

REGION II
CERCLA QUALITY ASSURANCE MANUAL

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FORWARD

This CERCLA Quality Assurance Manual has been prepared by the Monitoring Management Branch of the Environmental Services Division for use by the Emergency and Remedial Response Division Project Managers of the Region II Superfund (CERCLA/SARA) program in their daily working with contractors. Its use is intended to ensure that quality assurance and quality control practices (QA/QC) are fully built into all monitoring project designs.

Part I of this Manual, Administrative Procedures, describes the roles and responsibilities of the various Region II organizational units involved in the Superfund program. Part I is designed to be used as a guide so that Project Managers understand what quality assurance activities are required, who the key individuals responsible for carrying out these activities are, and where and how to obtain information and assistance in meeting these requirements.

Part II of this Manual provides Region II's quality assurance/quality control requirements for CERCLA sampling and analysis. Quality assurance procedures are used to verify that field and laboratory measurement systems operate within acceptable, defined limits. The effectiveness of the overall Quality Assurance Program demands that all personnel are aware of the QA/QC requirements for any investigation and that the quality assurance objectives are understood. This Part outlines all aspects of quality control in a monitoring program: minimum requirements necessary, and the rationale behind the requirements. The quality control procedures outlined in Part II of this Manual should be incorporated into all field/project/site operations plans and/or quality assurance project plans prepared for CERCLA work. Recommendations and requirements presented herein should be incorporated into project designs to the fullest extent possible. Where deviations from these recommendations and requirements is necessary, full justification must be presented in writing.

This Manual is meant to be a dynamic document. It will periodically be reviewed and updated, however it is not meant to provide definitive answers to all site-specific concerns. This is, rather, an attempt to provide the rationale behind the most common site-specific concerns which could be extrapolated for use in new situations.

Disclaimer

This Manual has been prepared for use by the Environmental Services and the Emergency and Remedial Response Divisions of the USEPA, Region II. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Agency.

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PART I

Administrative Procedures

I. CERCLA QUALITY ASSURANCE PROGRAM

A. Definition of Quality Assurance

Quality Assurance (QA) is the review and oversight at the planning, implementation, and completion stages of an environmental data collection activity to assure that when data is provided to data users it is of the quality needed. A QA program is a system of documented checks that ensures monitoring data is valid.

B. Basis for Quality Assurance in the CERCLA Program

All activities associated with the collection of physical and chemical data are required to be incorporated into the Agency's formal quality assurance program (EPA Administrator's Policy Statement, EPA Order 6350.1, May 30, 1979). These activities include all phases of sampling, analysis, and data handling that can affect the validity of the data. Any monitoring activity that generates data for EPA use must be collected under a formal QA program that adheres to Agency requirements (40 CFR Part 300.68 (k) of the National Contingency Plan).

The QA requirements for Region II and CERCLA are spelled out in the Region II Quality Assurance Program Plan (QAPP). The QAPP is approved annually by the Regional Administrator, concurred by the Region II Division Directors and distributed to regional managers and staff personnel. A QA program is needed in CERCLA to ensure that the data collected are of the type and quality required for the specific decision to be made, and to ensure defensible quality.

II. CERCLA Quality Assurance Organization

A. Emergency and Remedial Response Division (ERRD) - ERRD is responsible for the development, implementation and coordination of Regional activities under CERCLA/SARA. ERRD manages a comprehensive program for site evaluation, planned and immediate removals and long-term remedial actions including cost recovery actions. ERRD serves as the focal point for all emergency response and emergency contingency planning activity. ERRD is responsible for spill control and monitoring programs under Section 311 of the Clean Water Act. Within ERRD there are seven branches:

- Removal Action Branch (RAB)**
- Response and Prevention Branch (RPB)**
- N.Y./Caribbean Remedial Action Branch (NY/CRAB)**
- New Jersey Remedial Action Branch (NJRAB)**
- N.Y./Caribbean Compliance Branch (NY/CCB)**
- New Jersey Compliance Branch (NJCB)**
- Program Support Branch (PSB)**

The Removal Action Branch and the Response and Prevention Branch together comprise the Removal and Emergency Preparedness Program which responds to spills, manages the Spill Prevention, Countermeasure and Control Program (SPCC), manages the Superfund removal program, manages the Technical Assistance Team (TAT) and the Emergency Response Cleanup Service (ERCS) contracts, develops contingency plans and ensures response capabilities at remedial action sites.

The New Jersey and New York/Caribbean Remedial Action Branches carry out remedial investigations (RIs), conduct feasibility studies (FSs), manage EPA remedial contractor activities, overview remedial design (RD) activities, serve as liaisons with the Corps of Engineers and manage EPA responsibilities for operation and maintenance of facilities constructed at Superfund sites.

The New Jersey Compliance Branch and the NY/Caribbean Compliance Branch conduct hazard assessments, manage CERCLA technical enforcement activities, draft administrative orders, carry out remedial investigation/feasibility study (RI/FS) responsibilities for the sites classified as enforcement lead, develop cost recovery cases, negotiate settlements, and follow up on compliance by responsible parties with orders and negotiated settlements.

The Program Support Branch is responsible for several Superfund program tracking and data management systems as well as policy dissemination and implementation. The Branch also manages the Superfund site assessment and investigation programs, federal facility Superfund sites, dioxin sites, and site deletion activities. Many site investigations (SIs) are conducted by the FIT contractor in which case the projects are managed by the Environmental Services Division (ESD). The Branch also manages the REM, ARCS, and TES contracts.

B. Environmental Services Division (ESD) - ESD is responsible for setting priorities and assuring that resources are available to collect environmental samples, analyze collected samples, and evaluate the resulting data in support of monitoring programs. ESD directs and coordinates the field and laboratory support, directs the implementation of the QAPP, and directs special studies, investigations and surveys to support the Regional enforcement actions or define environmental quality programs. Within the ESD there are four branches:

- Technical Support Branch (TSB)
- Pesticides and Toxic Substances Branch (PTSB)
- Monitoring Management Branch (MMB)
- Surveillance and Monitoring Branch (SMB)

The Technical Support Branch consists of an Organic Chemistry Section, an Inorganic Chemistry Section, and a Sanitary Chemistry and Microbiology Section. This Branch is responsible for chemical and microbiological testing of pollutants in support of CERCLA, RCRA, CWA, TSCA, etc. activities.

The Pesticides and Toxic Substances Branch is responsible for the implementation of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) and the Toxic Substances Control Act (TSCA). The FIFRA program has been delegated to all Region II States and is basically an oversight program providing both technical and financial assistance. The TSCA program is an enforcement effort with major emphasis on polychlorinated biphenyl (PCB) chemicals and friable asbestos in primary and secondary schools.

The Monitoring Management Branch is responsible for conducting the Region's quality assurance and data management programs. MMB plans, coordinates, provides technical assistance and evaluates activities with EPA, State, local and other Federal and private laboratory and field operations. MMB develops quality assurance and data management plans and agreements with State and local agencies; plans and develops quality assurance and data management programs for activities of all Agency programs carried out in the Region.

MMB also carries out reviews of data quality objectives, QAPjPs and standard operating procedures; provides management and technical systems audits and evaluations of data quality; and operates a proficiency testing program and acts as a focal point for EPA methodology requirements and quality assurance services. In addition, the monitoring management function maintains an inventory of all monitoring projects in the Region, provides the data necessary for the Environmental Status Reports and reviews all State grantee outputs for monitoring activity.

The Surveillance and Monitoring Branch is responsible for the collection and evaluation of environmental data in all Agency monitoring and enforcement programs. SMB conducts investigations and studies of surface and ground water and air quality, RCRA

regulated facilities and industrial and municipal waste site field investigations and studies in support of Superfund remedial, removal, enforcement, and emergency response activities. SMB provides technical assistance to municipal treatment plants to improve operating procedures.

C. Superfund Contractor Services - Federal Contractors are major participants in Superfund environmental monitoring and data collection. Contractors provide support for removal, pre-remedial, and remedial activities. All contractors must implement a QAPP which will ensure data of known and adequate quality to meet the requirements of their Statements of Work (SOW). The development and implementation of a QAPP and individual QAPjPs also include auditing and corrective actions within which contractor auditors report to contractor corporate management. The following are brief descriptions of Superfund contractor activities.

Technical Enforcement Support (TES) - provides technical support such as health endangerment assessments, hydrological/geological studies and other special studies in support of litigation and negotiations. TES collects very little environmental data. Future TES contracts are expected to provide more collection of environmental data, including oversight of responsible party actions. Contract oversight is provided by ERRD.

TES V - Camp Dresser and McKee Incorporated
TES VI - Alliance Technologies Corporation

Environmental Services Assistance Team (ESAT) - provides analytical support, data review, logistical and administrative support, QA/QC support, and management and reporting services to ESD. R.F. Weston is the ESAT contractor. Oversight of ESAT contractors is provided by TSB/ESD.

Emergency Response Cleanup Services (ERCS) - provides implementation support to the removal program. ERCS contractors supply all personnel, material, and equipment for conducting removal operations. Mini-ERCS provide the same services for projects with smaller dollar amounts. OH Materials is the principal ERCS contractor. Oversight of ERCS contractors is done by the RPB/ERRD.

Technical Assistance Team (TAT) - provides technical and management support to EPA during removal actions. TAT activities include site assessments, sampling and monitoring, documenting project costs, QA, data management and reporting, enforcement support, community relations, and contingency planning. Roy F. Weston is the principal TAT contractor at this time, and is overseen by RPB/ERRD.

Field Investigation Team (FIT) - provides technical services in support of preliminary site investigations and a variety of special studies at remedial sites. NUS Corporation is the principal FIT contractor. FIT contractors are overseen by the SMB/ESD, especially through the RSCC.

Remedial Planning Team (REM) - provides support to enforcement and remedial response activities. REM services encompass remedial investigations, data management, engineering feasibility studies, technical support, and oversight of responsible parties, remedial design and planning and implementation activities. Contract oversight is provided by the PSB/ERRD. REM contractors are divided by region as below:

- REM I - NUS Corporation (expired 9/86)
- REM II - Camp, Dresser and McKee, Inc. (expired 6/89)
- REM III - Ebasco Services, Inc.
- REM IV - CH2M Hill, Inc.
- REM V - Williams, Russell, and Johnson, Inc.
- REM VI - Peer Consultants

Alternate Remedial Contracting Strategy (ARCS). Provides support to enforcement and remedial response activities from the RI/FS stage to the remedial designs and implementation activities. Contract oversight is provided by the PSB/ERRD. ARCS contractors are divided by the amount of work designated in each contract:

- Major
 - ARCS Ebasco Services, Incorporated
 - ARCS Camp Dresser and McKee Incorporated
 - ARCS Malcom Pirnie

- Minor
 - ARCS TAMS Consulting
 - ARCS ICF
 - ARCS R.F. Weston

III. Data Quality Objectives

A. Definition - "Data Quality Objectives (DQOs) are qualitative and quantitative statements which specify the quality of data required to support Agency decisions during remedial response activities. DQOs are determined based on the end uses of the data to be collected." (Guidance on Data Quality Objectives, Quality Assurance Management Staff, September 25, 1984) Therefore, a unique set of DQOs must be developed for each site and integrated into the project planning process for each data collection activity. DQOs apply to fund lead, federal or state enforcement lead, and potentially responsible party lead projects especially during the remedial investigation (RI), but should also be applied to some degree during feasibility studies (FS), remedial designs (RD), and remedial actions (RA).

B. Roles and Responsibilities of Key Personnel - Decision Maker (ERRD Program Director) - The decision maker is the individual responsible for deciding on the remedial design and remedial action to be taken for NPL sites, and deciding on the "level of risk DQO" needed.

Data User (ERRD Regional Project Manager) - The data user is the individual responsible for deciding on the amount and quality of data needed to determine degree and extent of contamination, the remedial design, and the remedial action to be taken. The data user is responsible for developing DQOs for each decision to be made.

Quality Assurance Officer (Regional within MMB) - The Quality Assurance Officer (QAO) advises and assists on the data collection design. The QAO prescribes the appropriate QA/QC measurements employed to determine the quality of data needed for the decision to be made.

C. DQO Guidance - Guidance on the development of DQO statements can be found in two documents:

1. Data Quality Objectives for Remedial Response Activities - Development Process, EPA/540/G-87/003, March 1987.

2. Data Quality Objectives for Remedial Response Activities - Example Scenario:RI/FS Activities at a Site with Contaminated Soils and Ground Water, EPA/540/G-87/004, March 1987.

IV. Preparation of Quality Assurance Project Plans (QAPjP)

A. Definition - A QAPjP presents in specific terms the policies, organization objectives, functional activities, and specific QA/QC activities designed to achieve the data quality goals or objectives of a specific project or continuing operation. All removal, pre-remedial, and remedial contractors involved in environmental monitoring or sampling activities must develop QAPjPs. QAPjPs should be prepared according to "Interim Guidelines and Specifications for Preparing QA Project Plans", QAMS-005/80, December 29, 1980, and "Guidance For Preparation of Combined Work/Quality Assurance Project Plans for Water Monitoring", OWRS-1, May 1984, provided in Appendix I. In order to save duplication of effort, it is allowable for QAPjPs to be incorporated into Project/Site Operations Plans (Plan).

1. Site-specific QA Project Plans - A site-specific QAPjP is required for each site which requires a focused approach that is unique to the site (e.g. - number of monitoring wells, monitoring of waste lagoons, waste piles, or metal drums containing waste).

2. Generic QA Project Plans - When a group of monitoring projects are carried out for the same purpose and with the same personnel and/or procedures, a "generic" QAPjP may be used to address this group of projects. Generic QAPjPs for Superfund activities may be developed only for site investigations and emergency removals.

B. Procedures for Preparation, Submittal, and Approval of QAPjPs

1. Federal-Lead Sites - RPMs are responsible for ensuring that EPA contractors prepare QAPjPs for site investigations, remedial investigations/feasibility studies (RI/FS), remedial design (RD), remedial actions (RA), and emergency removals. QAPjPs are first submitted to the RPM for review according to guidance criteria. Once the RPM is satisfied that all QA elements have been addressed, the plan is submitted to the Chief, THWS, MMB/ESD for review and approval at least 30 days prior to commencement of sampling. THWS will approve or request changes in writing within 15 workdays of receipt. It is important to keep in mind that QAPjPs must be approved by MMB before sampling may begin. Once MMB approves a plan, the QAO assigned to the project notifies the RSCC and RPM of approval and submits the approved analytical methods and parameter list to the RSCC to facilitate the CLP sample booking procedures. The RSCC will not schedule CLP analyses until they receive this approval memo; and the RSCC must be given appropriate lead time in order to obtain laboratory space for sample bookings. Lead time is discussed in Section VI of Part I.

2. State-Lead Sites (Remedial and Enforcement) - State project managers are responsible for ensuring that their contractors prepare QAPjPs. These QAPjPs are submitted to the state Superfund QAO for review and approval. Copies of the final, approved QAPjPs and the review comments are kept on file with the state and reviewed periodically by MMB/ESD.

3. **Federal Facility Sites** - These include the Department of Defense, U.S. Army Toxic and Hazardous Materials Agency, the Department of Energy, the Department of the Interior, and the United States Army Corps of Engineers. RPMs are responsible for ensuring that federal facilities prepare QAPjPs which follow the guidance described in this Manual for Responsible Party Sites. The QAPjP produced is submitted through the PSB to MMB for review and approval. Federal agencies are required under Section 120 of Superfund Amendments and Reauthorization Act (SARA) to comply with CERCLA both procedurally and substantively. This includes adherence to guidance and provisions set forth in the National Contingency Plan (NCP). Section 300.68 k(2) of the NCP states: "In fund-financed actions or actions under CERCLA Section 106, the quality assurance/site sampling plan must be reviewed and approved by the Remedial Project Manager with a coordination signature from the Quality Assurance Officer."

4. **Responsible Party Sites** - With the enactment of the SARA, Congress gave EPA specific authority to settle CERCLA actions, and it gave specific instructions respecting the type of settlement, administrative or judicial, to be used for each kind of response activity, as follows:

a) cost recovery actions may be settled either with a judicial consent decree or an administrative order.

b) abatement actions (abatement of a "danger" or "threat") must be settled through judicial consent decrees.

c) actions (removal actions and investigative activities, including RI's and FS's) may be settled with the use of either judicial consent decrees or administrative orders.

- **Administrative Orders** - Administrative orders (AO) are issued either by consent of the responsible parties ("administrative orders on consent") after negotiation of the terms, or on a mandatory basis by the Agency ("unilateral orders"). Negotiations are conducted between EPA and the potentially responsible parties (PRPs), within the jurisdiction of the Agency. Under administrative orders, the RPMs are responsible for ensuring that the PRP or their contractors prepare QAPjPs. The RPM reviews this document, and when satisfied that all QA elements have been addressed, submits it to the Chief of THWS for review and approval at least 30 days prior to commencement of sampling. THWS will approve the QAPjP or request changes in writing within 15 workdays.

- **Judicial Consent Decrees** - Consent decrees differ from administrative orders, in that the monitoring requirements for the QAPjPs are "negotiated" by EPA, the Department of Justice, and the PRP under the authority of a federal district court, usually in the jurisdiction in which the Superfund site is located. For this reason it is important for the RPM to request assistance from the ESD at negotiation sessions on technical requirements for monitoring and quality assurance. The RPM is responsible for ensuring that the PRP submits a QAPjP that addresses the available guidance and the recommendations of the ESD technical negotiators.

- EPA Oversight of Responsible Parties - If EPA oversight contractors take split samples from a PRP's contractor, procedures for split sampling and analysis must be prepared and submitted to MMB in a Short Form for approval. The Short Form is discussed in Part II of this Manual.

C. Guidance Documents for the Preparation of QAPjPs - QAPjPs should be prepared according to "Interim Guidelines and Specification For Preparing Quality Assurance Project Plans", QAMS-005/80, December 29, 1980, or "Guidance For Preparation of Combined Work/Quality Assurance Project Plans for Environmental Monitoring", OWRS, May, 1984, provided in Appendix I, and Part II of this Manual. A QAPjP can be combined into another document, such as a Project Operations Plan, Site Operations Plan, or Field Sampling Plan (generally referred to as the Plan) to avoid duplication. This is the preferred practice.

D. QAPjP Pre-Development Meetings - In order to reduce the time needed to resolve deficiencies in QAPjPs, up-front meetings are held between personnel responsible for preparing QAPjPs (RPMs, contractors, PRPs, consultants) and EPA technical personnel responsible for monitoring and quality assurance. Pre-development meetings should be convened prior to QAPjP submittal and at least 60 days prior to sampling.

V. Audit Programs

In general, QA audits will be performed by MMB staff. The various types of audits conducted by the Region are defined as follows.

A. Management Systems Audit (MSA) - An MSA is generally a QAPP review, checking managerial implementation of the approved QAPP. It evaluates the unit's QA organization and its activities, as well as the degree of management support afforded the program. Specifically, the audit covers the following:

- QAPjP development and approval,
- DQO development (where implemented),
- Standard Operating Procedure (SOP) development and approval,
- audit schedules and procedures,
- tracking systems for QA activities and corrective actions,
- managerial support, including financial and resource support, and
- QA responsibilities of personnel including Project Managers, field and laboratory staff, and QA staff.

B. Technical Systems Audit (TSA) - A TSA is generally an on-site audit of project-specific monitoring activities, either field, laboratory or both. It focuses on actual quality control activities of environmental data collection systems, and uses the approved QAPjP as a reference. TSAs are conducted on intramural projects and extramural monitoring which the Region supports or requires.

Specific activities vary with the scope of the audit, but can include review of:

- sample collection and analytical activities,
- equipment calibration techniques and records,
- decontamination and equipment cleaning,
- equipment suitability and maintenance/repair,
- background and training of personnel,
- laboratory control charts and support systems,
- QC samples such as duplicates, trip and field blanks, method blanks, unknown performance evaluation samples,
- sample containers, preservation techniques, and chain-of-custody,
- data logs, data transfer, data reduction and data validation, and
- monitor siting.

EPA REM, ARCS, and FIT contractors are required by contract to conduct TSAs of their field activities.

C. Data Quality Audit (DQA) - A DQA focuses on collected data by evaluating whether sufficient information exists to support the assessment of the data's quality. It will determine if the data set undergoes any validation procedure by the collector or data user to establish whether the data can be used to support the decision making process.

If DQOs exist, the data set(s) will be evaluated against them. If deficiencies are found, DQAs will be able to determine the causes, whether technical, managerial or both. DQAs are to be distinguished from data validation activities which are considered to be part of the data generation process. In Region II, DQAs are not normally conducted alone, but rather are conducted as part of TSAs.

D. Performance Evaluations (PE) - A PE is a means of evaluating laboratory performance with a sample of specific contaminants in an appropriate matrix. The true values of performance evaluation components are unknown to the laboratory analyst.

In some cases, PEs are performed on field operations that also perform analytical functions. This includes, for example, audits of ambient air monitoring operations in which cylinders of gas mixtures or audit devices are sent to field operators to check the calibration/operation of the monitors.

On an as-needed basis, MMB arranges for PEs to be submitted to all laboratories providing CERCLA analytical services. PE analyses are required for laboratories which participate in CLP every three months. PEs are also required for all non-CLP laboratories which have not analyzed PEs within the last six months. MMB sends the results of their PE audits to ERRD project managers along with their recommendation of capability. See Part II Section XII for further information.

VI. Superfund Contract Laboratory Program

The majority of Superfund sample analyses are performed within the Superfund Contract Lab Program (CLP). The program was created to handle the excess analytical demand that could not be handled by the regional laboratories.

Each Region has a Regional Sample Control Center (RSCC). In Region II, the RSCC resides in the SMB/ESD and can be reached at FTS 340-6705. The RSCC schedules sample analyses with CLP laboratories through the Sample Management Office (SMO) in Alexandria, VA. Each contractor is assigned a contact who may book samples through the RSCC. The contractor is responsible for ensuring that their subcontractors understand how to properly use the CLP. Primary contractors may not refer their subcontractors to the RSCC for guidance or to schedule samples. The December 1988 "User's Guide to The Contract Laboratory Program" (available through the RSCC) contains a thorough discussion of the CLP program.

After a QAPjP or Plan and all SAS requests have been approved by MMB, samples may be booked with the RSCC. The required lead time for all requests is :

1. Routine Analytical Services (RAS)- Verbal requests for RAS must be submitted to the RSCC on the Tuesday two weeks prior to the scheduled date of sample collection.

2. Special Analytical Services (SAS)- SAS requests must be submitted to the RSCC, in writing, by the Tuesday four weeks prior to the scheduled date of sample collection. (In instances of restricted funding longer lead time may be required.)

3. Exception SAS Requests- Exception SAS requests require a four to five week lead time. SMO must obtain program approval through Headquarters before soliciting laboratories.

Examples of exception SAS requests are the following:

- a. All non-Superfund requests.
- b. Non-invitation for bid (IFB) parameters or compounds requested for the first time.
- c. All requests requiring use of non-approved analytical procedures (methods which are not routinely requested through CLP).
- d. All requests specifying specific remedial parameters for waste samples (for example, compatibility, grain size distribution, permeability, viscosity, Atterburg limits, etc.)
- e. Requests which will incur a cost greater than \$25,000.

