DoD
PERCHLORATE HANDBOOK

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PREPARED BY
THE DEPARTMENT OF DEFENSE ENVIRONMENTAL
DATA QUALITY WORKGROUP

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LIST OF ACRONYMS AND ABBREVIATIONS

AFCEE	Air Force Center for Environmental Excellence
ASTM	American Society of Testing and Materials
CCV	continuing calibration verification
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CSM	conceptual site model
CWA	Clean Water Act
DNAPLs	dense non-aqueous-phase liquids
DoD	Department of Defense
DOE	Department of Energy
DQO	data quality objective
EDQW	DoD Environmental Data Quality Workgroup
EPA	U.S. Environmental Protection Agency
FIELDS	Field Environmental Decision Support
FFRRO	Federal Facilities Restoration and Reuse Office
GPS	Global Positioning System
HPLC	high performance liquid chromatography
HT	holding times
HTRW	Hazardous, Toxic, and Radioactive Waste
IC	ion chromatography
IC/EC	ion chromatography/electric conductivity
IC/MS	ion chromatography/mass spectrometry
ICV	initial calibration verification
IDQTF	Intergovernmental Data Quality Task Force
IPC	instrument performance check
IQG	Information Quality Guidelines
IRIS	Integrated Risk Information System
IS	internal standard
ITRC	Interstate Technology and Regulatory Council
JATO	jet-assisted takeoff
LC/MS	liquid chromatography/mass spectrometry
LCS	laboratory control sample
LNAPLs	light non-aqueous phase liquids

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LOD	limit of detection
LOQ	limit of quantitation
MCT	matrix conductivity threshold
MDL	method detection limit
MPC	measurement performance criteria
MRL	method reporting limit
MS	mass spectrometry
MS/MS	tandem mass spectrometry
NELAC	National Environmental Laboratory Accreditation Conference
NELAP	National Environmental Laboratory Accreditation Program
NPDES	National Pollutant Discharge Elimination System
PDB	passive diffusion bag
ppb	parts per billion
PQO	project quality objective
PT	proficiency testing
PVC	polyvinyl chloride
PWS	public water system
QA	quality assurance
QAPP	quality assurance project plan
QC	quality control
QSM	DoD Quality Systems Manual for Environmental Laboratories
RCRA	Resource Conservation and Recovery Act
RPD	relative percent difference
SADA	Spatial Analysis and Decision Assistance
SAP	sampling and analysis plan
SDWA	Safe Drinking Water Act
SPP	Systematic Planning Process
TDS	total dissolved solids
UCL	upper confidence level
UCMR	Unregulated Contaminant Monitoring Rule
UFP-QAPP	Uniform Federal Policy for Quality Assurance Project Plans
UFP-QS	Uniform Federal Policy for Implementing Environmental Quality Systems
USACE	U.S. Army Corps of Engineers
VOC	volatile organic compounds

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VSP	Visual Sample Plan
µg/L	micrograms per liter (equivalent to parts per billion)

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PART 1 – INTRODUCTION

This handbook was developed to assist DoD facilities in complying with current DoD policy governing perchlorate sampling and testing activities for both environmental restoration/cleanup and compliance monitoring programs. Intended users of this document include DoD Remedial Project Managers (RPMs), contractor project managers, and field-sampling personnel.

In February 2004, the Deputy Assistant Secretary of the Navy for Environment issued the EDQW *Interim Guidance on Sampling and Testing for Perchlorate*. This handbook replaces the EDQW Interim Guidance, and it supplements, but does not replace, any Component-specific policies. An electronic version of this handbook and associated appendices may be downloaded from http://www.navylabs.navy.mil. **Users of this handbook must obtain and follow the latest, approved DoD and Component-specific policy and guidance affecting perchlorate sampling and testing.**

Purpose and Scope

This handbook was prepared by the Department of Defense (DoD) Environmental Data Quality Workgroup (EDQW). Chartered under the leadership of the Department of the Navy, this inter-Component task force is responsible for promoting "the generation of environmental data of known and documented quality." This handbook has the following objectives:

- Ensure cost-effective and consistent approaches across DoD for sampling and testing activities involving perchlorate,
- Ensure that collected data are of the quality necessary to support decision-making, and
- Ensure that information disseminated to the public associated with perchlorate sampling and testing complies with the DoD Information Quality Guidelines. [1]

This handbook includes guidance on the following:

- Using conceptual site models (CSMs) to develop project quality objectives (PQOs) associated with sampling and analysis for perchlorate,
- Designing sampling strategies and implementing appropriate sampling techniques,
- Selecting qualified analytical laboratories and analytical methods, based on required performance objectives, and
- Documenting the above in project planning documents in accordance with the *Uniform Federal Policy for Quality Assurance Project Plans*, March 2005 (UFP-QAPP).

DoD RPMs and contractor project managers are expected to be trained and experienced in using the Systematic Planning Process (SPP), developing conceptual site models (CSMs), and

[1] In February 2003, DoD issued the DoD *Information Quality Guidelines* (DoD IQG) to comply with the Federal Data Quality Act (Public Law 106-554) and the Office of Management and Budget implementing guidelines. Under the DoD IQG, information that is disseminated to the public must meet basic quality standards: objectivity, utility, and integrity. In addition, those "situations involving influential scientific, financial or statistical analytical results" require that such information be "capable of being substantially reproduced."

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preparing and implementing project planning documents such as Quality Assurance Project Plans (QAPPs) or Sampling and Analysis Plans (SAPs). Appendix A provides a list of resources providing general guidance on those processes.

Summary of Perchlorate Uses and Sources

Perchlorate (ClO_4^-) is a soluble anion that forms solid salts with various cations, including ammonium, potassium, sodium, lithium, and magnesium. Once dissolved in water, perchlorate is very stable. It resists degradation in the subsurface and does not readily adsorb to mineral surfaces.

Perchlorate salts were first produced on a large scale in the 1940s. The military services have used perchlorate salts as components in solid propellant for rockets and missiles. The salts have also been used in some explosive and incendiary munitions fillers and in smoke-producing compounds, training simulators, and signal flares.

Non-military sources include pyrotechnics, fertilizers, black powder and black powder substitutes, air bag inflators, road flares, and the use of perchloric acid in laboratories and manufacturing. Perchlorate has been used medicinally to manage hyperthyroidism. Numerous studies are underway to investigate the natural occurrence of perchlorate. Perchlorate occurs naturally in some minerals and materials formed under evaporative conditions. Evidence also suggests it can be produced atmospherically.[2] For a comprehensive discussion of perchlorate uses and sources, readers should consult *Perchlorate: Overview of Issues, Status, and Remedial Options*, September 2005, prepared by the Interstate Technology and Regulatory Council (ITRC) Perchlorate Team.

Historical data on the occurrence of perchlorate in the environment have been compiled from a variety of sources. A national picture of contamination is still being developed. Detections have been in groundwater, with some detections reported in both soil and surface water. The analytical methods most commonly used to generate historical data have been various modifications of EPA Method 314.0. Sources of uncertainty for Method 314.0 include: (1) the method is non-specific for perchlorate, (2) it may be subject to interferences, (3) the Method stated reporting limit (MRL) is 4 parts per billion (ppb) in drinking water and (4) the method was specifically developed for the analysis of drinking water and has not been systematically validated in other materials. Due to the lack of published methods, sources of uncertainty also exist for historical data produced by Mass Spectrometry (MS). (Appendix G of this handbook defines quality control criteria (e.g., internal standard and isotope ratio) based on recently published EPA methods that must be achieved when using MS methods to determine perchlorate in matrices of concern to DoD.)

Federal and State Laws Regulating Perchlorate

Project teams should consult the appropriate Federal, State, and local regulations to determine current requirements at the time site-specific studies are initiated. The Safe Drinking Water Act (SDWA) directs EPA to periodically publish a list of contaminants that are known or anticipated to occur in public water systems and that may need a National Primary

[2]P.K. Dasgupta et al., "The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes," *Environmental Science & Technology* 39(6)*: 1569-75.*

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Drinking Water Regulation. This list is called the Contaminant Candidate List or CCL. EPA published the first CCL of 60 contaminants in March of 1998. Perchlorate was included on the first CCL. EPA decided not to regulate nine contaminants listed on the first CCL and carried forward the remaining 51 contaminants onto its second CCL, which was published in February 2005. EPA included perchlorate on its second CCL and it is currently undergoing evaluation as to whether a drinking water regulation is needed. In 1999 and under the authority of SDWA, EPA developed the Unregulated Contaminant Monitoring Rule (UCMR) in coordination with the CCL to provide a national perspective on the occurrence of unregulated contaminants in public water systems. Monitoring for perchlorate under the first UCMR occurred during the 2001-2005 timeframe. EPA has proposed to monitor for perchlorate under its second UCMR, which was proposed on August 22, 2005 and has not yet been promulgated.

The Clean Water Act (CWA) National Pollutant Discharge Elimination System (NPDES) permit program is administered by authorized States in most cases. Perchlorate may be one of the analytes that are regulated under site-specific permits. At the time this document was published, no regulations associated with the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) or the Resource Conservation and Recovery Act (RCRA) specifically address perchlorate.[3] Several States have issued advisory or guidance levels for perchlorate; however, at the time this handbook was published, no State had promulgated perchlorate standards.

The National Academy of Sciences' National Research Council (NRC) issued a report, *Health Implications of Perchlorate Ingestion* (January 2005), which recommended an oral reference dose (RfD) for perchlorate of 0.0007 mg/kg/day. EPA has based its RfD (0.0007 mg/kg/day) on the NRC-recommendation RfD and published it in the Integrated Risk Information System (IRIS).

PART 2 – KEY REQUIREMENTS

Key requirements for perchlorate sampling and testing at DoD facilities follow:

Implementing Environmental Quality Systems

The *Uniform Federal Policy for Implementing Environmental Quality Systems* (UFP-QS) and the *Uniform Federal Policy for Quality Assurance Project Plans* (UFP-QAPP) explain essential elements of quality systems for environmental data collection performed by Federal agencies. The documents were developed by the Intergovernmental Data Quality Task Force (IDQTF), a joint initiative involving DoD, the Department of Energy (DOE), and EPA. (Copies of these documents (UFP-QS and UFP-QAPP)) may be downloaded from the EPA Federal Facilities website at www.epa.gov/fedfac/documents/intergov_qual_task_force.htm.) These policies were developed to ensure that:

- Environmental data are of known and documented quality, suitable for their intended uses;

[3] Some EPA Regions have screening criteria or preliminary remediation goals for perchlorate, which may be used under CERCLA or RCRA.

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- Environmental data collection and technology programs meet applicable requirements; and
- Federal agencies achieve consistency across all regions with respect to acceptable minimum quality assurance requirements.

Organizations involved in perchlorate sampling and testing for DoD are expected to have a quality system in place that complies with the UFP-QS. Project-specific planning documents must address all quality requirements described in the UFP-QAPP. Appendix B describes the UFP-QAPP worksheets that guide the development of project-specific planning documents. Use of the worksheets, while optional, will ensure that project-specific planning documents address all UFP-QAPP requirements. Their use will also facilitate the review and approval of project planning documents by regulatory authorities, when required.

Selecting Qualified Environmental Testing Laboratories

Laboratories performing analyses for DoD projects must have a documented quality system that complies with ISO/IEC 17025:1999 and the latest approved version of the *Department of Defense Quality Systems Manual for Environmental Laboratories* (DoD QSM) (a copy may be downloaded from http://www.navylabs.navy.mil or https://www.denix.osd.mil). Laboratories must comply with Component-specific requirements and are subject to project-specific on-site assessments by DoD representatives. Laboratories must have appropriate State certifications or be accredited by a nationally recognized accreditation body, such as National Environmental Laboratory Accreditation Program (NELAP), for the applicable test method, as appropriate. Laboratories must provide documentation of their ability to achieve the project-specific method reporting limit (MRL) using the specified method in each matrix to be analyzed.

Applying the Systematic Planning Process

The Systematic Planning Process (SPP) must be used for the collection of all environmental data at environmental restoration/cleanup sites and training ranges. The Systematic Planning Process involves the following steps:

- Establishing the project team,
- Identifying decision-makers and stakeholders,
- Defining the specific problem to be addressed,
- Determining the scope, boundaries and schedule of the study,
- Developing the preliminary conceptual site model (CSM), and
- Identifying project quality objectives (PQOs).

Examples of the SPP

Two common examples of the SPP are EPA's Data Quality Objectives (DQO) Process (EPA QA/G-4) and the U.S. Army Corps of Engineers' Technical Project Planning Process.

Systematic planning ensures that the correct types, quantity and quality of data will be collected to satisfy the study objectives. General guidance on the SPP is provided in the UFP-QAPP. Appendix C outlines agreements that should be reached by the project team during the Systematic Planning Process for perchlorate investigations.

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Developing Conceptual Site Models

A conceptual site model (CSM) is a set of hypotheses about the following:

- Sources—the source of perchlorate contamination at a site.
- Pathways—the mechanisms that may lead to the release and transport of perchlorate contamination. For perchlorate, the groundwater pathway is of primary interest.
- Receptors—the human and ecological systems that may be exposed to the contamination, and the mechanisms that may lead to their exposure. The exposure mechanism of primary concern for perchlorate is ingestion.

The use of CSMs will aid in the development of PQOs and sampling plans for perchlorate sampling and testing at environmental restoration/cleanup sites and training ranges. Because the UCMR regulations and NPDES permits describe specific sampling and analysis requirements, including sampling points, it is not necessary to develop CSMs for compliance sampling and testing conducted under these programs.

A project's CSM can be depicted graphically, described in narrative form, or both. It is continually updated as data are collected. The U.S. Army Corps of Engineers' *Conceptual Site Models for OE and HTRW Projects* (EM 1110-1-1200) provides comprehensive guidance on the development of a CSM. A new Triad web site (http:www.triadcentral.org) discusses the use of CSMs in a dynamic planning process. Appendix D provides information about perchlorate sources, pathways, and receptors for use in generating CSMs for environmental restoration/cleanup projects and training range assessments.

Developing Project Quality Objectives

Appendix E provides guidance on developing site-specific PQOs for perchlorate sampling and testing. PQOs are qualitative and quantitative statements developed through the systematic planning process. They describe the types, quantity, and quality of data necessary to support defensible decisions.

The development of PQOs encompasses the following steps:

Step 1: Define the environmental problem and describe decisions to be made.

Step 2: Identify and describe the acceptable level of uncertainty for those decisions.

Step 3: Specify the measurement performance criteria (i.e., the data quality) required to support the acceptable level of uncertainty.

Step 4: Determine the appropriate uses and limitations of other available data, that is, data that are not generated in the current investigation but that may be used in making the current decision.

Step 5: Determine the types and quantity of new data required to support the decisions identified in step 1.

The PQOs are the entire set of qualitative and quantitative statements that result from each of these five steps. Appendix E focuses on developing PQOs for environmental restoration/cleanup projects. The development of PQOs for regulatory compliance sampling is much less complex because the permit or regulation generally dictates the type, quantity, and quality of data to be collected and reported.

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PART 3 – PERCHLORATE SAMPLING AND SAMPLE DESIGNS

For compliance sampling conducted under UCMR2 or NPDES permits, the sample design and sampling procedures are dictated by the regulation or permit. Sampling and sample design considerations for use when planning environmental restoration/cleanup projects must be developed for each project. Appendix F contains Technical Guides for use by field sampling personnel. These guides provide recommended procedures for collecting groundwater, drinking water, wastewater, and soil/sediment samples for perchlorate analysis. These Technical Guides can be used in the development of project-specific standard operating procedures (SOPs) for sample collection.

The development of sample designs for biota is outside the scope of this handbook. For guidance on this topic, users should consult the U.S. Department of Agriculture, Fish and Wildlife Service. Because perchlorate does not bioaccumulate in respiring receptors, biological tissue sampling is not recommended.

Sample Design Software

The federal government has funded the development of three software packages that support various aspects of sample design. (The use of any of these software packages is optional.) These packages, which are available for free download, are:

- Field Environmental Decision Support (FIELDS) (www.epa.gov/region5fields/)
- Spatial Analysis and Decision Assistance (SADA) (www.tiem.utk.edu/~sada/)
- Visual Sample Plan (VSP) (dqo.pnl.gov/)

FIELDS is a suite of sample design, database query, geospatial modeling, and analysis modules, implemented in ArcView, to support integrated environmental decision-making. FIELDS has implemented random and systematic sample design and provides a link to VSP to import and export sample designs to that software.

SADA is an integrated set of spatial analysis, statistical, risk assessment, and second-round sampling design tools to assist analysts in environmental decision-making. SADA provides data visualization and geospatial modeling tools, risk assessment modules, and decision analysis tools.

VSP provides simple tools for defining an optimal, technically defensible sampling scheme for site characterization. VSP is applicable to any two-dimensional sampling design, including those involving surface soil, building surfaces, surface water bodies, or other similar applications.

Properties of perchlorate affecting sampling

When dissolved in groundwater, perchlorate is a highly soluble and stable ion that migrates at the same velocity as the groundwater flow. Perchlorate does not adsorb to mineral surfaces typically found in subsurface materials. Perchlorate salts may, in certain rare circumstances, form solutions that have densities significantly higher than that of groundwater. If these solutions enter the subsurface, they may behave in the same manner as dense non-aqueous-phase liquids (DNAPLs) and should be sampled accordingly (See Appendix D for more information on this topic).

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Dissolved perchlorate has low volatility, so agitation of the sample or entrained air bubbles from the sampling equipment will not interfere with the analytical results. If additional sample collection is required for other analytes, then sampling methods and procedures will be dictated by the sampling requirements for the most sensitive parameters. Typically, organic compounds are collected first, and nonmetallic inorganic compounds are sampled last.

