HAZARDOUS WASTE PROGRAM

QUALITY ASSURANCE PROGRAM PLAN

Douglas A. Ducey, Governor

Henry R. Darwin, Director

ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

Waste Programs Division

Date: January 12, 2015

Revision A

A.1 TITLE AND APPROVAL PAGE

This QA Program Plan is hereby recommended for approval and commits the Department to follow the elements described within.

Arizona Department of Environmental Quality

Laura L. Malone, Director, Waste Programs Division

Signature: Laura L. Malone Date: 1/21/15

Robin Thomas, Manager, Hazardous Waste Permits Section

Signature: _____ Date: 1-20-15

Randall Matas, Manager, Inspections and Compliance Section

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Becky Soter, Safety and Quality Management Specialist, ADEQ

Signature: Becky Soter Date: 1-20-15

EPA Region 9

Eugenia McNaughton, Quality Assurance Manager, EPA Region 9

Signature: _____ Date: _____

The Arizona Department of Environmental Quality (ADEQ) has prepared this Quality Assurance (QA) Program Plan titled **Hazardous Waste Program Quality Assurance Program Plan** following the *EPA Requirements for Quality Assurance Project Plans (EPA QA/R-5)* dated March 2001, the *EPA Guidance for Quality Assurance Project Plans (EPA QA/G-5)* dated December 2002, the *EPA Region 9 Requirements for Quality Assurance Program Plan (R9QA/03.2)* dated March 2012, and the *ADEQ Quality Management Plan* dated August 2010.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105

January 12, 2015

MEMORANDUM

SUBJECT: Hazardous Waste Program Arizona Department of Environmental Quality (ADEQ) Quality Assurance Program Plan [QA Office Document Control Number RCRA0240PV2]

FROM: David R. Taylor, Ph.D., Sr. Document Reviewer
Quality Assurance Office (MTS-3)

THROUGH: Eugenia McNaughton, Ph.D., Manager
Quality Assurance Office (MTS-3)

TO: Marc Mowrey, Project Officer
Land Division, LND-1-1

The revised subject draft Quality Assurance Program Plan (QAPrP), prepared by the Arizona Department of Environmental Quality (ADEQ) dated March 20 2014, but received December 18, 2014, has been reviewed. A Response to Comments (RTC) was also received. The review was based on *EPA Region 9 Guidance for Quality Assurance Program Plans* (R9QA/03.2, March 2010); *EPA Requirements for Quality Management Plans* (EPA R-2, December 2001); *EPA Requirements for Quality Assurance Project Plans* (EPA QA/R-5, March 2001); *EPA Guidance for Quality Assurance Project Plans* (EPA QA/G-5, December 2002); *Guidance for the Data Quality Objectives Process* (EPA QA/G-4, August 2000); and a QA Office Memorandum dated November 20, 2014.

The QA Program Plan is approved. All previous concerns have been addressed. Original comments are reproduced below in bold face type. An evaluation of the revised plan flows in normal type.

If you have any questions or need further information please feel free to contact me by phone at 415-972-3803 or by email at <Taylor.David@epa.gov>.

Concerns

1A. [Section A.4.1.1, Organization Roles and Responsibilities; Environmental Laboratory Services] **The plan should clarify how Environmental Laboratory Services requirements apply to permittees and organizations submitting data to ADEQ.**

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ACRONYMS AND ABBREVIATIONS

AAC	Arizona Administrative Code
ADEQ	Arizona Department of Environmental Quality
ADHS	Arizona Department of Health Services
ADQ	Audit of Data Quality
AOC	Area of Concern
ARS	Arizona Revised Statutes
ASTM	American Society for Testing and Materials
CASOC	Corrective Action Schedule of Compliance
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
CLP	Contract Laboratory Program
CMI	Corrective Measures Implementation
CMS	Corrective Measures Study
CSM	Conceptual Site Model
CWA	Clean Water Act
DQA	Data Quality Assessment
DQI	Data Quality Indicator
DQO	Data Quality Objective
EDD	Electronic data deliverable
EPA	Environmental Protection Agency
HASP	Health and Safety Plan
HSWA	Hazardous and Solid Waste Amendments
HWICU	Hazardous Waste Inspections and Compliance Unit
HWM	Hazardous Waste Management
HWPU	Hazardous Waste Permits Unit
ICP	Inductively Coupled Plasma
IDW	Investigative Derived Waste

ITRC	Interstate Technical Regulatory Council
LCS	Laboratory Control Sample
MDL	Method Detection Limit
MQO	Measurement Quality Objective
MS/MSD	Matrix Spike and Matrix Spike Duplicate
MSR	Management System Review
MI	Multi-increment
MPC	Measurement Performance Criteria
NIST	National Institute of Standards and Testing
NOV	Notice of Violation
NPDES	National Pollutant Discharge Elimination System
PARCCS	Precision, Accuracy, Representativeness, Completeness, Comparability, and Sensitivity
PE	Performance Evaluation
PID	Photo Ionization Detector
PPE	Personnel Protective Equipment
PQL	Practical Quantitation Limit
PRQL	Project Required Quantitation Limit
PWSS	Public Water Supply System
QA	Quality Assurance
QAPjP	Quality Assurance Project Plan
QC	Quality Control
QCSR	Quality Control Summary Report
QMP	Quality Management Plan
RCRA	Resource Conservation and Recovery Act
RFA	RCRA Facility Assessment
RFI	RCRA Facility Investigation
RP	Remedial Plan
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SDG	Sample Delivery Group
SDWA	Safe Drinking Water Act
SOP	Standard Operating Procedure
SWMU	Solid Waste Management Unit
TSA	Technical System Audit
TSD	Transport, Storage and Disposal
VOA	Volatile Organic Analysis
VOC	Volatile Organic Compound
WPD	Waste Programs Division

Distribution List

Hazardous Waste Management Program Staff
ADEQ Technical Support Staff
Robin Thomas, Permits Section Manager
Randall Matas, Inspections and Compliance Section Manager
Becky Soter, Safety and Quality Management Specialist
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GROUP A: PROGRAM MANAGEMENT

Introduction

The United States Environmental Protection Agency (EPA) requires that all environmental monitoring and measurement efforts mandated or supported by EPA have in place a centrally managed Quality Assurance (QA) Program Plan. The purpose of the QA Program Plan is to provide guidance on how quality assurance (QA) and quality control (QC) procedures are applied in order to produce data that are:

- Scientifically valid.
- Of documented quality.
- Legally defensible.

The format and elements of this QA Program Plan are in accordance with EPA guidance, including EPA Requirements for Quality Assurance Project Plans for Environmental Data Operations EPA QA/R-5 (March 2001) and EPA Guidance for Quality Assurance Project Plans EPA QA/G-5 (December 2002). Specific elements required in a QA Program Plan include: project management, measurement data acquisition, assessment and oversight, data review and verification, and usability.

Any party generating data under ADEQ's Hazardous Waste Management (HWM) program (see Arizona Revised Statutes (A.R.S.) Title 49, Chapter 5, Article 2) has the responsibility to implement minimum procedures to assure that the precision, accuracy, completeness, comparability and representativeness of its data are known and documented. All QA/QC procedures must be in accordance with applicable professional technical standards, EPA requirements, government regulations and guidelines, and specific project goals and requirements. The QA Program Plan is a management tool that will help guarantee that data is of sufficient known quality to withstand scientific and legal challenge relative to the use for which the data is obtained.

Under the Federal Resource Conservation and Recovery Act (RCRA) as amended, cooperative enforcement, corrective actions, closures and inspection agreements have been developed between the EPA and the Arizona Department of Environmental Quality (ADEQ) HWM Program. ADEQ is the state lead agency for RCRA regulatory programs and is authorized under the Arizona Revised Statutes to conduct RCRA enforcement, compliance, inspection, corrective action, closures and permitting programs. Examples of activities within these programs include the inspection of hazardous waste generators, complaint investigations for hazardous waste dumping (illegal disposal) and permitting duties and oversight of hazardous waste treatment, storage and disposal (TSD) facilities. Many of these activities include the sampling and analysis of various media to verify possible violations for enforcement purposes or to establish site conditions during the operation or closure of regulated facilities. Monitoring programs for groundwater protection are established by the ADEQ at permitted RCRA facilities, and at facilities undergoing corrective actions for the purpose of site characterization and remediation.

Sampling activities overseen by ADEQ's Hazardous Waste Inspections and Compliance Unit (HWICU) and the Hazardous Waste Permits Unit (HWPU) are associated with the activities outlined above. Inspections of hazardous waste generators and complaint investigations for hazardous waste dumping (illegal disposal) are handled by HWICU. Permitting duties and oversight of hazardous waste treatment, storage and disposal (TSD) facilities are handled by HWPU. For the purpose of this document, a HWM facility can be a facility that generates hazardous wastes, is a permitted TSD facility, or both. When a

distinction needs to be made between a permitted TSD facility and a HWM facility that is not a permitted TSD, the acronym TSD will be used.

ADEQ can require the HWM facility/responsible party to conduct the sampling or designate agency personnel who are responsible for collecting such samples and/or documenting field collection activities. Those activities will occur within a framework that is well-defined by specific documentation requirements. Most activities will be conducted along a coordinated flow path consisting of the submittal and review of documents. To support the activities of ADEQ's HWM Program, media and waste samples are submitted to an Arizona Department of Health Services (ADHS) licensed laboratory.

A4: Program Organization and Planning Documentation

ADEQ's HWM Program operates within the Waste Programs Division of the ADEQ. This Division functions as a consolidated source of environmental cleanup in the State of Arizona, with authorities and responsibilities arising from delegated authorities through the RCRA, the Clean Water Act (CWA) and from cooperative work agreements through Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). The HWM Program is one component of the Waste Programs Division and consists of several full-time employees along with multiple managers/supervisors. Two of the units within the HWM Program are the HWICU and the HWPU.

ADEQ employs a decentralized approach to QA management, whereby each Division of ADEQ is responsible for deciding how they will specifically implement the general policies and procedures of ADEQ's Quality Management Plan. The ADEQ Director has delegated day-to-day responsibility for overseeing the Quality Management Plan to ADEQ's Quality Assurance/Quality Control (QA/QC) Steering Committee, chaired by ADEQ's Safety and Quality Management Specialist (QA/QC Supervisor). The QA/QC Supervisor functions as the Agency technical QA expert. The Steering Committee is to be made up of designated QA/QC personnel from each of the three environmental Divisions and the QA/QC Supervisor, who resides in the Office of Administrative Counsel for reasons of autonomy. The Steering Committee has not yet been created and that until such time as it is created, the QA/QC Supervisor will assume its responsibilities.

The QA/QC Supervisor is not routinely involved with the day-to-day activities of the HWM Program. The QA/QC Supervisor does not routinely participate in any of the planning phases of a project or is involved in the review/approval of submitted reports. The QA/QC Supervisor, though, can be requested to assist in the review of data when necessary. Please see Section A4.1.2 under Q/QC Supervisor for a full description of the QA/QC Supervisor's role.

A4.1 Program/Task Organization

The HWM Program, as described below, performs inspections and compliance, reviews permit applications, reviews reports generated by a HWM facility and collects samples when necessary. A HWM facility can be a facility that generates hazardous wastes, is a TSD facility, or both.

The operation of this program involves a number of parties with specific responsibilities related to data quality; these individuals represent four different organizational entities with specific functions related to the management of the HWM Program. The following paragraphs discuss these organizations and their

general responsibilities, followed by discussions of specific responsibilities held by various individuals within those organizations.

An organizational chart showing all the parties involved in the data quality system has been included as Figure A1: Components of the Quality System for ADEQ's HWM Program. Entities are identified based on their applicable data roles: data quality management, data generators or data users. The defined HWM Program includes the ADEQ Waste Programs Permits Section Manager, Inspections and Compliance Section Manager, HWPU and HWICU Unit Supervisors, HWM Program Technical Support and staff level personnel. EPA Region 9 Arizona Project Officer is also shown in Figure A1. The prospective data users include the HWM facility owner/operator and local government.

A4.1.1 Organizational Roles and Responsibilities

Environmental Protection Agency (EPA)
EPA works closely with Arizona in implementing the hazardous waste management program by providing grant funding, setting national goals and priorities, and conducting program oversight. Each year, EPA identifies the national priorities for implementing all of its programs, including the RCRA Subtitle C and D programs. These priorities form the basis for EPA and ADEQ workload negotiations for the upcoming year as part of the establishment of grant funding. Also, EPA regional staff has oversight responsibilities to promote national consistency in RCRA implementation, encourage coordination and agreement between EPA and ADEQ on technical and management issues, ensure proper enforcement by the ADEQ and ensure appropriate expenditure of federal grant funds.

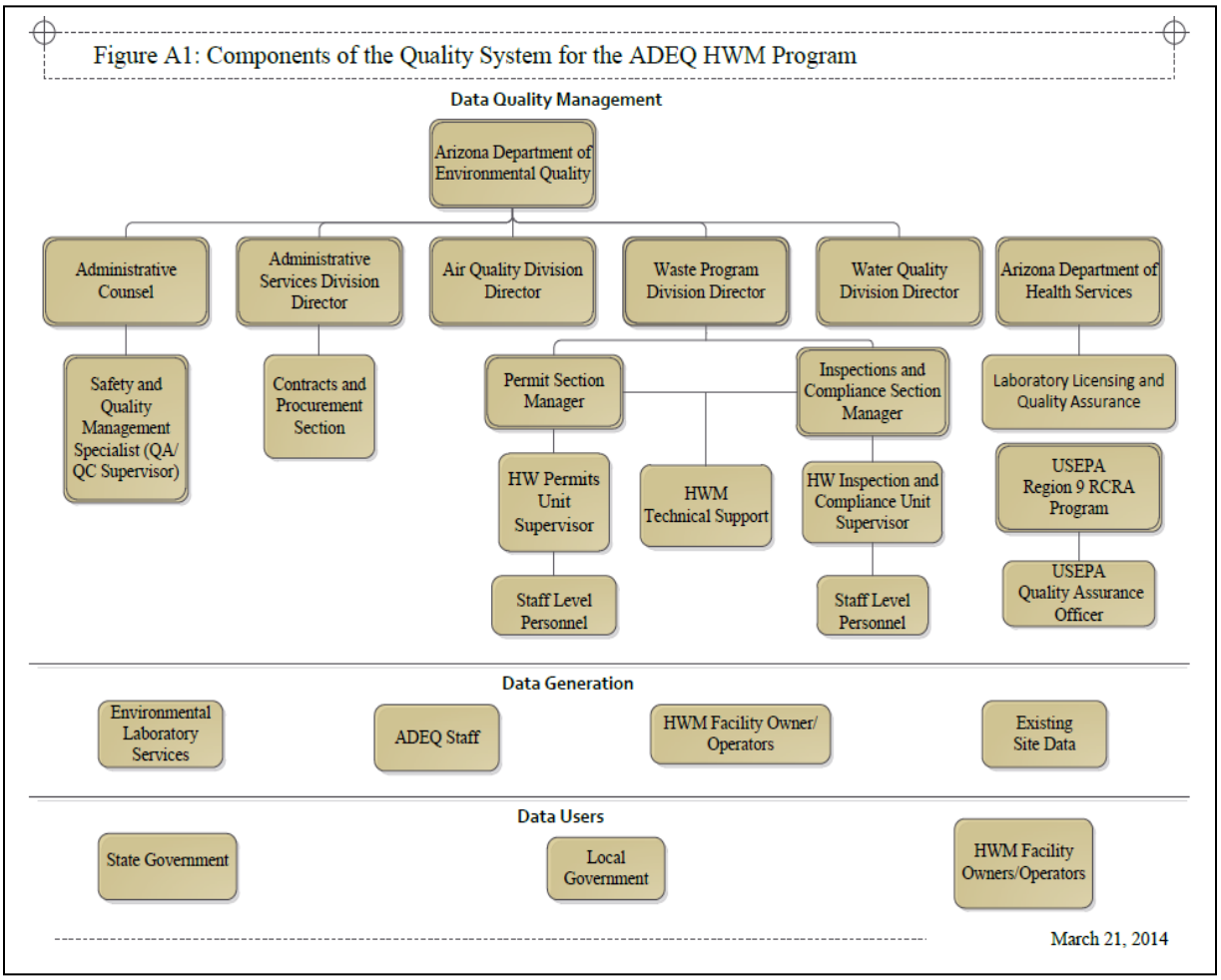
Arizona Department of Environmental Quality
The ADEQ is responsible for the operation of the HWM Program. All programmatic activities reside in the Waste Programs Division of ADEQ. The main functions of the HWM Program are carried out by the HWPU within the Permits Section and the HWICU of the Inspections and Compliance Section of the Waste Programs Division. Each of these sections and units has designated Section Managers and Unit Supervisors (two Section Managers and two Unit Supervisors in total).

Environmental Laboratory Services
All permittees and organizations submitting data generated for and submitted to ADEQ's HWM Program are required to use analytical laboratories licensed by the Arizona Department of Health Services (ADHS). The licensed analytical laboratories are required to follow all Arizona Administrative Code for Department of Health Services Laboratories (Appendix A). The data produced from the analysis of environmental samples are used to make informed decisions relating to the health and welfare of Arizona's citizens. These data must be of known quality, technically sound and legally defensible.

Upon application for an environmental laboratory license, ADHS shall issue the license if, after investigation, ADHS determines that the application conforms by the standards established by ADHS.

The ADHS Director shall prescribe rules providing for minimum standards of proficiency, methodology, quality assurance, operation, and safety for environmental laboratories and may prescribe standards for personnel education, training, and experience to meet Federal environmental statutes or regulation. The ADHS Director may also allow reciprocity with other states, and prescribe the manner and form in which compliance testing results are reported. The rules shall be developed in cooperation with the Director of the Department of Environmental Quality and shall be consistent with Title 49 (Section 49-101 et seq.).

Unless exempted by A.R.S. § 36-495.02, no person may operate or maintain an environmental laboratory without a license issued by the ADHS pursuant to A.R.S. §§ 36-495.03 through 36-495.14.



Hazardous Waste Management Facility Owners/Operators

As primary data generators, the HWM Facility Owner/Operators – either directly or through their environmental contractors - are responsible for the implementation and documentation of a number of QC elements, such as collection and analysis of field blanks, field duplicates and rinsate samples, to satisfy the requirements of the QA Program Plan. Please note that Section B.5 of this QA Program Plan discusses Quality Control in detail.

Please note: Some HWM Facility owner/operators employ staff that are qualified to satisfy the requirements of a QA Program Plan and, therefore, do not hire environmental contractors to generate environmental data. Also, please note that all documents requiring professional judgment must be sealed by a certified Arizona Board of Technical Registration registrant of an appropriate discipline.

The documentation of all environmental data collection activities must meet the following minimum requirements:

- Data must be documented directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.
- All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample identification, station or location identification (if applicable), name (signature or initials) of the person collecting the data, and date of data collection.
- Any changes to the original (raw data) entry must not obscure the original entry. The reason for the change must be documented, the change must be initialed and dated by the person making the change.

Also, SOPs for data collection should be developed following "Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations" (EPA 1995). SOPs should be included as an appendix of all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program. Any QA and QC reports (see Sections C2.2 and C2.3 can be included as an appendix of all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program. The field team should document reasoning for any deviations from an SOP and include that documentation in all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program.

A.4.1.2 Individual Roles and Responsibilities

In addition to those general responsibilities maintained by the above organizations, specific responsibilities for QA have been assigned to individuals involved in the HWM Program. These individuals will be referred to only as a given project title or position, since these assigned duties will be unaffected by staff changes within these positions. The listed individuals below correspond to the organization structure outlined above. They are described according to the level of direct oversight those individuals provide in the HWM Program's QA system.

<u>EPA Region 9, Arizona Project Officer</u>
The EPA Arizona Project Officer for the RCRA grant has responsibility for:

- Monitoring all activities and ADEQ's progress on the meeting grant commitments;
- Review progress reports to ensure ADEQ is performing the work as agreed and approved in the grant application;
- Serving as the focal point for programmatic and technical issues;
- Ensure completion of EPA's programmatic terms and conditions; and
- Maintaining documentation.

<u>Director, Arizona Department of Environmental Quality</u>
The ADEQ Director has overall responsibility for ADEQ's QA Program as outlined in EPA Order CIO 2105.0 (formerly 5360.1 A2). More specifically, the ADEQ Director is responsible for ensuring that QA is an identifiable activity having adequate resources allocated for the accomplishment of the mission's goals for ADEQ's divisions and Southern Regional office. These goals include providing the resources for the collection of the right type, quantity, and quality for all data generated in-house and externally.

Environmental Laboratory Services

The HWM Program relies on the ADHS licensing program for the satisfaction of many of the QA elements associated with laboratory operation and reporting (see Appendix A of this QA Program Plan). The ADHS is used to maintain oversight on analytical labs for quality control (QC) on all environmental samples submitted for analysis under a regulatory program—either the CWA, Safe Drinking Water Act (SDWA) or RCRA. Licensed laboratory QA responsibilities are described in its QA plan, as required by Arizona Administrative Code (A.A.C.) R9-14-615.B. ADHS maintains a list of licensed laboratories and periodically inspects them to ensure compliance.

The HWM Program also has the option of having audits performed by ADEQ's QA/QC Supervisor on laboratories licensed by ADHS. All ADEQ laboratory audits must be performed in accordance with Section 2.3.2 of ADEQ's August 2010 Quality Management Plan.

Director, Waste Programs Division of ADEQ

All site investigations and cleanups conducted in the State of Arizona are overseen by the ADEQ through its combined authorities from state-delegated environmental programs. The Waste Programs Division Director is responsible for the administration of all these cleanup authorities. In addition, because site cleanup regulations play an integral part in the development of data quality guidelines, the Division Director also plays an important function in determining data quality and sufficiency for the Waste Programs of ADEQ, including the HWM Program.

The regulations governing investigations and cleanups (ARS Title 49 – The Environment) in Arizona determine, on a general level, the type and amount of data necessary to make decisions regarding issuance of permits, Notice of Violations (NOVs), compliance orders, and the issuance of determination letters (e.g. "no further action" letters). The Division Director is responsible for ensuring a consistent application of these regulations across all Waste Programs cleanup sites. All site information is available to the Division Director for review and consideration of site decisions. The Division Director also holds regular supervisor-level meetings to discuss ADEQ issues and Waste Programs operations.

Section Manager, Inspections and Compliance Section of Waste Programs Division

The Inspections and Compliance Section Manager is responsible for staff level participation in all the administrative and technical areas of the HWICU. The Inspections and Compliance Section Manager is responsible for ensuring that the HWICU performs its functions consistent with WPD policies and procedures. The Section Manager's level of review will routinely consist of ensuring that the proper staff members reviewed, commented and drafted an appropriate enforcement document (e.g. NOV), which routinely contains requirements for a Site Assessment Plan. The Inspections and Compliance Section Manager ensures that the Section meets program goals.

Unit Supervisor, Hazardous Waste Inspections and Compliance Unit of the Inspections and Compliance Section

The Unit Supervisor of the HWICU is responsible for staff level participation in all the administrative and technical areas of the HWICU. The Unit Supervisor's level of review will routinely consist of ensuring that proper staff members carry out inspections and review, comment on and draft an appropriate response to submitted Site Assessment Plans and site assessment reports. The Unit Supervisor will also edit, if necessary, any comment or approval letter. The Unit Supervisor is responsible for final approval of submitted Site Assessment Plans and site assessment reports.

Section Manager, Permits Section of Waste Programs Division
The Permits Section Manager is responsible for staff level participation in all the administrative and technical areas of the HWPU. The Permits Section Manager is responsible for ensuring that the HWPU performs its functions consistent with WPD policies and procedures. The Permits Section Manager approves the EPA Grant Work Plans, establishes the priorities for the HWPU, prepares and/or negotiates the overall budget, and develops contracts for permitting support designed to assist HWPU. Also, the Permits Section Manager is available for consultation regarding closures, corrective actions, and the review of permit applications.

Unit Supervisor, Hazardous Waste Permits Unit of Permits Section
The Unit Supervisor of the HWPU is responsible for ensuring that permitting, closures and corrective actions are performed in accordance with State and Federal rules and guidance. The Unit Supervisor assigns work, manages priorities, and reviews staff outputs, including comment letters and notices of deficiency, approvals and permits. The Unit Supervisor is responsible for final approval of work plans and any required reporting.

*Please note that the exception to this approval process is that final approval for HWM TSD facility permit applications, which include Closure Plans (see HWPU Processes, Documents and Deliverables in Section A4.2) lies with the Waste Programs Division Director. The Waste Programs Division Director approves HWM TSD facility permit applications.

Staff Level Personnel of the HWM Program
Staff level personnel consist of Environmental Engineers, Inspectors, and Environmental Program Specialists. Their responsibilities with quality control may involve reviewing Planning Documents and Reports (see Figure A2) submitted by the HWM Facility Owner/Operators – either directly or through their contractors - to investigate and remediate soil and groundwater contamination. Soil, groundwater and soil gas samples may be collected directly by staff during split sampling events or during facility inspections. Personnel can conduct announced or unannounced inspections to ensure a HWM facility maintains compliance with regulatory requirements.

The proposed investigation is typically detailed in a work plan or Site Assessment Plan, which is reviewed, commented upon and approved by a Unit Supervisor after resolution of all issues and before the investigation begins. After the data is collected, the results are submitted in a report which is reviewed. Appendix B details the information that is typically required in a Site Assessment Plan. The following is a short list of some of the most common goals for sampling:

a. To document a discharge;
b. To determine the substance discharged;
c. To document the source of discharge;
d. To document that the discharge meets certain parameters;
e. To establish the amount/concentration of a substance in a discharge;
f. To document the extent and degree of contamination; or
g. To document that an area is below clean-up standards.

On the infrequent occasions when ADEQ staff collects samples and has them analyzed by an

ADHS approved laboratory (i.e. during inspections and split sampling events), the Technical Support person is available to assist the various staff level personnel when necessary. The Technical Support person, upon request from the staff level personnel, Unit Supervisor or Section Manager, will review this data with regards to QA Program Plan requirements, sampling goals and DQO's.

Hazardous Waste Management Program, Technical Support

Technical support at the section level is available and may be requested by staff, Unit Supervisor or Section Manager to assist with site assessment or remediation issues to ensure the investigation and data collection efforts of the environmental consultant and facility meet quality assurance objectives. This is done through three major activities:

1 Review of Planning Documents (see Figure A2) — The Technical Support person will be available to assist the various staff members when necessary. The Technical Support person, upon request from the staff level personnel, Unit Supervisor or Section Manager, will review and comment on the submitted Planning Documents with regards to QA Program Plan requirements, project goals and Data Quality Objectives (DQO's).

2. Development of DQOs —prior to the preparation of Site Assessment Plans by the HWM facility/responsible party or its contractor, an initial scoping session may be held with all available stakeholders to outline project goals and DQOs. These initial meetings will roughly follow guidance for the standard DQO process developed by the EPA (EPA 2006 - Guidance on Systematic Planning using the Data Quality Objectives Planning Process). The results of these initial meetings will guide the development of the site-specific Site Assessment Plan and will be documented as part of the Site Assessment Plan or QA Project Plan preparation.

3. Review of Data Reports (see Figure A2) — the Technical Support person will be available to assist the various staff level personnel when necessary. The Technical Support person, upon request from the staff level personnel, Unit Supervisor or Section Manager, will review the submitted data reports generated under an approved work plan or Site Assessment Plan with regards to QA Program Plan requirements, project goals and DQO's.

On the infrequent occasions when ADEQ staff collects samples and has them analyzed by an ADHS approved laboratory (i.e. during inspections and split sampling), the Technical Support person is available to assist the various staff level personnel when necessary. The Technical Support person, upon request from the staff level personnel, Unit Supervisor or Section Manager, will review this data with regards to QA Program Plan requirements, sampling goals and DQO's.

When requested by the staff level personnel, Unit Supervisor or Section Manager, the Technical Support person will prepare comments for revision of the data reports.

QA/QC Supervisor:
The QA/QC Supervisor provides assessment of HWM Program activities through the activities listed below:

- Technical System Audits
- Performance Evaluations
- Audits of Data Quality
- Data Quality Assessments

Please see Section C1.2.2 – Assessment of Program Activities for details on these activities.
The QA/QC Supervision also reviews and can revise the QA Program Plan. The QA Program Plan will need to be updated to accommodate new developments in QA/QC. Revisions to the QA Program Plan may become necessary through several different routes, and the QA/QC Supervisor will be responsible for responding and making these revisions when appropriate. During regular contact with the EPA, the QA Officer may make suggestions for improving quality performance that could be incorporated into the QA Program Plan. During a Technical System Audit (TSA), the QA/QC Supervisor will examine the QA Program Plan and the performance of the HWM Program and may make suggestions for improved performance that result in revisions to the QA Program Plan.

The QA/QC Supervisor is not routinely involved with the day-to-day activities of the HWM Program. The QA/QC Supervisor does not routinely participate in any of the planning phases of a project or is involved in the review/approval of submitted documents. The QA/QC Supervisor, though, can be requested to assist in the review of data when necessary.

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As primary data generators, the HWM Facility Owner/Operators – either directly or through their contractors - are responsible for the implementation and documentation of a number of QC elements, such as collection and analysis of field blanks, field duplicates and rinsate samples, to satisfy the requirements of the QA Program Plan. Please note that Section B.5 of this QA Program Plan discusses Quality Control in detail.

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Also, SOPs for data collection should be developed following "Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations" (EPA 1995). SOPs should be included as an appendix of all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program. Any QA and QC reports (see Sections C2.2 and C2.3 can be included as an appendix of all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program. The field team should document reasoning for any deviations from an SOP and include that documentation in all Planning Documents and Reports (see Figure A2) submitted to ADEQ's HWM Program.

A4.2 Planning Documentation

Sampling activities conducted or overseen by the HWICU and the HWPU will be associated with an inspection, a site assessment, a site cleanup project or routine sampling as part of inspection and permitting requirements. Those activities will occur within a framework that is well-defined by specific documentation requirements. Most activities will be conducted along a coordinated flow path consisting of the submittal and review of documents. Therefore, each defined document will play a role in establishing QC elements to ensure the production of a usable, reliable final product.

Outlined below are: 1) HWICU defined processes, documents and deliverables that constitute a typical RCRA inspection and site assessment. These RCRA inspection and site assessment processes focus mainly on HWM facilities that generate hazardous waste; and 2) HWPU defined processes, documents and deliverables that constitute a corrective action, closure or site assessment and remedy project. The HWPU defined processes focus mainly on permitted TSD facilities. The documents listed are in the order that those documents will be produced during the course of an inspection, an enforcement process, permitting, a TSD facility closure or corrective action. Section B9: Non-direct Measurements explains the documentation and use of previously generated data. Later sections will discuss other documentation issues, particularly the development of audits.

HWICU Processes, Documents and Deliverables

1. HWICU Facility Inspection

During an inspection, an inspector may identify potentially noncompliant conditions. Some conditions indicating a possible need for sampling include: 1) a potentially hazardous waste is being handled as a non-hazardous waste; 2) HWM facility waste handling practices indicate that mislabeling/misidentification of waste is likely to occur; 3) HWM facility waste handling practices indicate that wastes may vary significantly in characteristic over time (and mismanaged as a result); 4) visible or other observable evidence of possible past or ongoing releases of hazardous wastes from waste management units, satellite storage areas, waste generating areas, etc.; and 5) mismanagement of wastes (i.e. inappropriate treatment).

2. Notice of Violation

If an inspector observes that a hazardous waste violation has occurred, an NOV will be issued to the HWM facility/responsible party. An NOV is an informal tool used to inform a person or business that a

statute, rule, state law, or permit condition has been violated. The purpose of an NOV is to initiate corrective action that will stop the mismanagement of hazardous waste from improper treatment, storage or disposal. If warranted, the NOV will include a condition for the responsible party to submit a Site Assessment Plan. The NOV will identify the media or wastes to be sampled, the physical locations at which sampling should occur (e.g., the location of a possible release), the steps within a treatment process to sample, the physical characteristics of the medium to be sampled (e.g., sludge, granular solid), and other relevant information.

ADEQ can also issue a Consent Order or Compliance Order to the responsible party. These Orders are formal tools used to compel responsible parties to perform corrective actions. Orders are usually issued only if the responsible party did not comply with the conditions set within an NOV.

3. Site Assessment Plan

A Site Assessment Plan, the primary planning document for sampling activities, will be prepared by the HWM facility/responsible party after the NOV has been issued. Sampling activities will require the drafting of a Site Assessment Plan by the HWM facility or its consultant. The Site Assessment Plan must meet all of the requirements outlined in the NOV. Typical requirements are provided in Appendix B of this QA Program Plan. The Site Assessment Plan will be submitted to the ADEQ by the HWM facility for review. No assessment or cleanup activities involving data generation will be undertaken until planning documents are approved. Primary responsibility for review of site assessment planning documents will reside with the HWICU.