In addition, the CLP Deputy Project Officer (DPO), who resides in MMB, is available to resolve technical problems on sample analysis or contract compliance. The DPO may also be contacted with questions on methodology.

VII. Data Validation / Data Useability

A. Data Validation - It is the policy of Region II that all data generated be validated. Data validation is a systematic process for reviewing a body of data against a set of criteria to provide assurance that the data are adequate for their intended use. Data validation consists of data editing, screening, checking, auditing, verifying, certifying, and reviewing. Data are validated according to Region II standard operating procedures (SOPs). The Region II SOPs are based on National CLP Functional Guidelines for CLP Data Review. At this time data validation is carried out by both EPA and contractor personnel.

In the case of data generated by the Contract Laboratory Program, data packages (identified by a specific case number) are sent to the RSCC from the CLP laboratories that performed the analyses. If the package is complete, the RSCC forwards it to the data validators. The package is sent back to the RSCC after validation, whereupon it is sent to the data requestor (RPM or EPA contractor).

All non-CLP data, such as PRP generated data, must be validated. PRP contracted laboratories or outside parties must validate their data according to Region II SOPs. Project Managers may request MMB to validate PRP data if it is deemed necessary. To do this, the data should be sent to the Toxic and Hazardous Waste Section of MMB. In addition, all the CLP required deliverable information must accompany the data, so that MMB can adequately evaluate it. See Section XIV of Part II for more information.

B. Data Useability - In addition to reviewer/RPM interactions data useability meetings can be arranged with the MMB. These meetings can assist RPMs in the use of data for other than enforcement or risk assessment purposes. Data reviewers are required to reject data with questionable quantitative value. However, even though the true value is unknown, the data may still be of such value as to allow the user to make decisions based on maximum or minimum possible concentration.

ACRONYM LIST

AWS - Air and Water Section
AO - Administrative Order
ARCS - Alternate Remedial Contracting Strategy
CERCLA- Comprehensive Environmental Response Compensation and Liability Act
CFR - Code of Federal Regulations
CLP - Contract Laboratory Program
DPO - Deputy Project Officer
DQA - Data Quality Audit
DQO - Data Quality Objective
ERCS - Emergency Response Clean-up Services
ERRD - Emergency and Remedial Response Division
ERT - Emergency Response Team
ESAT - Environmental Services Assistance Team
ESD - Environmental Services Division
FIFRA - Federal Insecticide, Fungicide and Rodenticide Act
FIT - Field Investigation Team
FOP - Field Operations Plan
FR - Federal Register
FS - Feasibility Study
MMB - Monitoring Management Branch
MSA - Management Systems Audit
NCP - National Contingency Plan
NPL - National Priority List
NJRAB - New Jersey Remedial Action Branch
NY/CRAB- New York/Caribbean Remedial Action Branch
OSC - On-Scene Coordinator
PCB - Polychlorinated Biphenyl
PE - Performance Evaluation
POP - Project Operations Plan
PRP - Potentially Responsible Party
PSB - Public Support Branch
PTSB - Pesticides and Toxic Substances Branch
QA - Quality Assurance
QAO - Quality Assurance Officer
QAPjP - Quality Assurance Project Plan
QAPP - Quality Assurance Program Plan
QA/QC - Quality Assurance/Quality Control
RA - Remedial Action
RD - Remedial Design
REM - Remedial Contractor Program
RI - Remedial Investigation
RPB - Response and Prevention Branch
RPM - Regional Project Managers

RSCC - Regional Sample Control Center
SAP - Sampling and Analysis Plan
SARA - Superfund Amendments and Reauthorization Act
SCB - Site Compliance Branch
SI - Site Investigation
SMB - Surveillance and Monitoring Branch
SMO - Sample Management Office
SOP - Standard Operating Procedure
SOW - Statement of Work
SPCC - Spill Prevention, Countermeasure and Control Program
TAT - Technical Assistance Team
TES - Technical Enforcement Support
THWS - Toxic and Hazardous Waste Section
TSA - Technical Systems Audit
TSB - Technical Services Branch
TSCA - Toxic Substances Control Act

PART II

Quality Control Handbook for CERCLA Sampling and Analysis

I. SAMPLING DESIGN AND STRATEGY

A. Sampling Plan Components

Detail of sampling and analysis is a necessary part of each field/site/project operations plan, sampling and analysis plan, or quality assurance project plan (from hereon referred to as the Plan) in order to ensure uniform and acceptable sampling and analytical protocol for each project. The Plan describes the objectives and details how the individual tasks of a sampling and analytical effort will be performed. The Plan must discuss the following topics at a minimum, and it must include a Parameter Table, an example of which is included in Appendix IV. For EPA oversight contractors, a completed "Combined Work/QA Short Form" is the only required documentation that must be submitted for review and approval. An example of the "Short Form" is attached in Appendix I. Also, when booking samples through CLP SAS, a copy of the SAS Request Form must be submitted to MMB for review and approval, along with the Plan. All analytical methodology and special analytical requests should be incorporated by reference and/or attached to the plan.

- * Objectives of sampling design and selection of representative sampling sites.

Discussion of site history and sampling design rationale must be provided, so that reviewers of the Plan have the necessary information. The discussion should include topics such as the history of the contamination, the matrices involved, the dimensions of the site, etc.

- * Sampling Design

- * Selection of Parameters to be measured.

Parameters to be measured are usually dictated by the purpose of an investigation and should be based on knowledge of the problem being investigated. An in-depth discussion of parameter selection is out of the scope of this document as it is a process requiring much background and expertise in dealing with hydrogeologic systems, chemistry, and engineering. No criteria for parameter selection can be put forth in the format of a standard operating procedure.

- * Selection and preparation of sampling equipment.
- * Sampling equipment construction materials.
- * Required sample volumes.
- * Selection and preparation of sample containers.
- * Sample collection and handling.

- * Sample preservation.
- * Sample chain-of-custody and identification.
- * Use of field instrumentation.
- * Field quality control samples.
- * Choice of laboratories and validation of data.

These topics are further discussed within this Manual.

B. Purpose and Objective of Sampling

The basic objective of any sampling campaign is to collect a sample which is representative of the media under investigation. More specifically, the purpose of sampling at hazardous waste sites is to acquire information that will aid investigators in determining the presence and identity of on-site contaminants and the extent to which they have become integrated into the surrounding environment. This information can then be used as support for future litigations or as input to remedial investigations and risk assessments.

The validity of environmental data is dependent in part on the integrity of the field procedures employed in obtaining a sample. Proper sampling techniques must be employed to obtain a sample which is representative of the area or container of interest. A sample is representative if it possesses the same qualities or properties as the material under consideration. Due to the complexity of most hazardous substances and site conditions, no universal sampling methods can be recommended. Procedures must be adapted for use in various matrices and site-specific restrictions.

C. Types of Samples

Before defining the general sample types, the nature of the media or materials under investigation must be discussed. Materials can be described as homogeneous or heterogeneous. Homogeneous materials are generally defined as having uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in composition of the material over distance and time.

When discussing types of samples, it is important to distinguish between the type of media to be sampled and the sampling technique that yields a specific type of sample. In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

1. Environmental Samples

Environmental samples (ambient air, soils, surface water, groundwater, sediment or biota) are generally dilute (in terms of pollutant concentration) and usually do not require the special handling procedures used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

2. Hazardous Samples

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, etc., and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling any wastes believed to be concentrated, regardless of the degree.

D. Types of Measurement

In general, two basic types of sample measurements are recognized, both of which can be used for either environmental or concentrated samples. They are: 1) samples which are collected and subsequently analyzed in the laboratory and, 2) samples which are analyzed in-situ.

1. Laboratory Measurement

There are two types of samples which are collected and analyzed in a laboratory. These are grab samples and composite samples.

a. Grab Samples

A grab sample is defined as a single sample representative of a specific location at a given point in time. The sample is collected all at once and at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

b. Composite Samples

Composites are combinations of more than one sample collected at various sampling locations and/or different points in time. Analysis of composite yields an average value and can, in certain instances, be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

For sampling situations involving hazardous wastes, grab sampling techniques are

generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing. Compositing is often used for environmental samples, including dioxin samples, to determine vertical or horizontal spatial variability of parameters. This procedure provides data that can be useful by providing an average concentration over a number of locations and can serve to keep analytical costs down; however, it is important to understand that sensitivity is sacrificed when samples are composited due to dilution of individual grab samples. If contamination occurs in "hot" spots on site and "hot" grabs are composited with clean samples, a true vertical or horizontal distribution of contamination will appear to be a uniform distribution at a level lower than the true value of any one individual component(7). This is especially a concern when doing dioxin sampling with an action level of 1 ppb. Compositing is further discussed in Section IX.

2. In-Situ Measurement

In-situ measurements are made on samples in the environment. Measurements for pH, conductivity, and temperature must be taken in the field. Use of instrumentation such as an OVA, HNu and other gas analyzers is also considered in-situ measurement.

II. ANALYTICAL METHODS, PRESERVATION AND HOLDING TIMES

A. Methodology Available for use in the CERCLA Program

The CERCLA program has no legally mandated analytical methods. Methods from other programs or methods which are proven to be scientifically valid can be used for CERCLA work. The bulk of the analytical methods used presently are, however, from the Contract Laboratory Program (CLP).

The Contract Laboratory Program supports the Agency's Superfund effort by providing a range of chemical analytical services on a high volume, cost effective basis. Its purpose is to provide legally defensible analytical data. The program is managed by the National Program Office in Headquarters, and the Contractor-operated Sample Management Office receives the analytical requests from the Regions and coordinates and schedules sample analyses. Analytical Statements of Work exist for organics, inorganics and dioxin in water and soil/sediment matrices.

In addition to standardized analyses provided under the Routine Analytical Services (RAS) program, the CLP's Special Analytical Services (SAS) program provides clients with limited customized or specialized analyses, different from or beyond the scope of the RAS contract protocols. Services provided by SAS include: quick turn around analyses, verification analyses, analyses requiring lower detection limits than RAS methods provide, identification and quantification of non-Target Compound List (TCL) constituents, general waste characterizations, analysis of non-standard matrices, and other specific analyses. Consult the "User's Guide to the Contract Laboratory Program", December 1988 for further information.

As stated above, the CLP parameters of interest for RAS were titled under the 10/86 Statement of Work (SOW) the "Target Compound List". Under previous SOWs the TCL was titled the "Hazardous Substance List". Neither of these lists has been published in the Federal Register (FR) or Code of Federal Regulations (CFR) and thus are strictly lists defined by contract.

The "Priority Pollutant List" was established in the consent decree of the Natural Resources Defense Council (NRDC) vs. Train, in 1976. Although not published in the Federal Register under that title, it was published in a more generalized form in 44 FR 44502, July 30, 1979 as the "Toxic Pollutants" list under the Federal Water Pollution Control Act, and was amended in 46 FR 2266, January 8, 1981, and 46 FR 10724, February 4, 1981. Thus, the "Priority Pollutant" list as it now stands is comprised of 126 compounds or elements.

The Priority Pollutant and Target Compound Lists are presented in Appendix II which shows the differences between the two. They are not interchangeable; neither list is a subset of the other, both contain compounds not found on the other. The only Priority Pollutants which are not on TCL are: asbestos, benzidine, 1,2-diphenylhydrazine, N-nitrosodimethylamine, endrin aldehyde, 2-chloroethyl vinyl ether, acrolein, and

acrylonitrile. Refer to the Appendix for those compounds which are on TCL but not considered Priority Pollutants.

A discussion of available references, methods, holding times and preservatives follows.

B. Analytical References

The following is a listing of selected analytical references containing methods available for use in the CERCLA program.

1. Aqueous/solid matrices

a. 40 CFR Part 136, as updated yearly.

b. 7/88 CLP Statement of Work for Inorganics, the 9/87 Statement of Work for Dioxin, the 2/88 revision of the Organics Statement of Work, and as updated.

The CLP standardized organic analytical methods are based on the CFR methods 608, 613, 624, and 625 modified for use in the analysis of both water and soil matrices. The standardized inorganic analytical methods are based on FR methods, EPA Methods for Chemical Analysis of Water and Wastes (MCAWW), and Test Methods for Evaluating Solid Waste (SW-846), Third Edition for the analysis of water and soil matrices. Appendix II provides a listing of the CLP organic and inorganic Target Compound/Analyte Lists as taken from the most recent SOWs and includes the RAS detection limits.

The dioxin Routine Analytical Services (RAS) contract method determines the presence of the 2,3,7,8-tetrachloro-dibenzo-p-dioxin isomer in water and soil/sediment matrices.

c. Standard Methods, 15th and 16th eds., or as revised.

d. Methods for Chemical Analysis of Water and Wastes(MCAWW), Revised 1983, EPA 600/4-79-020.

e. American Society for Testing and Materials.

f. Test Methods for Evaluating Solid Waste-SW-846, Third Edition, November 1986.

g. Procedures for Handling and Chemical Analysis of Sediment and Water Samples, May 1981, Technical Report CE/81-1, NTIS#AD-A103788.

h. Methods for the Determination of Organic Compounds in Drinking Water (500 Series Methods), December 1988, EPA 600/4-88/039.

2. Air

Detailed analytical procedures for air analyses must be provided with any QAPjP. These procedures must accompany the SAS request and the air samples to the laboratory.

The following references contain the most commonly used lab methods for measuring various air contaminants. Whenever practicable EPA methods should be used for air analyses. However if EPA methods do not exist for the compounds of interest, other common methods, eg. NIOSH methods, may be specified provided that they have been validated at the detection limits of interest to the project.

Air Monitoring References

- a. Riggin, R.M. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/4-83-027. U.S. Environmental Protection Agency, Research Triangle Park, NC, 1983.
- b. NIOSH Manual of Analytical Methods, Volumes 1-2, 3rd edition. P. Eller, ed. National Institute for Occupational Safety and Health, Cincinnati, OH, 1984.
- c. Riggin, R.M. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, EPA-600/4-89-017. U.S. EPA, Research Triangle Park, NC, 1988.
- d. 40 CFR Part 50 Appendices A-J.
- e. SOP for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax, June 1984. EMSL/RTP-SOP-EMD-020.

3. Non-Aqueous Phase Liquids

- a. Test Methods for Evaluating Solid Waste, SW-846, Third Edition, November 1986.
- b. Interim Methods for the Measurement of Organic Priority Pollutants in Sludges, Revised Draft June 1980.
- c. Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils, Sept. 1982. EPA 600/4-81-045.

C. Preservation, Methodology and Holding Times

Complete and unequivocal preservation of samples is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations such as iron and lead may also adsorb onto surfaces (glass, plastic, quartz, etc.). Biological changes taking place in a sample may change the valence of an element or a radical. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration and freezing(8).

Appendix IV contains a copy of Table 2 from 40 CFR Part 136, July 1, 1987 and a tabular presentation of the CLP holding time and preservation requirements. The Table is comprised of approved "conventional" parameter (meaning those analyses not considered part of the most commonly used "organic" and "inorganic" sets of analyses) methodology for an aqueous matrix. The holding times and preservation requirements of these conventional parameters are to be followed.

Appendix IV also includes two tables of holding time and preservation requirements. One table applies to the Contract Laboratory Program's contractual stipulations and the requirements listed must be adhered to when using the CLP. Holding times begin at the Verified Time of Sample Receipt (VTSR) when the Contract Laboratory Program has been engaged. The second table contains requirements for all analyses which do not entail utilizing the CLP. Holding times on this table begin on the date of sample collection.

Various studies including a project funded by EPA and the Department of Defense and performed by the Oak Ridge Laboratory determined that aqueous volatile organic

samples (VOAs) can be held for extended periods of time with preservation using hydrochloric acid (HCl) to a pH less than 2 without significant loss of constituents. It is now a requirement when using CLP that all samples taken for volatile organics analysis be preserved with hydrochloric acid to a pH less than 2. When not using CLP, if non-preservation is chosen, then samples must be analyzed within 7 days of the sampling date. If preservation methods are chosen, then samples must be preserved as for CLP, ie. acidify with HCl to pH<2 as per the procedure below.

The following procedure, adapted from the drinking water methods should be used for acidification of volatile organic samples with HCl to a pH less than 2.

Adjust the pH of the sample to <2 by carefully adding 1:1 HCl drop by drop to the required 2 (40 ml) VOA sample vials. The number of drops of 1:1 HCl required should be determined on a third portion of sample water of equal volume.

It should be noted that if acidification of the sample causes effervescence, the sample should be submitted without preservation except for cooling to 4 degrees C. This sample property should be appropriately noted when present. When adding sodium thiosulfate to samples containing residual chlorine, the thiosulfate should be added to the vial prior to addition of the sample followed by addition of HCl. The 1:1 HCl solution should be made up with concentrated HCl (12N) and demonstrated analyte-free deionized water.

The pH testing and the determination of the appropriate volume of acid required to achieve pH<2 must be performed at each groundwater monitoring well prior to sampling unless monitoring is performed on the same wells on a continuous basis.

When samples are to be iced to 4 degrees C., it is intended that the sample bottle be surrounded by bags of ice or by ample packets of "Blue Ice" to ensure that the proper temperature is achieved and maintained during transport. It is not acceptable to put bags of ice around only the necks of the bottle or to use only a few packets of "Blue Ice" since these techniques do not ensure the attainment of the proper temperature. All samples must be shipped to the lab within 24 hours from the time of collection. Further information can be found in the User's Guide to the CLP of December 1988.

When booking samples through CLP SAS, a copy of the SAS Client Request must be attached to the Plan.

D. QC Criteria for 40CFR Part 136 and SW-846 Third Edition Methods

If the Contract Laboratory Program is used for the analysis of target compound list

(TCL) analytes, the laboratory analyzing the samples will perform specific quality control procedures to assure that the data is valid. However, Superfund PRP and RCRA analyses will usually be performed outside of the CLP program. The methods listed in 40 CFR Part 136 and SW-846 Third Edition do not specify detailed quality control procedures, so data analyzed under those methods may not be amenable to validation. In order to use 40 CFR Part 136 or SW-846 Third Edition methods for the analysis of TCL compounds, the Plan must specify proposed quality control criteria for spikes, blanks, surrogates, detection limits, and internal standards. We strongly recommend that CLP procedures be used to analyze all TCL compounds.

When SW-846 Third Edition methods are used, the generic QC procedures listed in Chapter One, and the specific QC procedures listed in Section Eight of each method must be followed. For the analysis of TCL analytes, the lab may use the CLP criteria for surrogates, internal standards, pesticide linearity and retention time shift shown on the Chapter One QC forms, or the lab may propose their own QC criteria based on SW-846 protocol. When non-TCL analytes are analyzed by SW-846 methods, the lab must propose all QC criteria before samples are analyzed.

These proposals must be submitted to MMB in the Quality Assurance Project Plan for review and approval, prior to the commencement of the sampling event.

III. DOCUMENTATION PROCEDURES

A. Chain-of-Custody

1. Definition and Reference

According to the USEPA Office of Enforcement and Compliance Monitoring National Enforcement Investigations Center (NEIC) Policies and Procedures, May 1978 revised May 1986, a sample is under custody if:

1. it is in your possession, or
2. it is in your view, after being in your possession, or
3. it was in your possession and you locked it up, or
4. it is in a designated secure area.

Possession must be traceable from the time the samples are collected.

2. Recordkeeping and Procedures

a. General

The method of sample identification utilized depends on the type of sample collected. In-situ field analyses are those conducted for specific field analyses or measurements where the data are recorded directly in bound field logbooks or recorded directly on the chain-of-custody record, with identifying information, while in the custody of the sampling team. Examples of such in-situ field measurements and analyses include pH, temperature, and conductivity. Also included in this category are those field measurements or analyses such as flow measurements, geophysical measurements, surveying measurements, etc. that are made with field instruments or analyzers, where no sample is actually collected.

Samples, other than those collected for in-situ field measurements or analyses, are identified by using a standard sample tag which is attached to the sample container. In some cases, particularly with biological samples, the sample tag may have to be included with or wrapped around the sample and waterproofed. The sample tags are sequentially numbered and are accountable documents after they are completed and attached to a sample or other physical evidence. The following information shall be included on the sample tag:

- a. site name
- b. field identification or sample station number
- c. date and time of sample collection
- d. designation of the sample as a grab or composite
- e. type of sample (matrix), and a brief description of the sampling location
- f. the signature of the sampler

- g. whether the sample is preserved or unpreserved
- h. the general types of analyses to be conducted

If a sample is split with another party, sample tags with identical information shall be attached to each of the sample containers.

The chain of custody record is used to record the custody of samples. It must accompany samples at all times. The following information must be supplied to complete the chain of custody record:

- a. project name
- b. signature of samplers
- c. sampling station number, date and time of collection, grab or composite sample designation, and a brief description of the type of sample and sampling location,
- d. tag numbers
- e. signatures of individuals involved in sample transfer, i.e., relinquishing and accepting samples. Individuals receiving the samples shall sign, date and note the time that they received the samples on the form.

Sample analysis request sheets serve as official communication to the laboratory of the particular analyses required for each sample and provide further evidence that the chain of custody is complete.

Shipping containers should be secured to ensure samples have not been disturbed during transport by using nylon strapping tape and EPA custody seals. The custody seals should be placed on the container so that it cannot be opened without breaking the seal.

b. CLP

The CLP documentation system provides the means not only to track and identify each sample, but to support the use of sample data in potential enforcement actions. Appendix V provides copies of CLP documentation described below.

RAS organic and inorganic samples are documented with corresponding CLP sample Traffic Reports (TRs), a four part carbonless form. Each TR may document up to twenty samples shipped to one CLP laboratory under one Case Number and one RAS analytical program. Samplers must complete the appropriate TRs for every shipment of RAS samples to a CLP laboratory. An adhesive sample label printed with the sample number is affixed to each container, and, in order to protect the label from water and solvent attack, each label is covered with clear waterproof tape. The sample labels permanently identify each sample collected and link each sample component throughout the analytical process. A custody seal is then placed over the lid of the container to ensure the samples are not opened prior to arrival at the laboratory. Sample documentation for the RAS dioxin program utilizes the CLP Dioxin Shipment

Record (DSR) and samples are individually numbered using pre- printed labels.

For SAS samples, a SAS Packing List (PL) is used along with adhesive sample labels.

Sample tags, containing the necessary information as required by NEIC, are attached to each sample container at the time of collection. Following sample analysis, sample tags are retained by the laboratory as physical evidence of sample receipt and analysis.

The Chain-of-Custody Record is employed as physical evidence of sample custody. One Record accompanies each cooler shipped from the field to the laboratory. In Region II, the Environmental Services Division Chain-of- Custody Record is used.

Shipping coolers are secured and custody seals placed across cooler openings. As long as custody forms are sealed inside the sample cooler and the custody seals remain intact, commercial carriers are not required to sign off on the custody form.

Whenever samples are split with a source or government agency, a separate Chain-of-Custody Record must be prepared for those samples, indicating with whom the samples are being split and sample tag serial numbers from splits (13).

If errors are made when completing any of these forms, the error must be crossed out with a single line and initialed and dated by the sampler.

Information regarding the information contained within, completion of, or obtaining these forms can be found in the CLP User's Guide available from the Region II RSCC.