In solids, perchlorate can be present as precipitated salts or dissolved in interstitial pore water. Perchlorate may also be present in propellant particles. The distribution of precipitated perchlorate salts and propellant particles in soil has been found to be extremely heterogeneous. The sampling design and sample collection procedures must take this heterogeneity into account, and composite (or incremental) sampling techniques should be used when sampling solids.

Standard soil sampling equipment and procedures may be used to collect samples for perchlorate analysis. Examples include those described in the American Society of Testing and Materials (ASTM) publication ENVSITE 02, *ASTM Standards Related to Environmental Site Characterization*, 2nd edition and ASTM D4700-91(1998) *Standard Guide for Soil Sampling from the Vadose Zone*. If it is necessary to collect samples of interstitial pore water, then a vadose zone sampler can be used. Vadose zone samplers include suction samplers and free-drainage samplers for collecting the pore water.

Because of its high solubility, it is unlikely that perchlorate will reside in sediments, and it will be unnecessary to sample sediments in most situations. Sediment sampling may be required in rare situations where 1) large quantities of perchlorate have been released, 2) an evaporative environment exists (e.g. waste impoundment associated with munitions demilitarization activities), or 3) perchlorate is entrained in fillers or other substrates that could inhibit dissolution. If one or more of these situations exist, standard procedures for sampling sediment, such as those described in the ASTM documents, should be employed.

Sample Collection Devices

Perchlorate will not react with materials typically used in sample collection devices or in the construction of groundwater monitoring wells (e.g., Teflon®, stainless steel, polyvinyl chloride (PVC), polyethylene, and polypropylene). Since these materials are all suitable for perchlorate sampling, cost may be the main consideration in choosing one type of material over another. Detailed information on the design and installation of groundwater monitoring wells can be found in a number of sources, including *Groundwater and Wells*, by F. Driscoll, and *Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells*, by L. Aller et al.

In rare situations, high-concentration perchlorate solutions (total dissolved solids greater than 1,000 mg/L or $C1^-$ greater than 500 mg/L) may cause corrosion in wells constructed from steel. Since the majority of groundwater monitoring wells installed are constructed of PVC, this usually will not be a concern.

To avoid issues associated with trace perchlorate contamination found in commonly used laboratory detergents, samplers should use dedicated or disposable equipment for perchlorate sampling where practical, and collect samples into new, precleaned sample containers. Where non-dedicated sampling equipment is used, decontamination will be required between sampling events. If perchlorate is the only target analyte, an acceptable procedure is to use a non-phosphate

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soap wash, followed by a deionized water rinse and air drying. If the investigation includes additional target analytes, then samplers should follow standard decontamination practices for those analytes, except that non-phosphate detergent must be used. Field samplers should collect a rinsate blank to verify that decontamination has been effective.

Investigating Potential Source Areas

When investigating known or suspected source areas, it is important to also identify all potential non-DoD and background sources of perchlorate (Refer to ITRC, September 2005). When developing sample designs, professional judgment will be used to decide which media to sample and select sample locations. Where the CSM indicates the potential for an extensive or ongoing perchlorate release, or where an arid climate is conducive to the continuing presence of perchlorate in the soil, the sample design should define the extent of contaminated soils. Where the CSM provides little information about potential source areas, statistically-based sampling designs (e.g. systematic or random sampling) should be used.

Investigating to Determine Migration Pathways

In areas where the presence of a perchlorate release has been established, the focus of the investigation will be to evaluate migration pathways and exposure pathways. Experience has shown that groundwater is a pathway of concern. The sampling objectives will include determining (or verifying) groundwater flow characteristics as well as plume geometry. Knowledge of the plume geometry in a three-dimensional perspective will aid in the understanding of perchlorate transport at a particular site. Concentrations can vary greatly by both depth and location. Concentrations can also vary over time because of seasonal changes in aquifer characteristics.

Variations in depth to groundwater can be used to evaluate seasonal variations in aquifer in hydrogeologic characteristics. These data can be used in conjunction with results from discrete quarterly or monthly sampling events to determine whether the data represent a seasonally adjusted high or low condition for contaminant concentrations.

The sample design for evaluating the groundwater pathway will involve judgmental sample placement, and monitoring wells generally should be installed for that purpose. Site-specific information about geology, hydrogeology, and the anticipated magnitude of the release will determine the number and locations of groundwater samples to be collected. For this reason, a registered or certified geologist or hydrogeologist must be involved in the development of all groundwater sample designs. In some investigations, depth-discrete sampling may be important for identifying contaminant flow zones at specific depths within the aquifer. This type of sampling may require the installation of cluster wells or depth-specific monitoring wells.

If it becomes necessary to estimate the total mass of perchlorate released (for example, when designing remediation systems) the most useful measure of perchlorate amount may be mass flux; that is, the mass of perchlorate moving through the aquifer per unit of time. The accurate calculation of mass flux requires three-dimensional information about the distribution of perchlorate throughout the plume.

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Sampling for High-Density Perchlorate Solutions

In the rare instance where there is potential for high-density perchlorate solutions to occur, depth-discrete groundwater samples should be collected across the thickness of the aquifer. This will allow the creation of a vertical profile of perchlorate concentrations and identification of zones containing high-density brines. Monitoring wells should be targeted specifically at horizons where the stratigraphic conditions are favorable for brines to accumulate (i.e. horizons immediately above low-permeability confining layers and local stratigraphic low points in aquifer horizons), and they should have short screened intervals to prevent mixing of zones of differing densities. Depth-discrete sampling may also be accomplished using direct-push groundwater samplers or multilevel groundwater monitoring systems, which allow several discrete zones to be independently monitored from an installation in a single borehole. These multilevel systems can provide significant cost savings where multiple zones must be repeatedly sampled over a period of time.

Sampling for Perchlorate when DNAPLS or LNAPLS are Present

Some sites may be contaminated with either light or dense, non-aqueous-phase liquids (LNAPLs or DNAPLs) or both, in addition to perchlorate. The presence of DNAPLs and LNAPLs should not affect the sampling procedures for perchlorate. If possible, the sample should be collected above the DNAPLs or below the LNAPLs in wells that contain these contaminants.

PART 4 – LABORATORY ANALYSIS, DATA DELIVERABLES, DATA REVIEW AND REPORTING

Analytical requirements for perchlorate testing will vary depending on the regulatory drivers. If sampling and testing activities have been requested by a regulatory agency, or those activities are subject to regulatory oversight, then installations should seek the regulators' input and concurrence on the analytical methods to be used through their participation in the systematic planning process. Regardless of the method used, each laboratory must demonstrate and document a Method Reporting Limit (MRL), in the matrix of concern, that is equal to or less than the applicable regulatory limit or concentration of concern specified in the PQOs.

Important Definitions for Selection of Perchlorate Methods

Selectivity: The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances.

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest.

Approaches to perchlorate analysis for environmental matrices include ion chromatography with electric conductivity (IC/EC) detection, and ion chromatography (IC) or liquid chromatography (LC) with either single or dual mass spectrometry (MS and MS/MS) detection. At the time of publication of this handbook, there was no standard, published method for preparation of solid samples for the analysis of perchlorate. Until SW-846 Methods 6850 and 6860 are published, laboratories must follow the sample preparation procedure detailed in Appendix G when analyzing solid samples for DoD. If testing of biota or food products is

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required, the Food and Drug Administration (FDA) developed IC/MS/MS method that should be followed (http://www.cfsan.fda.gov/~dms/clo4meth.html).

Sampling and Testing for Regulatory Compliance

Use of EPA Method 314.0 was mandatory for the analysis of perchlorate in drinking water under the Unregulated Contaminant Monitoring Rule that expired in December 2003 (UCMR). States may require the use of Method 314.0 in some existing NPDES permits. This is the only circumstance under which Method 314.0 should be used.

The UCMR2, which was published in August 2005, allows for the use of Method 314.0 (enhanced), 314.1 331.0 or 332.0 for perchlorate analysis. **Only the mass spectrometry methods (331.0 and 332.0) should be used for analysis of drinking water samples for DoD**. In situations where either Method 314.0 (enhanced) or 314.1 is used, all results above the method reporting limit ***must*** be confirmed using MS.

Sampling and Testing for Environmental Restoration/Cleanup and Range Assessments

Methods employing IC/EC (e.g. Methods 314.0, 314.0 (enhanced) and 314.1) are not appropriate for sampling and testing associated with environmental restoration/cleanup or range assessment projects. Only methods employing MS are to be used for environmental restoration/cleanup or range assessment projects.

Selection of the analytical method for a particular project must be based on project-specific Measurement Performance Criteria (MPCs). Table 1 provides a summary of information about each of the recommended perchlorate methods. For the sake of completeness, Table 2 provides information about other available methods that are not recommended for testing in accordance with the DoD Perchlorate Policy.

Table 1 - Recommended Methods for Perchlorate Analysis

Method (Technique)	Applicability	Limitations	Target Reporting Limits
EPA 331.0 (LC/MS) (LC/MS/MS)	• DoD Owned Drinking Water Systems (UCMR 2) • Applicable to drinking water samples, including those with high TDS	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking Water 0.1 µg/L (LC/MS) 0.02 µg/L (LC/MS/MS)
EPA 332.0 (IC/MS) (IC/MS/MS)	• DoD Owned Drinking Water Systems (UCMR 2) • Applicable to drinking water samples, including those with high TDS	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking Water 0.1 µg/L (IC/MS) 0.02 µg/L (IC/MS/MS)
SW6850 (LC/MS)	• Environmental Restoration • Operational Ranges • DoD Wastewater Effluent Discharges • Aqueous samples including those with high TDS • Soil and sludge samples	• Requires a proprietary column· • Final method not published	Drinking Water and Groundwater 0.2 µg/L Soil 2 µg/Kg

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Method (Technique)	Applicability	Limitations	Target Reporting Limits
SW6860 (IC/MS) (IC/MS/MS)	• Environmental Restoration • Operational Ranges • DoD Wastewater Effluent Discharges • Aqueous samples to include those with high TDS • Soil and sludge samples	• Pretreatment recommended for samples with high concentrations of sulfate • Final method not published	Drinking Water and Groundwater 0.2 µg/L Soil 2 µg/Kg
FDA Method (IC/MS/MS)	• Low moisture foods, bottled water, and milk	• None noted	Low moisture foods 3.0 µg/Kg Bottled Water 0.5 µg/L Milk 3.0 µg/L

Table 2 – Other Available Methods

Method (Technique)	Applicability	Limitations	Target Reporting Limits
EPA 314.0 (IC)	• Mandatory for drinking water samples reported under UCMR 1 • Aqueous samples with low dissolved solids (conductivity < 1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each • Not proposed for UCMR 2	• Subject to false positives due the lack of specificity of the conductivity detector • Validated for drinking water samples only • Inappropriate for use in samples with high TDS •	Drinking Water 4 µg/L
EPA 314.0 "enhanced" (IC)	• Drinking Water samples • Proposed option for UCMR 2	• No revision of Method 314.0 that documents these "Enhancements" has been published • Enhancements are only listed in the Federal Register notice • Subject to false positives due the lack of specificity of the conductivity detector • Limited commercial availability • Requires confirmation of perchlorate results above reporting limit when used for UCMR 2	Drinking water - 0.57 µg/L

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EPA 314.1	• Drinking water samples • Planned option for UCMR 2	• Reduces but does not eliminate the potential for false positives· • Validated for drinking water samples only • Long analytical run time • Limited commercial availability· • Requires confirmation of perchlorate results above reporting limit when used for UCMR 2	Drinking Water 0.13 µg/L
Draft SW9058 (IC)	• Aqueous samples with low dissolved solids (conductivity < 1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each	• Subject to false positives due the lack of specificity of the conductivity detector • Inadequate quality control criteria • Method is expected to undergo significant revision prior to publication	Low TDS Groundwater 4 µg/L

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Data Deliverable Requirements

The data package provided by the laboratory must meet the specifications contained in the most recent version of the DoD-QSM. The following is a summary of the minimum contents of the data package for perchlorate analysis:

- Analytical results for all samples (including LOQs and LODs),
- Dilution factors,
- Case narrative documenting any problems encountered during the analysis of the samples and resulting actions taken by the laboratory to resolve those problems,
- Use of DoD flags as specified in Appendix G,
- Summary results for calibrations, blanks, and all QC samples,
- All chromatograms and instrument printouts for calibration standards, instrument performance check, and associated QC samples,
- Summaries of ion area counts (if not already included on instrument printouts),
- Retention time window summaries, and
- Internal standard area count and retention time summaries.

Electronic data deliverables for compliance projects should meet the Staged Electronic Data Deliverable (SEDD) Stage 2a specification. Electronic data deliverables for environmental restoration/cleanup and range assessment projects should meet the SEDD Stage 2b specification. A future update to this handbook will include document type definitions for the SEDD files.

Data Review

Project planning documents must identify responsible personnel and describe specific data review procedures that will be used for all perchlorate investigations. *Data verification* is for the most part a completeness check. It is most effective when performed internally and then spot-

checked externally. *Data validation* is a check for compliance and conformance to specifications. It can be performed externally by the project chemist or QA coordinator, but it can also be performed by a third-party organization. This is often the case for highly visible projects. The *data usability assessment* looks at the big picture; it evaluates whether the data can be used as intended to support the project-specific decisions. Data usability may be initiated by the project quality assurance officer, but it requires participation by project decision-makers.

The principle of a graded approach applies to all phases of data review, just as it applies to the specifications on which the review is based. The level or detail of review depends on the importance of the decisions being made as expressed in the PQOs. An overview of the data review process is provided in Figure 37 of the UFP-QAPP. Project planning documents must describe all data review procedures and identify personnel responsible for each step.

Appendix G, Tables G-1 and G-2 summarize the data review criteria and corrective actions to be used for perchlorate analyses. Upon completion of internal verification, any necessary corrective action (including specified data flagging) will be implemented. Only after this is done will the data be approved for release in the final laboratory data report.

Data Reporting

DoD policy requires all perchlorate sampling and testing results to be reported to the responsible service branch for inclusion in their respective perchlorate database.

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APPENDIX A

SOURCES AND RESOURCES

Users of this handbook may wish to consult the following sources for additional information.

Policy

Department of Defense. ***Policy on DoD Required Actions Related to Perchlorate***. OSD memorandum, 26 January 2006.
Web site: http://www.dodperchlorateinfo.net/

U.S. EPA. ***Assessment Guidance for Perchlorate***. 26 January 2006.
Web site: http://epa.gov/newsroom/perchlorate.pdf

Department of Defense. ***Ensuring the Quality of Information Disseminated to the Public by the Department of Defense; Policy and Procedural Guidance.*** 10 February 2003.
Web site: http://www.whitehouse.gov/omb/inforeg/agency_quality-dod.pdf

Department of the Army. ***Department of Army Guidance for Assessing Potential Perchlorate Contamination***, Memorandum, 11 June 2004.
Web site: http://www.epa.gov/fedfac/pdf/armygu0604.pdf

Publications

Aller, L., et al. Handbook of Suggested Practices for the Design and Installation of Ground-Water Monitoring Wells. EPA/600/4-89/034, 1991.

American Society for Testing and Materials (ASTM) International. ***Standard Guide for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-water Quality Investigations***. Standard D 6771-02.
ASTM. ***Standard Practice for Expedited Site Characterization of Vadose Zone and Ground Water Contamination at Hazardous Waste Contaminated Sites.*** Standard D6235-98.

Dasgupta, P.K., K. Martinelango, W.A. Jackson, T.A. Anderson, K. Tian, R.W. Tock, and Srinath Rajagopalan. ***The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes***, *Environmental Science & Technology Online.* Release date 29 January 2005.

DiRienzo, R.P., K. Lin, T.T. McKay, and R.W. Wade. ***Analysis of Perchlorate in Drinking Water, Groundwater, Saline Water, Soil and Biota by LC/MS***. Presentation at DoD Environmental Training and Data Quality Workshop, Reno, NV, May 2004.

Driscoll, F.G. ***Groundwater and Wells***. 2nd edition, 1986, pp. 395-495.

Flowers, T.C, and J.R. Hunt. ***Long-Term Release of Perchlorate as a Potential Source of Groundwater Contamination.*** Chapter 14 in Perchlorate in the Environment, E.T. Urbansky, ed. New York: Kluwer/Plenum.

Food and Drug Administration, ***Rapid Determination of Perchlorate Anion in Food by Ion Chromatography Tandem Mass Spectrometry,*** Revision 1, 27 July 2004.
Web site: http://www.cfsan.fda.gov/~dms/clo4meth.html

Gilbert, R.O. ***Statistical Methods for Environmental Pollution Monitoring***, John Wiley and Sons, 1987.

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Hautman D.P., D.J. Munch, A.D. Eaton, and A.W. Haghani. ***Method 314.0 Determination of Perchlorate in Drinking Water Using Ion Chromatography,*** Revision 1.0, U.S. EPA, Office of Water, Cincinnati, OH, EPA/815/B-99/003, 1999.
Web site: http://www.epa.gov/ogwdw/methods/met314.pdf

National Environmental Laboratory Accreditation Conference (NELAC). ***2003 NELAC Standards.*** EPA/600R-04/003, June 2003.
Web site: http://www.epa.gov/nelac/

Orris, G.J. ***Preliminary Analysis for Perchlorate in Selected Natural Materials and Their Derivative Products.*** U.S. Geological Survey, Open file report 03-314, 2003.
Web site: http://geopubs.wr.usgs.gov/open-file/of03-314/

Pitzer, G. ***Confronting a Legacy of Contamination: Perchlorate.*** *Western Water*, May/June 2003.

Puls, R.W. and M.J. Barcelona, ***Low-Flow (Minimal Drawdown) Groundwater Sampling Procedures***, U.S. EPA, Ground Water Issue, EPA/540/5-95-504, 1996.