4. Planning Documentation Approval

After review of the planning document, HWICU will take one of three actions through written correspondence to the responsible party. These actions are:

a. If the planning document is found to be fully satisfactory, Staff Level Personnel will draft an approval letter and the Unit Supervisor will give Final Approval to the letter.
b. Where there are minor deficiencies in a plan, Staff Level Personnel will draft a conditional approval letter, which will dictate corrections in the plan, without requiring re-drafting of the documentation. These corrections will be considered part of the approved plan. The Unit Supervisor will give Final Approval to letter.
c. Where there are major deficiencies in a plan, Staff Level Personnel will draft a comment letter, indicating the plan deficiencies and suggesting corrections for re-drafting of the plan. The Unit Supervisor will issue Final Approval to the comment letter. Technical Support will be available at all stages of the process for consult.

Figure A2 details the review process for submitted Plans and required reports.

During the review process, a HWM facility is welcome to request a technical assistance meeting between the HWICU, and, if desired, the contractors involved with the project to further discuss any deficiencies that need to be addressed in the Site Assessment Plan.

5. Field Documentation

Though largely discussed elsewhere in this document, certain levels of field documentation will be required to be produced and maintained by the environmental consultant to help demonstrate compliance

with approved methods and to assist reviewers in making QA conclusions. Examples of required field documentation would include field logs, monitoring well sampling logs and chain-of-custody forms for environmental samples. Along with the analytical laboratory data package, field documentation can be requested as part of the independent data validation. Field documentation will be submitted as part of the required report in hard copy format.

6. Laboratory Analytical Package

The data package produced by the analytical laboratory should be sufficiently detailed to allow for review of analytical methods through data verification and validation processes and to determine appropriateness of data quality. The requirements for the specific content of laboratory data packages will be discussed in other sections of this QA Program Plan. The laboratory data package should be attached in an electronic format, with the exception of the chain of custody forms and the laboratory analytical sheets, which should be included in hard-copy format.

7. Approval of Site Assessment Reports

All site information generated during the assessment or cleanup must be collected, tabulated and considered in the reports generated by the HWM facility to document the project. Before the report is finalized, a draft version must be submitted to the HWICU to allow for comments and consideration of the quality and format of presented data. The format of the report will depend on the project goals. HWICU recommends that the HWM Facility owner/operator and their contractors use the report formatting described in EPA's Document Report Formatting and Presentation Guidelines available at http://www.epa.gov/evaluate/pdf/tools/report-formatting-presentation-guidelines.pdf.

Supporting documentation relevant to data generation and data quality must be attached to the final report, either in a hard-copy or electronic format. Generally, all field documentation will need to be attached to the report in a hard-copy format. The laboratory data package should be attached in an electronic format, with the exception of the chain of custody forms and the actual laboratory analytical sheets, which should be included in hard-copy format.

If ADEQ determines that the draft version of the required report does not demonstrate that project objectives were met, the HWICU may require the collection of additional data for inclusion into a final report. Otherwise, the responsible party may make the appropriate revisions to a report as outlined in any comment letters sent by ADEQ.

During the review process, a HWM facility is welcome to request a technical assistance meeting between the HWICU, and, if desired, the contactor involved with the project to further discuss any deficiencies that need to be addressed in the site assessment report.

Figure A2 details the review process for submitted Plans and required reports.

8. Project Closeout, Project Completion Letter

Project closeout for the HWM facility will be granted by ADEQ upon receipt of the approved final report. Closeout will be in the form of a written notification, commonly an NOV closure letter, to the HWM facility.

HWPU Processes, Documents and Deliverables

Each TSD Facility is required to have a written Closure Plan (see bullet 1a below). The owner/operator must submit the Closure Plan with the permit application, and it must be approved by the ADEQ Director as part of the permit issuance procedures of the HWM Program. In addition, the HWM Permit may contain requirements for Corrective Action to address historic or current releases of solid waste, hazardous waste, or hazardous waste constituents.

1. HWM TSD Facility Closure

a. Closure Plan – The Closure Plan must identify steps necessary to perform partial or final closure of the TSD Facility at any point of its active life. The closure plan must contain the following:

i. a description of how each hazardous waste management unit at the facility will be closed in accordance with hazardous waste rules and guidance;

ii. an estimate of the maximum inventory of hazardous wastes ever onsite over the active life of the facility and provide a detailed description of the methods to be used during closure, including methods for removing, transporting, treating, storing, or disposing of all hazardous wastes;

iii. a detailed description of the steps needed to remove or decontaminate all hazardous waste residues and contaminated containment system components, equipment, structures, and soils during closure, including procedures for cleaning equipment and removing contaminated soils, methods for sampling and testing surrounding soils, and criteria for determining the extent of decontamination required to satisfy the closure performance criteria; and

iv. a detailed description of other activities necessary during the closure period to ensure that the closure satisfies the closure performance standard, including groundwater monitoring, leachate collection, and run-on and run-off control.

The owner/operator of the TSD Facility must close the facility when it will no longer receive hazardous waste. The owner/operator must complete closure within 180 days after receiving the final volume of hazardous waste, unless extended by the ADEQ Director. If the owner/operator is not able to perform closure, ADEQ may draw on the financial assurance provided by the owner/operator and direct its contractor to complete closure.

b. Closure Report – Each Closure Plan requires the owner/operator to submit a Closure Report upon completion of closure. The Closure Report is described in the Permit. At a minimum the Closure Report requires that the following information be submitted:

i. a summary of results, significant observations, and conclusions;

ii. a detailed discussion of the closure procedures followed for each unit including: a) the procedures followed for contamination of the hazardous waste management unit, including disposition of residues; b) the equipment used for decontamination of the hazardous waste management unit; c) the sampling procedures used; d) the equipment used for sampling; e) the remedial procedures (if applicable) used; f) the equipment used for remediation; g) the analytical procedures and methods used; h) the analytical equipment used; i) the procedures used to prevent hazards and protect field personnel during closure; j) the equipment used to prevent hazards and protect field personnel during closure; k) drawings and photographs where appropriate; and l) description of any deviations from the approved closure plan;

iii. data generated from sampling and analysis activities performed pursuant to the plan including field notes, manifests, bills of lading, land disposal restriction forms, laboratory submittal forms, chain-of-custody forms, laboratory reports, and drilling logs;
iv. risk assessment discussion (if applicable), including methodology, data, references, and assumptions;
v. certification from the engineer and the owner/operator; and
vi. other information requested by the Director**.**

2. Corrective Actions

RCRA Section 3004(u), as amended by the Hazardous and Solid Waste Amendments (HSWA) and A.A.C. R18-8-264.A (40 CFR 264.101 and 40 CFR Subpart S) requires that Permits issued after November 8, 1984, address corrective action for releases of hazardous waste and hazardous waste constituents from any Solid Waste Management Unit (SWMU) at the facility, regardless of when the waste was placed in the unit. Alternatively, when the Permittee discovers a new SWMU or an area of concern (AOC) at the facility, or determines a release has occurred, the HWM facility must comply with the Corrective Action Schedule of Compliance (CASOC). The CASOC includes the RCRA Facility Assessment (RFA), RCRA Facility Investigation (RFI), the Corrective Measures Study (CMS), and Corrective Measures Implementation (CMI). With the exception of the RFA, each of these phases may require the TSD Facility to identify the media or wastes to be sampled, physical locations at which sampling should occur (e.g., the location of a possible release), and collection of other relevant site-specific information.

a. RCRA Facility Assessment – The objective of the RFA is to identify potential and actual releases from solid waste management units (SWMUs) and make preliminary determinations about releases, the need for corrective action, and interim measures. The RFA is conducted by ADEQ and generally occurs prior to permit issuance. If the HWM facility is in interim status and is not seeking a permit, the RFA may take place before the facility closes. The RFA begins with a file review of information about the facility. ADEQ may then conduct a visual site inspection to confirm available information on SWMUs and to note any visual evidence of releases. Finally, a sampling visit may be performed to collect data at the suspected release areas/locations to determine whether a RCRA Facility Investigation is warranted.

b. RCRA Facility Investigation Work Plan and Report – The RFI may take place when a release has been identified and further investigation is necessary. The purpose of the RFI is to gather enough data to fully characterize the nature, extent, and rate of migration of contaminants so that an appropriate response action can be determined.

   The investigation typically focuses on the specific units, releases, and exposure pathways that have been identified as problematic. Permittees may be required to submit one or more work plans for conducting an RFI. Upon completion of work plan activities, the Permittee may be required to submit an RFI Report that presents all information gathered under the approved RFI Work Plan. Typical information in an RFI Report details the type and extent of contamination at the facility, sources and migration pathways, and actual or potential receptors. The RFI Report must contain adequate information to support further corrective action decisions at the facility.

c. Corrective Measures Study Work Plan and Report – If the Director has reason to believe, after review of the RFI Report, that a SWMU has released concentrations of hazardous constituents that may pose a threat to human health and the environment, the Director may require the

owner/operator to conduct a Corrective Measures Study (CMS). The CMS Work Plan shall provide the following information:

i. a description of general approach to investigate and evaluate potential remedies;
ii. a definition of the overall study objectives;
iii. the specific plans and factors for evaluating remedies to ensure compliance with remedy standards, as stated in Permit Condition IV.H (Remedy Selection);
iv. the schedules for conducting the study; and
v. the proposed format for presentation of the information.

Upon completion of work plan activities, the owner/operator may be required to submit a report that summarizes the findings of the CMS. The CMS Report shall include:

i. a summary of the results of investigations and any bench-scale or pilot tests conducted for each remedy studied;
ii. a description and evaluation of each remedial alternative which passed through the initial screening of corrective measure technologies;
iii. all information gathered under the approved CMS Work Plan; and
iv. the recommended corrective measure(s) and a justification for selection of the recommended corrective measure(s).

d. Remedy Selection - Based on results of the CMS and any evaluations of additional remedies, the Director shall select a remedy that:

i. assures the protection of public health and welfare and the environment;
ii. to the extent practicable, provide for the control, management or cleanup of regulated substances so as to allow the maximum beneficial use of the water and soil of Arizona;
iii. is reasonable, necessary, cost-effective and technically feasible; and
iv. meets all applicable waste management requirements.

e. Corrective Measures Implementation Work Plan and Report - After receipt of the Director's Remedy Selection, the owner/operator may be required to submit a Corrective Measures Implementation (CMI) Work Plan. The CMI Work Plan must provide details of specific remedies (i.e. remove-and-treat or treat-in-place) to be taken which achieve compliance with cleanup standards, and a description of the remedy's technical features that are necessary to achieve cleanup standards, including:

i. requirements for quality sampling and analysis - including a plan for CMI groundwater monitoring that demonstrates an effective post-closure compliance or assessment monitoring program;
ii. requirements for removal, decontamination, closure, or post-closure of units, equipment, devices or structures used to implement remedy;
iii. a list of cleanup standards including, but not limited to hazardous constituents list for each medium (i.e. soil, groundwater);
iv. compliance points and compliance period;
v. management of hazardous waste;
vi. a schedule for initiating and completing all major technical features and milestones of remedy; and

vii. requirements for submission of semi-annual reports, other information, and modifications if above regulations cannot be met.

3. Site Assessment and Remedy (for releases with limited extent)

Site Assessment and Remedy may be required to assess and possibly remedy sites consisting of suspected historic releases of small areal/volumetric extent and for which no groundwater contamination has occurred or threatens to occur. Site Assessment and Remedy shall consist of a Site Assessment Plan and, if necessary, a Remedial Plan (RP).

The TSD facility owner/operator may be required to follow the provisions of the RFI, CMS, and CMI processes if, during performance of the Site Assessment Plan or RP, extensive contamination is found or if it is found that groundwater may be impacted by the historic release. The contents of Site Assessment Plan and RP's are included in Appendix B – General Requirements for Quality Assurance Project Plans/Site Assessment Plans.

4. Planning Documentation Approval

After review of a planning document, HWMU will take one of three actions through written correspondence to the environmental consultant. These actions are:

a. If the planning document is found to be fully satisfactory, Staff Level Personnel will draft an approval letter and the Unit Supervisor will give Final Approval to the letter.
b. Where there are minor deficiencies in a plan, Staff Level Personnel will draft a conditional approval letter, which will provide conditional approval while dictating corrections in the plan, without requiring re-drafting of the documentation. The Unit Supervisor will give Final Approval to the letter. These corrections will be considered part of the approved plan.
c. Where there are major deficiencies in a plan, Staff Level Personnel will draft a comment letter, indicating the plan deficiencies and suggesting corrections for re-drafting of the plan. The Unit Supervisor will issue Final Approval to the comment letter. Technical Support will be available at all stages of the process for consult.

Figure A2 details the review process for submitted Plans and required reports.

During the approval process, a HWM TSD facility is welcome to request a technical assistance meeting between the HWMU, and, if desired, the contractors involved with the project to further discuss any deficiencies that need to be addressed in the planning document.

5. Field Documentation

Though largely discussed elsewhere in this document, certain levels of field documentation will be required to be produced and maintained by the environmental consultant to help demonstrate compliance with approved methods and to assist reviewers in making QA conclusions. Examples of required field documentation would include field logs, monitoring well sampling logs and chain-of-custody forms for environmental samples. Along with the analytical laboratory data package, field documentation can be requested as part of the independent data validation. Field documentation will be submitted as part of the required report in hard copy format.

6. Laboratory Analytical Packages

The data package produced by the analytical laboratory should be sufficiently detailed to allow for review of analytical methods through data verification and validation processes and to determine appropriateness of data quality. The requirements for the specific content of laboratory data packages will be discussed in other sections of this QA Program Plan. The laboratory data package should be attached in an electronic format, with the exception of the chain of custody forms and the laboratory analytical sheets, which should be included in hard-copy format.

7. RFI, CMS and CMI Report Approval

All site information generated during the assessment or cleanup must be collected, tabulated and considered in the final reports generated by the TSD facility to document the project. The format of the report will depend on the project goals. HWPU recommends that the TSD Facility owner/operator and their contracotrs use the report formatting described in EPA's Document Report Formatting and Presentation Guidelines available at http://www.epa.gov/evaluate/pdf/tools/report-formatting-presentation-guidelines.pdf.

Unless otherwise specifically described in the TSD Facility Closure, Corrective Actions, and Site Assessment and Remedy sections detailed in bullets 1 through 3 above, general requirements for the final report would be the documentation of all work/field activities, presentation of all environmental data in a tabular and/or spatial format, and a section where the consultant uses their professional judgment to draw conclusions from the site data in the context of project goals. Through review of the draft reports, the HWPU will evaluate the acceptability of the presentation.

Supporting documentation relevant to data generation and data quality must be attached to the final report, either in a hard-copy or electronic format. Generally, all field documentation will need to be attached to the report in a hard-copy format. The laboratory data package should be attached in an electronic format, with the exception of the request for analysis forms and the actual laboratory analytical sheets, which should be included in hard-copy format.

Figure A2 details the review process for submitted Plans and required reports.

8. Comment Letters

If the HWPU requires revisions to the draft work plans and reports, those revisions will be communicated to the TSD facility or the TSD facility's consultant through the drafting of a comment letter. If the work plan or report is submitted as a component of a permit modification request, the comment letter will follow the license timeframe regulatory requirements of Arizona Administrative Code Title 18, Chapter 1, Article 5 concerning formal notices to the applicant. Comment letters and/or notices will include both suggested and required revisions. It will be the responsibility of the HWPU to determine whether the statements provided by the TSD Facility owner/operator or their consultant in the submittals are technically supported or are supported by the data, and whether the technical support or the data are of sufficient quality and quantity to meet project objectives.

9. Final Report

The final output of a project will be the submittal of a final Closure Report, RFI Report, CMS Report, CMI Report, or Site Assessment Report or Remedial Action Report to the ADEQ.

10. Project Closeout, Project Completion Letter
Project closeout for the HWM facility will be granted by ADEQ upon receipt of the approved final report. For a HWM Facility Closure closeout will be in the form of a written "Acknowledgement of Closure" letter. Corrective Actions and projects involving Site Assessment and Remedy may be closed out by a written "No Further Action" letter to the HWM facility. In the event that the Closure, Corrective Action, or Site Assessment and Remedy project is submitted as a permit modification request, project closeout may require formal approval of the permit modification request.

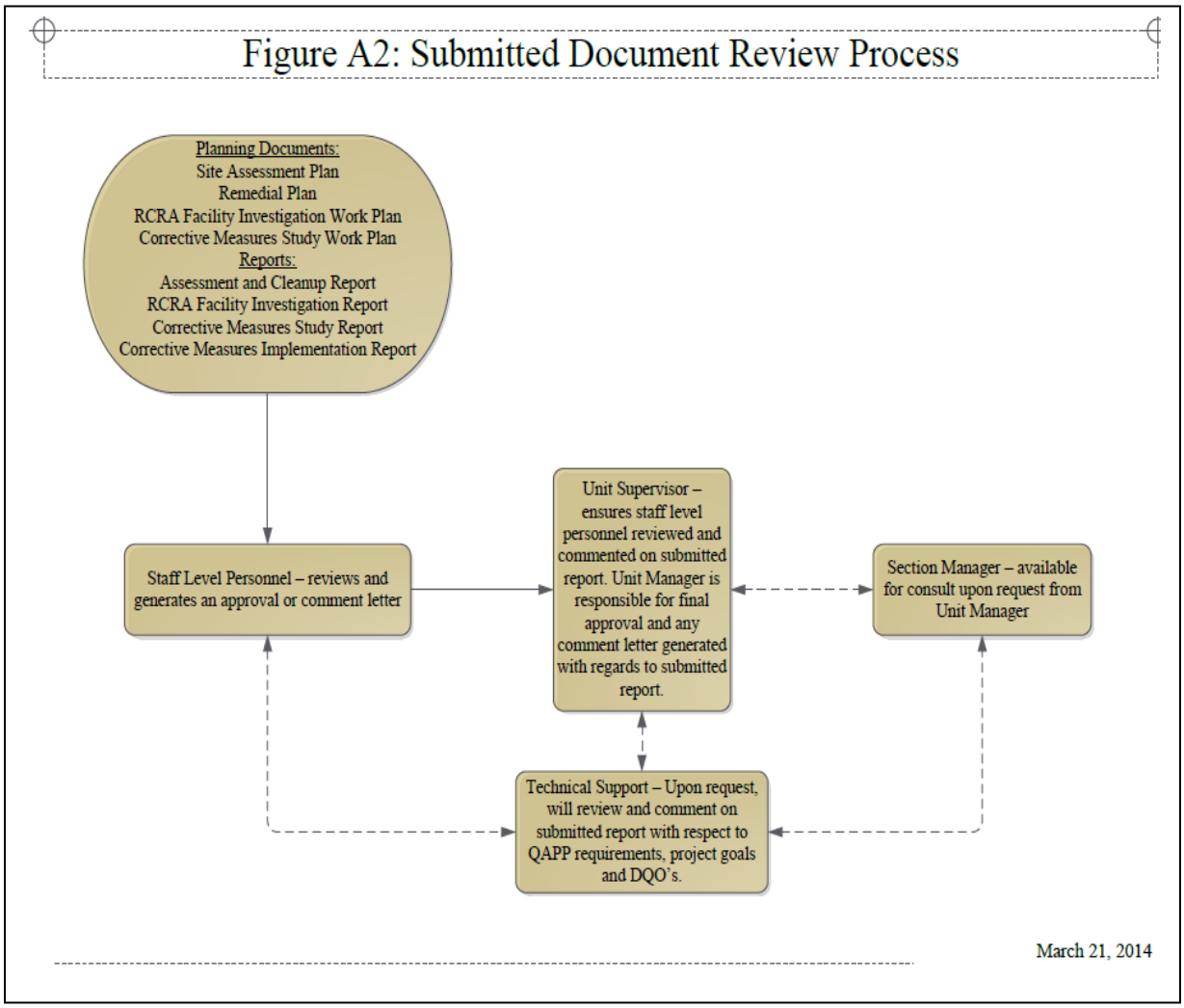
A5: Problem Definition/Background

The ADEQ HWM Program administers RCRA Subtitle C requirements for hazardous waste through Arizona's Revised Statutes and Administrative Code. The Subtitle C regulations establish a system for controlling hazardous waste from the time it is generated until its ultimate disposal — in effect, from "cradle to grave." To this end, there are Subtitle C regulations for the generation; transportation; and treatment, storage or disposal of hazardous wastes. In practical terms, this means regulating a large number of hazardous waste handlers. In administering RCRA Subtitle C, the HWM Program also:

- Conducts compliance and complaint inspections to ensure that hazardous wastes are safely managed and properly managed;
- Permits facilities that treat, store or dispose of hazardous waste;
- Performs education and outreach for facilities and general public;
- Manages ADEQ's pollution prevention (P2) program and other activities aimed at eliminating or reducing the use of toxic substances and the generation of hazardous wastes;
- Tracks manifests and annual reports and issuing HWM facility EPA identification numbers.

Past and present activities at *RCRA facilities sometimes result in the need for corrective action which may include site investigation. Additionally, when facilities close, site investigations may be required to determine whether releases have occurred. The requirement for corrective action is a result of the 1984 HSWA passed by Congress. These amendments require the cleanup of contamination due to improper waste management practices both prior and after the passage of RCRA. These amendments require responsible parties that are seeking a permit to treat, store or dispose of hazardous wastes to clean up environmental contaminants at their sites regardless of the time of release. CFR Title 40, 264, Subpart F - Releases From Solid Waste Management Units is of particular interest to site investigations as they relate to groundwater assessment.

** RCRA focuses only on active facilities (both operating and closing) and future facilities and does not address abandoned or historical sites which are managed under CERCLA – commonly known as Superfund.*



A6: Program/Task Description

Please see Sections A.4.1.2 (Staff Level Personnel HWM Program), A4.2 and A5 for details on the HWM Program and Task Descriptions.

A7: Quality Objectives and Criteria for Measurement Data

This section is broken into two parts, consistent with EPA Region 9 guidance for QA Program Plans. The first section documents regulatory action levels that are specific to the ADEQ; these action levels serve as the driver for site assessments and cleanup. The second section discusses MQOs and data quality indicators (DQIs) under the HWM Program.

DQI's, as defined by EPA, involve precision, accuracy, representativeness, completeness, comparability,

and sensitivity, also known as "PARCCS" parameters. It is expected that these indicators be used in data evaluation, but in general, the criteria by which DQIs are evaluated are based on project data quality needs, i.e., the MQOs. The extent to which program or project QC results meets MQOs determines whether data are acceptable for the intended use.

MQOs are the acceptance thresholds or goals for project data, usually based on the individual DQIs for each matrix and analyte group or analyte. MQOs are project-or method-specific quality acceptance criteria established to support project-specific DQOs, as well as the decisions that will be made based on the quality of the data. MQOs define whether the data are usable and meet project needs. Like DQOs, MQOs can be quantitative or qualitative statements.

MQOs specify what the QC acceptance criteria are for each analysis. A.A.C. R9-14-615 (see Appendix A) details QA requirements for ADHS licensed laboratories. Regardless of how the laboratory evaluates performance, the laboratory's acceptance criteria must meet the needs of each project. This QA Program Plan provides general requirements, but individual Site Assessment Plans or other submitted documents (see A4.2 Planning Documentation) will provide project-or site-specific requirements. Tables A1 through A3 are examples of the QC data from laboratories ADEQ typically receives.

Table A1. Typical QC data from laboratories. This is an example for water samples using EPA Method 8260B.

Compound (Laboratory Method - EPA Method 8260B)	**Matrix Spike (% Recovery Limits)**	**Laboratory Control Sample (% Recovery Limits)**	**Method Blank Result (ug/l)**	**Surrogates (% Recovery Limits)**
	Matrix Spike Duplicate (Relative % Difference)	**Laboratory Control Sample Duplicate (Relative % Difference)**	**Method Detection Limit (ug/l)**	
Benzene	68-131	68-130	ND	
	32	20	2.0	
Carbon Tetrachloride	65-147	60-150	ND	
	35	25	5.0	
PCE	67-131	70-130	ND	
	31	20	2.0	
TCE	66-132	70-130	ND	
	29	20	2.0	
Dibromofluoromethane				70-130
Toluene				70-130
4-Bromorfluorobenzene				70-130

Table A2. Typical QC data from laboratories. This is an example for soil samples using EPA Method 8310.

Compound (Laboratory Method - EPA Method 8310)	**Matrix Spike (% Recovery Limits)**	**Laboratory Control Sample (% Recovery Limits)**	**Method Blank Result (mg/l)**
	Matrix Spike Duplicate (Relative % Difference)	**Laboratory Control Sample Duplicate (Relative % Difference)**	**Reporting Limit (mg/l)**
Naphthalene	10-143	38-126	ND
	50	18	0.20
Benzo[a]pyrene	18-134	48-137	ND
	50	32	0.010
Chrysene	23-136	69-128	ND
	50	31	0.020
Dibenz[a,h]anthracene	21-137	73-130	ND
	49	31	0.010
Surrogate % Recovery Limits	2-Chloroanthracene 18-128	2-Chloroanthracene 62-124	2-Chloroanthracene 18 -128

Table A3. Typical QC data from laboratories. This is an example for water samples using EPA Method 8081A.

Compound (Laboratory Method 8081AZ)	**Matrix Spike (% Recovery Limits)**	**Laboratory Control Sample (% Recovery Limits)**	**Method Blank Result (ug/l)**
	Matrix Spike Duplicate (Relative % Difference)	**Laboratory Control Sample Duplicate (Relative % Difference)**	**Method Detection Limit (ug/l)**
4,4-DDT	10-161	61-126	ND
	20%	35%	0.007
Aldrin	10-143	43-120	ND
	20%	33%	0.009
Endrin	10-147	67-122	ND
	20%	35%	0.007
Heptachlor	10-157	51-124	ND
	20%	33%	0.008
Surrogate % Recovery Limits		Decachlorobiphen 10 -103%	
Surrogate % Recovery Limits		TCMX(S) 10-132%	

A7.1 Regulatory Action Levels

The ADEQ has authority to require owners and operators to conduct corrective/remedial actions at the site of a release. A remedial action is defined at A.R.S. § 49-281 and a corrective action is defined at A.R.S. § 49-1001. The terms are similar in that each refers to actions intended to stop, minimize and mitigate damage to the public health and the environment. Therefore, ADEQ has the authority to set action levels for soil, groundwater and surface water.

Two areas in Arizona's regulations will be discussed below. These two areas are (1) the release reporting regulations, which govern the initiation of a site cleanup project, and (2) the establishment of action levels specific to site media. These two topics are discussed below.

A7.1.1 ADEQ Release Reporting Regulations

The State of Arizona has adopted regulations that govern the reporting of releases of pollutants,

contaminants, petroleum products and hazardous substances. These regulations are contained in the A.A.C. Title 18. The enabling authority for these regulations is contained in several statutes adopted by the Arizona Legislature. Title 49 – The Environment of the Arizona Revised Statutes (A.R.S.) - contains provisions for the regulation of Water Quality, Air Quality, Solid Waste Management, Hazardous Waste Disposal and Underground Storage Tanks.

These enabling authorities allow Arizona to adopt reporting requirements that would be protective of state water resources and would also be consistent with federal hazardous waste requirements. The model for the State release reporting regulations comes from two federal sources: (1) reportable quantities of hazardous substance as contained in CERCLA and (2) reportable quantities of petroleum product described in RCRA Subchapter IX.

A7.1.2 Establishment of Media-Specific Action Levels

The ADEQ has authority to require owners and operators to conduct corrective/remedial actions at the site of a release. A remedial action is defined at A.R.S. § 49-281 and a corrective action is defined at A.R.S. § 49-1001. The terms are similar in that each refers to actions intended to stop, minimize and mitigate damage to the public health and the environment. Therefore, ADEQ has the authority to set action levels for soil, groundwater and surface water.

Remediation Standards for Soils
Remediation standards for soils are established in Arizona Administrative Code Title 18, Chapter 7 Article 2 (Soil Remediation Standards). ADEQ has three standards for soil: Background, Pre-determined and Site Specific. The Soil Remediation Standards rule is presented in Appendix D and details how each standard is established. The weblink for Soil Remediation Standards is http://www.azsos.gov/public_services/Title_18/18-07.htm.

Water Quality Standards for Groundwater and Surface Water
Remediation standards for groundwater and surface water are established in A.A.C. Title 18, Chapter 11 (Water Quality Standards). Water Quality Standards for surface water and aquifer water are established in Articles 1 and 4, respectively. The Water Quality Standards rule is presented in Appendix E. The weblink for Water Quality Standards is http://www.azsos.gov/public_services/Title_18/18-11.htm

Please note that for those chemicals that do not have an established Aquifer Water Quality Standard, the Narrative Aquifer Water Quality Standards (A.A.C. R18-11-405) apply.

A7.2 Measurement Quality Objectives and Data Quality Indicators

Analysis involves the characterization of samples based on chemical and/or physical properties. Analyses result in generating raw data from instrumental analysis, chemical analysis, or physical testing. The analytical methods used will be specific, sensitive enough to answer the question posed by the HWM objectives and meet the data quality goals associated with those objectives.

MQOs are the project or program QC criteria defined for various DQIs. During the planning phase, these set pre-determined limits on the acceptability of the data in regards to accuracy /bias, and precision, completeness and sensitivity.

ADEQ Project/Case Managers may consult with the ADEQ QA/QC Supervisor, or research a variety of published or written materials, to aid them in selecting or developing measurement technologies. The ADEQ QA/QC Supervisor shall maintain a file of in-house procedures and practices used in the measurement process. DQOs and ADEQ's QA/QC Supervisor's professional knowledge, are used to identify appropriate analytical procedures.

DQI's involve precision, accuracy, representativeness, completeness, comparability, and sensitivity, also known as "PARCCS" parameters. It is expected that these indicators be used in data evaluation, but in general, the criteria by which DQIs are evaluated are based on project data quality needs, i.e., the MQOs. The extent to which program or project QC results meets MQOs determines whether data are acceptable for the intended use.

Each DQI is defined to help interpret and assess specific data quality needs for each sample medium/matrix and for each associated analytical operation. The principals along with a brief summary of information related to assessing each DQI is given below:

Precision

Precision is the degree of agreement among repeated measurements of the same parameter under the same or similar conditions. Precision is reported as either relative percent difference (RPD) or relative standard deviation (RSD), depending on the end use of the data. Field precision is assessed through the collection and analysis of field duplicate samples. Laboratory precision is based upon laboratory matrix spike/matrix spike duplicate (MS/MSD) analyses.

Accuracy

Accuracy is the extent of agreement between an observed or measure value and the accepted reference, or true, value of the parameter being measured. For example, the objective for accuracy of the field sample collection procedures is to ensure that samples are not affected by sources external to the sample, such as sample contamination by ambient conditions or inadequate equipment decontamination procedures. Evaluating the results of equipment and trip blank samples for contamination is an assessment of sampling accuracy. For laboratories, accuracy can be assessed by determining percent recoveries from the analysis of laboratory control samples (LCSs) or standard reference materials.

Representativeness

Representativeness is a qualitative term that describes the extent to which a sampling design adequately reflects the environmental conditions of the site. It also reflects the ability of the sample team to collect samples and laboratory personnel to analyze those samples in such manners that the data generated accurately and precisely reflect the conditions at the site.

Completeness
Completeness is defined as the measure of the quantity of valid data obtained from a measurement system compared to the quantity that was expected under normal conditions. While a completeness goal of 100 percent is desirable, an overall completeness goal of 90 percent may be realistically achieved under normal field sampling and laboratory analysis conditions.

Comparability
The confidence with which one data set can be compared to another is a measure of comparability. The ability to compare data sets is particularly critical when a set of data for a specific parameter is compared to historical data for determining trends. Ensuring that property specific Site Assessment Plans are adhered to and that all samples are properly handled and analyzed will satisfy the comparability of field data.

Sensitivity
Sensitivity is the ability of a method or instrument to detect a parameter to be measured at a level of interest. For example, the sensitivity of the field instruments selected to measure temperature, pH, conductivity, and turbidity of groundwater should be measured by analyzing calibration check solutions, where appropriate, that equate to the lower end of the expected concentration range.

Sensitivity is related to the reporting limit. In this context, sensitivity refers to the capability of a method or instrument to detect a given analyte at a given concentration and reliably quantitate the analyte at that concentration. The investigator should be concerned that the instrument or method can detect and provide an accurate analyte concentration that is not greater than an applicable standard and/or screening level. Analytical results for samples that are non-detect for a particular analyte that have reporting limits greater than the applicable cleanup standards and/or screening levels cannot be used to demonstrate compliance with the applicable cleanup standards and/or screening levels.