B. Field Records

Field records must be kept by contractor personnel for each site. All aspects of sample collection and handling as well as visual observations must be documented in the logbooks. The following information must be recorded:

1. sample collection equipment;
2. field analytical equipment;
3. any other equipment used to make field measurements;
4. calculations;
5. results, and;
6. calibration data for equipment.

All entries must be dated, initialed, and legible (9).

All maintenance and calibration records for equipment must be traceable through field records to the person using the instrument and to the specific piece of instrumentation itself. Equipment should be labeled with the calibration date and when it is due for the next calibration. The calibration of the pH and conductivity meters must be checked

daily. Appendix VI describes the required quality assurance procedures for field analysis and equipment.

Standard operating procedures (SOPs) for use of any field instrumentation must be provided in the form of a manual or individually in the Plan itself. The SOPs should address calibration, maintenance and use of the instrumentation and should reflect what is currently being done in the field.

IV. GLASSWARE REQUIREMENTS

A. Bottle Suppliers

The CLP Sample Bottle Repository (SBR) provides cleaned, contaminant-free sample containers for use by groups performing hazardous waste sample collection activities under the Superfund program. Within this contract, sample containers are cleaned by defined procedures and representative containers undergo strict quality testing prior to shipment. This contributes to the integrity of sample data and supports its viability for use in enforcement case actions. The contractor uses approved techniques and instrumentation to procure, prepare, clean, label, store, package and ship sample containers and component materials. Appendix VII contains the Statement of Work for Maintenance of a Quality-Controlled Prepared Sample Container Repository, dated 4/87, revised 7/87 and 8/87, in which the specific requirements for quality control are delineated.

It is the policy of this office at this time that bottles supplied by any party performing Superfund work who does not obtain those bottles from the SBR must be cleaned and quality controlled in the same manner as is defined in the SBR SOW. Therefore, if containers are not being procured from the Repository, the container construction, cleaning and quality controlling must be the same as that described in the SOW presented in Appendix VII. A statement that the bottle supplier will follow the SBR SOW must be included in the Plan.

B. Volume and Type of Container

The volume of sample obtained should be sufficient to perform all required analyses with an additional amount collected to provide for quality control needs, split samples, or repeat analyses.

The sample container requirements may be found in the SBR SOW, the CLP User's Guide, or in 40 CFR Part 136.

NOTE: It is the policy of this office at this time that the 40 ml glass vial with Teflon septum must be used to collect volatile organics in a soil/sediment matrix.

C. Quality Control and Storage

As stated above, the SBR Statement of Work must be followed when it comes to procuring, preparing, cleaning, labeling, storing and quality controlling containers. This involves analysis/testing of one or more representative containers from each lot or batch after they have been cleaned and designation of a storage QC container for future analysis if contamination should be suspected at a later time. All storage QC containers should be kept in a separate contaminant-free area, See Appendix VII for detail. Contractors who store containers for any period of time must also comply with

storage requirements.

V. FIELD/LABORATORY DECONTAMINATION OF SAMPLING APPARATUS

A. General Considerations

All sampling apparatus must be properly decontaminated prior to its use in the field to prevent cross-contamination. The equipment should be pre-cleaned in a laboratory situation, or if the duration of the sampling event prohibits pre-cleaning in a lab, then equipment should be decontaminated once a day in an area outside of the contaminated zone. Enough equipment must be available to be dedicated to sampling points each day.

Also to avoid cross-contamination, disposable gloves must be worn by the sampling team and changed between sampling points. While performing the decontamination procedure, phthalate-free gloves must be used in order to prevent phthalate contamination of the sampling equipment by interaction between the gloves and the organic solvent(s).

B. Decontamination Procedures

The required decontamination procedure for all sampling equipment is:

- a. wash and scrub with low phosphate detergent
- b. tap water rinse
- c. rinse with 10% HNO₃, ultrapure
- d. tap water rinse
- e. an acetone only rinse or a methanol followed by hexane rinse (solvents must be pesticide grade or better)
- f. thorough rinse with deionized demonstrated analyte free water**
- g. air dry, and
- h. wrap in aluminum foil for transport

*See page 59 for water criteria.

+The volume of water used during this rinse must be at least five times the volume of solvent used in Step e.

Tap water may be used from any municipal water treatment system. The use of an untreated potable water supply is not an acceptable substitute. If metals samples are not being collected, the 10% nitric acid (HNO₃) rinse may be omitted, and, conversely, if organics samples are not being taken, the solvent rinse may be omitted.

When it is necessary to use split spoon sampling devices which are composed of carbon steel instead of stainless steel, the nitric acid rinse may be lowered to a concentration of 1% instead of 10% so as to reduce the possibility of leaching metals from the spoon itself.

VI. DECONTAMINATION OF PERIPHERAL EQUIPMENT

A. Well Evacuation Equipment

All tubing and evacuation equipment such as submersible pumps which are put into the borehole must be rinsed with soapy water and deionized water before use. All tubing must be dedicated to individual wells, i.e., tubing cannot be reused. If bailers are used to evacuate wells they must be decontaminated with the same procedure listed in Section V.

B. Well Casings

Well casings must be steam cleaned prior to installation to ensure that all oils, greases, and waxes have been removed. Because of the softness of casings and screens made of fluorocarbon resins, these materials should be detergent washed, not steam cleaned prior to installation. They should be rested on clean polyethylene sheeting to keep the possibility of contamination to a minimum.

C. Field Instrumentation

Instrumentation should be cleaned as per manufacturer's instructions. Probes such as those used in pH and conductivity meters must be rinsed after each use with deionized water.

D. Drilling Equipment and Other Large Pieces of Equipment

All drilling equipment that comes in contact with the soil must be steam cleaned before use and between boreholes. This includes drill rods, bits and augers, dredges, or any other large piece of equipment. Sampling devices such as split spoons and shelby tubes must be decontaminated as per Section V between boreholes.

VII. MONITORING WELL DESIGN AND CONSTRUCTION

A. Well Drilling and Development Methods

1. General Discussion and Preferred Methods

There are various well drilling methods for application in geologic conditions ranging from hard rock to unconsolidated sediments. Particular drilling methods have become dominant in certain areas because they are most effective in penetrating the local formation.

The recommended types of ground water well drilling techniques are presented in Appendix VIII. This list has been adopted from "The Practical Guide to Ground Water Sampling" (4). The selected methods for drilling ground water monitoring wells is a site specific decision. The Hollow Stem Augering technique is the preferred method for drilling into unconsolidated sediments of up to one hundred feet in depth, because this process potentially disturbs the formation the least. If a fluid rotary method is used, clean water should be used (see water criteria, page 59), and the fluids carefully controlled to minimize impact on the ground water system.

The mud rotary method has been the alternative chosen most often in the region, but may add foreign materials into the formation. Effects of this can be minimized by utilizing high-grade pure bentonite drilling fluids, coupled with rigorous well development, and purging to remove the fluid residues from the formation. This method should only be used if site subsurface conditions warrant its use.

Procedures designed to maximize well yield are included in the term "well development". Development has two broad objectives: 1) repair damage done to the formation by the drilling operation so that the natural hydraulic properties are restored, and 2) alter the basic physical characteristics of the aquifer near the borehole so that water will flow more freely to a well. These objectives are accomplished by applying some form of energy to the screen and formation (10). More importantly wells must be developed to provide water free of suspended solids for sampling. Improperly developed monitoring wells will produce samples containing suspended sediments that will bias the chemical analysis of the collected samples (4).

The first step in well development involves the movement of water at alternately high and low velocity into and out of the wellscreened gravel pack to break down the mud pack on the well bore and loosen fines in the materials being monitored. This step is followed by pumping to remove these materials from the well and the immediate area outside the well screen. This procedure should be continued until the water pumped from the well is visually free of suspended materials or sediments (4). Methods of development include overpumping, backwashing, mechanical surging, high velocity jetting, and air development procedures (10). Of these methods, high velocity jetting and air development procedures are unacceptable without modification.

High velocity jetting involves the use of a horizontal water or air stream forced through the well screen to agitate and rearrange the particles surrounding the screen. Although this is an effective method of development, its major disadvantage is the introduction of either air or water into the formation. Water jetting is acceptable only if the water used has a controlled source so cross contamination does not occur. If potable water is used for water jetting development, analysis of a water blank is required to ensure that the water is not introducing contaminants into the borehole. Air jetting is acceptable only if the air injected into the well has a controlled source. Due to frequent contamination of formations with petroleum hydrocarbons from the air jetting process, the use of an oil filter between the compressor pump and the borehole to control the purity of the air introduced downhole is a requirement.

As each monitoring well represents a unique circumstance involving formation characteristics, well parameters and pumping requirements, current USEPA policy does not require a minimum waiting period between development and sampling for most development procedures, but relies on the technical expertise of the drilling contractors to define the time required for the aquifer to return to stability. For the processes of high velocity jetting and air development, however, a ten to fourteen day waiting period has been defined as necessary by the Robert S. Kerr Environmental Research Laboratory and the New Jersey Department of Environmental Protection Geologic Survey, and is therefore required by Region II, for the stabilization of aquifer flow and to allow recovery of the aquifer from the stresses of development.

B. Well Filter Pack and Annular Sealant

The materials used to construct the filter pack should be chemically inert (e.g., clean quartz sand, silica, or glass beads), well rounded, and dimensionally stable. Natural gravel packs are acceptable, provided that a sieve analysis is performed to establish the appropriate well screen slot size and determine chemical inertness of the filter pack materials in anticipated environments.

The materials used to seal the annular space must prevent the migration of contaminants to the sampling zone from the surface or intermediate zones and prevent cross contamination between strata. The materials should be chemically compatible with the anticipated waste to ensure seal integrity during the life of the monitoring well and chemically inert so they do not affect the quality of the ground water samples. An example of an appropriate use of annular sealant material is using a minimum of two feet of certified sodium bentonite pellets immediately over the filter pack when in a saturated zone. The pellets are most appropriate in a saturated zone because they will penetrate the column of water to create an effective seal. Coarse grit sodium bentonite is likely to hydrate and bridge before reaching the filter pack. A cement and bentonite mixture, bentonite chips, or anti-shrink cement mixtures should be used as the annular sealant in the unsaturated zone above the certified-bentonite pellet seal and below the frost line. Again, the appropriate clay must be selected on the basis of the environment

in which it is to be used. In most cases, sodium bentonite is appropriate(5).

The selected seal must not interfere with the water chemistry. Bentonite clay has appreciable ion exchange capacity which may interfere with the chemistry on collected samples when grout seal is in close proximity to the screen or well intake. Similarly, expanding cement which does not harden properly may affect the pH of water from monitoring wells when in close proximity to the well screen or intake.

To minimize these potential interferences, a 1-foot layer of silica sand should be placed above the selected gravel pack. Then, if possible, 1-2 feet of pure bentonite pellets should be placed in the hole to prohibit the downward migration of bentonite slurry or neat cement(4).

The untreated sodium bentonite seal should be placed around the casing either by using a tremie pipe or, if a hollow-stem auger is used, putting the bentonite between the casing and the inside of the auger stem. Both of these methods present a potential for bridging. In shallow monitoring wells, a tamping device should be used to reduce this potential. In deeper wells, it may be necessary to pour a small amount of clean water down the casing to wash the bentonite down the hole.

The cement-bentonite mixture should be prepared using clean water and placed in the borehole using a tremie pipe. The tremie method ensures good sealing of the borehole from the bottom.

The remaining annular space should be sealed with expanding cement to provide for security and an adequate surface seals. Locating the interface between the cement and bentonite-cement mixture below the frost line serves to protect the well from damage due to frost heaving. The cement should be placed in the borehole using the tremie method(5).

C. Well Casing Selection

1. General Discussion

Well construction materials must be durable enough to resist degradation thereby retaining their long-term stability and structural integrity and be relatively inert to minimize alteration of ground water and collected samples.

In general, the more inert (i.e., less reactive) the casing material, the more assured one is that the ground water sample withdrawn from the well is representative of the actual ground water. The major potential alterations of the sample resulting from interactions with the well casing/screen materials are: (1) adsorption/absorption reactions, both of organics and inorganics; and (2) desorption reactions, meaning leaching of chemical constituents from the well casing material into the ground water or desorption of newly adsorbed material. Casing materials can also be affected by chemical attack, i.e., corrosion/deterioration, and microbial colonization and attack(4).

These processes may lead to the observation of false trends in analyte concentrations, highly variable water chemistry and the identification of artifacts resultant from surface release or sorptive interactions. As with the errors which sampling mechanisms can introduce into the chemical data, casing materials' related errors can be quite significant and difficult to predict. Appropriate choice of materials for each application must be made on the basis of long-term durability, cleanability, and the minimization of the secondary effects of sorption or leaching. Structural integrity over time is, therefore, the primary criterion for making reliable material choices. The materials must neither be attacked nor degraded during the course of the monitoring program(4).

A variety of construction materials have been used for casing and well screens, including virgin fluorocarbon resins (Teflon), stainless steel (304 or 316), cast iron, galvanized steel, polyvinylchloride (PVC), polyethylene and polypropylene. Many of these materials, however, may affect the quality of ground water samples and may not have the long-term structural characteristics necessary for site specific needs. For example, steel casing deteriorates in corrosive environments; PVC deteriorates when in contact with ketones, esters and aromatic hydrocarbons; polyethylene deteriorates in contact with aromatic and halogenated hydrocarbons; and polypropylene deteriorates in contact with oxidizing acids, aliphatic hydrocarbons, and aromatic hydrocarbons. In addition, steel, PVC, polyethylene and polypropylene may adsorb and leach constituents that may affect the quality of ground water samples(5).

The selection of well casing and screen material should be made with due consideration to geochemistry, anticipated lifetime of the monitoring program, well depth, chemical parameters to be monitored and other site specific factors. Fluorocarbon resins or stainless steel should be specified for use in the saturated zone when volatile organics are to be determined during long term monitoring. Where high corrosion potential exists or is anticipated, fluorocarbon resins are preferable to stainless steel. National Sanitation Foundation (NSF) or ASTM-approved polyvinylchloride (PVC) well casing and screens may be appropriate if only trace metals or non-volatile organics are the contaminants anticipated(5).

Any well casing material may be used in the vadose zone, however, one combination that should be avoided is the use of dissimilar metals, such as stainless steel and galvanized steel, without an electrically isolating (dielectric) bushing. If such dissimilar metals are in direct contact in the soil, a potential difference is created and leads to accelerated corrosion of the galvanized steel (in this example). More generically, in the Galvanic series the less noble metal becomes the anode to the more noble metal and is corroded at an accelerated rate. In well construction, this acceleration in corrosion at the point of connection will lead to failure of the construction materials. Thus, a dielectric coupling should be used for connecting dissimilar metals above the saturated zone.

Plastic pipe sections must be flush threaded or have the ability to be connected by another mechanical method that does not introduce contaminants such as glue or

solvents into the well(5).

2. Selection Criteria SOP

Appendix X presents the "Standard Operating Procedure for Selecting Ground Water Well Construction Material at CERCLA Sites", dated December 15, 1986. The appendix to the SOP provides a "Summary Table for Comparing Features of Various Ground Water Well Construction Materials", which was used to develop the criteria presented for selecting the appropriate casing material. The considerations involved in the process include duration of intended well use, use of data, desired detection limits, and known site conditions and contaminants. The numerical cut-off values presented except for the chloride and pH conditions on page 4 of the SOP were designed to be ball-park figures intended to guide decision making but they were not intended to be absolute limitations. They were, as all of the criteria were, devised after digestion of the current literature and using best professional judgement.

The Summary Form presented on page 5 of the SOP should be filled out by the EPA Project Manager and presented with the Plan for review for each site.

D. Well Screens

Monitoring well screens should be 5 to 10 feet in length to avoid dilution of the contaminated groundwater with water from less contaminated zones in the aquifer (5). If site specific circumstances dictate the use of longer screens, this issue should be clearly discussed in the Plan. The well depth should ensure that the screened section is always submerged, considering seasonal water level fluctuations. In cases where light, non-aqueous phase liquids are expected to pose a significant problem, the screened interval should intersect the water table throughout the year. If dense, non-aqueous phase liquids or denser than water dissolved contaminants are suspected to pose a problem, then the screened interval for the deeper wells should be positioned immediately above any significant confining layer.

E. Evaluation of Existing Wells

If it is desired that a well already existing on-site be sampled in conjunction with newly installed wells, the Project Manager should consider the ramifications of utilizing data from those wells if, according to the "SOP for Selecting Ground Water Well Construction Material", the existing well casing is not compatible with the type of ground water contamination or the sensitivity of analysis needed.

VIII. SAMPLE COLLECTION DEVICES, MATERIALS AND QUALITY CONTROL PRACTICES

A. References for Selection of Sampling Devices

Sampling at hazardous waste sites requires many different types of sampling devices. Selection of a device should be based on practicality, economics, representativeness, compatibility with analytical considerations, and safety. There are many documents which compile sampling methods and materials suitable to address most needs that arise during investigations. The following is a list of the most commonly used references compiling sampling equipment and methodology, however it is not meant to be an exhaustive listing of all the references available.

1. Characterization of Hazardous Waste Sites-A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076. December 1984. Available from ORD Publications in Cincinnati at (513)569-7562.
2. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029. September 1982. Available from ORD Publications.
3. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018. January 1980. Available from ORD Publications.
4. Practical Guide for Ground-Water Sampling. EPA 600/2-85/104. September 1984. Available from ORD Publications.
5. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, September, 1986. Office of Waste Programs Enforcement and Office of Solid Waste and Emergency Response. Available from RCRA Hotline at 800-424-9346.
6. A Guide to the Selection of Materials for Monitoring Well Construction and Ground Water Sampling. Barcelona, Gibb, Miller. Illinois State Water Survey, Champaign, Illinois. January 1984. NTIS publication #PB84-126929.
7. Test Methods for Evaluating Solid Waste, Physical and Chemical Methods. SW-846, Third Edition. Office of Solid Waste and Emergency Response. GPO publication #955-001-00000-1, at (202) 783-3238.
8. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, April 1984. EPA 600/4-84-041. Available from ORD Publications.
9. SOP for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax. June 27, 1984. EMSL/RTP-SOP-EMD-020. Available through USEPA at Research Triangle Park, NC at (919)541-2777.
10. USEPA Dioxin Strategy. November 28, 1983. Office of Water Regulations and

Standards and the Office of Solid Waste and Emergency Response in conjunction with the Dioxin Strategy Task Force, Washington, D.C., 20460.

11. Sampling Guidance Manual for the National Dioxin Study, May 16, 1984. Office of Water Regulations and Standards, Washington, D.C.

12. Soil Sampling Quality Assurance User's Guide, Draft. May 1984. EMSL-LV. EPA 600/4-84-043. Available from ORD Publications.

13. Data Quality Objectives for Remedial Response Activities. Development Process. EPA/540/G-87/003. March 1987.

14. Data Quality Objectives for Remedial Response Activities. Example Scenario: RI/FS Activities at a Site With Contaminated Soils and Ground Water. EPA/540/G-87/004. March 1987.

B. Groundwater

1. Sampling Design

Samples from a monitoring well represent a small part of the horizontal and vertical extent of the aquifer. Unlike its surface counterpart, where a sample can be arbitrarily taken at any point in the system, moving a ground water sampling point implies the installation of additional monitoring wells. There is a need to be concerned not with the point data as an end in itself, but as a component of a network approach wherein information on the ground water system is developed as a basis for extrapolating information to areas where samples were not collected and/or for predicting the effects of natural and man-made stresses on the subsurface systems(2). Discussion of the areas of consideration for location of ground water sampling points can be found in references listed above.

2. Well Evacuation

In order to obtain a representative sample of ground water, the water that has stagnated and stratified in the well casing must be purged or evacuated. Prior to evacuating the well, however, the presence or absence of immiscible phases (i.e., "floaters" and "sinkers") must be determined. "Floaters" are those relatively insoluble organic liquids that are less dense than water and which spread across the potentiometric surface. "Sinkers" are those relatively insoluble organic liquids that are more dense than water and tend to migrate vertically through the sand and gravel aquifers to the underlying confining layer. The detection of these immiscible layers requires specialized equipment that must be used before the well is evacuated for conventional sampling. The Plan should specify the device to be used to detect light phases and dense phases, as well as the procedures to be used for detecting and sampling these contaminants. Procedures for identifying and sampling "floaters" and "sinkers" can be found in section 4.2.2 of the RCRA Ground-Water Monitoring Technical Enforcement Guidance

Document dated September 1986.

Water that has remained in the well casing for extended periods of time (i.e., more than about two hours) has the opportunity to exchange gases with the atmosphere and to interact with the well casing material. The chemistry of the water stored in the well casing is dissimilar to that of the aquifer and, thus, should not be sampled(4).

Evacuating the well allows for fresh formation ground water to enter the well. When indicator parameters such as pH, temperature and specific conductance are observed to vary less than 10% over the removal of two successive well volumes, the well is presumed to be adequately flushed for representative sampling. Evacuation of at least 3-5 well volumes is required for high yielding wells, however, in wells with very low recoveries this may not be practical. In this case the well may be evacuated to near dryness once and allowed to recover sufficiently for samples to be taken. A well must be sampled within three hours of evacuation. If a well is allowed to sit longer than three hours after evacuation, it should be re-evacuated since the water contained in the casing may no longer be representative of the aquifer conditions(4).

Any device used to evacuate the well must be cleaned as per Section V to ensure that cross contamination between wells does not occur. When a pump is used to evacuate, the tubing which comes in contact with water should be made of polyethylene or Teflon, and must be dedicated to individual wells. The intake should be placed just below the water level and lowered as the water level lowers while pumping to ensure that all the water within the well bore is exchanged with fresh water.

A bailer may be used to evacuate the well and to sample it. Bailers must be constructed of Teflon or stainless steel. Bailer cords are to be stainless steel single stranded wire, or polypropylene monofilament such as fishing line. Braided or twisted cords of any type are not allowed as complete decon would be difficult resulting in possible cross contamination between wells. Ten foot leaders may be used of these acceptable materials, with nylon cord above. ANY down-hole equipment having neoprene fittings, PVC, tygon tubing, silicon rubber bladders, neoprene impellers, or viton are not acceptable. A bailer which is used to evacuate the well may also be used to sample it without any additional cleaning.

Bailer cord must be cleaned with soap and deionized water before use. Cord can be reused; it is not necessary to dedicate it to individual wells. If a ten foot or greater length leader (any cord of unacceptable material may not contact the water) is being used, only the leader need be cleaned. See Section VIII for acceptable bailer cord materials.

Any water that is removed from the well during evacuation can no longer be considered a representative portion of the aquifer and should not be reintroduced into the well after sampling.

3. Sampling Considerations

After evacuation of the required volume of water from the well, sampling may occur.

The unstable nature of many chemical, physical and microbial constituents in ground water limit the sample collection options. Certain factors should be considered when collecting representative samples:

- * Temperatures are relatively constant in the subsurface, therefore the sample temperature may change significantly when brought to the surface. This change can alter chemical reaction rates, reverse cationic and anionic ion exchanges on solids, and change microbial growth rates.
- * A change in pH can occur due to carbon dioxide adsorption and subsequent changes in alkalinity. Oxidation of some compounds may occur.
- * Dissolved gases may be lost at the surface.
- * The integrity of organic samples may be affected by problems associated with either adsorption or contamination from sampling materials and volatility(2).

