

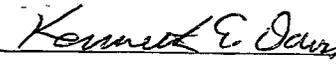
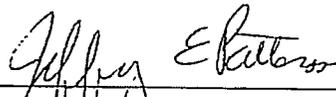
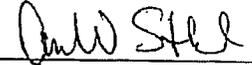
**FIELD SAMPLING PLAN
FOR PILOT STUDY OF THE
DONA PARK NEIGHBORHOOD
CORPUS CHRISTI
NUECES COUNTY, TEXAS**



Texas Commission on Environmental Quality
12100 Park 35 Circle, Bldg D
Austin, Texas 78753

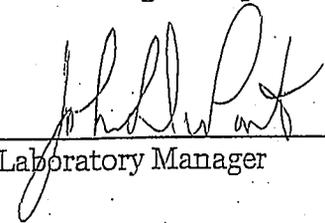
October 2010

Table 1: FSP Approval and Key Participants

NAME	RESPONSIBILITY	PHONE NUMBER/ EMAIL	ORGANIZATION	FSP APPROVAL SIGNATURE	APPROVAL DATE
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Laboratory Acknowledgement

I am responsible for the laboratory activities specified in the applicable work order conducted under this Field Sampling Plan (FSP). I have reviewed this FSP and the *TCEQ Quality Assurance Project Plan (QAPP)* (Document No. 200919.6). I understand this FSP and the QAPP together constitute the Sampling and Analysis Plan (SAP) for the site, and I understand that the terms of the current Assessment Investigation and Remedial Services Contract (AIRS) apply. I understand the project objectives and acknowledge receipt of the SAP.


Laboratory Manager

DHL Analytical
Company Name

10/15/10
Date

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1.0 INTRODUCTION

The Texas Commission on Environmental Quality (TCEQ) has prepared this Field Sampling Plan (FSP) for a Pilot Study at select residences in the Dona Park neighborhood in Corpus Christi, Nueces County, Texas. The neighborhood is located due south of the former American Smelting and Refining Company (ASARCO) zinc smelter, in Corpus Christi, Texas (the facility). Since 1994, a number of investigations and soil removal activities have been performed in this community. Due to the proximity of the neighborhood to the former zinc smelter and residents' and Citizens for Environmental Justice (CFEJ) concerns over the adequacy of previous investigations and soil removal activities, lead, zinc, and cadmium concentrations of residential soils are of concern.

The Sampling and Analysis Plan (SAP) for this Pilot Study consists of this site-specific FSP, applicable *TCEQ Standard Operating Procedures* (TCEQ SOPs) included in this FSP, and the *TCEQ Quality Assurance Project Plan* (QAPP) (Document No. 200919.7), as revised or amended by Section 8 of this FSP.

The TCEQ has requested that Weston Solutions, Inc., and Daniel B. Stephens and Associates, Inc., (hereafter referred to as CONTRACTOR) implement the tasks described in this FSP under TCEQ's current Assessment Investigation and Remedial Services Contract (AIRS).

This FSP presents the requirements and procedures for conducting field operations and other data collection efforts. This FSP has been prepared to ensure that the data quality objectives for the field and laboratory are satisfied, the field sampling methods are implemented in an appropriate manner, and the data collected are scientifically valid and defensible. A separate Health and Safety Plan (HASP) has been prepared to insure the safety of all field personnel during field implementation of this FSP.

This FSP is required reading for all CONTRACTORS, subcontractors, and TCEQ staff participating in the work effort. This FSP will be in the possession of the field teams collecting the samples. All involved CONTRACTORS, subcontractors, and TCEQ staff will have access to this FSP and are required to comply with the procedures documented herein.

To ensure that the current approved version of this FSP is being used, the TCEQ Project Manager (PM) and CONTRACTOR PM will be responsible for distributing the approved FSP and any revisions and/or addenda to the personnel involved in the project in their respective organizations and to subcontractors. The FSP distribution list is included as Table 1.

1.1 Purpose

This FSP describes the methods and objectives of the Pilot Study which will utilize discrete and composite soil samples analyzed by field portable x-ray fluorescence (XRF)

spectrometry and laboratory analysis to determine the concentrations of Target Chemicals of Concern (COCs) in residential soils. The objectives of the Pilot Study are:

- determine the concentrations of the COCs in soils of residential yards,
- establish a correlation between laboratory analyses and the XRF analyses of soils, and
- establish the optimal depth interval for soil samples.

1.2 Project Organization

The project team for the Pilot Study is presented in Table 1. Lines of communication for the project are shown in Figure 1 (Project Organization Chart). These individuals are responsible for communicating and planning to ensure all data obtained can be used for its intended purposes and to provide the direction and supervision needed to ensure that technically sound decisions are made within their areas of expertise.

In addition to the roles and responsibilities set forth in Element A.4 of the QAPP, the following additional responsibilities are assigned:

The TCEQ PM is responsible for:

- determining the project data quality objectives (DQOs),
- planning the project and completing the activities described in the SAP,
- directing the activities of the CONTRACTOR, and
- distributing the approved SAP and each addendum to the TCEQ personnel on the distribution list.

The TCEQ Quality Assurance (QA) Specialist is responsible for:

- reviewing and approving the analytical chemistry QA/QC aspects of the project,
- reviewing and approving the FSP for the project,
- reviewing the laboratory submittals specified in the Work Order (WO),
- ensuring the measurement quality objectives (MQOs) for the project were met by the CONTRACTOR and analytical laboratory, and
- reviewing the data usability summary (DUS) and other CONTRACTOR deliverables associated with analytical data.

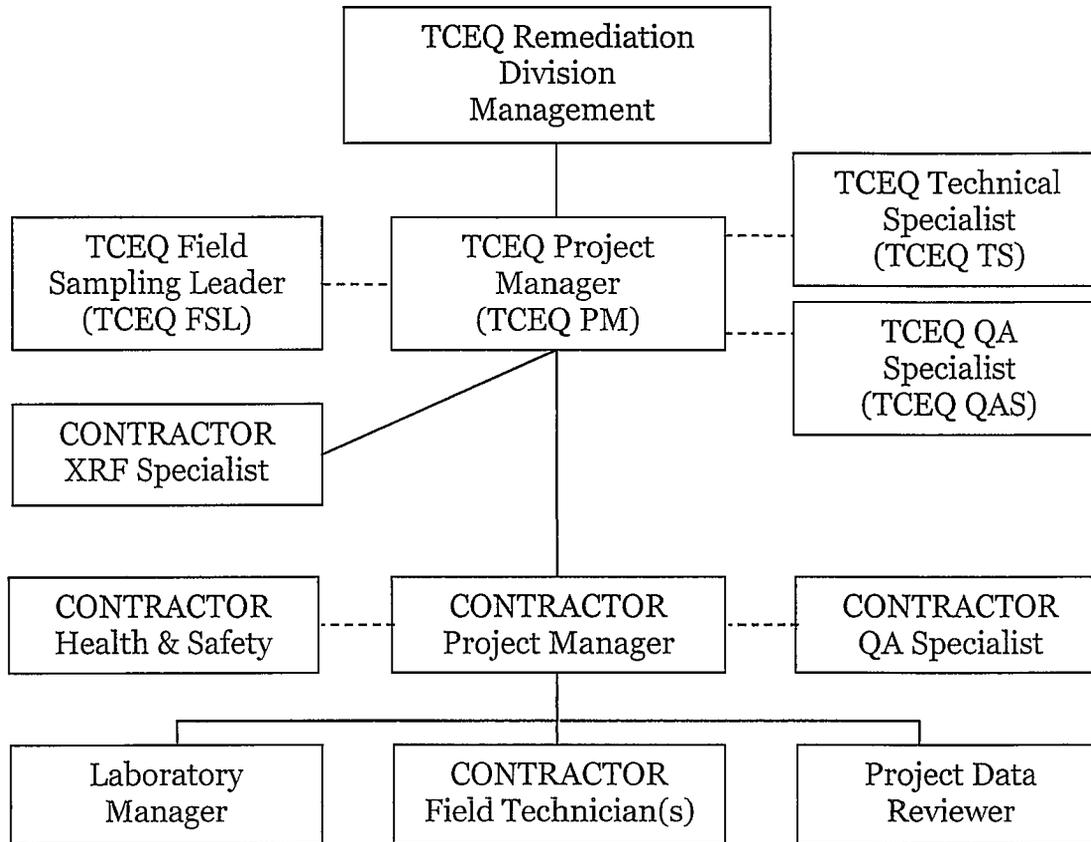
The TCEQ Field Sampling Leader is responsible for:

- communicating and coordinating with residents whose yards are being sampled;
- administering the resident questionnaire ahead of field work at a Study Unit;
- documenting field activities in the TCEQ field log book;
- determining sample locations;
- directing and overseeing all aspects of CONTRACTORS' field work, which will include taking photographs, collecting Global Positioning System (GPS) points, documenting sample locations, and conducting other activities described in this FSP;
- ensuring overall CONTRACTOR adherence to the applicable contract, WO, and SAP; and
- communicating project status and progress to the Project Manager from the field.

The CONTRACTOR PM is responsible for:

- distributing the approved SAP and addendums to the CONTRACTOR's and subcontractor's personnel;
- securing the signature from the subcontracted laboratory documenting that the laboratory has reviewed the analytical specifications of the SAP and can meet the analytical project objectives;
- performing and reviewing work (including work performed by subcontracted laboratories and all other subcontractors) which meets the requirements of the applicable contract, WO, and SAP;
- communicating with the TCEQ PM and following instructions issued by the TCEQ PM in accordance with the applicable contract; and
- oversight of and communication with subcontractors.

Figure 1: Project Organization Chart



2.0 SITE AND PROJECT SUMMARY

2.1 Study Area Description

The Study Area is immediately south of the former ASARCO/Encycle facility and includes 57 residences in the Dona Park neighborhood north of Interstate 37 and south of Up River Road along Manchester Avenue, Golla Drive, Dona Drive, and Vernon Drive (Figures 2 and 3). These 57 residential properties (lots) comprising the Study Area were identified by Dona Park residents and CFEJ as areas where assessment and/or removal activities possibly were not adequately performed. Each lot is divided into the front yard and back yard and each of these yards is defined as a Study Unit. This scheme results in two Study Units comprising a lot. These lots were identified by Dona Park residents and CFEJ as areas where assessment and/or removal activities possibly were not adequately performed. The closest Study Unit to the ASARCO smokestack (the stack) is located approximately 950 feet to the south of the stack.

Figure 2: Site Location

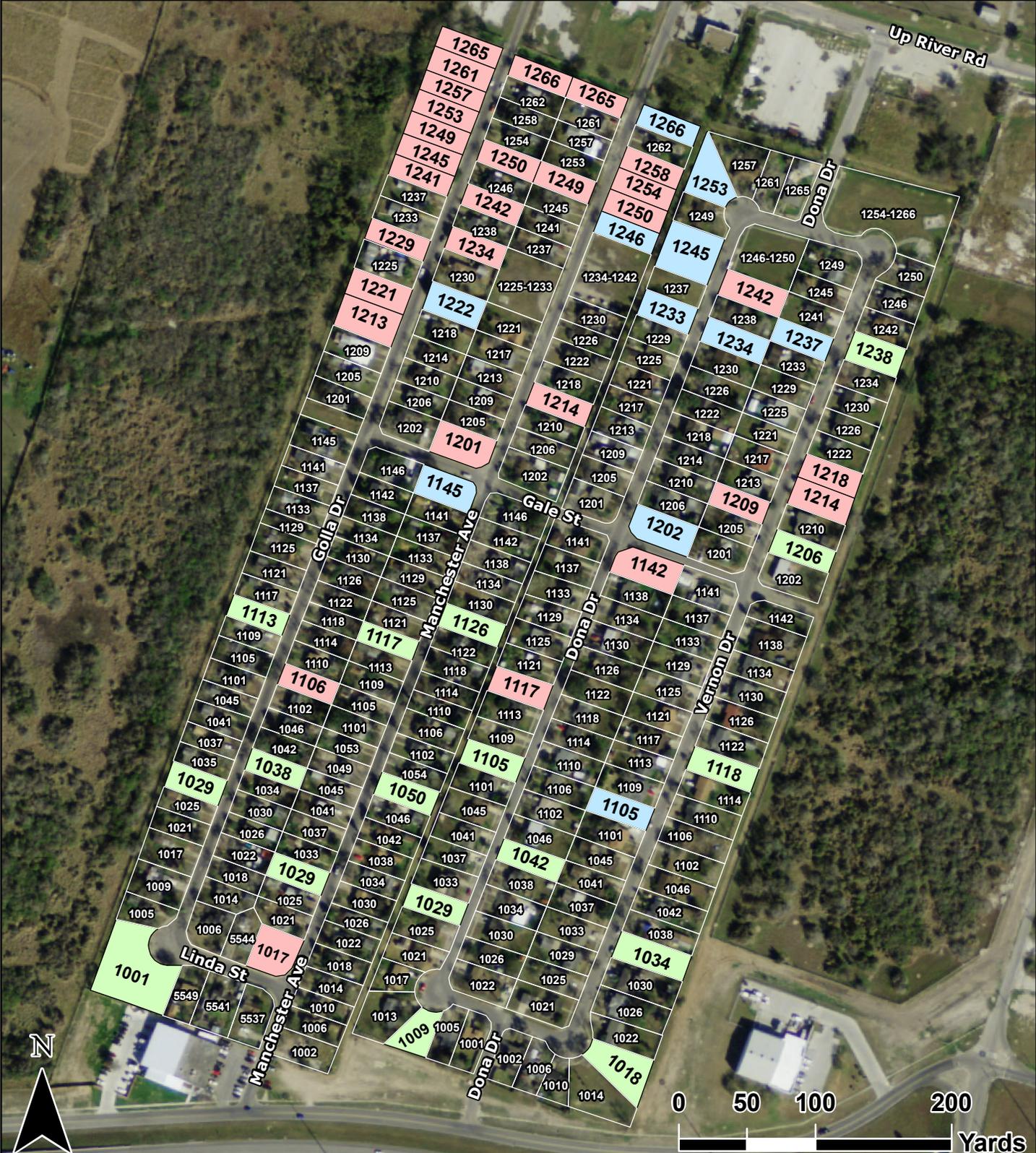


Corpus Christi



The base data used for this map is the 2009 USDA-FSA National Agriculture Imagery Program aerial imagery of Texas. Map Projection: NAD 1983, UTM Zone 14 N. This map was generated by the Remediation Division of the Texas Commission on Environmental Quality. No claims are made to the accuracy or completeness of the data, or to the suitability of the map for a particular use.

Figure 3: Pilot Study Subject Lots



- Community Referred Lots
- Verification Sampling Lots
- Depth Interval & Verification Sampling Lots

The base data used for this map is the 2009 USDA-FSA National Agriculture Imagery Program aerial imagery of Texas. Map Projection: NAD 1983, UTM Zone 14 N. This map was generated by the Remediation Division of the Texas Commission on Environmental Quality. No claims are made to the accuracy or completeness of the data, or to the suitability of the map for a particular use.

2.2 Previous Investigations

The neighborhood has been the subject of a number of investigations and soil removal actions since 1994. Dona Park resident's and CFEJ concerns over the adequacy of previous investigations and soil removal activities and the proximity of the former smelter to the neighborhood prompted this Pilot Study.

2.3 Chemicals of Concern (COCs)

Based on previous investigations and process knowledge of the facility, lead, cadmium, and zinc are the target COCs for the Pilot Study. Tables 2 and 3 list the analytical methods and analytes for the specified samples. All analytes listed in Tables 2 and 3 will be quantified by the laboratory. The COCs known or suspected to be associated with current or former activities at the site are Target COCs and are indicated with an "X" in Table 2.

The Texas Risk Reduction Program (TRRP) Rule, Title 30 Texas Administrative Code (TAC) Chapter 350, established protective concentration levels (PCLs) for numerous chemicals, including lead, cadmium, and zinc. These PCLs are derived through risk assessment procedures and are used as the default cleanup concentration standards for determining if further evaluation of a Study Unit is warranted. The TRRP residential 30 acre Tier 1 total soil combined PCLs ($T_{ot}S_{oil}C_{omb}$ PCLs) for lead, cadmium, and zinc are 500 mg/kg, 52, mg/kg, and 9,900 mg/kg, respectively. A concentration of 50 mg/kg for cadmium, appropriately established as concentrations of interest by TCEQ toxicologists during previous assessments, will be adopted for the pilot study. In summary, concentrations of 500 mg/kg for lead, 50 mg/kg for cadmium, and 9900 mg/kg for zinc will be referred to as the "Action Levels" for the purposes of this Pilot Study.

Table 2: Method SW6020A for Soil – Metals

Target COC	Analyte	CAS No.	QAPP MQL (mg/kg)	Dona Park Action Levels (mg/kg)	TRRP Residential PCL 30 Acre Source ^{Tot} Soil _{Comb} (mg/kg)	Lab MQL (mg/kg)	Is Lab MQL ≤ LORP? (Y/N)
<input type="checkbox"/>	Aluminum	7429-90-5	2.0	64000	64000	12.5	Y
<input type="checkbox"/>	Antimony	7440-36-0	0.1	15	15	1	Y
<input type="checkbox"/>	Arsenic	7440-38-2	1.0	24	24	1	Y
<input type="checkbox"/>	Barium	7440-39-3	0.3	7800	7800	2	Y
<input type="checkbox"/>	Beryllium	7440-41-7	0.3	38	38	0.3	Y
<input checked="" type="checkbox"/>	Cadmium	7440-43-9	0.2	50	52	0.3	Y
<input type="checkbox"/>	Chromium (total)	7440-47-3	0.4	27000	27000	2	Y
<input type="checkbox"/>	Cobalt	7440-48-4	0.8	21	21	2	Y
<input type="checkbox"/>	Copper	7440-50-8	0.6	550	550	2	Y
<input checked="" type="checkbox"/>	Lead (inorganic)	7439-92-1	0.2	500	500	0.3	Y
<input type="checkbox"/>	Manganese	7439-96-5	0.2	3400	3400	2	Y
<input type="checkbox"/>	Nickel and compounds	7440-2-0	0.2	830	830	2	Y
<input type="checkbox"/>	Selenium	7782-49-2	0.1	310	310	0.5	Y
<input type="checkbox"/>	Silver	7440-22-4	0.2	95	95	0.2	Y
<input type="checkbox"/>	Thallium and compounds (as thallium chloride)	7791-12-0	0.1	6.3	6.3	1	Y
<input checked="" type="checkbox"/>	Zinc	7440-66-6	2.5	9900	9900	2.5	Y

QAPP = Quality Assurance Project Plan for the Superfund Program: Document Number (200919.7)
 TRRP PCL = Texas Risk Reduction Program Protective Concentration Limit (last revised March 31, 2010)
 MQL = Method quantitation limit
 LORP = Level of required performance (denoted by bold font)

Table 3: Method SW7471B for Soil – Mercury

Target COC	Analyte	CAS No.	QAPP MQL (mg/kg)	TRRP Residential PCL 30 Acre Source ^{Tot} Soil _{comb} (mg/kg)	Lab MQL (mg/kg)	Is Lab MQL ≤ LORP? (Y/N)
<input type="checkbox"/>	Mercury (pH = 4.9)	7439-97-6	0.1	2.1	0.04	Y

QAPP = Quality Assurance Project Plan for the Superfund Program: Document Number (200919.7)

TRRP PCL = Texas Risk Reduction Program Protective Concentration Limit (last revised March 31, 2010)

MQL = Method quantitation limit

LORP = Level of required performance (denoted by bold font)

2.4 Conceptual Site Model

For the purposes of this investigation, it is assumed that the smokestack (the stack) formerly used during the ASARCO smelter operation was a potential source of lead, cadmium, and zinc concentrations via aerial transport and deposition onto residential soils. Particulate emissions from waste piles and other sources at the facility may have also contributed to the concentrations of these COCs in neighborhood soils. The ASARCO stack is located approximately 950 feet to the north of the nearest study unit.

Soils located near roadways can exhibit higher concentrations of lead due to the extensive use of leaded gasoline prior to 1975. Additionally, lead paint used on older homes is known to flake off and potentially contribute to the lead concentrations in nearby soils. For these reasons, collection of soil samples from areas near roadways and driveways, house drip-lines, and other potential sources of lead paint or automobile emissions will be avoided to the extent practical during this study. However, the determination of whether or not historical use of leaded gasoline and/or lead paint has contributed to the lead concentrations in soils in the Study Area is beyond the scope of the Pilot Study.

Extensive environmental industry experience has shown that in most situations transport of metal contaminants via air deposition results in the highest concentrations of metal COCs within the first few inches of soil. Further transport of metal COCs through infiltration, human activities, or other mechanisms to depths beyond the first few inches is not commonly observed. Additionally, industry experience has shown concentrations of metals generally decrease rapidly downward through the soil column in air deposition situations. The human health risk models used to determine action levels assume that human exposure generally occurs at the surface where soils are more readily contacted than at depth. Numerous previous sampling events in the Study Area have demonstrated that lead, cadmium, and zinc concentrations are highest within the top few inches of soil. However, this Pilot Study will investigate the soil samples down to 6 inches to verify the highest concentrations are found in the first few inches and to determine the optimal sample collection depth interval via sampling and analysis (discussed further below).

2.5 Schedule of Activities

The Pilot Study will consist of two distinct sampling events (i.e. Phase I and Phase II). The objectives and procedures of each phase are described in Section 4.0.

Phase I: Optimal Depth Interval Sampling

TCEQ and CONTRACTORS will mobilize to the field the week of October 18, 2010 to implement Phase I sampling. Phase I will generate data required for Phase II sampling.

Phase II: Determination of COC concentrations in Pilot Study Lots

Phase II activities will be scheduled after the Phase I data have been evaluated to determine the optimal depth interval and required soil moisture conditions.