Robbat, Jr., Albert, ***A Guideline for Dynamic Workplans and Field Analytics: The Keys to Cost-Effective Site Characterization and Cleanup***, Tufts University Chemistry Department in cooperation with U.S. EPA, Region I.
Web Site: http://www.epa.gov/tio/download/char/dynwkpln.pdf

U.S. Army Center for Health Promotion and Preventive Medicine (CHPPM). ***Just the Facts … Perchlorate in Drinking Water***. Publication 31-003-0502, May 2002.
Web site: http://chppm-www.apgea.army.mil/documents/FACT/31-003-0502.pdf

U.S. EPA, National Exposure Research Laboratory, Office of Research and Development. ***Method 332.0, Determination of Perchlorate in Drinking Water by Ion Chromatography with Suppressed Conductivity and Electrospray Ionization Mass Spectrometry***, EPA Document # EPA/600/R-05/049, Revision 1.0, March 2005

U.S. EPA, Technical Support Center, Office of Ground Water and Drinking Water. ***Method 331.0, Determination of Perchlorate in Drinking Water by Liquid Chromatography Electrospray Ionization Mass Spectrometry***, Revision 1.0, January 2005

U.S. EPA, Technology Innovation Program. ***Occurrence and Potential Sources of Perchlorate Releases to the Environment as of April, 2003.*** Web site:
http://www.clu-in.org/download/contaminantfocus/perchlorate/perchlorateoccurrenceapril03a.pdf

U.S. EPA, Office of Research and Development. ***Perchlorate Environmental Contamination: Toxicological Review and Risk Characterization***, External Review Draft. NCEA-1-0503, 16 January 2002.

Information Sources

Agency for Toxic Substances and Disease Registry (ATSDR)
Division of Toxicology, U.S. Department of Health and Human Services, Public Health Service
Web site: http://www.atsdr.cdc.gov

American Society for Testing and Materials (ASTM) International
Web site: http://www.astm.org

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Department of Defense (perchlorate information)
Web site: https://www.denix.osd.mil/denix/Public/Library/Water/Perchlorate/perchlorate.html
Web site: http://dodperchlorateinfo.net

Triad Resource Center
Web site: http://www.triadcentral.org/

U.S. EPA, EPA Quality System
Web site: http://www.epa.gov/quality/qa_docs.html

U.S. EPA, Federal Facilities Restoration and Reuse Office
Web site: http://www.epa.gov/fedfac/
Perchlorate links: http://www.epa.gov/fedfac/documents/perchlorate_links.htm

U.S. EPA, Field Analytical Technologies Encyclopedia
Module: Systematic Planning and Developing a Conceptual Site Model
Web site: http://fate.clu-in.org

U.S. EPA, Hazardous Waste Clean-up Information (CLU-IN) (perchlorate information)
Web site: http://clu-in.org/contaminantfocus/default.focus/sec/perchlorate/cat/Overview/

U.S. EPA, Office of Groundwater and Drinking Water
http://www.epa.gov/ogwdw

U.S. EPA, Quality Staff, Quality Systems Documents
Web site: http://www.epa.gov/quality/qa_docs.html

U.S. EPA, Technology Innovation Program
Web site: http://www.clu-in.org/triad/

U.S. EPA, Triad Approach
Web site: http://www.epa.gov/tio/triad/

U.S. Navy Environmental Sampling and Testing Programs (perchlorate information)
Web site: http://www.navylabs.navy.mil/Perchlorate.htm

Guidance

Department of Defense. ***DoD Quality Systems Manual for Environmental Laboratories*** **(DoD-QSM)**, Final Version 3, 2006 Web site:
https://www.denix.osd.mil/denix/Public/Library/Compliance/EDQW/DoDV2_Jun02_Final.pdf.

Intergovernmental Data Quality Task Force (IDQTF). ***Uniform Federal Policy for Implementing Environmental Quality Systems.*** EPA/505/F-03/001, January 2003.
Web site: http://www.epa.gov/fedfac/documents/qualityassurance.htm

IDQTF. ***Uniform Federal Policy for Quality Assurance Project Plans***, IDQTF Final.
EPA/505/B-04/900, July 2004.
Web site: http://www.epa.gov/fedfac/documents/qualityassurance.htm

U.S. Army Corps of Engineers. ***Conceptual Site Models for OE and HTRW Projects,*** USACE EM 1110-1-1200, February 2003.
Web site: http://www.usace.army.mil/inet/information/usace-docs/eng-manuals/em1110-1-1200/toc.htm

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U.S. Army Corps of Engineers. ***Technical Project Planning (TPP) Process***. USACE EM 200-1-2, 31 August 1998.
Web site: http://www.usace.army.mil/publications/eng-manuals/em200-1-2/toc.htm

U.S. EPA. ***Data Quality Objectives Process for Hazardous Waste Site Investigations*** **(EPA QA/G-4HW)**. EPA/600/R-00/007, January 2000.
Web site: http://www.epa.gov/quality/qs-docs/g4hw-final.pdf

U.S. EPA. ***Guidance for the Data Quality Objectives Process*** **(EPA QA/G-4)**. EPA/600/R-96/055, August 2000.
Web site: http://www.epa.gov/quality/qs-docs/g4-final.pdf

U.S. EPA. ***Guidance for Quality Assurance Project Plans*** **(EPA QA/G-5)**. EPA/240/R-02/009, December 2002 or most recent revision.
Web site: http://www.epa.gov/quality1/qs-docs/g5-final.pdf

U.S. EPA. ***Guidance for Geospatial Data Quality Assurance Project Plans*** **(EPA QA/G-5G).** EPA/240/R-03/003, March 2003 or most recent version.
Web site: http://www.epa.gov/quality/qs-docs/g5g-final.pdf.

U.S. EPA. ***Guidance for Preparing Standard Operating Procedures*** **(EPA QA/G-6)**. EPA/240/B-01/004, March 2001 or most recent revision.
Web site: http://www.epa.gov/quality1/qs-docs/g6-final.pdf

U.S. EPA. ***Guidance for Quality Assurance Project Plans for Modeling*** (EPA QA/G-5M), EPA/240/R-02/007, December 2002 or most recent version
Web site: http://www.epa.gov/quality1/qs-docs/g5m-final.pdf

U.S. EPA. ***Guidance on Choosing a Sampling Design for Environmental Data Collection*** **(G-5S).** EPA/240/R-02/005, December 2002.
Web site: http://www.epa.gov/quality/qs-docs/g5s-final.pdf

U.S. EPA. ***Requirements for Quality Assurance Project Plans*** **(EPA QA/R-5)**, March 2001 or most recent revision. Web site: http://www.epa.gov/quality1/qs-docs/r5-final.pdf.

U.S. Navy. ***Navy Installation Restoration Chemical Data Quality Manual (IR CDQM)***, September 1999. Web site: http://enviro.nfesc.navy.mil/ps/guidance/ircdqm/.

U.S. Air Force. ***Quality Assurance Project Plan***, HQ Air Force Center for Environmental Excellence Version 3.1, July 2001 or most recent revision.
Web site: http://www.afcee.brooks.af.mil/products/techtrans/quality.asp

U.S. Army Corps of Engineers. ***Chemical Quality Assurance for HTRW Projects.*** EM-200-1-6, 10 October 1997, or most recent revision.
Web site: http://www.usace.army.mil/inet/usace-docs/eng-manuals/em.htm

U.S. Army Corps of Engineers. ***Requirements for the Preparation of Sampling and Analysis Plans***. USACE EM 200-1-3, 1 February 2001.
Web site: http://www.usace.army.mil/inet/usace-docs/eng-manuals/em.htm

U.S. Navy. ***Navy Environmental Compliance Sampling and Field Testing Procedures Manual***. NAVSEA T0300-AZ-PRO-010.
Web site: http://www.navylabs.navy.mil/Archive/TOC.html

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Tools

Field Environmental Decision Support (FIELDS)
Web site: http://www.epa.gov/region5fields/

Spatial Analysis and Decision Assistance (SADA)
Web site: http://www.tiem.utk.edu/~sada/

Visual Sample Plan (VSP)
Web site: http://dqo.pnl.gov/

Statutes and Regulations

Unregulated Contaminant Monitoring Rule (UCMR), 40 CFR Parts 9, 141, 142
Safe Drinking Water Act (SDWA), 42 U.S.C. § 300f et seq.

Clean Water Act (CWA), 33 U.S.C. § 1251 et seq.

Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), 42 U.S.C. § 9601 et seq.

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APPENDIX B

DOCUMENTATION OF PROJECT-PLANNING DOCUMENTS IN CONFORMANCE WITH THE UFP-QAPP

Part 2A of the Uniform Federal Policy for Quality Assurance Project Plans (UFP-QAPP) provides worksheets to help document key QAPP elements. A copy of Part 2A can be downloaded from the EPA Federal Facilities website (http://www.epa.gov/fedfac/documents/qualityassurance.htm). If information required by these worksheets is provided in other project planning documents (such as a sampling and analysis plan or work plan), the relevant sections should be referenced in the QAPP and the text attached, if possible.

PROJECT MANAGEMENT

- **Worksheet #1, Title and Approval Page** – Identifies the QAPP preparer, QA officer, and project manager(s), and provides spaces for approval signatures.
- **Worksheet #2, QAPP Identifying Information** – Describes the nature of the project, the regulatory program under which the QAPP is prepared, dates of scoping sessions, partners involved in preparing the QAPP, data users, and relationships to other QAPPs. The worksheet includes a table for documenting whether specific QAPP elements are relevant, based on the project scope and decisions to be made. If information is documented in a different project planning document, it should be noted in this worksheet.
- **Worksheet #3, Distribution List** – Identifies QAPP recipients, contact information, and document control numbers.
- **Worksheet #4, Project Personnel Signoff Sheet –** Documents that project personnel have read the relevant portions of the QAPP.
- **Worksheet #5, Project Organizational Chart –** Identifies reporting relationships between all organizations involved in the project.
- **Worksheet #6, Communication Pathways** – Describes pathways for soliciting and obtaining approval for any changes that may be necessary.
- **Worksheet #7, Personnel Responsibilities and Qualifications** – Identifies personnel associated with each organization and documents their responsibilities, education, and relevant experience.
- **Worksheet #8, Special Personnel Training Requirements** – Provides space for the documentation of any specialized training.
- **Worksheet #9, Project Scoping Session Participants Sheet** – Identifies participants in project scoping sessions.
- **Worksheet #14, Summary of Project Tasks** – Provides a brief summary of all the required project activities. This is an overview of the details provided in other worksheets.
- **Worksheet #16, Project Schedule/Timeline Table** – Documents the project schedule, including anticipated initiation and completion dates, deliverables, and deliverable due dates.

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PROJECT QUALITY OBJECTIVES

- **Worksheet #10, Problem Definition** – Provides questions that may help to guide the problem definition process, and space to summarize the answers to the questions. The problem-definition should include reference to the CSM. Documentation of the CSM can include site maps, narrative descriptions, graphics, and diagrams, if the situation warrants.
- **Worksheet #11, Project Quality Objectives/Systematic Planning Process Statements** – Provides a series of questions that can help to guide the PQO development process, and includes space to record the responses.
- **Worksheet #12, Measurement Performance Criteria Table** – Provides a table to record MPCs for sampling and analysis.
- **Worksheet #13, Secondary Data Criteria Limitations Table** – Provides a table to record secondary data criteria and limitations.
- **Worksheet #15, Reference Limits and Evaluation Table** – Provides a list of target analytes and the project-required action limits and LOQs established during project scoping. The table should also include method detection limits and LOQs documented in validated methods and achieved by individual laboratories.

SAMPLE DESIGN

- **Worksheet #17, Sampling Design and Rationale** – Requires that the project sampling approach be provided in appropriate detail. The rationale for the selection of sampling locations, matrices, and concentration levels must be provided. Reference to a map is permitted.
- **Worksheet #18, Sampling Locations and Methods/SOPs Requirement Tables** – Documents the sampling location ID number, matrix, depth, concentration level, total number of samples, rationale for the sampling location, and sampling SOP(s) references.

SAMPLING REQUIREMENTS

- **Worksheet #19, Analytical Requirements Table** – Documents the matrix, concentration, sample volume, container number and size, preservation requirements, and holding times for each analytical and preparation method. This ensures that the appropriate amount of sample is collected for the specified analytical procedure.
- **Worksheet #20, Field Quality Control Sample Summary Requirements Table** – Requires that the number and type of field quality control samples be summarized by matrix and concentration level. This information would include the number of field duplicates, blanks, proficiency testing samples, etc.
- **Worksheet #21, Project Sampling SOP Reference Table** – Requests that all sampling SOPs associated with the project be listed and asks whether any SOPs have been modified for the project. The types of sampling SOPs include sample collection and preservation; sampling equipment cleaning and decontamination; equipment inspection, testing, and maintenance; and sample handling and custody.
- **Worksheet #22, Field Equipment, Calibration, Maintenance, Testing, and Inspection Table** – Identifies all field equipment and instruments, other than analytical instrumentation, that require calibration, maintenance, testing, or inspection. The frequency of each activity, acceptance criteria,

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and corrective action must also be documented. The SOP reference number for each type of equipment must be provided.

- **Worksheet #26, Sample Handling System** – Documents the components of the project-specific handling system. Documentation includes recording the personnel, along with their organizational affiliation, who are responsible for ensuring the proper handling, custody, and storage of field samples at the time of collection, at laboratory delivery, and at final sample disposal.
- **Worksheet #27, Sample Custody Requirements** – Requires a description of each procedure used for sample custody and integrity. These include field sample custody procedures, laboratory sample custody procedures, sample identification procedures, and chain-of-custody procedures.

ANALYTICAL REQUIREMENTS

- **Worksheet #23, Analytical SOP Reference Table** – Documents all analytical SOPs that will be used for either on-site or off-site analysis. Each SOP should be identified as a screening or a definitive analytical method and should indicate whether it has been modified for project work.
- **Worksheet #24, Analytical Instrument Calibration Table** – Identifies all analytical instrumentation that requires calibration. Identifies the SOP number and documents the calibration frequency, acceptance criteria, and corrective action requirements.
- **Worksheet # 25, Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table** – Identifies all analytical instrumentation that requires maintenance, testing, or inspection. Identifies the SOP number and documents the frequency, acceptance criteria, and corrective action requirements.
- **Worksheet #28, QC Samples Table** – For each sampling technique, analytical SOP, matrix, and concentration level, documents the type of QC sample, frequency, acceptance limits, corrective action, responsible person, data quality indicators, and measurement performance criteria.

DATA MANAGEMENT AND DATA REVIEW

- **Worksheet #29, Project Documents and Records Table** – Identifies all of the documents and records that will be generated for all project phases, including sample collection, field measurement, on-site and off-site analysis, and data assessment.
- **Worksheet #30, Analytical Services Table** – Documents all organizations and laboratories providing analytical services. This includes on-site and off-site screening and definitive analytical work. Subcontract laboratories should be identified if they will be doing any analytical work.
- **Worksheet # 34, Sampling and Analysis Verification (Step I) Process Table** – Describes all data verification processes. Identifies how verification will be conducted and what documentation is required.
- **Worksheet # 35, Sampling and Analysis Validation (Steps IIa and IIb) Process Table** – Describes that data validation process. Identifies each input to the validation process, the documentation required, and the person responsible.
- **Worksheet # 36, Sampling and Analysis Validation (Steps IIa and IIb) Summary Table** – Identifies the matrices and concentration levels for each validation criteria that will be used to validate the data.
- **Worksheet # 37, Data Usability Assessment** – Describes the procedures, methods, and activities that will be used to determine whether the data are of sufficient quality and quantity to support the

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environmental decisions. Discusses how the issues of data quality will be addressed and how any limitations on data use will be managed.

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APPENDIX C

AGREEMENTS TO BE REACHED DURING PROJECT SCOPING

Agreements to Be Reached	Information Needed
What is the purpose for conducting perchlorate sampling and analysis?	• A concise description of all decisions that need to be made.
Where are potential source areas for perchlorate?	• Past and current uses of the site • Past and current disposal practices • Information on past and current uses of surrounding land (DoD and non-DoD) • Relevant data on naturally-occurring perchlorate
If a release has occurred, what are the potential exposure pathways?	• Physical site characteristics • Climate conditions • Identification and locations of potential receptors
What are the relevant action/decision levels?	• Regulatory requirements • Permit limits • Analytical method reporting limits
Is there any existing data? Can it be used for current decision-making?	• The purpose for collection • Sampling/analysis methods used and method performance criteria • Data usability assessment
What analytical method should be used?	• Site-specific action level, regulatory limit, or permit limit • Measurement Performance Criteria
What type of data review will be required?	• Intended uses and users of the data • Importance/visibility of decisions to be made • Likelihood that data could be challenged • The manner in which limitations on the data will be conveyed to decision-makers
What are the next steps if site-specific decision/action levels are exceeded?	• Permit requirements • Current regulatory requirements (federal and state) • DoD and Component-specific policy

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APPENDIX D

GUIDANCE ON DEVELOPING CONCEPTUAL SITE MODELS FOR PERCHLORATE INVESTIGATIONS

This appendix provides information to assist in developing Conceptual Site Models (CSM) for environmental restoration/cleanup sites and training ranges, where analytes of concern include perchlorate. The development of CSMs is not required for compliance monitoring. The CSM is the set of hypotheses about the following:

- Sources – the source of perchlorate contamination at a site
- Pathways – the mechanisms that may lead to the release and transport of perchlorate contamination. For perchlorate, a primary pathway of interest is from the ground surface to groundwater aquifers.
- Receptors – the humans and ecological systems that may be exposed to the contamination, and the mechanisms that may lead to their exposure. The exposure mechanism of concern for perchlorate is ingestion.

Developing a CSM by systematically addressing the site-specific sources, pathways, and receptors provides a structured approach to organizing available information about a site. The CSM should be updated as new information is uncovered. The effort that a project team puts into developing this framework for understanding a site at the outset of an investigation will provide a solid base on which to build a perchlorate investigation project plan.