The only acceptable sampling devices for pH sensitive and volatile parameters are:

1. Teflon or stainless steel bladder pumps having adjustable flow control;
2. Teflon or stainless steel bottom-filling bailers; and,
3. Teflon or stainless steel syringe bailers.

Appropriate operating precautions for these sampling devices include:

- * Bladder pumps must be operated in a continuous manner so that they do not produce pulsating samples that are aerated in the return tube or upon discharge. Pumping rates should not exceed 100ml/min when samples are being taken for dissolved gases, volatile organic constituents, TOX and TOC;
- * Check valves must be designed and inspected to ensure that fouling problems do not reduce delivery capabilities or result in aeration of the sample;
- * Sampling equipment (especially bailers) must never be dropped into the well because this will cause degassing of the water upon impact;
- * The bailer's contents must be transferred to a sample container in a way that will minimize agitation and aeration without transferring the sample to an intermediate container, or utilizing a mechanical device; the bailer should not be "acclimated" by discharging the first bailer- full of water onto the ground since this unnecessarily agitates the water column prior to the volatile sensitive parameters being taken;
- * Clean sampling equipment must not be placed directly on the ground or other contaminated surface. When not in use, these devices should be placed on polyethylene sheeting or aluminum foil.

When sampling, heavy gauge aluminum foil or polyethylene sheeting should be placed on the ground around each well to prevent contamination of sampling equipment in the event that equipment is dropped or otherwise comes in contact with the ground.

When a number of rounds or phases of sampling will take place, the same type of sampling equipment should be used consistently throughout the entire project in order to increase the reproducibility in analytical results by eliminating the variability in sample collection technique.

Other sampling devices, including positive displacement pumps, gas lift devices, centrifugal pumps, and venturi pumps, may be used for collection of non-volatile or non-pH sensitive parameters (most parameters ARE pH- sensitive), provided that they are constructed of Teflon or stainless steel(5).

The preferred order of sample collection is as follows:

1. In-situ measurements: temperature, pH, specific conductance
2. Volatile organics (VOA)
3. Purgeable organic carbon (POC)
4. Purgeable organic halogens (POX)
5. Total organic halogens (TOX)
6. Total organic carbon (TOC)
7. Extractable organics
8. Total metals
9. Dissolved metals
10. Phenols
11. Cyanide
12. Sulfate and Chloride
13. Turbidity
14. Nitrate and Ammonia
15. Radionuclides

Detailed discussions of sample evacuation and collection procedures can be found in references #1,2,4,5 found in the Bibliography of this document.

For a discussion on the collection of filtered and non-filtered sample fractions for metals analysis, see Section XI.

4. Microbiological Sampling

There are several different methods for obtaining a ground water sample. Each of these methods differ in their advantages and disadvantages for obtaining samples for microbiological analyses.

The majority of ground water samples obtained for microbiological analysis are obtained

using preexisting wells which have existing in-place pumps. This limits the precautions the sampler must take to ensure a non-contaminated sample. Samples should be obtained from outlets as close as possible to the pump and should not be collected from leaky or faulty spigots or spigots that contain screens or aeration devices. The pump should be flushed for 5 to 10 minutes before the sample is collected. A steady flowing water stream at moderate pressure is desirable in order to prevent splashing and dislodging particles in the faucet or water line.

To collect the sample, remove the cap or stopper carefully from the sample bottle. Do not lay the bottle closure down or touch the inside of the closure. Avoid touching the inside of the bottle with your hands or the spigot. The sample bottle should not be rinsed out and it is not necessary to flame the spigot. The bottle should be filled directly to within 2.5 cm (1 inch) from the top. The bottle closure and closure covering should be replaced carefully and the bottle should be placed in a cooler (4 to 10 degrees C) unless the sample is going to be processed immediately in the field.

If a well does not have an existing in-place pump, samples can be obtained by either using a portable surface or submersible pump or by using a bailer. Each method presents special problems in obtaining an uncontaminated sample.

The main problem in using a sterilized bailer is obtaining a representative sample of the aquifer water without pumping or bailing the well beforehand to exchange the water in the bore for fresh formation water. This is difficult since such pre-sampling activities must be carried out in such a way as to not contaminate the well. Care must also be taken with bailers to not contaminate the sample with any scum on the surface of the water in the well. This is usually done by using a weighted, sterilized sample bottle suspended by a cord of acceptable material and lowering the bottle rapidly to the bottom of the well.

The use of portable pumps provides a way of pumping out a well before sampling and thus providing a more representative sample, but presents a potential source of contamination if the pumping apparatus cannot be sterilized beforehand. The method of sterilization will depend on what other samples are taken from the well since the use of many disinfectants may not be feasible if the well is also sampled for chemical analyses. If disinfection is not ruled out by other considerations, a method of sterilizing a submersible pump system is to submerge the pump, and any portion of the pump tubing which will be in contact with the well water, into a disinfectant solution and circulating the disinfectant through the pump and tubing for a recommended period of time.

The most widely used method of disinfection is chlorination due to its simplicity. Chlorine solutions may be easily prepared by dissolving either calcium or sodium hypochlorite in water. Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is available in a granular or tablet form usually containing about 70% of available chlorine by weight and should be stored under dry and cool conditions. Sodium hypochlorite, NaOCl , is available only in liquid form and can be bought in strengths up to 20% available chlorine. Its most

available form is household laundry bleach, which has a strength of about 5% available chlorine, but should not be considered to be full strength if it is more than 60 days old. The original percentage of available chlorine will be on the label. Fresh chlorine solutions should frequently be prepared because the strength will diminish with time. After disinfection the pump should be carefully placed in the well and then pumped to waste until the chlorine is thoroughly rinsed from the pump system.

If the pump cannot be disinfected, then the pump and tubing should be carefully handled to avoid gross surface contamination and the well should be pumped for 3 to 10 bore volumes before taking a sample. It may be desirable after pumping to pull the pump and take the sample with a sterile bailer.

In those cases where the water level in the well is less than 20 to 30 feet below the surface, a surface vacuum pumping system can be used for flushing out the well and withdrawing a sample.

Lastly, interpretation of analytic results may be difficult in some cases since surface contamination of wells due to poor drilling and completion practices is common. In cases where drinking water supplies are involved, a thorough inspection of the well is required to eliminate surface contamination down the well bore as a source of contaminants. Disinfection of the well by approved methods and resampling may be advisable, if disinfection will not affect the well for other sampling purposes(2).

C. Surface Water

1. Sampling Design

There are at present no quality assurance requirements for site location for sampling surface waters. References #1 and #2 in Part A of this Section can be consulted for design guidance.

2. Sampling Devices

Appendix XI provides a tabular comparison of surface water sample collection devices.

Samples from shallow depths can be readily collected by merely submerging the sample container. However, preservatives cannot be present in the container when it is lowered into the water. The method is advantageous when the sample might be significantly altered during transfer from a collection vessel into another container. This is the case with samples collected for oil and grease analysis since considerable material may adhere to the sample transfer container and as a result produce inaccurately low analytical results. Similarly the transfer of a liquid into a small sample container for volatile organic analysis, if not done carefully, could result in significant aeration and resultant loss of volatile species. Though simple, representative, and generally free from substantial material disturbances, it has significant shortcomings

when applied to a hazardous waste, since the external surface of each container would then need to be decontaminated.

In general the use of a sampling device constructed of a nonreactive material such as glass, stainless steel, or Teflon, is the most prudent method. The device should have a capacity of at least 500 ml, if possible, to minimize the number of times the liquid must be disturbed, thus reducing agitation of any sediment layers.

A 1-liter stainless steel beaker with pour spout and handle or large stainless steel ice scoops and ladles available from commercial kitchen and laboratory supply houses can be used.

It is often necessary to collect liquid samples at some distance from shore or the edge of the containment. In this instance an adaptation which extends the reach of the sampler is advantageous. Such a device is the pond sampler. It incorporates a telescoping heavy-duty aluminum pole with an adjustable beaker clamp attached to the end. The beaker previously described, a disposable glass container, or the actual sample container itself, can be fitted into the clamp.

It may on occasion be necessary to sample large bodies of water where a near surface sample will not sufficiently characterize the body as a whole. In this instance a peristaltic pump may be used in which the sample is drawn in through heavy walled Teflon tubing and pumped directly into the sample container. This method, however, is not suitable for pH sensitive or volatile samples in which stripping would occur.

Situations may still arise where a sample must be collected from depths beyond the capabilities of a peristaltic pump. In this instance an at-depth sampler may be required, such as a Kemerer, ASTM Bomb (Bacon Bomb) or Van Dorn sampler. These devices work well; however, care must be utilized in selecting devices that are made of materials that will not contaminate the sample. Van Dorn samplers are not generally recommended for organics as they rely on an elastic closing mechanism that can effect samples. They are readily available in a totally nonmetallic design which is very useful for sample collection for trace metal analysis.

Kemerer samplers are available on special order or adaptable for sample collection for organic analysis by substituting Teflon for the rubber or plastic stoppers. If the device is further ordered with stainless steel metallic parts in addition to Teflon stoppers it becomes a very versatile sampler(1).

Consult "Characterization of Hazardous Waste Sites-A Methods Manual:Volume II. Available Sampling Methods, Second Edition" for specific collection techniques using these devices. See Part B.4 of this Section for collection of microbial samples.

D. Sediment

Sediment is defined as the deposited material underlying a body of water.

1. Sampling Design

Streams, lakes, and impoundments will likely demonstrate significant variations in sediment composition with respect to distance from inflows, discharges or other disturbances. It is important, therefore, to document exact sampling location by means of triangulation with stable reference points on the banks of the stream or lake.

At the present time, however, there are no quality control requirements for choosing site location when sampling sediments. Reference #2 in Part A of this Section can be consulted and sediment transport and deposition modeling along with statistical considerations can be found in "Sediment Sampling Quality Assurance User's Guide," EPA 600/4-85-048, July 1985, NTIS #PB85- 233542.

2. Sampling Devices

Appendix XII provides a tabular comparison of some bottom grab and coring devices.

Samples can be taken with stainless steel spoons or trowels or the sample container itself if there is little or no water on top of the sediment. If the water above the sediment is a few feet deep a stainless steel corer or corer having a removable glass or Teflon liner may be used. This will help ensure the integrity of the surface layer of sediment and will minimize the loss of fine grained material. In deeper water the bottom grab samplers presented in Appendix XII may be used(1).

If at any time surface water samples are being taken in conjunction with sediment samples, the water samples should be taken first. The sampler should approach the location from the downstream direction with the container pointed upstream to ensure collection of an undisturbed sample.

Sediment samples collected for all analyses except VOA and TOX should be thoroughly mixed before being placed in appropriate sample containers. Rocks, twigs, and other debris should be removed from the sample prior to homogenization, if they are not considered part of the environmental sample. In this way stratification of constituents will not affect analytical results. VOA and TOX samples should be taken as individual grab samples, never homogenized. See Section IX for the procedure used for homogenization of samples.

E. Soil

1. Sampling Design

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. In the sampling of a soil matrix, sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the

population has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample are unbiased (accurate) estimators of true population parameters. In other words, the sample is representative of the population. One of the most common methods of selecting a random sample is to divide the population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers to be sampled through the use of a random-numbers table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population. A detailed discussion of random sampling can be found in SW-846, Third Edition, November 1986, Volume 2, Chapter 9.

In a biased sampling approach, site history, available information and professional judgement are used to determine the sampling locations in which contamination is expected to be found. In this case the most information is gotten from the least number of samples thereby allowing a cost savings. However, this approach to sampling design is more appropriate to a site investigation than a remedial investigation (RI) because it is not a comprehensive view of site conditions(7). Use of a biased approach during an RI must be justified in the Plan.

2. Sampling Devices

When sampling soil, stainless steel, Teflon or glass utensils should be used. The only exception is split spoons which are most commonly available in carbon steel. These are acceptable for use provided they are not excessively rusty.

A stainless steel spatula should be used to remove sample from the opened spoons, not the sampler's fingers, as the gloves may introduce organic interferences into the sample. As per water sampling, volatile organics and TOX samples should be taken immediately upon opening the spoon. Any rocks, twigs, leaves or other debris should be removed from the sample before homogenization, if they are not considered part of the environmental sample. All samples except those for volatile organics and TOX must be homogenized before being put into sample containers. Section IX provides a discussion on homogenization. Samples for VOA and TOX should never be homogenized as they both contain volatile parameters.

F. Potable Water

When sampling potable water the same quality control requirements apply as for sampling groundwater, where applicable.

The "Manual for the Certification of Laboratories Analyzing Drinking Water," EPA 570/9-82-002, October 1982, states that the sample needs to be representative of the potable water system, and that the tap water must be sampled after maintaining a

steady flow of 2 or 3 minutes to clear the service line. This flushing period is a minimum requirement and more time can be allowed if a large holding tank is in place and it is desirable to purge an entire tank volume. A tap must be free of any aerator, strainer, hose attachment, or water purification devices. When sampling chlorinated waters for organics and bacterial analyses, sodium thiosulfate should be added to the sample bottles. Consult the reference for details.

G. Dust/Wipe

The following Standard Operating Procedure has been developed by Region II for use in taking wipe samples.

1. Materials needed:

- a. cotton swabs, solvent rinsed and completely air dried;
(use of synthetic materials requires checking for compatibility with solvents)
- b. acetone, pesticide grade;
- c. hexane, pesticide grade;
- d. deionized water;
- e. HCl or HNO₃, redistilled
- f. stainless steel clamps or plastic clamps (only for taking metals samples);
- g. appropriate sample bottles.

2. A square area, of a size sufficient to give the required amount of sample for each fraction as provided in the analytical methodology to be used, should be marked off. This may require taking cotton swabs and a balance into the field, wiping a certain area and weighing the swab before and after to determine how much area should be wiped to give the required weight of sample.

3. Swabs for semi-volatile, pesticide and PCB samples should be moistened in a 1:4 acetone/hexane mixture. Swabs for volatile organic samples should be moistened with hexane alone, and those for metals with deionized water. While holding the swab in a clean, metal clamp, moisten the cotton swab with the appropriate solution.

4. While still holding the cotton swab in the clamp, wipe the sampling area back and forth repeatedly, applying moderate pressure. Wipe the entire area so that all the sample material is picked up.

5. Place the used swab in the appropriate sample container and seal.

6. Clean the clamps between each sample with both solvent and 10% HCL or HNO₃.

7. As a blank, moisten a clean swab with the solvent or water (for each collection medium), place it in a separate jar, and submit it with the other samples.

8. When samples are submitted for analysis, the laboratory should be told to rinse the sample jars with solvent or 10% HCL or HNO₃, depending on the analysis to be performed, when transferring sample to the extraction glassware.

The samples should be analyzed with the appropriate methodology for a soil/sediment matrix, and a sufficient quantity of material must be collected as called for in the analytical methodology in order for method detection limits to be achieved.

H. Dioxin

For guidance on conducting dioxin sampling events refer to "Sampling Guidance Manual for the National Dioxin Study", May 16, 1984. The sampling material requirements are the same as those present in this document for the matrix being sampled, with the following additions.

The equipment decontamination procedure is the same as that presented in Section V however samplers must use trichloroethylene as the solvent rinse in step e of the procedure.

Homogenization must be performed on dioxin samples of a solid matrix.

Homogenization may be performed in a laboratory or in the field and it should be done using either the coning and quartering method (see Section IX) or by using stainless steel blenders. Homogenization of wet sediment samples is more easily accomplished using the coning and quartering method. Specific quality control samples for dioxin sampling events are presented in Section X.

I. Drums

For sampling of non-homogenous or multi-phased materials in drums, tanks, waste piles, lagoons, etc., refer to SW-846, Third Edition, Volume 2 for guidance. The Plan must include a detailed approach in terms of basic strategy and sampling equipment if such containers are to be sampled.

IX. METHODS OF SAMPLE PREPARATION

A. Homogenization

The homogenization of a sample is the process of mixing individual grab samples in order to minimize any bias of sample representativeness introduced by the natural stratification of constituents within the sample.

To homogenize a sample of a soil/sediment matrix, first rocks, twigs, leaves and other debris should be removed if they are not considered part of the sample. The soil/sediment should be removed from the sampling device and placed in a stainless steel pan, then thoroughly mixed using a stainless steel spoon. The sediment in the pan should be scraped from the sides, corners and bottom of the pan, rolled to the middle of the pan, and initially mixed. The sample should then be quartered and moved to the four corners of the pan. Each quarter of the sample should be mixed individually, and then rolled to the center of the container and the entire sample mixed again.

Homogenization of an aqueous sample is only necessary if stratification of constituents is of concern, for example when sampling a lagoon or containerized liquid. Then homogenization would be performed by mixing in a stainless steel bowl.

B. Compositing

Compositing of samples is performed when samplers desire to obtain an average concentration of contaminants over a certain number of sampling points. Anytime compositing is performed, the concentration of contaminant in individual grab samples is diluted proportionately to the number of samples taken. Not only is the contaminant diluted, the detection limits for each individual sample are raised proportionally to the number of samples added to the composite. For instance, if a sampler wishes to composite two discrete samples into one, and the method detection limit for a target compound is 330 ppb, the detection limit for the target compound does not change for the composite, however, the detection limit for the compound in the individual samples which make up the composite is two times the normal detection limit or $2 \times 330 = 660$ ppb. This is important to keep in mind because it is possible that if a contaminant were present in only one of the two composited samples, and if it were at a level between 330 and 660 ppb, that contaminant would not be quantified or possibly even identified due to the effective dilution of the contaminant concentration in the composite. This concept should be taken into account when determining the data quality objectives of a composite sampling event, to ensure that useful data is collected. It is advisable that if a positive identification is made in the course of analyzing a composite sample, that the discrete samples then be analyzed individually to determine the true distribution of contaminant throughout each component of the composite.

Compositing of a solid matrix is accomplished by mixing equal volumes of grab samples in stainless steel pans with stainless steel spoons. Compositing is never performed on samples for volatile organics analysis (or any analysis involving a volatile portion such

as TOX), and, for a solid matrix, should never be done by placing equal portions of grab samples directly into sample jars, as the occurrence of error introduced by the sampler is highly probable.

C. Splitting

Splitting of samples is performed when two or more parties wish to have a portion of the same sample. They are most often collected in enforcement actions to ensure that sample results generated by Potentially Responsible Parties (PRPs) are accurate. Splitting of samples, however, is not as useful as providing blind performance evaluations samples to a laboratory since analytical performance and accuracy differs from laboratory to laboratory, and therefore one laboratory cannot be considered a "referee" whose performance can be considered the standard against which another's can be measured. Performance evaluation samples provide information on a laboratory's performance based upon analysis of that sample which contains parameters of a known and defined concentration.

Soil/sediment samples taken for volatile analysis cannot be split. In this case samples must be taken as co-located grabs. Then, a large quantity of material can be collected, homogenized, split and used to fill the remaining containers. Note that enough sample must be collected at one time in order to fill all the necessary sample containers. It may be necessary to co-locate or depth integrate collection so enough sample volume is available. A description of this process should be provided in the Plan.

When splitting aqueous samples, homogenization of the sample is only necessary if heterogeneity is suspected, for example when sampling a small lagoon or containerized liquid; however VOA and TOX samples are never homogenized. It is not generally necessary to homogenize ground water or surface water samples when splitting, and it is likewise generally unnecessary to divide a bailer's contents among several bottles.

Please note, duplicate samples, trip blanks and field equipment rinse blanks must be included as part of those samples which are split between the two or more parties involved.

X. FIELD QUALITY CONTROL SAMPLES

A. All Analyses Except Dioxin

1. Duplicates

Environmental duplicate samples are collected to demonstrate the reproducibility of sampling technique. Environmental duplicate samples must be taken at a frequency of at least 5% (1 in 20). This is a separate duplicate from the duplicates a laboratory must run, and cannot be replaced by a laboratory generated duplicate. This applies to every matrix sampled. Environmental duplicates are representative of field sampling precision, whereas laboratory duplicates are a measure of analytical precision. Both pieces of information are essential to determining the quality of data generated for a project.

2. Blanks

Blank water generated for use in the Region II CERCLA program must be "demonstrated analyte-free". By this term we mean water of a known quality which is defined by the Quality Assurance office.

The criteria for analyte-free water is as follows. The assigned values for the Contract Required Detection Limits (CRDLs) and Contract Required Quantitation Limits (CRQLs) can be found in the most recent CLP SOWs or in Appendix III enclosed. These criteria apply to all blank water used for fund-lead as well as PRP projects whether or not EPA CLP analytical methods are employed. If the levels of detection needed on a specific site are lower than the CLP CRDLs/CRQLs, then those levels are used to define the criteria for analyte free water.

purgeable organics	<10 ppb
semi-volatile organics	<CRQL
pesticides	<CRQL
PCBs	<CRQL
inorganics	<CRDL

However, specifically for the common laboratory contaminants listed below, the allowable limits are three times the respective CRQLs.

methylene chloride
acetone
toluene
2-butanone
phthalates

The analytical testing required for the water to be demonstrated as analyte free must be performed prior to the start of sample collection. The results must either be sent to the Region II QAO assigned to the specific project or be kept on-site for review by EPA

personnel during a field audit. In addition, the contractors shall maintain quality control records for each source of water which is used. These records shall demonstrate over time the presence/absence and level of contaminants found in each water supply. EPA personnel will randomly audit throughout the year the records kept by the generators/contractors.

If potable water is used during the drilling process and is introduced into the borehole, a sample of the water should be collected and analyzed to ensure contaminants are not being introduced via the water supply.

a. Trip Blanks

When sampling for volatile organics, a trip blank, consisting of demonstrated analyte free water sealed in 40 ml Teflon lined septum vials, must be taken into the field where sampling is going on. It should be taken at a minimum frequency of one per day when volatile organics in an aqueous matrix are being collected. Note that it is not necessary to take an aqueous trip blank when a non-aqueous medium is being sampled. Trip blanks are used to determine if any on-site atmospheric contaminants are seeping into the sample vials, or if any cross contamination of samples is occurring during shipment or storage of sample containers. Trip blanks are only analyzed for volatile organics.

b. Field Rinse Blanks

Rinse blanks consist of pouring demonstrated analyte free water over decontaminated sampling equipment as a check that the decontamination procedure has been adequately carried out and that there is no cross-contamination of samples occurring due to the equipment itself. Analysis of rinse blanks is performed for all analytes of interest. One blank should be collected for each type of equipment used each day a decontamination event is carried out. It is required that rinse blanks be performed on bowls and pans used to homogenize samples as well as on any filtration device used on aqueous samples being analyzed for "dissolved" metals. It is permissible to use the same aliquot of water on all equipment associated to a particular sample matrix for analysis of semi-volatile organics, pesticides, PCBs and inorganics. This rinse must be performed sequentially on all sampling equipment. However, a separate field rinse blank must be collected for each piece of equipment associated to a particular sample matrix which will be analyzed for volatile organics.