The issue of analytical sensitivity may be one of the most difficult to address as it pertains to data usability evaluations. Samples that are contaminated with sufficient quantity of material, such that dilutions are performed, are a leading cause of reporting limits exceeding applicable criteria. However, there may be instances where such exceedances are insignificant relative to the site specific DQOs. As an example, the project may be on-going and/or other compounds are "driving" the cleanup such that not meeting applicable criteria for all compounds at that particular juncture is not an issue.

A8: Special Training/Certification

A8.1 Responsibilities

ADEQ's Program Unit Supervisors are responsible for ensuring that each staff member involved with collecting or analyzing environmental data has the necessary technical, quality assurance, and project management training required for his or her assigned tasks and functions. Section Managers are also

responsible for ensuring that technical staff maintains the necessary level of proficiency to effectively meet ADEQ's QA/QC responsibilities. ADEQ's QA/QC Supervisor will serve as the Agency resource for arranging for, and assisting in, defining QA/QC training needs on a regular basis to update Program staff with developing QA/QC issues.

A8.2 Identification of Training Needs

Core training will be coordinated through the QA/QC Supervisor in conjunction with various Division supervisory personnel. Intermediate and advanced skill training will be arranged when the appropriate Agency staff identify the need. The QA/QC Supervisor, in conjunction with Program management, will identify continuing professional training requirements and address those requirements utilizing external resources for the latest technological advances and evolution in industry standards.

A8.3 Implementation of Training Requirements

ADEQ staff members are encouraged by supervisors to draw upon their educational background, experience, technical training, and on-the-job training to enhance their understanding and performance of QA-related procedures.

ADEQ's training program will offer, or arrange for through a third-party vendor, the following courses on a schedule and frequency suited to meet the needs of ADEQ's staff with QA responsibilities:

- An Orientation to Quality Assurance Management
- Establishing Data Quality Objectives
- Preparing Quality Assurance Project Plans
- How to Perform a Preliminary Data Review
- Public and Confidential Records Management

In addition, they will be encouraged to attend meetings and seminars, and to take formal training, in accordance with ADEQ's training policy, to enhance their understanding of Program specific QA requirements within the Programs they work. ADEQ's QA/QC Supervisor will maintain a record of all QA training taken by staff and managers responsible for environmental data generation.

A9: Documents and Records

A9.1 QA Program Plan Revisions

Throughout the life of the HWM Program, there may be changes to program requirements, or modifications to the way environmental data are collected, or changes to how enforcement activities are defined. Therefore, this QA Program Plan is recognized as a dynamic document that is subject to revision, as needed. The HWM Program, technical support and QA/QC personnel will examine and revise this QA Program Plan annually, although the plan will only be resubmitted to EPA Region 9 QA manager for review once every five years or as otherwise needed. Approved revisions will be disseminated to personnel included on the Distribution List (page 6).

A9.2 Environmental Data Documentation

This QA Program Plan and referenced policy, guidance and Standard Operating Procedures (SOPs) include written procedures for all methods and procedures related to the collection, processing, analysis, reporting and tracking of environmental data. All data generated for and submitted to ADEQ's HWM Program must be of sufficient quality to withstand challenges to their validity, accuracy and legibility. To meet this objective, data are recorded in standardized formats and in accordance with prescribed procedures. The documentation of all environmental data collection activities must meet the following minimum requirements:

- Data must be documented directly, promptly, and legibly. All reported data must be uniquely traceable to the raw data. All data reduction formulas must be documented.
- All original data records include, as appropriate, a description of the data collected, units of measurement, unique sample identification, station or location identification (if applicable), name (signature or initials) of the person collecting the data, and date of data collection.
- Any changes to the original (raw data) entry must not obscure the original entry. The reason for the change must be documented, the change must be initialed and dated by the person making the change.

Other specific documentation requirements are discussed throughout this QA Program Plan and referenced SOPs.

A9.2.1 Field Documentation and Forms

Records are maintained for each field activity to ensure that samples and data are traceable and defensible. Field records will be documented on field forms or in designated field logbooks to provide a secure record of field activities, observations and measurements during sampling. Field data and observations will be recorded in real time on activity-specific data forms. Completion of appropriate field documentation and forms for each sample is the responsibility of the field personnel. Section "B5.1 – Quality Control in the Field" provides a more complete description of the types of recorded field information.

A9.2.2 Project Files

HWM personnel are responsible for the maintenance of the project file. The project file will consist of all site documents specifically listed in Section A4.2 of this QA Program Plan. Additionally, HWM personnel will collect and include in the project file all other relevant project documentation in the file. These additional documents may include any official correspondence that does not correspond to any of those previously listed documents. The project file will also include all information not related to data generation, including documentation of all public involvement or community notification efforts.

A9.3 Routine Records Management Quality Assurance

The ADEQ Records Management Process addresses the system employed by the Agency for handling documents. This plan outlines the roles and responsibilities for management and staff concerning chain of custody procedures and records management.

ADEQ document control procedures require that documents generated, or obtained, by Agency personnel be accounted for when a project is completed. ADEQ's Records Management System dictates the procedures for checking-in and checking-out files for ADEQ staff, external clients, and the public.

ADEQ management will assure that the objectives of the Records Management Process are achieved. These objectives include the following:

- Prevent the creation of unnecessary records in any media;
- Promote the continuous development of filing systems and structures that allow for the efficient organization, maintenance, and retrieval of records;
- Ensure that records of continuing value are preserved, but that valueless or noncurrent information is disposed of or transferred to storage in a timely manner in accordance with ADEQ and/or ADHS records retention requirements;
- Ensure that the acquisition and use of all direct paper to microform systems and equipment, or electronic digital imaging, are technically feasible, cost-effective, and most importantly, satisfy Program needs;
- Preserve and protect information that is vital to the essential functions or mission of the organization. Preserve and protect information that is essential to the legal rights and interests of individual citizens and the government.

GROUP B: DATA GENERATION AND ACQUISITION

B1: Sampling Design/Experimental Design

HWM Program site assessments are conducted to determine if site media are contaminated. If the initial phase of the assessment finds evidence of contamination, then follow-on phases are conducted to determine characteristics of the contamination. Characterization includes evaluating the threat posed by the contamination and determining potential solutions for cleanup of the contamination. This QA Program Plan documents the planning, implementation and assessment procedures for data generated for and submitted to ADEQ's HWM Program. It describes how specific QA and QC activities are applied throughout the course of investigations and cleanup.

A HWM Program site assessment routinely involves one or more of the following activities: a background investigation on the history of site use, a field investigation that includes sample collection and analysis, an evaluation of cleanup options and costs and an assessment of the usability of resulting data. Typically, the first step is to conduct an investigation of site history to identify past uses of the property, including types and amounts of chemicals that may have been used onsite and any disposal activities that may have contributed to contamination.

This QA Program Plan includes requirements for measurements collected for a typical HWM facility. The specific design and extent of a HWM facility site assessment will be dictated largely by the conceptual site model (CSM), the availability of resources and the required level of data quality and QC. Project-specific DQOs and sampling design should be documented in the site-specific planning documents that are developed for each HWM facility Site Assessment Plan.

The following sections describe the sampling and analysis requirements under the HWM Program. Site-specific information required in the Site Assessment Plan for each HWM Program site includes the number and location of samples, types of samples to be collected, measurement parameters, sampling frequencies, design of sampling networks for monitoring and the time period over which sampling activities are to occur. All Site Assessment Plans prepared for the HWM Program must be reviewed and approved by ADEQ HWM Program personnel.

Section B5.1 has additional discussion on sampling and equipment decontamination procedures.

B1.1 Sampling Design

A sampling design specifies the number and location of samples to be collected at a site. Sampling design strategies are guided by study objectives and should factor in the conditions unique to the site being considered for redevelopment, including data gaps in the CSM, exposure potential, projected site reuse and available resources. As noted above, possible sampling design strategies are identified during the DQO process, and the details of the sampling design strategy are described in the site-specific Site Assessment Plan.

Typical designs for the collection of samples at HWM Program sites include biased sampling, statistically based sampling, one-time events and ongoing (multi-phase) events. Biased sampling specifies sampling locations based on the judgment of the field team leader and sampling plan designer. Statistically based

sampling designs use random or systematic sampling locations designed to avoid bias. A single sampling event may not provide an adequate characterization of the contamination onsite, especially when the CSM contains significant data gaps. In these situations multi-phase sampling may be helpful. The need for this sort of investigation should be identified during the DQO process.

Additional information on the development of sampling strategies is available in EPA's 2002 Guidance on Choosing a Sampling Design for Environmental Data Collection, EPA's 2006 Guidance on Systematic Planning Using the Data Quality Objectives Process and EPA's 2007 Guidance for Developing Standard Operating Procedures.

B1.1.1 Sample Types and Matrices

Sample types typically include surface soil, subsurface soil, groundwater and surface water. Some sites require sampling of sediment, pore water, sludge, air (soil gas or vapors) and other non-routine matrices such as building materials. Samples may be collected as discrete (grab) or composite samples. Discrete samples are useful for identifying and quantifying chemicals in areas of a site where contamination is suspected. The number of discrete samples should be determined during the DQO process. Composite samples are useful for identifying the average concentrations of contaminants across a site. Composite samples are composed of more than one discrete sample collected from different locations; the samples are mixed into a single homogeneous sample and submitted to the analytical laboratory as a single sample. Multi-increment (MI) samples represent a specific type of composite sample (see Incremental Sampling Methodology, ITRC February 2012 http://itrcweb.org/ism-1/). The number of composite samples and the number of individual samples within a composite sample should be based on the goals established during the DQO process.

Background samples should be collected from the same media as site samples, from areas on or near the site that are unlikely to be contaminated by site-related chemicals. Background samples are analyzed for the same parameters as the site samples to establish background concentrations of chemicals. Typically, background data are collected for naturally occurring inorganic chemicals, such as metals, whereas the background concentrations of manmade organic chemicals are assumed to be zero. It is the responsibility of the applicant to demonstrate if there is an "anthropogenic background" for organic chemicals that is unrelated to site activities.

B1.1.2 Sampling Locations and Frequencies

The sampling locations and the schedule for sampling are also specified during the DQO planning process. The duration over which samples are collected and the frequency of sampling or whether the work will be done in phases is also determined during the DQO process. For instance, if initial investigations indicate that contaminant levels in soils are below cleanup standards, no additional sampling would be required. If initial investigations indicate contaminant levels in soils are above cleanup standards, additional sampling would be required during remedial activities and/or post remedial activities.

B1.1.3 Parameters of Interest

The measurements to be collected at a site depend on the characteristics and history of the site. This QA Program Plan provides QA/QC information for parameters and media typically analyzed for HWM Program sites. Unusual parameters and matrices will necessitate preparation of a site-specific Site Assessment Plan. This topic is discussed in more detail in Section B2 of this QA Program Plan.

B1.1.4 Sampling Event Planning

Advance planning for field sampling events is required to ensure that the necessary arrangements are in place and that equipment is ready. The following will be considered when planning the sampling event:

1) Sample Handling and Custody Procedures — Field personnel will make arrangements with the appropriate laboratory for proper sample containers and custody procedures (described further in Section B3).

2) Equipment — Prior to collection of any sample, field personnel will ensure that all sampling equipment has been properly assembled, decontaminated, calibrated and is functioning properly prior to use. Equipment will be used according to manufacturer's instructions, and should generally be decontaminated according to the EPA SOP-Sampling Equipment Decontamination (see Appendix F of this QA Program Plan).

3) Field Forms — Field personnel will need to ensure that all necessary field forms, such field log books, soil and groundwater sampling forms and boring logs are assembled prior to the sampling event. Such field forms will be developed individually for each site based on the site's specific needs (see Appendix G of this QA Program Plan).

4) Health and Safety — Field personnel will ensure that all site-specific health and safety procedures are considered, and that personal protective equipment (PPE) is gathered.

5) Investigation-Derived Waste — Field personnel will plan for the generation of investigation-derived waste (IDW), and should assemble the appropriate IDW containers prior to the sampling event.

6) Field Audits — Field personnel will plan to conduct periodic field system audits for ongoing sampling events.

7) Paperwork and Permits — Field personnel will also ensure prior to the sampling event that other applicable paperwork is in order, such as permits and access agreements.

B2: Sampling Methods

Site-specific sampling methods as well as the numbers and types of samples are specified during the DQO process and documented in the site-specific Site Assessment Plan. Details of sample collection methods will depend upon site conditions, equipment limitations, chemicals of concern, sample matrices and cost, and will be described in a site-specific Site Assessment Plan. Collection methods will follow an ADEQ or EPA approved sampling protocol, unless unforeseen circumstances do not allow for an approved collection method. The following sections present general information on sampling methods for various media, including surface water, groundwater, drinking water, soil, sediment, pore water, sludge, air and non-routine matrices, such as building materials.

Additional methods may be used with approval of the HWM Program. General guidelines for field sampling are included in the EPA Standard Operating Procedure (SOP) on General Field Sampling Guidelines (see Appendix F). EPA SOPs for field sampling methods are available for download at http://www.ert.org/mainContent.asp?section=Products&subsection=List .

B2.1 Soil Samples

Soil samples collected at HWM Program sites may include surface and subsurface samples. Sample types may be discrete or composite samples. There are a variety of acceptable methods for collection of soil samples, and selection of an appropriate method will depend on site conditions and the sampling design. Methods commonly used to collect soil samples include drilling soil borings, digging test pits, sampling via hand auger and digging with a shovel or trowel. Additional information on the collection of soil samples can be found in EPA's Preparation of Soil Sampling Protocols: Sampling Techniques and Strategies (1992) and in the referenced EPA SOP for soil sampling (see Appendix F of this QA Program Plan).

B2.2 Groundwater Samples

Samples of groundwater may be collected during HWM Program site assessments and cleanups. Collection of groundwater samples may be one-time or ongoing and periodic. Groundwater samples can be collected from soil borings, temporary well points, monitoring wells and existing wells (e.g., municipal or community supply wells, domestic water wells, irrigation wells, or industrial supply wells). Groundwater samples may also be collected from shallow, intermediate, deep and perched aquifers.

Groundwater samples collected using soil borings allow for the collection of one-time discrete groundwater samples at a specific depth interval at a point in time. One-time groundwater samples are often used to help select locations for future monitoring wells. These one-time samples may be collected using a direct-push method, which is described in the SOP for direct-push groundwater sampling (see Appendix F of this QA Program Plan).

Groundwater samples may also be collected from permanently installed monitoring wells. All monitoring wells should be properly installed according to state regulations (see A.R.S. Title 45, Chapter 2, Article 10) and developed according to an Arizona Department of Water Resources (ADWR), ADEQ or EPA-approved protocol. Non-standard wells or problems encountered during well installation and sampling should be noted in the field logbook and in subsequent reports. Collection of groundwater samples from

monitoring wells is described in the EPA SOPs for groundwater well sampling, monitoring well installation and monitoring well development (see Appendix F of this QA Program Plan).

The following procedures should be employed when sampling residential water supplies or water-supply wells of any kind:

- Obtain permission to access property and obtain samples for analysis
- Inspect the water system to locate the tap nearest to the wellhead. Samples should be collected prior to any treatment units (e.g., ultra-violet light, reverse osmosis, etc.) if possible.
- Purge the water lines to flush the plumbing and holding tanks before collecting samples from drinking water, irrigation, or industrial wells, so that the sample collected is as representative as possible. Remove any faucet aerators and reduce water flow before collecting samples.

B2.3 Surface Water Samples

Surface water sampling may be conducted during HWM Program site assessments and cleanups to evaluate whether contaminants have migrated to nearby surface water bodies. Physical evidence such as odors, organic films on water surfaces and soil discoloration in the vicinity of surface water are indicators of possible contamination. Surface water samples include representative liquid samples collected from streams, brooks, rivers, lakes, ponds, lagoons, seeps, estuaries, drainage ways, sewers, channels, wetlands, surface water impoundments and other surface water bodies. These samples can also be collected from the surface or at depth within the water body. Surface water samples will be collected in general accordance with the EPA SOP for surface water sampling (see Appendix F of this QA Program Plan).

B2.4 Pore Water Samples

Pore water is water contained within the upper few centimeters of sediments just below the surface water/sediment interface. This interface is known as the hyporheic zone. Sampling of this zone can be done with equipment such as seepage meters and push-point pore water samplers or lysimeters. Discharge of groundwater to surface water through the hyporheic zone is unlikely to be homogeneous; therefore, determining locations for pore water sampling can involve additional investigative steps.

B2.5 Sediment Samples

Sediment samples can be collected for analysis of biological, chemical, or physical parameters. There are many factors to consider when choosing sediment sampling equipment, including, but not limited to, site access, sample volume requirements, sediment texture, target depth for sediment collection and flowing versus standing water. In general, piston samplers are best used for soft, fine-grained sediments where sediments at depth are required. Grab/dredge samplers are best for coarse, shallow sediments and where large volumes of sediment are required. Additional information on the collection of sediment samples is provided in EPA's SOP for sediment sampling (see Appendix F of this QA Program Plan).

B2.6 Sludge Samples

Sampling of sludge could involve a number of different situations and will likely depend upon site conditions. Therefore, details of collecting sludge samples will be described in a site-specific Site Assessment Plan. Common settings where sludge is sampled include catch basins and drywells.

B2.7 Air/Soil Vapor Samples

Air sampling is typically conducted at sites where vapor inhalation may be an exposure issue with regards to contaminants. Soil vapor samples are routinely collected to investigate releases of VOCs. Air sampling and soil vapor sampling is more complex than soil or water sampling because of the reactivity of chemical compounds in the gas matrix and sample interaction with the sampling equipment and media. Air and soil vapor sampling equipment is selected based on a number of factors including site conditions, sampling objectives, chemicals of concern, analytical methods and cost. Methods to sample air at active facilities include (but are not limited to) soil gas sampling or sampling with flux chambers. Typical sampling containers include tedlar bags, stainless steel Summa canisters, gas tight syringes and glass sorbent traps used with sampling pumps. More information on air and soil vapor sampling and analysis can be found at: http://www.airtoxics.com in EPA's SOP for general air sampling guidelines (Appendix F) and ADEQ's Soil Vapor Sampling Guidance (http://www.azdeq.gov/environ/waste/download/svsg.pdf).

B2.8 Building Materials Samples

Because sampling at HWM Program sites can involve non-routine sampling of unusual sample matrices, such as building materials. These matrices include concrete slabs or other types of building materials. Site-specific sample collection procedures will be developed, if needed, for sampling such non-routine matrices. Sampling personnel will coordinate with the analytical laboratory on the anticipated sample collection and handling methods to ensure that the sample data will meet all QA/QC requirements. Additional information on the collection of non-routine sample matrices is in EPA's SOP for chip, wipe and sweep sampling (see Appendix F of this QA Program Plan).

B3: Sample Handling and Custody

Chain of custody procedures differ among laboratories. Title 9, Chapter 14, Article 6 of the Arizona Administrative Code (R9-14-615) details the necessary documentation for sample control activities at an ADHS licensed laboratory. Custody procedures of the analyzing laboratory are identified prior to field activities. Field personnel must make arrangements with the appropriate laboratory for proper sample containers, preservatives, holding times and chain of custody forms. The custody of a sample must be traceable from the time of sample collection until results are reported. Chain of custody procedures provide a mechanism for documenting information related to sample collection and handling. A chain-of-custody form must be completed after sample collection and prior to sample shipment or release. The chain-of-custody form, sample labels and field documentation must be crossed checked to verify sample identification, date and time sample was collected, type of analyses, number of containers, sample volume, preservatives and type of containers. Additional information on sample handing and custody procedures can be found in EPA's SOPs for specific sample collection methods. SOPs and forms for sample handling, custody (chain-of-custody forms) and transport are referenced in Appendix F of this QA Program Plan.

B4: Analytical Methods

All analytical methods used to analyze samples must comply with relevant requirements of applicable federal or state programs for which they were collected, such as the CWA, SDWA, RCRA, Clean Air Act, or use other EPA-approved alternate methods. The most recently approved methods under the CWA and SDWA were promulgated in 40 CFR Part 136 on July 21, 2003. Currently approved methods under RCRA SW-846 can be obtained from the EPA website at http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm. Exhibit 1 of Title 9, Chapter 14 of the Arizona Administrative Code details ADHS approved methods with corresponding analytes.

Table B1 lists the classes of analytes that are typically of the greatest interest during HWM Program site assessments, as well as the ADEQ's preferred analytical methods. This table provides a starting point for selecting analytical methods for HWM Program site assessments. Additional methods may be available and appropriate; consult with the HWM Program or Exhibit 1 of Title 9, Chapter 14, Article 6 (http://www.azsos.gov/public_services/Title_09/9-14.htm) of the Arizona Administrative Code for alternate methods. The site-specific Site Assessment Plan should identify analytical methods and equipment, decontamination procedures, waste disposal requirements and performance requirements.

B5: Quality Control

QC requirements are integral to the success of a QA program. QC covers the overall system of technical activities that measure the performance of a process against defined standards to verify that they meet predefined requirements. Because errors can occur in the field, laboratory, or office, it is necessary for QC to be part of each of these functions. This QA Program Plan describes and defines the general quality objectives of the HWM Program. Site-specific quality objectives are further defined in project-specific Site Assessment Plans. This approach to quality system management ensures that quality activities are conducted throughout the data generation process, but allows for the flexibility to tailor quality-related activities to individual site specific data needs, depending on the complexity of the HWM Program site.

QA and QC parameters apply to the two primary types of data — definitive and non-definitive data — regardless of whether the data collection activity is associated with field measurements or laboratory measurements. Non-definitive data are frequently collected during the first stage of a multi-phase screening assessment, using rapid, less precise methods of analysis with less rigorous sample preparation. Non-definitive data can provide analyte identification and quantification, although both may be relatively imprecise. Typically, 5 to 10 percent of non-definitive samples or all critical samples are confirmed using analytical methods, QA/QC procedures and criteria associated with definitive data. Non-definitive data without associated confirmation data are of unknown quality. Qualitative, non-definitive data identify the presence of contaminants and classes of contaminants and can help focus the collection of definitive data, which is generally the more expensive of the two. Some data uses, such as risk assessments, require definitive data.

SOPs for data collection should be developed following “Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations” (EPA 1995). SOPs should be included as an appendix of all Planning Documents and Reports (see Figure A2) generated for and submitted to ADEQ’s HWM Program. The project field team should document reasoning for any deviations from an SOP and include

that documentation in all Planning Documents and Reports (see Figure A2) generated for and submitted to ADEQ's HWM Program.

B5.1 Quality Control in the Field

QC parameters should be described in detail for each step of field work and should also include specific corrective actions to be taken if difficulties are encountered in the field. Evaluation of field sampling procedures requires the collection and evaluation of field QC samples. Trip blanks, rinsate blanks, field duplicates and extra volume for matrix spikes and matrix spike duplicates will be collected and submitted to the analytical laboratory to provide a means of assessing the quality of data resulting from the field sampling program. Collection frequencies for field QC samples are noted in subsequent paragraphs contained in this section of this QA Program Plan.

Field QC requirements and documentation of all field sampling and observations are critical for providing a historical record for analysis of the usability of the data produced. The official field log book will contain documentation of field activities that involve the collection and measurement of environmental data. Additional forms may be used in the field to record related activities as explained below.

SOPs delineate the step-by-step approach that field personnel must follow in collecting samples, taking field measurements, decontaminating equipment, handling IDW and calibrating instruments. Most qualified sampling contractors and State and Federally certified laboratories develop SOPs and analytical methods as part of their overall QA program. SOPs should be developed following "Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations" (EPA 1995). SOPs should be included as an appendix of all Planning Documents and Reports (see Figure A2) generated for and submitted to ADEQ's HWM Program. The project field team should document reasoning for any deviations from an SOP and include that documentation in all Planning Documents and Reports (see Figure A2) generated for and submitted to ADEQ's HWM Program.

Non-disposable equipment used for sample collection must be cleaned according to the specific procedures documented in each sampling SOP. Sampling SOPs will be prepared by the group responsible for sampling and will be submitted to HWM Program for review and approval as part of the sampling plan. All sampling tools will be decontaminated before sampling begins and between sample locations. Soil and water sampling tools, including stainless-steel spoons, bowls, hand augers, split spoons, pumps and Hydropunch equipment, will be decontaminated by scrubbing in a solution of potable water and nonphosphate detergent (Alconox or Liquinox). EPA SOPs call for use of a 10 percent nitric acid (for metal analytes) or a solvent such as acetone for organic compound analytes (see Appendix F). The tools are then double-rinsed with distilled water. Sampling tools that are not used immediately after decontamination will be allowed to air dry and wrapped in aluminum foil. Larger equipment, such as the drilling rods and augers, will be decontaminated between boring locations. A temporary decontamination pad will be constructed near the site and a high-pressure steam cleaner will be used to clean the end of the rig and all augers, drill rods and core samplers. Decontamination fluids will be placed in containers and disposed of in accordance with the procedures outlined in the SOP for IDW.

B5.1.1 Field Instrument/Equipment Inspection and Calibration

Sampling and analysis generally requires the use of different pieces of equipment and tools in the gathering of environmental data. A field preventive maintenance protocol involves ensuring that all field equipment has been properly calibrated, charged and inspected prior to and at the end of each working day and that replacement parts are available.

All field equipment needs to be inspected to determine if it is adequate and appropriate for the media, parameters and tests to be performed. Data may be generated onsite through the use of real-time equipment, such as photoionization detectors (PIDs), organic vapor analyzers and pH meters. A more detailed analysis may call for relevant to later assessments of the usability of data generated by a mobile laboratory.

For field-testing and mobile laboratories, the team should track the transfer of samples and equipment should be examined to ensure that it is in working condition and properly calibrated. The calibration of field instruments should be performed according to the method and schedule specified in an SOP, which is usually based on the manufacturer's operating manual. Calibration of field equipment should be performed more often than specified in the SOP if equipment is used under adverse or extreme field conditions.

B5.1.2 Field Documentation

The field team should record field activities in indelible ink, in a permanently bound notebook with pre-numbered pages or on a preprinted form. For each sampling event, the field team must provide the site name, physical location, date, sampling start and finish times, names of field personnel, level of protection, documentation of any deviation from protocol and signatures of field personnel. For individual samples, field teams should ensure that field logbooks document the exact location and time the sample was taken, any measurement made (with real-time equipment), a physical description of the sample, sample ID number, sampling depth, sample volume and type of sample and the equipment used to collect the sample. This information can be critical to later evaluations of the resulting data's usability.

Complete and accurate documentation is essential to demonstrate that field measurement and sampling procedures are carried out as described in this QA Program Plan or the Site Assessment Plans. Field personnel will use permanently bound field logbooks with sequentially numbered pages to record and document field activities. The logbook will list the contract name and number, the project name, the site name, and the names of subcontractors, the service client and the project manager. At a minimum, the following information will be recorded in the field logbook:

- Name and affiliation of all on-site personnel or visitors
- Weather conditions during the field activity
- Summary of daily activities and significant events
- Notes of conversations with coordinating officials
- References to other field logbooks or forms that contain specific information

- Discussions of problems encountered and their resolution
- Discussions of deviations from the Site Assessment Plans or other governing documents
- Description of all photographs taken

The contractors performing field work are expected to develop field forms to record field activities.

Individual samples should be labeled in the field. Labels should include sample location, sample number, date and time of collection, sample type, sampler's name and method used to preserve the sample, if applicable. Sample preservation involves the treatment of a sample usually through the addition of a compound that adjusts pH to retain the sample properties, including concentrations of substances, until it can be analyzed. The field team should create a table listing the total number of samples, types of sample matrices, all analyses planned for each sample differentiating critical measurements and other information that may be relevant to later assessments of the data usability.

B5.1.3 Trip Blanks

Trip blank samples are used to evaluate whether the shipping and handling procedures are introducing contaminants into the samples or if cross-contamination in the form of migration of VOCs between the collected samples. One trip blank will be submitted to the laboratory for analysis each day that samples are collected. Trip blanks for soil and water samples are VOA vials filled with purged deionized water that are transported to the field and then returned to the laboratory without being opened.

B5.1.4 Rinsate Blanks

Rinsate blanks are collected to evaluate the potential for cross-contamination of samples during collection. Rinsate blanks will be collected at a rate of one per day per matrix when non-dedicated and non-disposable sampling equipment is used in the field. Equipment rinsate blanks will be obtained by passing organic-free water through or over the decontaminated sampling equipment and collecting the rinse water in appropriate sample containers.

Rinsate blanks will be analyzed for the same parameters as the associated field samples. Rinsate blanks should not contain detectable concentrations of target analytes greater than the PRQL for the compound. Any detection of target analytes in a rinsate blank will result in an investigation to determine effect on overall data usability, and affected results will be qualified as estimates or as nondetects at an elevated PRQL as appropriate.

B5.1.5 Field Duplicate Samples

Field duplicate samples of water and air samples are samples that are collected simultaneously in separate containers. The purpose of field duplicates is to allow evaluation of the contribution of random error from sampling to the total error associated with the data. One set of field duplicates will be collected and submitted for every twenty field samples collected (and at least one per sampling day if less than twenty are collected) for water, soil and air. Field duplicate precision will be evaluated as described below.

B5.1.6 Matrix Spike/Matrix Spike Duplicates (Field Requirements)

Double sample volume should be collected at a rate of one per twenty samples per matrix (minimum of once per sampling event) to ensure that the laboratory has sufficient volume to perform matrix spikes and matrix spike duplicates (MS/MSDs).

B5.1.7 Inter-laboratory Split Samples (Field Requirements)

Inter-laboratory split samples are field duplicates (liquid matrices) or split samples (solid matrices) that are submitted to both the primary laboratory and a secondary or QC laboratory. Inter-laboratory split samples are collected simultaneously with a sample from the same source under identical conditions into separate containers. Results from the split samples are used to assess laboratory performance by comparison of qualitative and quantitative results from the two laboratories, including indications of matrix interferences such as elevated PRQLs. In order to provide useful information, however, the split sample must be directly associated with the original (primary) sample to evaluate laboratory performance. The association will be determined by field personnel and maintained during the data import process.

B5.2 Quality Control in the Laboratory

Compliance monitoring on ADHS licensed laboratories is conducted by the Arizona Department of Health Services (ADHS) as described in Title 9, Chapter 14, Article 6 of the Arizona Administrative Code (A.A.C. R9-14-605 – Compliance Monitoring). ADEQ also conducts Technical Systems Audits on ADHS licensed laboratories (ADEQ contract laboratories and contract laboratories of contractors who submit analytical data to ADEQ). The primary goals of TSAs will be to review the laboratory organization, operation, and capabilities; determine the reliability of data; and note corrective action for any apparent deficiencies. Auditors for TSAs will be selected by the ADEQ QA/QC Supervisor based on their technical proficiency in the subject area. The designated auditors will be responsible for planning and conducting the audit, and reporting the findings to the laboratory manager and to the ADEQ QA/QC Supervisor.

B5.3 Data Quality Indicators (DQIs)

Identifying DQIs and establishing Quality Control (QC) samples and Measurement Performance Criteria (MPC) to assess each DQI, as introduced in Section 1.7, are key components of project planning and development. These components demonstrate an understanding of how "good" the data need to be to support project decisions, and help to ensure there is a well-defined system in place to assess that data quality once data collection/generation activities are complete.

When faced with addressing data quality needs in a Site Assessment Plan, one of the first terms you may come across is DQIs. DQIs (Precision, Accuracy/Bias, Representativeness, Comparability, Completeness, and Sensitivity) include both quantitative and qualitative terms. Each DQI is defined to help interpret and assess specific data quality needs for each sample medium/matrix and for each associated analytical operation. Section A7.2 of this QA Program Plan explains the principals along with a brief summary of information related to assessing each DQI. In addition to Section A7.2 of this QA Program Plan, ADEQ has established the following policies, procedures, and/or guidance for sample collection and analytical techniques. These procedures, where relevant, apply to all analytical data being generated for use by the

HWM Program. These procedures should be followed unless special exceptions have been requested and approved, and/or deviations are outlined in a HWM Program Site Assessment Plan. The following documents can be found in their entirety in Appendix G.

- ADEQ Temperature/Preservation Guidance;
- Substantive Policy 0154 - Addressing Spike And Surrogate Recovery As They Relate To Matrix Effects In Water, Air, Sludge And Soil Matrices Policy; and
- Substantive Policy 0170 - Implementation of EPA Method 5035 - Soil Preparation For EPA Method 8015B, 8021B and 8260B.

B6: Instrument/Equipment Testing, Inspection and Maintenance

All field and laboratory analytical instruments and equipment will be tested, inspected and maintained according to the manufacturer's guidelines and recommendations. Data collected from improperly functioning equipment will not be used.

Records for equipment testing, inspection and maintenance will be maintained in a bound logbook for each piece of equipment. The date, time, name of inspector, what was inspected and the results of testing and inspection will be recorded in the logbook. All equipment or systems requiring periodic maintenance will be inspected.