For comprehensive general guidance on the development of CSMs, consult the U.S. Army Corps of Engineers' *Conceptual Site Models for OE and HTRW Projects.* The Triad website, http:www.triadcentral.org, discusses the use of CSMs in a dynamic planning process.

Identifying Sources of Perchlorate Releases

The first step in determining whether a perchlorate release may have occurred is to determine whether perchlorate was used at that site. Historically, perchlorate has been manufactured as salts of ammonium, potassium, magnesium, and sodium. These perchlorate salts have been used as oxidizer components for solid rocket fuels and as explosive components for both military munitions and civilian uses.

Other uses of perchlorate salts have included pyrotechnics (fireworks), flares, and air bag inflators. Perchloric acid is used in various laboratory applications, as well as in various manufacturing processes. The use of perchlorate containing minerals in the production of some fertilizers may be a key factor in non-point-source perchlorate findings. Sodium chlorate, used as a defoliant and nonselective herbicide, may contain perchlorate as a by-product of the manufacturing process. Sodium hypochlorite and other chlorine compounds commonly used for water disinfection and bleaching may also contain traces of perchlorate. In addition, perchlorate is a naturally occurring compound in some types of minerals. For a more comprehensive discussion of uses and sources of perchlorate, the reader should refer to *Perchlorate: Overview of Issues, Status, and Remedial Options*, September 2005, published by the Interstate Technology and Regulatory Council (ITRC).

It is important to note that while this appendix lists activities and circumstances that may lead to a perchlorate release, the information presented does not imply that perchlorate releases would have occurred on every site where these activities took place. Each project team will need to identify site-specific sources and establish the magnitude of any background levels of perchlorate by developing a

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CSM that takes into account *all* the possible sources of perchlorate release. This appendix describes some situations in which perchlorate releases are known to have occurred, for both DoD and non-DoD-related activities, as well as provides information about the emerging understanding of naturally occurring perchlorate. It also provides guidance on developing site-specific models for perchlorate release and suggests sources of information that can help to describe those releases.

Perchlorate Releases Related to DoD Activities

This section provides suggestions regarding activities on DoD sites that could result in perchlorate releases and gives potential locations of those releases. ***The simple fact that one or more of these activities occurred, however, should not be interpreted as evidence that perchlorate has been released.*** Perchlorate releases may have occurred at sites where the following activities took place:

- The manufacture, storage, or disposal of perchlorate salts, perchlorate-containing propellants, rocket fuels, explosives, perchlorate containing munitions, munitions components, or training devices. These activities have occurred primarily at ammunition plants, arsenals, and depots.
- Research, development, testing, and use of perchlorate containing propellants, rocket fuels, explosives, munitions, or munitions components.
- Training with perchlorate containing munitions or training simulators.

DoD munitions, munitions components, and training devices that may have contained perchlorate include the following:

- Solid fuel rockets
- Mines
- Torpedo warheads
- Smoke-generating compounds
- Signal flares
- Parachute flares
- Star rounds for pistols (illumination rounds)
- Thermite-type incendiaries
- Tracer rounds
- Incendiary bombs
- Fuzes
- Jet-assisted takeoff (JATO) devices
- Training simulators

In addition to DoD technical manuals and bulletins for specific munitions, the Munitions Items Disposition Action System (MIDAS) database contains detailed information on the constituents (propellants, explosives, and pyrotechnics) found in specific munitions, although the database does not usually contain information on obsolete munitions.[1]

[1] MIDAS database is restricted to username and password holders. The web site for the database is https://midas.dac.army.mil.

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Perchlorate Releases Related to non-DoD Activities

A number of documented perchlorate release sites are owned by other (non-DoD) Federal agencies, including sites related to explosives research at the Department of Energy's national laboratories and one NASA site. The following are other potential non-DoD sources:

- Commercial blasting (for construction) with perchlorate-containing explosives[2]
- Use of perchloric acid in manufacturing processes
- Perchlorate-containing fertilizer
- Perchlorate-containing sodium chlorate used as a herbicide
- Commercial manufacture of perchlorate salts or perchlorate-containing items (e.g., pyrotechnics and flares)

Natural Occurrence of Perchlorate

Perchlorate may occur in fertilizer produced from nitrate ores from the Atacama Desert of northern Chile. Recent work by the U.S. Geological Survey (USGS) has indicated that perchlorate can also occur naturally in other minerals and materials.[3] Perchlorate has been detected in samples of the mineral hanksite, in sylvinite (potash) ore, and in a number of playa crust materials. It is not currently known whether the perchlorate occurs as a potassium or sodium salt, and whether it is an impurity in the crystal structure of another mineral or is trapped as an anion within fluid inclusions in minerals that form these materials.

Research is being undertaken to better define the circumstances under which perchlorate may naturally occur. A recent study conducted by Texas Tech University suggests that it can be produced atmospherically.[4] Additional research is needed to determine mechanisms that may introduce naturally occurring perchlorate into groundwater or surface water, thereby making it a potential source of background contamination. A comprehensive discussion on the natural occurrence of perchlorate is included in the ITRC document, September 2005.

Development of Site-Specific CSM for Sources of Perchlorate Releases

If a perchlorate release is suspected at a DoD site, research should be undertaken to determine the types of activities that led to the releases, the types of munitions associated with the releases (if applicable), and the potential magnitudes of those releases. The following sources of information can be used:

- The technical specifications (e.g., technical manuals, technical pamphlets, or special weapons ordnance manuals) for the munitions in question. These specifications provide the amount of perchlorate salt in the propellant or filler.
- Ammunition request and issue documents (e.g., DD 581 forms). These forms provide information about the number of perchlorate-containing munitions requested for a training or research facility. They also provide information about the number of munitions issued for use in training activities.

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[2] Carrie Simmons, "Blasting May Have Contaminated Town Water," *Westford Eagle* (Mass.), 10 September 2004.
[3] This discussion is based on the information in *Preliminary Analyses for Perchlorate in Selected Natural Materials and Their Derivative Products*, Orris et al., U.S. Geological Survey Open-File Report 03-314, 2003, at http://geopubs.wr.usgs.gov/open-file/of03-314/OF03-314.pdf.
[4] P.K. Dasgupta et al., "The Origin of Naturally Occurring Perchlorate: The Role of Atmospheric Processes," *Environmental Science & Technology* 39(6)*: 1569-75.*

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- Disposal reports from Explosive Ordnance Disposal Detachments associated with the facility.
- Records associated with demilitarization, recycling, and destruction of munitions.
- For manufacturing facilities: technical documents, specifications, and disposal reports for the compounds or munitions manufactured.
- For research and test facilities: technical and operational evaluation plans. Operational evaluation plans describe the field evaluation of new munitions. The evaluation may have occurred at a "normal" training facility, that is, a facility not specifically related to research and testing.

In addition to this information, historical facility maps should be used to begin to determine the likely locations of potential releases. For manufacturing facilities, locations of potential releases will include wastewater impoundments, other areas where perchlorate-containing process fluids are used or disposed, areas that receive runoff from manufacturing operations that use perchlorate salts, and areas where disposal of dry perchlorate wastes occurred. For training facilities, such locations may include firing points and target areas. For all facilities, disposal areas (e.g., open burn/open detonation areas) will be likely locations for potential perchlorate releases.

Table D-1 outlines some of the activities, primary sources, and release mechanisms that can lead to perchlorate releases. These are provided to help project teams determine whether a particular military-related activity may have resulted in a release, and to suggest some types of activities and areas that might warrant investigation.

Table D-1: Activities, Sources, and Mechanisms That Could Lead to Perchlorate Releases

Activity	Primary Sources	Release Mechanism
Manufacturing	Wastewater impoundments	Leaching, surface water runoff
	Storage areas	Spills, surface water runoff (outside storage)
	Wastewater outflow points	Spills, surface water runoff, leaching, septic systems
	Open burn areas	Incomplete burning and associated leaching
	Landfills	Precipitation and leaching of buried waste material
Storage	Disposal facility for retrograde propellant/fuel	Discharge of washout for disposal operation
	Open burn/open detonation facilities	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching
Research and Development	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching
	Wastewater impoundments	Leaching, surface water runoff
	Wastewater outflow points	Spills, surface water runoff, leaching, septic systems
	Landfills	Precipitation and leaching of buried waste material
	Recycling operations	Mishandling and spills, washout
Testing	Target area	Incomplete detonation or deflagration after deployment
	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching
	Firing points	Burning of excess propellant, burial of excess munitions
Training	Target areas	Incomplete detonation or deflagration after deployment
	Open burn/open detonation areas	Incomplete detonations, kickouts from open detonation, incomplete burning and associated leaching
	Firing points	Burning of excess propellant, burial of excess munitions

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Conceptual site models of sources for perchlorate release should also address potential sources of anthropogenic perchlorate contamination not related to DoD activities. These sources could include any non-DoD Federal facilities or commercial facilities in the vicinity that have been involved in perchlorate-related manufacture, storage, disposal, or research and testing; commercial facilities where perchloric acid is used; the use of fertilizers of herbicides containing perchlorate; and, in the Southwest, the use of Colorado River water for irrigation or the infiltration of irrigation water into local aquifers. Conceptual site models should also consider potential natural occurrences of perchlorate from minerals (e.g. caliche) in arid and semi-arid areas.

Identifying Migration Pathways

Once the project team suspects or confirms a perchlorate release, it should analyze potential migration and exposure pathways to provide focus for further planning. Because of the high solubility and low sorption characteristics of perchlorate, the primary media of concern will be groundwater and surface water, although soil may also be of concern under some circumstances. The following sections describe some common scenarios for the transport of perchlorate into surface water and groundwater, the circumstances under which perchlorate contamination might be present in soils, and guidance and resources for constructing a site-specific analysis of perchlorate migration pathways.

Perchlorate in Groundwater and Surface Water

The presence of perchlorate has been documented in both groundwater and surface water, although the majority of the reported detections have been for groundwater. Surface water may be the final medium of concern in the investigation, or it may be a pathway to groundwater. The primary pathways of perchlorate into surface waters are either through direct release (e.g., as a wastewater discharge), or through soil contamination that is dissolved by precipitation and transported via surface runoff into nearby water bodies. Surface water may also be contaminated by perchlorate-containing groundwater discharging to a surface water body.

Perchlorate can enter groundwater through various pathways. The primary pathways include the following:

- Residual contaminants (salts) at the ground surface dissolve by contact with water (e.g., precipitation) and then migrate through the underlying media to the groundwater aquifer.
- Buried contaminants dissolve by contact with water moving downward through the vadose zone or by contact with shallow groundwater.
- Contaminated surface waters enter groundwater flow systems in recharge areas in a number of ways: by recharge to groundwater due to natural hydraulic gradients, by infiltration induced by pumping wells near the surface water body, by flowing down abandoned boreholes and improperly sealed wells, or by seeping into solution conduits in karst settings.
- Perchlorate-contaminated surface water is used for artificial recharge of groundwater.
- Surficial aquifers contaminated as a result of any of the mechanisms described above serve as a source of contamination for deeper aquifers.

Climatic conditions can affect the transport of contaminants released at the ground surface to an aquifer and then through the aquifer. Climate affects weathering processes, which will influence the hydraulic characteristics (i.e., soil texture, soil type, and permeability) of the matrix. Climate will also affect the amount of water recharging the aquifer and, therefore, the groundwater flow rates. In arid or semi-arid

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regions, evaporation rates often exceed precipitation, resulting in a negative infiltration rate. Precipitation infiltrates short distances into the unsaturated zone before being removed by evaporation. This can result in the concentration of residual salts (caliche or hardpan layers) and surface contaminants in evaporative horizons in the shallow subsurface. Significant changes in land use may substantially alter local recharge conditions. Industrial, agricultural and residential development in arid regions can result in new localized sources of recharge to groundwater due to concentrated stormwater runoff, wastewater discharges, irrigation, etc. These increases in recharge may mobilize naturally-occurring and anthropogenic salts in the vadose zone soils and result in impacts to groundwater that would not occur under natural recharge conditions.

Once the contaminant enters the aquifer, factors that will affect its transport in the aquifer include the chemistry, temperature, hydraulic conductivity and transmissivity, hydraulic gradient, flow directions, dilution, dispersion, diffusion, retardation potential, pumping stresses, recharge, regional discharge, aquifer porosity, spatial extent and orientation of the aquifer, and structural geologic features. When dissolved, the perchlorate ion will migrate with the same velocity as the groundwater flow.

Natural Attenuation

Once it is dissolved in groundwater, perchlorate is very stable, and natural degradation is not generally expected to occur in aerobic conditions. Studies have shown, however, that natural attenuation can occur under anaerobic conditions, when sufficient carbon material, the right kind of microbes, and sufficient residence times exist. Research has been undertaken to determine the extent to which these conditions occur naturally and to identify useful methods for recognizing and monitoring natural attenuation of perchlorate when it does occur. In proceeding through the investigation, project teams must consider whether changes in perchlorate concentration occur as a result of dilution during seasonal changes or natural attenuation.

Seasonal Variations in Concentration

Responses of aquifers to seasonal changes are a more common cause of changes in perchlorate concentrations than natural attenuation. The response to these seasonal changes can be observed as a direct or indirect correlation. The direct correlation between weather and the contaminant concentration is observed when the water table rises or falls and the contamination concentration changes proportionally. The indirect correlation is demonstrated as a delayed response that is observed either as an increase or as a decrease in the concentration that cannot be immediately correlated to a seasonal change. The indirect correlation may be due to an external man-made or induced factor that may also be indirectly tied to seasonal variation.

The direct correlation relates to how perchlorate is transported into the aquifer matrix with seasonal change. The correlation will be specific to the region in question. For example, desert regions are characterized by sparse, heavy rains during monsoonal periods. In contrast, the Eastern states typically receive rain during most of the year. If perchlorate is being transported from the source area by dissolving in rainwater and infiltrating into the aquifer, then seasonal increases in concentration may be more pronounced in the arid regions.

The indirect correlation relates to how weather affects other modes of transport. For example, during dry conditions irrigation water may be applied to croplands. If the irrigation water is from a contaminated surface water source, such as the Colorado River, then during the irrigation period, when plant growth is

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slow, the excess irrigation water could infiltrate through the vadose zone and recharge the underlying aquifer. This may be manifested as a seasonal spike in the groundwater contaminant concentration beneath a field. This spike may decrease as the plant roots develop and begin to take up water at higher rates during evapotranspiration. If there are multiple plantings (e.g., lettuce), then this pattern may be repeated with each planting, growth, and harvest cycle. The plants have been observed to take up the perchlorate into the cell structures, which results in contaminated plant matter. Thus, groundwater samples collected in these settings may exhibit seasonal changes in response to irrigation practices, which may be indirectly correlated to climatic conditions.

In areas with large deciduous trees, the growth of the leaf canopy and consumption of water during the summer can cause a decline in the water table. Consumptive use occurs when the tree roots penetrate into the vadose zone or the capillary fringe of the aquifer, take up water during the summer growth cycle, and evapotranspirate this water through the leaves. If this water is contaminated with perchlorate, then perchlorate can become concentrated in the trees' leaves and stems. Woody plants store perchlorate in their leaves and biodegrade it in their root zones, so the concentration in soils with a large number of trees might decrease.[5] The consumptive use of water by various plants and tree species can be determined through value estimates in the literature or by actual measurement.

Density-Driven Migration of High Concentration Perchlorate Brines

Due to the extremely high solubility of many perchlorate salts, it is possible to form solutions of those salts in water with densities significantly higher than that of groundwater. Research into migration of brine solutions in the subsurface indicates that a density difference between the brine and ambient groundwater of 0.8 mg/cm^3 can result in migration of the brine according to gravitational forces as opposed to groundwater gradients.[6] Situations where this may occur are limited to those such as the discharge of concentrated solutions from manufacturing operations or the concentration of perchlorate solutions through evaporation. If such brine solutions enter the subsurface, mixing of the brine with groundwater may be very limited, and the movement of brines will be controlled by gravity and the subsurface topography of low permeability confining layers.[7] Perchlorate brine may accumulate on or in confining layers where the rate of its release into groundwater is limited by diffusion. In the few instances where high-density brine solutions may be present, the solution should be sampled in the same manner as a DNAPL (i.e. vertical profiling of aquifer concentrations and screening selected wells in areas of likely brine accumulation at the bottom of the aquifer).

Perchlorate in Soils

Perchlorate is extremely soluble in water, so precipitation (rainfall and snowmelt) may quickly deplete the ground surface contaminant mass (source area). Sufficient rainfall will ultimately transport these contaminants, as dissolved salts, away from the source area. Thus, the basis for suspecting soil contamination by perchlorate will depend on site-specific details such as the amount of suspected residual

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[5] Laboratory Characterization of Phyto-transformation Products of Perchloroethylene (PCE), Trichloroethylene (TCE) and Perchlorate, Final Report by Valentine A. Nzengung. Web site: http://clu-in.org/download/contaminantfocus/perchlorate/Nzengung1.html.

[6] Schincariol, R.A.; Schwartz, F.W. "An experimental investigation of variable density flow and mixing in homogeneous and heterogeneous media." *Water Resources Research* 1990, 26, 2317-2329.

[7] Flowers, T.C., Hunt, J.R., "Long-Term Release of Perchlorate as a Potential Source of Groundwater Contamination ", *Perchlorate in the Environment*, edited by Urbansky, 177-188, Kluwer Academic/Plenum Publishers, New York, 2000

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contaminant mass at the ground surface, whether the source area is an active or continuous problem, the surface topography and geology, and the climatic conditions. Perchlorate does not adhere to soil particles; however, dissolved perchlorate can be trapped within the soil pores by capillary forces of surface tension (molecular attraction) or become trapped in dead-end pore spaces. Perchlorate can be retained in some propellant matrices and distributed in soil, and thus not be immediately dissolved. The project team should consider this phenomenon, because some of the source investigations performed by manufacturers have proved this to be a source of perchlorate in soil, particularly in areas with little precipitation.