The blank should be collected at the beginning of the day prior to the sampling event and that blank must accompany those samples which were taken that day. This is a necessary procedure so that the blank will be associated with the proper samples during data validation. If all samples collected that day are not validated with the field rinse blank sample, it is the contractor's responsibility to ensure the application of the blank's results to the group of samples. It is also the contractor's responsibility to monitor the field rinse blank results over time in order to assess the performance of the sampling team with respect to the adequacy of the decontamination procedure. This will help reduce the number of samples needing reanalysis as well as the number of

results being qualified and/or rejected due to contamination of the field rinse blank sample.

3. Matrix Spike/Matrix Spike Duplicate Analyses

When performing CLP organic extractable analysis, the laboratory must be supplied with triple sample volume for each Sample Delivery Group (SDG) in order to perform matrix spike and matrix spike duplicate analyses. This does not include field or trip blanks. Blanks do not require separate matrix spike or duplicate analyses regardless of their matrix.

As stated in the SOW, the limits on an SDG are:

- *each Case of field samples, or
- *each 20 field samples within a Case, or
- *each fourteen calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SDG), whichever comes first.

B. Dioxin

When dioxin sampling is performed a batch of quality control samples must accompany environmental samples whether the samples are sent through the Contract Laboratory Program or to a privately contracted laboratory.

The quality control sample requirements for every group of 24 dioxin samples collected or every 24 samples collected over a period of two days, whichever comes first, are:

- a. two performance evaluation samples from EMSL-LV fortified with a known amount of native 2,3,7,8-TCDD (unknown to the laboratory);
- b. one environmental duplicate - designated as a duplicate by the sampling team;
- c. one blind blank (blind blank to the laboratory)-this sample does not go through the homogenization on-site;
- d. one known blank - this is an uncontaminated soil/sediment and/or water sample that is to be fortified by the lab with 2,3,7,8-TCDD at a concentration of 1 ug/kg for soils and 10 ng/L for aqueous samples. This sample must be designated by the contractor sampling team to the laboratory as "for spiking".
- e. one blender blank-this is blank soil homogenized in the field to check for cross-contamination during the blending process, and is only necessary if blenders are used to homogenize the samples.
- f. rinsate blank - rinsate blanks consist of pouring spectrophotometric grade

trichloroethene (minimum 200 mls) over decontaminated sampling equipment as a check that the decontamination procedure has been adequately carried out and that no cross contamination of samples has occurred due to the equipment itself. Analysis of rinsate blanks is performed for all isomers of interest.

Samples a, c, and d above will be ordered by the Regional Quality Assurance Officer from EMSL-LV at the request of the EPA Project Manager only.

XI. FILTERED AND NON-FILTERED FRACTIONS OF GROUND WATER SAMPLES

A. General Discussion

In certain situations it may be desirable to consider filtration of ground water samples in order to obtain information about the "dissolved" species of the contaminant in solution as opposed to that portion of contaminant which may adhere to silt or clay particles. The real concern in this issue is whether or not the contaminant is a component of the ground water, which implies that if the contaminant is truly a component of the ground water, then it must flow with the ground water. If the contaminant flows with the ground water on or under a site then there is the potential for the contaminant to be moved to and from impact areas outside of the site.

There has been a general assumption that water and soil are the only distinct constituents of an aquifer system; there is also a false assumption that water and completely solvated solutes are the only constituents of the system that are mobile. In fact, components of the solid phase in the colloidal size range may be mobile in subsurface environments (11). The colloidal state refers to a two phase system in which one phase in a very finely divided state is dispersed through a second. In ground water, colloidal particles are generally smaller than one micrometer (1 μm) in diameter. Since the clay fraction is defined by the USDA as being 2 μm and smaller, not all clay is strictly colloidal, but even the larger clay particles have colloid-like properties (12). There is ample evidence, as can be seen in the literature, that colloid particles can move in aquifers (11).

There are two distinct types of colloidal matter, inorganic and organic, which exist in intimate intermixture. The inorganic is present almost exclusively as clay minerals of various kinds; the organic is represented by humus (12). These colloidal particles can sorb organic and inorganic contaminants and stabilize them in the mobile phase of the aquifer. Association of contaminants with mobile colloidal particles may enhance the transport of highly adsorbed pollutants, or deposition of colloidal particles in porous media may decrease permeability and reduce contaminant transport (11).

The separation of "dissolved" and "particulate" sample fractions is most commonly accomplished by filtration through a 0.45 μm membrane filter. The convention of using a 0.45 μm pore size filter was borrowed from the microbiological science where it was used as the separation point for filtering bacteria out of aqueous media. This convention was borrowed by other organizations for use in the analysis of aqueous metals samples, and now is specified as the pore size through which will pass those constituents that are "dissolved". Those constituents which are retained on the 0.45 μm filter are labeled "suspended", and "total" metals is the sum of the "dissolved" and "suspended" fractions.

It would be more accurate, however, to term the fractions "filterable" and "non-filterable" instead of "dissolved" and "total" or "particulate" given the operational nature of the separation. The 0.45 um distinction is not useful when one is concerned with true soil/water chemistry but has its sole value at present in the fact that it is convention and is used as such in ground water characterization throughout the country.

The policy in Region II on filtering ground water has been that only samples for metals analyses may be filtered, and when taking metals samples, "total" metals should be taken with the option to take a "dissolved" sample if so desired. The filtration of aqueous samples for organics analyses has not been allowed in the Region since, 1)volatile contaminants would be released during filtration, and 2)the membrane filters used for the filtration of metals samples will adsorb the organics, thereby giving falsely negative results.

The rationale behind the policy is this: rather than rely totally on "dissolved" metals data, which will generally give results that are lower than the true amount of contaminant which moves with ground water, the Region has chosen to be more conservative in its use of metals data by preferring to consider "total" metals data, thereby erring on the side of finding more metals in a sample than actually may be mobile in the ground water phase. Obviously, in some cases when samples are silty, the "total" metals values will be high due to the addition of metals which were bound to particles of greater size than the colloidal range. Unfortunately the use of either "total" or "dissolved" metals data alone is inappropriate when one wishes to consider the true portion and constituents which move with ground water.

The Regional policy as presented here will continue to be enforced in spite of the limitations until such time as a technically well-founded alternative is developed. If exceptions or modifications to this policy are desired based on site specific needs, the Project Manager should consult the Quality Assurance Officer assigned to the project.

B. Procedures for Filtration of Aqueous Metals Samples

1. Decontamination of Apparatus

When filtering aqueous metals samples, a device made of polyethylene, polypropylene or borosilicate glass should be used. The apparatus should be pre-cleaned by rinsing with a 10% HNO₃ solution, followed by a demonstrated analyte-free deionized water rinse, and should be cleaned in the same manner between samples. Also, a field rinse blank must be collected for this apparatus. See Section X for further details.

2. Filtration Procedures and Preservation

The filter used should be a cellulose-based membrane filter of 0.45 um nominal pore

size. Samples must be filtered immediately after their collection to minimize changes in the concentration of the substances of interest. Samples are only passed through the filtration apparatus once, they are not to be passed through repeatedly until they are free of turbidity. Samples are then preserved immediately with undiluted ultrapure HNO₃ and the pH checked to ensure proper pH has been attained. No samples for cyanide, conventional parameters, or organics may be filtered in this manner. All paperwork accompanying the samples to the laboratory should clearly state that the samples have been field filtered, in order to avoid a second filtration at the lab.

XII. LABORATORY QUALIFICATIONS

A. Use of CLP vs. non-CLP Laboratories

Most analytical work performed for Federal fund-lead CERLCA sites within the Region utilizes the USEPA Contract Laboratory Program. However, it is not mandatory that all analyses supporting the CERCLA program be performed by a Contract Laboratory, whether the project is a fund-lead or enforcement-lead site. Laboratories which do not participate in CLP may be used at any time, provided they adhere to Region II QA/QC requirements which are described here.

If a non-CLP laboratory is used, that laboratory must supply to the Regional Quality Assurance Officer (QAO), a copy of their in-house QA/QC manual which is applicable to the analyses to be performed. The QA/QC manual should cover the following topics:

- resumes
- personnel training and experience
- organizational structure
- equipment available
- reference materials/reagents
- control charts
- standard operating procedures
- data reduction/reporting
- chain-of-custody
- glassware preparation

Also, that laboratory must perform acceptably on performance evaluation samples supplied by the EPA or a State certified program for those parameters of interest to the project. A formal request for EPA performance evaluation samples should be sent from the EPA Project Manager for the site to the EPA QAO in MMB.

A non-CLP laboratory must also undergo a technical systems audit performed by the party independent to the analysis in order to evaluate the laboratory's capability to perform the work. A copy of the resultant report should be sent directly to the EPA QAO. A State audit report, outlining the laboratory's performance within the last year, will be acceptable. The format of the audit checklist can be taken from the CLP Invitation for Bid (IFB). Agreement from the laboratory to perform these tasks must be made before the plan is approved. Only after this information has been provided and found to be acceptable, can sampling and analysis begin. The CLP IFBs are available from the Sample Management Office at (703) 557-2490.

XIII. USE OF MOBILE LABORATORIES

A. Qualifications and Methods

There has been a growing demand throughout the Region for use of field analytical laboratories in order to screen samples and generate real-time results which can be used to make decisions in the field. These laboratories commonly use "quick and dirty" techniques since strict precision and accuracy requirements are not necessary for the intended use of the data, and since, in most cases, critical sampling locations, where quality data is important, are split for analysis by a CLP laboratory also.

However, there are certain quality control requirements for use of mobile laboratories. First, the data quality objectives (DQOs) for the screening event must be determined and documented. The DQOs should take into account the fact that "quick and dirty" screening methods do not generally give high quality precision and accuracy and some confirmational analysis with a CLP or other commercial laboratory is necessary. Confirmational analysis should be run on those sample locations which are most critical to the project, for instance, the boundary area of a removal action. Secondly, if a methodology is developed for use, that method must be documented and validated. Proof of the validation must be provided to the EPA QAO and the QAO must consider it satisfactory before the method can be used. The method validation should address the following points, where applicable.

- a. analytical objectives
- b. method detection limits
- c. analytical procedure
- d. precision and accuracy
- e. calibration
- f. quantitation
- g. data reduction/validation
- h. holding times

Finally, as for any data generated within the Region and which is not validated by Regional personnel, the contractor's quality assurance officer must sign a summary statement which describes the quality control measures followed, the quality control sample results, what data was rejected due to exceedances, etc. This statement should be supplied to the EPA Project Manager.

XIV. VALIDATION OF DATA

A. Contract Laboratory Program

All data generated for use by Region II which is produced by CLP is validated by the Region with in-house protocol. These data validation standard operating procedures for organics, inorganics and dioxin data are updated yearly for the current set of CLP contracts. Application of a protocol which standardizes data useability criteria ensures that all data which is used in the Region is of comparable and acceptable quality and utility. The Region II data validation standard operating procedures are presented in Appendix XIII.

B. Non-CLP

Data which is generated outside of CLP for use in Region II must be validated in the same manner as all other data is validated so that a standard useability criteria is applied to all data used in the Region. All data should be of comparable quality.

The Plan must identify the laboratory to be used if the laboratory is not to be engaged through the CLP program or if the laboratory does not participate in CLP. All data produced by laboratories which do not participate in CLP (or if they do participate but are not directly contracted by EPA) must be validated by the laboratory or primary engineering contractor according to Region II validation SOPs. Note that these SOPs apply only to the CLP methodologies and that if different analytical method references are used (such as SW-846 or Methods for Chemical Analysis of Water and Wastes) the validation criteria will have to be modified according to the quality control criteria called for in that methodology used. The QAO of the laboratory must be identified and a detailed discussion of the validation criteria to be used when data is generated must be provided in the Plan.

After data is generated a validation report must be provided to the EPA Quality Assurance Officer in MMB assigned to the site. This will ensure that the data has been validated in accordance with the Region II protocol, or, if quality control criteria had to be established according to the dictates of the method, the party performing the validation is responsible for establishing precision and accuracy protocol and for validating the data and meeting criteria based on that protocol. Quality assurance summary sheets, and, if applicable, the Region II SOP validation checklist should be provided to the Project Manager. The summary sheets should be taken from the CLP SOW, the third edition of SW-846 or be based thereon. Data analysis sheets must be provided for each environmental sample listing quantities found or detection limits.

If the Project Manager wishes to have the validation of data checked by the MMB staff, or if upon review of the validation report provided a revalidation of a certain percentage of data is deemed necessary, CLP deliverables must be made available. This may mean notifying the PRP in advance that CLP deliverables may be requested from their

laboratory at a future date.

XV. FIELD AUDITING AND OVERSIGHT

A. Audits Initiated by EPA and Primary Contractor

On-site audits of EPA contracted and PRP contracted field sampling teams takes place on a random basis within the Region. EPA personnel performing the audits look for good sampling technique and ensure that approved Plans are being implemented in the field. Auditors do make suggestions to contractors in the field but they do not stop work unless a discrepancy severe enough to invalidate data results is observed. If a severe discrepancy is observed the Project Manager is notified by phone when the auditors return to the office that day.

EPA personnel send written audit reports to the EPA Project Manager following the audit and request written response from the contractor when inadequacies are found.

B. Contractors in an Oversight Capacity

Contractors retained in an oversight capacity should be looking for good sampling technique and adherence to an approved Plan when overseeing other contractors in the field. Logbooks should be kept by the oversight contractor and any poor practices or discrepancies with the Plan should be noted and the EPA Project Manager notified of the findings by phone.

C. Audits Performed by States

State Quality Assurance personnel routinely perform audits of Federal-lead sites. Although State auditors can make suggestions to improve sampling technique and to ensure that approved Plans are being implemented, they do not have the authority to stop work in the field or to change any part of the Plan. If a disagreement with State auditors arises in the field, the contractor should contact the Project Manager for guidance.

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**REGION II
CERCLA QUALITY ASSURANCE MANUAL**

PART II: QUALITY CONTROL HANDBOOK FOR CERCLA SAMPLING AND ANALYSIS

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I. FORWARD

A.Intent

This CERCLA Quality Assurance Manual has been prepared by the Monitoring Management Branch of the Environmental Services Division for use by the Emergency and Remedial Response Division Project Managers of the Region II Superfund (CERCLA) program in their daily working with contractors. It's use is intended to ensure that quality assurance and quality control practices (QA/QC) are fully built into all monitoring project designs.

This Manual provides Region II's quality assurance/quality control requirements for CERCLA sampling and analysis. Quality assurance procedures are used to verify that field and laboratory measurement systems operate within acceptable, defined limits. The effectiveness of the overall Quality Assurance Program demands that all personnel are aware of the QA/QC requirements for any investigation and that the quality assurance objectives are understood. This Volume outlines of all aspects of QC in a monitoring program, minimum requirements necessary, and the rationale behind the requirements. This Manual is meant to be a dynamic document. It will periodically be reviewed and updated, however it is not meant to provide definitive answers to all site-specific concerns. This is, rather, an attempt to provide a rationale behind the most common site-specific concerns which could be extrapolated for use in new situations.

The quality control procedures outlined in this Manual should be incorporated into all field/project/site operations plans and/or quality assurance project plans prepared for CERCLA work. Recommendations and requirements presented herein should be incorporated into project designs to the fullest extent possible. Where deviations from these recommendations and requirements is necessary, full justification must be presented in writing.

B. Disclaimer

This Manual has been prepared for use by the Environmental Services and the Emergency and Remedial Response Divisions of the USEPA, Region II. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the Agency.

II. SAMPLING DESIGN AND STRATEGY

A. Sampling Plan Components

Detail of sampling and analysis is a necessary part of each field/site/project operations or quality assurance project plan (from hereon referred to as the Plan) in order to ensure uniform and acceptable sampling and analytical protocol for each project. The Plan describes the objectives and details how the individual tasks of a sampling and analytical effort will be performed. The Plan must include the following topics as a minimum.

- * Objectives of sampling design and selection of representative sampling sites.**

Discussion of site history and sampling design rationale must be provided, so that reviewers of the Plan have the necessary information. The discussion should include topics such as the history of the contamination, the matrices involved, the dimensions of the site, etc.

- * Sampling Design**
- * Selection of Parameters to be measured.**

Parameters to be measured are usually dictated by the purpose of an investigation and should be based on knowledge of the problem being investigated. An in-depth discussion of parameter selection is out of the scope of this document as it is a process requiring much background and expertise in dealing with hydrogeologic systems, chemistry, and engineering, and no criteria for parameters can be put forth in the format of an SOP.

- * Selection and preparation of sampling equipment.**
- * Sampling equipment construction materials.**
- * Required sample volumes.**
- * Selection and preparation of sample containers.**
- * Sample collection and handling.**
- * Sample preservation.**
- * Sample chain-of-custody and identification.**
- * Use of field instrumentation.**
- * Field quality control samples.**

- * Choice of laboratories and validation of data.

These topics are further discussed within this Manual.

B. Purpose and Objective of Sampling

The basic objective of any sampling campaign is to collect a sample which is representative of the media under investigation. More specifically, the purpose of sampling at hazardous waste sites is to acquire information that will aid investigators in determining the presence and identity of on-site contaminants and the extent to which they have become integrated into the surrounding environment. This information can then be used as support for future litigations or as input to remedial investigations and risk assessments.

The validity of environmental data is dependent in part on the integrity of the field procedures employed in obtaining a sample. Proper sampling techniques must be employed to obtain a sample which is representative of the area or container of interest. A sample is representative if it possesses the same qualities or properties as the material under consideration. Due to the complexity of most hazardous substances and site conditions, no universal sampling methods can be recommended. Procedures must be adapted for use in various matrices and site-specific restrictions.

C. Types of Samples

Before defining the general sample types, the nature of the media or materials under investigation must be discussed. Materials can be described as homogeneous or heterogeneous. Homogeneous materials are generally defined as having uniform composition throughout. In this case, any sample increment can be considered representative of the material. On the other hand, heterogeneous samples present problems to the sampler because of changes in composition of the material over distance and time.

When discussing types of samples, it is important to distinguish between the type of media to be sampled and the sampling technique that yields a specific type of sample. In relation to the media to be sampled, two basic types of samples can be considered: the environmental sample and the hazardous sample.

1. Environmental Samples

Environmental Samples (ambient air, soils, surface water, groundwater, sediment or biota) are generally dilute (in terms of pollutant concentration) and usually do not require the special handling procedures used for concentrated wastes. However, in certain instances, environmental samples can contain elevated concentrations of pollutants and in such cases would have to be handled as hazardous samples.

2. Hazardous Samples

Hazardous or concentrated samples are those collected from drums, tanks, lagoons, pits, waste piles, fresh spills, etc., and require special handling procedures because of their potential toxicity or hazard. These samples can be further subdivided based on their degree of hazard; however, care should be taken when handling any wastes believed to be concentrated, regardless of the degree.

D. Types of Measurement

In general, two basic types of sample measurements are recognized, both of which can be used for either environmental or concentrated samples. They are: 1) samples which are collected and subsequently analyzed in the laboratory and, 2) samples which are analyzed in-situ.

1. Laboratory Measurement

There are two types of samples which are collected and analyzed in a laboratory. These are grab samples and composite samples.

a. Grab Samples

A grab sample is defined as a single sample representative of a specific location at a given point in time. The sample is collected all at once and at one particular point in the sample medium. The representativeness of such samples is defined by the nature of the materials being sampled. In general, as sources vary over time and distance, the representativeness of grab samples will decrease.

b. Composite Samples

Composites are combinations of more than one sample collected at various sampling locations and/or different points in time. Analysis of composite yields an average value and can, in certain instances, be used as an alternative to analyzing a number of individual grab samples and calculating an average value. It should be noted, however, that compositing can mask problems by diluting isolated concentrations of some hazardous compounds below detection limits.

For sampling situations involving hazardous wastes, grab sampling techniques are generally preferred because grab sampling minimizes the amount of time sampling personnel must be in contact with the wastes, reduces risks associated with compositing unknowns, and eliminates chemical changes that might occur due to compositing. Compositing is often used for environmental samples, including dioxin samples, to determine vertical or horizontal spatial variability of parameters. This procedure provides data that can be useful by providing an average concentration over a number of locations and can serve to keep analytical costs down; however, it is

important to understand that sensitivity is sacrificed when samples are composited due to dilution of individual grab samples. If contamination occurs in "hot" spots on site and "hot" grabs are composited with clean samples, a true vertical or horizontal distribution of contamination will appear to be a uniform distribution at a level lower than the true value of any one individual component(7). This is especially a concern when doing dioxin sampling with an action level of 1 ppb. Information on methods of compositing are presented in Section X.

2. In-Situ Measurement

In-situ measurements are made on samples in the environment. Measurements for pH, conductivity, and temperature must be taken in the field. Use of instrumentation such as an OVA, HNu and other gas analyzers is also considered in-situ measurement.

III. ANALYTICAL METHODS, PRESERVATION AND HOLDING TIMES

A. Methodology Available for use in the CERCLA Program

The CERCLA program has no legally mandated analytical methods. Methods from other programs or methods which are proven to be scientifically valid can be used for CERCLA work. The bulk of the analytical methods used presently are, however, from the Contract Laboratory Program (CLP).

The Contract Laboratory Program supports the Agency's Superfund effort by providing a range of chemical analytical services on a high volume, cost effective basis. Its purpose is to provide legally defensible analytical data. The program is managed by the National Program Office in Headquarters, and the Contractor-operated Sample Management Office receives the analytical requests from the Regions and coordinates and schedules sample analyses. Analytical Statements of Work exist for organics, inorganics and dioxin in water and soil/sediment matrices.

In addition to standardized analyses provided under the Routine Analytical Services (RAS) program, the CLP's Special Analytical Services (SAS) program provides clients with limited customized or specialized analyses, different from or beyond the scope of the RAS contract protocols. Services provided by SAS include: quick turn around analyses, verification analyses, analyses requiring lower detection limits than RAS methods provide, identification and quantification of non-Target Compound List (TCL) constituents, general waste characterizations, analysis of non-standard matrices, and other specific analyses. Consult the "User's Guide to the Contract Laboratory Program", December 1986 for further information.

As stated above, the CLP parameters of interest for RAS were titled under the 10/86 Statement of Work (SOW) the "Target Compound List". Under previous SOWs the TCL was titled the "Hazardous Substance List". Neither of these lists has been published in the Federal Register (FR) or Code of Federal Regulations (CFR) and thus are strictly lists defined by contract.

The "Priority Pollutant List" was established in the consent decree of the Natural Resources Defense Council (NRDC) vs. Train, in 1976. Although not published in the Federal Register under that title, it was published in a more generalized form in 44 FR 44502, July 30, 1979 as the "Toxic Pollutants" list under the Federal Water Pollution Control Act, and was amended in 46 FR 2266, January 8, 1981, and 46 FR 10724, February 4, 1981. Thus, the "Priority Pollutant" list as it now stands is comprised of 126 compounds or elements.

The Priority Pollutant and Target Compound Lists are presented in Appendix I to which shows the differences between the two. They are not interchangeable terms; neither list is a subset of the other, both contain compounds not found on the other. The only Priority Pollutants which are not on TCL are: asbestos, benzidine, 1,2-diphenylhydrazine, N-nitrosodimethylamine, endrin aldehyde, 2-chloroethyl vinyl

ether, acrolein, and acrylonitrile. Refer to the Appendix for those compounds which are on TCL but not considered Priority Pollutants.