Preventive maintenance for most field equipment is carried out in accordance with procedures and schedules recommended in (1) the equipment manufacturer's literature or operating manual, or (2) SOPs that describe equipment operation associated with particular applications of the instrument. However, more stringent testing, inspection and maintenance procedures and schedules may be required when field equipment is used to make critical measurements.

A field instrument that is out of order will be segregated, clearly marked and not used until it is repaired. The field team leader will be notified of equipment malfunctions so that service can be completed quickly or substitute equipment can be obtained. When the condition of equipment is suspect, unscheduled testing, inspection and maintenance should be conducted. Any significant problems with field equipment will be reported in the daily field QC report.

The equipment testing, inspection and maintenance logs for all contractor equipment must be made available to the HWM Program upon request.

B7: Instrument/Equipment Calibration and Frequency

Calibration of all analytical instrumentation is required to ensure that the analytical system is operating correctly and functioning at the sensitivity that is required to meet project-specific DQOs. Each instrument will be calibrated with standard solutions appropriate to the instrument and analytical method, in accordance with the methodology specified and at the QC frequency specified in laboratory or field sampling SOPs.

B7.1 Field-Based Instruments

Field equipment, if used, will be calibrated at the beginning of the field effort and at prescribed intervals. The calibration frequency depends on the type and stability of equipment, the intended use of the equipment and the recommendation of the manufacturer. Detailed calibration procedures for field equipment are available from the specific manufacturers' instruction manuals, and general guidelines are included in SOPs. All calibration information will be recorded in a field logbook or on field forms. A label that specifies the scheduled date of the next calibration will be attached to the field equipment. If this type of identification is not feasible, equipment calibration records will be readily available for reference. Field-based analytical instruments, such as turbidometers and pH electrodes must be calibrated following manufacturers' instructions and frequency recommendations (or following appropriate SOPs) before they may be used for collecting data.

B7.2 Laboratory Instruments

Calibration and maintenance of analytical instruments will be conducted in accordance with the QC requirements identified in each laboratory SOP and in QA manuals, along with the manufacturers' instructions. General requirements are discussed below.

The history of calibration and maintenance for instruments in the subcontract laboratory is an important aspect of the project's overall QA/QC program. As such, all initial and continuing calibration procedures will be implemented by trained personnel following the manufacturer's instructions and in accordance with applicable EPA protocols to ensure the equipment is functioning within the tolerances established by the manufacturer and the method-specific analytical requirements.

The laboratory will obtain calibration standards from commercial vendors for both inorganic and organic compounds and analytes. Stock solutions for surrogate standards and other inorganic mixes will be made from reagent-grade chemicals or as specified in the analytical method. Stock standards will also be used to make intermediate standards that will be used to prepare calibration standards. Special attention will be paid to expiration dating, proper labeling, proper refrigeration and freedom from contamination. Documentation on receipt, mixing and use of standards will be recorded in the appropriate laboratory logbook. Logbooks must be permanently bound. Additional specific handling and documentation requirements for the use of standards may be provided in subcontractor laboratory QA plans.

The verification standards for initial calibrations should be analyzed after the instrument calibration to verify the preparation and concentration of the calibration standards. The verification standards for continuing calibrations should be analyzed (as per method requirements) to verify the calibration of the analytical system over time.

Analytical balances will be calibrated annually according to manufacturer's instructions and have a calibration check before each use by laboratory personnel. Balance calibration shall be documented in hardbound logbooks with pre-numbered pages.

All refrigerators and incubators will be monitored for proper temperature by measuring and recording internal temperatures on a daily basis. At a minimum, thermometers used for these measurements will be calibrated annually, according to manufacturers' instructions.

The subcontract laboratories will maintain an appropriate water supply system that is capable of furnishing ASTM Type II polished water to the various analytical areas.

B8: Inspection/Acceptance of Supplies and Consumables

The laboratory shall inspect supplies and consumables prior to their use in analysis. The description of materials provided in the method shall be used as a guideline for establishing the acceptance criteria for these materials. Purity of reagents shall be monitored by analysis of LCSs. An inventory and storage system for these materials shall assure use before manufacturers' expiration dates and storage under safe and chemically compatible conditions.

Analytical laboratories are required to provide certified clean containers for all analyses. These containers must meet EPA standards described in EPA's 1992 "Specifications and Guidance for Obtaining Contaminant-Free Sampling Containers".

Procedures for receiving supplies and consumables in the field are similar. When supplies are received, the project manager or field team leader will log the supplies into a supply logbook and then inspect all items against the acceptance criteria. Any deficiencies or problems will be noted in the field logbook, and deficient items will be returned for immediate replacement.

B9: Non-direct Measurements

Environmental data generation typically involves planning, sampling, analysis, assessment and data review. In planning their investigations, project teams generally use existing data to develop sampling designs and to decide how much and what type of data to collect. The term existing data is used interchangeably with "secondary data" and "non-direct measurements". Existing data may come from a number of sources, including other studies, government databases, etc. The original purpose for collecting these secondary data may be very different from that of the current investigation. Also, these secondary data may have been collected using different sampling methods (composite vs. grab, random vs. hot spot sampling), and/or analytical methods than those selected for the current investigation.

Basing decisions on existing data may result in errors if secondary data were not generated for the same purpose or using the same methods as the current investigation. Data could be biased and final conclusions could be impacted.

Therefore, before using secondary data, project team members should evaluate the data to identify any limitations on their use. Also, to ensure transparency in decision making, criteria and reasons for ***including*** and ***excluding*** certain data from use must be clearly documented. Failure to clearly document why data are included or excluded can result in the appearance of biased data selection and diminish the product's credibility.

Project personnel should describe the processes for selecting and for evaluating existing data in the quality assurance plan in accordance with ***EPA Requirements for Quality Assurance Project Plans*** QA/R-5 http://www.epa.gov/quality/qs-docs/r5-final.pdf.

For an in-depth discussion on when and how to use existing data in environmental projects, refer to EPA Guidance for Quality Assurance Project Plans QA/G-5 "Chapter 3: Projects Using Existing Data" http://www.epa.gov/quality/qs-docs/g5-final.pdf.

Sources of secondary data include the following:

- Environmental indicator data obtained from federal/state/local databases and records
- Existing sampling and analytical data from a previous investigation of the area
- Computer model simulations and applications pertaining to other studies
  Historical data (e.g., from organization's/facility's corporate records and/or federal/state local records pertaining to previous monitoring events, site assessments, investigations, etc.)
- Background information/data from organization's/facility's corporate records and/or federal/state/local records pertaining to site-specific industrial processes, process by-products, past and current chemical uses, raw material and finished product testing, waste testing and disposal practices, and potential chemical breakdown products
- Data generated to verify innovative technologies and methods
- Data obtained from computer databases (such as manufacturers' process/product information, waste management or effluent information, and EPA or state data bases)
- Literature files/searches
- Publications
- Photographs
- Topographical maps
- Meteorological data

B10: Data Management

Field data generated for ADEQ's HWM Program, such as sample ID and latitude/longitude coordinates, should be recorded on field data sheets or hand-held computers. Field data are reported to the Project Manager through submission of field notebooks or field sampling data sheets, if used, by contractor field staff.

Laboratory analytical reports will include QC results and any other necessary analytical information, enabling reviewers to determine data quality. Laboratory data should be submitted to the ADEQ Project Manager in both printed and electronic form. Rapid turnaround data from the laboratory are reported to the Project Manager, if requested, but rapid turnaround is generally not required. Copies of field logs, a copy of chain-of-custody forms, original preliminary and final lab reports and electronic media reports must be kept for review by the ADEQ. The field crew must retain original field logs. The contract laboratory shall retain chain-of-custody forms. The contract laboratory will retain copies of the preliminary and final data reports.

Table B1. Common Contaminants at HWM Facilities and Recommended Methods for Analysis of Soil, Groundwater or Materials Samples

Laboratory Analytical Methods for Investigations			
Test Method →	EPA Method 8260B	EPA Method 8310 or 8270 SIM	See Footnote 3
Products			
VOCs[1,2]	X		
SVOCs		X	
Metals			X
Organochlorine Pesticides	EPA Method 8081A		

Footnotes:

1. Soil gas samples to be collected when analysis from soils are not expected to yield results that would be a satisfactory demonstration of whether or not a Product Type was released into the environment (e.g. soil has coarse lithology). The analytical method should be TO-15.
2. VOCs are to be analyzed using the current EPA Method 8260B (full list). For UST systems in place during 1996 or before, EPA Method 504.1 should be used to investigate for the presence of EDB (water only).
3. Metals to be analyzed are: arsenic, cadmium, chromium (total), lead and mercury. Use EPA methods 6000 and 7000 series for the analyses. Make a due diligent effort to obtain the background levels of the metals analyzed for comparison purposes.

Abbreviations: VOC = volatile organic compounds; SVOCs = semi-volatile organic compounds

Please note that when requesting compound specific analyses and the sample is petroleum based, the laboratory will be informed as such.

GROUP C: ASSESSMENT AND OVERSIGHT

C1: Assessments and Response Actions

Assessment and response actions are part of the quality system for ensuring and documenting that the procedures required by this QA Program Plan are being followed during the generation of data that will be included in all Planning Documents and Reports (see Figure A2) generated for and submitted to ADEQ's HWM Program.

C1.1 Purpose/Background

During the planning process, many options for sampling, sample handling, sample analysis and data reduction are evaluated. Selection of specific options depends on the nature of the corrective action or monitoring activity. This section of the QA Program Plan describes the internal and external checks necessary to ensure that all elements are correctly implemented. In addition, checks are needed to ensure that the quality of the data is adequate and that corrective actions are implemented in a timely and effective manner. Documenting all internal assessments is a critical component of the quality system.

C1.2 Assessment Activities and Program Planning

ADEQ employs several QA assessment tools designed to provide a better understanding of the components of, and the basis for improving, the ADEQ Quality Management System. Internal (Programmatic) and External QA audits are one of the principal tools for determining the effectiveness of the ADEQ QA/QC components. QA audit frequency and scheduling will vary with the type of review conducted.

C1.2.1 Assessment of Subsidiary Organizations

A. Management System Reviews (MSRs)

An MSR is an independent assessment of a Program's QA management practices and data collection procedures, and is generally performed by the ADEQ QA/QC Supervisor. The MSR will qualitatively assess a program to determine if the ADEQ Quality Management System is adequate to ensure the quality of the Program's data. MSRs address the effectiveness of management controls in achieving and assuring data quality, the adequacy of resources and personnel devoted to QA functions, the effectiveness of training and assessments, and the applicability of data quality requirements. While MSRs can identify significant QA concerns and areas of needed improvement, they also point out noteworthy accomplishments.

Most MSRs will examine the following elements:

- An assessment of the overall effectiveness of the QA management system, as measured by its adherence to the approved QMP
- Procedures for developing Data Quality Objectives (DQOs);
- Procedures for developing and approving QA Program Plans and QAPjPs;
- The effectiveness of existing QA Program Plan guidance and QAPjPs;

- Procedures for developing and approving SOPs;
- Procedures, criteria, and schedules for conducting QA audits;
- Tracking systems for assuring that the QA Program is operating effectively, and that corrective actions disclosed by QA audits have been taken;
- Responsibilities and authorities of various line managers, and QA personnel, for implementing the QA program;
- The degree of management support;
- The level of financial and other resources committed to implementing the QA Program

MSRs performed or arranged by the ADEQ QA/QC Supervisor will be conducted in accordance with EPA's 2003 Guidance on Assessing Quality Systems (Management Systems Review Process).

The reviews for the individual ADEQ Quality Assurance Programs are intended to accomplish the following objectives:

- Identify any data quality problems;
- Identify benchmark practices that could be used in other Agency Programs;
- Propose recommendations for resolving quality problems;
- Confirm implementation and effectiveness of any recommended corrective actions.

C1.2.2 Assessment of Program Activities

Technical Systems Audits (TSAs)
A Technical Systems Audit is conducted to assess the sampling and analytical quality control procedures used to generate environmental data. TSAs entail a comprehensive, on-site evaluation of the field equipment; sampling and analyses procedures; documentation; data validation; and training procedures for collecting or processing environmental data.

Both laboratory and field TSAs can be performed:

Laboratory TSAs
TSAs will be conducted on the Arizona Department of Health Services State Laboratory, ADEQ contract laboratories, and contract laboratories of contractors who submit analytical data to ADEQ. The primary goals of TSAs will be to review the laboratory organization, operation, and capabilities; determine the reliability of data; and note corrective action for any apparent deficiencies. Auditors for TSAs will be selected by ADEQ's QA\QC Supervisor based on their technical proficiency in the subject area. The designated auditors will be responsible for planning and conducting the audit, and reporting the findings to the laboratory manager and to ADEQ's QA\QC Supervisor.

Field TSAs
Oversight of field operations is an important part of the quality assurance process, and the ADEQ QA/QC Supervisor will conduct QA audits of field sampling activities, both for its own field operations, and on those contractors that collect samples for Programs sponsored by EPA. ADEQ will specify frequency and procedures for conducting field TSAs within specific Program areas. When project specific Site Assessment Plans are reviewed, and also during any MSRs or other QA audits, ADEQ's QA/QC Supervisor will determine the necessity of field TSAs.

Specific items that may be observed during the audit include:

- Availability of approved project plans such as the Site Assessment Plan and Health and Safety Plan (HASP) to all project members
- Documentation of personnel qualifications and training
- Sample collection, identification, preservation, handling and shipping procedures
- Decontamination procedures used to clean sampling equipment
- Equipment calibration and maintenance
- Completeness of logbooks and other field records (including nonconformance documentation)

Performance Evaluations

Performance Evaluations (PEs) samples are used to assess the ability of a laboratory, or field measurement system, to provide reliable data. PEs samples will be considered for laboratories providing analytical services, directly or indirectly, for ADEQ and will be traceable, whenever possible, through the National Institute of Standards and Technology (NIST). The evaluation consists of providing a reference, "blind" or "double blind" sample, to the laboratory for analysis. A PE sample contains known concentrations of chemical constituents, or pollutants, of interest and will normally be in the appropriate media (e.g., soil, water, air). The analytical results obtained by the laboratory are compared to the known concentrations of the chemical constituents contained in the PE sample(s), as a means of determining if the laboratory demonstrated its ability to properly identify, and quantify, pollutants within established, or calculated, control limits.

PE samples will be scheduled by the HWM Program on an as-needed basis depending on the laboratory. All PE studies performed for ADEQ, whether required on a regular basis or performed on a one time basis, will be coordinated through or requested from the ADEQ QA/QC Supervisor or designee. For external projects requiring PEs, the Task/Work Assignment, Task/Delivery Order, or similar document needs to outline the specific details of the Performance Evaluation so the associated costs can be included in the contractor proposal. The results of PEs provide a means for assessing overall data integrity, and may be used as criteria for selecting candidates for on-site evaluations.

Audits of Data Quality

EPA 2001 Guidance for Quality Assurance Project Plans defines an audit of data quality (ADQ) as "a qualitative and quantitative evaluation of the documentation and procedures associated with environmental measurements to verify that the resulting data are of acceptable quality." This assessment primarily involves an evaluation of the completeness of the documentation of field and analytical procedures and quality control results, and usually involves tracing the paper trail accompanying the data from sample collection and custody to analytical results and entry into a database. This technique is commonly used to verify the process involved in entering data residing in large regulatory databases.

Results of both DQAs and data quality audits can be used in a number of ways. First, they can be used in making recommendations for changes in the design and performance of data collection efforts, and in the use and documentation of QC procedures. Secondly, they can be used as a guide for the planning and acquisition of supplemental data for the project and potentially for other related projects. Problems identified through DQAs may trigger the need for an MSR to determine management deficiencies, or a TSA to identify technical problems.

Data Quality Assessments (DQAs)*

A DQA refers to the process used to determine whether the quality of a given data set is adequate for its intended use. DQAs can be performed on all, or selected projects and/or data generation processes. The purpose of this type of evaluation is to determine whether the data collected are acceptable to the decision-maker or end user. Assessments generally take place at one of two points in the data generation process. First, as data are generated, aspects of the project such as surveillance of field and laboratory operations, consistency of the data with MQOs, successfully completing performance evaluation sample studies, and so forth, can be used to arrive as an assessment of whether the data are valid and acceptable. Rejected or questionable data cannot be used by ADEQ in its decision making, except in limited circumstances, such as a rough site screening.

Once data have been examined and assessed, and they are found to be of known and acceptable quality, then the results can be evaluated in the context of the Data Quality Objectives for the project. In some, but not all, cases, this may involve a statistical evaluation such as null hypothesis testing. EPA 2006 Data Quality Assessment - A Reviewers Guide guidance and EPA 2006 Data Quality Assessment - Statistical Methods for Practitioners discusses the types and uses of statistical analyses. In others in may involve a comparison to regulatory action levels. An assessment must also be made as to whether there is a sufficient quantity of data to support program or project decisions, and whether the original sampling design was appropriate. In some cases, the data may suggest that additional data are required to achieve a higher statistical confidence level. This could be because too many data points were invalidated, that samples were not collected over a long enough time period, or that a vital sampling area not previously considered important, was missed. In other cases, an assessment might show that data of a different type are required, or that the sensitivity of the instrument used in the measurement was not adequate to meet project objectives. Thus, both types of assessments are vital to the successful completion of a project.

If necessary, ADEQ's QA/QC Supervisor can review data generated by the ADHS State Laboratory, and by contract laboratories, for the various ADEQ Programs. These data review activities use checklists, standard operating procedures, and standardized qualification codes to indicate data quality.

*DQAs are performed on data generated for and submitted to ADEQ's HWM Program. DQA's are performed on an on-going basis.

Peer Reviews

Peer reviews are not strictly an internal QA function; rather, they are technical scientific reviews that evaluate assumptions, calculations, methods and conclusions. The ADEQ will use internal expertise to evaluate different technical aspects of the reports produced by contractors.

C1.3 Documentation of Assessments

This section identifies the organization and the person(s) that will perform the assessments, as well as the

documentation of information collected during the audit.

C1.3.1 Number, Frequency and Types of Assessments

An MSR for every major Agency Program is attempted once every four years. TSAs may be routinely planned by ADEQ's QA/QC Supervisor, specifically requested by ADEQ's Project/Case Manager, or result from the findings of another audit or review. Results will be reported to the audited organization in the form of a written report within 14 calendar days of the completion of the audit, or a mutually agreed upon alternative. Written comments by ADEQ's Project/Case Manager must be supplied to ADEQ's QA/QC Supervisor within 14 calendar days of receipt of the audit findings, or a mutually agreed upon alternative. Copies of the TSA Audit Final Report will be stored in the project file and also with ADEQ's QA/QC Supervisor. Additional copies will be distributed as appropriate.

C1.3.2 Assessment Personnel

MSRs and TSAs are generally conducted by ADEQ's QA/QC Supervisor and focuses on the HWM Program's adherence to the approved Agency QMP and its Quality Assurance Program Plan.

C1.3.3 Schedule of Assessment Activities

See Section C1.3.1 above.

C1.3.4 Reporting and Resolution of Issues

Nonconformance to practices and procedures outlined in this QA Program Plan or project-specific Site Assessment Plan will be addressed in a timely manner to ensure that nonconforming issues or deficiencies are corrected. The ultimate responsibility to ensure that all issues and deficiencies are satisfactorily resolved rests with the Unit Supervisors.

The HWM Program will have 30 days to prepare a written response to the reviewer's assessment memorandum. If the evaluation report recommends corrective actions, the HWM Program should address these recommendations and include a schedule for making any appropriate changes in its quality assurance procedures. These reviews will be used by the ADEQ Leadership team to gauge the effectiveness of the Agency QMP and of the HWM Program approach to data quality management.

C2: Reports to Management

Effective management of environmental data collection requires (1) timely assessment and review of all activities and (2) open communication, interaction and feedback among all project participants. This section outlines the reporting requirements for activities conducted under the HWM Program.

C2.1 Purpose/Background

Planned reports provide a structure for evaluating the management of program schedules, assessing the

effect of deviations from approved program and project plans on data quality and determining the potential uncertainties in decisions made based on the data. QA reports keep managers and project members informed on the performance of QA/QC activities. QA reports summarize the results of project-specific audits, list any significant problems and discuss the solutions and corrective actions implemented to resolve QA/QC problems.

C2.2 Frequency, Content and Distribution of Reports

A QA report is generated by field, technical, laboratory or QA personnel and sent to the HWM Program, as required throughout the duration of the project. The laboratory QA report is prepared by the Laboratory Manager or designee with the assistance of senior staff. The report is submitted in written or oral form, depending on the problems observed. The report can be included in one of the Planned Documents listed in Figure A2.

The contractor field team will record daily activities in a field log book to summarize activities throughout the field investigation. This daily log book will describe sampling and field measurements, equipment used, subcontractor personnel on site, QA/QC and health and safety activities, problems encountered, corrective actions taken, deviations from the QA Program Plan or Site Assessment Plan and explanations for the deviations. The daily log book is prepared by the field team leader and submitted to the HWM Program, if requested. The content of the daily log book will be summarized and included in the final report submitted for the field investigation.

The QA reports submitted for the project should include discussion of the following, if appropriate:

- Sampling and support equipment that were used, other than those specified in the approved QA Program or Site Assessment Plan
- Preservation or holding-time requirements for any sample that were not met
- QC checks (field and laboratory) that were found to be unacceptable
- Analytical requirements for precision, accuracy, or MDL/PQL that were not met
- Sample collection protocols or analytical methods specified in the QA Program Plan that were not met
- Any activity or event that affected the quality of the data
- Any corrective actions that were initiated as a result of deficiencies
- Any internal or external systems or performance audits that were conducted

The following example contains a list of recommended topics that may be used to develop a comprehensive QA Report. The information listed below should be contained within a QA Report, if appropriate.

Title Page – The following information must be listed:
Time period of the report,

QA Project Plan Title and/or Plan number
Laboratory name, address and phone number
Preparer's name and signature

Table of Contents – Should be included I f the report is more than ten pages long

Audits – in table form, summarize all project specific audits that were performed during the specified time period

Performance audits must include the following
- Date of the audit
- System tested
- Who administered the audit
- Parameters analyzed
- Reported results
- True values of the samples (if applicable)
- If any deficiencies or failures occurred, summarize the problem area and the corrective action

System audits must include the following:
- Date of the audit
- System tested
- Who administered the audit (agency or department)
- Parameters analyzed
- Results of tests
- Parameters for which results were unacceptable (include the reported and true values, if applicable)
- Explanation of the unacceptable results. Include probable reasons and the corrective action.

Copies of documentation such as memos, reports, etc., shall be enclosed

Significant QA/QC Problems
- Identify the problem, and the date it was found
- Identify the individual who reported the problem
- Identify the source of the problem
- Discuss the solution and corrective actions taken to eliminate the problem

Corrective Actions Status
- Discuss the effectiveness of all corrective actions taken durin ghte specified time frame as well as any initiated durin gth eprevious report period.
- Discuss any additional measures that may be implemented as the result of any corrective action.

The field team will prepare a QC summary report (QCSR) that will be submitted to the HWM Program, along with (or included within) the final report for the field investigation. The QCSR will include a summary and evaluation of QA/QC activities, including any field or laboratory assessments, completed during the investigation. The QCSR will also indicate the location and duration of storage for the complete data packages. Particular emphasis will be placed on evaluating whether project MQOs were met and whether data are of adequate quality to support the required decisions as stated in the DQOs for the project.

C2.3 Identify Responsible Organizations and Individuals

The HWM facility owner or operator – either directly or through its contractor - is responsible for preparing Planning Documents and Reports and incorporating any comments received from ADEQ HWM Program personnel. The HWM facility owner or operator is responsible for ensuring that a complete environmental laboratory report is included in all Planning Documents and Reports generated for and submitted to ADEQ's HWM Program. Organizational and individual roles and responsibilities are described in detail in Section A4.1 of this QA Program Plan. A list of Planning Documents and Reports is included in Figure A2.

GROUP D: DATA REVIEW

D1: Data Verification, Validation and Assessment

This section describes the procedures that are planned to review, verify and validate field and laboratory data. This section also discusses procedures for verifying that the data are sufficient to meet DQOs and MQOs for the project.

D1.1 Purpose/Background

Data verification, validation and assessment are done to ensure that environmental programs and decisions are supported by data of the type and quality needed and expected for the intended use.

D1.2 Data Verification

Data verification is the process of evaluating the completeness, correctness, conformance and compliance of a specific data set against the method, procedural or contractual requirements. Data verification evaluates whether sampling protocols, SOPs, analytical methods and project specific planning documents (Site Assessment Plans) were followed during data generation. Verification also involves examining the data for errors or omissions. Field and laboratory staff can verify that the work is producing appropriate outputs.

D1.3 Data Validation

Data validation is a systematic process for reviewing a body of data against a pre-established set of acceptance criteria defined in this QA Program Plan and in project-specific Site Assessment Plans. Data validation is an analyte-and sample-specific process that extends the evaluation of data beyond data verification and is performed to determine the analytical quality of a specific data set.

ADEQ's HWM Program performs a partial validation on selected analytical data routinely generated for and submitted to ADEQ's HWM Program. This partial validation involves an examination of the data package to determine whether MQOs for precision, accuracy and sensitivity have been met. Partial validation is based on discrepancies noted during the verification step. For example, perhaps some, but not all, surrogates in a method requiring an organic extraction are outside method defined acceptance criteria, but other QC data such as precision of the measurements and blank data are acceptable. This might lead to a review that centered on surrogate recoveries. The intent of the partial validation is to qualify data so that the user is alerted that s/he should understand the limitations when making decisions based on the data. Full data validation may occur if results are used in court cases.

D1.4 Data Quality Assessment

A Data Quality Assessment (DQA) refers to the process used to determine whether the quality of a given data set is adequate for its intended use. DQAs can be performed on all, or selected projects and/or data generation processes. The purpose of this type of evaluation is to determine whether the data collected are acceptable to the decision-maker of end user. Assessments generally take place at one of two points in the data generation process. First, as data are generated, aspects of the project such as surveillance of field

and laboratory operations, consistency of the data with MQOs, successfully completing performance evaluation sample studies, and so forth, can be used to arrive at an assessment of whether the data are valid and acceptable. Rejected or questionable data cannot be used by ADEQ in its decision making, except in limited circumstances, such as a rough site screening.

Once data have been examined and assessed, and they are found to be of known and acceptable quality, then the results can be evaluated in the context of the DQO's for the project. In some, but not all, cases this may involve a statistical evaluation such as null hypotheses testing. In others, it may involve a comparison to regulatory action levels. An assessment must also be made as to whether there is a sufficient quantity of data to support program or project decisions, and whether the original sampling design was appropriate. In some cases, the data may suggest that additional data are required to achieve a higher statistical confidence level. This could be because too many data points were invalidated, that samples were not collected over a long enough time period, or that a vital sampling area not previously considered important, was missed. In other cases, an assessment might show that data of a different type are required, or that the sensitivity of the instrument used in the measurement was not adequate to meet project objectives. Thus, both types of assessments are vital to the successful completion of a project.

If necessary, ADEQ's QA/QC Supervisor can review data generated by the ADHS State Laboratory and contract laboratories for the various ADEQ Programs. These data review activities use checklists, standard operating procedures, and standardized qualification codes to indicate data quality. The use of checklists and SOPs help standardize the data review process. The extent and level of verification for individual data sets should clearly be defined in the project Site Assessment Plan.

D2: Approaches to Verification, Validation and Assessment

The integrity of the data generated over the life of the project is confirmed by data verification and validation. The process for determining if the data satisfy program-defined requirements involves evaluating and interpreting the data, in addition to verifying that QC requirements were met. Projects planned using EPA's DQO process should produce data that provide answers to critical study questions.

The process for verifying and validating data is presented in EPA 2002 Guidance on Environmental Data Verification and Data Validation. Section 5 of this EPA guidance provides tools and techniques for data verification and validation: http://www.epa.gov/QUALITY/qs-docs/g8-final.pdf

D2.1 Approaches to Data Verification

Project team personnel will verify field data through reviews of data sets to identify inconsistencies or anomalous values. Any inconsistencies discovered will be resolved as soon as possible by seeking clarification from field personnel responsible for data collection. All field personnel will be responsible for following the sampling and documentation procedures described in the project Site Assessment Plan so that defensible and justifiable data are obtained.

Laboratory personnel will verify analytical data at the time of analysis and reporting and through subsequent reviews of the raw data for any nonconformances to the requirements of the analytical method. Laboratory personnel will make a systematic effort to identify any outliers or errors before they

report the data. Outliers that are found to be the result of errors will be identified and corrected; outliers that cannot be attributed to errors in analysis, transcription, or calculation will be clearly identified in the case narrative section of the analytical data package. All analytical data generated for and submitted to ADEQ's HWM Program are to be verified by the laboratory.

Verified data are checked for a variety of topics including transcription errors, correct application of dilution factors, appropriate reporting of dry weight versus wet weight and correct usage of conversion factors, among others. Verified data may have laboratory qualifiers. Verified data are one output of this process.

A second output from the verification process is documentation, which may include a certification statement signed by the laboratory manager and included in the data package. Narratives on technical issues, non-compliance and any corrective action taken are included in the laboratory data package. Records from field activities are likely to be logbooks or handwritten notes, all of which should be dated and signed.

The laboratory QA manual must be used to accept, reject or qualify the data generated by the laboratory. ADEQ, though, makes the decision on whether or not to use the data. The laboratory management is responsible for validating the data generated by the laboratory. The laboratory personnel must verify that the measurement process was "in control" (i.e., all specified MQOs for the DQIs were met, or acceptable deviations are explained) for each batch of samples before proceeding with analysis of a subsequent batch. In addition, each laboratory must establish a system for detecting and reducing transcription and/or calculation errors prior to reporting data. Only data that have acceptable deviations explained, shall be submitted by the laboratory. When QA requirements have not been met, the samples will be reanalyzed when possible, and only the results of the reanalysis will be submitted, provided these results are acceptable.

D2.2 Approaches to Data Validation

Data validation determines the analytical quality of data within a specific data set; it is an analyte-and sample-specific process based on achieving the MQOs set forth in the planning documents for the project. Validation assesses whether data quality goals specified in the planning phase have been achieved. Unlike data verification, which may be done by the laboratory, data validation is typically performed by a qualified person who is not affiliated with the laboratory. Validation of analytical data generated for and submitted to ADEQ's HWM Program is performed by the Unit Supervisor, staff level personnel or, upon request, Technical Support.

The level of data validation depends on the size and complexity of the project and the decisions to be made. Basically, data validation is the process of evaluating the available data against the project MQOs to make sure that the objectives are met. Cursory validation is performed on data generated for and submitted to ADEQ's HWM Program. If full data validation is ever needed on a HWM Program project, the QA/QC supervisor will be notified. Criteria for data validation are summarized in Table D-1.

The personnel validating the data should be familiar with the project-specific MQOs. So, the validator should have access to the QA Program Plan, Site Assessment Plans, SOPs and approved analytical methods. The validator must identify these and other project records, obtain records produced during data

verification, and validate the records by determining whether the data quality meets goals established in the planning documents.

Data validation generally includes the following steps:

Validation of Field Data

1 Evaluate field records for completeness and consistency

2 Review field QC information

3 Summarize deviations and determine effects on data quality

4 Summarize number and type of samples collected

Validation of Laboratory Data

1 Assemble planning documents and data to be validated. Review data records to determine method, procedural and contractual QC compliance or noncompliance;

2 Review verified, reported sample results collectively for the data set as a whole, including laboratory qualifiers;

3 Summarize data and QC deficiencies and evaluate the impact on overall data quality;

ADEQ uses Arizona Data Qualifiers that are revised periodically with the consensus of the Arizona Environmental Laboratory Advisory Committee (ELAC). The most up to date version should be used when applying qualifiers to data and can be found on the ADHS and ADEQ websites or at the following weblink: http://www.azdeq.gov/function/programs/download/azdatqa.pdf.

Any field or laboratory data that did not meet the quality goals established in the planning documents are summarized in a comment letter to the party responsible for performing the Site Assessment.

D2.3 Approaches to Data Assessment

The purpose of a data assessment is to integrate all aspects of data generation to determine the usability of the data. The final step in the process is to compare the data obtained to the DQOs established by the program in its QA Program Plan or else in project-specific planning documents. Aspects of the sampling program evaluated during the data assessment include sampling design, sample collection procedures and sample handling. Analytical procedures (both field and laboratory) and QC procedures are also reviewed during the process. Field and laboratory instrument calibration logbooks are maintained by the environmental consultant and laboratories, respectively, and are reviewed by the appropriate personnel (Unit Supervisors, staff level personnel, Technical Support and/or QA/QC Supervisor) on an as needed basis. Criteria for evaluating all aspects are provided in the following paragraphs.