In most cases, the perchlorate sources have been directly released to the soil through disposal or training activities. Another potential pathway to soil is the accumulation of perchlorate at the ground surface in areas that are subject to evaporation or to evapotranspiration and where perchlorate-laden groundwater discharges at the surface. The perchlorate can precipitate as salts or bioaccumulate in plant matter. [8] [9]

Dissolved perchlorate can be held between soil particles as a result of the specific retention capacity of the soil matrix. Within the vadose zone, for example, retention capacity ranges from 0.01 percent for granite, to 3 percent for sand, to 48 percent for clay. Retention capacity can provide a general indicator as to whether perchlorate can be retained within the soil column. Under most circumstances, soil columns with high specific retention capacities should be considered as media of concern for perchlorate.

In arid environments, the transport of perchlorate to groundwater will be limited by the net infiltration derived from precipitation. When evapotranspiration is high, dissolved perchlorate may migrate only a short distance through the soils before the water bearing it evaporates. The precipitated perchlorate may accumulate at shallow depths within subsurface caliche deposits or be held within the soil matrix. Typically, there will be little adsorption of the perchlorate in the soil.

Perchlorate in soils will remain either as precipitated salts that are present between the soil particles or as dissolved perchlorate in the interstitial pore water. Perchlorate in soil should be considered at sites with any of the following conditions:

- Large quantities of perchlorate have been used, disposed of, or burned at the site in the past.
- A perchlorate source is likely to be present, and the soils and vadose zone matrix have an affinity to retain interstitial water.
- The climatic conditions result in high evapotranspiration rates.
- Perchlorate-laden groundwater or surface water can discharge to the ground surface and are subject to high evaporation rates.
- A perchlorate source is ongoing because of on-site testing, use, or disposal.
- Groundwater contamination is elevated and suggests the presence of ongoing soil contamination emanating from an unknown source area.

Development of a Site-Specific Conceptual Model of Perchlorate Pathways

To fully understand the nature of the geologic setting and the variables that contribute to contaminant transport at a site, the investigator should consult county, State, and Federal agencies to gather available

[8] FDA study "Exploratory Data on Perchlorate in Food," at http://www.cfsan.fda.gov/~dms/clo4data.html.

[9] Bosque-Leon Watershed Study, U.S. Army Corps of Engineers, Fort Worth District

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information on the climatic conditions, soil morphologies, topography, hydrology, and geologic conditions for the area of interest. The following are typical sources of information:

- USGS and State Geological Surveys at http://www.usgs.gov
- National Climatic Data Center at http://www.ncdc.noaa.gov
- Department of Natural Resources and water resources agencies for the States
- U.S. Department of Agriculture–Forest Service at http://www.fs.fed.us and Natural Resources Conservation Service–Soils at http://soils.usda.gov
- U.S. EPA and States' departments of environmental protection
- County and regional water supply agencies
- Private consulting firms (hydrogeological and engineering)
- Private industries (mining, quarrying, well drilling, blasting, etc.)
- Professional associations (National Groundwater Association, Geological Society of America, and others)
- Local colleges and universities (soil science, agriculture, geology, hydrogeology, and civil engineering programs)

Identifying Receptors

The exposure mechanism of concern for perchlorate is ingestion of contaminated drinking water and food containing perchlorate. Researchers are just beginning to collect data on perchlorate contamination of produce and hays. Indications are that plants readily absorb perchlorate present in their growth media.[10] Studies also show that dairy cows fed hay that contains perchlorate will produce milk that contains perchlorate.[11]

The information indicates that the most likely complete human exposure pathway will be through drinking water, but it also shows that human exposure through contamination of water used to irrigate food crops (both for humans and for dairy cows, if not other livestock) must also be considered.

If drinking water contamination is suspected at a site, one potential source of confirmatory evidence is the information from the UCMR testing. Investigators should check the current UCMR database for public water systems (PWS) in the vicinity of DoD sites that tested for and may have detected perchlorate.

Although consulting the available information about perchlorate in public water systems is helpful, the team developing a CSM must remember that documented perchlorate presence or absence is only part of the picture. If a PWS has detected perchlorate, it does not mean that the source was DoD-generated, and if a PWS adjacent to a site with a known release has not detected perchlorate, it does not mean that the drinking water pathway will not be completed in the future. It may only mean that the contamination has not yet reached the PWS water source. The latest UCMR database can be found through the EPA Office of Groundwater and Drinking Water web site.

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[10] For example, see the recent FDA study "Exploratory Data on Perchlorate in Food," at http://www.cfsan.fda.gov/~dms/clo4data.html.

[11] *Perchlorate in Drinking Water: A Science and Policy Review* (Chapter 3) contains a succinct summary of the current understanding of the occurrence of perchlorate in food. The document was published by the Urban Water Research Center at the University of California, Irvine, in June 2004 and is available from http://www.urban-water.uci.edu.

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APPENDIX E

GUIDANCE ON DEVELOPING PROJECT QUALITY OBJECTIVES FOR PERCHLORATE INVESTIGATIONS

This appendix provides guidance on developing site-specific project quality objectives (PQOs) for perchlorate sampling and testing. PQOs are qualitative and quantitative statements developed through the systematic planning process. They describe the types, amount, and quality of data that will be necessary to support defensible decisions. The development of PQOs encompasses the following steps:

Step 1: Define the environmental problem and describe decisions to be made.

Step 2: Identify and describe the acceptable level of uncertainty for those decisions.

Step 3: Specify the measurement performance criteria (i.e., the data quality) required to support the acceptable level of uncertainty.

Step 4: Determine the appropriate uses and limitations of other available data, that is, data that are not generated in the current investigation but that may be used in making the current decision.

Step 5: Determine the types and quantity of new data required to support the decisions.

The PQOs are the entire set of qualitative and quantitative statements that result from each of these five steps. Although the development of PQOs is discussed as a linear progression, in practice it is iterative; therefore, project teams should be prepared to revisit prior steps if the results of step 5 prove to be inadequate. The major emphasis of this chapter will be on developing PQOs for environmental investigations. The development of PQOs for regulatory compliance sampling is much less complex because the permit or regulation generally dictates the type, quantity, and quality of data to be collected and reported.

Step 1: Define the Environmental Problem and Describe Decisions to Be Made

The general problem statement for perchlorate investigations is the following: Is there an unacceptable risk to human health (or the environment) as a result of a DoD release of perchlorate? Developing a site-specific conceptual site model (CSM), as described in Appendix D, is the initial step in addressing this problem. The tasks involved in developing the CSM make it possible to identify what is known and what additional information is needed to answer the following questions:

- Has a perchlorate release occurred, or is it likely to occur?
- If a release has occurred, or one is likely, are there complete exposure pathways to human receptors?
- If there are complete exposure pathways, then how much perchlorate is present?

Breaking the general problem statement down into a series of more specific problems or questions allows the investigation to proceed in a logical sequence. At each stage of the investigation, the CSM should be updated to reflect the latest information.

In a "dynamic" work plan, the CSM is updated in real time as the field work progresses. This allows the work plan to be modified or refined in the field as the understanding of the problem becomes more complete. It also allows course corrections if the field work reveals that any of the initial assumptions were incorrect.

Has a Perchlorate Release Occurred?

The project team may not need to perform sampling and testing to determine whether a perchlorate release is likely to have occurred at a site. Historical research may provide a sufficient basis for

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concluding that perchlorate either has or has not been released at the site. If historical research is inconclusive, then preliminary sampling and analysis may need to be performed to screen for perchlorate in various media.

As discussed in Appendix D, project teams will need to make informed judgments about the completeness and accuracy of historical records, including existing analytical data. The following environmental questions should be posed:

- Could past or current uses of the site result in the release of perchlorate?
- What do the historical records indicate about the possible magnitude of perchlorate use and/or release at the site?
- Do historical records indicate potential locations for release (e.g., wastewater impoundments or disposal areas)?

The problem statement and decision statements ("if/then" statements) are used to guide the investigation so that it proceeds in a logical sequence of activities. The following are some examples:

Problem Statement:

Historical research will be conducted for [specified time period and area of interest] to determine whether it is likely that perchlorate was released at the site.

Decision Statements:

If an examination of [specified set of records] indicates that perchlorate was stored at this site between [specified date] and the present, then additional research will be conducted to determine whether there are potential on-site disposal or release locations.

If research provides evidence that perchlorate was not used or stored at the site between [specified date] and the present, then no further investigation will be conducted.

If research provides evidence of on-site release or disposal of perchlorate, then sampling and analysis will be conducted to determine whether perchlorate is present in soil, groundwater, or surface water at concentrations that could present an unacceptable risk to human health.

If a Release Has Occurred, Are There Complete Exposure Pathways to Human Receptors?

Once the occurrence of a release has been established, investigations necessary to determine exposure pathways may require further records searches, sampling and testing for perchlorate in the appropriate media, and the collection of site-specific hydrogeological data. Environmental questions that can help define this problem include the following:

- Is there perchlorate in the soil?
  - What is the approximate extent of contamination?
  - What is the depth to groundwater?
- Is there perchlorate in the surface water?
  - Is there a pathway from the surface water to the groundwater?
- Is there perchlorate in the groundwater?

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  - What are the boundaries of the perchlorate plume?
  - At what rate is the plume spreading?

- Can perchlorate be transported off-site in the surface water or groundwater?
- Does the surface water or groundwater serve as a source or potential source for drinking water?
- Is surface water or groundwater used for irrigation?

The following are examples of a problem statement and decision statements for this phase of an investigation:

Problem Statement:

A groundwater investigation will be conducted to determine whether there is a complete groundwater pathway from [specified source] to [specified receptor].

Decision Statements:

If groundwater modeling studies based on [specified set of data] indicate the potential for a complete pathway from [specified source] to [specified receptor], then groundwater samples will be collected and analyzed from [specified area intercepting suspected pathway].

If modeling studies indicate no complete pathway, then groundwater will be excluded as a medium of concern.

If groundwater samples are collected and all perchlorate results are below [site-specific screening level or action level], then no further samples will be collected, and groundwater will be excluded as a medium of concern.

If groundwater samples are collected, and the result of any sample exceeds the [site-specific screening or action level], then further studies will be designed and conducted to characterize the suspected source area and groundwater quality.

If There Are Complete Exposure Pathways, How Much Perchlorate Is Present?

If a complete exposure pathway has been confirmed, it will be necessary to determine the amount of perchlorate to which humans might be exposed and to compare this to the established reference dose.

The primary questions for quantifying perchlorate are the following:

- What is the concentration of perchlorate in each medium of concern?
- What is the site-specific concentration of concern (action level) for each medium (e.g., soil, surface water, and groundwater)?

The following are examples of a problem statement and decision statements for this phase of an investigation:

Problem Statement:

Groundwater samples will be collected from [specified locations] to determine whether the perchlorate concentration exceeds the [site-specific, risk-based] action level of [X ppb].

Decision Statements:

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If the average concentration of perchlorate in groundwater samples collected from [specified locations] is greater than or equal to the action level, then the aquifer will be excluded from use as a drinking water supply until a final remedy is developed and implemented.

If the average concentration of perchlorate in groundwater is between [X ppb] and the action level, then quarterly monitoring will be conducted for [specified time period].

If the average concentration of perchlorate in groundwater is less than [X ppb], then no further action will be taken.

Step 2: Identify the Acceptable Level of Decision Uncertainty

The primary factor to consider in determining the acceptable level of uncertainty is the importance of the decision. In other words, what are the potential consequences of making a wrong decision, in terms of human health, the environment, and project resources? The team should consider the following:

- **The resources available to complete the project –** Given available project resources, what level of uncertainty is achievable?
- **The expected difficulty in discerning between the different decision conditions** – For example, is the actual concentration expected to be close to the selected action level? Or is it expected to be so much higher or lower than the action level that it will be straightforward to assess the results against the action level?
- **The variability of the data being used to make the decision –** Both site heterogeneity and variability introduced during the sampling and analysis processes contribute to overall uncertainty.

Decision Uncertainty for Investigating Perchlorate Releases

To determine the tolerable level of uncertainty for this stage of the investigation, the project team should consider the following issues:

- What are the limitations of the existing data used to generate the CSM?
  - If there is a strong indication (i.e., records are judged to be relatively complete and accurate) that perchlorate was used at the site, and the locations of potential source areas (e.g., open burn areas) are known, then the primary source of decision uncertainty in verifying the presence or absence of a release will be the capability of the analytical method to detect and quantify perchlorate in the media of concern at the concentration of concern.
  - If current information indicates that it is unlikely that perchlorate was used at the site, then the project team must determine what kind of data must be collected to confirm, at an acceptable level of uncertainty, that perchlorate was not released at the site.
  - If little is known about the site, or if existing information is deemed unreliable, then the level of uncertainty will be influenced by the availability of records to help confirm perchlorate use and identify possible release locations. Filling these data gaps may require a more rigorous sample design. What effect would a release have on receptors? The more likely it is that receptors could be exposed, the lower the tolerance for uncertainty in determining whether perchlorate was released.
- If sampling and analysis are to be done, which analytical methods should be used? Does the laboratory's SOP include procedures for managing potential matrix interference? The achievable level of uncertainty will be determined in part by matrix characteristics.

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- With regard to the site-specific action or decision levels, will the analytical method be able to distinguish contaminated samples from uncontaminated samples?

The following are some examples of PQOs designed to control measurement uncertainty:

- *Groundwater samples from the six existing monitoring wells at ABC Air Force Base will be collected and analyzed for perchlorate using EPA Method 331.0. Assuming the data are normally distributed, if the 95% Upper Confidence Limit (UCL) of the mean concentration exceeds the State action level (AL) of X ppb, then a groundwater investigation will be initiated to evaluate whether complete exposure pathways exist.*
- *If the 95% UCL of the mean concentration is less than the State AL, a second round of samples will be collected in 6 months to verify the absence of impacts from perchlorate.*
- *If the 95% UCL of the mean concentration is less than the State AL for both rounds of groundwater sampling, then no further action will be taken.*

These PQOs address several sources of measurement uncertainty: geospatial variability in aquifer characteristics, sampling uncertainty, analytical uncertainty, and seasonal changes.

Decision Uncertainty for Investigating Exposure Pathways

To determine the tolerable level of uncertainty for this stage of the investigation, the project team should consider the following issues, in addition to the issues discussed above:

- How well is local geology/hydrogeology understood? For example, are there complicating factors (e.g., Karst formations) that make groundwater flow characteristics particularly difficult to model?
- How well have potential source areas been characterized?
- Is current land use stable or subject to change?
- How does the stage of investigation affect the appropriate level of uncertainty? For example, is the investigation being done to rule out a potentially complete pathway, or is it being done for the purpose of developing a remedial design?

The following are some examples of PQOs designed to control measurement uncertainty:

- *A groundwater modeling study will be conducted for ABC Air Force Base to determine whether a potentially complete groundwater pathway exists from Trout Pond to the City public water supply. Hydrogeolgical data used as input to the model will be derived only from monitoring wells 5-10, as these were the only wells that were installed according to State guidelines, and they are the only wells for which detailed boring logs are available. Climatological data will be obtained for the past 10 years from the county weather service. Groundwater infiltration rates will be derived from data for the calendar year of highest precipitation within the past 10 years.*
- *If the modeling study is able to demonstrate with 90% certainty that a complete pathway will not exist under conditions described above, then groundwater will be excluded as a pathway of concern.*
- *If the modeling study is not able to rule out a complete pathway with 90% certainty, then further studies will be conducted as necessary to evaluate the potential for complete exposure pathways.*

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Note that these examples rely on existing data, but judgments have been made about the source and characteristics of data that are deemed to be sufficiently reliable for the intended purposes. The PQOs address sources of uncertainty resulting from spatial and temporal variability in hydrogeological characteristics.

Decision Uncertainty for Investigating for Perchlorate Amount

The key parameter that affects the acceptable decision uncertainty in this case is how close the actual concentration is expected to be to the action or decision level. An example of a PQO follows:

The analytical results from 2 rounds of ground water samples collected from monitoring wells 1-20 will be used in conjunction with hydrogeological data from wells 6-20 to estimate the size and orientation of the ground water plume. Samples will be analyzed using EPA Method 331.0. The assumed edges of the plume will correspond to sample results that are less than or equal to one half the perchlorate MCL.

Step 3: Specify Measurement Performance Criteria

Measurement performance criteria (MPCs) are the specific quality control acceptance criteria that are used to judge whether the collected data meet the PQOs. Both data users and quality assurance (QA) personnel must be involved in the development of the MPCs. MPCs specify performance standards for specific data acquisition activities, whether they are record searches, sampling and analysis, or hydrogeological investigations. MPCs do not specify how the data will be acquired.

MPCs are described in terms of data quality indicators (DQIs), which include precision, accuracy/bias, representativeness, comparability, sensitivity, selectivity, and completeness. The criteria for the DQIs can be either quantitative or qualitative, depending on the type of decision, the type of data, and the DQI itself. Part 2B of the UFP-QAPP is a *Quality Assurance/Quality Control Compendium* that outlines minimum QA/QC activities appropriate for different types of investigations. The UFP-QAPP and the Compendium describe which QC samples are used to assess each DQI. These minimum requirements should be factored into sampling and testing activities for perchlorate investigations.

For analytical data, MPCs are measured through specific QC samples designed for that purpose. Appendix G, Table G-3 provides specific measurement performance criteria for perchlorate analytical methods.