A discussion of available references, methods, holding times and preservatives follows.

B. Analytical References

The following is a listing of selected analytical references containing methods available for use in the CERCLA program.

1. Aqueous/solid matrices

1. 40 CFR Part 136, as updated yearly.

2. 7/87 CLP Statement of Work for Inorganics, the 10/86 Statement of Work for Dioxin, the 1/87 revision of the Organics Statement of Work, and as updated.

The CLP standardized organic analytical methods are based on the CFR methods 608, 613, 624, and 625 modified for use in the analysis of both water and soil matrices. The standardized inorganic analytical methods are based on FR methods, EPA Methods for Chemical Analysis of Water and Wastes (MCAWW), and Test Methods for Evaluating Solid Waste (SW-846), Third Edition, or as revised, for the analysis of water and soil matrices. Appendix II provides a listing of the CLP organic and inorganic Targeted Compound/Element Lists as taken from the most recent SOWs and includes the RAS detection limits.

The dioxin Routine Analytical Services (RAS) contract method determines the presence of the 2,3,7,8-tetrachloro-dibenzo-p-dioxin isomer in water and soil/sediment matrices.

3. Standard Methods, 15th and 16th eds., or as revised.

4. Methods for Chemical Analysis of Water and Wastes(MCAWW), Revised 1983, EPA 600/4-79-020.

5. American Society for Testing and Materials.

6. Test Methods for Evaluating Solid Waste-SW-846, Third Edition, November 1986.

7. Procedures for Handling and Chemical Analysis of Sediment and Water Samples, May 1981, Technical Report CE/81-1, NTIS#AD-A103788.

2. Air

1. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, April 1984. EPA 600/4-84-041.

2. SOP for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax, June 1984. EMSL/RTP-SOP-EMD-020.

3. Non-Aqueous Phase Liquids

1. Test Methods for Evaluating Solid Waste, SW-846, Third Edition, November 1986.

2. Interim Methods for the Measurement of Organic Priority Pollutants in Sludges, Revised Draft June 1980.

3. Determination of Polychlorinated Biphenyls in Transformer Fluid and Waste Oils, Sept. 1982. EPA 600/4-81-045.

C. Preservation, Methodology and Holding Times

Complete and unequivocal preservation of samples is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations such as iron and lead may also adsorb onto surfaces (glass, plastic, quartz, etc.). Biological changes taking place in a sample may change the valence of an element or a radical. Soluble constituents may be converted to organically bound materials in cell structures, or cell lysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition.

Methods of preservation are relatively limited and are intended generally to (1) retard biological action, (2) retard hydrolysis of chemical compounds and complexes, (3) reduce volatility of constituents, and (4) reduce absorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration and freezing(8).

Appendix III contains a copy of Table 2 from 40 CFR Part 136, July 1, 1987 and a tabular presentation of the CLP holding time and preservation requirements. The Table is comprised of approved "conventional" parameter (meaning those analyses not considered part of the most commonly used "organic" and "inorganic" sets of analyses) methodology for an aqueous matrix. The holding times and preservation requirements of these conventional parameters are to be followed.

Appendix III also includes a table of CLP holding time and preservation requirements.

These requirements are to be followed not only for CLP methodology, but also for 40 CFR Part 136 and SW-846 methodology used for organic and inorganic analyses of aqueous or solid matrices. Holding times begin from the time of sample collection unless the Contract Laboratory Program has been engaged, in which case holding times begin at the Verified Time of Sample Receipt (VTSR) due to contractual requirements.

Recent studies including a project funded by EPA and the Department of Defense and performed by the Oak Ridge National Laboratory determined that aqueous volatile organic samples (VOAs) could be held for extended periods of time with preservation with hydrochloric acid (HCl) to pH less than 2 without significant loss of constituents. Thus, it is now a requirement that all samples taken for volatile organics analysis be preserved with hydrochloric acid to pH less than 2. This applies to samples analyzed by CLP or any other laboratory using any accepted methodology. Note, however, that this does not change the CLP holding time requirements.

The following procedure, adapted from the drinking water methods should be used for acidification of volatile organic samples with HCl to a pH less than 2.

Adjust the pH of the sample to <2 by carefully adding 1:1 HCl drop by drop to the required 2 (40 ml) VOA sample vials. The number of drops of 1:1 HCl required should be determined on a third portion of sample water of equal volume.

It should be noted that if acidification of the sample causes effervescence, the sample should be submitted without preservation except for cooling to 4 degrees C. This sample property should be appropriately noted when present. Also, the 1:1 HCl solution should be made up with demonstrated analyte-free deionized water.

When samples are to be iced to 4 degrees C., it is intended that the sample bottle be surrounded by bags of ice to ensure that the proper temperature is achieved and maintained during transport. It is not acceptable to put bags of ice around only the necks of the bottle or to use "Blue Ice" since the use of these devices does not ensure the attainment of the proper temperature.

When booking samples through CLP SAS, a copy of the SAS request must be attached to the parameter table in the Plan.

IV. DOCUMENTATION PROCEDURES

A. Chain-of-Custody

1. Definition and Reference

According to the USEPA Office of Enforcement and Compliance Monitoring National Enforcement Investigations Center (NEIC) Policies and Procedures, May 1978 revised May 1986, a sample is under custody if:

1. it is in your possession, or
2. it is in your view, after being in your possession, or
3. it was in your possession and you locked it up, or
4. it is in a designated secure area.

Possession must be traceable from the time the samples are collected.

2. Recordkeeping and Procedures

a. General

The method of sample identification utilized depends on the type of sample collected. In-situ field analyses are those conducted for specific field analyses or measurements where the data are recorded directly in bound field logbooks or recorded directly on the chain-of-custody record, with identifying information, while in the custody of the sampling team. Examples of such in-situ field measurements and analyses include pH, temperature, and conductivity. Also included in this category are those field measurements or analyses such as flow measurements, geophysical measurements, surveying measurements, etc. that are made with field instruments or analyzers, where no sample is actually collected.

Samples, other than those collected for in-situ field measurements or analyses, are identified by using a standard sample tag which is attached to the sample container. In some cases, particularly with biological samples, the sample tag may have to be included with or wrapped around the sample and waterproofed. The sample tags are sequentially numbered and are accountable documents after they are completed and attached to a sample or other physical evidence. The following information shall be included on the sample tag:

- a. site name
- b. field identification or sample station number
- c. date and time of sample collection
- d. designation of the sample as a grab or composite
- e. type of sample (matrix), and a brief description of the sampling location
- f. the signature of the sampler

- g. whether the sample is preserved or unpreserved
- h. the general types of analyses to be conducted

If a sample is split with another party, sample tags with identical information shall be attached to each of the sample containers.

The chain of custody record is used to record the custody of samples. It must accompany samples at all times. The following information must be supplied to complete the chain of custody record:

- a. project name
- b. signature of samplers
- c. sampling station number, date and time of collection, grab or composite sample designation, and a brief description of the type of sample and sampling location,
- d. tag numbers
- e. signatures of individuals involved in sample transfer, i.e., relinquishing and accepting samples. Individuals receiving the samples shall sign, date and note the time that they received the samples on the form.

Sample analysis request sheets serve as official communication to the laboratory of the particular analyses required for each sample and provide further evidence that the chain of custody is complete.

Shipping containers should be secured to ensure samples have not been disturbed during transport by using nylon strapping tape and EPA custody seals. The custody seals should be placed on the container so that it cannot be opened without breaking the seal.

b. CLP

The CLP documentation system provides the means not only to track and identify each sample, but to support the use of sample data in potential enforcement actions. Appendix IV provides copies of CLP documentation described below.

A sample Traffic Report (TR), which has a unique sample identification number, is assigned to each sample collected. An adhesive sample label printed with the TR sample number is affixed to each container, and, in order to protect the label from water and solvent attack, each label is covered with clear waterproof tape. The sample labels, which bear the TR identification number, permanently identify each sample collected and link each sample component throughout the analytical process. A custody seal is then placed over the lid of the container to ensure the samples are not opened prior to arrival at the laboratory.

Sample documentation for the RAS dioxin program utilizes the CLP Dioxin Shipment Record (DSR) and samples are individually numbered using pre-printed labels.

For SAS samples, a SAS Packing List (PL) is used along with adhesive sample labels.

Sample tags, containing the necessary information as required by NEIC, are attached to each sample container at the time of collection. Following sample analysis, sample tags are retained by the laboratory as physical evidence of sample receipt and analysis.

The Chain-of-Custody Record is employed as physical evidence of sample custody. One Record accompanies each cooler shipped from the field to the laboratory. In Region II, the Environmental Services Division Chain-of- Custody Record is used.

Shipping coolers are secured and custody seals placed across cooler openings. As long as custody forms are sealed inside the sample cooler and the custody seals remain intact, commercial carriers are not required to sign off on the custody form.

Whenever samples are split with a source or government agency, a separate Chain-of-Custody Record should be prepared for those samples, indicating with whom the samples are being split and sample tag serial numbers from splits (13).

Information regarding the information contained within, completion of, or obtaining these forms can be found in the CLP User's Guide available from the Region II RSCC.

B. Field Records

Field records should be kept by contractor personnel for each site. All aspects of sample collection and handling as well as visual observations should be documented in the logbooks. The following information should be recorded:

1. sample collection equipment;
2. field analytical equipment;
3. any other equipment used to make field measurements;
4. calculations;
5. results, and;
6. calibration data for equipment.

All entries should be dated and initialed and must be legible (9).

All maintenance and calibration records for equipment should be traceable through field records to the person using the instrument and to the specific piece of instrumentation itself. Equipment should be labeled with the calibration date and when it is due for the next calibration. The calibration of the pH and conductivity meters must be checked daily. Appendix V describes the required quality assurance procedures for field analysis and equipment.

Standard operating procedures (SOPs) for use of any field instrumentation must be provided in the form of a manual or individually in the Plan itself. The SOPs should address calibration, maintenance and use of the instrumentation and should reflect what is currently being done in the field.

V. GLASSWARE REQUIREMENTS

A. Bottle Suppliers

The CLP Sample Bottle Repository (SBR) provides cleaned, contaminant-free sample containers for use by groups performing hazardous waste sample collection activities under the Superfund program. Within this contract, sample containers are cleaned by defined procedures and representative containers undergo strict quality testing prior to shipment. This contributes to the integrity of sample data and supports its viability for use in enforcement case actions. The contractor uses approved techniques and instrumentation to procure, prepare, clean, label, store, package and ship sample containers and component materials. Appendix VI is the Statement of Work for Maintenance of a Quality-Controlled Prepared Sample Container Repository, dated 4/87, revised 7/87 and 8/87, in which the specific requirements for quality control are delineated.

It is the policy of this office at this time that bottles supplied by any party performing Superfund work who does not obtain those bottles from the SBR must be cleaned and quality controlled in the same manner as is defined in the SBR SOW. Therefore, if containers are not being procured from the Repository, the container construction, cleaning and quality controlling must be the same as that described in the SOW presented in Appendix VI. A statement that the bottle supplier will follow the SBR SOW must be included in the Plan.

B. Volume and Type of Container

The volume of sample obtained should be sufficient to perform all required analyses with an additional amount collected to provide for quality control needs, split samples, or repeat analyses.

The sample container requirements may be found in the SBR SOW, the CLP User's Guide, or in 40 CFR Part 136.

C. Quality Control and Storage

As stated above, the SBR Statement of Work must be followed when it comes to procuring, preparing, cleaning, labeling, storing and quality controlling containers. This involves analysis/testing of one or more representative containers from each lot or batch after they have been cleaned and designation of a storage QC container for future analysis if contamination should be suspected at a later time. All storage QC containers should be kept in a separate contaminant-free area. See Appendix V for detail. Contractors who store containers for any period of time must also comply with storage requirements.

VI. FIELD/LABORATORY DECONTAMINATION OF SAMPLING APPARATUS

A. General Considerations

All sampling apparatus must be properly decontaminated prior to its use in the field to prevent cross-contamination. The equipment should be pre-cleaned in a laboratory situation, or if the duration of the sampling event prohibits pre-cleaning in a lab, then equipment should be decontaminated once a day in an area outside of the contaminated zone. Enough equipment must be available to be dedicated to sampling points each day.

B. Decontamination Procedures

The required decontamination procedure for all sampling equipment is:

- a. wash and scrub with low phosphate detergent
- b. tap water rinse
- c. rinse with 10% HNO₃, ultrapure
- d. tap water rinse
- e. an acetone rinse or a methanol followed by hexane rinse (solvents must be pesticide grade or better)
- f. deionized demonstrated analyte free water rinse
- g. air dry, and
- h. wrap in aluminum foil, shiny side out, for transport

Tap water may be used from any municipal water treatment system. The use of an untreated potable water supply is not an acceptable substitute. If metals samples are not being collected, the 10% nitric acid (HNO₃) rinse may be omitted, and, conversely, if organics samples are not being taken, the solvent rinse may be omitted.

When it is necessary to use split spoon sampling devices which are composed of carbon steel instead of stainless steel, the nitric acid rinse may be lowered to a concentration of 1% instead of 10% so as to reduce the possibility of leaching metals from the spoon itself.

Bailer cord must be cleaned with soap and deionized water before use. Cord can be reused; it is not necessary to dedicate it to individual wells. If a ten foot or greater length leader (any cord of unacceptable material may not contact the water) is being used, only the leader need be cleaned. See Section IX for acceptable bailer cord materials.

VII. DECONTAMINATION OF PERIPHERAL EQUIPMENT

A. Well Evacuation Equipment

All tubing and evacuation equipment such as submersible pumps which are put into the borehole must be rinsed with soapy water and deionized water before use. All tubing must be dedicated to individual wells, i.e., tubing cannot be reused. If bailers are used to evacuate wells they must be decontaminated with the same procedure listed in Section VI.

B. Well Casings

Well casings must be steam cleaned prior to installation to ensure that all oils, greases, and waxes have been removed. Because of the softness of casings and screens made of fluorocarbon resins, these materials should be detergent washed, not steam cleaned prior to installation. They should be rested on clean polyethylene sheeting to keep the possibility of contamination to a minimum.

C. Field Instrumentation

Instrumentation should be cleaned as per manufacturer's instructions. Probes such as those used in pH and conductivity meters must be rinsed after each use with deionized water.

D. Drilling Equipment and Other Large Pieces of Equipment

All drilling equipment that comes in contact with the soil must be steam cleaned before use and between boreholes. This includes drill rods, bits and augers, dredges, or any other large piece of equipment. Sampling devices such as split spoons and shelby tubes must be decontaminated as per Section VI between boreholes.

VIII. MONITORING WELL DESIGN AND CONSTRUCTION

A. Well Drilling and Development Methods

1. General Discussion and Preferred Methods

There are various well drilling methods for application in geologic conditions ranging from hard rock to unconsolidated sediments. Particular drilling methods have become dominant in certain areas because they are most effective in penetrating the local formation.

The recommended types of ground water well drilling techniques are presented in Appendix VII. This list has been adopted from "The Practical Guide to Ground Water Sampling" (4). The most widely used method of drilling in the Region is the mud rotary technique, however, as presented in Appendix VII, "The Effects of Grouts, Sealants, and Drilling Fluids on the Quality of Ground-Water Samples," drilling fluids and additives may introduce contamination into the well which may persist even after development and can affect the chemical and biological quality of the samples. The use of mud rotary is not recommended, particularly for investigation of organic contaminant situations. Where possible, hollow stem auger, cable tool, or air rotary should be used to install wells. Where fluid rotary methods are employed, clean water should be used, and fluids carefully controlled to minimize impact on the ground water system. Vigorous development and purging should be employed to remove the filtrable solid residue from the wall cake and invasive filtrate (10).

Procedures designed to maximize well yield are included in the term "well development". Development has two broad objectives: 1) repair damage done to the formation by the drilling operation so that the natural hydraulic properties are restored, and 2) alter the basic physical characteristics of the aquifer near the borehole so that water will flow more freely to a well. These objectives are accomplished by applying some form of energy to the screen and formation (10). More importantly wells must be developed to provide water free of suspended solids for sampling. Improperly developed monitoring wells will produce samples containing suspended sediments that will bias the chemical analysis of the collected samples (4).

The first step in well development involves the movement of water at alternately high and low velocity into and out of the wellscreened gravel pack to break down the mud pack on the well bore and loosen fines in the materials being monitored. This step is followed by pumping to remove these materials from the well and the immediate area outside the well screen. This procedure should be continued until the water pumped from the well is visually free of suspended materials or sediments (4). Methods of development include overpumping, backwashing, mechanical surging, high velocity jetting, and air development procedures (10). Of these methods, high velocity jetting and air development procedures are unacceptable without modification.

High velocity jetting involves the use of a horizontal water or air stream forced through the well screen to agitate and rearrange the particles surrounding the screen. Although this is an effective method of development, its major disadvantage is the introduction of either air or water into the formation. Water jetting is acceptable only if the water used has a controlled source so cross contamination does not occur. If potable water is used for water jetting development, analysis of a water blank is required to ensure that the water is not introducing contaminants into the borehole. Air jetting is acceptable only if the air injected into the well has a controlled source. Due to frequent contamination of formations with petroleum hydrocarbons from the air jetting process, the use of an oil filter between the compressor pump and the borehole to control the purity of the air introduced downhole is a requirement.

As each monitoring well represents a unique circumstance involving formation characteristics, well parameters and pumping requirements, current USEPA policy does not require a minimum waiting period between development and sampling for most development procedures, but relies on the technical expertise of the drilling contractors to define the time required for the aquifer to return to stability. For the processes of high velocity jetting and air development, however, a ten to fourteen day waiting period has been defined as necessary by the Robert S. Kerr Environmental Research Laboratory and the New Jersey Department of Environmental Protection Geologic Survey, and is therefore required by Region II, for the stabilization of aquifer flow and to allow recovery of the aquifer from the stresses of development.

B. Well Filter Pack and Annular Sealant

The materials used to construct the filter pack should be chemically inert (e.g., clean quartz sand, silica, or glass beads), well rounded, and dimensionally stable. Natural gravel packs are acceptable, provided that a sieve analysis is performed to establish the appropriate well screen slot size and determine chemical inertness of the filter pack materials in anticipated environments.

The materials used to seal the annular space must prevent the migration of contaminants to the sampling zone from the surface or intermediate zones and prevent cross contamination between strata. The materials should be chemically compatible with the anticipated waste to ensure seal integrity during the life of the monitoring well and chemically inert so they do not affect the quality of the ground water samples. An example of an appropriate use of annular sealant material is using a minimum of two feet of certified sodium bentonite pellets immediately over the filter pack when in a saturated zone. The pellets are most appropriate in a saturated zone because they will penetrate the column of water to create an effective seal. Coarse grit sodium bentonite is likely to hydrate and bridge before reaching the filter pack. A cement and bentonite mixture, bentonite chips, or anti-shrink cement mixtures should be used as the annular sealant in the unsaturated zone above the certified-bentonite pellet seal and below the frost line. Again, the appropriate clay must be selected on the basis of the environment in which it is to be used. In most cases, sodium bentonite is appropriate(5).

The selected seal must not interfere with the water chemistry. Bentonite clay has appreciable ion exchange capacity which may interfere with the chemistry on collected samples when grout seal is in close proximity to the screen or well intake. Similarly, expanding cement which does not harden properly may affect the pH of water from monitoring wells when in close proximity to the well screen or intake.

To minimize these potential interferences, a 1-foot layer of silica sand should be placed above the selected gravel pack. Then, if possible, 1-2 feet of bentonite pellets should be placed in the hole to prohibit the downward migration of bentonite slurry or neat cement(4).

The untreated sodium bentonite seal should be placed around the casing either by using a tremie pipe or, if a hollow-stem auger is used, putting the bentonite between the casing and the inside of the auger stem. Both of these methods present a potential for bridging. In shallow monitoring wells, a tamping device should be used to reduce this potential. In deeper wells, it may be necessary to pour a small amount of formation water down the casing to wash the bentonite down the hole.

The cement-bentonite mixture should be prepared using clean water and placed in the borehole using a tremie pipe. The tremie method ensures good sealing of the borehole from the bottom.

The remaining annular space should be sealed with expanding cement to provide for security and an adequate surface seals. Locating the interface between the cement and bentonite-cement mixture below the frost line serves to protect the well from damage due to frost heaving. The cement should be placed in the borehole using the tremie method(5).

C. Well Casing Selection

1. General Discussion

Well construction materials must be durable enough to resist degradation thereby retaining their long-term stability and structural integrity and be relatively inert to minimize alteration of ground water and collected samples.

In general, the more inert (i.e., less reactive) the casing material, the more assured one is that the ground water sample withdrawn from the well is representative of the actual ground water. The major potential alterations of the sample resulting from interactions with the well casing/screen materials are: (1) adsorption/absorption reactions, both of organics and inorganics; and (2) desorption reactions, meaning leaching of chemical constituents from the well casing material into the ground water or desorption of newly adsorbed material. Casing materials can also be affected by chemical attack, i.e., corrosion/deterioration, and microbial colonization and attack(4).

These processes may lead to the observation of false trends in analyte concentrations, highly variable water chemistry and the identification of artifacts resultant from surface release or sorptive interactions. As with the errors which sampling mechanisms can introduce into the chemical data, casing materials' related errors can be quite significant and difficult to predict. Appropriate choice of materials for each application must be made on the basis of long-term durability, cleanability, and the minimization of the secondary effects of sorption or leaching. Structural integrity over time is, therefore, the primary criterion for making reliable material choices. The materials must neither be attacked nor degraded during the course of the monitoring program(4).

A variety of construction materials have been used for casing and well screens, including virgin fluorocarbon resins (Teflon), stainless steel (304 or 316), cast iron, galvanized steel, polyvinylchloride (PVC), polyethylene and polypropylene. Many of these materials, however, may affect the quality of ground water samples and may not have the long-term structural characteristics necessary for site specific needs. For example, steel casing deteriorates in corrosive environments; PVC deteriorates when in contact with ketones, esters and aromatic hydrocarbons; polyethylene deteriorates in contact with aromatic and halogenated hydrocarbons; and polypropylene deteriorates in contact with oxidizing acids, aliphatic hydrocarbons, and aromatic hydrocarbons. In addition, steel, PVC, polyethylene and polypropylene may adsorb and leach constituents that may affect the quality of ground water samples(5).

The selection of well casing and screen material should be made with due consideration to geochemistry, anticipated lifetime of the monitoring program, well depth, chemical parameters to be monitored and other site specific factors. Fluorocarbon resins or stainless steel should be specified for use in the saturated zone when volatile organics are to be determined during long term monitoring. Where high corrosion potential exists or is anticipated, fluorocarbon resins are preferable to stainless steel. National Sanitation Foundation (NSF) or ASTM-approved polyvinylchloride (PVC) well casing and screens may be appropriate if only trace metals or non-volatile organics are the contaminants anticipated(5).