D2.3.1 Sampling Design

Samples should conform to the type and location specified in the project-specific Site Assessment Plan. Any deviations should be noted, along the likely effect on the usability of the data for its intended purpose. An overview of sampling design is also discussed in Section B1.1 of this QA Program Plan. EPA also provides guidance in its 2002 Guidance on Choosing a Sampling Design for Environmental Data Collection: http://www.epa.gov/QUALITY/qs-docs/g5s-final.pdf

D2.3.2 Sample Collection Procedures

The data reviewer (i.e. typically the field team leader from the contracted environmental consultant) should verify that the appropriate specified methods were used during sampling. The reviewer should:

1 Evaluate the field records for consistency
2 Review QC information
3 Summarize deviations and determine their effect on data quality
4 Summarize the samples collected
5 Prepare a field data verification summary

Improper field practices can compromise the useability of a data set. Specific issues to look for include mislabeling of sample containers, problems with field instruments, improper documentation (such as failure to properly fill in the log book), improper collection of VOC samples (such as leaving a cap off a container or collecting VOC samples from a well-mixed composite sample), biasing sampling locations or forgetting to obtain location information for each sample, improper purging of monitoring wells, improper decontamination procedures or intentionally cutting corners by collecting many samples from one location to save time.

For preparation of the field data verification summary, the field team leader evaluates field records and notebooks for consistency with field methods and procedures described in the Site Assessment Plan to assure that these procedures were followed properly or that deviations from the procedures still yield data of acceptable quality. The verification summary should include observations on (1) the consistency and completeness of field records, (2) the adequacy of field QC information, (3) any deviations from Site Assessment Plan procedures and the probable effect of the deviations on data quality and (4) the number and types of samples collected and how this compares with specifications in the Site Assessment Plan. The different parts of the data verification summary are typically incorporated into the final deliverable to ADEQ HWM Program personnel for review. ADEQ HWM Program personnel can request from the HWM facility owner/operator copies of field records and notebooks for their own review on an as needed basis.

Most qualified sampling contractors and State and Federally certified laboratories develop SOPs and analytical methods as part of their overall QA program. SOPs should be developed following EPA 1995 Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations. The field team should document which SOPs they are using in the field and any deviations from an SOP. Appendix F lists references and weblinks to EPA generated SOPs.

D2.3.3 Sample Handling

QA personnel should confirm that samples were handled in accordance with protocols required in the QA Program Plan and project-specific Site Assessment Plan. Sample containers and preservation methods should be confirmed as appropriate for the nature of the sample and type of data generated from the sample. Chain-of-custody records and storage conditions should be checked to ensure the representativeness and integrity of the samples.

D2.3.4 Analytical Procedures

Section B4 of this QA Program Plan identified the requirements of analytical methods used to generate the data. Each sample should be verified to ensure that the procedures used to generate the data were implemented as specified. Acceptance criteria for these data follow those used in data validation, with suitable codes to characterize any deviations from the procedure.

D2.3.5 Quality Control

Section B5 of this QA Program Plan specified the QC checks that should be performed during sample collection, handling and analysis. Here, the QA reviewer should confirm that results for QC samples were evaluated against acceptance criteria (i.e., MQOs) specified in Section B.

D2.3.6 Calibrations

Section B7 of this QA Program Plan addressed the calibration of instruments and equipment and the information required to ensure that the calibrations (1) were performed within an acceptable timeframe prior to generation of measurement data; (2) were performed in proper sequence, included the proper number of calibration points; (3) were performed using standards that bracketed the range of reported measurements (i.e., were within the linear working range of the instrument) and (4) had acceptable linearity checks to ensure the measurement system was stable when the calibration was performed. The environmental consultant performing the field work for the HWM facility owner/operator is responsible for the calibration of all field sampling equipment. Contracted environmental laboratories are responsible for the calibration of all laboratory equipment used to analyze samples associated with all samples collected for the data generated for and submitted to ADEQ's HWM Program. All equipment and instrument calibrations shall be recorded in an appropriate log book and be made available to ADEQ HWM Program personnel upon request.

D2.3.7 Data Reduction and Processing

Internal checks by laboratory staff should verify the integrity of the raw data generated by the analyses. Electronic data deliverables (EDDs) automatically produced by the laboratory should help minimize data entry errors. Steps in data reduction should be clearly documented so that the validity of the analysis can be properly assessed.

Data should be cross-checked to confirm consistency or comparability in analytical methods and detection limits, units of measurement, compatibility of file types or software and other critical factors that affect how the data will ultimately be interpreted to influence conclusions and recommendations.

D3: Reconciliation with Data Quality Objectives

After the data have been verified and validated, the data are evaluated against project DQOs. Implementation of the DQA process completes the data life cycle by providing the assessment needed to determine if project objectives were achieved.

Two 2006 EPA guidance documents on DQA are available from EPA at http://www.epa.gov/quality/qa_docs.html. DQA is the scientific and statistical evaluation of environmental data to determine if they meet the planning objectives of the project, and thus are of the right type, quality and quantity to support their intended use. Data Quality Assessment - A Reviewers Guide broadly describes the statistical aspects of DQA in evaluating environmental data sets. A more detailed discussion on implementation of graphical and statistical tools is found in the companion guidance document on statistical methods for practitioners (Data Quality Assessment - Statistical Methods for Practitioners). These EPA guidance documents discuss the use of DQA to support environmental decision-making (e.g., compliance determinations).

The DQA process is built on a fundamental premise: data quality is meaningful only when it relates to the intended use of the data. Data quality does not exist in a vacuum; a reviewer needs to know in what context a data set is to be used, in order to establish a relevant yardstick for judging whether or not the data are acceptable. By applying the DQA process, a reviewer can answer four important questions:

1 Can a decision (or estimate) be made with the desired level of certainty, given the quality of the data?

2 How well did the sampling design perform?

3 If the same sampling design strategy is used again for a similar study, would the data be expected to support the same intended use with the desired level of certainty?

4 Is it likely that sufficient samples were taken to enable the reviewer to see an effect if there really were an effect? That is, is the quantity of data sufficient?

D3.1 Purpose/Background

This section outlines methods for evaluating the results obtained from the sampling and analysis. Scientific and statistical evaluations of the data are used to determine if the data collected are of the right type, quantity and quality to support their intended use and to adequately address the primary study questions.

Please note that statistical evaluations of data generated for and submitted to ADEQ's HWM Program are rarely employed. This is because judgmental sampling is most always the appropriate method for collecting samples for situations encountered. For the rare occasion when a project needs a statistical evaluation, confidence intervals (step 3 of the "Five Steps of Statistical DQA" in Section D3.2 below) is the statistic that would most likely best fit the project. If statistical evaluation other than confidence

intervals is needed, a contractor may be selected to perform independent statistical evaluations in accordance with the DQA process outlined in this QA Program Plan.

D3.2 Reconciling Results with Program Objectives or DQOs

EPA guidance documents for data evaluation (EPA 2006) describe an iterative five-step process called the "Five Steps of Statistical DQA":

1 Review the DQOs and sampling design described in the project planning documents.

2 Conduct a preliminary data review or exploratory data analysis to understand the character and structure of the data set and to evaluate whether there are any anomalies in the data that may not have been noticed during data verification and validation. Are there outliers or other anomalies that should be further investigated before continuing with statistical testing?

3 Select a statistical test. Choose appropriate statistical tests based on the characteristics of the data and the questions that the investigation was intended to address.

4 Verify the assumptions of the statistical tests and assess the effect that violations of test assumptions may have on the result (i.e., is the test sufficiently robust to provide a valid result at a reasonable level of confidence?) and consider other factors (i.e., Are there effects of seasonality that must be considered? Would alternative statistical tests be better suited to the data than the tests proposed in the planning documents?).

5 Draw conclusions from the data. Using multiple lines of evidence, the results of statistical tests and professional judgment, the data analyst should be able to provide conclusions and recommendations for the site. In some cases, the conclusion may be that more data are needed to answer the primary study questions.

If DQOs have not been adequately developed, the analyst may need to review the planning documents and sampling design, and then define the statistical hypotheses to be tested and establish tolerable limits on decision errors.

When the DQOs are qualitative, judgmental sampling is utilized and statistical tools are not appropriate, the ADEQ will still systematically assess data quality and data usability. This DQA assessment – Four Steps of DQA for Qualitative DQOs - will include the following:

1. A review of the sampling design and sampling methods to verify that these were implemented as planned and are adequate to support project objectives;

2. A review of project-specific MQOs for precision, accuracy, representativeness, completeness, comparability and quantitation limits to evaluate whether acceptance criteria have been met;

3. A review of project-specific DQOs to assess whether they have been achieved by the data collected; and

4. An evaluation of any limitations associated with the decisions to be made based on the data

collected. For example, if data completeness is only 90 percent compared to a project-specific completeness objective of 95 percent, the data may still be usable to support a decision, but at a lower level of confidence.

D3.2.1 Review DQOs and Sampling Design

Step 1 of the DQA process should (1) document or define the project specific DQOs, (2) verify that the hypothesis is consistent with project objectives and (3) identify any deviations from the sampling plan and assess the potential effect of the deviations.

The objectives of the study should be reviewed in order to provide a context for analyzing the data. If a systematic planning process has been implemented before the data are collected, then this step reviews the study objectives to evaluate whether project goals have been met and whether the study questions have been adequately answered. If no clear planning process was used, the reviewer should:

- Develop a concise definition of the problem (DQO Step 1) and of the methodology of how the data were collected (DQO Step 2). These two steps should provide the fundamental reason for collecting the environmental data and identify all potential actions that could result from the data analysis.

- Identify the target population and determine if any essential information is missing (DQO Step 3). If so, either collect the missing information before proceeding, or select a different approach to resolving the problem.

- Specify the scale of determination (any subpopulations of interest) and any boundaries on the study (DQO Step 4) based on the sampling design. The scale of determination is the smallest area or time period to which the conclusions of the study will apply. The apparent sampling design and implementation may restrict how small or how large the scale of determination can be.

- Evaluate whether the data support the conclusions offered (DQO Step 5)

The overall type of sampling design and the manner in which data were collected will likely place constraints on how the data can be used and interpreted. The data analyst should assess whether features of the design support or contradict the stated objectives of the study. Were there deviations from the planned design? What might be the effect of these deviations? Are data adequate to address the primary study questions? How do these objectives translate into statistical hypotheses (null and alternative hypotheses)?

The design and sampling strategy should be discussed in clear detail in the project-specific Site Assessment Plan. The overall type of sampling design and the manner in which samples were collected or measurements were taken will place conditions and constraints on how the data can be used and interpreted.

A key distinction in sampling design is between judgmental sampling (also called authoritative or biased sampling), in which sample numbers and locations are selected based on expert knowledge of the problem, and probability-based sampling, in which sample numbers and locations are selected based on randomization, and each member of the target population has a known probability of being included in

the sample. Judgmental sampling has some advantages and is appropriate in some cases. This type of sampling should be considered when the objectives of the investigation are not of a statistical nature (for example, when the objective of a study is to identify specific locations of leaks/hot spots or when the study is focused solely on the sampling locations themselves). Generally, conclusions drawn from judgmental samples apply only to those individual samples.

Probabilistic sampling typically takes more effort to implement than judgmental sampling, because systematic or random locations must be selected for sampling. However, a probability-based sampling design has the advantage of allowing the use of statistical tests, which permit confidence and uncertainty of the results to be specified. Probability-based designs do not preclude the use of expert knowledge or the use of existing data to establish the sampling design. An efficient sampling design is one that uses all available prior information to stratify the site (in order to improve the representativeness of the resulting samples) and set appropriate parameters. Common types of probabilistic sampling designs include the following:

- Simple random sampling – the method of sampling where samples are collected at random times or locations throughout the sampling period or study area.

- Stratified sampling – a sampling method where a population is divided into nonoverlapping subpopulations called "strata," and sampling locations are selected randomly within each stratum using a random or systematic sampling design.

- Systematic and grid sampling – a randomly selected unit (in space or time) establishes the starting place of a systematic pattern that is repeated throughout the population. With some important assumptions, can be shown to be equivalent to simple random sampling.

- Ranked set sampling – a field sampling design where expert judgment or an auxiliary measurement method is used in combination with simple random sampling to determine which locations should be sampled.

- Adaptive cluster sampling – a sampling method in which some samples are taken using simple random sampling, and additional samples are taken at locations where measurements exceed some threshold value.

- Composite sampling – a sampling method in which multiple samples are physically mixed into a larger sample and samples for analysis drawn from this larger sample. This technique can be highly cost-effective (but at the expense of variability estimation) and had the advantage it can be used in conjunction with any other sampling design. (Multi-increment sampling is a particular form of composite sampling, and may be an effective design for certain types of sites to answer certain types of questions).

Regardless of the type of sampling scheme, the reviewer should review the description of the sampling design and look for design features that support the project objectives. For example, if the goal of the study is to make a decision about the average (defined here as the arithmetic mean) concentration of a contaminant in an effluent stream over time, then composite samples may be an appropriate sampling

design. On the other hand, if the goal of the study is to find hot spots of contamination at a hazardous waste site, compositing should be used with caution, to avoid "averaging away" hot spots.

The reviewer should also look for potential problems in the implementation of the sampling design. For example, if simple random sampling was used to collect the data, can the reviewer be confident that the sampling locations or data point were truly random? Small deviations from a sampling plan probably have minimal effect on the conclusions drawn from the data set, but the effects of significant or substantial deviations should be carefully assessed. Finally, the reviewer should verify that the data are consistent with the project-specific Site Assessment Plan and the overall objectives of the study.

D3.2.2 Conduct Preliminary Data Review

Step 2 of the DQA process reviews graphical representations of the data and calculates some basic statistical quantities. By reviewing the data both numerically and graphically, the reviewer can understand the structure of the data, and thereby identify appropriate use of the data.

Statistical quantities numerically describe the data. The quantities that are typically calculated include the arithmetic or geometric mean, the median and other percentiles and the standard deviation. These quantities provide estimates of characteristics for the sample population and allow one to make inferences about the population from which the data were drawn. Graphical representations permit the reviewer to identify patterns and relationships within the data, confirm or disprove assumptions and identify potential problems.

The preliminary data review allows the reviewer to understand the structure and characteristics of the data set and the population from which these data were drawn. Graphical depictions of the data permit the analyst to identify anomalies that may require further investigation or perhaps even reanalysis by the laboratory. Output from DQA Step 2 typically includes (1) tables of summary statistics and (2) graphs and/or statistical plots of the data.

D3.2.3 Select Statistical Test

Under Step 3 of the DQA process, the data analyst selects the most appropriate statistical test or method for evaluating the data. The statistical method will be selected based on the sampling plan used to collect the data, the type of data distribution and the assumptions made in setting the DQOs, noting any deviations from these assumptions. Conclusions about other aspects of the data set or the stated null hypothesis are made based on the results of this evaluation. EPA DQA guidance provides a discussion (with mathematical formulas and examples for conducting statistical tests) of the process for statistically evaluating environmental data. Detailed technical information that reviewers can use to select appropriate procedures may be found in Chapter 3 of EPA's 2006 Data Quality Assessment: Statistical Methods for Practitioners.

For the rare occasion when a HWM Program project needs a statistical evaluation, confidence intervals (step 3 of the "Five Steps of Statistical DQA" in Section D3.2 above) is the statistic that would most likely best fit the HWM Program project. For example, the project's objective may be to estimate the average level of pollution for a particular contaminant. A reviewer can describe the desired (or achieved)

degree of uncertainty in the estimate by establishing confidence limits within which one can be reasonably certain that the true value will lie. When interpreting a confidence interval statement such as "The 95% confidence interval for the mean is 19.1 to 26.3", the implication is that the best estimate for the unknown population mean is 22.7 (halfway between 19.1 and 26.3), and that we are 95% certain that the interval 19.1 to 26.3 captures the unknown population mean.

If a particular statistical procedure was specified in the project Site Assessment Plan, the reviewer should use the results of the preliminary data review to determine if the procedure is appropriate for the data collected. If not, then the reviewer should document why the procedure is deemed inappropriate, and then select a different method. Chapter 3 of EPA 2006 Data Quality Assessment: Statistical Methods for Practitioners provides alternatives for several statistical procedures. If a particular procedure has not been specified, then the reviewer should select a statistical test or method based on the study objectives, results of the preliminary data review, and key assumptions necessary for the method.

All statistical tests make assumptions about the data. For instance, the t-test, which is a parametric test used to compare two data sets, assumes that each data set approximates a normal distribution and that the two data sets have approximately equal variance. In contrast to parametric tests like the t-test, nonparametric tests make much weaker assumptions about the distributional form of the data. However, both parametric and nonparametric tests assume that the data are derived from statistically independent samples Common assumptions of statistical tests include distributional form of the data, independence, dispersion characteristics, approximate homogeneity and the basis for randomization in the sampling design. For example, the one-sample t-test assumes random and independent samples, an approximately normal distribution, no outliers and no more than a small percentage of non-detections.

Statistical methods that are insensitive to small or moderate departures from the assumptions are called "robust." However, some tests rely on the data meeting certain key assumptions in order for the test results to be valid. The reviewer should note any sensitive assumptions where relatively small deviations could jeopardize the validity of the test results.

After completing Step 3 of the DQA process, the data analyst or reviewer should have selected appropriate statistical tests and noted the critical assumptions of the statistical tests.

D3.2.4 Verify Assumptions of Statistical Tests

The validity of a statistical test or method depends on the key assumptions underlying the test, and whether the data violate these assumptions. Minor deviations from assumptions are usually not critical if the statistical technique is sufficiently robust to compensate for such deviations.

If the data do not show serious deviations from the key assumptions of the statistical method, then the DQA process continues to Step 5, 'Draw Conclusions from the Data.' However, it is possible that if one or more of the assumptions are called into question, this could require a reevaluation of which test may be most appropriate for the data. It is true that some deviations do not invalidate the results of a statistical test, but this should be confirmed here in Step 4 of the DQA process. For example, deviation from normality may not be seriously important for a large sample size, but could be critically important for a small sample size.

This step in the DQA process is an important check on the validity and reliability of the conclusions that are drawn. Outputs from this step include documentation of the method used to verify assumptions and verification that the test results are valid. Additionally, the reviewer should provide a description of any corrective actions that were taken.

D3.2.5 Draw Conclusions from Data

Step 5 of the DQA process represents the culmination of the planning, implementation and assessment phases of the project operations. In this step, the data analyst draws conclusions that address the project objectives. All of the analysis and review conducted in Steps 1 through 4 should ensure that the conclusions drawn in Step 5 adequately address project objectives in a scientifically defensible manner.

In Step 1, the project objectives are reviewed (or developed retrospectively) and the sampling design is evaluated. In Step 2, the implementation of the sampling scheme is reviewed and a preliminary picture of the data set is developed. In Step 3, the appropriate statistical tests are selected. Finally, the underlying assumptions of the statistical test are verified in Step 4.

Conclusions drawn in the final step of the DQA process allow the reviewer or data analyst to present valid statistical results with a specified level of significance. The confidence and power of the tests are stated, along with the study conclusions in plain English. Finally, the data analyst provides an assessment of the overall performance of the sampling design and identifies additional data that may be needed (that is, data gaps are identified).

If data were collected using a judgmental sampling design or if few samples were collected, professional judgment rather than formal statistical testing may be applied to draw conclusions. Or, statistical tests may be applied, recognizing that the results may present a biased "worst-case scenario." For example, if the data from biased samples (e.g., selective sampling of visibly stained soils) are used in a one-sample statistical test to compare concentrations against a cleanup standard or action level, and test results show that concentrations do not exceed the action level, then a conclusion can be drawn. If test results show that concentrations do exceed the action level, then, in formulating conclusions, the reviewer should balance the test results against the knowledge that the data were biased toward the sampling of "hot spots."

D4: Revisions to the QA Program Plan

Throughout the life of ADEQ's HWM Program, there may be changes to program requirements, or modifications to the way environmental data are collected, or changes to how enforcement activities are defined. Therefore, this QA Program Plan is recognized as a dynamic document that is subject to revision, as needed. ADEQ HWM Program personnel, Technical Support and QA/QC personnel will examine and revise this QA Program Plan annually, although the plan will only be resubmitted to EPA Region 9 QA manager for review once every five years or as otherwise needed. Approved revisions will be disseminated to personnel included on the Distribution List (page 6).

Table D1 – Criteria for Partial and Full Data Validation

Analytical Group	Criteria for Partial Data Validation	Criteria for Full Data Validation
CLP Organic Analyses	● Holding times ● Calibration ● Blanks ● Surrogate recovery ● Matrix spike and matrix spike duplicate recovery ● Laboratory control sample or blank spike ● Internal standard performance ● Field duplicate sample analysis ● Temperature ● Overall assessment of data for an SDG	● Holding times ● Gas Chromotography/Mass Spectroscopy tuning ● Calibration ● Blanks ● Surrogate recovery ● Matrix spike and matrix spike duplicate recovery ● Laboratory control sample or blank spike ● Internal standard performance ● Field duplicate sample analysis ● Compound identification ● Target compound list identification ● Compound quantitation and reported detection limits ● Tentatively identified compounds ● System performance ● Temperature ● Overall assessment of data for an SDG
CLP Inorganic Analyses	● Holding times ● Calibration ● Blanks ● Matrix spike recovery ● Matrix duplicate sample analysis ● Laboratory control sample or blank spike ● Field duplicate sample analysis ● Temperature ● ICP serial dilution ● Overall assessment of data for an SDG	● Holding times ● Calibration ● Blanks ● ICP interference check sample ● Matrix spike recovery ● Matrix duplicate sample analysis ● Laboratory control sample ● Field duplicate sample analysis ● Graphite furnace atomic absorption QC ● Sample result verification ● Temperature ● ICP serial dilution ● Detection limits ● Overall assessment of data for an SDG

Notes:
CLP Contract Laboratory Program
ICP Inductively coupled plasma (emission spectroscopy)
SDG Sample delivery group
QC Quality Control

Appendix A Arizona Administrative Code for Department of Health Services Laboratories

Below is the hyperlink to the Arizona Administrative Code for Title 9 (Health Services) Chapter 14 (Department of Health Services Laboratories):

http://www.azsos.gov/public_services/Title_09/9-14.htm

Appendix B General Requirements for Quality Assurance Project Plans/Site Assessment Plans

EPA's document QA/R-5 - EPA Requirements for a Quality Assurance Project Plan - indicates that the level of detail of the QA Project Plan should be based on a graded approach. This is so that the level of detail in each QA Project Plan will vary according to the nature of the work being performed and the intended use of the data. As a result, an acceptable QA Project Plan for some environmental data operations may require a qualitative discussion of the experimental process and its objectives while others may require extensive documentation to adequately describe a complex environmental program.

Site Assessment Plan Projects of Limited Scope

EPA's document R9QA/008.1 - Sampling and Analysis Plan Guidance and Template, Version 2 – provides a template for Site Assessment Plans for projects of limited scope. This template combines the basic elements of a Quality Assurance Project Plan and Field Sampling Plan.

A.A.C. R18-8-280(D)(2) states a "… site assessment plan shall describe in detail the procedures to determine the nature, extent and degree of hazardous waste contamination in the environment". Site assessment plans should be designed to combine the basic elements of a Quality Assurance Project Plan and Field Sampling Plan. Notices of Violations and Compliance Orders routinely ask for the following information with regards to Site Assessment Plans of limited scope:

a. An introduction, including purpose, problem, brief scope of the Site Assessment Plan, and project manager(s) or contact individual(s);
b. A facility description, including street address, property owner, tenant if other than owner, and legal description of property;
c. Facility operation, including manufacturing process(es), chemical usage, storage, disposal, and facility layout;
d. Facility/property history, including former processes performed at the facility and past spills/releases of solid or hazardous wastes;
e. Provisions for the submission of an amended Site Assessment Plan, in the event that activities conducted did not meet the terms and conditions set forth in the approved SAP;
f. Provisions for submitting a remedial plan (RP) to ADEQ if warranted by information obtained during the implementation of the approved SAP;
g. Scope of assessment activities to be undertaken and a schedule for all work activity;
h. Rationale for assessment activities including a description of why the particular activity has been selected;
i. A list of the contaminants of concern based upon historical and current chemical usage, or as determined from preliminary sampling at the site or vicinity;
j. Sampling methodologies and equipment to be used to obtain samples;
k. Sample locations and depths with rationale for location selections;
l. Site specific depth to groundwater information;
m. Maps and figures depicting:

i. Sample locations
ii. Property boundaries
iii. Above and below ground utilities and structures
iv. Areas of contamination
v. Exclusion and decontamination zones

n. Quality Assurance/Quality Control (QA/QC) procedures for obtaining, preserving and transporting samples, including decontamination procedures, chain of custody, sample labeling and identification;
o. Laboratory certification and QA/QC procedures. All contracted laboratories must be certified by the Arizona Department of Health Services. Typical QC data from laboratories reported to ADEQ are tabled in Section A7 of this document;
p. A description of how investigative derived hazardous and/or potentially hazardous waste(s) will be handled;
q. Tables summarizing the following:

i. Soil sampling information including sample location identification number and sampling depth interval; and
ii. Itemized schedule of implementation and completion of each activity of the SAP including dates for submittal to ADEQ of documentation or reports.

r. Appendices containing the following items:
i. Any drawings larger than 11.5" x 17"; and
ii. References.

Projects Involving Extensive Characterization, Monitoring or Remediation

For projects involving extensive characterization, monitoring or remediation, EPA's document *QA/R-5 EPA Requirements for a Quality Assurance Project Plan* should be utilized to document the QA/QC procedures to be utilized for project activities.

(1) Site Assessment Plan - Any SP submitted by the owner/operator shall contain the following:

(a) A description of the purpose for the SP;
(b) A general description of the site including a site diagram or drawing. Identify as applicable:
(i) property boundaries;
(ii) buildings and fences;
(iii) process and maintenance areas;
(iv) active and inactive waste generation, handling treatment, storage, disposal, and spill areas;
(v) water wells, dry wells, sumps, storm sewers, industrial and sanitary sewers, septic tanks, surface waters (including intermittent washes, discharges or irrigation ditches, canals, etc);
(vi) depth to ground water;

(vii) soil coverings (asphalt, concrete, vegetation, etc);
(viii) topography and drainage patterns

(c) Identity of each waste which has been stored, treated, or disposed at the site, and the identity of each hazardous constituent present in that waste;

(d) The method(s) used to determine sample locations and depths (random, systematic, biased, or combination) and a rationale for the number of samples taken;

(e) A diagram showing the number, type, and location of samples;

(f) Detailed sampling procedures describing:
(i) Contents of the field notebook
(ii) Sampling equipment used
(iii) Sample sizes
(iv) Use of any sample compositing
(v) Sample containers, labels, and seals
(vi) Field and trip blanks
(vii) Sample preservatives
(viii) Quality assurance procedures (blind field duplicates, use of a check lab, and chain of custody)
(ix) Sample packaging and shipment
(x) Reserved samples (samples to be taken but not immediately analyzed)
(xi) Backfilling and grouting of sample borings
(xii) Equipment decontamination procedures, including disposal of spent solutions

(g) Analytical parameters and the rationale for choosing such parameters. Typical QC data from laboratories reported to ADEQ are tabled in Section A7 of this document.

(h) Provision for expanding the SP if contamination is found to have migrated

(i) Provision for the submittal of a Site Assessment Report within 90 days of performance of the SP, providing the following information:
(i) A summary of results, significant observations, and conclusions.
(ii) A discussion of the sampling followed for each site, including a description of:
a. The sampling procedures used;
b. The equipment used for sampling;
c. The analytical procedures and methods used;
d. The analytical equipment used; and
e. The quality assurance procedures used.
(iii) The procedures used to prevent hazards and protect field personnel;
(iv) The equipment used to prevent hazards and protect field personnel;
(v) Drawings and photographs where appropriate;
(vi) Description of any deviations from the approved SP;
(vii) Data generated from sampling and analysis activities performed pursuant to the plan, including field notes, manifests, bills of lading, LDR forms, laboratory submittal forms, chain-of-custody forms, laboratory reports, and drilling logs.

(j) Provision for the submittal of a Remedial Plan, if any hazardous constituents are found above the applicable soil remediation standards of Title 18, Chapter 7, Article 2 or if any hazardous constituents may be expected to migrate to ground water.

(k) Provision for a request of a Finding of No Further Action from the Director, if no hazardous constituents are found above the applicable soil remediation standards of Title 18, Chapter 7, Article 2, or if no hazardous constituents may be expected to migrate to ground water.

(l) The final approved SP is incorporated into the owner/operator's HWM Permit.

(2) Remedial Plan - Any Remedial Plan (RP) submitted by the owner/operator shall contain the following:

(a) A description of the process to be used in the removal of all hazardous waste, hazardous waste constituents, and/or soils determined to be contaminated with hazardous waste or hazardous waste constituents;

(b) An estimate of the amount of waste or soils to be generated, including a site map indicating the location and vertical and horizontal extent of the area to be remediated;

(c) Identification of the personnel to be used during the remediation, including the name of the project officer who will be responsible for managing the site;

(d) A provision for a site safety plan which will be enforced during the remediation. At a minimum, the site safety plan should specify the precautions to be taken and monitoring to be performed which ensures the safety of the site workers and the surrounding community;

(e) The method(s) used to determine sample locations and depths (random, systematic, biased, or combination) and a rationale for the number of samples taken;

(f) A diagram showing the number, type, and location of samples to be taken;

(g) Detailed sampling procedures describing:

(i) Contents of the field notebook
(ii) Sampling equipment used
(iii) Sample sizes
(iv) Use of any sample compositing
(v) Sample containers, labels, and seals
(vi) Field and trip blanks
(vii) Sample preservatives
(viii) Quality assurance procedures (blind field duplicates, use of a check lab, chain of custody)
(ix) Sample packaging and shipment
(x) Reserved samples (samples to be taken but not immediately analyzed)
(xi) Backfilling and grouting of sample borings
(xii) Equipment decontamination procedures, including disposal of spent solutions;

(h) Analytical parameters and the rationale for choosing such parameters. Typical QC data from laboratories reported to ADEQ are tabled in Section A7 of this document;

(i) The chain of custody procedures to be followed;

(j) If the remediation may be expected to include the storage of hazardous waste or soils contaminated with hazardous constituents on-site, the storage method, location, and expected duration must be detailed. The description must specify the precautions to be taken to protect the facility and surrounding community from exposure to the waste or soils contaminated with hazardous constituents;

(k) If the remediation entails excavation, the steps which will be taken to limit access to the excavated area must be described;

(l) If the remediation entails the use of imported back-fill, provisions for documenting that the back-fill is clean;

(m) The decontamination procedures and disposal techniques to be employed for all decontaminated solutions and personal protective equipment;

(n) The disposal method and identification of the disposal site(s) of all hazardous wastes and contaminated soils generated during the remediation;
(o) A schedule for performance of the remedy, including provision for prior ADEQ notification (5 days);
(p) Provisions for amendment of the RP should confirmatory sampling indicate the presence of hazardous waste or hazardous waste constituents~~,~~ are found above the applicable soil remediation standards of Title 18, Chapter 7, Article 2 or if any hazardous constituents may be expected to migrate to ground water;
(q) Documentation that the site has been flagged prior to remediation;
(r) Provisions for the submittal of a Remedial Report within 90 days of completion of the remedy providing:
    (i) A summary of results, significant observations, and conclusions.
    (ii) A discussion of the sampling followed for each site, including a description of:
    a. the sampling procedures used;
    b. the equipment used for sampling;
    c. the analytical procedures and methods used;
    d. the analytical equipment used;
    e. the quality assurance procedures used;
    (iii) The procedures used to prevent hazards and protect field personnel;
    (iv) The equipment used to prevent hazards and protect field personnel
    (v) Drawings and photographs where appropriate
    (vi) Description of any deviations from the approved RP.
    (vii) Data generated from the remedy and confirmatory sampling and analysis activities performed pursuant to the RP, including field notes, manifests, bills of lading, LDR forms, laboratory submittal forms, chain-of-custody forms, laboratory reports, and drilling logs;
(s) Provision for a request of a Finding of No Further Action from the Director, through a Class 1 Permit Modification request, if no hazardous constituents remain above the applicable soil remediation standards of Title 18, Chapter 7, Article 2, and if no hazardous constituents may be expected to migrate to ground water;
(t) The final approved RP is incorporated into the owner/operators HWM Permit.