MPCs for Investigating the Occurrence of Perchlorate Release

For investigations relying on historical records, the primary DQIs are completeness and accuracy. Criteria for completeness can be described in terms of the availability of records for the specific area and time period under study. Verifying and documenting the accuracy of historical records is important, especially if anecdotal information is to be part of the study.

The following are examples of MPCs for historical records:

Completeness: Records will be missing for no more than 20 percent of the total time period addressed by this study.

Accuracy: Any information obtained from interviews on the location of potential perchlorate releases will be confirmed by documentary evidence or field sampling.

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For analytical data, MPCs are specified in terms of specific quality control samples and procedures, which are described in Appendix G. For investigations employing sampling and analysis, selectivity will be an important DQI, and the team will need to develop a strategy to confirm any results obtained using nonspecific analytical methods (e.g., those employing IC/EC).

MPCs for Investigating for Complete Pathways and Determining the Amount of Perchlorate

Analytical methods employing mass spectrometry must be used for these stages of the investigation. Analytical method performance criteria are provided in Appendix G. When determining hydrogeological characteristics, accuracy and representativeness will be important DQIs. Hydrogeological characteristics can be very heterogeneous (i.e., subject to both spatial and temporal variability). Depending on the importance of the decision to be made and the complexity of the site hydrogeology, the investigation may require a large number of measurements in order to adequately represent the spatial and temporal distribution of the characteristics.

The following are examples of MPCs for hydrogeological data:

Accuracy: It is estimated that groundwater flow direction can be determined with an accuracy of plus or minus 15 degrees.

Representativeness: Estimates of seasonal changes in depth to groundwater and groundwater flow will be based on quarterly groundwater measurements on wells 1-10 collected over the past 5 years.

Step 4: Determine Appropriate Uses and Limitations of Available Data

Available data may include historical records and analytical results that were collected to answer different questions than those posed in the current investigation. They may not necessarily represent the time period or areas under study. They also may not meet the specified MPCs. The use of such data — for conducting groundwater modeling, for example — may result in erroneous decisions; therefore, it is essential to evaluate how relevant and reliable the data are, given the decisions to be made in the current investigation.

It may be possible to use existing data during any phase of the investigation, provided they are evaluated against project-specific DQOs and MPCs, and qualified accordingly. Existing data can include information on source areas, perchlorate concentrations, groundwater flow direction, or connectivity between surface water and groundwater. Determining the appropriate uses and limitations of such data involves examining the supporting records or raw data and examining the availability of corroborating evidence. Examples of questions that should be asked to address data uses and limitations include the following:

For historical records:

- Are the records complete and well organized?
- Do they contain all the necessary information?
- Are there gaps for certain time periods?
- For reports of previous investigations, is supporting documentation (e.g., field logs, analytical reports) present?
- For information based on interviews, is the interview documented? Is the information corroborated by another source?

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For existing analytical data:

- Why were the data collected (i.e., what problem was being addressed, and what decisions were being made)?
- Were data generated according to an approved QAPP or SAP?
- What were the laboratory's qualifications?
- Was the laboratory accredited for relevant fields of testing? Was it assessed by a DoD Component? Did it have a documented quality system?
- If EPA Method 314.0 was used for matrices other than drinking water, how was it modified?
- Was a standard operating procedure (SOP) provided for the method?
- Is the laboratory report, including quality control information, available?
- What was the reporting limit in each matrix? How was it determined? How were results below the reporting limit reported and qualified?
- How did the laboratory address matrix interference? Were results confirmed using a perchlorate-specific method?
- Were the data verified and validated?

For geological/hydrogeological data:

- Are the data from a reliable source? Are they site-specific or based on regional information?
- If drilling was performed, what was the purpose? Did it follow a work plan?
- Was drilling supervised by a registered geologist?
- Are drilling logs available?

Step 5: Determine the Type and Quantity of New Data

The types and quantities of new data required depend on the outcome of the previous four steps, that is, the decisions to be made, the acceptable level of uncertainty, the MPCs, and the availability or suitability of other available data.

Investigators must also consider the types of supporting data that are needed. Supporting data include information that will help interpret the results and put the study in context; for example, the locations and depths of all sampling points. When collecting surface water or groundwater samples, it may be necessary to measure additional analytes (e.g., pH, conductivity, total dissolved solids, chloride, bicarbonate/carbonate, and sulfate) to assess potential matrix interferences.

When conducting groundwater sampling, the supporting hydrogeological data that should be collected include depth to water, depth to the well bottom, length of the screened interval, well diameter, appearance of the sample, and any observational data related to the well yield (e.g., changes in the water level within the well, or in nearby wells) during sampling.

The CSM is a helpful tool for identifying the type and quantity of new data needed at every stage of the investigation. Data collection should then focus on filling gaps in the CSM at each stage. For example, when investigating whether a perchlorate release has occurred, the CSM should contain sufficient information about perchlorate use and handling to permit potential source areas to be located. Data requirements will include the concentration of perchlorate in the media of concern.

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When investigating pathways, hydrogeological data and analytical data will be collected to fill any data gaps in the CSM. Data to be collected may include the following:

- Aquifer depths and flow characteristics
- Connectivity between aquifers or between surface water and groundwater
- Groundwater recharge rates
- General groundwater quality
- Location and size of source areas or plumes
- Soil characteristics

Determining the concentrations of perchlorate in complete pathways is the basis for subsequent risk assessment and risk management decisions. Because of the importance of these decisions, the tolerance for uncertainty will be low, measurement performance criteria will be stringent, and a large number of samples could be required to ensure that the study represents actual conditions.

PQOs for Regulatory Compliance Sampling

For regulatory compliance sampling, the environmental problem will be defined in the governing regulation or permit. In general, the decision statements will also be specified; however, in some circumstances, the project team might find it useful to clearly state the decisions and the consequences of possible outcomes in order to help clarify the appropriate level of data quality. The following is an example of such a decision statement (Note: Actual decision statements must be consistent with both the regulations and the permit conditions):

- *Quarterly sampling will be undertaken to determine whether the concentration of perchlorate in the wastewater exceeds the permit limit.*
  - *If the concentration is determined to exceed the permit limit, then confirmatory analysis will be undertaken.*
  - *If the original concentration exceeds the permit limit, but confirmatory analysis results are below the permit limit, then both results will be reported to the permitting authority, and follow-up actions will be negotiated on a case-by-case basis.*
  - *If the confirmatory analysis indicates that the concentration exceeds the permit limit, then the permitting authority will be informed, and weekly sampling will be initiated and will continue until the source of the problem is identified and corrected.*
  - *If the concentration does not exceed the permit limit, then quarterly sampling will continue for a period of 2 years.*
  - *If the concentration of perchlorate remains below the permit limit for 2 years, then quarterly monitoring for perchlorate will be discontinued.*

For regulatory compliance sampling, the tolerance for decision uncertainty will be directly tied to the penalties for exceeding a regulatory level (e.g., a NPDES permit level).

The PQOs will need to address the level of certainty associated with specific results (e.g., non-detects, concentrations near the specified action level, or concentrations significantly above the specified action level). The following is an example PQO for drinking water:

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- *Demonstrate that the 95 percent Upper Confidence Limit on the mean concentration is less than or equal to the action level of [X ppb].*

Measurement performance criteria for this PQO come in part from the DoD-QSM and include the following:

- *The laboratory will verify the Limit of Detection (LOD) with a check sample spiked at two times the laboratory-identified LOD.*
- *The Level of Quantitation (LOQ) will be three times the LOD and less than or equal to the specified action level of [X ppb].*

Limitations on the use of existing data depend on the analytical method used:

- If perchlorate was previously detected in the wastewater, what analytical method was used to detect it?
- If EPA Method 314.0 was used, was the concentration confirmed using a perchlorate-specific method?

The type of data required for compliance monitoring of perchlorate will be the analytical results for drinking water or wastewater samples. The quantity of data is usually specified in the permit or regulation. Supporting data requirements could include measurements of total dissolved solids (TDSs), chloride, bicarbonate/carbonate, and sulfate.

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APPENDIX F
PERCHLORATE FIELD SAMPLING TECHNICAL GUIDES

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TECHNICAL GUIDE

COLLECTING DRINKING WATER SAMPLES FOR PERCHLORATE

Prepared by: DoD Environmental Data Quality Workgroup **Date:**_____

Reviewed by: _____ **Date:**_____

Approved by: _____ **Date:** _____

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1.0 Scope & Application

1.1 This Technical Guide (TG) has been developed to generate consistency across DoD for the collection and analysis of drinking water samples for perchlorate.

1.2 The use of this TG is restricted to individuals trained and experienced in drinking water sampling methods. It should be used in conjunction with professional judgment, taking site-specific requirements into consideration.

1.3 If sampling and testing activities have been requested by a regulatory agency, or are subject to regulatory oversight, then installations should obtain regulatory authority review and comment on the QAPP or SAP.

2.0 Summary of Method

2.1 Samples may be collected using standard drinking water sampling procedures.

2.2 Materials typically used in the sampling of drinking water do not affect sampling for perchlorate.

2.3 Analyses of perchlorate samples must be performed by laboratories that meet the requirements of the *DoD Perchlorate Handbook* and the *DoD Quality Systems Manual for Environmental Laboratories* (DoD-QSM) (http://www.navylabs.navy.mil/ManualsDocs.htm).

3.0 Health and Safety Warnings

3.1 This guide does not attempt to address all health and safety issues. The user must determine applicable requirements and establish appropriate health and safety protective measures.

3.2 Users of this guide should review the site health and safety plan with specific emphasis placed on hazards related to drinking water sampling tasks. Follow standard safe operating practices.

3.3 When working with potentially hazardous materials, follow U.S. EPA, OSHA and Service-specific health and safety regulations, policies and procedures.

4.0 Interferences

4.1 Filtration is used to remove microorganisms and suspended solids.

5.0 Equipment and Supplies

5.1 Sampling equipment is typically constructed from polyethylene, or polypropylene. These materials are all suitable for perchlorate sampling. All sampling equipment and containers must be sterile.

6.0 Sample Collection

6.1 Standard drinking water sampling procedures may be used to collect samples for perchlorate analysis. Dissolved perchlorate will not volatilize so agitation of the sample or entrained air bubbles will not interfere with the analytical results.

6.2 If sample collection is required for other analytes, sampling methods and procedures will be dictated by the sampling requirements for the most sensitive parameters.

6.2.1 Samples must be collected in order of decreasing volatility of target analytes. Samples for volatile organic compounds are normally collected first, followed

by semivolatile organic compounds and finally inorganic compounds. The sampling order will be specified by the sampling and analysis plan or permit.

6.3 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

7.0 Sample Handling and Preservation

7.1 Filter the sample through a sterile 0.2µm filter, to remove microorganisms and eliminate suspended solids. Collect 80 mL filtered sample in the sterile sample container. After filtering, store the samples with headspace in order to minimize the possibility of anaerobic conditions developing during sample storage.

7.2 Samples should be cooled as specified by the applicable method. If no guidance is provided, store the samples at 4 ± 2 °C.

7.3 Samples that are stored and collected in the manner described in this TG may be held for a maximum of 28 days before analysis.

8.0 Data and Records Management

8.1 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

8.2 Logbooks should be used and contain such things as: sample locations, time and date of collection, list of all personnel involved with sample collection and any field measurements take (e.g. pH).

9.0 Field Sample Quality Control and Quality Assurance

9.1 The following field quality control samples/checks shall be performed:

9.1.1 Field Duplicate – One field duplicate sample must be taken per sampling event, or one per 10 samples, whichever is more frequent.

9.1.2 Matrix Spike/Matrix Spike Duplicate – One sample per sampling event, or one per 20 samples per matrix, whichever is more frequent, must be designated for use as a Matrix Spike/Matrix Spike Duplicate.

10.0 Laboratory Selection, Quality Control, and Quality Assurance

10.1 The laboratory selected to perform the analysis must be approved by a DoD Component and meet the requirements of the National Environmental Laboratory Accreditation Program (NELAP) and the latest version of the DoD QSM. More information about laboratory and method selection is contained in Appendix G of the *DoD Perchlorate Handbook*.

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TECHNICAL GUIDE

COLLECTING GROUNDWATER SAMPLES FOR PERCHLORATE

Prepared by: DoD Environmental Data Quality Workgroup **Date:**_____

Reviewed by: _____ **Date:**_____

Approved by: _____ **Date:** _____

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1.0 Scope & Application

1.4 This Technical Guide (TG) has been developed to generate consistency across DoD for the collection and analysis of groundwater samples for perchlorate.

1.5 The use of this TG is restricted to individuals familiar with groundwater sampling methods.

2.0 Summary of Method

2.1 Low-Flow Purging and Sampling (LFPS) procedures are the preferred method for sampling groundwater wells for perchlorate. However, because of the solubility and stability of perchlorate, samples may be collected using any standard groundwater sampling method that meets the project-specific data quality objectives (DQOs) for sample representativeness.

2.2 Materials typically used in the construction of wells or the manufacture of sampling equipment do not affect perchlorate.

2.3 Analyses of perchlorate samples must be performed by laboratories that meet the requirements of the *DoD Perchlorate Handbook* and the *DoD Quality Systems Manual for Environmental Laboratories* (DoD-QSM) (http://www.navylabs.navy.mil/ManualsDocs.htm).

3.0 Health and Safety Warnings

3.1 This guide does not attempt to address all health and safety issues. The user must determine applicable requirements and establish appropriate health and safety protective measures.

3.2 Users of this guide should review the site health and safety plan with specific emphasis placed on hazards related to well sampling tasks. Follow standard safe operating practices.

3.3 When working with potentially hazardous materials, follow U.S. EPA, OSHA and Service-specific health and safety regulations, polices and procedures.

4.0 Interferences

4.1 The use of disposable/dedicated sampling equipment is recommended to eliminate the potential for sample contamination from documented sources of interferences such as detergents.

4.2 If non-disposable/dedicated sampling equipment is used, proper field decontamination techniques must be followed.

4.3 If perchlorate is the only target analyte, an acceptable decontamination procedure is to use a non-phosphate soap wash, followed by a deionized water rinse and air drying.

4.4 If the investigation includes additional target analytes, then samplers should follow standard decontamination practices for those analytes, except that non-phosphate detergent must be used.

4.5 Field samplers must use a rinsate blank to determine that the decontamination has been effective.

4.6 Filtration is used to remove microorganisms and suspended solids.

5.0 Equipment and Supplies

5.1 Sampling equipment is typically constructed from Teflon®, stainless steel, PVC, polyethylene, or polypropylene. These materials are all suitable for perchlorate sampling.

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6.0 Sample Collection

6.1 Standard groundwater sampling equipment and procedures may be used to collect groundwater samples for perchlorate analysis. Dissolved perchlorate will not volatilize, so agitation of the sample or entrained air bubbles from the sampling equipment does not interfere with the analytical results. Standard Low-Flow Purging and Sampling (LFPS) procedures are the preferred method to be used to collect representative groundwater samples. Examples of low-flow purging and sampling procedures are:

- EPA Region I Low Stress (low flow) Purging and Sampling Procedure for the Collection of Ground Water Samples from Monitoring Wells, July 30, 1996, Revision 2.
- Puls, R.W. and Barcelona, M.J., "Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedure", U.S. Environmental Protection Agency, Office of Research and Development, Publication # EPA/540/5-95/, pp. 12.
- ASTM D6771-2, "Standard Practice For Low Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations"

6.1.1 Wells that are continuously pumped or under regular use, so that water in the wells does not have an opportunity to become stagnant (e.g., operating recovery wells, municipal supply wells, and domestic supply wells), can be sampled without additional purging. In such cases the well can be sampled using any appropriate technique. Approval by the regulatory agency may be required.

6.1.2 In those situations where the groundwater conditions and well construction make it appropriate, no-purge sampling methods with devices (e.g. Hydrasleeve and Snap sampler) that are demonstrated to collect representative samples for perchlorate may be used. Approval by the regulatory agency may be required.

6.2 If sample collection is required for other analytes, sampling methods and procedures will be dictated by the sampling requirements for the most sensitive parameters.

6.2.1 Samples must be collected in order of decreasing volatility of target analytes. Samples for volatile organic compounds are normally collected first, followed by semivolatile organic compounds and finally inorganic compounds. The sampling order will be specified by the sampling and analysis plan or permit.

6.3 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

6.4 Some sites may be contaminated with light non-aqueous-phase liquids (LNAPLs) or dense non-aqueous-phase liquids (DNAPL), or both, in addition to perchlorate. The presence of DNAPLs and LNAPLs should not affect the sampling procedures for perchlorate. When possible, collect the sample above the DNAPLs or below the LNAPLs.

6.5 If there is potential for high-density perchlorate solutions to occur at a site (Perchlorate concentrations > 10,000 ppm) the solution will likely behave like a DNAPL. If monitoring for perchlorate is required in the presence of a high-density perchlorate brine solution, consult the DoD Perchlorate Handbook for additional guidance.

7.0 Sample Handling and Preservation

7.4 Filter the sample through a sterile 0.2µm filter, to remove microorganisms and eliminate

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suspended solids. In cases where it is difficult to filter the sample through the 0.2µm filter, pre-filtering through a 0.45µM may be necessary. Collect 80 mL filtered sample in the sterile sample container. After filtering, store the samples with headspace in order to minimize the possibility of anaerobic conditions developing during sample storage.

7.5 Samples should be cooled as specified by the applicable method. If no guidance is provided, store the samples at 4 ± 2 °C.

7.6 Samples that are stored and collected in the manner described in this TG may be held for a maximum of 28 days before analysis.

8.0 Data and Records Management

8.1 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

8.2 Logbooks should be used and, as with any groundwater sampling event, the logbook should contain such things as: maps showing sample locations, a narrative of the sampling event, a list of all personnel involved with sample collection, water depth, volume purged, and sampling method.