Each day during each sampling event, the Health and Safety Officer (HSO) will conduct a safety briefing which will review the following:

- potential hazards;
- routes of egress from potentially contaminated areas and the site in general;
- routes to the hospital;
- telephone numbers for TCEQ managers, local emergency workers, and other local contacts; and
- emergency assignments and procedures.

Following the safety briefing, the TCEQ or CONTRACTOR PM will discuss the following in preparation for the day's activities:

- team roles, responsibilities, and assignments;
- sample locations and sampling procedures;
- decontamination procedures;
- QA/QC activities; and
- the schedule for the day.

3.0 ANALYTICAL REQUIREMENTS AND DATA QUALITY OBJECTIVES

3.1 Analytical Requirements

In accordance with the standard practice of the TCEQ, the most recent updated versions of EPA methods from *SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* will be used for all sample analyses. Requirements for these analytical methods are briefly described in the QAPP and the site-specific exceptions, additions, or changes to the requirements of the QAPP are described in Section 8 of this FSP.

A principle objective of the Pilot Study is to correctly determine if the true mean concentration of lead, cadmium, or zinc in each Study Unit (front or back yard) is above

or below the Action Levels. Study Units with mean concentrations exceeding the Action Level of one or more COC will be considered for further evaluation; Study Units with mean concentrations for all COCs below the Action Levels will require no further evaluation.

LABORATORY METHODS

Lead, cadmium, and zinc are routinely analyzed at commercial environmental laboratories throughout the United States using EPA SW-846 6020A for metals in soil by inductively coupled plasma-mass spectrometry and using SW-846 Method 7471B for mercury in soil by cold-vapor atomic absorption. Precise and accurate analysis of the Target COCs can be obtained using these laboratory methods. These analytical methods will be used to analyze samples collected under this FSP.

FIELD PORTABLE X-RAY FLUORESCENCE ANALYSIS (XRF)

Samples collected under this FSP will be analyzed by SW-846 Method 6200 field screening method in conjunction with confirmatory laboratory analytical methods. The SW846-6200 method is an XRF method with the capability for analyzing the sample both *in-situ*, i.e., in place without removing the soil from the ground, and *ex-situ*, i.e., out of place as in collected and containerized. This method can be used to rapidly analyze lead, cadmium, and zinc in soil at a large number of locations in the field. The lower limits of detection using this method are typically sufficient for the analytical requirements of this study. The appropriateness of XRF use for this particular study will be determined through an evaluation of the correlation between the field analytical results and the confirmatory laboratory analytical results as described below.

The sampling and analysis plan for the Pilot Study will consist of a combination of laboratory analysis and field XRF analysis. Field analytical methods are generally less sensitive and precise than laboratory methods. However, field analytical methods allow for a larger number of samples to be collected and analyzed in a more cost effective and time efficient manner than laboratory methods and can be used to determine concentrations of COCs in the Study Unit.

CORRELATION BETWEEN LABORATORY AND FIELD ANALYSES

The laboratory method is more sensitive, accurate, and precise, and is expected to provide the best estimate of the COC concentrations in individual samples. However, because XRF allows more samples to be analyzed, the XRF provides a better overall decision for the Study Units. Therefore, the XRF results will be compared with the laboratory analytical results. During the Pilot Study, most samples will undergo laboratory as well as field XRF analysis (as explained below, core samples to determine the appropriate depth interval will undergo only laboratory analyses).

Linear regression will be used to compare laboratory results with XRF results. Because laboratory samples are more extensively prepared (mixed, ground, and digested) than XRF samples, field analyses can result in an underestimation of actual concentrations.

However, underestimation can be accounted for in the decision process. The results of the Pilot Study linear regression will be used to determine the correlation between the laboratory and XRF estimates and any underestimation trend in the XRF estimates. If necessary, an XRF Action Level lower than the Dona Park Action Level listed in Table 2 will be developed to protect against decision errors.

3.2 Level of Required Performance (LORP)

The Level of Required Performance (LORP) is the concentration around which the laboratory shall demonstrate the method can quantify analytical responses. The laboratory will use a method having a calibration standard run at a concentration lower than the LORP or will clearly identify the COCs that the laboratory method cannot quantify at the LORP due to technical limitations. The laboratory method quantitation limit (MQL) will be less than the LORP or the laboratory will advise the CONTRACTOR that the laboratory cannot meet the LORP. If the laboratory cannot meet the LORP, i.e., the method MQL exceeds the LORP for a specified COC, the laboratory will verify the method proposed for use is the most sensitive method for the COC in the matrix of concern and will provide the laboratory's method detection limit (MDL) supported by a successful detectability check sample (DCS) analysis to the CONTRACTOR. The CONTRACTOR is responsible for ensuring the laboratory MQLs are below the LORPs and for securing concurrence from the TCEQ PM when the laboratory proposes the use of a method with an MQL greater than the LORP.

3.3 Data Validation and Usability

There are three components of the review of analytical chemistry data specified in the QAPP; these three components are termed: Laboratory Data Review (LDR), Data Usability Review (DUR), and Data Validation. Each of these components is discussed below and additional guidance on LDR, DUR, and Data Validation can be found in the QAPP.

3.3.1 Laboratory Data Review

Laboratory Data Review (LDR) is the routine review performed by the laboratory during and soon after sample analysis. It consists of laboratory personnel applying their expertise in assessing the generated data against specified quality control criteria and other requirements. LDR will be performed in accordance with the applicable preparation and analytical methods as well as documented internal laboratory operating procedures. For each analysis, the laboratory will perform LDR on the reportable and supporting data (as defined in Elements A.9.2.2 and A.9.3, respectively, of the QAPP) in accordance with the requirements listed in Element D.2.1.1 of the QAPP. The results of the LDR will be documented in the Laboratory Review Checklist (LRC) and, as necessary, in Exception Reports (ERs) as described in Element A.9.2.1, Element A.9.2.1.1, and Attachment 2 of the QAPP.

3.3.2 Data Usability Review (Independent Data Review)

Data Usability Review (DUR) is the review of the reportable data by a party independent of the analyzing laboratory. Like all data review, the DUR consists of the comparison of certain quality control results with the QC acceptance criteria specified in this FSP and the QAPP.

If specified in the WO, CONTRACTOR will perform a DUR on each analytical batch as specified in Element D.2.1.2 of the QAPP. CONTRACTOR will identify and report issues and concerns encountered during the DUR and will implement recommended corrective actions, as necessary, after discussion with the TCEQ Quality Assurance Specialist. The results of analyses will be flagged with the final DUR qualifiers, qualifier codes, and bias codes in accordance with criteria given in Element D.1.1 of the QAPP.

3.3.3 Data Validation

Validation of project data is performed on a minimum of 10 percent of the project analytical batches (or at least one analytical batch per sampling event if there are fewer than 10 batches). Data validation is implemented to provide a quality check on the laboratory system generating the data. All of the QC results which were reported on the laboratory test reports (or summary forms) as being outside of the acceptance criteria shall be checked against the Laboratory Review Checklist to evaluate whether problems were identified and reported. Ten percent of the data in the data packages being validated shall be checked for transcription errors and calculation errors. If systematic or frequent errors are encountered, 100 percent of the data packages shall be reviewed for errors analogous to those identified in the initial review. The data validation will be completed by the CONTRACTOR as specified in QAPP Element D.2.1.3.

3.3.4 Data Validation Memorandum

If specified in the WO, CONTRACTOR will document the results of the DUR and/or Data Validation in the Data Review Memoranda (DRM) and Data Validation Memoranda (DVM), respectively, prepared in accordance with the applicable contract specifications. The DRM and DVM will briefly summarize the results of the data review or data validation and identify issues and concerns encountered during the data review or data validation, including any significant QC problems or anomalies, rejected data, and any corrective action taken or recommended for future analyses.

3.4 Sampling Objectives and Data Quality Objectives

Data Quality Objectives (DQOs) are qualitative and quantitative statements that translate non-technical project goals into technical project-specific decision goals. The

sampling approach was developed with community input in an effort to design an appropriate data collection scheme that generates the data required for the Pilot Study. The sample rationale and sampling plan design is discussed in Section 4. A two-phased sampling approach will be used. The purpose of Phase I is to determine the optimal depth interval for sampling; the purpose of Phase II is to collect samples at the optimal depth to determine the mean concentration of COCs for each Study Unit.

Since the TRRP Rule dictates that exposure areas be limited to the size of existing yards or 1/8th acre, each front yard and each back yard residence included in the Pilot Study will be designated as a separate Study Unit.

The Pilot Study is designed to answer the following questions:

- Is the mean concentration of lead, cadmium, and zinc in a Study Unit greater than the Action Level?
- Is there a reasonable correlation between the mean concentration of the in-situ discrete XRF (IDX) measurements and the ex-situ composite laboratory (ECL) measurements?
- Is there a reasonable correlation between the ex-situ composite XRF (ECX) measurements and the ex-situ composite laboratory (ECL) measurements?
- Is there a sample collection depth interval that consistently yields the highest concentration?

4.0 SAMPLING PLAN DESIGN

4.1 Sample Locations

The Pilot Study will consist of implementing the sampling protocols described below on 57 residential yards consisting of 114 Study Units (front and back yards). The surface area for each Study Unit will be estimated with a measuring wheel to exclude impervious surfaces and driveways, house drip-lines, and other potential sources of lead.

The term “in-situ” will be used to describe soil that remains in place during the measurement process. “Ex-situ” means the soil at the Sample Location is removed and collected in a sample container. “Core Location” is the position in the Study Unit from which a soil core is extracted during Phase 1 activities. “Sample Locations” are geospatial positions in a Study Unit from which an in-situ discrete XRF measurement is performed or an ex-situ discrete sample or an ex-situ composite aliquot is collected during Phase 2 activities.

PHASE I: Determining the Optimal Depth Interval for Sample Collection

EX-SITU DISCRETE CORE SAMPLES

In order to determine the optimal depth interval for subsequent samples, Phase 1 of the Pilot study will consist of the collection of ex-situ discrete core (“Core”) samples from 11 selected lots. Lots with the highest historical lead or cadmium concentrations, that were never remediated, were selected for Phase I sampling and are listed in Table 4.

One six-inch soil core will be collected from a single Core Location at each of the Study Units designated for core sampling. One or more cores will be extracted from each Core Location as needed to provide sufficient sample volume to meet volume requirements of the laboratory. Additional cores will be extracted from as near to the original core location as is feasible.

Six separate interval samples will be collected from the extracted cores at each Core Location as follows:

- 0-1 inch interval,
- 1-2 inch interval,
- 2-3 inch interval,
- 3-4 inch interval,
- 4-5 inch interval, and
- 5-6 inch interval.

The depth intervals will be established against the extracted soil core using an appropriate measurement device. Using a cutting tool, the CONTRACTOR will carefully separate each soil core into the depth intervals described above.

The first three samples (from 0-1, 1-2, and 2-3 inches deep) will be shipped to the laboratory for immediate analyses. The remaining three samples from each core sample location (from 3-4, 4-5 and 5-6 inches deep) will be sent to the laboratory, but retained for future analyses at the instruction of the TCEQ PM. The decision on whether or not to analyze these deeper core samples will be based on the sample results of the shallower core samples. If, as anticipated, Target COC concentrations diminish with depth (or are already less than the Action Levels) there will be no need to analyze the deeper core samples. If on the other hand, the shallower core samples do not indicate a reduction of Target COC concentrations with depth, all or some of the deeper core samples will be analyzed based on instruction from the TCEQ PM.

Four Split Samples collected from community-selected Study Units and depth intervals (from 0-1, 1-2, and 2-3 inches deep) will also be shipped to EPA’s Region 6 Laboratory in Houston, Texas, for independent analysis.

Table 4: Phase I Optimal Depth Interval Core Sampling Lots

Address	Street	Yard
1202	Dona Drive	Front
1233	Dona Drive	Back
1234	Dona Drive	Front
1245	Dona Drive	Front
1253	Dona Drive	Front
1222	Golla Drive	Front
1145	Manchester Avenue	Back
1246	Manchester Avenue	Front
1266	Manchester Avenue	Back
1105	Vernon Drive	Front
1237	Vernon Drive	Front

PHASE II: Determining the Mean Concentration for Each Study Unit

DISCRETE IN-SITU XRF MEASUREMENTS

Twenty approximately equally-spaced Sample Locations will be marked with flags in each Study Unit. At each Sample Location, vegetative cover and soil will be removed to reach the optimal depth interval and the XRF will be used to make an in-situ discrete XRF (“IDX”) measurement. Each individual IDX measurement will be recorded and the mean concentration of the twenty measurements calculated and recorded as the IDX estimate of the mean concentration in that Study Unit. Tables 5 and 6 identify the 57 lots where IDX measurements will be taken. Table 5 lists lots that were referred to TCEQ by CFEJ and community residents. Table 6 lists lots that were selected by TCEQ to ensure the Pilot Study adequately covers the entire community.

Table 5: Phase II Community Referred Lots

Address	Street	Yard
1117	Dona Drive	Both
1142	Dona Drive	Both
1242	Dona Drive	Both
1106	Golla Drive	Both
1213	Golla Drive	Both
1221	Golla Drive	Both
1229	Golla Drive	Both
1234	Golla Drive	Both
1241	Golla Drive	Both
1242	Golla Drive	Both
1245	Golla Drive	Both
1249	Golla Drive	Both
1250	Golla Drive	Both
1253	Golla Drive	Both
1257	Golla Drive	Both
1261	Golla Drive	Both
1265	Golla Drive	Both
1266	Golla Drive	Both
1017	Manchester Avenue	Both
1201	Manchester Avenue	Both
1214	Manchester Avenue	Both
1249	Manchester Avenue	Both
1250	Manchester Avenue	Both
1254	Manchester Avenue	Both
1258	Manchester Avenue	Both
1265	Manchester Avenue	Both
1209	Vernon Drive	Both
1214	Vernon Drive	Both
1218	Vernon Drive	Both

Table 6: Phase II Verification Sampling Lots

Address	Street	Yard
1009	Dona Drive	Both
1029	Dona Drive	Both
1042	Dona Drive	Both
1105	Dona Drive	Both
1202	Dona Drive	Both
1233	Dona Drive	Both
1234	Dona Drive	Both
1245	Dona Drive	Both
1253	Dona Drive	Both
1001	Golla Drive	Both
1029	Golla Drive	Both
1038	Golla Drive	Both
1113	Golla Drive	Both
1222	Golla Drive	Both
1029	Manchester Avenue	Both
1050	Manchester Avenue	Both
1117	Manchester Avenue	Both
1126	Manchester Avenue	Both
1145	Manchester Avenue	Both
1246	Manchester Avenue	Both
1266	Manchester Avenue	Both
1018	Vernon Drive	Both
1034	Vernon Drive	Both
1105	Vernon Drive	Both
1118	Vernon Drive	Both
1206	Vernon Drive	Both
1237	Vernon Drive	Both
1238	Vernon Drive	Both

COLLECTION OF EX-SITU COMPOSITE SAMPLES

Following in-situ discrete XRF measurement, an equal volume aliquot of soil from the optimal depth interval from each Sample Location will be removed and placed in an appropriate sample bag using a suitable coring device. The ex-situ composite sample will then be thoroughly disaggregated and mixed in the field as described in the XRF SOP. Sample bags, containers, and sampling devices are described in Section 5 of this FSP. Twenty such aliquots from each Study Unit will comprise the ex-situ composite sample for that Study Unit.

EX-SITU COMPOSITE XRF MEASUREMENTS

Following disaggregation and mixing, the mean concentration in the Study Unit will be determined through XRF measurements in the field. Five XRF measurements will be made on the ex-situ composite sample by subjecting the sample to XRF at five separate locations on the outside of the sample bag. Each individual ex-situ composite XRF (ECX) measurement will be recorded in the field logbook and the calculated mean of the five measurements will constitute the ECX estimate of the mean concentration in the Study Unit. After approximately three Study Units have been tested each day, the TCEQ project scientists (Project Manager, Field Team Leader and Technical Specialist) will determine whether the number of ECX measurements on each ex-situ composite sample may be reduced if the percent relative standard deviation between the five ECX measurements is less than or equal to 15% for each Target COC.

EX-SITU COMPOSITE LABORATORY SAMPLES

Following ECX measurements, an appropriate volume of the ex-situ composite sample will be transferred to a laboratory container, labeled, and shipped to the laboratory. The laboratory method will then be used to analyze the ex-situ composite laboratory (ECL) sample and produce the laboratory estimate of the mean concentration in the Study Unit. The remaining sample volume will be cataloged and retained until the TCEQ PM specifically instructs the CONTRACTOR that it should be discarded.

4.2 Sample Analyses

The laboratory analyses for each sample are listed in Tables 2 and 3. XRF measurements for lead, cadmium, and zinc will be made in the field as described in Appendix C: XRF SOP.

4.3 Field Quality Control Samples

Field QC samples listed in Table 7 will be collected in accordance with SOP 6.5 (Collection of QA/QC Samples).

Table 7: Frequency of Collection of Field Quality Control Samples

Type of QC Sample	Frequency of Collection
Matrix Spike/ Matrix Spike Duplicate (MS/MSD)	One per 20 project samples of each matrix. Collect the MS/MSD at a sample location suspected to be contaminated with low to medium levels of COCs. Do not use highly contaminated samples for the MS/MSD.
Equipment Rinsate Blank (ER)	One at the start of sample collection on the first day of the sampling event, and one at the end of each day for each matrix are required when non-dedicated sampling equipment is used.
Field Duplicates (FD)	One per day per 10 project samples of each matrix. Collect the field duplicate at a sample location known or suspected to be contaminated with COCs, immediately after the sample is collected.
Temperature Blank	One per cooler.
Split Samples	EPA will analyze four split samples during Phase I and 10% of Phase II samples.

5.0 SAMPLING METHODS AND SAMPLE HANDLING

5.1 Field Sampling Procedures

All samples will be collected in accordance with this FSP, the QAPP, and the SOPs referenced in the appendices.

5.1.1 Sample Collection

Sample collection techniques are described below. Field sampling personnel will wear non-lubricated nitrile disposable gloves, or other suitable disposable gloves, during the handling of sampling equipment and during sampling. The disposable gloves will be changed between each Study Unit. Prior to sampling activities, sampling equipment will be handled and decontaminated in accordance with SOP 1.5 (Decontamination), as described in Section 7.2 of this FSP.

5.1.1.1 Soil Samples

All soil samples will be collected with decontaminated sampling equipment and placed into certified clean sample jars or sample bags consistent with TCEQ SOPs, *Appendix B: Sampling and Analysis Procedures*, *Appendix C: XRF Standard Operating Procedure*, and *Appendix E: EPA Method 6200 - Field Portable X-Ray Fluorescence Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment*.

SOP 10.5: Soil Sampling Using a Shelby Tube Sampler procedures are amended per procedures outlined in *Appendix B*. A slam bar sampler will be used in lieu of drilling equipment as the shallow sampling depths do not require drilling. Also, procedures in the SOP relating to volatile organic compounds (VOCs) are not applicable to this Pilot Study.

5.2 Sample Containers, Sample Preservation, and Holding Time

A summary of the requirements for containers, preservation techniques, sample volumes, and holding times for each sample analyte is presented in Table 8: Containers, Sample Volumes, Preservation Techniques, and Holding Times. All sample containers will have a minimum amount of head space present when capped. All samples will be cooled in an ice chest to a temperature ≤ 4 C.

Table 8: Containers, Sample Volumes, Preservation Techniques, and Holding Times

Matrix	Parameter	Required Volume	Container	Preservative	Holding Time
Soil	Metals	4 ounces	One 4-oz wide-mouth glass jar with Teflon®-lined cap	Cool to 4°C	6 months

5.3 Chain-of-Custody Procedures

Handling, packing, and chain-of-custody procedures to track all samples collected and shipped to laboratories will be conducted in accordance with SOP 6.4 (Sample Handling and Control).

6.0 FIELD SURVEY AND MEASUREMENTS

6.1 Property Access

It is the policy of the TCEQ that formal access agreements documenting a landowner's permission for the TCEQ and its CONTRACTORS to investigate and sample their property be obtained, if possible. Form TCEQ-10452 will be used whenever possible to obtain access agreements between landowners and the TCEQ prior to the initiation of sample collection activities. In the event that the TCEQ is unable to secure a written access agreement from a property owner, verbal agreement for access will be obtained whenever possible and documented in the field logbook. If the property is abandoned, or the owner cannot be determined or contacted, the TCEQ PM will determine further courses of action in conjunction with TCEQ management.

6.2 Global Positioning System (GPS) Data

GPS data will be collected pursuant to SOP 17.1 (GPS Data Collection and Submission). GPS coordinates will be obtained for all core samples using appropriately certified GPS equipment operated by appropriately certified GPS technicians. All core sample locations and the IDX Sample Location in the northwest corner of each Study Unit will have GPS coordinates determined. The Sample Location in the northwest corner of each Study Unit will be assigned Sample Location 1 for that Study Unit.

7.0 ADDITIONAL FIELD ACTIVITIES

7.1 Sample Identification and Documentation

All sample locations will be visually inspected, described in the field logbook, and photographed. Information regarding sample collection will be entered into the field logbook in accordance with SOP 6.1 (Field Activity Documentation and Reporting). The following information will be recorded in the field logbook:

- date and time of sample collection;
- sample collection method;
- sample preservation;
- name of the person who collected the sample;
- sample identification number and depth measured from ground surface;
- field measurements made on the sample during collection;
- GPS file number;
- photograph number;
- date and time of photograph with a description of the purpose of the photograph
- name of the person who took the photograph and direction the person was facing when the photograph was taken;
- relevant observations such as soil color, obvious staining, and weather conditions; and
- deviations from the FSP, QAPP, or SOP.