Appendix C Arizona Administrative Code for Soil Remediation Standards

Below is the hyperlink to the Arizona Administrative Code for Title 18 (Environmental Quality) Chapter 7 (Department of Environmental Quality Remedial Action) Article 2 (Soil Remediation Standards):

http://www.azsos.gov/public_services/Title_18/18-07.htm

Appendix D Arizona Administrative Code for Water Quality Standards

Below is the hyperlink to the Arizona Administrative Code for Title 18 (Environmental Quality) Chapter 11 (Department of Environmental Quality Water Quality Standards):

http://www.azsos.gov/public_services/Title_18/18-11.htm

Appendix E Standard Operating Procedures

This appendix contains references and web addresses for numerous standard operating procedures (SOPs) from the U.S. Environmental Protection Agency (EPA). General sampling guidelines are included in the EPA SOP on General Field Sampling Guidelines. SOPs delineate the step-by-step approach that field personnel must follow in collecting samples, taking field measurements, decontaminating equipment, handling IDW and calibrating instruments. Most qualified sampling contractors and State and Federally certified laboratories develop SOPs and analytical methods as part of their overall QA program. SOPs should be developed following "Guidance for Preparation of Standard Operating Procedures for Quality-Related Operations" (EPA 1995). The field team should document which SOPs they are using in the field and any deviations from an SOP.

EPA SOPs for field sampling methods are available for download at:

http://www.ert.org/mainContent.asp?section=Products&subsection=List

Field personnel will ensure that all sampling equipment has been properly assembled, decontaminated and calibrated, and is functioning properly prior to use. Equipment will be used according to manufacturer's instructions, and should generally be decontaminated according to the EPA SOP for Sampling Equipment Decontamination.

The following list provides references and web addresses for a variety of SOPs provided by the EPA:

#1702 Sentex Scentograph Gas Chromatograph Field Use
#1703 Summa Canister Cleaning Procedures
#1704 Summa Canister Sampling
#1705 GC/MS Analysis of Tenax/CMS Cartridges and Summa Canisters
#1706 Summa Canister Field Standards
#1707 X-MET 880 Field Portable X-Ray Fluorescence Operating Procedures
#1708 Low Level Methane Analysis for Summa Canister Gas Samples
#1713 Spectrace 9000 Field Portable X-Ray Fluorescence Operating Procedure
#2001 General Field Sampling Guidelines
#2006 Sampling Equipment Decontamination
#2007 Groundwater Well Sampling
#2008 General Air Sampling Guidelines
#2009 Drum Sampling
#2010 Tank Sampling
#2011 Chip, Wipe, and Sweep Sampling
#2012 Soil Sampling
#2013 Surface Water Sampling
#2015 Asbestos Air Sampling
#2016 Sediment Sampling
#2017 Waste Pile Sampling
#2020 7-Day Standard Reference Toxicity Test Using Larval *Pimephales promelas*
#2021 24-Hour Range Finding Test Using *Daphnia magna* and *Daphnia pulex*
#2022 96-Hour Acute Toxicity Test Using *Pimephales promelas*
#2023 24-Hour Range Finding Test Using Larval *Pimephales promelas*
#2024 48-Hour Acute Toxicity Test using *Daphnia magna* and *Daphnia pulex*
#2025 Three Brood Static Renewal Toxicity Test Using *Ceriodaphnia dubia*
#2026 7-Day Static Renewal Toxicity Test Using Larval *Pimephales promelas*
#2027 96-Hour Static Toxicity Test Using *Selenastrum capricornutum*
#2028 10-Day Chronic Toxicity Test Using *Daphnia magna* and *Daphnia pulex*

#2030 Chlorophyll Determination
#2033 Plant Protein Determination
#2034 Plant Biomass Determination
#2035 Plant Peroxidase Activity Determination
#2036 Tree Coring and Interpretation
#2037 Terrestrial Plant Community Sampling
#2038 Vegetation Assessment Field Protocol
#2042 Soil Gas Sampling
#2043 Manual Water Level Measurements
#2044 Monitor Well Development
#2045 Controlled Pumping Test
#2046 Slug Tests
#2048 Monitor Well Installation
#2050 Model 5400 Geoprobe Operation
#2084 Activity-Based Air Sampling for Asbestos
#2101 Retrieving Meteorological Information
#2102 Tedlar Bag Sampling
#2103 Charcoal Tube Sampling in Ambient Air
#2104 Tenax/CMS Tube Sampling
#2107 Photovac 10A10 Portable Gas Chromatograph Operation
#2108 Photovac 10S50, 10S55, and 10S70 Gas Chromatograph Operation
#2109 Photovac GC Analysis for Soil, Water, and Air/Soil Gas
#2110 Microsensor P200
#2114 Photoionization Detector (PID) HNU
#2119 Air Sampling For Metals (NIOSH Method 7300, Elements)
#2120 Remote Meteorological Station
#2121 High Volume Polyurethane Foam Sampling
#2123 ALOHA 5.2.3 Air Model
#2124 CAMEO 1.2 Software System
#2129 Met One Remote Meteorological Station
#2138 Installation and Use of the MicroMet Plus® Software
#2200 Dry Suit Diving
#2201 Surface Supplied Diving Operations
#3019 Dive Operation Safety

The following list provides references and web addresses for a variety of SOPs provided by ASTM:
ASTM D 5088- 02(2008) Standards Practice for Decontamination of Field Equipment Used at Waste Sites

ASTM D 5679-95a. 1995. Standard Practice for Sampling Consolidated Solids in Drums or Similar Containers

ASTM D 5680-95a. 1995. Standard Practice for Sampling Unconsolidated Solids in Drums or Similar Containers.

ASTM D 5743-97. 1997. Standard Practice for Sampling Single or Multilayered Liquids, With or Without Solids, in Drums or Similar Containers

ASTM D 6063-96. 1996. Standard Guide for Sampling of Drums and Similar Containers by Field Personnel

ASTM D6232 - 2008 Standard Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities

Appendix F Field Forms

Contractors working on projects for HWM Facilities are expected provide their own field log sheets and field forms for common tasks, such as drilling and logging borings, drilling and installing monitoring wells, and sampling environmental media. Daily field logbook entries also constitute part of the record and should be included as an appendix to site assessment reports prepared for the HWM Program.

Copies of the chain-of-custody forms should be reported along with the analytical data from the laboratory. These are typically reported as a separate appendix in the investigation report. Sampling sheets filled out during sample collection should correlate with the information reported on the chain-of-custody forms.

For the occasions when the ADEQ HWM Program staff level personnel collect field samples, sample collection field sheets are used. Examples of these field sheets are included in the appendix.

Appendix G ADEQ Specific Quality Assurance Guidance and Policies

0154.000 **ADDRESSING SPIKE AND SURROGATE RECOVERY AS THEY RELATE TO MATRIX EFFECTS IN WATER, AIR, SLUDGE AND SOIL MATRICES POLICY**

Level One **Arizona Department of Environmental Quality**

Originator: Kenyon C. Carlson, Manager
Quality Assurance/Quality Control (QA/QC) Unit

Contact for Information: Kenyon C. Carlson, Manager
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Issue Date: October 23, 1998

PURPOSE

The Arizona Department of Health Services (ADHS) has not established a comprehensive policy on the issue of matrix spike or surrogate recoveries because they do not have the authority to establish criteria by which ADEQ will either accept or reject data.

This policy will assure that all data submitted to ADEQ meets regulatory requirements and are legally defensible by establishing alternative criteria for when the established method recovery acceptance criteria for matrix spikes and/or surrogates are exceeded.

ADEQ is concerned with the assumption that if spike and/or surrogate recoveries exceed method acceptance criteria and that if those results can be duplicated without re-extracting the sample, the failure of that quality control criteria is a result of matrix effects. Duplication of out-of-range results can be the result of influences other than matrix effects and could be indicative of the method or instrument being out-of-control.

The ADEQ QA/QC Unit believes a more accurate and reliable assessment of possible matrix effects can be established using either a (1) dilution technique, (2) the method of standard additions, or (3) analyzing a laboratory fortified blank (LFB) or a laboratory control sample (LCS). Because ADEQ is a regulatory agency, compliance results must be able to meet all legal constraints and uphold all analytical method requirements.

AUTHORITY

A.A.C. R18-4-106 and R9-14-608.

DEFINITIONS

Data: For the purposes of this policy, data is defined as `raw data' (examples include but are not limited to calibration curves, chromatograms, spectras, sample preparation and injection logs

etc.) and does not include laboratory reports. (Contact the QA unit for further information.)

Laboratory Fortified Blank (LFB): (aka blank spike)An aliquot of organic free reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology (analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Fortified Blank Duplicate (LFBD): (aka blank spike duplicate) A duplicate sample of the aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFBD is analyzed exactly like a sample, and its purpose is to determine whether the methodology (analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Control Sample (LCS): A sample of clean dirt or sand to which known quantities of the method analytes are added in the laboratory. The LCS is extracted and analyzed exactly like a sample, and its purpose is to determine whether the methodology (sample preparation and analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Control Sample Duplicate (LCSD): A duplicate sample of clean dirt or sand to which known quantities of the method analytes are added in the laboratory. The LCSD is extracted and analyzed exactly like a sample, and its purpose is to determine whether the methodology (sample preparation and analytical process) is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

Laboratory Fortified Sample Matrix (LFM): (aka matrix spike) An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and therefore determines to what degree the method is successful in analyzing the target analytes. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

Laboratory Fortified Sample Matrix Duplicate (LFMD): (aka matrix spike duplicate) A duplicate sample of the aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFMD is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results and therefore determines to what degree the method is successful in analyzing the

target analytes. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFMD corrected for background concentrations.

Matrix: The predominant material, component or substrate which contains the analyte of interest. Matrix is not necessarily synonymous with phase (liquid or solid).

Matrix Interference: Also referred to as matrix effects. Matrix spike interference are those chemical and/or physical interferences that impede the analytical instrumentation in detecting the true value concentration of a target analyte within a sample. One possible source of matrix interferences may be caused by contaminants that are co-extracted from the sample and result in a positive or negative bias. The extent of matrix interferences will vary considerably from source to source, depending upon the nature and diversity of the sample matrix.

Method of Standard Additions: A technique used most commonly in metals analysis by atomic absorption; however, it can be applied in many areas of the laboratory. It serves to correct for matrix effects in the sample. Aliquots of a sample are spiked with at least three different concentrations of a standard.

Surrogate: A pure analyte, which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amounts before extraction and is measured with the same procedures used to measure other sample components. A surrogate behaves similarly to the target analyte and its use is most often used with organic analytical procedures. The purpose of a surrogate analyte is to monitor method performance with each sample.

POLICY

ADEQ will not accept test results for regulatory purposes when the LFM and/or surrogate recovery exceed the acceptance criteria unless the laboratory has demonstrated that the sample itself is responsible for the QC results exceeding the methods acceptance criteria.

RESPONSIBILITY

The *ADEQ Program staff* will be responsible for reviewing the final report or the quality control summary sheets which accompany the final results of the laboratory analysis to verify that matrix spikes and/or surrogate recoveries were within the acceptance criteria. If the program staff are uncertain as to how to evaluate the final report, or if required information is missing, it shall be the responsibility of the program staff to forward the information to the ADEQ QA/QC Unit for review and recommendations.

The *ADEQ QA/QC Unit* will review data referred by program staff to ensure that the procedures outlined in Attachment A of this policy

were followed by the laboratory and to report their findings to the appropriate ADEQ program staff.

APPLICABILITY

This policy is applicable to all types of water, air, sludge, and soil matrices regardless of the method of analysis.

PROCEDURES

The *ADEQ program staff* shall review the final report or the quality control (QC) summary sheet which accompanies the final report. ADEQ program staff shall assess the results of the LFM and LFMB on the QC Summary sheet to determine if the recoveries are within the acceptance range. If the LFM or LFMB results exceed the established recovery criteria, ADEQ program staff will assess the recovery criteria for those out of range analytes in either the LFB/LFBD or LCS/LCSD. If the required information is not included with the final report or program staff are uncertain as how to evaluate the final report, they shall notify the QA/QC Unit so the QA/QC staff can perform a more thorough evaluation of the results.

The *ADEQ QA/QC staff*, if necessary, shall request a laboratory data package to review the raw data, determine the validity of the results and compliance with the ADEQ data reporting policy. The QA/QC Unit shall also submit in writing, to the program staff, the data validation findings and the ADEQ QA/QC Unit's recommendations.

ATTACHMENT

ATTACHMENT A

LABORATORY PROCEDURES

The ADEQ policy for addressing spike and surrogate recovery as they relate to matrix effects in water, air, sludge and soil matrices suggests three different techniques (analysis of an LFB/LFBD or LCS/LCSD pair, dilution procedure, or the standard additions technique) which may adequately explain the out-of-range QC results of samples. These three techniques do not represent an all inclusive list for demonstrating matrix effects within a sample and laboratories may have alternate and valid techniques to demonstrate matrix interference. These alternate techniques should be discussed with and approved by the ADEQ QA Unit prior to analysis to avoid the rejection of data.

ADEQ also requires the analyses of either an LFB/LFBD, LCS/LCSD or LFM/LFMD pair to satisfy the precision requirements for drinking water methods. More useful information can be obtained regarding precision when comparing samples containing target analytes. Very little useful precision information is obtained when comparing the instrument precision using two samples that are non detect. Whenever included in the analytical batch, the laboratory must report the results of the LFB/LFBD or LCS/LCSD in addition to the LFM/LFMD to ADEQ and shall include the numerical values established by the laboratory for the QC acceptance criteria whenever the method has not provided any.

While the method would require a re-extraction of that sample, to confirm matrix interference, if the LFM and/or the LFMB fall outside the method's acceptance criteria, ADEQ will accept the results of the LFB/LFBD or LCS/LCSD which demonstrate that the analytical process is in control. The LFB/LFBD and LCS/LCSD provide an interference free matrix such that if the surrogates and/or matrix spike analytes are within the method's acceptance criteria, then there is compelling data that an instrument is operating properly, the extraction procedure provided no bias, and the method is in control. The LFB/LFBD must be analyzed with the same batch as the LFM/LFMD for ADEQ to accept the LFB/LFBD results. The LCS/LCSD samples must be extracted and analyzed with the same batch as the LFM/LFMD samples for ADEQ to accept the results of the LCS/LCSD samples. The laboratory shall include the numerical values established by the laboratory for the QC acceptance criteria whenever the method has not provided any.

Another option is the dilution technique. The dilution technique is particularly well suited for demonstrating matrix effects in the LFM samples for analyses that don't require extraction procedures. Laboratories performing analytical work for ADEQ that suspect matrix interference in LFM samples may dilute that sample such that all suspected matrix effects are diluted out as well prior to spiking. Once the matrix effects have been diluted out, recovery of the matrix spikes and surrogates should fall within the

acceptable recovery criteria established by the method, or the lab if none are given in the method. The dilution of samples suspected of having matrix interference such that interference is no longer a factor strongly suggests that there may have been matrix effects in the sample and the recovery of the spiked analytes within the acceptance range demonstrates the instrumentation and method are in control. ADEQ will accept use of the dilution technique to demonstrate matrix effects in LFM and LFMD samples because not every sample is matrix spiked and it cannot be assumed that the matrix effects observed in one sample are representative of the entire sample batch.

Because the dilution technique raises the reporting level of an analyte, it may not be a suitable technique to demonstrate matrix interference if the resulting reporting level exceeds the regulatory (trigger) or action level. The method of standard additions would be a preferred technique to help correct for positive or negative bias in the samples because this technique is unlikely to raise the reporting level of regulated contaminants that may be present in the sample. The method of standard additions usually employs aliquots of a digested or extracted sample which are spiked with at least three different concentrations of a standard. The standard additions are chosen to bracket the unknown sample concentration and the response of the instrument must be linear.

Those samples whose matrix spikes or surrogate recoveries continue to fall outside the acceptance criteria after any of the above three techniques, or an alternate method pre-approved by the ADEQ QA Unit have been employed, shall be reviewed by ADEQ on a case-by-case basis. Any results reported which are affected by matrix interference shall be flagged as an estimated quantitation.

0154.000 ADDRESSING SPIKE AND SURROGATE RECOVERY AS THEY RELATE TO MATRIX EFFECTS IN WATER, AIR, SLUDGE AND SOIL MATRICES POLICY

Level One **Arizona Department of Environmental Quality**

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0170.000 IMPLEMENTATION OF EPA METHOD 5035 - SOIL PREPARATION FOR EPA METHODS 8015B, 8021B AND 8260B.

LEVEL TWO **Arizona Department of Environmental Quality**

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Issue Date:

Next Scheduled Review Date: 2 years from issuance

Authority: Arizona Revised Statutes (A.R.S.) §49-104(A)

I. PURPOSE

The EPA Office of Solid Waste promulgated Method 5035, ***Closed-System Purge-and-Trap Extraction for Volatile Organics in Soil and Waste Samples*** (Attachment 1), in June 1997 in SW-846, Update III. The Arizona Department of Health Services (ADHS) Office of Laboratory Licensure, Certification and Training adopted Method 5035 in May 1998 and Method 5035 became enforceable on March 1, 1999 in Arizona. The collection and analytical procedures for the approved method are flexible and, without further guidance, could result in multiple interpretations.

This policy establishes the sampling options and the preservation holding time requirements for individual programs within the ADEQ's Waste Programs Division. This policy is necessary to provide an understanding of the options set forth by the method and the limitations imposed on specific field sampling requirements. This policy does not eliminate the need to read and understand EPA Method 5035. The method, in conjunction with this policy, will provide a technically defensible and consistent approach to sampling for Volatile Organic Compounds (VOCs) in soils.

II. DEFINITIONS: (FOR PURPOSES OF EPA METHOD 5035 ONLY) -

1.	Sample Preservation:	The addition of methanol or sodium bisulfate to an unpreserved sample in the field or in the laboratory.
2.	Sample Extraction:	The addition of methanol to an unpreserved sample in the laboratory. After extraction, the methanol is transferred to a vial and can be stored at 4°C (± 2°C) until analysis.
3.	Hermetically Sealed:	For the purposes of this policy a hermetically sealed container shall be defined as a sample storage device that consistently shows less than 10% loss from volatilization over the intended storage holding time (usually 14 days) or a minimum of 48 hours for the compounds of concern at a given site.
4.	Sample Freezing:	A preservation technique in which the sample is frozen and stored at 0°C (32°F), or lower upon receipt at the laboratory. Blue ice is unacceptable.
5.	Calcareous Soil:	A soil whose content of carbonate is sufficient to cause effervescence when tested with hydrochloric acid. (Reference: Bates R. L. and Jackson J. A.. (1987). Glossary of Geology. (3rd ed.) Alexandria: American Geological Institute.)

III. POLICY

Method 5035 is structured as a 2-tier approach for low and high concentration sampling[1]. Preservation is recommended for both low and high contaminant concentrations as stated in the Method. Based upon program requirements, preservation can be conducted in the field or subsampled in an EnCore™ Sampler and the sample preserved in accordance with sample handling.

A. Sample collection options for low reporting limits (<200 µg/kg):

I. Methanol Preservation-

EPA has permitted the use of methanol preservation for low level analysis if the target analyte(s) can be quantitated below 200µg/kg. As a result, laboratories must demonstrate their ability to detect below 200 µg/kg to the client and ADHS. Samples preserved in the field with methanol using a 40 ml glass VOA vial with a plastic screw cap and a Teflon septa must be analyzed within 14 days from the time of sample collection.

ii. EnCore™ Sampler-

The sample can be collected using either a 5-gram or 25-gram EnCore™ Sampler. The sample must be stored at 4°C (±2°C) and preserved or extracted within 48 hours if not preserved. Approved preservatives include either methanol or sodium bisulfate. Once preserved, the sample must be analyzed within 14 days from the time of sample collection. The EnCore™ Sampler 48-hour preservation hold time as required in the method applies only to the EnCore™ Sampler option and is based on manufacturers' studies. Freezing the unpreserved sample in the EnCore™ Sampling device can extend the

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[1]Refer to EPA Method 5035 (Attachment 1) and Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices, June 23, 1999 (Attachment 2).

holding time up to seven days (e.g., 48 hours unfrozen and 5 days frozen.)

iii. Sodium Bisulfate Preservation-

Samples preserved in the field with sodium bisulfate must be analyzed 14 days from the time of sample collection. This technique should be used if detection limits in the range of 2 - 5 µg/kg are desired. Calcareous samples, however, may effervesce upon contact with the sodium bisulfate preservative solution (thereby liberating the volatile gases) and compromise the integrity of the sample. In these instances, sodium bisulfate preservative solution cannot be utilized to attain the lower reporting levels and one of three alternative sample collection methods must be employed.

a) The sample can be collected in a VOA vial containing 10 ml of reagent grade water, sealed with a plastic screw cap containing a Teflon septa and stored at 4°C (±2°C.) This sample must be analyzed within 48 hours from the time of sampling using a closed system purge and trap.

b) The sample can be collected in a dry VOA vial, sealed with a plastic screw cap containing a Teflon septa and stored at 4°C (±2°C.) Once at the lab, water must be introduced through the septa and analyzed by closed purge and trap within 48 hours from the time of sample collection. Freezing the unpreserved sample can extend the holding time an additional 5 days for a total of 7 days from the time of sample collection.

c) The sample can be collected in an EnCore™ Sampler, stored at 4°C (±2°C) and analyzed within 48 hours from the time of sample collection. Freezing the unpreserved sample can extend the holding time up to seven days.

iv. Bulk Sampling-

The rationale for the collection of bulk samples must be clearly documented and approved by the appropriate program in a work or sampling plan or other written

communication with ADEQ. If samples are not preserved in the field, the reasons for not preserving must be clearly documented and approved by the relevant program.

ADHS rules require laboratories to flag data generated from samples that have not been preserved in the field or have not been collected in recommended containers if the reporting levels are below 200 µg/kg.

B. Sample collection options for high reporting limits (>200µg/kg):

I. Methanol Preservation-

This technique may be used if the reporting limits are above 200 µg/kg. Samples preserved in the field with methanol using a 40 ml glass VOA vial with a plastic screw cap and a Teflon septa must be analyzed within 14 days from the time of sample collection.

ii. EnCore™ Sampler-

The sample can be collected using an EnCore™ Sampler. Methanol must be added within the 48-hour period immediately following sample collection. The EnCore™ Sampler 48-hour preservation hold time as required in the method is applicable specifically only to the EnCore™ subcoring device and is based on the manufacturers' studies. After collection the sample must be stored on ice at 4°C (±2°C) until analyzed. Freezing the unpreserved sample in the EnCore™ Sampling device can extend the holding time up to seven days (e.g., 48 hours unfrozen and 5 days frozen.) Once the sample is preserved, it must be analyzed within 14 days from the time of sample collection.

iii. Bulk Sampling-

The rationale for collection of bulk samples must be clearly documented and approved by the

appropriate program in a work or sampling plan or other written communication with ADEQ. If samples are not preserved in the field or subsampled in EnCore™ Samplers, the reasons for not preserving must be clearly documented and approved by the relevant program.

Significant volatile loss occurs when samples are collected in glass jars and transported to a laboratory for analysis[2]. Therefore, **glass jars with Teflon™ -lined lids containing no preservative ARE NOT ACCEPTABLE** for the collection of soil for VOC analysis, unless otherwise specified in this policy (Program Specific Requirements) or prior approval has been received from the relevant program.

III. Program Specific Requirements[3]:

1. WQARF, Hazardous Waste Compliance, Solid Waste Programs

When utilizing the field preservation option of the 5035 method, samples must be preserved immediately after collection with minimal handling to be considered reliable compliance samples. Samples maybe collected and held on ice at 4°C (±2°C) for a maximum of 2 hours before preserving or analyzing the sample. This option of holding samples on ice for up to 2 hours is accepted, but not encouraged, due to the known volatile loss over time.

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[2]Siegrist, R.L., and P.D. Jennsen, 1990. Evaluation of Sampling Method Effects of Volatile Organic Compound Measurements in Contaminated Soil, *Environmental Science and Technology*, Vol.24, pp. 1387-1392.

[3]For specific programs, a sample collected in a brass/steel sleeve is acceptable under the conditions noted in Section IV. The brass or steel sleeves must have each end covered with a sheet of Teflon, aluminum foil (aluminum is optional, but preferred) and sealed with a plastic cap. The plastic caps must be secured and the capped sleeve should be placed in a plastic ziplock bag which is then taped to ensure the caps are secure. The use of tape to bind the cap to the end of the sleeve is discouraged. The length of time a sample can be held in this container is finite and subject to specific program requirements set forth in Section V.

Samples collected and preserved or analyzed after 2 hours will be considered bulk samples and not suitable for compliance purposes. Data generated from samples collected and transported to a laboratory in this manner has limited compliance value and may not be accepted by the above referenced programs.

2. ***Hazardous Waste Inspections and Emergency Response Programs***

For planned field sampling events, samples must be preserved immediately after collection, with minimal handling, to be considered compliance samples. The sample may be held on ice at 4°C (±2°C) for a maximum of 2 hours before preserving or analyzing the sample.

For unanticipated sampling events, where significant difficulties exist for preserving samples onsite, bulk soil samples may be collected and stored at 4°C (±2°C) but must be preserved within 72 hours with the approval of the program.

3. ***UST Program***

When site-specific sampling conditions prevent the use of appropriate sample collection and preservation techniques as defined in Section I or Section II, samples may be submitted in properly sealed brass sleeve containers maintained at 4°C (±2°C) for laboratory analysis of VOCs. The laboratory must document sample holding time and flag the associated analytical results if sample preservation or extraction exceeds 48 hours, regardless of the reporting limit. Reasons for lack of field preservation within the 48 hour period and submittal of bulk samples for laboratory analysis must be clearly documented.

IV. Quality Control for unpreserved samples:

Unpreserved samples submitted to the laboratory should have matrix spikes and surrogates added directly to an aliquot of the sample before extraction. The laboratory should be requested to provide a narrative describing

the procedures for sample spiking and flag all data in which the matrix was not directly spiked prior to extraction.

V. Example of Holding Time Calculations for Frozen Samples:

Example 1 Sample is placed in a vial without chemical preservative in the field and stored at 4°C (±2°C).

The sample must be analyzed within 48 hours of collection.

Example 2 The sample is collected in a hermetically sealed subcoring and storage device in the field, stored at 4°C (±2°C) and transferred into a vial without chemical preservative in the laboratory.

The sample must be analyzed within 48 hours of collection.

Example 3 The sample is collected in a hermetically sealed subcoring and storage device, transported/stored at 4°C (±2°C), frozen at the laboratory 18 hours after collection, thawed (at ambient temperature) after 4 days and transferred into a vial without a chemical preservative in the laboratory.

The sample must be analyzed within 30 hours from the time the sample is defrosted to 4°C (±2°C).

48 hours allowed before analysis - 18 hours before freezing = 30 hours allowed from thawing (at ambient temperature) to analysis.

Freezing can only extend the holding times for unpreserved samples. Freezing is an alternative to preserving samples in the field. Freezing can never extend the holding times of samples beyond the analytical methods required holding time. (Ex. Freezing cannot extend the holding time from 14 days to 19 days).

VI. RESPONSIBILITY

All staff in the respective Waste Programs Division programs are responsible for knowledge and implementation of this policy. Supervisors are responsible for ensuring that the information contained in this policy is consistently and equitably applied by all staff. It is the responsibility of the sampler to inform the laboratory receiving personnel which program requirements are appropriate for the sample.

0000.000 IMPLEMENTATION OF EPA METHOD 5035 - SOIL PREPARATION FOR EPA METHODS 8015B, 8021B, AND 8260B POLICY

LEVEL TWO: Waste Programs Division

Originator: David Esposito, Director
Waste Programs Division

Contact: Kenyon C. Carlson, Manager
ADEQ QA/QC Unit

Issue Date:

Next Scheduled Review Date:

APPROVED BY:

Mark D. Charles for: 4/20/00
David Esposito, Date
Director
Waste Programs Division

4/21/00
Mark Santana Date
Administrative Counsel
Office of Administrative Counsel

The Policy Review Committee has posted, reviewed and accepted this policy by motion as of April 19, 2000.

Juanita Guidry Copeland 4/21/2000
Juanita Guidry Copeland Date
Acting Policy Coordinator

METHOD 5035

CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a closed-system purge-and-trap process for the analysis of volatile organic compounds (VOCs) in solid materials (e.g., soils, sediments, and solid waste). While the method is designed for use on samples containing low levels of VOCs, procedures are also provided for collecting and preparing solid samples containing high concentrations of VOCs and for oily wastes. For these high concentration and oily materials, sample collection and preparation are performed using the procedures described here, and sample introduction is performed using the aqueous purge-and-trap procedure in Method 5030. These procedures may be used in conjunction with any appropriate determinative gas chromatographic procedure, including, but not limited to, Methods 8015, 8021, and 8260.

1.2 The low soil method utilizes a hermetically-sealed sample vial, the seal of which is never broken from the time of sampling to the time of analysis. Since the sample is never exposed to the atmosphere after sampling, the losses of VOCs during sample transport, handling, and analysis are negligible. The applicable concentration range of the low soil method is dependent on the determinative method, matrix, and compound. However, it will generally fall in the 0.5 to 200 µg/kg range.

1.3 Procedures are included for preparing high concentration samples for purging by Method 5030. High concentration samples are those containing VOC levels of >200 µg/kg.

1.4 Procedures are also included for addressing oily wastes that are soluble in a water-miscible solvent. These samples are also purged using Method 5030..

1.5 Method 5035 can be used for most volatile organic compounds that have boiling points below 200°C and that are insoluble or slightly soluble in water. Volatile, water-soluble compounds can be included in this analytical technique. However, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency.

1.6 Method 5035, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5035 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Method 8021 in series with Method 8015.

1.7 As with any preparative method for volatiles, samples should be screened to avoid contamination of the purge-and-trap system by samples that contain very high concentrations of purgeable material above the calibration range of the low concentration method. In addition, because the sealed sample container cannot be opened to remove a sample aliquot without compromising the integrity of the sample, multiple sample aliquots should be collected to allow for screening and reanalysis.

1.8 The closed-system purge-and-trap equipment employed for low concentration samples is not appropriate for soil samples preserved in the field with methanol. Such samples should be analyzed using Method 5030 (see the note in Sec. 6.2.2).

1.9 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Low concentration soil method - generally applicable to and soils and other solid samples with VOC concentrations in the range of 0.5 to 200 µg/kg.

Volatile organic compounds (VOCs) are determined by collecting an approximately 5-g sample, weighed in the field at the time of collection, and placing it in a pre-weighed vial with a septum-sealed screw-cap (see Sec. 4) that already contains a stirring bar and a sodium bisulfate preservative solution. The vial is sealed and shipped to a laboratory or appropriate analysis site. The entire vial is then placed, unopened, into the instrument carousel. Immediately before analysis, organic-free reagent water, surrogates, and internal standards (if applicable) are automatically added without opening the sample vial. The vial containing the sample is heated to 40°C and the volatiles purged into an appropriate trap using an inert gas combined with agitation of the sample. Purged components travel via a transfer line to a trap. When purging is complete, the trap is heated and backflushed with helium to desorb the trapped sample components into a gas chromatograph for analysis by an appropriate determinative method.

2.2 High concentration soil method - generally applicable to soils and other solid samples with VOC concentrations greater than 200 µg/kg.

The sample introduction technique in Sec. 2.1 is not applicable to all samples, particularly those containing high concentrations (generally greater than 200 µg/kg) of VOCs which may overload either the volatile trapping material or exceed the working range of the determinative instrument system (e.g., GC/MS, GC/FID, GC/EC, etc.). In such instances, this method describes two sample collection options and the corresponding sample purging procedures.

2.2.1 The first option is to collect a bulk sample in a vial or other suitable container without the use of the preservative solution described in Sec. 2.1. A portion of that sample is removed from the container in the laboratory and is dispersed in a water-miscible solvent to dissolve the volatile organic constituents. An aliquot of the solution is added to 5 mL of reagent water in a purge tube. Surrogates and internal standards (if applicable) are added to the solution, then purged using Method 5030, and analyzed by an appropriate determinative method. Because the procedure involves opening the vial and removing a portion of the soil, some volatile constituents may be lost during handling.

2.2.2 The second option is to collect an approximately 5-g sample in a pre-weighed vial with a septum-sealed screw-cap (see Sec 4) that contains 5 mL of a water-miscible organic solvent (e.g., methanol). At the time of analysis, surrogates are added to the vial, then an aliquot of the solvent is removed from the vial, purged using Method 5030 and analyzed by an appropriate determinative method.

2.3 High concentration oily waste method - generally applicable to oily samples with VOC concentrations greater than 200 µg/kg that can be diluted in a water-miscible solvent.

Samples that are comprised of oils or samples that contain significant amounts of oil present additional analytical challenges. This procedure is generally appropriate for such samples when they are soluble in a water-miscible solvent.

2.3.1 After demonstrating that a test aliquot of the sample is soluble in methanol or polyethylene glycol (PEG), a separate aliquot of the sample is spiked with surrogates and diluted in the appropriate solvent. An aliquot of the solution is added to 5 mL of reagent water in a purge tube, taking care to ensure that a floating layer of oil is not present in the purge tube. Internal standards (if applicable) are added to the solution which is then purged using Method 5030 and analyzed by an appropriate determinative method.