9.0 Field Sample Quality Control and Quality Assurance

9.1 The following field quality control samples/checks shall be performed:

9.1.1 Field Duplicate – One field duplicate sample must be taken per sampling event, or one per 10 samples, whichever is more frequent.

9.1.2 Field Equipment or Rinse Blank – One rinsate blank must be taken per sampling event. (Only required when decontamination of sampling equipment is performed in the field.)

9.1.3 Matrix Spike/Matrix Spike Duplicate – One sample per sampling event, or one per 20 samples, whichever is more frequent, must be designated for use as a Matrix Spike/Matrix Spike Duplicate.

10.0 Laboratory Selection, Quality Control, and Quality Assurance

10.1 The laboratory selected to perform the analysis must be approved by a DoD Component and meet the requirements of the National Environmental Laboratory Accreditation Program (NELAP) and the latest version of the DoD QSM. More information about laboratory and method selection is contained in Appendix G of the *DoD Perchlorate Handbook*.

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TECHNICAL GUIDE

COLLECTING SURFACE WATER AND WASTEWATER SAMPLES FOR PERCHLORATE

Prepared by: DoD Environmental Data Quality Workgroup **Date:**_____

Reviewed by: _____ **Date:**_____

Approved by: _____ **Date:** _____

Draft Final

1.0 Scope & Application

1.6 This Technical Guide (TG) has been developed to generate consistency across DoD for the collection and analysis of surface water and wastewater samples for perchlorate.

1.7 The use of this TG is restricted to individuals trained and experienced in surface water or wastewater sampling methods. It should be used in conjunction with professional judgment, taking site-specific requirements into consideration.

1.8 If sampling and testing activities have been requested by a regulatory agency, or are subject to regulatory oversight, then installations should obtain regulatory authority review and comment on the QAPP or SAP.

2.0 Summary of Method

2.1 Samples may be collected using the same process specified in the current permit or standard wastewater sampling procedures, as detailed in *Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Section, "1060 - Collection and Preservation of Samples".

2.2 Materials typically used in the sampling of surface water and wastewater do not affect sampling for perchlorate.

2.3 Analyses of perchlorate samples must be performed by laboratories that meet the requirements of the *DoD Perchlorate Handbook* and the *DoD Quality Systems Manual for Environmental Laboratories* (DoD-QSM) (http://www.navylabs.navy.mil/ManualsDocs.htm).

3.0 Health and Safety Warnings

3.1 This guide does not attempt to address all health and safety issues. The user must determine applicable requirements and establish appropriate health and safety protective measures.

3.2 Users of this guide should review the site health and safety plan with specific emphasis placed on hazards related to surface water and wastewater sampling tasks. Follow standard safe operating practices.

3.3 When working with potentially hazardous materials, follow U.S. EPA, OSHA and Service-specific health and safety regulations, policies and procedures.

4.0 Interferences

4.1 The use of disposable or dedicated sampling equipment is recommended to eliminate the potential for sample cross-contamination.

4.2 If non-disposable/dedicated sampling equipment is used, proper field decontamination techniques must be followed.

4.3 If perchlorate is the only target analyte, an acceptable decontamination procedure is to use a non-phosphate soap/detergent wash, followed by a deionized water rinse and air drying.

4.4 If the investigation includes additional target analytes, then samplers should follow standard decontamination practices for those analytes, except that non-phosphate detergent must be used.

4.5 A rinsate blank should be collected to demonstrate that the decontamination has been effective.

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5.0 Equipment and Supplies

5.1 Sampling equipment is typically constructed from stainless steel, PVC, polyethylene, or polypropylene. These materials are all suitable for perchlorate sampling.

6.0 Sample Collection

6.1 Standard surface water or wastewater sampling procedures may be used to collect samples for perchlorate analysis (*Standard Methods for the Examination of Water and Wastewater*, 20th Edition, Section, "1060 - Collection and Preservation of Samples"). Dissolved perchlorate will not volatilize so agitation of the sample or entrained air bubbles will not interfere with the analytical results.

6.2 If sample collection is required for other analytes, sampling methods and procedures will be dictated by the sampling requirements for the most sensitive parameters.

6.2.1 Samples must be collected in order of decreasing volatility of target analytes. Samples for volatile organic compounds are normally collected first, followed by semivolatile organic compounds and finally inorganic compounds. The sampling order will be specified by the sampling and analysis plan or permit.

6.3 If waste stream has multiple phases, each phase needs to be collected and analyzed separately.

7.0 Sample Handling and Preservation

7.7 Collect 80 mL of sample and store with headspace in order to minimize the possibility of anaerobic conditions developing during sample storage.

7.8 Samples should be cooled as specified by the applicable method. If no guidance is provided, store the samples at 4 ± 2 °C.

7.9 Samples that are stored and collected in the manner described in this TG may be held for a maximum of 28 days before analysis.

8.0 Data and Records Management

8.1 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

8.2 Logbooks should be used and contain such things as: sample locations, time and date of collection, list of all personnel involved with sample collection and any field measurements take (e.g. pH).

9.0 Field Sample Quality Control and Quality Assurance

9.1 Matrix Spike/Matrix Spike Duplicate – One sample per sampling event, or one per 20 samples per matrix, whichever is more frequent, must be designated for use as a Matrix Spike/Matrix Spike Duplicate.

10.0 Laboratory Selection, Quality Control, and Quality Assurance

10.1 The laboratory selected to perform the analysis must be approved by a DoD Component and meet the requirements of the National Environmental Laboratory Accreditation Program (NELAP) and the latest version of the DoD QSM. More information about laboratory and method selection is contained in Appendix G of the *DoD Perchlorate Handbook*.

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TECHNICAL GUIDE

COLLECTING SOLID SAMPLES FOR PERCHLORATE

Prepared by: DoD Environmental Data Quality Workgroup **Date:**_____

Reviewed by: _____ **Date:**_____

Approved by: _____ **Date:** _____

Draft Final

1.0 Scope & Application

1.9 This Technical Guide (TG) has been developed to generate consistency across DoD for the collection and analysis of solid for perchlorate.

1.10 The use of this TG is restricted to individuals trained and experienced in soil and sediment sampling methods. It should be used in conjunction with professional judgment, taking site-specific requirements into consideration.

1.11 If sampling and testing activities have been requested by a regulatory agency, or are subject to regulatory oversight, then installations should obtain regulatory authority review and comment on the QAPP or SAP. In this case, the collection of split samples is strongly recommended (i.e. where a portion of each sample is sent to a second laboratory).

2.0 Summary of Method

2.1 Solid samples for perchlorate can be collected with many types of sampling equipment (e.g. trowels, hand augers, split spoons, direct-push samplers, Ekman dredges, Ponar dredges, Gravity corers).

2.2 Care must be taken to ensure that each sample represents the location, sample medium, and depth being evaluated. Poor sampling techniques will produce misleading results and lead to incorrect decisions.

2.3 Analysis of perchlorate samples must be performed by laboratories that meet the requirements of the *DoD Perchlorate Handbook* and the *DoD Quality Systems Manual for Environmental Laboratories* (DoD QSM) (http://www.navylabs.navy.mil/ManualsDocs.htm).

2.4 Definitive methods (e.g., those employing mass spectrometry (MS)) must be used for the analysis of soil and sediment samples for perchlorate. At this time, the EPA has not published any methods for the analysis of solid samples; therefore, required sample preparation procedures and analytical method performance criteria are specified in Appendix G of the DoD Perchlorate Handbook. The use of EPA Method 314.0 or one of its modifications is not appropriate.

3.0 Health and Safety Warnings

3.1 This guide does not attempt to address all health and safety issues. The user must determine applicable requirements and establish appropriate health and safety protective measures.

3.2 Users of this guide should review the site health and safety plan with specific emphasis placed on hazards related to soil and sediment sampling tasks. Follow standard safe operating practices.

3.3 When working in the presence of potentially hazardous materials, energetics or ordnance, follow U.S. EPA, OSHA and Service-specific health and safety regulations, policies and procedures.

4.0 Interferences

4.1 The use of disposable or dedicated sampling equipment is recommended to eliminate the potential for sample cross-contamination.

4.2 If non-disposable/dedicated sampling equipment is used, proper field decontamination techniques must be followed.

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4.3 If perchlorate is the only target analyte, an acceptable decontamination procedure is to use a non-phosphate soap/detergent wash, followed by a deionized water rinse and air drying.
4.4 If the investigation includes additional target analytes, then samplers should follow standard decontamination practices for those analytes, except that non-phosphate detergent must be used.
4.5 A rinsate blank to should be collected to demonstrate that the decontamination has been effective.

5.0 Equipment and Supplies

5.1 Sampling equipment is typically constructed from Teflon®, stainless steel, PVC, polyethylene, or polypropylene. These materials are all suitable for perchlorate sampling.

6.0 Sample Collection

6.1 Because of its high solubility, it is unlikely that perchlorate will reside in sediments. For this reason, in most situations it will be unnecessary to sample sediments for perchlorate. Sediment sampling may be required in rare situations where large quantities of perchlorate have been released and an evaporative environment exists (waste impoundment associated with munitions demilitarization activities). When this situation exists, standard procedures for sampling sediment should be employed.
6.2 Standard soil sampling equipment and procedures may be used to collect samples for perchlorate analysis. Examples include those described in ASTM publication ENVSITE 02, *ASTM Standards Related to Environmental Site Characterization*, 2nd edition and ASTM D4700-91(1998) *Standard Guide for Soil Sampling from the Vadose Zone*.
6.3 Avoid unusual areas, such as eroded areas, rock outcroppings, and fence lines, unless these features have been specifically designated as sample points in the SAP.
6.4 If no contradictory guidance is provided in the QAPP or SAP, remove debris such as sticks, rocks, and vegetation from the soil surface before collecting the samples.
6.5 If perchlorate is expected to be distributed homogeneously (e.g. a former wastewater impoundment area at a manufacturing plant) then discrete samples can be taken. If the distribution is expected to be heterogeneous (e.g. retained in propellant matrices, distributed in soil, and not immediately dissolved) or is unknown, then composite (or incremental) soil sampling techniques are recommended. In this case, a sample representing a particular sampling unit (area or volume of soil) should consist of at least five subsamples collected within the sampling unit. Subsamples should be as close to the same size (in terms of mass) as possible.
6.6 Following the collection of all subsamples representing a particular sample unit, the sample should be mixed until it achieves a consistent physical appearance.
6.7 Well-mixed samples should be placed in clean 4-oz amber glass bottles.

7.0 Sample Handling and Preservation

7.10 Samples should be cooled as specified by the applicable method. If no guidance is provided, the samples should be stored at 4 ± 2 °C.
7.11 Samples that are stored and collected in the manner described in this TG may be held for a maximum of 28 days before analysis.

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8.0 Data and Records Management

8.1 Once sampling is complete, all field documentation records and chain-of-custody forms must be completed.

8.2 Logbooks should be used and, as with any sampling event, they include: maps showing sample locations, a narrative description of the sampling event, a list of all personnel involved with sample collection, and sampling method.

9.0 Field Sample Quality Control and Quality Assurance

9.1 Field Duplicate (Field Split) – One field duplicate sample must be taken per sampling event, or one per 10 samples, whichever is more frequent.

9.2 Field Equipment or Rinsate Blank – One rinsate blank must be taken per sampling event. (Only required when decontamination of sampling equipment is performed in the field.)

9.3 Matrix Spike/Matrix Spike Duplicate – One sample per matrix per sampling event, or one per 20 samples of the same matrix, whichever is more frequent, must be designated for use as a Matrix Spike/Matrix Spike Duplicate.

10.0 Laboratory Selection, Quality Control, and Quality Assurance

10.1 The laboratory selected to perform the analysis must be approved by a DoD Component and meet the requirements of the National Environmental Laboratory Accreditation Program (NELAP) or the American Association for Laboratory Accreditation (A2LA) and the latest version of the DoD QSM. More information about laboratory and method selection is contained in Appendix G of the *DoD Perchlorate Handbook*.

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APPENDIX G
SELECTING ANALYTICAL METHODS AND SERVICES

This appendix provides guidance on the following:

- The selection of appropriate analytical methods for the analysis of perchlorate
- The preparation of solid samples for perchlorate analysis
- The specification of analytical method performance criteria

Analytical Methods

The selected analytical method must be able to quantitate perchlorate at the concentration of concern, in the matrices to be analyzed. The specific procedure used by the laboratory must meet the project-specific measurement performance criteria (MPCs). Approaches to perchlorate analysis include ion chromatography with conductivity (IC/EC) detection, and ion chromatography or liquid chromatography (LC) with either single or tandem mass spectrometry (MS or MS/MS) detection.

Important Definitions for Selection of Perchlorate Methods

Selectivity: The capability of a test method or instrument to respond to a target substance or constituent in the presence of non-target substances.

Sensitivity: The capability of a method or instrument to discriminate between measurement responses representing different levels (e.g., concentrations) of a variable of interest.

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Ion Chromatography/Conductivity

How it works: Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate mixtures of ions based on their affinity for the resin. As the ions elute from the column, they can be quantified using a conductivity detector. Identification and quantitation of perchlorate within a sample are based on the response of the conductivity detector during the retention time window for perchlorate, that is, the time during which perchlorate is expected to elute from the IC column.
Advantages: Historically, IC/EC has been slightly less expensive than MS techniques.
Limitations: The conductivity detector is nonspecific. Any ion eluting within the retention time window is reported as perchlorate. EPA IC methods have not been validated for use in matrices other than drinking water.
Improvements and Ongoing Work: To improve the performance of IC/EC the EPA developed Method 314.1, which employs the use of pre-concentration and second column confirmation. While these modifications improve method sensitivity, they do not eliminate the potential for false positive results.

Mass Spectrometry

How it works: Either IC or LC is used to separate perchlorate from other sample constituents based on its affinity for the column. The IC or LC is interfaced to either a single or tandem MS through an electrospray ionization probe. The MS isolates the perchlorate ion and its isotopes from ions of differing masses. This selectivity for the specific ion masses allows the MS detector system to be definitive in its identification and quantitation of perchlorate.

In a tandem MS system, the perchlorate ion and its isotope collide with gas molecules, causing them to fragment into product ions. The second MS isolates the product ions of interest. This step adds another level of selectivity to the method. Both single and tandem MS methods employ the use of an enriched isotope internal standard, ^{18}O-perchlorate, to facilitate the accurate identification and quantitation of perchlorate.

Advantages: Mass spectrometry methods are definitive and more sensitive than IC/EC. In situations where extremely low reporting limits are required, or where the sample stream is subject to interference that may require significant dilution prior to analysis, a tandem MS method will likely be required to meet project quality objectives (PQOs).

Limitations: The electrospray ionization probe can experience problems with high-conductivity samples (i.e., those containing high concentrations of total dissolved solids, or TDS). Procedures to minimize this impact include the use of specialized pretreatment columns and matrix diversion techniques. Typically MS-based methods have been more expensive than the IC/EC methods; however, the costs are expected to decrease as demand increases.

Improvements and Ongoing work: The EPA Office of Water has published an IC-based MS (or MS/MS) method (Method 332.0) and an LC-based MS (or MS/MS) method (Method 331.0). The EPA Office of Solid Waste is currently validating both an IC-based MS method (SW-846 Method 6860) and an LC-based MS method (SW- 846 Method 6850).

Other Methods

If testing of biota or food products is required, the Food and Drug Administration (FDA) has developed an IC/MS/MS method similar to EPA Method 331.0 (available at FDA's web site at http://www.cfsan.fda.gov/~dms/clo4meth.html). This method uses an IC column in a high-performance liquid chromatography (HPLC) system. The method includes preparation procedures for produce that could be applied to other types of vegetation. The preparation procedure involves grinding the sample, adding an appropriate amount of internal standard, and then extracting with water. After filtration, the resulting extract can be analyzed the same as any other aqueous sample.

Table G-1 contains a list of perchlorate methods that are recommended for use by DoD.
For the sake of completeness, Table G-2 identifies other available methods; however, the use of these methods is not recommended.