In order to avoid mistakes, sample bottles may be temporarily labeled on the container surface prior to or immediately after sample collection. Sample bottles will be permanently labeled as soon as possible after collection. Sample labels will include:

- field sample ID,
- project name and number,
- sampling date and time,
- name of the sample collector,
- method of sample preservation, and
- laboratory analyses required.

A residential lot, consisting of two Study Units (i.e. front yard and back yard), that is sampled will be identified with a unique number specific to that lot. This identification method will ensure sample results specific to a residential lot will remain confidential when the results are shared with the public. Residents whose yards are sampled will be provided their individual sample results specific to their lots.

Field sample identification number (ID) nomenclature indicating sample type (i.e. in-situ discrete or ex-situ composite), residential lot, depth interval or grid number, and Study Unit will be used to identify individual samples.

- **“Core” sample** IDs will consist of the prefix **“Core”** followed by the unique residential lot number and ending with a dash followed by a two-digit number indicating the depth interval of the core sample followed by an **“F”** or a **“B”** indicating the depth interval and specific Study Unit of the core sample (e.g., **“Core1-01-F”** means Core sample collected from “Residential Lot 1” at the 0-1 inch interval in the front yard Study Unit).
- **In-situ discrete XRF measurement** IDs will consist of the prefix **“IDX”** followed by the unique residential lot number, then a dash and a number indicating the sample grid location, and ending with a dash and an **“F”** or **“B”** to indicate the Study Unit (i.e. front or back yard).
- The calculated **mean estimate of the 20 in-situ discrete XRF measurements** collected from each Study Unit will be identified with the prefix **“IDX”** followed by the unique residential lot number, then a dash and the word **“mean,”** and ending with a dash and an **“F”** or **“B”** to indicate the Study Unit (i.e. front or back yard).
- **Ex-situ composite XRF measurement** IDs will consist of the prefix **“ECX”** followed by the unique residential lot number, then a dash and a number indicating the XRF sample number, and ending with a dash and an **“F”** or **“B”** to indicate the Study Unit (i.e. front or back yard, respectively).
- **The calculated mean estimate of the ex-situ composite XRF measurements** collected from each Study Unit will be identified with the prefix **“ECX”** followed by the unique residential lot number, then a dash and the word **“mean,”** and ending with a dash and an **“F”** or **“B”** to indicate the Study Unit (i.e. front or back yard, respectively).
- **Ex-situ composite laboratory sample** IDs will consist of the prefix **“ECL”** followed by the unique residential lot number and ending with a dash and an **“F”** or **“B”** to indicate the Study Unit (i.e. front or back yard).

Field duplicate samples will have a sample number randomly selected by the TCEQ PM. The identification of duplicate samples will not include any information that may reveal

to the laboratory their identity as duplicates. Associated duplicate samples will be identified in the field logbook. Duplicate sample collection times will be a random increment of time after the collection time of the primary sample.

Equipment rinsate blanks will be identified as "ER" samples, and split samples will be identified by "SS" in front of the corresponding nomenclature described above.

The CONTRACTOR will document each Study Unit with a photograph which depicts as many Sample Locations as possible in a single photo. The photo will be taken from the vicinity of the northwest Sample Location which will be designated as Sample Location one (1). The photo will include permanent landmarks such as buildings, other structures, or old-growth trees.

The CONTRACTOR will document the general dimensions and layout of each Study Unit with a site sketch. The sketch will include GPS points, photograph location, Sample Locations, measurements between Sample Locations and other features of the Study Unit.

7.2 Decontamination

Any non-dedicated equipment potentially coming into contact with contaminated media will be decontaminated according to SOP No. 1.5 (Decontamination). Plastic sheeting will be used to provide a clean working area around each sample location and, to the extent possible, prevent contaminated soil from contacting sampling equipment. Smaller decontamination areas for personnel and portable equipment will be provided as necessary, in accordance with the HASP. All disposable Personal Protective Equipment (PPE) will be decontaminated such that it can be disposed of as Class 3 waste.

Dedicated sampling equipment will be used whenever it is available. Sampling equipment and tools will be decontaminated in accordance with SOP No. 1.5 (Decontamination), as modified in Section 7.2 of this FSP, between sampling locations. Non-dedicated sampling equipment will be decontaminated prior to use and between each Study Unit. An equipment rinsate sample will be collected as specified in Table 7. The TCEQ PM may modify the decontamination frequency as appropriate. Decontamination of field equipment will be performed in accordance with SOP 1.5 (Decontamination), modified as follows:

Following Step 4 in SOP 1.5 for large equipment and following Step 2 for small equipment:

- rinse all equipment with potable water;
- clean equipment with a brush in a solution of laboratory grade detergent (Liquinox, Alconox, or equivalent);
- rinse with potable water;

- if samples are for metals/cyanide analysis, rinse with 10% nitric acid solution (trace metals grade);
- rinse with distilled or deionized water;
- rinse with reagent grade isopropanol if analyzing for organic compounds;
- rinse with deionized water;
- allow equipment to completely dry, then collect an equipment rinsate sample using ultra-deionized water, seal the rinsate sample container with a custody seal, and place the sample in the shipment cooler;
- place the equipment on clean plastic sheeting and allow to air dry; and
- if the equipment is not to be used immediately, place small equipment in plastic sealable bag and place a custody seal across the sealed opening of the bag.

7.3 Investigation Derived Waste

Investigation Derived Waste (IDW) will be handled in accordance with SOP No. 1.4 (Management of Investigation Derived Waste). The CONTRACTOR will be responsible for the collection and containerization of all IDW. IDW will be stored temporarily in acceptable containers such as U.S. Department of Transportation (DOT) approved steel 55-gallon drums or tanks. The containers will be transported to a staging area in a manner to prevent spillage or evaporative loss.

The CONTRACTOR will label all IDW containers with the date of accumulation, description of the materials, the source of the materials, and the field sample numbers of the samples which will be used to classify them. All IDW containers may be temporarily stored in an appropriate staging area designated for that purpose. A completed log of all IDW information and labeling and a rough sketch of the IDW locations with the numbers (or other identifiers) of each IDW container will be included in the field logbook. It is the CONTRACTOR's responsibility to correctly label, characterize, transport and dispose of all IDW generated via this field effort in a timely manner consistent with issued TCEQ WOs and all applicable rules and regulations.

7.4 Site Restoration

The work site and sampling locations will be restored to their original condition in accordance with SOP 1.3 (Site Restoration). Efforts will be made to minimize impacts to work sites and sampling locations, particularly residential properties and those properties in or near sensitive environments.

7.5 Health and Safety Plan

All personnel involved in the sampling event will comply with the HASP applicable to the site. The designated TCEQ and/or CONTRACTOR HSO will conduct a daily safety briefing prior to initiating field work each day to advise workers of site-specific physical and chemical hazards associated with executing the FSP. The topics for this safety meeting are discussed in the HASP and briefly outlined in Section 2.5.

7.6 Deviations, Modifications, and/or Departures from the FSP or QAPP

Each deviation, modification, and/or departure from this approved FSP or QAPP will be recorded, with a discussion of the rationale for each, in the field logbook.

8.0 EXCEPTIONS, ADDITIONS, AND CHANGES TO THE TCEQ QAPP

Changes to QAPP Table B5.1.16-3: Summary of Calibration and QC Procedures for Method SW6020A Applicable Parameters: ICP/MS Metals: Table B5.1.16-3 specifies that a method detection limit (MDL) study be performed "Once per 12 month period." The following phrase will be added: "or perform Detectability Check Samples (DCS) on a quarterly basis throughout the year to verify the MDL." In addition, the acceptance criteria in these tables will be changed from "Detection limits shall be \leq $\frac{1}{2}$ the MQLs in Table B5.1.16-1." to "Detection limits shall be \leq $\frac{1}{2}$ the MQLs listed in Table 2 of the FSP."

Addition to QAPP Element B.4.1 (Screening Methods): SW-846 Method 6200 will be utilized for the field portable x-ray fluorescence (XRF) analysis of soil samples. The XRF SOP to be utilized for this sampling event is provided in Appendix C; SW-846 Method 6200 is included in Appendix E.

Table 9: TCEQ Standard Operating Procedures (SOPs) Checklist

<input type="checkbox"/>	SOP #	SOP Title	<input type="checkbox"/>	SOP #	SOP Title
<input type="checkbox"/>	1.1	Initial Site Reconnaissance	<input type="checkbox"/>	8.4	Surface Water Sampling Using a Pump
<input type="checkbox"/>	1.2	(Site) Preparation and Control	<input type="checkbox"/>	8.5	Surface Water Sampling Using a Bomb Sampler
<input checked="" type="checkbox"/>	1.3	Site Restoration	<input type="checkbox"/>	9.1	Sediment Sampling Using a Trowel
<input checked="" type="checkbox"/>	1.4	Management of Investigative Derived Waste	<input type="checkbox"/>	9.2	Sediment Sampling Using a Bucket Auger
<input checked="" type="checkbox"/>	1.5	Decontamination	<input type="checkbox"/>	9.3	Sediment Sampling Using a Dredge
<input type="checkbox"/>	2.1	Land Survey	<input type="checkbox"/>	9.4	Sediment Sampling Using a Push Core
<input type="checkbox"/>	2.2	Water Use Survey	<input type="checkbox"/>	10.1	Soil Sampling Using a Trowel
<input type="checkbox"/>	2.3	Receptor Survey	<input type="checkbox"/>	10.2	Soil Sampling Using a Split Barrel Sampler
<input type="checkbox"/>	2.4	Utility Survey	<input type="checkbox"/>	10.3	Soil Sampling Using a Hand Auger
<input checked="" type="checkbox"/>	6.1	Field Activity Documentation and Reporting	<input type="checkbox"/>	10.4	Soil Sampling Using Direct Push
<input type="checkbox"/>	6.2	Homogenization of Soil Samples	<input checked="" type="checkbox"/>	10.5	Soil Sampling Using a Shelby Tube Sampler
<input type="checkbox"/>	6.3	Collection of VOC Samples	<input type="checkbox"/>	11.1	Source Sampling of a Homogenous Liquid
<input checked="" type="checkbox"/>	6.4	Sample Handling and Control	<input type="checkbox"/>	11.2	Source Sampling of a Heterogeneous or Stratified Liquid
<input checked="" type="checkbox"/>	6.5	Collection of QA/QC Samples	<input type="checkbox"/>	11.3	Source Sampling of a Homogenous Solid
<input type="checkbox"/>	7.1	Water Level/Sediment Measurement	<input type="checkbox"/>	11.4	Source Sampling of a Heterogeneous or Stratified Solid
<input type="checkbox"/>	7.2	Purging a Monitoring Well with a Bailer	<input type="checkbox"/>	12.1	Asbestos Air Sampling
<input type="checkbox"/>	7.3	Purging a Monitoring Well with a Pump	<input type="checkbox"/>	12.2	Asbestos Solids Sampling
<input type="checkbox"/>	7.4	Micro Purging a Monitoring Well	<input type="checkbox"/>	14.1	Air Sampling and Monitoring Design
<input type="checkbox"/>	7.5	Measurement of Field Parameters	<input type="checkbox"/>	14.2	Air Sampling Using a High Volume Sampler
<input type="checkbox"/>	7.6	Groundwater Sampling Using a Bailer	<input type="checkbox"/>	14.3	Air Sampling Using a PM-10 Sampler
<input type="checkbox"/>	7.7	Groundwater Sampling Using a Pump	<input type="checkbox"/>	14.4	Air Sampling Using a PS-1 Sampler
<input type="checkbox"/>	7.8	Groundwater Sampling Using a Low-flow Techniques	<input type="checkbox"/>	14.5	Air Sampling Using a Summa Canister for VOC Sampling
<input type="checkbox"/>	8.1	Surface Water Sampling Using the Direct Method	<input type="checkbox"/>	14.6	Real-time Air Monitoring
<input type="checkbox"/>	8.2	Surface Water Sampling Using a Kemmerer Bottle	<input type="checkbox"/>	14.7	Collection of Meteorological Data
<input type="checkbox"/>	8.3	Surface Water Sampling Using a Dip Sampler	<input checked="" type="checkbox"/>	17.1	GPS Data Collection and Submission

APPENDIX A
TCEQ STANDARD OPERATING PROCEDURES



STANDARD OPERATING PROCEDURE NO. 1.3 SITE RESTORATION

SOP#: 1.3
DATE: 11/29/2001
REVISION #: 0
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1.0 METHOD SUMMARY

This standard operation procedure (SOP) describes the steps necessary for site restoration. Upon completion of field activities, the site should be repaired to its original condition when possible. All drums or waste containers should be staged in a designated staging area and all other waste should be removed. All borings should be backfilled.

2.0 EQUIPMENT/APPARATUS/REAGENTS

Varies depending on which of the following tasks are completed.

3.0 PROCEDURES

1. Minimize impacts to work sites and sampling locations, particularly those in or near sensitive environments, such as wetlands with the use of soil erosion fences or by diverting streams/brooks during work operations.
2. Fill boreholes and pits, re-vegetate or erect erosion fences as necessary, re-establish streams, brooks, etc, as applicable.
3. Remove all sampling, decontamination equipment, and other items introduced to the site upon completion of work.
4. Remove all drums, trash, and other waste upon completion of work at the site.
5. Transport decontamination and/or purge water and soil cuttings to the designated locations.

4.0 CAUTIONS AND INTERFERENCES

This section is not applicable to this SOP.



STANDARD OPERATING PROCEDURE NO. 1.4
MANAGEMENT OF
INVESTIGATIVE DERIVED WASTE

SOP#: 1.4
DATE: 11/29/2001
REVISION #: 0
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1.0 METHOD SUMMARY

This standard operating procedure (SOP) provides standard operating procedures for managing investigative derived waste (IDW) generated during field activities. Materials which may become IDW include:

- Personnel protective equipment (PPE) including disposable coveralls, gloves, booties, respirator canisters, splash suits, etc.
- Disposable equipment including plastic ground and equipment covers, aluminum foil, conduit pipe, composite liquid waste samplers (COLIWASAs), disposable bailers, rope or twine, Teflon® tubing, broken or unused sample containers, sample container boxes, tape, etc.
- Soil cuttings from drilling or hand augering.
- Excess soil sample material.
- Drilling mud or water used for water rotary drilling.
- Ground water obtained through well development or well purging.
- Cleaning fluids such as spent solvents and washwater.
- Packing and shipping materials.

2.0 EQUIPMENT/APPARATUS/REAGENTS

2.1 Equipment List

- 55-gallon drums
- Labels for drums
- Wrenches for securing drum lids
- Marking pens (for marking on labels and on drums)
- Lumber (for creating storage area)
- Plastic sheeting (for storage area)
- Plywood (for storage area flooring)
- 5-gallon buckets
- Manifests
- Drum log

3.0 PROCEDURES

Be sure to keep all hazardous waste separate from non-hazardous waste. Label each container properly and keep a log (Appendix A) of all the drums or containers, stating their identification number and contents. Drill cuttings from different holes can be put in the same drums provided they originate from similar areas of the site (e.g., upgradient, background borings, etc.).

3.1 Management of Non-Hazardous IDW

1. If necessary, compact the waste into a reusable container, such as a 55-gallon drum to reduce the volume of non-hazardous waste.
2. If the waste is generated from an active facility, seek permission from the operator of the facility to place the *non-hazardous* PPE, disposable equipment, and/or paper/cardboard wastes into the facility dumpsters. These materials may also be taken to a nearby permitted landfill. On larger studies, waste hauling services may be obtained and a dumpster located at the study site.



STANDARD OPERATING PROCEDURE NO. 1.4
MANAGEMENT OF
INVESTIGATIVE DERIVED WASTE

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3. Dispose of *non-hazardous* IDW such as drill cuttings, purge or development water, decontamination washwater, drilling muds, etc. in a unit with an environmental permit such as a landfill or sanitary sewer. These materials must not be placed into dumpsters.
4. Seek permission to place these types of IDW into the facility treatment system if the facility is active.

3.2 Management of Hazardous IDW

1. Properly contain and label all suspected or identified hazardous wastes. Wastes should be stored in labeled 55-gallon drums at a segregated staging facility with a secondary containment structure.
2. Take care to keep non-hazardous materials segregated from hazardous waste contaminated materials.
3. Review appropriate sample results to determine waste characterization and perform any specific analysis required by the permitted disposal facility.
4. Hazardous wastes may be stored on site for a maximum of 90 days before they must be manifested and shipped to a permitted treatment or disposal facility.
5. Dispose of hazardous IDW as specified in the USEPA and TNRCC regulations. If appropriate, place these wastes in an active facility waste treatment system.
6. Anticipate generation of hazardous IDW, if possible, to permit arrangements for proper containerization, labeling, transportation, and disposal/treatment in accordance with USEPA and TNRCC regulations.

4.0 CAUTIONS AND INTERFERENCES

1. All liquid and soil/sediment IDW *must* be containerized and analyzed before disposal.
2. The collection handling, and proposed disposal method must be specified in the site work plan.



**STANDARD OPERATING PROCEDURE NO. 1.4
MANAGEMENT OF
INVESTIGATIVE DERIVED WASTE**

SOP#: 1.4
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APPENDIX A



STANDARD OPERATING PROCEDURE NO. 1.5 DECONTAMINATION

SOP#: 1.5
DATE: 11/29/2001
REVISION #: 0
PAGE 1 of 2

1.0 METHOD SUMMARY

This standard operating procedure (SOP) provides a description of the methods used for preventing, minimizing, or limiting cross-contamination of samples due to inappropriate or inadequate equipment decontamination and to provide general guidelines for developing decontamination procedures for sampling equipment to be used during hazardous waste operations. This SOP does not address personnel decontamination.

Removing or neutralizing contaminants from equipment minimizes the likelihood of sample cross contamination, reduces or eliminates transfer of contaminants to clean areas, and prevents the mixing of incompatible substances. Gross contamination can be removed by physical decontamination procedures. These abrasive and non-abrasive methods include the use of brushes, air and wet blasting, and high and low pressure water cleaning.

2.0 EQUIPMENT/APPARATUS/REAGENTS

- Non-phosphate detergent
- Tap water
- Distilled or deionized water
- Long and short handled brushes
- Bottle brushes
- Drop cloth/plastic sheeting
- Paper towels
- Plastic or galvanized tubs or buckets
- Pressurized sprayers
- Aluminum foil
- Ziploc® bags
- Trash bags
- Appropriate personal protective equipment (PPE)
- Face shield (for hard hat)
- High pressure washer (if necessary)
- Fuel for high pressure washer
- 55-gallon drums
- Plywood
- Sump pump
- Landscape timbers, 4 x 4's, or 2 x 4's

3.0 PROCEDURES

3.1 Decontamination

The prime contractor shall describe all decontamination of drilling equipment, well construction materials, sampling equipment, tools, etc in the project work plan. All samples and equipment leaving the contaminated area of a site must be decontaminated to remove any contamination that may have adhered to equipment. This includes casing, drill bits, auger flights, the portions of drill rigs that stand above boreholes, sampling devices, and instruments, such as slugs and sounders. In addition, the contractor shall take care to prevent the sample from coming into contact with potentially contaminating substances, such as tape, oil, engine exhaust, corroded surfaces, and dirt.

The following procedures shall be used to decontaminate large pieces of equipment, such as casings, auger flights, pipe and rods, and those portions of the drill rig that may stand directly over a boring or well location or that come into contact with casing, auger flights, pipe, or rods:

1. Prepare the decontamination zone in accordance with SOP 1.2.
2. Don appropriate PPE.
3. Deposit the contaminated equipment on the plastic drop cloth/sheet or in a container inside the CRZ.
4. Place large pieces of equipment (e.g., auger flights) on sawhorses.



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5. Use a high-pressure washer and a low-phosphate soap (e.g, Alconox) to remove encrusted material from grossly contaminated equipment. If necessary, use a brush to scrub the equipment until all visible dirt, grime, grease, oil, loose paint, rust flakes, etc., have been removed.
6. Rinse all equipment with potable water.
7. Store the equipment on sawhorses or wrapped in clean plastic sheeting.
8. Decontamination water should be collected and transferred to a 55-gallon drum at the end of the day or whenever significant quantities of water have accumulated. Drums of investigative derived waste (IDW) should be managed in accordance with SOP 1.4.

The following procedures shall be used to decontaminate small pieces of sampling equipment such as split spoons, bailers, trowels/spoons and bowls:

1. Prepare the decontamination zone in accordance with SOP 1.2.
2. Don appropriate PPE.
3. Scrub the equipment with a solution of potable water and low-phosphate soap (e.g., Alconox).
4. If organic constituents are contaminants of concern, rinse the equipment with a pesticide-grade solvent, typically acetone. If acetone is a constituent of concern, substitute methanol as the rinse agent.
5. Rinse the equipment with copious quantities of distilled or deionized water.
6. Allow the equipment to air dry on a clean surface or rack elevated at least two feet above ground.
7. Wrap the sampling device in aluminum foil or place in Ziploc® bags prior to reuse.

At the completion of the decontamination activities, all fluids and solid waste should be containerized and managed in accordance with SOP 1.4.

If a particular contaminant fraction is not present at the site, the ten (10) step decontamination procedure specified above may be modified for site specificity. For example, the solvent rinse may be eliminated if organics are not of concern at a site. Modifications to the standard procedure should be documented in the site specific work plan or subsequent report.

4.0 CAUTIONS AND INTERFERENCES

1. The use of distilled/deionized water commonly available from commercial vendors is typically acceptable for decontamination of sampling equipment.
2. The use of an untreated potable water supply is not an acceptable substitute for tap water. Tap water may be used from any municipal or industrial water treatment system.
3. If solvents are utilized in decontamination they raise health and safety, and waste disposal concerns.
4. Damage can be incurred by solvent washing of complex and sophisticated sampling equipment.