2.3.2 Samples that contain oily materials that are not soluble in water-miscible solvents must be prepared according to Method 3585.

3.0 INTERFERENCES

3.1 Impurities in the purge gas and from organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running method blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed in sequence. Where practical, samples with unusually high concentrations of analytes should be followed by an analysis of organic-free reagent water to check for cross-contamination. If the target compounds present in an unusually concentrated sample are also found to be present in the subsequent samples, the analyst must demonstrate that the compounds are not due to carryover. Conversely, if those target compounds are <u>not</u> present in the subsequent sample, then the analysis of organic-free reagent water is not necessary.

3.4 The laboratory where volatile analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage area should be isolated from all atmospheric sources of methylene chloride, otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Sample Containers

The specific sample containers required will depend on the purge-and-trap system to be employed (see Sec. 4.2). Several systems are commercially available. Some systems employ 40-mL clear vials with a special frit and equipped with two PTFE-faced silicone septa. Other

systems permit the use of any good quality glass vial that is large enough to contain at least 5 g of soil or solid material and at least 10 mL of water and that can be sealed with a screw-cap containing a PTFE-faced silicone septum. Consult the purge-and-trap system manufacturer's instructions regarding the suitable specific vials, septa, caps, and mechanical agitation devices.

4.2 Purge-and-Trap System

The purge-and-trap system consists of a unit that automatically adds water, surrogates, and internal standards (if applicable) to a vial containing the sample, purges the VOCs using an inert gas stream while agitating the contents of the vial, and also traps the released VOCs for subsequent desorption into the gas chromatograph. Such systems are commercially available from several sources and shall meet the following specifications.

4.2.1 The purging device should be capable of accepting a vial sufficiently large to contain a 5-g soil sample plus a magnetic stirring bar and 10 mL of water. The device must be capable of heating a soil vial to 40°C and holding it at that temperature while the inert purge gas is allowed to pass through the sample. The device should also be capable of introducing at least 5 mL of organic-free reagent water into the sample vial while trapping the displaced headspace vapors. It must also be capable of agitating the sealed sample during purging, (e.g., using a magnetic stirring bar added to the vial prior to sample collection, sonication, or other means). The analytes being purged must be quantitatively transferred to an absorber trap. The trap must be capable of transferring the absorbed VOCs to the gas chromatograph (see 4.2.2).

NOTE: The equipment used to develop this method was a Dynatech PTA-30 W/S Autosampler. This device was subsequently sold to Varian, and is now available as the Archon Purge and Trap Autosampler. See the Disclaimer at the front of this manual for guidance on the use of alternative equipment.

4.2.2 A variety of traps and trapping materials may be employed with this method. The choice of trapping material may depend on the analytes of interest. Whichever trap is employed, it must demonstrate sufficient adsorption and desorption characteristics to meet the quantitation limits of all the target analytes for a given project and the QC requirements in Method 8000 and the determinative method. The most difficult analytes are generally the gases, especially dichlorodifluoromethane. The trap must be capable of desorbing the late eluting target analytes.

NOTE: Check the responses of the brominated compounds when using alternative charcoal traps (especially Vocarb 4000), as some degradation has been noted when higher desorption temperatures (especially above 240 - 250°C) are employed. 2-Chloroethyl vinyl ether is degraded on Vocarb 4000 but performs adequately when Vocarb 3000 is used. The primary criterion, as stated above, is that all target analytes meet the sensitivity requirements for a given project.

4.2.2.1 The trap used to develop this method was 25 cm long, with an inside diameter of 0.105 inches, and was packed with Carbopack/Carbosieve (Supelco, Inc.).

4.2.2.2 The standard trap used in other EPA purge-and-trap methods is also acceptable. That trap is 25 cm long and has an inside diameter of at least 0.105 in. Starting from the inlet, the trap contains the equal amounts of the adsorbents listed below. It is recommended that 1.0 cm of methyl silicone–coated packing (35/60 mesh, Davison, grade 15 or equivalent) be inserted at the inlet to extend the life of the trap. If

the analysis of dichlorodifluoromethane or other fluorocarbons of similar volatility is not required, then the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap.

4.2.2.2.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.2.2.2.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.2.2.2.3 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.2.2.3 Trapping materials other than those listed above also may be employed, provided that they meet the specifications in Sec. 4.2.3, below.

4.2.3 The desorber for the trap must be capable of rapidly heating the trap to the temperature recommended by the trap material manufacturer, prior to the beginning of the flow of desorption gas. Several commercial desorbers (purge-and-trap units) are available.

4.3 Syringe and Syringe Valves

4.3.1 25-mL glass hypodermic syringes with Luer-Lok (or equivalent) tip (other sizes are acceptable depending on sample volume used).

4.3.2 2-way syringe valves with Luer ends.

4.3.3 25-µL micro syringe with a 2 inch x 0.006 inch ID, 22° bevel needle (Hamilton #702N or equivalent).

4.3.4 Micro syringes - 10-, 100-µL.

4.3.5 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.4 Miscellaneous

4.4.1 Glass vials

4.4.1.1 60-mL, septum-sealed, to collect samples for screening, dry weight determination.

4.4.1.2 40-mL, screw-cap, PTFE lined, septum-sealed. Examine each vial prior to use to ensure that the vial has a flat, uniform sealing surface.

4.4.2 Top-loading balance - Capable of accurately weighing to 0.01 g.

4.4.3 Glass scintillation vials - 20-mL, with screw-caps and PTFE liners, or glass culture tubes with screw-caps and PTFE liners, for dilution of oily waste samples.

4.4.4 Volumetric flasks - Class A, 10-mL and 100-mL, with ground-glass stoppers.

4.4.5 2-mL glass vials, for GC autosampler - Used for ... waste samples extracted with methanol or PEG.

4.4.6 Spatula, stainless steel - narrow enough to fit into a sample vial.

4.4.7 Disposable Pasteur pipettes.

4.4.8 Magnetic stirring bars - PTFE- or glass-coated, of the appropriate size to fit the sample vials. Consult manufacturer's recommendation for specific stirring bars. Stirring bars may be reused, provided that they are thoroughly cleaned between uses. Consult the manufacturers of the purging device and the stirring bars for suggested cleaning procedures.

4.5 Field Sampling Equipment

4.5.1 Purge-and-Trap Soil Sampler - Model 3780PT (Associated Design and Manufacturing Company, 814 North Henry Street, Alexandria, VA 22314), or equivalent.

4.5.2 EnCore™ sampler - (En Chem, Inc., 1795 Industrial Drive, Green Bay, WI 54302), or equivalent.

4.5.3 Alternatively, disposable plastic syringes with a barrel smaller than the neck of the soil vial may be used to collect the sample. The syringe end of the barrel is cut off prior to sampling. One syringe is needed for each sample aliquot to be collected.

4.5.4 Portable balance - For field use, capable of weighing to 0.01 g.

4.5.5 Balance weights - Balances employed in the field should be checked against an appropriate reference weight at least once daily, prior to weighing any samples, or as described in the sampling plan. The specific weights used will depend on the total weight of the sample container, sample, stirring bar, reagent water added, cap, and septum.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 Methanol, CH_3OH - purge-and-trap quality or equivalent. Store away from other solvents.

5.3 Polyethylene glycol (PEG), $H(OCH_2CH_2)_nOH$ - free of interferences at the detection limit of the target analytes.

5.4 Low concentration sample preservative

5.4.1 Sodium bisulfate, $NaHSO_4$ - ACS reagent grade or equivalent.

5.4.2 The preservative should be added to the vial prior to shipment to the field, and must be present in the vial prior to adding the sample.

5.5 See the determinative method and Method 5000 for guidance on internal standards and surrogates to be employed in this procedure.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

Refer to the introductory material in this chapter, Organic Analytes, Sec. 4.1, for general sample collection information. The low concentration portion of this method employs sample vials that are filled and weighed in the field and never opened during the analytical process. As a result, sampling personnel should be equipped with a portable balance capable of weighing to 0.01 g.

6.1 Preparation of sample vials

The specific preparation procedures for sample vials depend on the expected concentration range of the sample, with separate preparation procedures for low concentration soil samples and high concentration soil and solid waste samples. Sample vials should be prepared in a fixed laboratory or other controlled environment, sealed, and shipped to the field location. Gloves should be worn during the preparation steps.

6.1.1 Low concentration soil samples

The following steps apply to the preparation of vials used in the collection of low concentration soil samples to be analyzed by the closed-system purge-and-trap equipment described in Method 5035.

6.1.1.1 Add a clean magnetic stirring bar to each clean vial. If the purge-and-trap device (Sec. 4.2) employs a means of stirring the sample other than a magnetic stirrer (e.g., sonication or other mechanical means), then the stir bar is omitted.

6.1.1.2 Add preservative to each vial. The preservative is added to each vial prior to shipping the vial to the field. Add approximately 1 g of sodium bisulfate to each vial. If samples markedly smaller or larger than 5 g are to be collected, adjust the amount of preservative added to correspond to approximately 0.2 g of preservative for each 1 g of sample. Enough sodium bisulfate should be present to ensure a sample pH of ≤2.

6.1.1.3 Add 5 mL of organic-free reagent water to each vial. The water and the preservative will form an acid solution that will reduce or eliminate the majority of the biological activity in the sample, thereby preventing biodegradation of the volatile target analytes.

6.1.1.4 Seal the vial with the screw-cap and septum seal. If the double-ended, fritted, vials are used, seal both ends as recommended by the manufacturer.

6.1.1.5 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.1.6 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

6.1.1.7 Because volatile organics will partition into the headspace of the vial from the aqueous solution and will be lost when the vial is opened, surrogates, matrix spikes, and internal standards (if applicable) should only be added to the vials after the sample has been added to the vial. These standards should be introduced back in the

laboratory, either manually by puncturing the septum with a small-gauge needle or automatically by the sample introduction system, just prior to analysis.

6.1.2 High concentration soil samples collected without a preservative

When high concentration samples are collected without a preservative, a variety of sample containers may be employed, including 60-mL glass vials with septum seals (see Sec. 4.4).

6.1.3 High concentration soil samples collected and preserved in the field

The following steps apply to the preparation of vials used in the collection of high concentration soil samples to be preserved in the field with methanol and analyzed by the aqueous purge-and-trap equipment described in Method 5030.

6.1.3.1 Add 10 mL of methanol to each vial.

6.1.3.2 Seal the vial with the screw-cap and septum seal.

6.1.3.3 Affix a label to each vial. This eliminates the need to label the vials in the field and assures that the tare weight of the vial includes the label. (The weight of any markings added to the label in the field is negligible).

6.1.3.4 Weigh the prepared vial to the nearest 0.01 g, record the tare weight, and write it on the label.

NOTE: Vials containing methanol should be weighed a second time on the day that they are to be used. Vials found to have lost methanol (reduction in weight of >0.01 g) should not be used for sample collection.

6.1.3.5 Surrogates, internal standards and matrix spikes (if applicable) should be added to the sample after it is returned to the laboratory and prior to analysis.

6.1.4 Oily waste samples

When oily waste samples are known to be soluble in methanol or PEG, sample vials may be prepared as described in Sec. 6.1.3, using the appropriate solvent. However, when the solubility of the waste is unknown, the sample should be collected without the use of a preservative, in a vial such as that described in Sec. 6.1.2.

6.2 Sample collection

Collect the sample according to the procedures outlined in the sampling plan. As with any sampling procedure for volatiles, care must be taken to minimize the disturbance of the sample in order to minimize the loss of the volatile components. Several techniques may be used to transfer a sample to the relatively narrow opening of the low concentration soil vial. These include devices such as the EnCore™ sampler, the Purge-and-Trap Soil Sampler ™, and a cut plastic syringe. Always wear gloves whenever handling the tared sample vials.

6.2.1 Low concentration soil samples

6.2.1.1 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.1.2 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the sample vial containing the preservative solution. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

NOTE: Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial. If the amount of gas generated is very small (i.e., several mL), any loss of volatiles as a result of such effervescence may be minimal if the vial is sealed quickly. However, if larger amounts of gas are generated, not only may the sample lose a significant amount of analyte, but the gas pressure may shatter the vial if the sample vial is sealed. Therefore, when samples are known or suspected to contain high levels of carbonates, a test sample should be collected, added to a vial, and checked for effervescence. If a rapid or vigorous reaction occurs, discard the sample and collect low concentration samples in vials that do not contain the preservative solution.

6.2.1.3 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.1.4 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.1.5 As with the collection of aqueous samples for volatiles, collect at least two replicate samples. This will allow the laboratory an additional sample for reanalysis. The second sample should be taken from the same soil stratum or the same section of the solid waste being sampled, and within close proximity to the location from which the original sample was collected.

6.2.1.6 In addition, since the soil vial cannot be opened without compromising the integrity of the sample, at least one additional aliquot of sample must be collected for screening, dry weight determination, and high concentration analysis (if necessary). This third aliquot may be collected in a 60-mL glass vial or a third 40-mL soil sample vial. However, this third vial must *not* contain the sample preservative solution, as an aliquot will be used to determine dry weight. If high concentration samples are collected in vials containing methanol, then two additional aliquots should be collected, one for high concentration analysis collected in a vial containing methanol, and another for the dry weight determination in a vial without either methanol or the low concentration aqueous preservative solution.

6.2.1 If samples are known or expected to co[illegible]n target analytes over a wide range of concentrations, thereby requiring the analyses of multiple sample aliquots, it may be advisable and practical to take an additional sample aliquot in a low concentration soil vial containing the preservative, but collecting only 1-2 g instead of the 5 g collected in Sec. 6.2.1.1. This aliquot may be used for those analytes that exceed the instrument calibration range in the 5-g analysis.

6.2.1.8 The EnCore™ sampler has not been thoroughly evaluated by EPA as a sample storage device. While preliminary results indicate that storage in the EnCore™ device may be appropriate for up to 48 hours, samples collected in this device should be transferred to the soil sample vials as soon as possible, or analyzed within 48 hours.

6.2.1.9 The collection of low concentration soil samples in vials that contain methanol is not appropriate for samples analyzed with the closed-system purge-and-trap equipment described in this method (see Sec. 6.2.2).

6.2.2 High concentration soil samples preserved in the field

The collection of soil samples in vials that contain methanol has been suggested by some as a combined preservation and extraction procedure. However, this procedure is not appropriate for use with the low concentration soil procedure described in this method.

NOTE: The use of methanol preservation has not been formally evaluated by EPA and analysts must be aware of two potential problems. First, the use of methanol as a preservative and extraction solvent introduces a significant dilution factor that will raise the method quantitation limit beyond the operating range of the low concentration direct purge-and-trap procedure (0.5-200 µg/kg). The exact dilution factor will depend on the masses of solvent and sample, but generally exceeds 1000, and may make it difficult to demonstrate compliance with regulatory limits or action levels for some analytes. Because the analytes of interest are volatile, the methanol extract cannot be concentrated to overcome the dilution problem. Thus, for samples of unknown composition, it may still be necessary to collect an aliquot for analysis by this closed-system procedure and another aliquot preserved in methanol and analyzed by other procedures. The second problem is that the addition of methanol to the sample is likely to cause the sample to fail the ignitability characteristic, thereby making the unused sample volume a hazardous waste.

6.2.2.1 When samples are known to contain volatiles at concentrations high enough that the dilution factor will not preclude obtaining results within the calibration range of the appropriate determinative method, a sample may be collected and immediately placed in a sample vial containing purge-and-trap grade methanol.

6.2.2.2 Using an appropriate sample collection device, collect approximately 5 g of sample as soon as possible after the surface of the soil or other solid material has been exposed to the atmosphere: generally within a few minutes at most. Carefully wipe the exterior of the sample collection device with a clean cloth or towel.

6.2.2.3 Using the sample collection device, add about 5 g (2 - 3 cm) of soil to the vial containing 10 mL of methanol. Quickly brush any soil off the vial threads and immediately seal the vial with the septum and screw-cap. Store samples on ice at 4°C.

6.2.2.4 When practical, use a portable balance to weigh the sealed vial containing the sample to ensure that 5.0 ± 0.5 g of sample were added. The balance should be calibrated in the field using an appropriate weight for the sample containers employed (Sec. 4.5.5). Record the weight of the sealed vial containing the sample to the nearest 0.01 g.

6.2.2.5 Alternatively, collect several trial samples with plastic syringes. Weigh each trial sample and note the length of the soil column in the syringe. Use these data to determine the length of soil in the syringe that corresponds to 5.0 ± 0.5 g. Discard each trial sample.

6.2.2.6 Other sample weights and volumes of methanol may be employed, provided that the analyst can demonstrate that the sensitivity of the overall analytical procedure is appropriate for the intended application.

6.2.2.7 The collection of at least one additional sample aliquot is required for the determination of the dry weight, as described in Sec. 6.2.1.6. Samples collected in methanol should be shipped as described in Sec. 6.3, and must be clearly labeled as containing methanol, so that the samples are not analyzed using the closed-system purge-and-trap equipment described in this procedure.

6.2.3 High concentration soil sample <u>not</u> preserved in the field

The collection of high concentration soil samples that are not preserved in the field generally follows similar procedures as for the other types of samples described in Secs. 6.2.1 and 6.2.2, with the obvious exception that the sample vials contain neither the aqueous preservative solution nor methanol. However, when field preservation is not employed, it is better to collect a larger volume sample, filling the sample container as full as practical in order to minimize the headspace. Such collection procedures generally do not require the collection of a separate aliquot for dry weight determination, but it may be advisable to collect a second sample aliquot for screening purposes, in order to minimize the loss of volatiles in either aliquot.

6.2.4 Oily waste samples

The collection procedures for oily samples depend on knowledge of the waste and its solubility in methanol or other solvents.

6.2.4.1 When an oily waste is <u>known</u> to be soluble in methanol or PEG, the sample may be collected in a vial containing such a solvent (see Sec. 6.1.4), using procedures similar to those described in Sec. 6.2.2.

6.2.4.2 When the solubility of the oily waste is <u>not</u> known, the sample should either be collected in a vial without a preservative, as described in Sec. 6.2.3, or the solubility of a trial sample should be tested in the field, using a vial containing solvent. If the trial sample is soluble in the solvent, then collect the oily waste sample as described in Sec. 6.2.2. Otherwise, collect an unpreserved sample as described in Sec. 6.2.3.

6.3 Sample ha.. .ng and shipment

All samples for volatiles analysis should be cooled to approximately 4°C, packed in appropriate containers, and shipped to the laboratory on ice, as described in the sampling plan.

6.4 Sample storage

6.4.1 Once in the laboratory, store samples at 4°C until analysis. The sample storage area should be free of organic solvent vapors.

6.4.2 All samples should be analyzed as soon as practical, and within the designated holding time from collection. Samples not analyzed within the designated holding time must be noted and the data are considered minimum values.

6.4.3 When the low concentration samples are strongly alkaline or highly calcareous in nature, the sodium bisulfate preservative solution may not be strong enough to reduce the pH of the soil/water solution to below 2. Therefore, when low concentration soils to be sampled are known or suspected to be strongly alkaline or highly calcareous, additional steps may be required to preserve the samples. Such steps include: addition of larger amounts of the sodium bisulfate preservative to non-calcareous samples, storage of low concentration samples at -10°C (taking care not to fill the vials so full that the expansion of the water in the vial breaks the vial), or significantly reducing the maximum holding time for low concentration soil samples. Whichever steps are employed, they should be clearly described in the sampling and QA project plans and distributed to both the field and laboratory personnel. See Sec. 6.2.1.2 for additional information.

7.0 PROCEDURE

This section describes procedures for sample screening, the low concentration soil method, the high concentration soil method, and the procedure for oily waste samples. High concentration samples are to be introduced into the GC system using Method 5030. Oily waste samples are to be introduced into the GC system using Method 5030 if they are soluble in a water-miscible solvent, or using Method 3585 if they are not.

7.1 Sample screening

7.1.1 It is highly recommended that all samples be screened prior to the purge-and-trap GC or GC/MS analysis. Samples may contain higher than expected quantities of purgeable organics that will contaminate the purge-and-trap system, thereby requiring extensive cleanup and instrument maintenance. The screening data are used to determine which is the appropriate sample preparation procedure for the particular sample, the low concentration closed-system direct purge-and-trap method (Sec. 7.2), the high concentration (methanol extraction) method (Sec. 7.3), or the nonaqueous liquid (oily waste) methanol or PEG dilution procedure (Sec. 7.4).

7.1.2 The analyst may employ any appropriate screening technique. Two suggested screening techniques employing SW-846 methods are:

7.1.2.1 Automated headspace (Method 5021) using a gas chromatograph (GC) equipped with a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series, or,

7.1.2.2 Extraction of the sample with hexadecane (Method 3820) and analysis of the extract on a GC equipped with a FID and/or an ECD.

7.1.3 The analyst may inject a calibration standard containing the analytes of interest at a concentration equivalent to the upper limit of the calibration range of the low concentration soil method. The results from this standard may be used to determine when the screening results approach the upper limit of the low concentration soil method. There are no linearity or other performance criteria associated with the injection of such a standard, and other approaches may be employed to estimate sample concentrations.

7.1.4 Use the low concentration closed-system purge-and-trap method (Sec. 7.2) if the estimated concentration from the screening procedure falls within the calibration range of the selected determinative method. If the concentration exceeds the calibration range of the low concentration soil method, then use either the high concentration soil method (Sec. 7.3), or the oily waste method (Sec. 7.4).

7.2 Low concentration soil method (Approximate concentration range of 0.5 to 200 µg/kg - the concentration range is dependent upon the determinative method and the sensitivity of each analyte.)

7.2.1 Initial calibration

Prior to using this introduction technique for any GC or GC/MS method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the determinative methods and Method 5000 provide specific information on calibration and preparation of standards. Normally, external standard calibration is preferred for the GC methods (non-MS detection) because of possible interference problems with internal standards. If interferences are not a problem, or when a GC/MS method is used, internal standard calibration may be employed.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.2 and that is connected to a gas chromatograph or a gas chromatograph/mass spectrometer system.

7.2.1.2 Before initial use, a Carbopack/Carbosieve trap should be conditioned overnight at 245°C by backflushing with an inert gas flow of at least 20 mL/minute. If other trapping materials are substituted for the Carbopack/Carbosieve, follow the manufacturers recommendations for conditioning. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 minutes at 245°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.3 If the standard trap in Sec. 4.2.2.2 is employed, prior to initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min, or according to the manufacturer's recommendations. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

7.2.1.4 Establish the purge-and-trap instrument operating conditions. Adjust the instrument to inject 5 mL of water, to heat the sample to 40°C, and to hold the sample at 40°C for 1.5 minutes before commencing the purge process, or as recommended by the instrument manufacturer.

7.2.1.5 Prepare a minimum of five initial calibration standards containing all the analytes of interest and surrogates, as described in Method 8000, and following the instrument manufacturer's instructions. The calibration standards are prepared in organic-free reagent water. The volume of organic-free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL added to the vial before shipping it to the field plus the organic-free reagent water added by the instrument). The calibration standards should also contain approximately the same amount of the sodium bisulfate preservative as the sample (e.g., ~1 g), as the presence of the preservative will affect the purging efficiencies of the analytes. The internal standard solution must be added automatically, by the instrument, in the same fashion as used for the samples. Place the soil vial containing the solution in the instrument carousel. In order to calibrate the surrogates using standards at five concentrations, it may be necessary to disable the automatic addition of surrogates to each vial containing a calibration standard (consult the manufacturer's instructions). Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as recommended by the manufacturer.

7.2.1.6 Carry out the purge-and-trap procedure as outlined in Secs. 7.2.3. to 7.2.5.

7.2.1.7 Calculate calibration factors (CF) or response factors (RF) for each analyte of interest using the procedures described in Method 8000. Calculate the average CF (external standards) or RF (internal standards) for each compound, as described in Method 8000. Evaluate the linearity of the calibration data, or choose another calibration model, as described in Method 8000 and the specific determinative method.

7.2.1.8 For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.8.1 Chloromethane is the most likely compound to be lost if the purge flow is too fast.

7.2.1.8.2 Bromoform is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.8.3 Tetrachloroethane and 1,1-dichloroethane are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.9 When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross-contamination and memory effects from a high concentration sample or even the standard are a common problem.

Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification

Refer to Method 8000 for details on calibration verification. A single standard near the mid-point of calibration range is used for verification. This standard should also contain approximately 1 g of sodium bisulfate.

7.2.3 Sample purge-and-trap

This method is designed for a 5-g sample size, but smaller sample sizes may be used. Consult the instrument manufacturer's instructions regarding larger sample sizes, in order to avoid clogging of the purging apparatus. The soil vial is hermetically sealed at the sampling site, and MUST remain so in order to guarantee the integrity of the sample. Gloves must be worn when handling the sample vial since the vial has been tared. If any soil is noted on the exterior of the vial or cap, it must be carefully removed prior to weighing. Weigh the vial and contents to the nearest 0.01 g, even if the sample weight was determined in the field, and record this weight. This second weighing provides a check on the field sampling procedures and provides additional assurance that the reported sample weight is accurate. Data users should be advised on significant discrepancies between the field and laboratory weights.

7.2.3.1 Remove the sample vial from storage and allow it to warm to room temperature. Shake the vial gently, to ensure that the contents move freely and that stirring will be effective. Place the sample vial in the instrument carousel according to the manufacturer's instructions.

7.2.3.2 Without disturbing the hermetic seal on the sample vial, add 5 mL of organic-free reagent water, the internal standards, and the surrogate compounds. This is carried out using the automated sampler. Other volumes of organic-free reagent water may be used, however, it is imperative that all samples, blanks, and calibration standards have exactly the same final volume of organic-free reagent water. Prior to purging, heat the sample vial to 40°C for 1.5 minutes, or as described by the manufacturer.

7.2.3.3 For the sample selected for matrix spiking, add the matrix spiking solution described in Sec. 5.0 of Method 5000, either manually, or automatically, following the manufacturer's instructions. The concentration of the spiking solution and the amount added should be established as described in Sec. 8.0 of Method 8000.

7.2.3.4 Purge the sample with helium or another inert gas at a flow rate of up to 40 mL/minute (the flow rate may vary from 20 to 40 mL/min, depending on the target analyte group) for 11 minutes while the sample is being agitated with the magnetic stirring bar or other mechanical means. The purged analytes are allowed to flow out of the vial through a glass-lined transfer line to a trap packed with suitable sorbent materials.

7.2.4 Sample Desorption

7.2.4.1 Non-cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode and preheat the trap to 245°C without a flow

of desorption gas. Start the flow of desorption gas . . 10 mL/minute for about four minutes (1.5 min is normally adequate for analytes in Method 8015). Begin the temperature program of the gas chromatograph and start data acquisition.

7.2.4.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure that the cryogenic interface is at -150°C or lower, and rapidly heat the trap to 245°C while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Methods 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C. Begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.5 Trap Reconditioning

After desorbing the sample for 4 minutes, recondition the trap by returning the purge-and-trap system to the purge mode. Maintain the trap temperature at 245°C (or other temperature recommended by the manufacturer of the trap packing materials). After approximately 10 minutes, turn off the trap heater and halt the purge flow through the trap. When the trap is cool, the next sample can be analyzed.

7.2.6 Data Interpretation

Perform qualitative and quantitative analysis following the guidance given in the determinative method and Method 8000. If the concentration of any target analyte exceeds the calibration range of the instrument, it will be necessary to reanalyze the sample by the high concentration method. Such reanalyses need only address those analytes for which the concentration exceeded the calibration range of the low concentration method. Alternatively, if a sample aliquot of 1-2 g was also collected (see Sec. 6.2.1.7), it may be practical to analyze that aliquot for the analytes that exceeded the instrument calibration range in the 5-g analysis. If results are to be reported on a dry weight basis, proceed to Sec. 7.5

7.3 High concentration method for soil samples with concentrations generally greater than 200 µg/kg.

The high concentration method for soil is based on a solvent extraction. A solid sample is either extracted or diluted, depending on sample solubility in a water-miscible solvent. An aliquot of the extract is added to organic-free reagent water containing surrogates and, if applicable, internal and matrix spiking standards, purged according to Method 5030, and analyzed by an appropriate determinative method. Wastes that are insoluble in methanol (i.e., petroleum and coke wastes) are diluted with hexadecane (see Sec. 7.3.8).

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were <u>not</u> preserved in the field are prepared using the steps below, beginning at Sec. 7.3.1. If solvent preservation was employed in the field, then the preparation begins with Sec. 7.3.4.

7.3.1 When the high concentration sample is <u>not</u> preserved in the field, the sample consists of the entire contents of the sample container. Do not discard any supernatant liquids. Whenever practical, mix the contents of the sample container by shaking or other mechanical means without opening the vial. When shaking is not practical, quickly mix the contents of the vial with a narrow metal spatula and immediately reseal the vial.

7.3.2 If the sample is from an unknown source, perform a solubility test before proceeding. Remove several grams of material from the sample container. Quickly reseal the container to minimize the loss of volatiles. Weigh 1-g aliquots of the sample into several test tubes or other suitable containers. Add 10 mL of methanol to the first tube, 10 mL of PEG to the second, and 10 mL of hexadecane to the third. Swirl the sample and determine if it is soluble in the solvent. Once the solubility has been evaluated, discard these test solutions. If the sample is soluble in either methanol or PEG, proceed with Sec. 7.3.3. If the sample is only soluble in hexadecane, proceed with Sec. 7.3.8.

7.3.3 For soil and solid waste samples that are soluble in methanol, add 9.0 mL of methanol and 1.0 mL of the surrogate spiking solution to a tared 20-mL vial. Using a top-loading balance, weigh 5 g (wet weight) of sample into the vial. Quickly cap the vial and reweigh the vial. Record the weight to 0.1 g. Shake the vial for 2 min. If the sample was not soluble in methanol, but was soluble in PEG, employ the same procedure described above, but use 9.0 mL of PEG in place of the methanol. Proceed with Sec. 7.3.5.

NOTE: The steps in Secs. 7.3.1, 7.3.2, and 7.3.3 must be performed rapidly and without interruption to avoid loss of volatile organics. These steps must be performed in a laboratory free from solvent fumes.

7.3.4 For soil and solid waste samples that were collected in methanol or PEG (see Sec. 6.2.2), weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum, shake for 2 min, as described above, and proceed with Sec. 7.3.5.

7.3.5 Pipet approximately 1 mL of the extract from either Sec. 7.3.3 or 7.3.4 into a GC vial for storage, using a disposable pipet, and seal the vial. The remainder of the extract may be discarded. Add approximately 1 mL of methanol or PEG to a separate GC vial for use as the method blank for each set of samples extracted with the same solvent.

7.3.6 The extracts must be stored at 4°C in the dark, prior to analysis. Add an appropriate aliquot of the extract (see Table 2) to 5.0 mL of organic-free reagent water and analyze by Method 5030 in conjunction with the appropriate determinative method. Proceed to Sec. 7.0 in Method 5030 and follow the procedure for purging high concentration samples.

7.3.7 If results are to be reported on a dry weight basis, determine the dry weight of a separate aliquot of the sample, using the procedure in Sec. 7.5, after the sample extract has been transferred to a GC vial and the vial sealed.

7.3.8 For solids that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste) dilute or extract the sample with hexadecane using the procedures in Sec. 7.0 of Method 3585.

7.4 High concentration method for oily waste samples

This procedure for the analysis of oily waste samples involves the dilution of the sample in methanol or PEG. However, care must be taken to avoid introducing any of the floating oil layer into the instrument. A portion of the diluted sample is then added to 5.0 mL of organic-free reagent water, purged according to Method 5030, and analyzed using an appropriate determinative method.

For oily samples that are not soluble in methanol or PEG (including those samples consisting primarily of petroleum or coking waste), dilute or extract with hexadecane using the procedures in Sec. 7.0 of Method 3585.

The specific sample preparation steps depend on whether or not the sample was preserved in the field. Samples that were not preserved in the field are prepared using the steps below, beginning at Sec. 7.4.1. If methanol preservation was employed in the field, then the preparation begins with Sec. 7.4.3.

7.4.1 If the waste was not preserved in the field and it is soluble in methanol or PEG, weigh 1 g (wet weight) of the sample into a tared 10-mL volumetric flask, a tared scintillation vial, or a tared culture tube. If a vial or tube is used instead of a volumetric flask, it must be calibrated prior to use. This operation must be performed prior to opening the sample vial and weighing out the aliquot for analysis.

7.4.1.1 To calibrate the vessel, pipet 10.0 mL of methanol or PEG into the vial or tube and mark the bottom of the meniscus.

7.4.1.2 Discard this solvent, and proceed with weighing out the 1-g sample aliquot.

7.4.2 Quickly add 1.0 mL of surrogate spiking solution to the flask, vial, or tube, and dilute to 10.0 mL with the appropriate solvent (methanol or PEG). Swirl the vial to mix the contents and then shake vigorously for 2 minutes.