Any well casing material may be used in the vadose zone, however, one combination that should be avoided is the use of dissimilar metals, such as stainless steel and galvanized steel, without an electrically isolating (dielectric) bushing. If such dissimilar metals are in direct contact in the soil, a potential difference is created and leads to accelerated corrosion of the galvanized steel (in this example). More generically, in the Galvanic series the less noble metal becomes the anode to the more noble metal and is corroded at an accelerated rate. In well construction, this acceleration in corrosion at the point of connection will lead to failure of the construction materials. Thus, a dielectric coupling should be used for connecting dissimilar metals above the saturated zone.

Plastic pipe sections must be flush threaded or have the ability to be connected by another mechanical method that does not introduce contaminants such as glue or solvents into the well(5).

2. Selection Criteria SOP

Appendix IX presents the "Standard Operating Procedure for Selecting Ground Water Well Construction Material at CERCLA Sites", dated December 15, 1986. The Appendix to the SOP provides a "Summary Table for Comparing Features of Various Ground Water Well Construction Materials", which was used to develop the criteria presented for selecting the appropriate casing material. The considerations involved in the process include duration of intended well use, use of data, desired detection limits, and known site conditions and contaminants. The numerical cut-off values presented except for the chloride and pH conditions on page 4 of the SOP were designed to be ball-park figures intended to guide decision making but they were not intended to be absolute limitations. They were, as all of the criteria were, devised after digestion of the current literature and using best professional judgement.

The Summary Form presented on page 5 of the SOP should be filled out by the EPA Project Manager and presented with the Plan for review for each site.

D. Evaluation of Existing Wells

If it is desired that a well already existing on-site be sampled in conjunction with newly installed wells, the Project Manager should consider the ramifications of utilizing data from those wells if, according to the "SOP for Selecting Ground Water Well Construction Material", the existing well casing is not compatible with the type of ground water contamination or the sensitivity of analysis needed.

IX. SAMPLE COLLECTION DEVICES, MATERIALS AND QUALITY CONTROL PRACTICES

A. References for Selection of Sampling Devices

Sampling at hazardous waste sites requires many different types of sampling devices. Selection of a device should be based on practicality, economics, representativeness, compatibility with analytical considerations, and safety. There are many documents which compile sampling methods and materials suitable to address most needs that arise during investigations. The following is a list of the most commonly used references compiling sampling equipment and methodology, however it is not meant to be an exhaustive listing of all the references available.

1. Characterization of Hazardous Waste Sites-A Methods Manual: Volume II. Available Sampling Methods, Second Edition. EPA-600/4-84-076. December 1984. Available from ORD Publications in Cincinnati at (513)569-7562.
2. Handbook for Sampling and Sample Preservation of Water and Wastewater. EPA-600/4-82-029. September 1982. Available from ORD Publications.
3. Samplers and Sampling Procedures for Hazardous Waste Streams. EPA-600/2-80-018. January 1980. Available from ORD Publications.
4. Practical Guide for Ground-Water Sampling. EPA 600/2-85/104. September 1984. Available from ORD Publications.
5. RCRA Ground-Water Monitoring Technical Enforcement Guidance Document, September, 1986. Office of Waste Programs Enforcement and Office of Solid Waste and Emergency Response. Available from RCRA Hotline at 800-424-9346.
6. A Guide to the Selection of Materials for Monitoring Well Construction and Ground Water Sampling. Barcelona, Gibb, Miller. Illinois State Water Survey, Champaign, Illinois. January 1984. NTIS publication #PB84-126929.
7. Test Methods for Evaluating Solid Waste, Physical and Chemical Methods. SW-846, Third Edition. Office of Solid Waste and Emergency Response. GPO publication #955-001-00000-1, at (202) 783-3238.
8. Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air, April 1984. EPA 600/4-84-041. Available from ORD Publications.
9. SOP for the GC/MS Determination of Volatile Organic Compounds Collected on Tenax. June 27, 1984. EMSL/RTP-SOP-EMD-020. Available through USEPA at Research Triangle Park, NC at (919)541-2777.
10. USEPA Dioxin Strategy. November 28, 1983. Office of Water Regulations and Standards and the Office of Solid Waste and Emergency Response in conjunction with

the Dioxin Strategy Task Force, Washington, D.C., 20460.

11. Sampling Guidance Manual for the National Dioxin Study, May 16, 1984. Office of Water Regulations and Standards, Washington, D.C.

12. Soil Sampling Quality Assurance User's Guide, Draft. May 1984. EMSL-LV. EPA 600/4-84-043. Available from ORD Publications.

13. Data Quality Objectives for Remedial Response Activities. Development Process. EPA/540/G-87/003. March 1987.

14. Data Quality Objectives for Remedial Response Activities. Example Scenario: RI/FS Activities at a Site With Contaminated Soils and Ground Water. EPA/540/G-87/004. March 1987.

B. Groundwater

1. Sampling Design

Samples from a monitoring well represent a small part of the horizontal and vertical extent of the aquifer. Unlike its surface counterpart, where a sample can be arbitrarily taken at any point in the system, moving a ground water sampling point implies the installation of additional monitoring wells. There is a need to be concerned not with the point data as an end in itself, but as a component of a network approach wherein information on the ground water system is developed as a basis for extrapolating information to areas where samples were not collected and/or for predicting the effects of natural and man-made stresses on the subsurface systems(2). Discussion of the areas of consideration for location of ground water sampling points can be found in references listed above.

2. Well Evacuation

In order to obtain a representative sample of ground water, the water that has stagnated and stratified in the well casing must be purged or evacuated. Prior to evacuating the well, however, the presence or absence of immiscible phases (i.e., "floaters" and "sinkers") must be determined. "Floaters" are those relatively insoluble organic liquids that are less dense than water and which spread across the potentiometric surface. "Sinkers" are those relatively insoluble organic liquids that are more dense than water and tend to migrate vertically through the sand and gravel aquifers to the underlying confining layer. The detection of these immiscible layers requires specialized equipment that must be used before the well is evacuated for conventional sampling. The Plan should specify the device to be used to detect light phases and dense phases, as well as the procedures to be used for detecting and sampling these contaminants. Procedures for identifying and sampling "floaters" and "sinkers" can be found in section 4.2.2 of the RCRA Ground-Water Monitoring Technical Enforcement Guidance Document dated September 1986.

Water that has remained in the well casing for extended periods of time (i.e., more than about two hours) has the opportunity to exchange gases with the atmosphere and to interact with the well casing material. The chemistry of the water stored in the well casing is dissimilar to that of the aquifer and, thus, should not be sampled(4). Evacuating the well allows for fresh formation ground water to enter the well. When indicator parameters such as pH, temperature and specific conductance are observed to vary less than 10% over the removal of two successive well volumes, the well is presumed to be adequately flushed for representative sampling. Evacuation of at least 3-5 well volumes is required for high yielding wells, however, in wells with very low recoveries this may not be practical. In this case the well may be evacuated to near dryness once and allowed to recover sufficiently for samples to be taken. A well must be sampled within three hours of evacuation. If a well is allowed to sit longer than three hours after evacuation, it should be re-evacuated since the water contained in the casing may no longer be representative of the aquifer conditions(4).

Any device used to evacuate the well must be cleaned as per Section VI to ensure that cross contamination between wells does not occur. When a pump is used to evacuate, the tubing which comes in contact with water should be made of polyethylene or Teflon, and must be dedicated to individual wells. The intake should be placed just below the water level and lowered as the water level lowers while pumping to ensure that all the water within the well bore is exchanged with fresh water.

A bailer may be used to evacuate the well and to sample it. Bailers must be constructed of Teflon or stainless steel with cords made of Teflon coated wire, stainless steel wire or polypropylene monofilament. Ten foot leaders may be used of these acceptable materials, with nylon cord above. ANY down-hole equipment having neoprene fittings, PVC, tygon tubing, silicon rubber bladders, neoprene impellers, or viton are not acceptable. A bailer which is used to evacuate the well may also be used to sample it without any additional cleaning.

Any water that is removed from the well during evacuation can no longer be considered a representative portion of the aquifer and should not be reintroduced into the well after sampling.

3. Sampling Organics and Inorganics

After evacuation of the required volume of water from the well, sampling may occur. The unstable nature of many chemical, physical and microbial constituents in ground water limit the sample collection options. Certain factors should be considered when collecting representative samples:

- * Temperatures are relatively constant in the subsurface, therefore the sample temperature may change significantly when brought to the surface. This change can alter chemical reaction rates, reverse cationic and anionic ion exchanges on solids, and change microbial growth rates.

* A change in pH can occur due to carbon dioxide adsorption and subsequent changes in alkalinity. Oxidation of some compounds may occur.

* Dissolved gases may be lost at the surface.

* The integrity of organic samples may be affected by problems associated with either adsorption or contamination from sampling materials and volatility(2).

The only acceptable sampling devices for pH sensitive and volatile parameters are:

1. Teflon or stainless steel bladder pumps having adjustable flow control;
2. Teflon or stainless steel bottom-filling bailers; and,
3. Teflon or stainless steel syringe bailers.

Appropriate operating precautions for these sampling devices include:

* Bladder pumps must be operated in a continuous manner so that they do not produce pulsating samples that are aerated in the return tube or upon discharge. Pumping rates should not exceed 100ml/min when samples are being taken for dissolved gases, volatile organic constituents, TOX and TOC;

* Check valves must be designed and inspected to ensure that fouling problems do not reduce delivery capabilities or result in aeration of the sample;

* Sampling equipment (especially bailers) must never be dropped into the well because this will cause degassing of the water upon impact;

* The bailer's contents must be transferred to a sample container in a way that will minimize agitation and aeration without transferring the sample to an intermediate container, or utilizing a mechanical device; the bailer should not be "acclimated" by discharging the first bailer- full of water onto the ground since this unnecessarily agitates the water column prior to the volatile sensitive parameters being taken;

* Clean sampling equipment must not be placed directly on the ground or other contaminated surface. When not in use, these devices should be placed on polyethylene sheeting or aluminum foil.

When sampling, heavy gauge aluminum foil or polyethylene sheeting should be placed on the ground around each well to prevent contamination of sampling equipment in the event that equipment is dropped or otherwise comes in contact with the ground.

When a number of rounds or phases of sampling will take place, the same type of sampling equipment should be used consistently throughout the entire project in order to increase the reproducibility in analytical results by eliminating the variability in sample collection technique.

Other sampling devices, including positive displacement pumps, gas lift devices, centrifugal pumps, and venturi pumps, may be used for collection of non-volatile or non-pH sensitive parameters (most parameters ARE pH- sensitive), provided that they are constructed of Teflon or stainless steel(5).

The preferred order of sample collection is as follows:

1. In-situ measurements: temperature, pH, specific conductance
2. Volatile organics (VOA)
3. Purgeable organic carbon (POC)
4. Purgeable organic halogens (POX)
5. Total organic halogens (TOX)
6. Total organic carbon (TOC)
7. Extractable organics
8. Total metals
9. Dissolved metals
10. Phenols
11. Cyanide
12. Sulfate and Chloride
13. Turbidity
14. Nitrate and Ammonia
15. Radionuclides

Detailed discussions of sample evacuation and collection procedures can be found in references #1,2,4,5 found in the Bibliography of this document.

For a discussion on the collection of dissolved and particulate sample fractions for metals analysis, see Section XII.

4. Sampling Microbiological

There are several different methods for obtaining a ground water sample. Each of these methods differ in their advantages and disadvantages for obtaining samples for microbiological analyses.

The majority of ground water samples obtained for microbiological analysis are obtained using preexisting wells which have existing in-place pumps. This limits the precautions the sampler must take to ensure a non- contaminated sample. Samples should be obtained from outlets as close as possible to the pump and should not be collected from leaky or faulty spigots or spigots that contain screens or aeration devices. The pump should be flushed for 5 to 10 minutes before the sample is collected. A steady flowing water stream at moderate pressure is desirable in order to prevent splashing and dislodging particles in the faucet or water line.

To collect the sample, remove the cap or stopper carefully from the sample bottle. Do

not lay the bottle closure down or touch the inside of the closure. Avoid touching the inside of the bottle with your hands or the spigot. The sample bottle should not be rinsed out and it is not necessary to flame the spigot. The bottle should be filled directly to within 2.5 cm (1 inch) from the top. The bottle closure and closure covering should be replaced carefully and the bottle should be placed in a cooler (4 to 10 degrees C) unless the sample is going to be processed immediately in the field.

If a well does not have an existing in-place pump, samples can be obtained by either using a portable surface or submersible pump or by using a bailer. Each method presents special problems in obtaining an uncontaminated sample.

The main problem in using a sterilized bailer is obtaining a representative sample of the aquifer water without pumping or bailing the well beforehand to exchange the water in the bore for fresh formation water. This is difficult since such pre-sampling activities must be carried out in such a way as to not contaminate the well. Care must also be taken with bailers to not contaminate the sample with any scum on the surface of the water in the well. This is usually done by using a weighted, sterilized sample bottle suspended by a cord of acceptable material and lowering the bottle rapidly to the bottom of the well.

The use of portable pumps provides a way of pumping out a well before sampling and thus providing a more representative sample, but presents a potential source of contamination if the pumping apparatus cannot be sterilized beforehand. The method of sterilization will depend on what other samples are taken from the well since the use of many disinfectants may not be feasible if the well is also sampled for chemical analyses. If disinfection is not ruled out by other considerations, a method of sterilizing a submersible pump system is to submerge the pump, and any portion of the pump tubing which will be in contact with the well water, into a disinfectant solution and circulating the disinfectant through the pump and tubing for a recommended period of time.

The most widely used method of disinfection is chlorination due to its simplicity. Chlorine solutions may be easily prepared by dissolving either calcium or sodium hypochlorite in water. Calcium hypochlorite, $\text{Ca}(\text{OCl})_2$, is available in a granular or tablet form usually containing about 70% of available chlorine by weight and should be stored under dry and cool conditions. Sodium hypochlorite, NaOCl , is available only in liquid form and can be bought in strengths up to 20% available chlorine. Its most available form is household laundry bleach, which has a strength of about 5% available chlorine, but should not be considered to be full strength if it is more than 60 days old. The original percentage of available chlorine will be on the label. Fresh chlorine solutions should frequently be prepared because the strength will diminish with time. After disinfection the pump should be carefully placed in the well and then pumped to waste until the chlorine is thoroughly rinsed from the pump system.

If the pump cannot be disinfected, then the pump and tubing should be carefully handled to avoid gross surface contamination and the well should be pumped for 3 to 10 bore volumes before taking a sample. It may be desirable after pumping to pull the

pump and take the sample with a sterile bailer.

In those cases where the water level in the well is less than 20 to 30 feet below the surface, a surface vacuum pumping system can be used for flushing out the well and withdrawing a sample.

Springs are unlikely to yield representative samples of an aquifer due to surface contamination close to a spring's discharge unless the spring has an extremely fast flow and the outlet is protected from surface contamination.

Lastly, interpretation of analytic results may be difficult in some cases since surface contamination of wells due to poor drilling and completion practices is common. In cases where drinking water supplies are involved, a thorough inspection of the well is required to eliminate surface contamination down the well bore as a source of contaminants. Disinfection of the well by approved methods and resampling may be advisable, if disinfection will not affect the well for other sampling purposes(2).

C. Surface Water

1. Sampling Design

There are at present no quality assurance requirements for site location for sampling surface waters. References #1 and #2 in Section IX can be consulted for design guidance.

2. Sampling Devices

Appendix X provides a tabular comparison of surface water sample collection devices.

Samples from shallow depths can be readily collected by merely submerging the sample container. However, preservatives cannot be present in the container when it is lowered into the water. The method is advantageous when the sample might be significantly altered during transfer from a collection vessel into another container. This is the case with samples collected for oil and grease analysis since considerable material may adhere to the sample transfer container and as a result produce inaccurately low analytical results. Similarly the transfer of a liquid into a small sample container for volatile organic analysis, if not done carefully, could result in significant aeration and resultant loss of volatile species. Though simple, representative, and generally free from substantial material disturbances, it has significant shortcomings when applied to a hazardous waste, since the external surface of each container would then need to be decontaminated.

In general the use of a sampling device constructed of a nonreactive material such as glass, stainless steel, or Teflon, is the most prudent method. The device should have a capacity of at least 500 ml, if possible, to minimize the number of times the liquid must be disturbed, thus reducing agitation of any sediment layers.

A 1-liter stainless steel beaker with pour spout and handle or large stainless steel ice scoops and ladles available from commercial kitchen and laboratory supply houses can be used.

It is often necessary to collect liquid samples at some distance from shore or the edge of the containment. In this instance an adaptation which extends the reach of the sampler is advantageous. Such a device is the pond sampler. It incorporates a telescoping heavy-duty aluminum pole with an adjustable beaker clamp attached to the end. The beaker previously described, a disposable glass container, or the actual sample container itself, can be fitted into the clamp.

It may on occasion be necessary to sample large bodies of water where a near surface sample will not sufficiently characterize the body as a whole. In this instance a peristaltic pump may be used in which the sample is drawn in through heavy walled Teflon tubing and pumped directly into the sample container. This method, however, is not suitable for pH sensitive or volatile samples in which stripping would occur.

Situations may still arise where a sample must be collected from depths beyond the capabilities of a peristaltic pump. In this instance an at-depth sampler may be required, such as a Kemerer, ASTM Bomb (Bacon Bomb) or Van Dorn sampler. These devices work well; however, care must be utilized in selecting devices that are made of materials that will not contaminate the sample. Van Dorn samplers are not generally recommended for organics as they rely on an elastic closing mechanism that can effect samples. They are readily available in a totally nonmetallic design which is very useful for sample collection for trace metal analysis.

Kemerer samplers are available on special order or adaptable for sample collection for organic analysis by substituting Teflon for the rubber or plastic stoppers. If the device is further ordered with stainless steel metallic parts in addition to Teflon stoppers it becomes a very versatile sampler(1).

Consult "Characterization of Hazardous Waste Sites-A Methods Manual:Volume II. Available Sampling Methods, Second Edition for specific collection techniques using these devices. See Section IX.B.4 for collection of microbial samples.

D. Sediment

Sediment is defined as the deposited material underlying a body of water.

1. Sampling Design

Streams, lakes, and impoundments will likely demonstrate significant variations in sediment composition with respect to distance from inflows, discharges or other disturbances. It is important, therefore, to document exact sampling location by means of triangulation with stable reference points on the banks of the stream or lake.

At the present time, however, there are no quality control requirements for choosing site location when sampling sediments. Reference #2 in Section IX can be consulted and sediment transport and deposition modeling along with statistical considerations can be found in "Sediment Sampling Quality Assurance User's Guide," EPA 600/4-85-048, July 1985, NTIS #PB85-233542.

2. Sampling Devices

Appendix XI provides a tabular comparison of some bottom grab and coring devices.

Samples can be taken with stainless steel spoons or trowels or the sample container itself if there is little or no water on top of the sediment. If the water above the sediment is a few feet deep a stainless steel corer or corer having a removable glass or Teflon liner may be used. This will help ensure the integrity of the surface layer of sediment and will minimize the loss of fine grained material. In deeper water the bottom grab samplers presented in Appendix XI may be used(1).

If at any time surface water samples are being taken in conjunction with sediment samples, the water samples should be taken first. The sampler should approach the location from the downstream direction with the container pointed upstream to ensure collection of an undisturbed sample.

Sediment samples collected for all analyses except VOA and TOX should be thoroughly mixed before being placed in appropriate sample containers. Rocks, twigs, and other debris should be removed from the sample prior to homogenization. In this way stratification of constituents will not affect analytical results. VOA and TOX samples should be taken as individual grab samples, never homogenized. See Section X for the procedure used for homogenization of samples.

E. Soil

1. Sampling Design

Statistical techniques for obtaining accurate and precise samples are relatively simple and easy to implement. In the sampling of a soil matrix, sampling accuracy is usually achieved by some form of random sampling. In random sampling, every unit in the population has a theoretically equal chance of being sampled and measured. Consequently, statistics generated by the sample are unbiased (accurate) estimators of true population parameters.

In other words, the sample is representative of the population.

One of the most common methods of selecting a random sample is to divide the population by an imaginary grid, assign a series of consecutive numbers to the units of the grid, and select the numbers to be sampled through the use of a random-numbers

table (such a table can be found in any text on basic statistics). It is important to emphasize that a haphazardly selected sample is not a suitable substitute for a randomly selected sample. That is because there is no assurance that a person performing undisciplined sampling will not consciously or subconsciously favor the selection of certain units of the population, thus causing the sample to be unrepresentative of the population. A detailed discussion of random sampling can be found in SW-846, Third Edition, November 1986, Volume 2, Chapter 9.

In a biased sampling approach, site history, available information and professional judgement are used to determine the sampling locations in which contamination is expected to be found. In this case the most information is gotten from the least number of samples thereby allowing a cost savings. However, this approach to sampling design is more appropriate to a site investigation than a remedial investigation (RI) because it is not a comprehensive view of site conditions(7). Use of a biased approach during an RI must be justified.

2. Sampling Devices

When sampling soil, stainless steel, Teflon or glass utensils should be used. The only exception is split spoons which are most commonly available in carbon steel. These are acceptable for use provided they are not excessively rusty.

A stainless steel spatula should be used to remove sample from the opened spoons, not the sampler's fingers, as the gloves may introduce organic interferences into the sample. As per water sampling, volatile organics and TOX samples should be taken immediately upon opening the spoon. Any rocks, twigs, leaves or other debris should be removed from the sample before homogenization. All samples except those for volatile organics and TOX must be homogenized before being put into sample containers. Section X provides a discussion on homogenization. Samples for VOA and TOX should never be homogenized as they both contain volatile parameters.

F. Potable Water

When sampling potable water the same quality control requirements apply as for sampling groundwater, where applicable.

The "Manual for the Certification of Laboratories Analyzing Drinking Water," EPA 570/9-82-002, October 1982, states that the sample needs to be representative of the potable water system, and that the tap water must be sampled after maintaining a steady flow of 2 or 3 minutes to clear the service line. This flushing period is a minimum requirement and more time can be allowed if a large holding tank is in place and it is desirable to purge an entire tank volume. A tap must be free of any aerator, strainer, hose attachment, or water purification devices. When sampling chlorinated waters for organics, cyanide and bacterial analyses, sodium thiosulfate should be added to the sample bottles.

F. Dust/Wipe

The following Standard Operating Procedure has been developed by Region II for use in taking wipe samples.

1. Materials needed:

- a. cotton swabs, solvent rinsed and completely air dried;
(use of synthetic materials requires checking for compatibility with solvents)
- b. acetone, pesticide grade;
- c. hexane, pesticide grade;
- d. deionized water;
- e. stainless steel clamps or plastic clamps (only for taking metals samples);
- f. appropriate sample bottles.

2. A square area, of a size sufficient to give the required amount of sample, for each fraction as provided in the analytical methodology to be used, should be marked off. This may require taking cotton swabs and a balance into the field, wiping a certain area and weighing the swab before and after to determine how much area should be wiped to give the required weight of sample.

3. Swabs for semi-volatile, pesticide and PCB samples should be moistened in a 1:4 acetone/hexane mixture. Swabs for volatile organic samples should be moistened with hexane alone, and those for metals with deionized water. While holding the swab in a clean, metal clamp, moisten the cotton swab with the appropriate solution.

4. While still holding the cotton swab in the clamp, wipe the sampling area back and forth repeatedly, applying moderate pressure. Wipe the entire area so that all the sample material is picked up.