STANDARD OPERATING PROCEDURE NO. 6.4
SAMPLE HANDLING AND CONTROL

SOP#: 6.4
DATE: 1/31/2001
REVISION #: 0
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1.0 METHOD SUMMARY

This SOP presents procedures for maintaining control of environmental samples following collection through shipment to the analytical laboratory. In addition, this SOP describes standard chain-of-custody protocols which should be followed to document the possession of samples from the time of collection until the laboratory report is submitted.

2.0 EQUIPMENT/APPARATUS/REAGENTS

Equipment needed for use in this SOP includes:

- Precleaned sample containers
- Preservatives (if not in containers)
- Sturdy cooler, in good repair
- Fiberglass strapping tape
- Duct tape
- Clear tape
- Bubble wrap or other packing material
- Ziploc-type bags
- Trash bags
- Ice
- Shipping labels
- Pens, markers, etc.

3.0 PROCEDURES

3.1 Sample Identification

The contractor should identify procedures for unique sample identification and the relation to field identification (i.e., how sample numbers are assigned). Samples shall be uniquely identified, labeled, and documented in the field at the time of collection. Samples collected for laboratory analysis are identified by using standard sample labels which are affixed to the sample containers. Most analytical laboratories will supply the necessary labels. The following information shall be included on the sample label at the time of collection using waterproof, non-erasable ink:

- Project number
- Field identification or sample station number
- Date and time of sample collection
- Designation of the sample as a grab or composite
- Whether the sample is preserved or unpreserved
- The types of analyses to be performed
- Any relevant comments (such as readily detectable or identifiable odor, color, or known hazardous properties)
- Signature or initials of the sampler(s)

3.2 Sample Packaging

Environmental samples should be packed prior to shipment using the following procedures:

1. Allow sufficient headspace (approximately 10 percent of the volume of the container) in all bottles (except volatile organic analysis (VOA) vials with a septum seal) to compensate for any pressure and temperature changes which may occur during shipment.
2. Ensure that the lids on all bottles are tight.
3. Select a sturdy cooler in good repair. Secure and tape the drain plug with fiberglass strapping tape or duct tape. Line the cooler with a heavy duty plastic garbage bag.



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4. Place glass sample bottles into bubble wrap bags or wrap a layer of bubble wrap around glass containers. Many laboratories provide bubble wrap bags for sample shipment. Place two to three VOA vials in a single bag.
5. Place the bottles in the cooler with larger bottles on the bottom inside the garbage bag. Insert polyethylene bottles between glass bottles for cushion. Put VOA vials (in bubble wrap bags) on their side on top of the larger sample containers.
6. Ensure that a trip blank has been included as appropriate for VOA samples and that a temperature blank (if supplied) is included as outlined in SOP No. 6.3, and SOP No. 6.5.
7. Place ice that has been "double bagged" on top of and/or between the samples. Fill remaining void space in the cooler with bubble wrap. Ensure that a sufficient quantity of ice has been placed into the cooler to maintain VOC samples at 4°C. In summer months, it may be necessary to fill as much as 50 percent of the cooler volume with ice to properly cool warm samples.
8. Securely fasten the top of the garbage bag with tape.
9. Place the Chain-of-Custody record into a Ziploc-type bag and tape the bag to the inside of the cooler lid.
10. Close the cooler and securely tape (preferably with fiberglass strapping tape) the top of the cooler shut. Chain-of-custody seals (preferably two) should be affixed to the cooler with clear tape so that the cooler can not be opened without breaking the seals.
11. Place the shipping label in a sealed pouch on the lid of the cooler for shipment. A label containing the name and address of the shipper and the destination should be placed on the outside of each additional cooler included in the shipment.

3.3 Sample Shipping

Samples collected in the field shall be transported to the laboratory or field testing site as expeditiously as possible (within 24 hours of sampling) to avoid hold time exceedances and to ensure that samples remain properly preserved. Samples for VOC analysis must be maintained at a temperature of 4°C.

In general environmental samples include drinking water, most ground water and ambient surface water, soil, sediment, treated municipal and industrial wastewater effluent, biological specimens, or any samples not expected to be contaminated with high levels of hazardous materials. Samples collected from process wastewater streams, drums, bulk storage tanks, soil, sediment, or water samples from areas suspected of being highly contaminated may require shipment as dangerous goods. Regulations for packing marking, labeling, and shipping of dangerous goods by air transport are promulgated by the International Air Transport Authority (IATA), which is equivalent to United Nations International Civil Aviation Organization (UN/ICAO). It is the responsibility of the shipper to ensure that shipments are made in accordance with all applicable laws, including contents and labeling.

3.4 Sample Chain-of-Custody

Procedures to ensure the custody and integrity of the samples should begin at the time of sampling and continue through transport, sample receipt, preparation, analysis and storage, data generation and reporting, and sample disposal. Records concerning the custody and condition of the samples are maintained in field laboratory records.

The contractor shall maintain chain-of-custody records for all field and field QC samples. A sample is defined as being within a person's custody if any of the following conditions exist:

- It is in their possession,
- It is in their view,



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SAMPLE HANDLING AND CONTROL**

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- It was in their possession and they secured it in a locked area, or
- It is in a designated secured area.

All sample containers shall be sealed in a manner that shall prevent or provide detection of tampering if it occurs. In no case shall tape be used to seal sample containers. Samples shall not be packaged with activated carbon unless prior approval is obtained from TCEQ.

The following minimum information concerning the sample shall be documented on the TCEQ chain-of-custody form (Attachment 1):

- Unique sample identification
- Date and time of sample collection
- Source of sample (including name, location, and sample type)
- Designation of matrix spike/matrix spike duplicate (MS/MSD)
- Preservative used
- Analyses required
- Number of sample containers
- Pertinent field data (pH, temperature, elevated headspace results or contaminant concentrations)
- Serial numbers of custody seals and transportation cases (if used)
- Name(s) of person(s) collecting the samples
- Custody transfer signatures and dates and times of sample transfer from the field to transporters and to the laboratory or laboratories
- Transporter tracking number (if applicable) or courier receipts

4.0 CAUTIONS AND INTERFERENCES

This section is not applicable to this SOP.



STANDARD OPERATING PROCEDURE NO. 6.5 COLLECTION OF QA/QC SAMPLES

SOP#: 6.5
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1.0 METHOD SUMMARY

Quality assurance/quality control samples are collected to attempt to determine if sample bottle preparation, sample shipment, handling, and storage procedures had an impact on the sample integrity. Data validation is an integral part of the sampling program and consists of reviewing and assessing the quality of data and determining the usability of the data based on previously defined objectives.

2.0 EQUIPMENT/APPARATUS/REAGENTS

The following equipment is used for collection of QA/QC samples:

- Pre-cleaned sample containers (with preservatives, if required)
- Analyte-free water (distilled or deionized)
- Stainless steel sampling bowl
- Stainless steel sampling spoon
- Other equipment as prescribed for collecting soil or water samples

3.0 PROCEDURES

3.1 Collection Field QA/QC Samples

3.1.1 Equipment Blanks

Equipment blanks should be collected using the following procedures:

1. Properly decontaminate the sampling device. Equipment blanks are not collected on disposable equipment (e.g., disposable bailers).
2. Select the proper sample containers and an appropriate quantity of analyte-free water (deionized or distilled).
3. Complete the sample labels with the appropriate information.
4. Slowly pour the analyte-free water through or over the sampling device until the sample bottle is filled to the appropriate level.
5. Securely tighten the cap on the bottle.
6. Prepare the bottle for shipment in accordance with SOP 6.5 (Sampling Handling and Control).

3.1.2 Field Blanks

Field blanks should be collected downwind of possible VOC sources. The procedures for collecting field blanks are:

1. Select the proper sample containers (VOC vials) for collecting the sample and an appropriate quantity of analyte-free water.
2. Complete the sample labels with the appropriate information.
3. Pour the water into the vial just to overflowing so that there is a meniscus at the top of the vials.
4. Securely tighten the lid on the sample vials.
5. Prepare the sample for shipment in accordance with SOP 6.5 (Sampling Handling and Control).

3.1.3 Field Duplicate Samples

Duplicate samples should be collected simultaneously or in immediate succession, using identical recovery techniques, and treated in an identical manner during storage, transportation, and analysis. If possible, collect duplicate samples in areas known to be contaminated to assess the laboratory's ability to measure contamination.

1. Select the proper sample containers for collecting a sample and a duplicate sample.



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2. Complete the sample labels with the appropriate information.
3. Collect the sample as required.
 - a. Groundwater Samples
 - i. Collect the sample in accordance with the appropriate sampling SOP.
 - ii. Fill the sample bottle half full with the pump or bailer then fill the duplicate sample bottle half full. Fill the remainder of the sample bottle then the remainder of the duplicate sample bottle. If a bailer is used, attempt to fill equal quantities from each bailer load into the sample and duplicate bottles.
 - b. Soil Samples
 - i. Collect the sample in accordance with the appropriate sampling SOP but collect double the required sample volume.
 - ii. Place the sample material into a stainless steel bowl and homogenize the sample with a stainless steel spoon. Do not homogenize samples for VOC analysis as the homogenization will cause a release of VOC constituents.
 - iii. Quarter the sample bowl and set aside two of the sample quarters.
 - iv. Homogenize the sample again.
 - v. Fill the appropriate sample jars using the material from the bowl, placing equal portions of sample into the sample bottles.
4. Securely tighten the caps on the sample bottles.
5. Prepare the sample for shipment in accordance with SOP 6.5 (Sampling Handling and Control).

3.1.4 Field Replicate (Split) Samples

If possible, collect field replicate samples from areas known to be contaminated to assess the laboratory's ability to measure contamination.

1. Select the proper sample containers for collecting a sample and a replicate sample.
2. Complete the sample labels with the appropriate information.
3. Prepare the sample using the same methods described in Section 3.1.3.
4. Place the field replicate samples in a separate cooler for shipment to the second laboratory.

3.1.5 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

Many laboratories can prepare the MS/MSD samples from the submitted sample volume. The sampler is only required to identify the sample for MS/MSD analysis on the chain of custody. If the sampler is required to collect MS/MSD samples, they should be collected as replicate samples but with three sets of samples (one original sample, one matrix spike sample, and one matrix spike duplicate).

3.1.6 Temperature Blank

Temperature blanks are typically prepared by the analytical laboratory and included in the shipment of sample coolers and containers. One temperature blank should be returned to the laboratory in each sample cooler.

3.1.7 Trip Blank



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COLLECTION OF QA/QC SAMPLES**

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Trip blanks are usually prepared by the analytical laboratory using analyte-free water and included in the shipment of sample coolers and containers. Trip blanks should only be submitted with samples requiring VOC analysis. One trip blank should be included in each sample cooler containing samples for VOC analysis. The procedures for submitting a trip blank are:

- Prepare the coolers for shipment to the laboratory. If possible, pack all samples for VOC analysis in one cooler so that only one trip blank is required.
- Identify the trip blank on the chain-of-custody record. If the project will continue for several days, be sure to number trip blanks sequentially so that multiple trip blanks with the same identification number are not submitted to the laboratory.
- Ensure that VOC analysis (or benzene, toluene, ethylbenzene, and xylenes (BTEX) at Leaking Petroleum Storage Tank (LPST) sites) is the selected analysis for the trip blank.

4.0 CAUTIONS AND INTERFERENCES

The types of QA/QC samples and frequency for collection are typically outlined in the project Quality Assurance Project Plan (QAPP). It is important to identify the sample frequency prior to beginning the field effort. QA/QC samples should be selected to match the sampling program (i.e., it is not necessary to collect trip blanks for sites where only samples for metals analysis are being collected).



STANDARD OPERATING PROCEDURE NO. 10.5 SOIL SAMPLING USING A SHELBY TUBE SAMPLER

SOP#: 10.5
DATE: 11/18/2003
REVISION #: 1
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1.0 METHOD SUMMARY

Subsurface sampling attempts to remove soil below the ground surface in a relatively undisturbed state in order to quantify the extent of contamination at specific depths. Soil samples shall be collected based on odors, discoloration, organic vapor meter readings, predetermined depth, and any other appropriate field screening method.

2.0 EQUIPMENT/APPARATUS/REAGENTS

The contractor shall describe the equipment to be used to collect the sample, field screening equipment including calibration and quality control (QC) requirements for the samples to be taken. Each instrument will be calibrated according to the manufacturer's operating manual prior to each day's use. Instrument calibrations will be documented in the field book. During this calibration, an appropriate maintenance check will be performed on each piece of equipment. If damaged or failed parts are identified during the daily maintenance check and it is determined that the damage can impact the instrument's performance, the instrument will be removed from service until the part or parts are replaced or repaired. An equivalent piece of equipment will be substituted for the malfunctioning instrument to maintain schedule, if possible. Typical equipment required for subsurface sampling includes:

- Tape measure (in tenths of feet)
- Shelby tube samplers
- Rig-mounted extruder
- Knife
- Field logbook
- Waterproof and permanent marking pens
- Duct tape
- Decontamination supplies
- Paper towels
- Appropriate personal protective equipment (PPE)
- Sample jars with labels
- Cooler with ice
- Zip-lock bags
- Drum for drill cuttings, if necessary
- Organic Vapor Meter
- Table for examining drilled cores

3.0 PROCEDURES

When soil samples are to be submitted for laboratory analysis, they shall be collected using stainless steel, continuous drive, Shelby tube samplers. These samplers are 24 inches in length and have an outside diameter (OD) of 2 inches. Shelby tube samplers are not appropriate for use on sandy, unconsolidated materials.

1. Decontaminate the Shelby tube sampler to be used for soil sampling.
2. Soil sampling using a Shelby tube sampler is performed in conjunction with SOP 5.1 (Hollow Stem Borehole Advancement) or 5.3 (Mud Rotary Borehole Advancement).
3. Attach the Shelby tube sampler to the center rods and lower the sampler to the bottom of the bore hole.
4. Drive the sampler a depth of 2 feet into undisturbed soil.
5. Pull the Shelby tube sampler out of the bore hole and detach the sampler from the center rods.
6. Place the Shelby tube with the "bottom" (the end of the tube with the shallowest sample) of the tube against the extruder head. Extrude the sample into a decontaminated trough.
7. As soon as the Shelby tube sample is extruded, monitor the sample for organic vapors using the PID or FID.
8. Record the results on the boring log and in the field log book.



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SOIL SAMPLING USING A SHELBY TUBE SAMPLER**

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Carefully split the sample core using a decontaminated stainless steel knife. Immediately cut center sections for VOC samples and place into appropriate sample containers, filling the container as full as possible. Immediately place the sample in an iced cooler held at a temperature below 4 degrees C.

Samples collected to be tested for other analytical parameters concurrently with VOCs shall be then collected. Soil chemistry samples not being analyzed for VOCs shall be placed in 8 or 16-ounce, laboratory cleaned, EPA-approved glass containers with Teflon-lined lids. This shall be done using clean stainless steel sampling tools and rubber gloves. If initial screening results indicate the presence of organic vapors, a headspace analysis shall be conducted on remaining portions of the sample.

Grab samples shall be collected by obtaining a representative volume of soil from the area to be sampled and placing it directly into the sample bottle.

If soil samples are being collected for VOC analysis, the sample collection procedures discussed in TCEQ Superfund Program SOP No. 6.3 (Collection of VOC Samples) must be followed.

Collection of QC samples shall be done in accordance with SOP 6.5 (Collection of QC Samples).

The sampling equipment shall be decontaminated in accordance with SOP 1.5 (Decontamination) between each sample, and new gloves should be worn each time.

4.0 CAUTIONS AND INTERFERENCES

Rock or impenetrable soil may be encountered during Shelby tube sampling. If this is the case, a different method may be used (drill rig, etc), or it may be necessary to move to another location. If access is a problem, different drilling methods or locations may solve this problem as well. Additionally, if loose, unconsolidated materials are encountered, a different sampling method, such as the use of split spoon sampling devices, will be necessary, therefore the contractor should be prepared for all scenarios and uncertainties.



**STANDARD OPERATING PROCEDURE NO. 6.1
FIELD ACTIVITY DOCUMENTATION AND REPORTING**

SOP#: 6.1
DATE: 09/25/03
REVISION #: 01
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1.0 METHOD SUMMARY

This SOP provides requirements for documenting and reporting site activities. The objective of the documentation program is to accurately and completely describe all field activities, thereby demonstrating that all field activities are conducted in accordance with the project specific Field Sampling Plan or Field Work Plan and applicable Superfund Program Standard Operating Procedures (SOPs).

2.0 EQUIPMENT/APPARATUS/REAGENTS

Equipment typically required for documenting the progress of the project includes:

- Field logbook (all weather or water resistant)
- Field forms
- Camera
- Video recorder (if necessary)
- Permanent marking pens
- Ink pens (with waterproof, black ink)

The field logbook shall contain the following information at a minimum:

- Location, date and time of each activity
- Weather conditions (changes)
- Activity being performed
- Identity of the person(s) performing the activity
- The numerical value and units of any field measurements
- The identity of, and the calibration results for, each field instrument being used
- All information required to demonstrate that the work is conducted in accordance with applicable Sampling Plans, Work Plans and SOPs
- visitors to the site

Specific information which shall be included for each sample includes:

- Sample type and sampling method
- The identity of each sample and depth(s) from which it was collected
- The amount of each sample
- Sample description (e.g., color, odor, clarity)
- Identification of sampling devices
- Identification of conditions that might affect the representativeness of a sample (e.g., refueling operations, damaged well casings)
- All information required to demonstrate that the work is conducted in accordance with applicable Sampling Plans, Work Plans and SOPs

All information relating to installation and development of monitor wells, installation of temporary groundwater sampling points, well development, well purging, groundwater sample collection and all other sampling activities or field work shall be recorded in a field logbook or field form(s). When field forms are used the field logbook shall reference the data noted on field forms and the field forms shall be dated and signed by the author. The field logbook will be bound with consecutively numbered pages and will be suitable for submission as evidence in legal proceedings. Each entry in the field logbooks will be signed and dated by the author. All original data recorded in the field logbook and other field forms will be written using permanent, waterproof ink. Errors



STANDARD OPERATING PROCEDURE NO. 6.1 FIELD ACTIVITY DOCUMENTATION AND REPORTING

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made in the field logbook will be corrected by the individual making the entry by crossing a line through the error, entering the correct information, and dating and initialing the correction. The field logbooks and field forms will become part of the project file, and should be kept in the project file at all times when not in the possession of the field team.

3.0 PHOTOGRAPHS

General guidelines (all types of photos):

- If possible, use a camera that has a time and/or date stamp. Record the date and time each photo was taken on the photo or with the photo file (as applicable) and in the field logbook.
- Do not use special lenses (i.e., wide-angle lenses) as they can distort the image
- A brief, accurate description of what the photograph shows, including the name of the site and location shall be recorded in the field logbook.
- Include the name of the photographer, and witness, as applicable.

When photographs are taken the record of each frame exposed/recorded is kept in the bound field logbook along with the information above required for each photograph. The field investigator shall then enter the required information on the prints, slides or CD (if digital photos) using the photographic record from the bound field logbook, to identify each photograph.

Conventional 35 mm Cameras

- Obtain negatives in one continuous, uncut sheet and include with the pictures.
- Arrange photos in album format and include the above information for each photo and submit with the field logbook.

Digital Cameras

- Submit a CD-R of the downloaded picture files in JPEG format (include the above information for each photo) and submit with the field logbook.
- Digital camera recording mode (dependent on camera's pixel resolution quality and picture quality mode) shall be set to achieve a minimum pixel resolution of 1600 x 1200 or higher.

4.0 OTHER FIELD FORMS

Other types of records which may be used in the field include:

- Drum inventory forms
- Well development/purging records
- Boring logs



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FIELD ACTIVITY DOCUMENTATION AND REPORTING**

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- Well construction diagrams (as-builts)

5.0 CAUTIONS AND INTERFERENCES

This section is not applicable to this SOP.



**STANDARD OPERATING PROCEDURE NO. 17.1
GLOBAL POSITIONING SYSTEM DATA
COLLECTION AND SUBMISSION**

SOP#: 17.1
DATE: 12/04/03
REVISION #: 0
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1.0 METHOD SUMMARY

TCEQ requires the use of Global Positional System (GPS) in conjunction with other technologies to collect and maintain positional data that provides physical and environmental site information about plume and contaminate changes over time. Also GPS technologies are used to provide the boundaries of buildings, real property, waste areas, locations of wells and other relevant site features.

2.0 GPS CERTIFICATION

To ensure that TCEQ receives reliable and accurate positional data, TCEQ OPP 8.12 requires that the GPS data collector must be certified. The TCEQ staff may obtain GPS certification by attending a training course presented by either an internal GPS trainer or by a manufacturer-certified GPS trainer. Non-TCEQ staff may obtain GPS certification from a manufacturer-certified GPS trainer. All GPS data collectors must verify that the certification instruction they have received meets the minimum elements listed in Table 1 - GPS Certified Training Minimum Elements in the Third Party GPS Training Certification section of this SOP.

3.0 EQUIPMENT / APPARATUS

A DGPS (Differential Global Positioning System) receiver can be either a stand alone unit, or a GPS module with Differential GPS antenna and relevant satellite subscription, plugged into a portable computer. The DGPS receiver must:

- Have six channel parallel reception or better.
- Have sub-meter horizontal accuracy.
- Employ these processing parameters:

Position acquisition rate-	1/second or better
Position mode	- 3D (uses 4 satellites)
Maximum PDOP	- 6(or less)
Minimum Elevation	- User-Selectable (record elevation accuracy)
- Have the ability to perform real-time differential correction (no post processing).
- Receive correction data from a recognized, reliable source, and which is appropriate for real-time correction in the geographic area in which the GPS measurements will be made.
- Output correction data in RTCM-SC104 (Radio Technical Commission of Maritime Service - Special Committee Paper No.104) format via an RS-232 cable or other compatible connection which matches the DGPS receiver.
- Have ability to store at least 180 position measurements.