Table G-1 Recommended Methods for Perchlorate Analysis

Method (Technique)	Applicability	Limitations	Target Reporting Limits
EPA 331.0 (LC/MS) (LC/MS/MS)	• DoD Owned Drinking Water Systems (UCMR 2) • Applicable to drinking water samples, including those with high TDS	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking Water 0.1 µg/L (LC/MS) 0.02 µg/L (LC/MS/MS)
EPA 332.0 (IC/MS) (IC/MS/MS)	• DoD Owned Drinking Water Systems (UCMR 2) • Applicable to drinking water samples, including those with high TDS	• Pretreatment recommended for samples with high concentrations of sulfate • Validated for drinking water samples only	Drinking Water 0.1 µg/L (IC/MS) 0.02 µg/L (IC/MS/MS)

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SW6850 (LC/MS)	• Environmental Restoration • Operational Ranges • DoD Wastewater Effluent Discharges • Aqueous samples including those with high TDS • Soil and sludge samples	• Requires a proprietary column· • Final method not published	Drinking Water and Groundwater 0.2 µg/L Soil 2 µg/Kg
SW6860 (IC/MS) (IC/MS/MS)	• Environmental Restoration • Operational Ranges • DoD Wastewater Effluent Discharges • Aqueous samples to include those with high TDS • Soil and sludge samples	• Pretreatment recommended for samples with high concentrations of sulfate • Final method not published	Drinking Water and Groundwater 0.2 µg/L Soil 2 µg/Kg
FDA Method (IC/MS/MS)	• Low moisture foods, bottled water, and milk	• None noted	Low moisture foods 3.0 µg/Kg Bottled Water 0.5 µg/L Milk 3.0 µg/L

Table G-2 –Other Available Methods (Not Recommended for use by DoD)

Method (Technique)	Applicability	Limitations	Target Reporting Limits
EPA 314.0 (IC)	• Mandatory for drinking water samples reported under UCMR 1 • Aqueous samples with low dissolved solids (conductivity < 1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each • Not proposed for UCMR 2	• Subject to false positives due the lack of specificity of the conductivity detector • Validated for drinking water samples only • Inappropriate for use in samples with high TDS	Drinking Water 4 µg/L
EPA 314.0 "enhanced" (IC)	• Drinking Water samples • Proposed option for UCMR 2	• No revision of Method 314.0 that documents these "Enhancements" has been published • Enhancements are only listed in the Federal Register notice • Subject to false positives due the lack of specificity of the conductivity detector • Limited commercial availability • Requires confirmation of perchlorate results above reporting limit when used for UCMR 2	Drinking water - 0.57 µg/L

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Method (Technique)	Applicability	Limitations	Target Reporting Limits
EPA 314.1	• Drinking water samples • Planned option for UCMR 2	• Reduces but does not eliminate the potential for false positives· • Validated for drinking water samples only· • Long analytical run time· • Limited commercial availability· • Requires confirmation of perchlorate results above reporting limit when used for UCMR 2	Drinking Water 0.13 µg/L
Draft SW9058 (IC)	• Aqueous samples with low dissolved solids (conductivity < 1 mS/cm TDS) and chloride, sulfate, and carbonate concentrations < 100 mg/L each	• Subject to false positives due the lack of specificity of the conductivity detector • Inadequate quality control criteria • Method is expected to undergo significant revision prior to publication	Low TDS Groundwater 4 µg/L

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Sample Preparation for Solid Samples

Currently there is no standard method for preparation of solid samples for the analysis of perchlorate. Prior to the publication of the SW-846 Methods 6850 and 6860 all solid samples processed for DoD must follow the procedure detailed below:

- Weigh 1 g of solid sample, recording the weight to 0.01 g. Transfer the sample to a 15 mL centrifuge tube.
- Add 10 mL of reagent water, 50 µL of internal standard spiking solution. Vortex the mixture, followed by sonication for a minimum of 10 minutes, followed by additional vortexing.
- Centrifuge the sample for 5 minutes to separate the solids from the extract solution.
- Filter the supernatant extract solution using a plastic syringe fitted with a 0.45-µm membrane filter. Dispense the extract sample into an autosampler vial for analysis.
- If large quantities of organic contaminants are present in the solid sample extract (i.e. supernatant extract is highly colored), a cleanup step using a C18 column may be performed to remove organic contaminants from the supernatant extract solution.
    - Activate the C18 cartridge column by pushing approximately 5 mL of methanol through the column, followed by 5 mL of reagent water. A flow rate of approximately 0.5 mL/min is recommended. Care should be taken not to let the column become dry.
    - Using gentle pressure, push approximately 6 mL of the supernatant extract solution through the activated column.
    - Discard the first 2 mL of eluted sample extract.

— Collect the remaining eluted sample extract (approximately 4 mL) in a clean container. Filter the sample extract using a plastic syringe fitted with a 0.45-µm membrane filter. Dispense the extract sample into an autosampler vial for analysis.

Measurement Performance Criteria

The analytical method should be selected based on the project-specific measurement performance criteria, as explained below:

- Sensitivity—The Method Reporting Limit (MRL) must be documented in the specific matrix of concern, at or below the applicable concentration of concern or regulatory limit. The MRL cannot be less than the lowest calibration standard.
- Selectivity—If the primary method used is nonselective (such as EPA Method 314.0), positive results above a regulatory limit, permit-specified limit, or project-specific action level must be confirmed using MS. Once results have been confirmed using MS, then use of an IC/EC method for long-term monitoring purposes may be acceptable. For investigative purposes, however, MS should be used for all analyses.
- Precision—To generate information on sample heterogeneity and laboratory precision, the project team can submit field duplicates or splits for analysis by one laboratory, or split samples can be submitted to multiple laboratories for confirmation purposes. Laboratory duplicates or matrix spike duplicates will provide information regarding analytical precision. A minimum of one laboratory duplicate or matrix spike duplicate per 20 samples per matrix must be analyzed.
- Accuracy—To determine method accuracy, matrix spike samples must be prepared on each matrix from the site. A minimum of one matrix spike per 20 samples per matrix must be collected and analyzed. One interference check sample (a laboratory-fortified synthetic sample matrix that has been spiked with perchlorate) per batch must be analyzed in order to verify that the selected method can accurately quantitate perchlorate in the presence of ionic suppressors that are common to some matrices. The interference check sample includes common ionic interference (chloride, sulfate, carbonate, and bicarbonate) and perchlorate.

Method Selection

When conducting sampling and testing for perchlorate in surface soil, drinking water, groundwater, surface water, sediments, or other environmental matrices, the selected method must be able to meet the specified MRL in the matrix of concern. If sampling and testing activities have been requested by a regulatory agency, or those activities are subject to regulatory oversight, then installations should secure approval from the regulatory authority for the use of the method. Regardless of the method used, each laboratory must demonstrate and document an MRL, in the matrix of concern, that is equal to or less than any applicable regulatory limit or concentration of concern specified in the PQOs.

<u>Regulatory Compliance Sampling</u>

Use of EPA Method 314.0 was mandatory for the analysis of perchlorate in drinking water under the Unregulated Contaminant Monitoring Rule that expired in December 2003. A number of

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States may continue to require the use of Method 314.0. States may also require the use of Method 314.0 to satisfy requirements for perchlorate testing at facilities operating under Clean Water Act NPDES permits. These are the only conditions under which Method 314.0 should be used.

The second Contaminant Candidate List under the UCMR, which was finalized in February 2005, allows for the use of Method 314.0, 314.1 331.0 or 332.0 for perchlorate analysis. Only the mass spectrometry methods (331.0 and 332.0) should be used for analysis of drinking water samples for DoD. In situations where either Method 314.0 or 314.1 is used, all results above the applicable regulatory limit *must* be confirmed using MS.

Sampling for Environmental Restoration/Cleanup and Range Sustainment Activities

IC/EC (Methods 314.0 and 314.1) is not appropriate for sampling and analysis associated with environmental restoration/cleanup or range assessment activities. Only methods employing MS are to be used for these projects.

Minimum Laboratory Qualifications

Laboratories must have a documented quality system that complies with ISO/IEC 17025:1999 and the Department of Defense Quality Systems Manual for Environmental Laboratories (DoD QSM). They also must certify conformance to the DoD QSM and are subject to project-specific on-site assessments by DoD representatives. Laboratories must have appropriate State certifications or be accredited by a nationally recognized accreditation body, such as NELAP, for the applicable test method, as appropriate. Laboratories must provide documentation of their ability to achieve the project-specific MRL using the specified method in each matrix to be analyzed.

Method Reporting Limit

The Method Reporting Limit is the minimum concentration that can be reported by a laboratory as a quantified value. Results at the MRL must meet the all the quality control criteria specified in table G-3. The MRL can not be lower than the concentration of the lowest calibration standard. While some of EPA's new methods (314.1, 331.0 and 332.0) allow less stringent quality control (QC) criteria for values reported at the MRL, the DoD does not concur with this practice. The QC criteria for the method must be consistent over the entire quantification range (see Table G-3).

Data Qualifiers

Data not meeting the minimum QC requirements outlined in the tables below should be qualified by the laboratory using the data-qualifier flags defined in the most recent version of the DoD QSM. Standard data qualifiers, which are to be used by laboratories only, are listed below. Additional data qualifiers (e.g., an R-flag for rejected data) may be used by data validators when they evaluate data usability.

U – Undetected at the limit of detection: The associated data value is the limit of detection, adjusted by any dilution factor used in the analysis.

J – Estimated: The analyte was positively identified; the quantitation is estimated (e.g., matrix interference, below standard, outside the calibration range).

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B – Blank contamination: The analyte was detected above one-half the reporting limit in an associated blank.

Q – Failure of one or more quality control criteria (e.g., LCS recovery, surrogate spike recovery, perchlorate isotope ratio): Data usability should be carefully assessed by the project team. DoD assessment may result in the rejection of data and potential withholding of payment to the laboratory based on unacceptable performance.

Minimum QC Requirements

The QC requirements for any method employing IC/EC must as a minimum meet the requirements detailed in Method 314.0. The minimum QC requirements for use with MS-based methods are detailed in Table G-3.

This appendix will be updated periodically to reflect new methods. Updates will be posted at http://www.navylabs.navy.mil.

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Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Holding Time (HT)	All samples	Headspace should be about one-third of the container. HT $\leq$ 28 days (to be consistent with other EPA requirements) with samples stored at 4 °C +/– 2 °C.	None, qualify data with a Q-flag.	
Method Reporting Limit	With every initial calibration	Documented in the specific matrix of concern, at or below the applicable regulatory limit. Equal to lowest calibration standard.		
Limit of Quantitation (LOQ)	With every initial calibration.	Documented in the specific matrix of concern, at or below the applicable regulatory limit. Equal to lowest calibration standard. At least 3 times the MDL/LOD.	Apply J-flag to all results between LOD and LOQ.	
Method Detection Limit (MDL)	A full MDL study is conducted at initial setup and subsequently once per 12-month period and when major changes occur in the method's operating procedures (addition of cleanup procedures, column changes, mobile phase changes). If no changes have been made to the method, quarterly MDL verification checks may be performed in lieu of the yearly MDL study.	MDL study must be performed in the matrix of interest using a standard at a concentration that is 1 to 10 times the estimated MDL value. MDL must be validated through the analysis of a low-level spike at ~ 2 times MDL taken through the entire preparation process. MDL verification checks must produce a signal at least 3 times the instrument's noise level.	Run MDL verification check at higher level and set MDL higher or re-perform MDL study.	Samples cannot be analyzed without a valid MDL.
Retention Time (window width calculated for each analyte and internal standard)	At method setup and after major maintenance (e.g., column change).	Width is $\pm$ 3 times standard deviation for each analyte retention time from 72-hour study.	N/A	N/A

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Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Retention Time Window (position establishment)	Once per ICAL and at the beginning of the analytical shift	Position shall be set using the midpoint standard of the calibration curve or the value in the CCV run at the beginning of the analytical shift.	N/A	N/A
Initial Calibration (ICAL)	Initial calibration prior to sample analysis.	Minimum of 5 calibration standards to establish linearity (daily), $r \geq 0.995$ or with an RSD for each analyte (including MRL) of $\leq$ 20%. The calibration is linear and shall not be forced through the origin. The concentration corresponding to the absolute value of the calibration curve's Y-intercept must be $\leq$ LOD.	Correct problem, then repeat initial calibration. Flagging criteria are not appropriate.	Problem must be corrected. No samples may be run until ICAL has passed.
Second Source Calibration Verification (SSCV)	Once after each multipoint calibration, analysis of a second source standard at the midpoint of the calibration.	Value of second source for perchlorate within $\pm$ 10% of expected value (initial source).	Correct problem and verify second source standard. Rerun SSCV. If that fails, correct problem and repeat initial calibration.	Problem must be corrected. No samples may be run until SSCV has passed.
Initial Calibration Verification Standard (ICV)	After initial calibration, daily analysis of a standard at the midpoint of the calibration.	%Difference $\leq$ 15% relative to initial value.	Correct problem and rerun ICV. If that fails, correct problem and repeat initial calibration. Flagging criteria are not appropriate. No samples may be run until calibration has been verified.	Problem must be corrected. No samples may be run until calibration has been verified.
Continuing Calibration Verification Standard (CCV)	Analysis of mid-level standard after every 10 samples. All samples should be bracketed by the analysis of a standard demonstrating that the system was capable of accurately detecting and quantifying perchlorate.	%Difference $\leq$ 15% relative to initial value.	Correct problem and rerun CCV and all samples analyzed since last successful CCV. If that fails, apply Q-flag to all results in all samples since the last acceptable calibration verification, if reanalysis is not possible.	No samples may be analyzed until the problem has been corrected.

Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Limit of Detection Verification Standard (LODV)	Analyze before and directly after every batch of samples is analyzed. It can be analyzed after every 10 samples in order to reduce the reanalysis rate.	Perchlorate spike concentration is approximately 2 times the limit of detection. Recovery within 30% of its true value. If a sample with perchlorate concentration at or between the LOD and RL is bracketed by a failing LODV, it must be reanalyzed. A sample with concentration above the RL can be reported.	Correct problem and rerun LODV and all samples analyzed since last successful LODV. If that fails, apply Q-flag to all results in all samples since the last acceptable calibration verification, if reanalysis is not possible.	No samples may be analyzed until the problem has been corrected.
Interference Check Sample (ICS)	One ICS is extracted with every batch of 20 samples. It verifies the method performance at the matrix conductivity threshold (MCT). At least one ICS must be analyzed daily.	Analysis of a standard containing perchlorate at the RL and interfering anions at the concentration determined by the interference threshold study. Monitor recovery of perchlorate and retention time. Recovery within 30% of the true value.	Correct problem and then reanalyze all samples in that batch. If poor recovery from the cleanup filters is suspected, a different lot of filters must be used to reextract all samples in the batch. If column degradation is suspected, a new column must be calibrated before the samples can be reanalyzed.	No samples may be reported that are associated with a failing ICS.
Method Blanks (MB)	One per batch. Undergoes same pretreatment steps as the samples.	< ½ of the RL.	Correct problem, reprep, then reanalyze method blank and all samples processed with the contaminated blank. Apply B-flag to all results for the specific analytes in all samples in the associated preparatory batch if reanalysis is unsuccessful.	
Laboratory Control Sample (LCS)	Once per analytical batch spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within method requirements or laboratory-generated limits, or 85-115% to verify calibration and to check method performance.	Correct problem, then reprep and reanalyze the LCS and all associated samples. If corrective action fails, apply Q-flag to all samples in the associated preparatory batch.	

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Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Matrix Spikes (MS)	Collect one per 20 samples per matrix, spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within 75-125%.	In the parent sample, apply J-flag if acceptance criteria are not met.	For matrix evaluation only. If MS results are outside the limits, the data must be evaluated to determine the source of the difference and to determine if there is a matrix effect or analytical error.
Matrix Spike Duplicates or Laboratory Duplicates (MS and MSD)	Collect one per 20 samples per matrix, spiked at the RL. Undergoes same pretreatment steps as the samples.	Recovery within MS limits, relative percent difference < 20%.	In the parent sample, apply J-flag if acceptance criteria are not met.	Evaluate the data to determine the source of the difference.
Laboratory Reagent Blank	Analyzed prior to calibration and after samples with overrange concentration of perchlorate and after each batch is analyzed.	Concentration < ½ RL.	Reanalyze reagent blank (until no carryover is observed) and all samples processed since the contaminated blank. Apply B-flag to all results not preceded by an acceptable reagent blank if reanalysis is not possible.	
Mass Tuning	Optimize setting of the mass spectrometer daily before sample analysis.	Tuning standards should contain the analytes of interest and meet acceptance criteria outlined in the laboratory SOP.	Retune instrument. If the tuning will not meet acceptance criteria, an instrument mass calibration must be performed and the tuning redone.	Sample analysis should not proceed without an acceptable tuning.

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Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Mass Calibration	Instrument must have a valid mass calibration prior to any sample analysis. The mass calibration is updated on an as-needed basis (QC failures, ion masses show large deviations from known masses, major instrument maintenance is performed, or the instrument is moved).	Mass calibration range must bracket the ion masses of interest without greatly exceeding the range. The most recent mass calibration must be used for an analytical run, and the same mass calibration must be used for all data files in an analytical run. Mass calibration must be verified by acquiring a full scan continuum mass spectrum of a perchlorate stock standard. Perchlorate ions should be within ± 0.3 *m/z* of mass 99, 101, and 107.	If the mass calibration fails, recalibrate. If it still fails, consult manufacturer instructions on corrective maintenance.	No samples may be analyzed under a failing mass calibration.
Isotope Ratio $^{35}Cl/^{37}Cl$	Every sample, spiked sample, and standard and method blank.	Monitor for both the parent ion at mass 99/101 and the daughter ion at mass 83/85 for MS-MS methods or just 99/101 for MS only. Theoretical ratio ~ 3.06. Must fall within 2.3 to 3.8.	If criteria are not met, the sample must be rerun. If the sample was not pretreated, the sample should be reextracted using cleanup procedures. If, after cleanup, the ratio still fails, use alternative techniques to confirm presence of perchlorate (i.e., a post spike sample, dilution to reduce any interference, etc.). Data should be qualified as estimated (J-flag) and should be noted in the case narrative.	Decision to report data failing ratio check should be thoroughly documented in case narrative.
Internal Standard (IS)	Addition of ^{18}O-labeled perchlorate to every sample, spiked sample, standard, instrument blank, and method blank.	Measured ^{18}O IS area within ± 50% of the value from the initial calibration. RRT of the perchlorate ion in a sample is the retention time of the perchlorate ion divided by the retention time of the internal standard. The RRT must be 1.0 ± 2% (0.98 – 1.02).	Rerun the sample at increasing dilutions until the ± 50% acceptance criteria are met. If criteria cannot be met with dilution, the interference are suspected and the sample must be reprepped using additional pretreatment steps. Data should be qualified as estimated with a Q-flag and should be discussed in the case narrative.	If peak is not within retention time window, presence is not confirmed. Use for quantitation and to ensure identification. Failing internal standard should be thoroughly documented in the case narrative.

Table G-3: Minimum QC Requirements for MS Methods

QC Element	Minimum Frequency	Criteria/Requirements	Corrective Action/Flagging Criteria	Comments
Interference Threshold Study	At initial setup and when major changes occur in the method's operating procedures (addition of cleanup procedures, column changes, mobile phase changes).	Measure the threshold of common suppressors (chloride, sulfate, carbonate, bicarbonate) that can be present in the system without affecting the quantitation of perchlorate. The threshold is the concentration of the common suppressors where perchlorate recovery falls outside an 85-115% window.	N/A	This study and site history will determine the concentration at which the ICS suppressors should be set.

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