5. Place the used swab in the appropriate sample container and seal.

6. Clean the clamps between each sample with both solvent and 10% HCL.

7. As a blank, moisten a clean swab with the solvent or water (for each collection medium), place it in a separate jar, and submit it with the other samples.

8. When samples are submitted for analysis, the laboratory should be told to rinse the sample jars with solvent or 10% HCL, depending on the analysis to be performed, when transferring sample to the extraction glassware.

The samples should be analyzed with the appropriate methodology for a soil/sediment matrix, and a sufficient quantity of material must be collected as called for in the analytical methodology, in order for method detection limits to be achieved.

H. Dioxin

For guidance on conducting dioxin sampling events refer to "Sampling Guidance Manual for the National Dioxin Study", May 16, 1984. The sampling material requirements are the same as those present in this document for the matrix being sampled, with the following additions.

The equipment decontamination procedure is the same as that presented in Section VI and samplers have the option of using methanol/hexane, acetone, or 1,1,1-trichloroethane as solvents.

Homogenization must be performed on dioxin samples of a solid matrix. Homogenization may be performed in a laboratory or in the field and it should be done using either the coning and quartering method (see Section X) or by using stainless steel blenders. Homogenization of wet sediment samples is more easily accomplished using the coning and quartering method. Specific quality control samples for dioxin sampling events are presented in Section XI.

I. Drums

For sampling of non-homogenous or multi-phased materials in drums, tanks, waste piles, lagoons, etc., refer to SW-846, Third Edition, Volume 2 for guidance. The Plan must include a detailed approach in terms of basic strategy and sampling equipment if such containers are to be sampled.

X. METHODS OF SAMPLE PREPARATION

A. Homogenization

The homogenization of a sample is the process of mixing individual grab samples in order to minimize any bias of sample representativeness introduced by the natural stratification of constituents within the sample.

To homogenize a sample of a soil/sediment matrix, first rocks, twigs, leaves and other debris should be removed if they are not considered part of the sample. The soil/sediment should be removed from the sampling device and placed in a stainless steel pan, then thoroughly mixed using a stainless steel spoon. The sediment in the pan should be scraped from the sides, corners and bottom of the pan, rolled to the middle of the pan, and initially mixed. The sample should then be quartered and moved to the four corners of the pan. Each quarter of the sample should be mixed individually, and then rolled to the center of the container and the entire sample mixed again.

Homogenization of an aqueous sample is only necessary if stratification of constituents is of concern, for example when sampling a lagoon or containerized liquid. Then homogenization would be performed by mixing in a stainless steel bowl.

B. Compositing

Compositing of samples is performed when samplers desire to obtain an average concentration of contaminants over a certain number of sampling points. Anytime compositing is performed, the concentration of contaminant in individual grab samples is diluted proportionately to the number of samples taken. Not only is the contaminant diluted, the detection limits for each individual sample are raised proportionally to the number of samples added to the composite. For instance, if a sampler wishes to composite two discrete samples into one, and the method detection limit for a target compound is 330 ppb, the detection limit for the target compound does not change for the composite, however, the detection limit for the compound in the individual samples which make up the composite is two times the normal detection limit or $2 \times 330 = 660$ ppb. This is important to keep in mind because it is possible that if a contaminant were present in only one of the two composited samples, and if it were at a level between 330 and 660 ppb, that contaminant would not be quantified or possibly even identified due to the effective dilution of the contaminant concentration. This concept should be taken into account when determining the data quality objectives of a composite sampling event, to ensure that useful data is collected. It is advisable that if a positive identification is made in the course of analyzing a composite sample, that the discrete samples then be analyzed individually to determine the true distribution of contaminant throughout each component of the composite.

Compositing of a solid matrix is accomplished by mixing equal volumes of grab samples in stainless steel pans with stainless steel spoons. Compositing is never performed on samples for volatile organics analysis (or any analysis involving a volatile portion such

as TOX), and, for a solid matrix, should never be done by placing equal portions of grab samples directly into sample jars, as the occurrence of error introduced by the sampler is highly probable.

C. Splitting

Splitting of samples is performed when two or more parties wish to have a portion of the same sample. They are most often collected in enforcement actions to ensure that sample results generated by Potentially Responsible Parties (PRPs) are accurate. Splitting of samples, however, is not as useful as providing blind performance evaluations samples to a laboratory since analytical performance and accuracy differs from laboratory to laboratory, and therefore one laboratory cannot be considered a "referee" who's performance can be considered the standard against which another's can be measured. Performance evaluation samples provide information on a laboratory's performance based upon analysis of that sample which is of a known and defined concentration.

Soil/sediment samples taken for volatile analysis cannot be split. In this case samples must be taken as co-located grabs. Then a large quantity of material can be collected, homogenized, split and used to fill the remaining containers. Note that enough sample must be collected at one time in order to fill all the necessary sample containers. It may be necessary to co-locate or depth integrate collection so enough sample volume is available. A description of this process should be provided in the Plan.

When splitting aqueous samples, homogenization of the sample is only necessary if heterogeneity is suspected, for example when sampling a small lagoon or containerized liquid; however VOA and TOX samples are never homogenized. It is not generally necessary to homogenize ground water or surface water samples when splitting, and it is likewise generally unnecessary to divide a bailer's contents among several bottles.

XI. FIELD QUALITY CONTROL SAMPLES

A. All Analyses Except Dioxin

1. Duplicates

Environmental duplicate samples are collected to demonstrate the reproducibility of sampling technique. Environmental duplicate samples must be taken at a frequency of at least 5% (1 in 20). This is a separate duplicate from the duplicates a laboratory must run, and cannot be replaced by a laboratory generated duplicate. This applies to every matrix sampled. Environmental duplicates are representative of field sampling precision, whereas laboratory duplicates are a measure of analytical precision. Both pieces of information are essential to determining the quality of data generated for a project.

2. Blanks

Blank water generated for use in the Region II CERCLA program must be "demonstrated analyte-free". By this term we mean water of a known quality which is defined by the Quality Assurance office.

The criteria for analyte-free water is as follows. The assigned values for the Contract Required Detection Limits (CRDLs) can be found in the most recent CLP SOWs.

purgeable organics	<10 ppb
semi-volatile organics	<CRDL
pesticides	<CRDL
PCBs	<CRDL
Inorganics	<CRDL

However, specifically for the common laboratory contaminants listed below, the allowable limits are three times the respective CRDLs.

methylene chloride
acetone
toluene
2-butanone
phthalates

The contractors shall maintain quality control records for each source of water which is used. These records shall demonstrate over time the presence/absence and level of contaminants found in each water supply. EPA personnel will randomly audit throughout the year the records kept by the generators/contractors.

If potable water is used during the drilling process and is introduced into the borehole, a sample of the water should be collected and analyzed to ensure contaminants are not being introduced via the water supply.

a. Trip Blank

When sampling for volatile organics, a trip blank, consisting of demonstrated analyte free water sealed in 40 ml Teflon lined septum vials, must be taken into the field where sampling is going on. It should be taken at a frequency of one per day per matrix sampled when volatile organics in an aqueous matrix are being collected. Note that it is not necessary to take an aqueous trip blank when a non-aqueous medium is being sampled. Trip blanks are used to determine if any on-site atmospheric contaminants are seeping into the sample vials, or if any cross contamination of samples is occurring during shipment or storage of sample containers. Trip blanks are only analyzed for volatile organics.

b. Field Rinse Blanks

Rinse blanks consist of pouring demonstrated analyte free water over decontaminated sampling equipment as a check that the decontamination procedure has been adequately carried out and that there is no cross- contamination of samples occurring due to the equipment itself. Analysis of rinse blanks is performed for all analytes of interest. One blank should be taken for each type of equipment used each time a decontamination event is carried out, whether that be daily or weekly. It is required also that rinse blanks be performed on bowls and pans used to homogenize samples.

The blank should be done at the beginning of the day prior to the sampling event and that blank must accompany those samples which were taken that day. This is a necessary procedure so that the blank will be associated with the proper samples for the purpose of data validation.

3. Matrix Spike/Matrix Spike Duplicate Analyses

When performing CLP organic extractable analysis, the laboratory must have triple sample volume for each Sample Delivery Group (SDG), which does not include field or trip blanks. Blanks do not require separate matrix spike or duplicate analyses regardless of their matrix.

As stated in the SOW, the limits on an SDG are:

- *each Case of field samples, or
- *each 20 field samples within a Case, or
- *each fourteen calendar day period during which field samples in a Case are received (said period beginning with the receipt of the first sample in the SGD), whichever comes first.

B. Dioxin

When dioxin sampling is performed a batch of quality control samples must accompany

environmental samples whether the samples are sent through the Contract Laboratory Program or to a privately contracted laboratory.

The quality control sample requirements for every 20 dioxin samples taken are:

- a. two performance evaluation samples from EMSL-LV containing 2,3,7,8-TCDD;
- b. one environmental duplicate;
- c. one blind blank (blind blank to the laboratory)-this sample does not go through the homogenization on-site;
- d. one known blank (the lab will spike with 1 ppb TCDD)-this does not go through homogenization on-site;
- e. one blender blank-this is blank soil homogenized in the field to check for cross-contamination during the blending process, and is only necessary if blenders are used to homogenize the samples.

These samples will be ordered by the Regional Quality Assurance Officer from EMSL-LV at the request of the EPA Project Manager only.

XII. FILTERED AND NON-FILTERED FRACTIONS OF GROUND WATER SAMPLES

A. General Discussion

In certain situations it may be desirable to consider filtration of ground water samples in order to obtain information about the "dissolved" species of the contaminant in solution as opposed to that portion of contaminant which may adhere to silt or clay particles. The real concern in this issue is whether or not the contaminant is a component of the ground water, which implies that if the contaminant is truly a component of the ground water, then it must flow with the ground water. If the contaminant flows with the ground water on or under a site then there is the potential for the contaminant to be moved to and to impact areas outside of the site.

There has been a general assumption that water and soil are the only distinct constituents of an aquifer system; there is also a false assumption that water and completely solvated solutes are the only constituents of the system that are mobile. In fact, components of the solid phase in the colloidal size range may be mobile in subsurface environments(11). The colloidal state refers to a two phase system in which one phase in a very finely divided state is dispersed through a second. In ground water, colloidal particles are generally smaller than one micrometer (1 μm) in diameter. Since the clay fraction is defined by the USDA as being 2 μm and smaller, not all clay is strictly colloidal, but even the larger clay particles have colloid-like properties (12). There is ample evidence, as can be seen in the literature, that colloid particles can move in aquifers (11).

There are two distinct types of colloidal matter, inorganic and organic, which exist in intimate intermixture. The inorganic is present almost exclusively as clay minerals of various kinds; the organic is represented by humus (12). These colloidal particles can sorb organic and inorganic contaminants and stabilize them in the mobile phase of the aquifer. Association of contaminants with mobile colloidal particles may enhance the transport of highly adsorbed pollutants, or deposition of colloidal particles in porous media may decrease permeability and reduce contaminant transport (11).

The separation of "dissolved" and "particulate" sample fractions is most commonly accomplished by filtration through a 0.45 μm membrane filter. The convention of using a 0.45 μm pore size filter was borrowed from the microbiological science where it was used as the separation point for filtering bacteria out of aqueous media. This convention was borrowed by other organizations for use in the analysis of aqueous metals samples, and now is specified as the pore size through which will pass those constituents that are "dissolved". Those constituents which are retained on the 0.45 μm filter are labeled "suspended", and "total" metals is the sum of the "dissolved" and "suspended" fractions.

It would be more accurate, however, to term the fractions "filterable" and "non-filterable"

instead of "dissolved" and "total" or "particulate" given the operational nature of the separation. The 0.45 um distinction is not useful when one is concerned with true soil/water chemistry but has its sole value at present in the fact that it is convention and is used as such in ground water characterization throughout the country.

The policy in Region II on filtering ground water has been that only samples for metals analyses may be filtered, and when taking metals samples, "total" metals should be taken with the option to take a "dissolved" sample if so desired. The filtration of aqueous samples for organics analyses has not been allowed in the Region since, 1) volatile contaminants would be released during filtration, and 2) the membrane filters used for the filtration of metals samples will adsorb the organics, thereby giving falsely negative results.

The rationale behind the policy is this: rather than rely totally on "dissolved" metals data, which will generally give results that are lower than the true amount of contaminant which moves with ground water, the Region has chosen to be more conservative in its use of metals data by preferring to consider "total" metals data, thereby erring on the side of finding more metals in a sample than actually may be mobile in the ground water phase. Obviously, in some cases when samples are silty, the "total" metals values will be high due to the addition of metals which were bound to particles of greater size than the colloidal range. Unfortunately the use of either "total" or "dissolved" metals data alone is inappropriate when one wishes to consider the true portion and constituents which move with ground water.

The Regional policy as presented here will continue to be enforced in spite of the limitations until such time as a technically well-founded alternative is developed. If exceptions or modifications to this policy are desired based on site specific needs, the Project Manager should consult the Quality Assurance Officer assigned to the project.

B. Procedures for Filtration of Aqueous Metals Samples

1. Decontamination of Apparatus

When filtering aqueous metals samples, a device made of polyethylene or borosilicate glass should be used. The apparatus should be pre-cleaned by rinsing with a 10% HNO₃ solution, followed by a demonstrated analyte-free deionized water rinse, and should be cleaned in the same manner between samples.

2. Filtration Procedures and Preservation

The filter used should be a cellulose-based membrane filter of 0.45 um nominal pore size. Samples must be filtered immediately after their collection to minimize changes in the concentration of the substances of interest. Samples are only passed through the filtration apparatus once, they are not to be passed through repeatedly until they are free of turbidity. Samples are then preserved immediately with undiluted ultrapure HNO₃ and the pH checked to ensure proper pH has been attained. No samples for

cyanide, conventional parameters, or organics may be filtered in this manner.

XIII. LABORATORY QUALIFICATIONS

A. Use of CLP vs. non-CLP Laboratories

Most analytical work performed for Federal fund-lead CERCLA sites within the Region utilizes the USEPA Contract Laboratory Program. However, it is not mandatory that all analyses supporting the CERCLA program be performed by a Contract Laboratory, whether the project is a fund-lead or enforcement-lead site. Laboratories which do not participate in CLP may be used at any time, provided they adhere to Region II QA/QC requirements which are described here.

If a non-CLP laboratory is used, that laboratory must supply to the Regional Quality Assurance Officer (QAO), a copy of their in-house QA/QC manual which is applicable to the analyses to be performed. The QA/QC manual should cover the following topics:

- resumes
- personnel training and experience
- organizational structure
- equipment available
- reference materials/reagents
- control charts
- standard operating procedures
- data reduction/reporting
- chain-of-custody
- glassware preparation

Also, that laboratory must perform acceptably on performance evaluation samples supplied by EPA for those parameters of interest to the project. A formal request for performance evaluation samples should be sent from the EPA Project Manager for the site to the EPA QAO.

A non-CLP laboratory must also undergo a technical systems audit performed by the primary engineering contractor in order to evaluate the laboratory's capability to perform the work. A copy of the resultant report should be sent to the EPA Project Manager and subsequently to the EPA QAO. The format of the audit checklist can be taken from the CLP Invitations for Bid (IFBs). Only after this information has been provided and is found to be acceptable can sampling and analysis begin. The CLP IFBs are available from the Sample Management Office at (703)557-2490.

XIV. USE OF MOBILE LABORATORIES

A. Qualifications and Methods

There has been a growing demand throughout the Region for use of field analytical laboratories in order to screen samples and generate real-time results which can be used to make decisions in the field. These laboratories commonly use "quick and dirty" techniques since strict precision and accuracy requirements are not necessary for the intended use of the data, and since, in most cases, critical sampling locations, where quality data is important, are split for analysis by a CLP laboratory also.

However, there are certain quality control requirements for use of mobile laboratories. First, the data quality objectives (DQOs) for the screening event must be determined and documented. The DQOs should take into account the fact that "quick and dirty" screening methods do not generally give high quality precision and accuracy and some confirmational analysis with a CLP or other commercial laboratory is necessary. Confirmational analysis should be run on those sample locations which are most critical to the project, for instance, the boundary area of a removal action. Secondly, if a methodology is developed for use, that method must be documented and validated. Proof of the validation must be provided to the EPA QAO and the QAO must consider it satisfactory before the method can be used. The method validation should address the following points, where applicable.

- a. analytical objectives
- b. method detection limits
- c. analytical procedure
- d. precision and accuracy
- e. calibration
- f. quantitation
- g. data reduction/validation
- h. holding times

Finally, as for any data generated within the Region and which is not validated by Regional personnel, the contractor's quality assurance officer must sign a summary statement which describes the quality control measures followed, the quality control sample results, what data was rejected due to exceedances, etc. This statement should be supplied to the EPA Project Manager.

XV. VALIDATION OF DATA

A. Contract Laboratory Program

All data generated for use by Region II which is produced by CLP is validated by the Region with in-house protocol. These data validation standard operating procedures for organics, inorganics and dioxin data are updated yearly for the current set of CLP contracts. Application of a protocol which standardizes data useability criteria ensures that all data which is used in the Region is of comparable and acceptable quality and utility. The Region II data validation standard operating procedures are presented in Appendix XII.

B. Non-CLP

Data which is generated outside of CLP for use in Region II must be validated in the same manner as all other data is validated so that a standard useability criteria is applied to all data used in the Region. All data should be of comparable quality.

The Plan must identify the laboratory to be used if the laboratory is not to be engaged through the CLP program or if the laboratory does not participate in CLP. All data produced by laboratories which do not participate in CLP (or if they do participate but are not directly contracted by EPA) must be validated by the laboratory or primary engineering contractor according to Region II validation SOPs. Note that these SOPs apply only to the CLP methodologies and that if different analytical method references are used (such as SW-846 or Methods for Chemical Analysis of Water and Wastes) the validation criteria will have to be modified according to the quality control criteria called for in that methodology used. The QAO of the laboratory must be identified and must provide a signed document to the EPA Project Manager stating that he/she has validated the data in accordance with the Region II protocol, or, if quality control criteria had to be established according to the dictates of the method, the laboratory is responsible for establishing precision and accuracy protocol and for validating the data and meeting criteria based on that protocol. A document delineating the criteria used must be provided along with quality assurance summary sheets, and, if applicable, the Region II SOP validation checklist. The summary sheets should be taken from the CLP SOW, the third edition of SW-846 or be based thereon. Data analysis sheets must be provided for each environmental sample listing quantities found or detection limits.

XVI. FIELD AUDITING AND OVERSIGHT

A. Audits Initiated by EPA and Primary Contractor

On-site audits of EPA contracted and PRP contracted field sampling teams takes place on a random basis within the Region. EPA personnel performing the audits look for good sampling technique and ensure that approved Plans are being implemented in the field. Auditors do make suggestions to contractors in the field but they do not stop work unless a discrepancy severe enough to invalidate data results is observed. If a severe discrepancy is observed the Project Manager is notified by phone when the auditors return to the office that day.

EPA personnel send written audit reports to the EPA Project Manager following the audit and request written response from the contractor when inadequacies are found.

B. Contractors in an Oversight Capacity

Contractors retained in an oversight capacity should be looking for good sampling technique and adherence to an approved Plan when overseeing other contractors in the field. Logbooks should be kept by the oversight contractor and any poor practices or discrepancies with the Plan should be noted and the EPA Project Manager notified of the findings by phone.

C. Audits Performed by States

State Quality Assurance personnel routinely perform audits of Federal-lead sites. Although State auditors can make suggestions to improve sampling technique and to ensure that approved Plans are being implemented, they do not have the authority to stop work in the field or to change any part of the Plan. If a disagreement with State auditors arises in the field, the contractor should contact the Project Manager for guidance.

LIST OF APPENDICES

- I. Priority Pollutant vs. Target Compound List
- II. CLP Statement of Work Target Compound/Element Lists
- III. 40 CFR Part 136, Table 2
CLP Holding Time and Preservation Requirements
- IV. CLP Documentation
- V. Quality Assurance Procedures for Field Analysis and Equipment
- VI. Sample Bottle Repository Statement of Work
- VII. Recommended Well Drilling Techniques
- VIII. "The Effects of Grouts, Sealants, and Drilling Fluids on the Quality of Ground Water Samples"
- IX. Region II Standard Operating Procedure for Selecting Ground Water Well Construction Material at CERCLA Sites
- X. Comparison of Surface Water Collection Devices
- XI. Comparison of Bottom Grab and Coring Devices
- XII. Region II Data Validation Standard Operating Procedures
TECHNICAL PRESERVATION AND HOLDING TIME
REQUIREMENTS*

ANALYTE

MATRIX

HOLDING TIME \

Volatile Organics

Solid

10 days

cool to 4

Extractable Organics	Solid	7 days to extraction, cool to 4 degrees C	
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		40 days to analysis	
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Cyanide	Solid	14 days	cool, 4
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Metals	Solid	6 months	none
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Mercury	Solid	28 days	cool to 4
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Dioxin (2,3,7,8-TCDD)	Solid	6 months	none
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Volatile Organics

Aqueous

preserved: 14 days low/medium conc.:

HCl to pH <2

unpreserved: 7 days

**cool 4
degrees C**

cool 4

degrees C

Extractable Organics

Aqueous

7 days to extraction, low/medium conc.:

40 days to analysis cool 4 degrees C

Cyanide

Aqueous

14 days

cool 4

NaOH

acid if
oxidizer
high conc.:6
ozglass
present
cadmium
carbonate if
S2- present

Metals

Aqueous

6 months

low/med conc.:

cool 4

HNO₃ pH<2

high conc.:
none

Mercury

Aqueous

28 days

low/med

cool 4

HNO3 pH<2

Dioxin (2,3,7,8-TCDD)	Aqueous	10 days to extraction,	high conc.: none cool 4
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40 days to analysis

* All holding times begin on date of sample collection.

CLP CONTRACTUAL PRESERVATION AND HOLDING TIME
REQUIREMENTS*

ANALYTE

MATRIX

HOLDING TIME

Volatile Organics

Solid

10 days

cool to 4

Extractable Organics	Solid	10 days to extraction,	cool to 4
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40 days to analysis

Cyanide	Solid	12 days	cool, 4
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Metals	Solid	6 months	none
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Mercury	Solid	26 days	cool to 4
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Dioxin (2,3,7,8-TCDD)

Solid

6 months

none

Volatile Organics

Aqueous

preserved: 10 days low/medium conc.:

HCl to pH <2

cool 4
degrees C

high conc.: none

Extractable Organics

Aqueous

5 days to extraction, low/medium conc.:

40 days to analysis cool 4 degrees C

high conc.:

Cyanide

Aqueous

12 days

cool 4

NaOH

acid if

Metals

Aqueous

6 months

low/med conc.:

**present
cadmium
carbonate if
S²⁻ present**

cool 4

HNO₃ pH<2

Mercury

Aqueous

26 days

**high conc.:
none**

low/med

cool 4

HNO₃ pH<2

high conc.:
none

Dioxin (2,3,7,8-TCDD)

Aqueous

10 days to extraction,

cool 4

40 days to analysis

* Contractual holding times being on date of Verified Time of Sample Receipt.

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