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GLOBAL POSITIONING SYSTEM DATA
COLLECTION AND SUBMISSION

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- Have ability to transfer almanac and position data to a personal computer via a serial port or USB connection.
- Include software to perform mission planning, differential correction, point data averaging, and conversion to common formats (Grid or ArcView).
- Have a water and shock resistant case.
- Include portable power source(s) which will last a full working day.
- All weather proof Field Log Book.
- A laser rangefinder (optional)

4.0 GPS DATA COLLECTION AND ACCURACY

Horizontal Accuracy - All horizontal positions collected using certified GPS units shall maintain sub-meter accuracy. In order to meet sub-meter accuracy, latitude and longitude coordinates should be carried out to at least 6 places for decimal degree and at least 2 place for decimal seconds.

DGPS - Differential Global Positioning System (DGPS) receiver which corrects the atmospheric effects. DGPS are used for realtime GPS mapping and tracking without the need for post-processing.

PDOP - Positional Dilution of Precision. A measure of the quality of a GPS measurement taken from a given set of four satellites at a given time. If the satellites are not widely distributed from the user's location, the PDOP value will be higher, and the quality of the measurement will be diminished. PDOP values greater than 6 are not acceptable.

Datum - A mathematical model used by cartographers to define the shape of the earth in a specific area. Always use North America Datum of 1983 (NAD 83).

Differential Correction - A process applied to raw GPS data that removes certain types of errors; primarily, the error introduced by Selective Availability. This process requires correction data from a reference GPS receiver operating from a precisely known location. Correction data must be obtained from a recognized, reliable source (such as the reference network maintained by the Texas Department of Transportation) or Racal LandStar, and certain Trimble units, provide a satellite delivered GPS correction service, which provide 24 hour accurate and reliable real time precise positioning on land and in the air. For full coverage in Texas, the differential signal is transmitted to the user by high-power geostationary satellites. The GPS and differential signal are both received by the GPS via a single antenna

A single position reading obtained through appropriate use of real-time correction must have sub-meter accuracy.

Collection Methods - GPS data may be collected using one of three methods:



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- Superimposed - The superimposed method involves standing on top of or next to the subject for which you are collecting GPS locational data. Collect 60-100 readings.
- Centroid - The centroid method is used when the superimposed method cannot be used (e.g. well inside a locked fence or structure). Take points equal distance from the desired point by starting and stopping the GPS and by averaging these points. The unit will average the point for each reading and then all the points as one point which will be the center of all the readings. Collect a minimum of 30 readings per point prior to averaging.
- Offset - The offset method is used when the superimposed method cannot be used and only when accurate offset measurements can be made (e.g. Using a laser rangefinder, tape measure, etc.) The potential error associated with the offset measurement must be added to the potential error associated with the GPS measurement. A note in the GPS logging software and the field log book of bearing and distance from the offset location can be used but location must be corrected before it is entered into a table or shape file.
- Points - The point is used for well and sample locations, gates, sub-meter objects, etc.
- Line - The line is used for trail, road, stream, berm, etc.
- Polygon - The polygon is used for buildings, site boundary, waste area, ponds or piles, etc. If it is hard to walk the entire perimeter, readings can be taken at each corner of the polygon by starting and stopping the GPS at the corners and within the same Station. The program will add the line in between the points of the Station to create a polygon.

5.0 DATA SUBMITTALS

Correction Status - All GPS data submitted must have a field indicating each record's differential correction status. There are only two selections available:

- Differential Correction - Indicates that the record has been differentially corrected.
- Uncorrected - Indicates that the record has not been differentially corrected.

Offset - The offset points must be noted in the field log book and actual points calculated before entering the station into the final database or shape file.

Events - Each event must be in separate data table or shape file.

Data Sets - Each data set must be in separate file or layer (e.g All wells, buildings, site boundaries, sample results/event, site features, roads, trails, utilities, etc. must be in separate layers/tables).



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Arc View files - All data must be in Decimal Degrees, NAD 83 exported to Arc View 3.2 as a shape files with the relevant metadata, a hard copy of the Arc View tables must accompany the electronic version for TCEQ submittal.

Field Log Book - Site name location and details of field activity must be noted in the field log book, including the name and coordinates of each station and bearing and distance details describing any station off-sets.

Minimum Attributes - All GPS data submitted to TCEQ should conform to the data attributes defined in Table 1.

Table 1			
GPS Data Attributes			
Attribute	Data Type	Field Length	Description
Latitude	Number	Double	Decimal Degree to a minimum of six decimal places
Longitude	Number	Double	Decimal Degree to a minimum of six decimal places
Site Name	Text	50	Superfund Site Name
Station Name	Text	50	Monitoring well number or Sample name
Station Reference / Comments	Text	50	Station Location Relative to Facility
Station Type	Text	10	Point, Line or Polygon
Collector Name	Text	50	Last Name, First Initial
GPS Certificate Number	Text	8	TCEQ GPS Certificate Number
Collection Method	Text	15	Superimposed, Centroid, Offset
Datum	Text	5	Horizontal Datum (NAD27, NAD83 or WGS84)
Max PDOP	Number	Single	Maximum PDOP value in effect during data collection (not > 6)
Receiver Type	Text	50	GPS model name & accuracy
Correction Status*	Text	50	Tells whether or not GPS data was differentially corrected
GPS Date	Date	N/A	Date GPS data was collected
GPS Time	Text	8	Time GPS data was collected
Total Positions Collected	Number	Integer	Number of positions collected/corrected



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* Data that is not differentially corrected will be rejected.

Data Format - GPS data submitted to TCEQ should be in electronic format (dBASE IV, .dbf file format is preferred). The following is an example of how the data table should be structured. The data may be submitted via email, on diskette, or CD.

**Table 2
Third Party GPS Data
Example Data Table**

Latitude	Longitude	Site Name	Station Name	Station Reference / Comments	Collector Name	TCEQ GPS Certificate Number	Datum	Collection Method	Max PDOP	Receiver Type	Correction Status	GPS Date	GPS Time	Total Positions
11.11100 0	99.999000	Pioneer	MW-21	NW Corner	Terry, D	95081107	NAD83	Superimposed	4.4	Trimble XRS DGPS	Differential Correction	5/22/00	10:10 AM	61
11.11110 0	99.999100	Pioneer	MW-22	Center of the facility	Terry, D	95081107	NAD83	Centroid	5.2	Trimble XRS DGPS	Differential Correction	5/22/00	10:25 AM	108
11.11120 0	99.999200	Pioneer	MW-23	S of entrance	Terry, D.	95081107	NAD83	Superimposed	3.5	Trimble XRS DGPS	Differential Correction	5/22/00	1:38 PM	66
11.11120 0	99.999200	Pioneer	site location	South Entrance of facility	Terry, D.	95081107	NAD83	Superimposed	3.5	Trimble XRS DGPS	Differential Correction	5/22/00	3:38 PM	60



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Third Party GPS Training Certification

Minimum Qualifications

Texas Natural Resource Conservation Commission

TCEQ OPP 8.12 requires all GPS training courses to include both lecture/classroom discussion and hands-on exercises. Table 1 contains the minimum elements that must be included in any TCEQ-recognized GPS certification training course

Table 1

GPS Certification Training

Minimum Elements

Minimum lecture and/or demonstration elements	Minimum hands-on exercises, to be successfully completed by each student
<input type="checkbox"/> Background of the Global Positioning System.	<input type="checkbox"/> Pre-planning, including data quality objectives, equipment and materials needed, logistics of field data collection, and prediction of GPS data collection conditions.
<input type="checkbox"/> GPS accuracy issues.	<input type="checkbox"/> Navigation to a given coordinate.
<input type="checkbox"/> Relevant Agency operating policies.	<input type="checkbox"/> Storing and transferring raw positional data.
<input type="checkbox"/> Operation of GPS equipment, including basic troubleshooting.	<input type="checkbox"/> Differential correction of raw data through post processing.
<input type="checkbox"/> Data collection procedures.	<input type="checkbox"/> Averaging corrected point data and outputting to a GIS file.
<input type="checkbox"/> Differential correction, both real time processing and post processing.	
<input type="checkbox"/> Coordinate averaging for point locations.	
<input type="checkbox"/> Data output in formats appropriate for import to GIS or tabular databases.	



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Class exercises shall also include computer plotting of point data to allow students to better understand GPS accuracy issues and the effects of differential correction and point data averaging.

Note:

All certified GPS users recognized by TCEQ must be recertified every 2 years;

- Sales or user demonstrations do NOT constitute GPS training;
- GPS training courses should last a minimum of six to eight hours;
- The TCEQ GPS operating policy is available online at: <http://www.tceq.state.tx.us/gis/gisply.html>

Individuals obtaining or with current GPS certification training must verify that the instruction they have received meets the minimum elements listed in Table 1. Therefore, fill out the attached form, along with copies of GPS training certificates, and return them to:

David P. Terry
TCEQ GPS Coordinator (MCC-155)
SWAP Team
Texas Commission on Environmental Quality
P.O. Box 13087
Austin, Texas 78711-3087
(512) 239 4755
Email: dterry@tceq.state.tx.us



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GPS Certification Verification Form
Texas Commission on Environmental Quality

Contact Information

GPS Training Coordinator Information			Training Provider Information	
Name			Organization Providing GPS Training	
Organization			Instructor	
Mailing Address			Course Name	
City	State	ZIP	Course Date	Course Hours
Email Address			GPS System (Trimble, Magellan, etc.)	Manufacturer Certified? Yes <input type="checkbox"/> No <input type="checkbox"/>

The following individual(s) have received GPS certification training that complies with TCEQ OPP 8.12 minimum training elements:

Name	Title

I hereby state that the information provided is true, accurate, and complete to the best of my abilities

Signature of GPS Training Coordinator or GPS Trainer

Title

Date

Printed Name

Telephone Number

Extension

APPENDIX B
SAMPLING AND ANALYSIS PROCEDURES

IN-SITU DISCRETE XRF (IDX) MEASUREMENTS

- 1) "In-situ" measurements are those measurements made on the surface of undisturbed, in-place soils (discrete samples). Twenty in-situ discrete XRF ("IDX") measurements will be made in each Study Unit.
- 2) IDX measurements will only be made during suitably dry conditions. During Phase 1 of the Project soil moisture content will be measured at a number of in-situ locations using the Field Scout soil moisture instrument. Suitable criteria for moisture content of soils for subsequent in-situ XRF measurements will then be developed prior to initiation of Phase 2 of the Project.
- 3) Twenty approximately equally-spaced Sample Locations within the Study Unit will be demarcated with flags. The Sample Locations will be purposefully selected in the field to provide approximately equal-spacing, complete coverage of the Study Unit and avoidance of locations potentially impacted by lead-paint and/or lead emissions from automobiles.
- 4) The Sample Locations will be numbered beginning with Sample Location 1 in the northwest corner of the Study Unit.
- 5) At each Sample Location, the vegetative cover will be removed from an approximate 6 inch by 6 inch area at the optimal depth.
- 6) The XRF operator will complete an IDX measurement for lead, cadmium, and zinc from the exposed surface soil at the approximate center of each Sample Location. The concentration value determined at each Sample Location will be documented in the field logbook.
- 7) The mean of the twenty IDX measurements will be calculated and defined as the "**IDX estimate of the mean concentration in the Study Unit**". One such calculated mean concentration will be established for each Study Unit.

EX-SITU SAMPLE COLLECTION, PREPARATION, AND XRF MEASUREMENT

Bulk Sample Aliquot Collection

1. Select 20 Sample Locations within the Study Unit (as described in the FSP).
2. Remove grass and other ground-cover to expose the optimal depth interval at each Sample Location.
3. Following IDX measurement, collect a 1-inch soil plug from the optimal depth interval using a suitable cylindrical coring device. Discard any soil collected below that 1-inch plug depth.
4. Collect 20 such soil plugs from 20 designated Sample Locations within the Study Unit.
5. In a suitable non-metallic mixing container, combine the 20 soil plugs into the bulk sample using the following procedures:

Bulk Sample Mixing

6. Remove large non-soil materials (rocks, sticks, leaves, etc.) from the bulk sample.
7. Disaggregate and mix the material using a stirring and mixing motion with a suitable non-metallic dedicated tool.
8. Sieve the bulk sample through a No. 10 (2mm) sieve.
9. Discard the un-sieved portion of the bulk sample.
10. Thoroughly mix the sieved portion of the bulk sample for 2 minutes.
11. Collect the bulk sample into a large labeled sample bag.

Cone and Quarter Splitting

12. Pour and pile the bulk sample onto a plastic lined cutting board to form a conical shape.
13. Flatten the coned pile into a circular shape with a uniform thickness of approximately 1/2 inch or less.
14. Split the bulk sample into pie-shaped quarters using the non-metallic trowel to drag and separate each quadrant.
15. Combine OPPOSITE quadrants into the mixing container.
16. Replace the other opposite quadrants into the original bulk sample bag.
17. Thoroughly mix the remaining bulk sample again.
18. Cone and quarter the remaining bulk sample again by following Steps 12 through 14 above.
19. Combine and mix ADJACENT quadrants.
20. Complete this coning and quartering procedure until approximately 4 ounces of Phase 1 sample remains for laboratory analysis and approximately 8 ounces of Phase 2 sample remains for laboratory analysis. For most samples, a total of 4 repetitions of the coning and quartering procedure should reduce the volume to the required laboratory sample volume. For field duplicate or split

samples, the required volume should result from 3 repetitions of the coning and quartering procedure.

21. Place the reduced volume sample material in a small sample bag.

Ex-Situ Composite XRF Measurement

22. For each sample (regular, duplicate, and split) perform ex-situ composite XRF measurements as described in Section 4 of the FSP and the XRF SOP in Appendix C.

Laboratory Sample Preparation

23. Move the sample from the sample bag to a properly labeled sample jar and prepare for shipping to the laboratory.

APPENDIX C
XRF STANDARD OPERATING PROCEDURE



1. Portable X-Ray Fluorescence Screening for Metals

This Standard Operating Procedure (SOP) establishes protocols for the collection of x-ray fluorescence (XRF) data at discrete in-situ locations as well as from composite ex-situ soil sample locations. This SOP has been prepared exclusively for use at the Dona Park Neighborhood Site (the Site) in Corpus Christi, Texas. This SOP addresses sample preparation and field methodologies to be employed during this sampling event. A total of 20 in-situ measurements and 1 composite sample will be collected in each study unit. The samples will be analyzed in the field using the NITON® XL3t Series analyzer. Lead, cadmium, and zinc are the contaminants of concern for the Site. The action levels for the Site are 500 milligrams per kilogram (mg/kg), 50 mg/kg, and 9,900 mg/kg for lead, cadmium, and zinc, respectively. The primary objective of this activity is to determine whether the XRF tool can be used to accurately measure concentrations of lead and cadmium in soils. The purpose of this SOP is to standardize the XRF sampling procedures to ensure data quality, defensibility, and reproducibility.

All or parts of the SOPs and SOGs described in this section may be reproduced and used in DBS&A reports, proposals, and work plans with the verbal consent of the President, the Quality Assurance Manager, or a DBS&A Division Director.

1.1 Procedures

XRF analysis is based on the principle of atomic excitation. Elements in a soil sample are irradiated with a beam of X-rays. Inner-orbital electrons in the atom are photoejected and leave the atom in an excited state as a result of electron vacancy. Relaxation occurs when an outer orbital electron with higher energy fills the vacancy and emits X-rays possessing energy unique to each element in the sample.

Field measurement of metals in soils with an XRF may be influenced by soil moisture, with errors in reporting increasing with increasing soil moisture contents. Because of this, this SOP also details the procedures to employ to ensure that the data collected are defensible.

These protocols refer to and depend upon the implementation of related Daniel B. Stephens & Associates, Inc. protocols on decontamination; instrument calibration, maintenance and use; quality control; field documentation, sample integrity, and chain-of-custody procedures.

1.1.1 Apparatus and Materials

The following apparatus and materials are required for metals screening in soils.

1. NITON® XL3t Series analyzer.
2. Field Scout TDR 300 Soil Moisture Meter
3. A stainless steel or plastic trowel or spatula for smoothing and compacting soil
4. Soil jars or sealable plastic bags for collecting samples
5. Marking pens, field notebook



1.2 Soil Moisture Readings

Soil moisture readings will be collected at the start, mid-point, and end of the day during each day when field XRF measurements are made. In the event that a precipitation event occurs during the sampling day, additional moisture measurements will be collected before proceeding with soil sampling activities. Moisture readings will be collected using a Field Scout TDR 300 Soil Moisture Meter capable of producing a percent moisture range from 0 to saturation (saturation is typically around 50% volumetric water) and with meter accuracy of approximately $\pm 3.0\%$.

Prior to collecting moisture readings, the soil moisture meter will be calibrated following the user's manual calibration process provided in Appendix 1 of this SOP. The meter should be wiped with a towel between tests to remove all excess dirt. Soil moisture measurements will be made at a minimum of four locations in the front and back yards at the first house sampled in the morning, the first house sampled after lunch, and the last house sampled during each field day. For each of these houses, the average soil moisture will be calculated and recorded in the field log book.

1.3 Go/No-Go Determination

Optimal moisture percentages will be determined in the field during Phase I of the Pilot Study, which will be conducted to determine the optimal sampling depth determination. Field soil moisture readings will be collected and compared to the laboratory derived percent moisture. Once optimal moisture percentages are determined for the site, this optimal moisture plus or minus 5% will be set as a Go/No-Go indicator for soil sample collection.

1.4 XRF Operations

The NITON® XL3t Series analyzer will be used to measure metal concentrations reported in parts per million (ppm) for both the in-situ samples as well as the ex-situ composite bagged soil samples. The XRF ex-situ composite bagged samples will be homogenized and five readings collected to achieve a mean sample result for each study unit. Five readings will be collected from the composite samples collected at the first three sample locations as a measure of precision. In the event that the readings at these locations vary by less than 15%, subsequent locations will only require a single set of readings.

The XRF unit will be factory prepared specifically for environmental soil analysis and will be factory calibrated prior to shipment so site-specific calibrations are not required. In the field, a field check will be conducted daily on the XRF prior to sampling using lead, cadmium, and zinc reference standards provided by NITON. A description of the field check procedure is provided in Appendix 2 in the NITON® XRF user's manual. Table 1 provides a summary of the QC procedures and the applicable acceptance criteria when using the XRF



Table 1. Summary of QC Procedures for Field XRF by Method SW-846 6200

Qc Check Sample	Minimum Frequency	QC Acceptance Criteria*	Required Corrective Action If QC Acceptance Criteria Not Met
Performance check at concentration near XRF decision level	1 at the beginning of the day, then 1 per every 100 analyses, and then 1 at the end of the working day.	$\pm 20\%$ difference (%D) of true value	Document performance outside the QC acceptance criteria for all samples analyzed prior the performance check and after the last acceptable performance check.
XRF precision check on <i>ex-situ</i> composite bagged samples**	3 samples at the beginning of each day; each sample analyzed 5 times in replicate	$\leq 15\%$ RSD	Document the calculated precision in the field logbook.
Blank sample check	Analyzed on each working day before and after sample analyses are conducted and once per every 100 analyses.	No target COC concentrations above the established detection limit.	If target COCs are detected in the blank sample, check probe window and blank sample for contamination and clean appropriately. If QA acceptance criteria remain unmet, contact vendor.

Notes:

* If the QC Acceptance Criteria are not met, the corrective actions given in Section 9.0 of SW846-6200 will be followed.

**The precision check should be performed on samples with varying concentration ranges to assess the effect of concentration on method precision.

1.4.1 In-Situ Discrete Sampling

Twenty (20) in-situ soil sample locations will be identified in each study unit prior to collecting XRF readings. Each study unit sample location will be uniquely identified. XRF soil sample collection will be in a gridded pattern. The optimal screening depth will be determined prior to XRF sampling and will be consistent for all in-situ soil sample locations. At the same time that sample depths are determined; optimal soil moisture content for the samples will also be calculated.

The sampling procedure will be programmed into the XRF prior to mobilizing to the field. This procedure will assure that the filters used and the sample collection time will be optimal for lead, cadmium, and zinc analysis and that the required detection limits for lead, cadmium, and zinc are achieved at each location. It is estimated that 4 to 5 minutes will be required at each soil sample location. The in situ measurement is taken by simply placing the analyzer probe on a prepared, flat area of soil.



The XRF soil sampling procedure for in-situ sampling is as follows:

1. The optimal sampling depth will be determined prior to XRF field sampling activities, and the field team will remove soils down to the optimal sampling depth.
2. Each sample location will be clearly marked and the study unit soil sample location documented.
3. In the event that a global positioning system (GPS) is linked to the XRF, the XRF will be programmed to automatically collect latitude and longitude points while the samples are being analyzed.
4. Remove any debris, such as leaves, twigs, grass, and stones, from the measurement surface.
5. Loosen the soil to a depth of 1.5 to 2.5 centimeters (cm) (0.5 inch (in) to 1 in) over an area of at least 10 cm (4 inch) diameter, and stir the loosened soil to achieve some homogenization with a dedicated trowel or stir wand.
6. Tamp the mixed and loosened soil to a relatively flat, smooth surface.
7. Set the XRF on the prepared surface location using the extend-a-pole accessory.
8. Measure the metal concentrations in the soils with the NITON® XL3t Series analyzer following the NITON SOP.
9. Record the date, time, sample location and results in ppm in the field logbook.

1.4.2 Ex-Situ Composite Sampling

The ex-situ composite samples will be formed by combining soil from several sample locations (estimated 20 soil sample locations per study unit). Equal volume aliquots will be collected from the in-situ soil sampling locations where the in-situ XRF readings were collected.