7.4.3 If the sample was collected in the field in a vial containing methanol or PEG, weigh the vial to 0.1 g as a check on the weight recorded in the field, add the surrogate spiking solution to the vial by injecting it through the septum. Swirl the vial to mix the contents and then shake vigorously for 2 minutes and proceed with Sec. 7.4.4.

7.4.4 Regardless of how the sample was collected, the target analytes are extracted into the solvent along with the majority of the oily waste (i.e., some of the oil may still be floating on the surface). If oil is floating on the surface, transfer 1 to 2 mL of the extract to a clean GC vial using a Pasteur pipet. Ensure that no oil is transferred to the vial.

7.4.5 Add 10 - 50 µL of the methanol extract to 5 mL of organic-free reagent water for purge-and-trap analysis, using Method 5030.

7.4.6 Prepare a matrix spike sample by adding 10 - 50 µL of the matrix spike standard dissolved in methanol to a 1-g aliquot of the oily waste. Shake the vial to disperse the matrix spike solution throughout the oil. Then add 10 mL of extraction solvent and proceed with the extraction and analysis, as described in Secs. 7.4.2 - 7.4.5. Calculate the recovery of the spiked analytes as described in Method 8000. If the recovery is not within the acceptance limits for the application, use the hexadecane dilution technique in Sec. 7.0 of Method 3585.

7.5 Determination of % Dry Weight

If results are to be reported on a dry weight basis, it is necessary to determine the dry weight of the sample.

NOTE: It is highly recommended that the dry weight determination only be made after the analyst has determined that no sample aliquots will be taken from the 60-mL vial for high

concentration analysis. This is to minimize loss of volatiles and to avoid sample contamination from the laboratory atmosphere. There is no holding time associated with the dry weight determination. Thus, this determination can be made any time prior to reporting the sample results, as long as the vial containing the additional sample has remained sealed and properly stored.

7.5.1 Weigh 5-10 g of the sample from the 60-mL VOA vial into a tared crucible.

7.5.2 Dry this aliquot overnight at 105°C. Allow to cool in a desiccator before weighing. Calculate the % dry weight as follows:

$$\% \text{ dry weight} = \frac{\text{g of dry sample}}{\text{g of sample}} \times 100$$

WARNING: The drying oven should be contained in a hood or vented. Significant laboratory contamination may result from a heavily contaminated hazardous waste sample.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat this demonstration whenever new staff are trained or significant changes in instrumentation are made. See Sec. 8.0 of Methods 5000 and 8000 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - See Sec. 8.0 in Method 5000 and Method 8000 for procedures to follow to demonstrate acceptable continuing performance on each set of samples to be analyzed. These include the method blank, either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis, a laboratory control sample (LCS), and the addition of surrogates to each sample and QC sample.

8.5 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Single laboratory accuracy and precision data were obtained for the method analytes in three soil matrices, sand, a soil collected 10 feet below the surface of a hazardous landfill, called the

C-Horizon, and a surface garden soil. Each sample was fortified with the analytes at a concentration of 20 ng/5 g, which is equivalent to 4 µg/kg. These data are listed in tables found in Method 8260.

9.2 Single laboratory accuracy and precision data were obtained for certain method analytes when extracting oily liquid using methanol as the extraction solvent. The data are presented in a table in Method 8260. The compounds were spiked into three portions of an oily liquid (taken from a waste site) following the procedure for matrix spiking described in Sec. 7.4. This represents a worst case set of data based on recovery data from many sources of oily liquid.

10.0 REFERENCES

1. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry" U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November 1991.

2. Siegrist, R. L., Jenssen, P. D., "Evaluation of Sampling Method Effects on Volatile Organic Compound Measurements in Contaminated Soils", Envir Sci Technol, 1990; 24; 1387-92.

3. Hewitt, A. D., Jenkins, T. F., Grant, C. L., "Collection, Handling and Storage: Keys to Improved Data Quality for Volatile Organic Compounds in Soil", Am Environ Lab, 1995; 7(1); 25-8.

4. Liikala, T. L., Olsen, K. B., Teel, S. S., Lanigan, D. C., "Volatile Organic Compounds: Comparison of Two Sample Collection and Preservation Methods", Envir Sci Technol, 1996; 30; 3441-7.

5. Lewis, T. E., Crockett, A. B., Siegrist, R. L., Zarrabi, K., "Soil Sampling and Analysis for Volatile Organic Compounds", Envir Monitoring & Assessment, 1994; 30; 213-46.

6. Hewitt, A. D., "Enhanced Preservation of Volatile Organic Compounds in Soil with Sodium Bisulfate", SR95-26, U. S. Army Cold Regions Research and Engineering Laboratory, Hanover, NH.

7. Hewitt, A. D., Lukash, N. J. E., "Sampling for In-Vial Analysis of Volatile Organic Compounds in Soil", Am Environ Lab, 1996; Aug; 15-9.

8. Hewitt, A. D., Miyares, P. H., Sletten, R. S., "Determination of Two Chlorinated Volatile Organic Compounds in Soil by Headspace Gas Chromatography and Purge-and-Trap Gas Chromatography/Mass Spectrometry", Hydrocarbon Contaminated Soils, 1993, 3; 135–45, Chelsea, MI, Lewis Publishers.

9. Hewitt, A. D., "Methods of Preparing Soil Samples for Headspace Analysis of Volatile Organic Compounds: Emphasis on Salting Out", 12th Annual Waste Testing and Quality Assurance Symposium, Washington, DC, 1996, 322-9.

10. Hewitt, A. D., Miyares, P. H., Leggett, D. C., Jenkins, T. F., "Comparison of Analytical Methods for Determination of Volatile Organic Compounds", Envir Sci Tech, 1992; 26; 1932-8.

TABLE 1

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH CONCENTRATION SOILS/SEDIMENTS

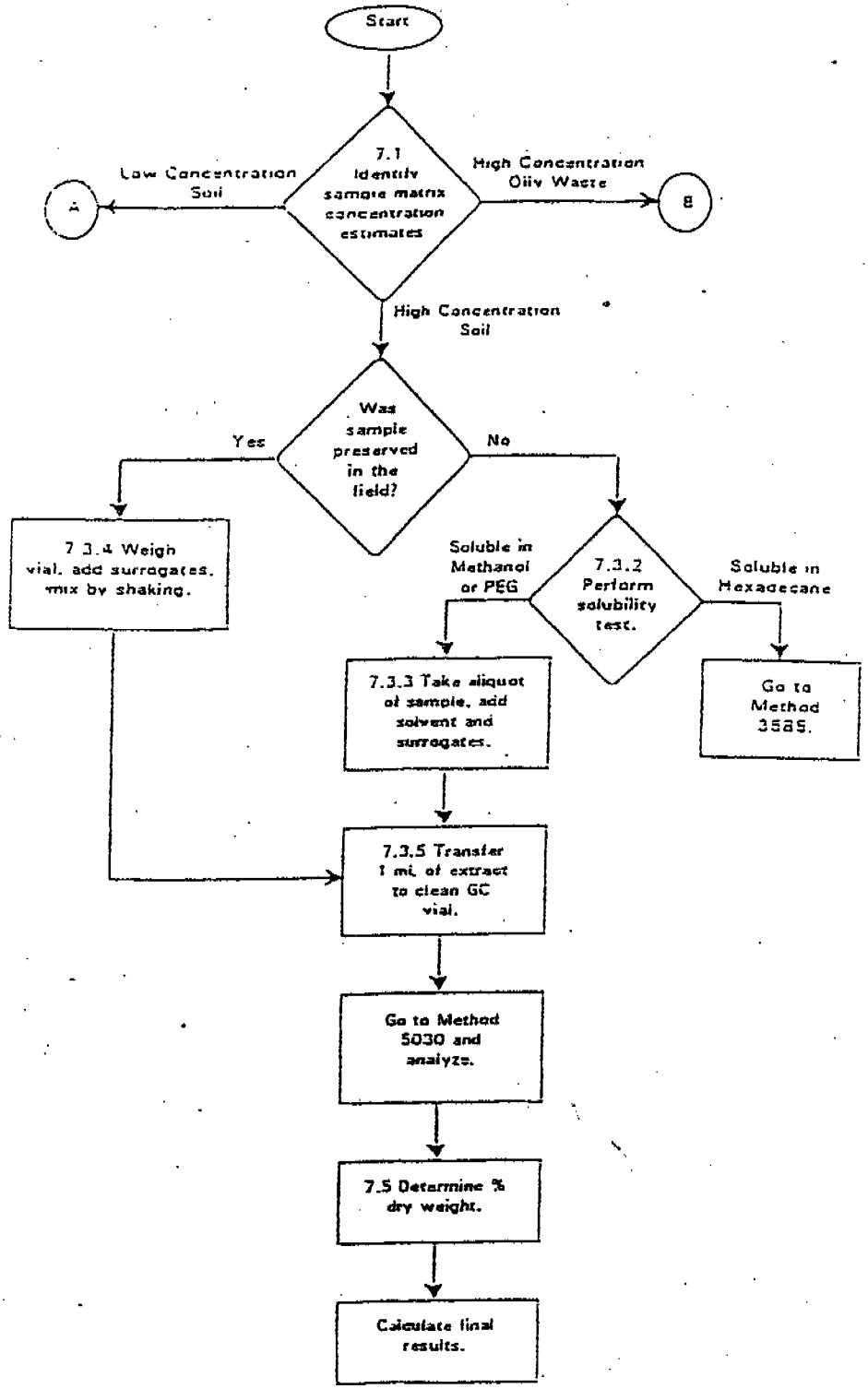
Approximate Concentration Range	Volume of Methanol Extract[a]
500 - 10,000 µg/kg	100 µL
1,000 - 20,000 µg/kg	50 µL
5,000 - 100,000 µg/kg	10 µL
25,000 - 500,000 µg/kg	100 µL of 1/50 dilution[b]

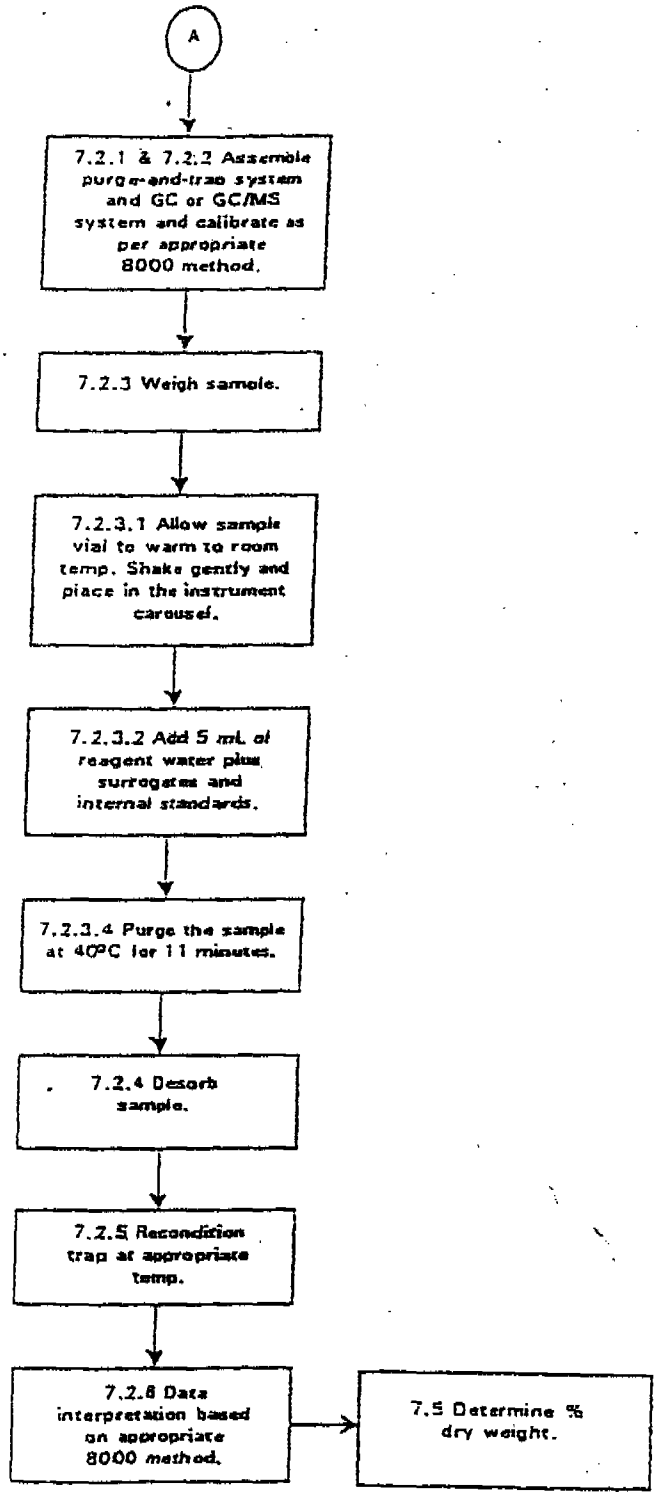
Calculate appropriate dilution factor for concentrations exceeding those in this table.

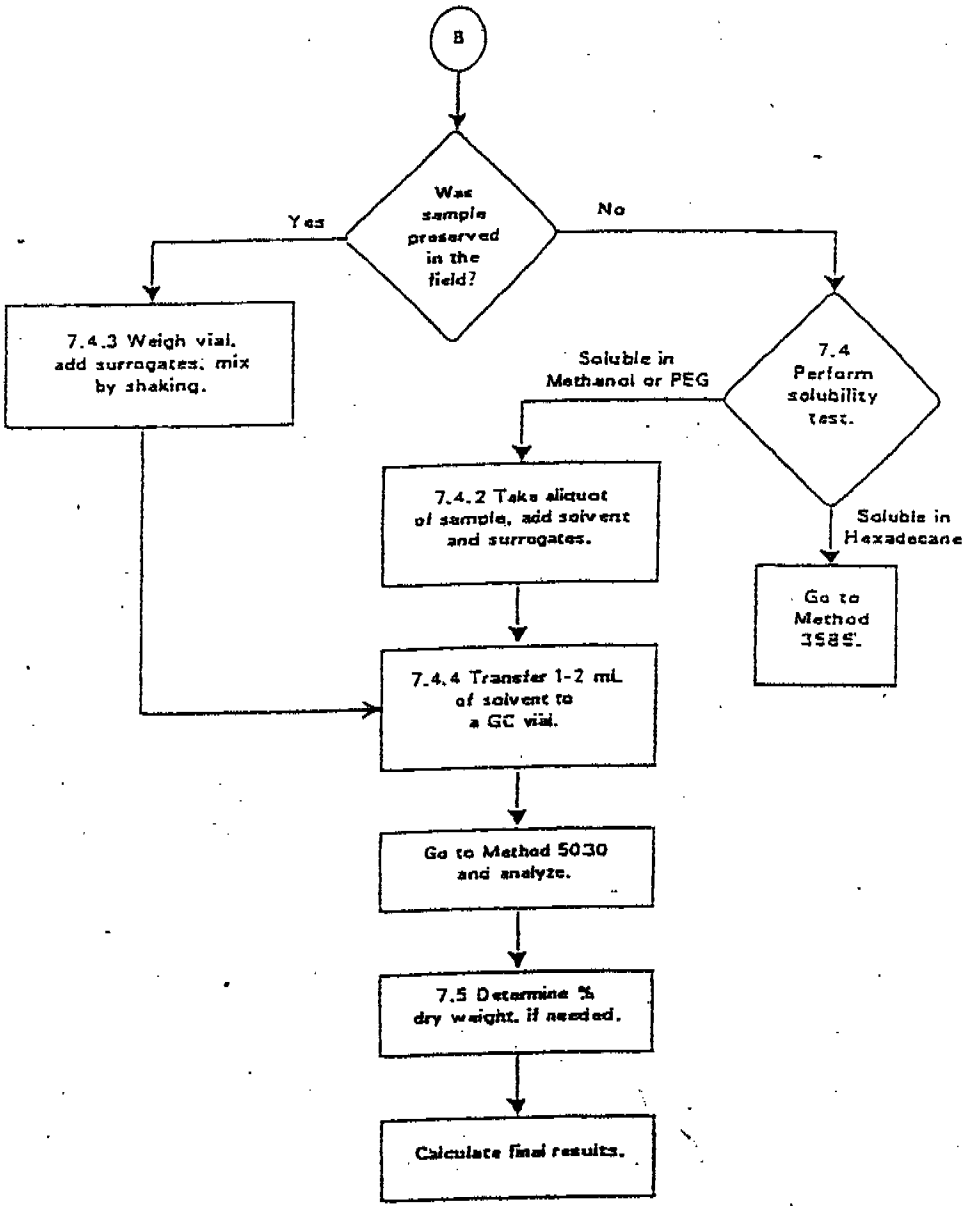
[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5-mL syringe whatever volume of methanol is necessary to maintain a total volume of 100 µL of methanol.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

METHOD 5035
CLOSED-SYSTEM PURGE-AND-TRAP AND EXTRACTION FOR VOLATILE ORGANICS IN SOIL AND WASTE SAMPLES




A
7.2.1 & 7.2.2 Assemble purge-and-trap system and GC or GC/MS system and calibrate as per appropriate 8000 method.
7.2.3 Weigh sample.
7.2.3.1 Allow sample vial to warm to room temp. Shake gently and place in the instrument carousel.
7.2.3.2 Add 5 mL of reagent water plus surrogates and internal standards.
7.2.3.4 Purge the sample at 40°C for 11 minutes.
7.2.4 Desorb sample.
7.2.5 Recondition trap at appropriate temp.
7.2.6 Data interpretation based on appropriate 8000 method.
7.5 Determine % dry weight.


B
Was sample preserved in the field?
Yes
No
7.4.3 Weigh vial, add surrogates, mix by shaking.
7.4 Perform solubility test.
Soluble in Methanol or PEG
Soluble in Hexadecane
7.4.2 Take aliquot of sample, add solvent and surrogates.
Go to Method 3585.
7.4.4 Transfer 1-2 mL of solvent to a GC vial.
Go to Method 5030 and analyze.
7.5 Determine % dry weight, if needed.
Calculate final results.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
REGION IX
75 Hawthorne Street
San Francisco, CA 94105-3901

June 23, 1999

MEMORANDUM

SUBJECT: Regional Interim Policy for Determination of Volatile Organic Compound (VOC) Concentrations in Soil and Solid Matrices.

FROM: Nora McGee, Assistant Regional Administrator
USEPA Region 9

TO: USEPA Region 9 Personnel and Parties Collecting Environmental Measurements Under Regional Programs.

Purpose

Appropriate methodologies to minimize volatilization and biodegradation losses in solid matrices have not been consistently implemented throughout Region 9. This memorandum articulates the Region's policy on the adoption of sampling and laboratory methodologies for the collection of volatile organic compound (VOC) data from soil or solid matrices. USEPA SW-846, Update III, Method 5035, "Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples," incorporating procedures to minimize VOC losses was finalized by USEPA in June 1997. This Region 9 policy requires the use of Method 5035, or an equally or more effective method, for the collection of representative and precise data for VOCs in soil and solid matrices. Additionally, this policy was developed to be consistent with the Agency's Data Quality Objectives (DQO) Process (outlined in "Guidance for the Data Quality Objectives Process," USEPA QA/G-4, September 1994) by allowing for a graded approach through the collection of representative data that meets project data quality needs.

Policy

Scope and Applicability

Environmental data collection activities performed under USEPA Region 9 programs for the determination of VOC concentrations in soil and solid matrices.

This policy is applicable to data collection activities conducted by USEPA staff and contractors, USEPA grantees, Federal Facilities, entities complying with USEPA regulatory requirements and/or other entities producing data for USEPA decision making. This includes data being collected under ongoing quality assurance plans and sampling plans.

INTERIM POLICY

Time Frame for Implementation

This policy should be adopted quickly and to the maximum practicable extent. Cases where it is not practicable to implement this policy should be brought to the attention of the USEPA Region 9 QA Office. This is being put forth as an interim policy, as USEPA is still evaluating technical information to further refine procedures for minimization of VOC losses. Please note, an amendment to this policy may be required.

Statement of Policy

Methods for the collection and analysis of VOCs in soil or other solid matrices must minimize volatile losses. Because USEPA SW-846 Method 5035 does not rigorously dictate specifics of field sample collection[1] and laboratory sample handling protocols, project specific procedures to minimize volatile losses must be developed and be included in the site/program quality assurance project plan (QAPP) or sampling and analysis plan (SAP). USEPA SW-846 Method 5021 "Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis," also incorporates procedures to minimize volatile losses. However, Method 5021 should be used with caution, as it can be reasonably interpreted and performed in a way which does not prevent loss of VOCs. USEPA Region 9 considers the following practices as minimum requirements to reduce volatile losses in soil samples:

1. Samples are handled as intact[2] soil cores in the field and laboratory.

2. Samples are stored in containers which can be reliably sealed to prevent volatilization losses[3] over the project specified analytical holding time.

3. Samples are analyzed or chemically, acid or methanol, preserved within 48 hours of collection, if any contaminant may undergo biodegradation.

4. Exposure of the sample core to the atmosphere in the field and laboratory should be minimized[4].

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1 ASTM Method D4547-98 "Standard Guide for Sampling Waste and Soils for VOCs," is a good reference for VOC sampling protocols.

2 Soils should always be collected and transferred using a coring device, such as a metal sleeve or cut off syringe. Use of transfer devices, such as spatulas, is not acceptable either in the field or laboratory.

3 Volatilization losses from sampling/storage containers must be less than what would be expected from a volatile organic analysis vial with a Teflon/silicon septa stored for 14 days, unless project DQOs require more stringent requirements.

4 Field sub-cores should be taken immediately upon exposing the soil core to ambient conditions. Sub samples should be directly extruded into the analysis containers. Total exposure of samples to ambient conditions should not be more than 15 seconds.

USEPA Region 9 will consider exceptions to this policy on a case-by-case basis. All deviations from procedures outlined in Method 5035 should be documented in a QAPP or a SAP which must be submitted to, and approved by, the Region 9 QA Office. Additionally, the party responsible for data collection must demonstrate that the methodologies proposed will result in data that meet project/program data quality objectives (DQOs).

Additional Considerations

Field Laboratories: The use of field laboratories, that analyze samples within several hours of collection, is an excellent choice to prevent loss of volatiles in transit and storage. However, the sample collection and analysis procedures used must prevent volatilization losses and comply with requirements 1 and 4 articulated in the Statement of Policy. Additionally, the quality control criteria and quality assurance system used by a field laboratory must be adequate for generation of data which will meet project DQOs.

Addition of Surrogates and Matrix Spiking Compounds in the Field: The most appropriate time for addition of analytical surrogate and matrix spiking compounds into soils is prior to sample extraction, by water or a solvent. Method 5035 does not incorporate the addition of the compounds prior to extraction in the field. Because this is an important control check on the analytical process, which begins at extraction, for some project/program DQOs it may be appropriate to incorporate a procedure which adds surrogate and/or matrix spiking compounds prior to extraction.

Holding Times: The holding time for preserved soil samples should be interpreted as 14 days from the time of sample collection(stored at 4±2°C). Due to potential biodegradation losses, samples stored in sealed containers, but not chemically preserved, should not be stored for more than 48 hours. On a project/program specific basis, USEPA Region 9 will consider other alternatives to extend the holding time of soils that have not been chemically preserved (see Attachment A). Holding time will be considered as cumulative (see Attachment B for holding time examples). Exceptions should be documented in a QAPP or a SAP submitted to and approved by the Region 9 QA Office.

Unconsolidated Solid Matrices: Solid Matrices that are not amenable to the use of a coring technique should be collected in such a way as to preserve the integrity of the sample matrix. Transferring of these soils with spatulas or similar devices into sampling containers is discouraged as this disrupts the sample pore spaces and greatly increases the sample surface area available for volatilization. For soil piles, fresh soil at an adequate depth should be sampled.

Calcareous Soils: Method 5035 notes that, "Soil samples that contain carbonate minerals (either from natural sources or applied as an amendment) may effervesce upon contact with the acidic preservative solution in the low concentration sample vial." Calcareous soils that effervesce on contact with the low-level preservative solution should be collected using an alternative preservation technique (see Attachment A).

Soil Gas: This policy is not intended to address the role of soil gas in the environmental decision making process. The Region recognizes that soil gas data is used extensively, in USEPA Region 9, for site decision making and in some cases soil gas is the preferred tool for gathering data on subsurface conditions. However, there are also scenarios where soil gas data are unacceptable for agency decision making (e.g., in excavated soils and when determining disposal options).

Drilling Techniques: This policy does not address the impact of drilling techniques on the collection of a representative VOC sample. Site/program QAPPs and SAPs should address the impact of all collection techniques on sample integrity and select those appropriate for the DQOs. Potential VOC losses due to drilling techniques include, but are not limited to: sample compression and loss of pore space; air introduction into the sample matrix; heat introduced in the drilling process; and volatilization from prolonged periods in a non-hermetically sealed sampling apparatus.

Background

Traditional practices for the sampling and analysis of volatile organic compounds (VOCs) in soil have been shown to have a significantly low bias of inconsistent magnitude (Grant, 1996) from volatilization (Hewitt, 1996) and biodegradation (Hewitt, 1994). Based on this and other research, the USEPA modified the methodology in SW846 for collection and analysis of volatiles in soil. Soil was deleted as an option from Method 5030 and Method 5035 and Method 5021 were added. These methods provide for handling of samples as intact soil cores, chemical preservation techniques, storage of samples in hermetically sealed containers and minimization of analyte losses due to direct volatilization (both in the field and the laboratory) and biodegradation.

"Traditional" collection techniques, such as transferring soils to a glass jar with minimal head space and collecting samples directly into a brass sleeve (e.g., CA Split Spoon) do not yield accurate or consistent results. It has been specifically demonstrated that capped brass sleeves show significant losses. Hewitt and Lukash (Hewitt, 1996) demonstrated capped sleeves can show substantial losses in less than one day. Hewitt and Lukash also demonstrated volatile losses in uncapped core liners of up to 90% in less than 40 minutes for trichloroethene (TCE). Because other analytes and matrix types can have higher mobility than those tested, substantial losses may occur in an even shorter period of time. Grant, Jenkins and Mudambi (Grant, 1996) examined split sampling results from a cross section of laboratories. For VOCs in soil they noted that, "The magnitude of this scatter [for a typical data comparison] is so large that it is

impossible to recommend effective limits of acceptability. Instead, we believe that steps are urgently needed to improve data quality." Hewitt noted (Hewitt, 1994) that biodegradation of Benzene and Toluene in soil samples stored in sealed glass ampules at 4 C for 14 days could be substantial, demonstrating a need for chemical preservatives. Turriff and Reitmeyer (Turriff, 1998) demonstrated that a variety of soil matrices could be held for 48 hours at 4 C, in sealed zero headspace containers, without substantial VOC losses. Additionally, Turriff and Reitmeyer demonstrated that freezing was an option to extend holding times of En Core™ sampling devices. Because volatile losses have been linked to disturbance of the soil matrix and exposure to the atmosphere, samples should be handled in intact soil cores and stored in hermetically sealed vessels in both the field and the laboratory.

This USEPA Region 9 policy is based on the best scientific information available at this time and is subject to further clarifications and additions as other research becomes available. If you have any questions please call Vance Fong at 415 744-1492 or Mathew Plate at 415 744-1493.

References

Hewitt, A.D. (1994) Concentration Stability of Four Volatile Organic Compounds in Soil Subsamples. US Army Cold Regions Research and Engineering Laboratory, Special Report 94-6.

Grant, C.L., T.F. Jenkins and A.R. Mudambi (1996) Comparison Criteria for Environmental Chemical Analyses of Split Samples Sent to Different Laboratories, Corps of Engineers Archived Data. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-9.

Hewitt, A.D. and J.E. Lukash (1996) Obtaining and Transferring Soils for In-Vial Analysis of Volatile Organic Compounds. US Army Cold Regions Research and Engineering Laboratory, Special Report 96-5.

Turriff, D. Ph.D. and C. Reitmeyer (1998) Validation of Holding Times for the EnCore™ Sampler. En Novative Technologies, Inc.

Attachment A

Preservation Alternatives: The following are preservation alternatives that may be appropriate for some projects/programs and are subject to project/program specific approval by the USEPA Region 9 QA Office.

> **Freezing of unpreserved samples:** It has been shown in several studies that freezing of unpreserved soils is an effective means of slowing the biodegradation process. At this time, USEPA Region 9 will accept freezing of unpreserved soils as a method to extend holding times up to seven days on a project specific basis. While there is some evidence that freezing for longer periods may also be acceptable for some data needs, USEPA Region 9 does not believe that the current scientific evidence supports a longer holding time for frozen samples in most cases. Samples should be frozen in containers that have an air tight seal and can maintain this seal while frozen. Because water expands in the freezing process, VOA vials with water or samples with extremely high moisture contents may rupture the storage container.
>
> **Preservatives**: Acids other than sodium bisulfate may be used to preserve low level samples. The choice of an alternative acid should be made in consultation with the USEPA Region 9 QA Office. In all cases the preserved sample pH should be 2.

Sampling Containers: Currently the Region recognizes three sample collection/storage alternatives which can be used (other than acid/water or methanol, as specified in Method 5035).

> 1. A VOA vial with 5 mL of water without preservative and approximately 5 g of sample. Which must be analyzed within 48 hours of collection by closed system purge and trap.
>
> 2. A VOA vial with approximately 5 g of sample. Water must be introduced through the septa at time of analysis by closed system purge and trap. Sample must be analyzed within 48 hours of collection if stored at 4±2°C or 7 days if frozen. (This alternative must be approved on a project specific basis.)
>
> 3. An En Core™ sampler which is analyzed or preserved within 48 hours of collection if stored at 4±2°C or analyzed within 7 days if frozen. (Freezing of En Core™ samplers must be approved on a project specific basis.)

If requested, USEPA Region 9 QA Office will consider the applicability of other sampling containers/devices that have been demonstrated, with appropriate supporting documentation, to be adequate for collection and storage of VOCs.

Attachment B Examples of Holding Time Policy

Example 1 Sample is placed into a vial without chemical preservative in the field (due to effervescence) and stored at 4±2°C.

Sample must be analyzed within 48 hours of collection.

Example 2 Sample is collected into a hermetically sealed sub-coring and storage device in the field, stored at 4±2°C and transferred into a vial without chemical preservative in the laboratory.

Sample must be analyzed within 48 hours of collection.

Example 3 Sample is collected into a hermetically sealed sub-coring and storage device, transported/stored at 4±2°C, frozen at the laboratory 28 hours after collection, defrosted after 2 days and transferred into a vial without chemical preservative in the laboratory.

Sample must be analyzed within 20 hours from the time the sample is defrosted to 4±2°C.
48 (hours allowed) - 28 (hours before freezing) = 20 (hours allowed from defrosting to analysis)

ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY

DATE: January 24, 2002

ADEQ TEMPERATURE/PRESERVATION GUIDANCE POLICY

To help assure the validity and documentation of data generated for use by ADEQ, the QA Unit requires that the elements listed below be fulfilled. If the requirements listed below are not fulfilled, the data *may* be considered unacceptable for compliance or enforcement purposes.

Temperature Documentation Requirements

The documentation of the presence of "wet" ice with samples is not a substitute for measuring temperature. At a minimum, the temperature of a temperature blank must be recorded for each cooler upon sample receipt. The preferred procedure for documenting sample temperature is to record the temperature on the chain of custody.

It is, however, *recommended* that the temperature of each sample be recorded upon sample receipt. The measurement of a temperature blank is not required if each sample temperature is documented.

The sole use of "blue" ice is strongly discouraged for use by laboratories generating data that will be submitted to ADEQ. "If 'blue' ice is used, it should be frozen at the time of sampling, the sample should be chilled before packing, and special notice must be taken at sample receipt to be certain the required temperature (4C) has been maintained." ***Manual for the Certification of Laboratories Analyzing Drinking Water***, page IV-3, section 6.2. There must be documentation substantiating that the "blue" ice was frozen at the time of sampling and that the sample was chilled before packing.

The QA Unit acknowledges that all samples may not have time to equilibrate to 4±2°C due to an insufficient time between sample collection and sample submittal to the laboratory. The rejection of data in these situations will not be automatic. Each of these occurrences will be evaluated on an individual basis to determine if a good faith effort has been made to maintain the samples at the required temperatures.

Chemical Preservation Requirements

All pH adjustments performed by the laboratory must be recorded.

The pH of a sample must be recorded by the laboratory either upon receipt or before analysis, as appropriate to the specific method. Recording the pH of a sample may be documented on the chain of custody or some other appropriate form.

In lieu of a laboratory verifying that a sample has been preserved to the appropriate pH in the field, written documentation such as a laboratory copy of a sampler's field notes also provides adequate documentation of proper preservation.