1. Equal aliquot collected from the study unit sampling locations will be placed in disposable lead-free sampling bags.
2. The bagged sample will be placed on a smooth surface that does not contain metal. A background measurement reading of the testing surface will be made with the XRF and documented in the field book for lead and cadmium levels. This testing surface should be used throughout the field events for consistency.
3. Prior to analyzing the sample, identify and discard materials in the sample which are not relevant for characterizing the site. Examples of extraneous material in soil samples include pieces of glass, twigs, leaves, rocks, etc.
4. Homogenize the bagged soils until uniform distribution is achieved per cone and quarter splitting sample preparation instructions in the field sampling plan (FSP). If soils are stiff clays that cannot be homogenized in a bag, a mortar and pestle should be used to homogenize the soils. A consistent homogenization method should be determined during the first discrete sampling event at the site and used throughout the XRF sampling activities.



5. The bagged soil should be placed in a way where the thickness across the sample is consistent and there should be no "void" areas where soils are absent.
6. Following thorough homogenization, five (5) XRF readings will be taken through the sampling bag. The mean of the five measurements will be the ex-situ composite XRF mean of the study unit.
7. At the completion of XRF readings on the bagged sample, the sample will be moved to the appropriate sampling container for submittal to laboratory for comparative analysis.

1.5 Field Documentation

The following data, at a minimum, shall be recorded in a field book, log, or form (or a combination thereof):

1. Date, time, and location
2. Name(s) of field operator
3. Equipment
4. Check sampler documentation
5. Sample identification and collection start time
6. Site conditions that could affect the integrity of the sample

Attachments

Appendix 1: Field Scout TDR 300 Soil Moisture Meter User's Manual

Appendix 2: NITON® XL3t Series analyzer User's Manual

APPENDIX D
FIELD SCOUT TDR 300 SOIL MOISTURE METER PRODUCT
MANUAL



DECLARATION OF CONFORMITY

Spectrum Technologies, Inc.
12360 S. Industrial Dr. East
Plainfield, IL 60585 USA

Model Numbers: 6430FS
Description: Portable Soil Moisture Probe
Type: Electrical Equipment for Measurement, Control, and Laboratory Use
Directive: 2004/108/EC
Standards: EN 61326-1:2006
EN 61000-4-2:1995, including A1:1998 and A2:2001.
EN 61000-4-3:2002
As a consequence of the meter's measurement principle, radio frequencies less than 950 MHz can affect the meter's readings. Operating the meter in areas where such transmissions are present should be avoided.
EN 55011:2007

Douglas L. Kieffer, Soil/Water Products Manager

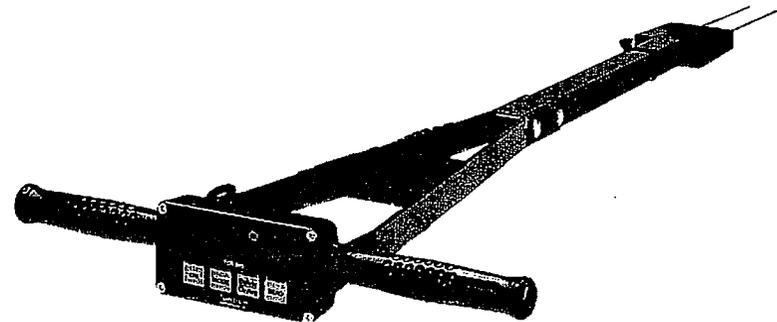
March 18, 2009



**TDR 300
Soil Moisture Meter**

PRODUCT MANUAL

Item # 6430FS



**Spectrum
Technologies, Inc.**

12360 S. Industrial Dr. E
Plainfield IL 60585
(800) 248-8873 or (815) 436-4440
Fax (815) 436-4460
E-Mail: info@specmeters.com
www.specmeters.com

**Spectrum
Technologies, Inc.**

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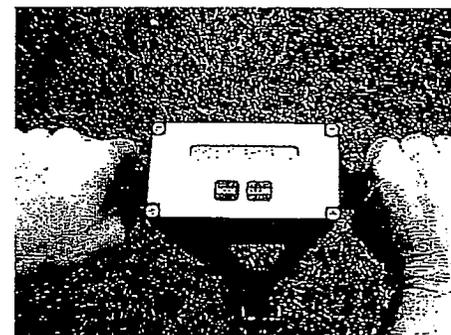
This manual will familiarize you with the features and operation of your new Field Scout™ TDR 300 Soil Moisture Meter. Please read this manual thoroughly before using your instrument. For customer support, or to place an order, call Spectrum Technologies, Inc. at (800) 248-8873 or (815) 436-4440 between 7:30 am and 5:30 p.m. CST
FAX (815) 436-4460
e-mail: info@specmeters.com
www.specmeters.com

GENERAL OVERVIEW

Thank you for purchasing the Field Scout™ TDR 300 Soil Moisture Meter. This manual describes the features and operation of the meter.

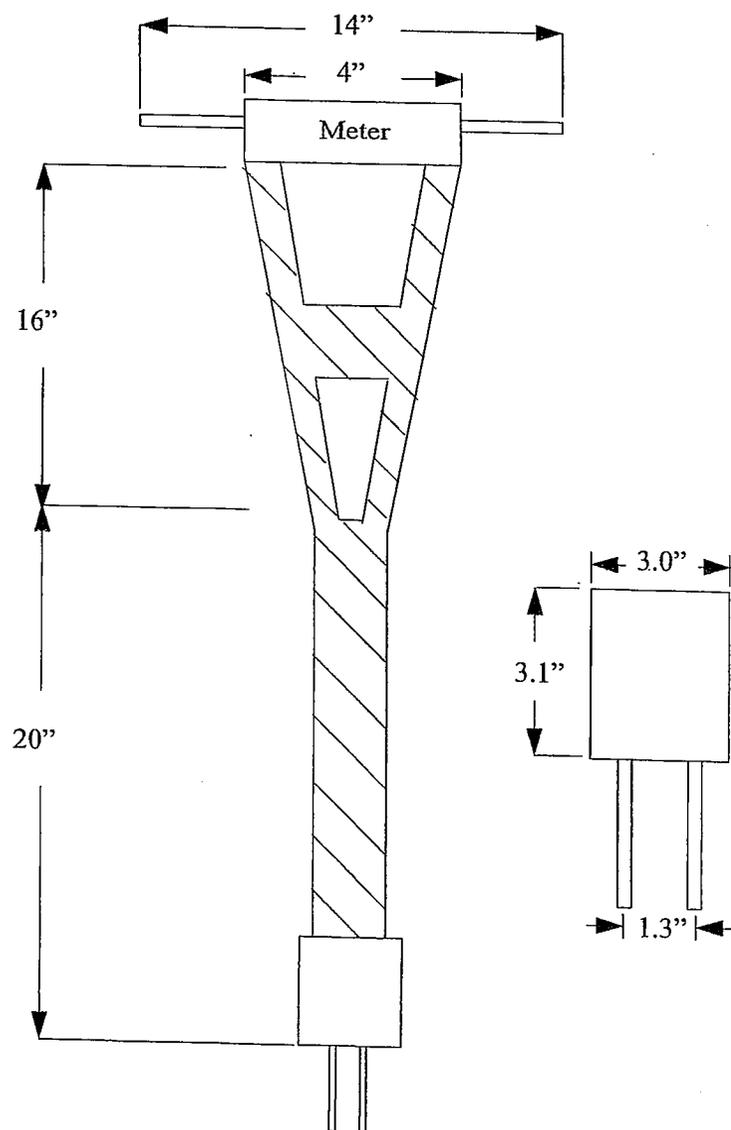
Soil moisture is a critical and potentially highly variable component of the soil environment. Time-domain reflectometry is a proven technology for quickly and accurately determining volumetric water content (VWC) in soil.

The Field Scout's shaft-mounted probe allows the user to easily and rapidly take many measurements. The user can quickly transition between taking VWC readings in standard and high-clay mode. The meter's built-in data logger can record data from several sites and eliminates the need to record data manually. Through the software (included) the user can download the data, change the logger settings and program the logger to record relative water content at multiple sites.



SHAFT DIMENSIONS

The following are the dimensions of a fully extended shaft. It is possible to reduce the length of the meter by 2" (5cm) by adjusting the lower half of the shaft.



SPECIFICATIONS

Measurement Units	Percent volumetric water content
Resolution	0.1%
Accuracy	±3.0% volumetric water content with electrical conductivity < 2 dS m ⁻¹
Range	0% to saturation (<i>Saturation is typically around 50% volumetric water.</i>)
Power	4 AAA alkaline batteries Approximately 12 month life
Logger Capacity	2700 readings without GPS, 1250 readings with GPS/DGPS
Display	16 character, 2 line LCD
Weight	3 lbs. (1.4 kg)
Probe Head Dimensions	3.1" x 3" x 1" (7.8cm x 7.5cm x 2.5cm)
Rod Dimensions	Length : 1.5" (3.8cm), 3" (7.6cm), 4.7" (12cm) or 7.9" (20cm) Diameter: 0.2" (0.5cm) Spacing: 1.3" (3.3cm)

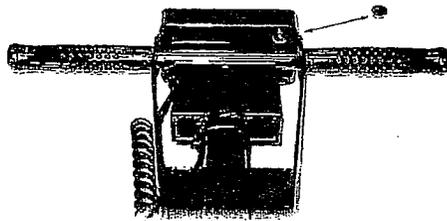
The internal data logger and RS-232 port are compatible with GPS/DGPS. The data logger's LCD screen will display the data in one of three modes (see MODE button p. 11):

1. Volumetric water content - in Standard or High Clay mode
2. Relative water content - up to 2 RWC modes can be established
3. Measurement period - in microseconds

COMPUTER INTERFACE/ CHANGING BATTERIES

Software Installation

Insert the CD for Field Scout software into your PC's disk drive. If auto-start is not enabled on your computer, select **Run** from the **Start** menu and type **D:\Setup.exe** (Substitute the appropriate drive letter for your CD drive). Click **OK** and follow the instructions on the screen.



*TDR 300
data port*

The data port on the underside of the TDR 300 meter (shown above) can be accessed by removing the plastic screw. It is through this port that the meter is connected to either a PC or to a GPS unit. The meter must be turned off before attempting communication with the software.

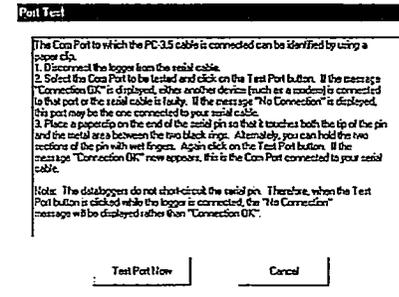
Connecting to a PC

The Field Scout software comes with a gray PC interface cable. This cable connects to the 9-pin serial port of your computer and to the meter's computer port. The meter's configuration can be modified by clicking on the **Meter Settings** button (see Meter Settings, p. 18). The **Com Port**, **Meter Type**, **Download**, **Clear Memory** and **Meter Settings** buttons are explained in the Field Scout Software Toolbar section (p. 16).

Changing the batteries

The battery compartment is accessed by removing the meter's face plate. The meter is powered by AAA batteries.

IDENTIFYING THE CORRECT COM PORT

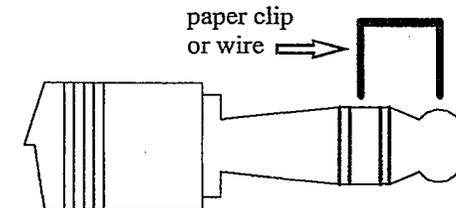


The computer **Communications Port** to which the PC-3.5 serial cable is connected can be identified by using a paper clip.

1. Disconnect the serial cable from the meter.

2. To bring up the **Port Selection** screen, click on the **Com Port Button**, select the com port to be tested and click the **Port Test** button. Click the **Test Port Now** button. If the message "Connection OK" is displayed, another device (such as a modem) is probably connected to that port. If the message "No Connection" is displayed, this port may be the one connected to your serial cable and you can proceed to the next step.

3. Place a paperclip on the end of the serial pin so that it touches both the tip of the pin and the metal area between the two black rings. Again click on the **Test Port Now** button. If the message "Connection OK" now appears, this is the com port connected to your serial cable.



NOTE: The dataloggers do not short-circuit the serial pin. Therefore, when the **Test Port** button is clicked while the meter is connected, the "No Connection" message will be displayed.

CONNECTING TO A GPS UNIT

The data logger function must be enabled using the Field Scout software in order to record a GPS signal (see Meter Settings p. 18).

The GPS unit must be plugged into the TDR 300 meter and running when the meter is first turned on. If a GPS signal is found at startup, the logger will search for a GPS signal for every reading. If no GPS signal is found when the meter is first turned on, the meter will not search for one when taking readings, thereby saving time when taking readings. In this case the LCD will display the **No GPS Found** message.

If the GPS signal is found while taking geo-referenced readings, the LCD will briefly display the message, "**Reading GPS ..**" before displaying the measurement. If the GPS signal is lost during a series of readings, or if the specified differential correction is not found, the LCD will read "**Reading GPS .. ERR**" before returning to measurement mode. In this case, the data will be recorded without latitude and longitude. During subsequent readings, the meter will again search for a GPS.

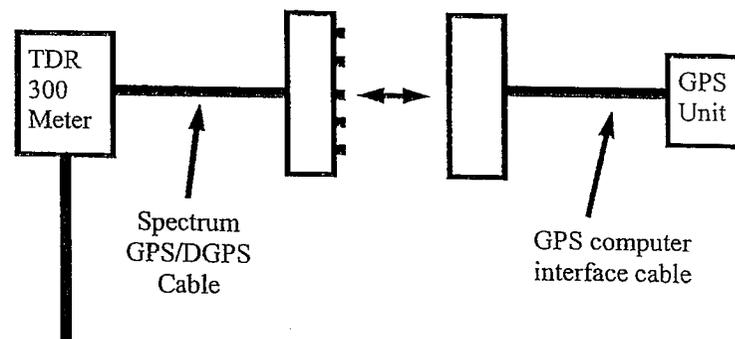
GPS Setting

Your GPS unit must be set for NMEA 0183 input/output messages. If the meter has trouble receiving the GPS signal, check that it has the following settings:

Data bits: 8	Stop bits: 1
Baud rate: 4800 bps	Parity: None
Timing: 1 second	GGA data string

Cable Connections

A GPS/DGPS cable (item # 2950CV5) is required to connect the TDR 300 meter to a GPS unit. This cable has a 9-pin male connection and a stereo pin that connects to the meter's data port. You will also need a cable that allows the GPS unit to connect to a 9-pin male serial port. If this cable doesn't come standard with your GPS unit, it should be available from the manufacturer. This cable is generally used to upload information from a computer to the GPS unit. These components should be connected as shown in the figure below.



Connecting the TDR 300 meter to a GPS unit

METER OPERATION

ON

The ON switch turns the meter/datalogger on and off. When the meter is turned on, it will display the battery status for 3 seconds. For the next 3 seconds, it will display how much logger memory has been used and, if the logger was enabled in the software, whether the GPS signal was found. If a GPS signal is found, latitude and longitude data will be included in the data file. The screen will then display the most recently used MODE screen.

Logger 75% Full
GPS=Yes DGPS=No

Logger 75% Full
No GPS Found

Sample meter power-up screens with datalogger enabled: left screen indicates GPS signal was found.

If you are using GPS, but the meter doesn't find the GPS signal when powering up, the meter will **not** search for the GPS signal when taking readings. Turn the meter off and on so it can look for the GPS signal. Once the signal is found, GPS information will be included in the data file until the signal is lost or the GPS unit is disconnected from the meter.

Note: If the data logger is disabled (see Meter Settings, p. 14), the meter will not seek the GPS signal when it is powered up. It will, instead, proceed immediately to the most recently used mode (see MODE button, p. 11) screen.

MODE

Pressing the MODE button allows the user to determine the type of measurement that will be taken or select the length of rods connected to the probe.

Data Collection Modes

Available measurement options are volumetric water content (VWC) using the standard or high clay mode (see p. 22), up to two relative water content modes (see p. 24), or measurement period (in microseconds). Relative water content options will only appear if they are configured in the software (see Meter Settings, p. 18). The period measurement is available for users interested in performing soil-specific calibrations (see Appendix 1).

Note: There is not a high clay measurement calibration for the 1.5" rods. The meter will display dashes if this mode/rod length combination is selected.

Changing Rod Length

ROD=MED (4.7in)
HIT DEL To Chnge

Rod Length Options Screen

In order to get accurate volumetric or relative water content (VWC or RWC) readings, the rod length setting must be correct. In the VWC modes, the currently selected rod length appears in the lower left corner of the LCD screen. The options are **T**urf (1.5"), **S**hort (3.0"), **M**edium (4.7"), and **L**ong (7.9") rods. Press the MODE button until the LCD displays the rod length options screen. Pressing the DELETE/CLR AVG button will allow you to toggle between the three choices.

Delete Clr Avg

When the DELETE/CLR AVG button is pressed and immediately released, the last data point will be taken out of the logger file and removed from the running average. Pressing and holding this button will reset the running average but will not affect data stored on the data logger.

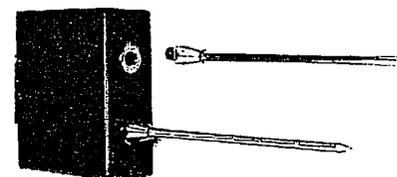
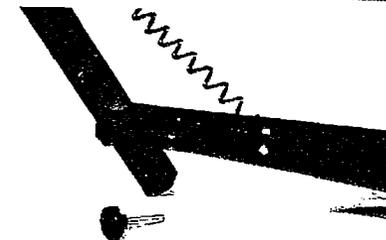
READ

Press the READ button to read the probe and update the screen values. Data values, along with GPS or DGPS information if applicable, are sent directly to the data logger. If the logger searches for, but doesn't find a GPS signal, an error message will briefly appear in the lower right corner. In this case, a data point will be stored without the GPS data. The data point can be cleared from memory with the DELETE/CLR AVG button (above).

When the data logger is full, the LCD will display the message "Error: Memory Full". To resume normal operation, the logger memory must be cleared using the **Clear Memory** button in Field Scout software (see p. 17)

TAKING READINGS

- Remove one of the hand screws from the shaft. This will allow you to unfold the shaft to its full length. Return the screw to lock the shaft in the extended position.



- Screw the rods into the sockets at the bottom of the probe block. The size of the nut at the base of the rods is 7/16".

- Turn on the meter and ensure that it is configured with the correct rod length setting (see Changing Rod Length, p. 11).

- Select the correct mode setting (see Data Collection Modes, p. 11). This will bring you to one of the data collection screens. The TDR 300 can be set to one of two VWC modes, Standard or High Clay. The Standard mode will be appropriate for most mineral soils. The High Clay mode will be more accurate for soils with higher clay contents (>27%). In VWC mode, the top line of the display shows the VWC mode and the water content. The bottom line has probe setting and data file information.

STNDRD VWC%=35.1
PL=S N015 A=36.3

Sample Data Screen

- PL:** Probe Length (**T**urf, **S**hort, **M**edium, or **L**ong rods)
N: Number of readings included in the Average
A: Average of all readings taken since meter was turned on or DELETE/CLR AVG button was pressed

Note, the internal calibrations are valid for a wide range of mineral soils. However, for soils that are high in clay, organic matter or salt, the meter will give values that are higher than the actual VWC. In this case, it is recommended that the meter be operated in relative water content mode (see p. 24) or that a soil-specific calibration be developed (see Appendix 1).

The meter can also be set to give the raw reading if it is set to **Period** mode. This mode is intended primarily for soil-specific calibrations (see Appendix 1).

- Push the rods into the soil. When taking a measurement, it is important that the rods be fully inserted into the soil. If not, part of the sampling volume will be composed of air and the reading will be inaccurately low. For the same reason, the probe should be inserted with a steady, downward pressure. If the rods are wiggled into the soil, air pockets can be created adjacent to the rods that will result in low readings. The probe should not be struck with a hammer or other blunt instrument as this can cause damage to the internal electronics. Also, care should be taken to ensure the rods are inserted as parallel to one another as possible. This

will not have a large affect on the reading but will decrease the chances the rods will be bent or broken. Likewise, it is best to avoid areas with rocks or other material that can cause the rods to deflect or bend. If the ground is especially hard or compact, you can use a Pilot Hole maker (item 6430PH) to make 1½” holes to aid in starting the insertion of the probe rods.

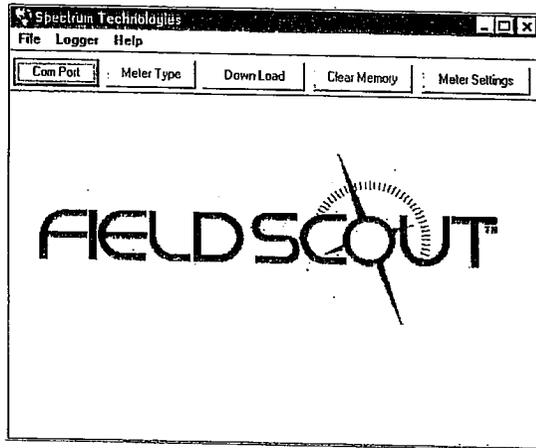
- Press the **READ** button to initiate the measurement sequence. The reading should appear almost instantaneously.

Note: The TDR rods are manufactured from type 303 stainless steel and are designed to bend if non-vertical force is applied to them. This serves to protect the TDR block electronics from potential damage that could be caused by excessive force.

Occasional rod bending is normal, and can be expected during the course of sampling. Longer rods will be more susceptible to bending than shorter rods. If bending occurs, rods should simply be bent back to parallel position, perpendicular to the TDR block. Measurements will continue to be accurate provided that rods are reasonably close to parallel.

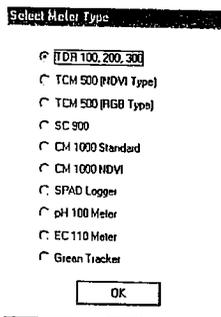
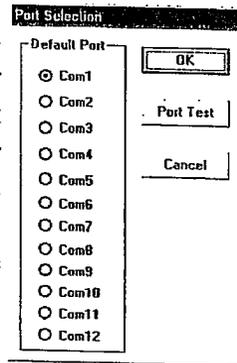
If care is not taken to reposition rods to a parallel position, subsequent pressure on the rods will accentuate the bending and may cause the rods to break. Rods should be considered maintenance items that may need to be replaced over time, depending upon the nature and frequency of sampling.

FIELD SCOUT SOFTWARE TOOLBAR



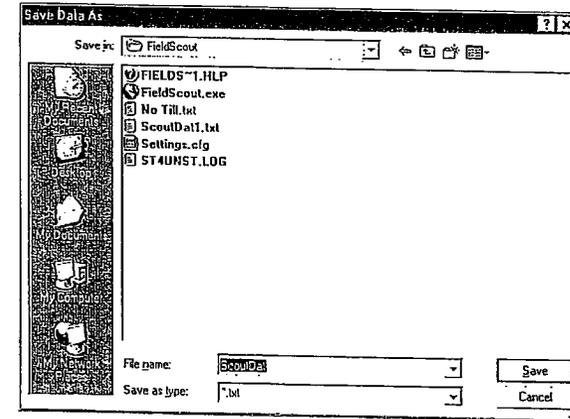
Com Port

The gray software cable connects the meter to the computer data port. Select the Com Port that is assigned to the computer data port. See Identifying the Correct Com Port (p. 7) for instructions on how to determine which port to select.



Meter Type

Select the TDR option from the list of available Field Scout meters.



Download

To download data from the internal data logger, turn the meter off and connect the gray serial cable to the RS-232 port on the underside of the meter. Click the **Download** button on the main software screen. In the **Save Data As** screen, give the file a descriptive name and select the location where it will be saved.

When the file has been saved, the software will give you the option of immediately viewing the file. The data file is stored as a comma-delimited text file and may be viewed in text editor or spreadsheet software.

Clear Memory

Data is not automatically removed from the logger memory after a download. The **Clear Memory** button clears all data from the logger memory.

Meter Settings

Click this button to configure the meter and data logger.

METER SETTINGS

Meter Settings

Meter Info:
 Serial #: 1 Model #: TDR 300 Firmware Version: 5.0
 Meter Name: Test
 (Max Length = 32 Characters)

Logger Settings:
 Enable Meter's Logging Function (Must Be Checked to Log Data)
 Set Meter to Record Only GPS Readings with Differential Correction
 Enter Time Zone Correction Number (i.e. 5 for USA Central Time Zone)

Units:
 Inches
 mm

Relative Water Content Set Points:

	Type 1	Type 2
Enable Display:	<input checked="" type="checkbox"/>	<input checked="" type="checkbox"/>
Type Name: (5 Chr Max)	Fld1	Fld4
Dry Set Point (%):	5	8
Wet Set Point (%):	35	50
Use Calibration:	Standard	High Clay

Save Cancel

The Meter Settings screen in the Field Scout software is used to configure the meter and data logger for your specific application. The fields are described below.

Meter Name: The name given the meter will be the title on the first line of the downloaded text file.

Logger Settings: The data logger is enabled and disabled by checking the first box. If the data logger is enabled, it will search for a GPS signal when the meter is turned on. If a signal is found, position data will be stored along with the soil moisture data. If no GPS signal is available when the logger is turned on, the logger will no longer look for one when measuring and recording soil moisture data. If the second box is checked, the logger will store the GPS value **only** if it has been differentially corrected. In general, this option should remain unchecked. If the differential cor-

rection is not found, only the soil moisture value will be stored in the data file. A time-zone correction should be entered in the third box.

Units: When operating the meter in Relative Water Content mode, the LCD can display the rod length options in English or metric units. The meter will calculate and display the water deficit (see Relative Water Content p. 24) in the same unit system.

Relative Water Content Set Points: Up to 2 Relative Water Content (see p. 24) modes can be programmed into the meter by entering the wet and dry set points into the appropriate boxes. From the dropdown menus near the bottom of the screen, select which VWC calibration (Standard or High Clay) should be used for each RWC mode. Each of these modes can be given a descriptive name of 5 characters. These names can be used to identify a certain field or soil type.

Finally, for an RWC mode to be available, it must be enabled by checking the Enable Display box. If this box is not checked, that RWC mode will not appear on the LCD during meter operation.

DATA FILES

	A	B	C	D	E	F
1	Name: Test					
2	Serial #: 1					
3	Datum: WGS 84					
4	Longitude	Latitude	No.	% Water	Type	Rod Length
5	Logger Started: 8:01:30					
6	-88.3582	41.31085	N=1	30.7	Standard VWC	7.9in
7	-88.3582	41.31085	N=2	30.7	Standard VWC	7.9in
8	-88.3582	41.31085	N=3	30.7	Standard VWC	7.9in
9	-88.3613	41.31134	N=4	17.3	Standard VWC	7.9in
10	Logger Started 9:06:10					
11	-88.3595	41.31217	N=1	22.1	Standard VWC	4.7in
12	-88.3595	41.31217	N=2	22.5	Standard VWC	4.7in
13	-88.3595	41.31217	N=3	22.5	Standard VWC	4.7in
14	-88.3595	41.31217	N=1	14.5	Hi Clay VWC	4.7in
15	-88.3595	41.31217	N=2	14.5	Hi Clay VWC	4.7in
16	-88.3595	41.31217	N=3	14.5	Hi Clay VWC	4.7in
17	Logger Started					
18			N=1	27	Asnle	3.0in
19			N=2	31	Asnle	3.0in
20			N=3	42	Asnle	3.0in
21			N=4	78	Asnle	3.0in
22	Logger Started					
23			N=1	2750	Period uS	7.9in
24			N=2	2770	Period uS	7.9in
25			N=3	2780	Period uS	7.9in
26			N=4	2760	Period uS	7.9in
27						
28						

Sample data showing results of data collected with and without GPS activated. Note: GPS signal not found when recording data in lines 17 through 26.

The data is stored in comma-delimited text files. These files can be opened with text-editing software (e.g. Microsoft Word) or spreadsheet software (e.g. Excel).

The first two lines of the data file give the logger's name and serial number. The third line indicates that latitude and longitude are referenced to the 1984 World Geodetic Survey datum. The fourth line shows the column headings for the rest of the data file.

Logging sessions are started and completed by turning the meter on and off. The start of a logging session is indicated by the data line "Logger Started." If a GPS signal was found at the start of a logger session, a time stamp is included on the "Logger Started" line.

The data is separated into 6 fields: Latitude and Longitude (blank if a GPS unit was not connected), sample number, value, measurement type, and rod length. The "measurement type" data field indicates whether the reading is volumetric water content, relative water content or measurement period. For volumetric water content data, the calibration equation (Standard or High Clay) for that data point will also be included in measurement type.

VOLUMETRIC WATER CONTENT MEASUREMENTS

Volumetric Water Content (VWC)

The soil can be thought of as being composed of soil, water and air. The volumetric water content (VWC) is the ratio of the volume of water in a given volume of soil to the total soil volume. This can be expressed as either a decimal or a percent. Three soil moisture levels of importance can be defined as follows:

Saturation: All soil pores are filled with water. The VWC will equal the percent pore space of the soil.

Field Capacity: The condition that exists after a saturated soil is allowed to drain to a point where the pull of gravity is no longer able to remove any additional water.

Permanent Wilting Point: The highest moisture content at which a plant can no longer extract water from the soil.

Additionally, we can define Plant Available Water as the amount of water between Permanent Wilting Point and Field Capacity. One rule of thumb is that irrigation should be initiated when half the Plant Available Water has been depleted.

Time Domain Reflectometry (TDR)

The underlying principal of TDR involves measuring the travel time of an electromagnetic wave along a waveguide. The speed of the wave in soil is dependent on the bulk dielectric permittivity (ϵ) of the soil matrix. The fact that water ($\epsilon = 80$) has a much greater dielectric con-

stant than air ($\epsilon = 1$) or soil solids ($\epsilon = 3-7$) is exploited to determine the VWC of the soil. The VWC measured by TDR is an average over the length of the waveguide.

Electronics in the TDR 300 generate and sense the return of a high energy signal that travels down and back, through the soil, along the waveguide composed of the two replaceable, stainless steel rods. The sampling volume is an elliptical cylinder that extends approximately 3 cm out from the rods. The high frequency signal information is then converted to volumetric water content. High amounts of clay or high electrical conductivity ($EC > 2$ dS/m) will attenuate the high-frequency signal and affect the reading displayed by the meter. Very high organic matter content will similarly affect the VWC reading.

RELATIVE WATER CONTENT MODE

RWC=25.5 D=3.17in
A=23.4 N=06 Asnte

In addition to displaying volumetric water content (VWC), the meter can also display the relative water content (RWC) and Water Deficit (see MODE button, p. 11). RWC is an index value calculated with respect to upper (wet) and lower (dry) VWC set points. The set points are configured with the software (refer to Meter Settings, p. 18). An RWC of 0 indicates the soil is at the dry set point while an RWC of 100 indicates the soil has reached the wet set point. (Example: Assume the dry set point is VWC=25% and the wet set point is VWC=40%. If the meter measured a VWC of 35%, this would translate to a RWC of 67 because 35% is 2/3 between 25% and 40%.) If the soil's volumetric water content is outside the range of the set points, it is possible to get a negative RWC or an RWC greater than 100.

If the volumetric water contents for field capacity and permanent wilting point are the wet and dry set points respectively, the RWC value will be equivalent to Plant Available Water (PAW). A general rule of thumb is to recommend irrigation when the soil has reached 50% of the PAW.

Also included on the first line is the Water Deficit. The Water Deficit is the amount of rain or irrigation water necessary to raise the soil water content to the wet set point. This calculation applies to a soil depth equal to the probe rod length. The water deficit can be extrapolated further into the profile if the porosity and water-holding characteristics are similar to the volume of soil sampled by the probe.

The second line of the LCD gives the Average (A) of all readings taken, the Number (N) of readings taken and the 5-symbol name given to this soil type in the Meter Settings screen (see p. 18).

APPENDIX 1

SOIL-SPECIFIC CALIBRATION

For maximum accuracy, you may choose to perform a soil-specific calibration

Period = 0950 uS N015

rather than use either of the internal (Standard or High Clay) soil calibrations coded into the TDR 300's firmware. In these cases, an independent soil moisture content measurement is required. A relation can then be developed that relates the meter's period reading (see MODE button, p. 11) to actual volumetric water content (VWC). This is most easily accomplished by doing a regression of one set of data against another.

VWC data can be obtained with a device such as a neutron probe, by measuring the weight of a saturated soil column of known volume as it is gradually dried, or by gradually wetting a known volume soil with the addition of known increments of water. In most cases, however, the calibration will be done with gravimetric sampling. This procedure is briefly described below.

In the field, establish a number of sites to sample. Each site should be wetted to a different soil moisture content by adding varying amounts of water. At each site a Field Scout TDR reading is taken followed by the extraction of a known volume of soil. Ideally, this would be an undisturbed soil core. The wet weight of this soil must be determined. If the soil cannot be weighed immediately, it should be stored in a plastic bag to reduce evaporation. The soil is then oven-dried (105°C for 48 hours is a common requirement) and weighed again. The volumetric water content is calculated as follows:

$$VWC = 100 * (M_{wet} - M_{dry}) / (\rho_w * V_{tot})$$

Where:

M_{wet}, M_{dry} = mass (g) of wet and dry soil respectively
 V_{tot} = total soil volume (ml)
 ρ_w = density of water (1g/ml)

An alternate, but equivalent, calculation can be obtained from the gravimetric water content and soil bulk density.

$$VWC = GWC * (\rho_b / \rho_w)$$

Where GWC is the gravimetric water content and ρ_b is the bulk density:

$$GWC = 100 * (M_{wet} - M_{dry}) / M_{dry}$$

$$\rho_b = M_{dry} / V_{tot}$$

The final step is to plot the calculated the measured period values with the readings obtained from Field Scout TDR meter. Regression analysis can then be performed on this data to develop an equation to convert from period to VWC.

APPENDIX 2

TROUBLESHOOTING

1. Unable to bring up the Meter Settings screen.

Generally, this indicates that the PC is not able to communicate with the meter. Check the following:

- The interface cable is securely connected to both the PC and the meter
- The meter has fresh batteries
- The meter is off
- The correct COM port is selected (see p. 7)
- The **Meter Type** is set to the TDR family (see p. 16)

2. Dashes on the data screen while in Turf mode.

Check that you are in **Standard** calibration mode. There is no **High Clay** calibration for the 1½" rods.

3. I am getting getting VWC values near 0% for all measurements, even in very wet soil.

Most likely a circuit component in the display is damaged and must be repaired. Contact Spectrum Technologies or your distributor to obtain a Return Goods Authorization (RGA) number.

4. When turning the meter on, it indicated it had found the GPS signal. However, when taking readings I get a GPS error message.

This can happen if the meter is set to only accept GPS readings that have been differentially corrected. In general, this is not necessary. On the **Meter Settings** screen (p. 18), uncheck the second box in the Logger Settings section.

5. The meter is not logging any data.

The meter is shipped with the data logger disabled. It must be enabled in the Meter Settings screen (p. 18).

6. My Average reading suddenly went to 0%.

The average is only calculated for a maximum of 65 readings. If additional readings are taken, the LCD will display a value of 0% for the average. Press and hold the **DELETE/CLR AVG** button (p. 12) to return to normal operating mode.

7. My LCD is stuck at N = 250.

250 is the maximum number the LCD will display. At this point, additional water content readings can be made, but the index number (N value) will stay at 250. Press and hold the **DELETE/CLR AVG** button (p. 12) to return to normal operating mode.

APPENDIX 3

TIME ZONE CORRECTIONS

Time Zone Correction	City
0	Dublin, Lisbon, London
3	Rio de Janeiro, Montevideo
4	Asuncion
5	Atlanta, Indianapolis, New York, Ottawa, Bogota, Montreal, Toronto
6	Guatemala City, Houston, New Orleans, Chicago, Mexico City, Winnipeg
7	Phoenix, Denver, Edmonton
8	San Francisco, Los Angeles, Vancouver
9	Anchorage
10	Honolulu
11	Wellington
13	Adelaide, Melbourne, Sydney
14	Vladivostok, Brisbane
15	Seoul, Tokyo
16	Beijing, Hong Kong, Manila, Singapore, Taipei
17	Hanoi, Jakarta, Vientiane
18	Calcutta, New Delhi
19	Kabul, Islamabad
20	Tehran, Abu Dhabi, Dubai
21	Moscow, Nairobi, Kampala, Riyadh
22	Ankara, Athens, Helsinki, Istanbul, Cairo, Johannesburg, Harare
23	Amsterdam, Barcelona, Berlin, Geneva, Paris, Prague, Rome, Brussels, Madrid, Stockholm, Warsaw, Lagos

WARRANTY

This product is warranted to be free from defects in material or workmanship for one year from the date of purchase. During the warranty period Spectrum will, at its option, either repair or replace products that prove to be defective. This warranty does not cover damage due to improper installation or use, lightning, negligence, accident, or unauthorized modifications, or to incidental or consequential damages beyond the Spectrum product. Before returning a failed unit, you must obtain a Returned Materials Authorization (RMA) from Spectrum. Spectrum is not responsible for any package that is returned without a valid RMA number or for the loss of the package by any shipping company.

APPENDIX E
METHOD 6200 - FIELD PORTABLE X-RAY FLUORESCENCE
SPECTROMETRY FOR THE DETERMINATION OF
ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

SW-846 is not intended to be an analytical training manual. Therefore, method procedures are written based on the assumption that they will be performed by analysts who are formally trained in at least the basic principles of chemical analysis and in the use of the subject technology.

In addition, SW-846 methods, with the exception of required method use for the analysis of method-defined parameters, are intended to be guidance methods which contain general information on how to perform an analytical procedure or technique which a laboratory can use as a basic starting point for generating its own detailed Standard Operating Procedure (SOP), either for its own general use or for a specific project application. The performance data included in this method are for guidance purposes only, and are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed below for soil and sediment samples. Some common elements are not listed in this method because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). These light elements are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed below are of environmental concern, while a few others have interference effects or change the elemental composition of the matrix, affecting quantitation of the analytes of interest. Generally elements of atomic number 16 or greater can be detected and quantitated by FPXRF. The following RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Antimony (Sb)	7440-36-0
Arsenic (As)	7440-38-0
Barium (Ba)	7440-39-3
Cadmium (Cd)	7440-43-9
Chromium (Cr)	7440-47-3
Cobalt (Co)	7440-48-4
Copper (Cu)	7440-50-8
Lead (Pb)	7439-92-1
Mercury (Hg)	7439-97-6
Nickel (Ni)	7440-02-0
Selenium (Se)	7782-49-2
Silver (Ag)	7440-22-4
Thallium (Tl)	7440-28-0
Tin (Sn)	7440-31-5

Analytes	CAS Registry No.
Vanadium (V)	7440-62-2
Zinc (Zn)	7440-66-6

In addition, the following non-RCRA analytes have been determined by this method:

Analytes	CAS Registry No.
Calcium (Ca)	7440-70-2
Iron (Fe)	7439-89-6
Manganese (Mn)	7439-96-5
Molybdenum (Mo)	7439-93-7
Potassium (K)	7440-09-7
Rubidium (Rb)	7440-17-7
Strontium (Sr)	7440-24-6
Thorium (Th)	7440-29-1
Titanium (Ti)	7440-32-6
Zirconium (Zr)	7440-67-7

1.2 This method is a screening method to be used with confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma-atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)). This method's main strength is that it is a rapid field screening procedure. The method's lower limits of detection are typically above the toxicity characteristic regulatory level for most RCRA analytes. However, when the obtainable values for precision, accuracy, and laboratory-established sensitivity of this method meet project-specific data quality objectives (DQOs), FPXRF is a fast, powerful, cost effective technology for site characterization.

1.3 The method sensitivity or lower limit of detection depends on several factors, including the analyte of interest, the type of detector used, the type of excitation source, the strength of the excitation source, count times used to irradiate the sample, physical matrix effects, chemical matrix effects, and interelement spectral interferences. Example lower limits of detection for analytes of interest in environmental applications are shown in Table 1. These limits apply to a clean spiked matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (100 -600 second) count times. These sensitivity values are given for guidance only and may not always be achievable, since they will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of performance-based sensitivity is presented in Sec. 9.6.

1.4 Analysts should consult the disclaimer statement at the front of the manual and the information in Chapter Two for guidance on the intended flexibility in the choice of methods, apparatus, materials, reagents, and supplies, and on the responsibilities of the analyst for demonstrating that the techniques employed are appropriate for the analytes of interest, in the matrix of interest, and at the levels of concern.

In addition, analysts and data users are advised that, except where explicitly specified in a regulation, the use of SW-846 methods is *not* mandatory in response to Federal testing requirements. The information contained in this method is provided by EPA as guidance to be used by the analyst and the regulated community in making judgments necessary to generate results that meet the data quality objectives for the intended application.

1.5 Use of this method is restricted to use by, or under supervision of, personnel appropriately experienced and trained in the use and operation of an XRF instrument. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use either sealed radioisotope sources or x-ray tubes to irradiate samples with x-rays. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This latter process is known as the photoelectric effect. When an atom absorbs the source x-rays, the incident radiation dislodges electrons from the innermost shells of the atom, creating vacancies. The electron vacancies are filled by electrons cascading in from outer electron shells. Electrons in outer shells have higher energy states than inner shell electrons, and the outer shell electrons give off energy as they cascade down into the inner shell vacancies. This rearrangement of electrons results in emission of x-rays characteristic of the given atom. The emission of x-rays, in this manner, is termed x-ray fluorescence.

Three electron shells are generally involved in emission of x-rays during FPXRF analysis of environmental samples. The three electron shells include the K, L, and M shells. A typical emission pattern, also called an emission spectrum, for a given metal has multiple intensity peaks generated from the emission of K, L, or M shell electrons. The most commonly measured x-ray emissions are from the K and L shells; only metals with an atomic number greater than 57 have measurable M shell emissions.

Each characteristic x-ray line is defined with the letter K, L, or M, which signifies which shell had the original vacancy and by a subscript alpha (α), beta (β), or gamma (γ) etc., which indicates the higher shell from which electrons fell to fill the vacancy and produce the x-ray. For example, a K_α line is produced by a vacancy in the K shell filled by an L shell electron, whereas a K_β line is produced by a vacancy in the K shell filled by an M shell electron. The K_α transition is on average 6 to 7 times more probable than the K_β transition; therefore, the K_α line is approximately 7 times more intense than the K_β line for a given element, making the K_α line the choice for quantitation purposes.

The K lines for a given element are the most energetic lines and are the preferred lines for analysis. For a given atom, the x-rays emitted from L transitions are always less energetic than those emitted from K transitions. Unlike the K lines, the main L emission lines (L_α and L_β) for an element are of nearly equal intensity. The choice of one or the other depends on what interfering element lines might be present. The L emission lines are useful for analyses involving elements of atomic number (Z) 58 (cerium) through 92 (uranium).

An x-ray source can excite characteristic x-rays from an element only if the source energy is greater than the absorption edge energy for the particular line group of the element, that is, the K absorption edge, L absorption edge, or M absorption edge energy. The absorption edge energy is somewhat greater than the corresponding line energy. Actually, the K absorption edge energy is approximately the sum of the K, L, and M line energies of the particular element, and the L absorption edge energy is approximately the sum of the L and M line energies. FPXRF is more sensitive to an element with an absorption edge energy close to but less than

the excitation energy of the source. For example, when using a cadmium-109 source, which has an excitation energy of 22.1 kiloelectron volts (keV), FPXRF would exhibit better sensitivity for zirconium which has a K line energy of 15.77 keV than to chromium, which has a K line energy of 5.41 keV.

2.2 Under this method, inorganic analytes of interest are identified and quantitated using a field portable energy-dispersive x-ray fluorescence spectrometer. Radiation from one or more radioisotope sources or an electrically excited x-ray tube is used to generate characteristic x-ray emissions from elements in a sample. Up to three sources may be used to irradiate a sample. Each source emits a specific set of primary x-rays that excite a corresponding range of elements in a sample. When more than one source can excite the element of interest, the source is selected according to its excitation efficiency for the element of interest.

For measurement, the sample is positioned in front of the probe window. This can be done in two manners using FPXRF instruments, specifically, in situ or intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. The sample cup is then placed on top of the window inside a protective cover for analysis.

Sample analysis is then initiated by exposing the sample to primary radiation from the source. Fluorescent and backscattered x-rays from the sample enter through the detector window and are converted into electric pulses in the detector. The detector in FPXRF instruments is usually either a solid-state detector or a gas-filled proportional counter. Within the detector, energies of the characteristic x-rays are converted into a train of electric pulses, the amplitudes of which are linearly proportional to the energy of the x-rays. An electronic multichannel analyzer (MCA) measures the pulse amplitudes, which is the basis of qualitative x-ray analysis. The number of counts at a given energy per unit of time is representative of the element concentration in a sample and is the basis for quantitative analysis. Most FPXRF instruments are menu-driven from software built into the units or from personal computers (PC).

The measurement time of each source is user-selectable. Shorter source measurement times (30 seconds) are generally used for initial screening and hot spot delineation, and longer measurement times (up to 300 seconds) are typically used to meet higher precision and accuracy requirements.

FPXRF instruments can be calibrated using the following methods: internally using fundamental parameters determined by the manufacturer, empirically based on site-specific calibration standards (SSCS), or based on Compton peak ratios. The Compton peak is produced by backscattering of the source radiation. Some FPXRF instruments can be calibrated using multiple methods.

3.0 DEFINITIONS

- 3.1 FPXRF -- Field portable x-ray fluorescence.
- 3.2 MCA -- Multichannel analyzer for measuring pulse amplitude.
- 3.3 SSCS -- Site-specific calibration standards.
- 3.4 FP -- Fundamental parameter.
- 3.5 ROI -- Region of interest.

3.6 SRM -- Standard reference material; a standard containing certified amounts of metals in soil or sediment.

3.7 eV -- Electron volt; a unit of energy equivalent to the amount of energy gained by an electron passing through a potential difference of one volt.

3.8 Refer to Chapter One, Chapter Three, and the manufacturer's instructions for other definitions that may be relevant to this procedure.

4.0 INTERFERENCES

4.1 The total method error for FPXRF analysis is defined as the square root of the sum of squares of both instrument precision and user- or application-related error. Generally, instrument precision is the least significant source of error in FPXRF analysis. User- or application-related error is generally more significant and varies with each site and method used. Some sources of interference can be minimized or controlled by the instrument operator, but others cannot. Common sources of user- or application-related error are discussed below.

4.2 Physical matrix effects result from variations in the physical character of the sample. These variations may include such parameters as particle size, uniformity, homogeneity, and surface condition. For example, if any analyte exists in the form of very fine particles in a coarser-grained matrix, the analyte's concentration measured by the FPXRF will vary depending on how fine particles are distributed within the coarser-grained matrix. If the fine particles "settle" to the bottom of the sample cup (i.e., against the cup window), the analyte concentration measurement will be higher than if the fine particles are not mixed in well and stay on top of the coarser-grained particles in the sample cup. One way to reduce such error is to grind and sieve all soil samples to a uniform particle size thus reducing sample-to-sample particle size variability. Homogeneity is always a concern when dealing with soil samples. Every effort should be made to thoroughly mix and homogenize soil samples before analysis. Field studies have shown heterogeneity of the sample generally has the largest impact on comparability with confirmatory samples.

4.3 Moisture content may affect the accuracy of analysis of soil and sediment sample analyses. When the moisture content is between 5 and 20 percent, the overall error from moisture may be minimal. However, moisture content may be a major source of error when analyzing samples of surface soil or sediment that are saturated with water. This error can be minimized by drying the samples in a convection or toaster oven. Microwave drying is not recommended because field studies have shown that microwave drying can increase variability between FPXRF data and confirmatory analysis and because metal fragments in the sample can cause arcing to occur in a microwave.

4.4 Inconsistent positioning of samples in front of the probe window is a potential source of error because the x-ray signal decreases as the distance from the radioactive source increases. This error is minimized by maintaining the same distance between the window and each sample. For the best results, the window of the probe should be in direct contact with the sample, which means that the sample should be flat and smooth to provide a good contact surface.

4.5 Chemical matrix effects result from differences in the concentrations of interfering elements. These effects occur as either spectral interferences (peak overlaps) or as x-ray absorption and enhancement phenomena. Both effects are common in soils contaminated with heavy metals. As examples of absorption and enhancement effects; iron (Fe) tends to absorb copper (Cu) x-rays, reducing the intensity of the Cu measured by the detector, while chromium (Cr) will be enhanced at the expense of Fe because the absorption edge of Cr is slightly lower in energy than the fluorescent peak of iron. The effects can be corrected mathematically through the use of fundamental parameter (FP) coefficients. The effects also can be compensated for using SSCS, which contain all the elements present on site that can interfere with one another.

4.6 When present in a sample, certain x-ray lines from different elements can be very close in energy and, therefore, can cause interference by producing a severely overlapped spectrum. The degree to which a detector can resolve the two different peaks depends on the energy resolution of the detector. If the energy difference between the two peaks in electron volts is less than the resolution of the detector in electron volts, then the detector will not be able to fully resolve the peaks.

The most common spectrum overlaps involve the K_{β} line of element Z-1 with the K_{α} line of element Z. This is called the K_{α}/K_{β} interference. Because the $K_{\alpha}:K_{\beta}$ intensity ratio for a given element usually is about 7:1, the interfering element, Z-1, must be present at large concentrations to cause a problem. Two examples of this type of spectral interference involve the presence of large concentrations of vanadium (V) when attempting to measure Cr or the presence of large concentrations of Fe when attempting to measure cobalt (Co). The V K_{α} and K_{β} energies are 4.95 and 5.43 keV, respectively, and the Cr K_{α} energy is 5.41 keV. The Fe K_{α} and K_{β} energies are 6.40 and 7.06 keV, respectively, and the Co K_{α} energy is 6.92 keV. The difference between the V K_{β} and Cr K_{α} energies is 20 eV, and the difference between the Fe K_{β} and the Co K_{α} energies is 140 eV. The resolution of the highest-resolution detectors in FPXRF instruments is 170 eV. Therefore, large amounts of V and Fe will interfere with quantitation of Cr or Co, respectively. The presence of Fe is a frequent problem because it is often found in soils at tens of thousands of parts per million (ppm).

4.7 Other interferences can arise from K/L, K/M, and L/M line overlaps, although these overlaps are less common. Examples of such overlap involve arsenic (As) K_{α} /lead (Pb) L_{α} and sulfur (S) K_{α} /Pb M_{α} . In the As/Pb case, Pb can be measured from the Pb L_{β} line, and As can be measured from either the As K_{α} or the As K_{β} line; in this way the interference can be corrected. If the As K_{β} line is used, sensitivity will be decreased by a factor of two to five times because it is a less intense line than the As K_{α} line. If the As K_{α} line is used in the presence of Pb, mathematical corrections within the instrument software can be used to subtract out the Pb interference. However, because of the limits of mathematical corrections, As concentrations cannot be efficiently calculated for samples with Pb:As ratios of 10:1 or more. This high ratio of Pb to As may result in reporting of a "nondetect" or a "less than" value (e.g., <300 ppm) for As, regardless of the actual concentration present.

No instrument can fully compensate for this interference. It is important for an operator to understand this limitation of FPXRF instruments and consult with the manufacturer of the FPXRF instrument to evaluate options to minimize this limitation. The operator's decision will be based on action levels for metals in soil established for the site, matrix effects, capabilities of the instrument, data quality objectives, and the ratio of lead to arsenic known to be present at the site. If a site is encountered that contains lead at concentrations greater than ten times the concentration of arsenic it is advisable that all critical soil samples be sent off site for confirmatory analysis using other techniques (e.g., flame atomic absorption spectrometry (FLAA), graphite furnace atomic absorption spectrometry (GFAA), inductively coupled plasma-

atomic emission spectrometry, (ICP-AES), or inductively coupled plasma-mass spectrometry, (ICP-MS)).

4.8 If SSCS are used to calibrate an FPXRF instrument, the samples collected must be representative of the site under investigation. Representative soil sampling ensures that a sample or group of samples accurately reflects the concentrations of the contaminants of concern at a given time and location. Analytical results for representative samples reflect variations in the presence and concentration ranges of contaminants throughout a site. Variables affecting sample representativeness include differences in soil type, contaminant concentration variability, sample collection and preparation variability, and analytical variability, all of which should be minimized as much as possible.

4.9 Soil physical and chemical effects may be corrected using SSCS that have been analyzed by inductively coupled plasma (ICP) or atomic absorption (AA) methods. However, a major source of error can be introduced if these samples are not representative of the site or if the analytical error is large. Another concern is the type of digestion procedure used to prepare the soil samples for the reference analysis. Analytical results for the confirmatory method will vary depending on whether a partial digestion procedure, such as Method 3050, or a total digestion procedure, such as Method 3052, is used. It is known that depending on the nature of the soil or sediment, Method 3050 will achieve differing extraction efficiencies for different analytes of interest. The confirmatory method should meet the project-specific data quality objectives (DQOs).

XRF measures the total concentration of an element; therefore, to achieve the greatest comparability of this method with the reference method (reduced bias), a total digestion procedure should be used for sample preparation. However, in the study used to generate the performance data for this method (see Table 8), the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r often exceeding 0.95, except for barium and chromium). The critical factor is that the digestion procedure and analytical reference method used should meet the DQOs of the project and match the method used for confirmation analysis.

4.10 Ambient temperature changes can affect the gain of the amplifiers producing instrument drift. Gain or drift is primarily a function of the electronics (amplifier or preamplifier) and not the detector as most instrument detectors are cooled to a constant temperature. Most FPXRF instruments have a built-in automatic gain control. If the automatic gain control is allowed to make periodic adjustments, the instrument will compensate for the influence of temperature changes on its energy scale. If the FPXRF instrument has an automatic gain control function, the operator will not have to adjust the instrument's gain unless an error message appears. If an error message appears, the operator should follow the manufacturer's procedures for troubleshooting the problem. Often, this involves performing a new energy calibration. The performance of an energy calibration check to assess drift is a quality control measure discussed in Sec. 9.2.

If the operator is instructed by the manufacturer to manually conduct a gain check because of increasing or decreasing ambient temperature, it is standard to perform a gain check after every 10 to 20 sample measurements or once an hour whichever is more frequent. It is also suggested that a gain check be performed if the temperature fluctuates more than 10° F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 This method does not address all safety issues associated with its use. The user is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals listed in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses.

NOTE: No MSDS applies directly to the radiation-producing instrument because that is covered under the Nuclear Regulatory Commission (NRC) or applicable state regulations.

5.2 Proper training for the safe operation of the instrument and radiation training should be completed by the analyst prior to analysis. Radiation safety for each specific instrument can be found in the operator's manual. Protective shielding should never be removed by the analyst or any personnel other than the manufacturer. The analyst should be aware of the local state and national regulations that pertain to the use of radiation-producing equipment and radioactive materials with which compliance is required. There should be a person appointed within the organization that is solely responsible for properly instructing all personnel, maintaining inspection records, and monitoring x-ray equipment at regular intervals.

Licenses for radioactive materials are of two types, specifically: (1) a general license which is usually initiated by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) a specific license which is issued to named persons for the operation of radioactive instruments as required by local, state, or federal agencies. A copy of the radioactive material license (for specific licenses only) and leak tests should be present with the instrument at all times and available to local and national authorities upon request.

X-ray tubes do not require radioactive material licenses or leak tests, but do require approvals and licenses which vary from state to state. In addition, fail-safe x-ray warning lights should be illuminated whenever an x-ray tube is energized. Provisions listed above concerning radiation safety regulations, shielding, training, and responsible personnel apply to x-ray tubes just as to radioactive sources. In addition, a log of the times and operating conditions should be kept whenever an x-ray tube is energized. An additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply, however, if the tube is properly positioned within the instrument, this is only a negligible risk. Any instrument (x-ray tube or radioisotope based) is capable of delivering an electric shock from the basic circuitry when the system is inappropriately opened.

5.3 Radiation monitoring equipment should be used with the handling and operation of the instrument. The operator and the surrounding environment should be monitored continually for analyst exposure to radiation. Thermal luminescent detectors (TLD) in the form of badges and rings are used to monitor operator radiation exposure. The TLDs or badges should be worn in the area of maximum exposure. The maximum permissible whole-body dose from occupational exposure is 5 Roentgen Equivalent Man (REM) per year. Possible exposure pathways for radiation to enter the body are ingestion, inhaling, and absorption. The best precaution to prevent radiation exposure is distance and shielding.

6.0 EQUIPMENT AND SUPPLIES

The mention of trade names or commercial products in this manual is for illustrative purposes only, and does not constitute an EPA endorsement or exclusive recommendation for

use. The products and instrument settings cited in SW-846 methods represent those products and settings used during method development or subsequently evaluated by the Agency. Glassware, reagents, supplies, equipment, and settings other than those listed in this manual may be employed provided that method performance appropriate for the intended application has been demonstrated and documented.

6.1 FPXRF spectrometer -- An FPXRF spectrometer consists of four major components: (1) a source that provides x-rays; (2) a sample presentation device; (3) a detector that converts x-ray-generated photons emitted from the sample into measurable electronic signals; and (4) a data processing unit that contains an emission or fluorescence energy analyzer, such as an MCA, that processes the signals into an x-ray energy spectrum from which elemental concentrations in the sample may be calculated, and a data display and storage system. These components and additional, optional items, are discussed below.

6.1.1 Excitation sources -- FPXRF instruments use either a sealed radioisotope source or an x-ray tube to provide the excitation source. Many FPXRF instruments use sealed radioisotope sources to produce x-rays in order to irradiate samples. The FPXRF instrument may contain between one and three radioisotope sources. Common radioisotope sources used for analysis for metals in soils are iron Fe-55 (^{55}Fe), cadmium Cd-109 (^{109}Cd), americium Am-241 (^{241}Am), and curium Cm-244 (^{244}Cm). These sources may be contained in a probe along with a window and the detector; the probe may be connected to a data reduction and handling system by means of a flexible cable. Alternatively, the sources, window, and detector may be included in the same unit as the data reduction and handling system.

The relative strength of the radioisotope sources is measured in units of millicuries (mCi). All other components of the FPXRF system being equal, the stronger the source, the greater the sensitivity and precision of a given instrument. Radioisotope sources undergo constant decay. In fact, it is this decay process that emits the primary x-rays used to excite samples for FPXRF analysis. The decay of radioisotopes is measured in "half-lives." The half-life of a radioisotope is defined as the length of time required to reduce the radioisotopes strength or activity by half. Developers of FPXRF technologies recommend source replacement at regular intervals based on the source's half-life. This is due to the ever increasing time required for the analysis rather than a decrease in instrument performance. The characteristic x-rays emitted from each of the different sources have energies capable of exciting a certain range of analytes in a sample. Table 2 summarizes the characteristics of four common radioisotope sources.

X-ray tubes have higher radiation output, no intrinsic lifetime limit, produce constant output over their lifetime, and do not have the disposal problems of radioactive sources but are just now appearing in FPXRF instruments. An electrically-excited x-ray tube operates by bombarding an anode with electrons accelerated by a high voltage. The electrons gain an energy in electron volts equal to the accelerating voltage and can excite atomic transitions in the anode, which then produces characteristic x-rays. These characteristic x-rays are emitted through a window which contains the vacuum necessary for the electron acceleration. An important difference between x-ray tubes and radioactive sources is that the electrons which bombard the anode also produce a continuum of x-rays across a broad range of energies in addition to the characteristic x-rays. This continuum is weak compared to the characteristic x-rays but can provide substantial excitation since it covers a broad energy range. It has the undesired property of producing background in the spectrum near the analyte x-ray lines when it is scattered by the sample. For this reason a filter is often used between the x-ray tube and the sample to suppress the continuum radiation while passing the characteristic x-rays from the anode. This filter is sometimes incorporated into the window of the x-ray tube. The choice of

accelerating voltage is governed both by the anode material, since the electrons must have sufficient energy to excite the anode, which requires a voltage greater than the absorption edge of the anode material and by the instrument's ability to cool the x-ray tube. The anode is most efficiently excited by voltages 2 to 2.5 times the edge energy (most x-rays per unit power to the tube), although voltages as low as 1.5 times the absorption edge energy will work. The characteristic x-rays emitted by the anode are capable of exciting a range of elements in the sample just as with a radioactive source. Table 3 gives the recommended operating voltages and the sample elements excited for some common anodes.

6.1.2 Sample presentation device -- FPXRF instruments can be operated in two modes: in situ and intrusive. If operated in the in situ mode, the probe window is placed in direct contact with the soil surface to be analyzed. When an FPXRF instrument is operated in the intrusive mode, a soil or sediment sample must be collected, prepared, and placed in a sample cup. For FPXRF instruments operated in the intrusive mode, the probe may be rotated so that the window faces either upward or downward. A protective sample cover is placed over the window, and the sample cup is placed on top of the window inside the protective sample cover for analysis.

6.1.3 Detectors -- The detectors in the FPXRF instruments can be either solid-state detectors or gas-filled, proportional counter detectors. Common solid-state detectors include mercuric iodide (HgI_2), silicon pin diode and lithium-drifted silicon $\text{Si}(\text{Li})$. The HgI_2 detector is operated at a moderately subambient temperature controlled by a low power thermoelectric cooler. The silicon pin diode detector also is cooled via the thermoelectric Peltier effect. The $\text{Si}(\text{Li})$ detector must be cooled to at least -90°C either with liquid nitrogen or by thermoelectric cooling via the Peltier effect. Instruments with a $\text{Si}(\text{Li})$ detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 L. Proportional counter detectors are rugged and lightweight, which are important features of a field portable detector. However, the resolution of a proportional counter detector is not as good as that of a solid-state detector. The energy resolution of a detector for characteristic x-rays is usually expressed in terms of full width at half-maximum (FWHM) height of the manganese K_α peak at 5.89 keV. The typical resolutions of the above mentioned detectors are as follows: HgI_2 -270 eV; silicon pin diode-250 eV; $\text{Si}(\text{Li})$ -170 eV; and gas-filled, proportional counter-750 eV.

During operation of a solid-state detector, an x-ray photon strikes a biased, solid-state crystal and loses energy in the crystal by producing electron-hole pairs. The electric charge produced is collected and provides a current pulse that is directly proportional to the energy of the x-ray photon absorbed by the crystal of the detector. A gas-filled, proportional counter detector is an ionization chamber filled with a mixture of noble and other gases. An x-ray photon entering the chamber ionizes the gas atoms. The electric charge produced is collected and provides an electric signal that is directly proportional to the energy of the x-ray photon absorbed by the gas in the detector.

6.1.4 Data processing units -- The key component in the data processing unit of an FPXRF instrument is the MCA. The MCA receives pulses from the detector and sorts them by their amplitudes (energy level). The MCA counts pulses per second to determine the height of the peak in a spectrum, which is indicative of the target analyte's concentration. The spectrum of element peaks are built on the MCA. The MCAs in FPXRF instruments have from 256 to 2,048 channels. The concentrations of target analytes are usually shown in ppm on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 3,000 to 5,000 sets of numerical analytical results. Most FPXRF instruments are menu-driven from software built into the

units or from PCs. Once the data-storage memory of an FPXRF unit is full or at any other time, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery and battery charger.

6.3 Polyethylene sample cups -- 31 to 40 mm in diameter with collar, or equivalent (appropriate for FPXRF instrument).

6.4 X-ray window film -- Mylar™, Kapton™, Spectrolene™, polypropylene, or equivalent; 2.5 to 6.0 μm thick.

6.5 Mortar and pestle -- Glass, agate, or aluminum oxide; for grinding soil and sediment samples.

6.6 Containers -- Glass or plastic to store samples.

6.7 Sieves -- 60-mesh (0.25 mm), stainless-steel, Nylon, or equivalent for preparing soil and sediment samples.

6.8 Trowels -- For smoothing soil surfaces and collecting soil samples.

6.9 Plastic bags -- Used for collection and homogenization of soil samples.

6.10 Drying oven -- Standard convection or toaster oven, for soil and sediment samples that require drying.

7.0 REAGENTS AND STANDARDS

7.1 Reagent grade chemicals must be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Pure element standards -- Each pure, single-element standard is intended to produce strong characteristic x-ray peaks of the element of interest only. Other elements present must not contribute to the fluorescence spectrum. A set of pure element standards for commonly sought analytes is supplied by the instrument manufacturer, if designated for the instrument; not all instruments require the pure element standards. The standards are used to set the region of interest (ROI) for each element. They also can be used as energy calibration and resolution check samples.

7.3 Site-specific calibration standards -- Instruments that employ fundamental parameters (FP) or similar mathematical models in minimizing matrix effects may not require SSCS. If the FP calibration model is to be optimized or if empirical calibration is necessary, then SSCSs must be collected, prepared, and analyzed.

7.3.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of 10 samples spanning the concentration ranges of the analytes of interest and of the interfering elements must be obtained from the site. A sample size of 4 to 8 ounces is recommended, and standard glass sampling jars should be used.

7.3.2 Each sample should be oven-dried for 2 to 4 hr at a temperature of less than 150 °C. If mercury is to be analyzed, a separate sample portion should be dried at ambient temperature as heating may volatilize the mercury. When the sample is dry, all large, organic debris and nonrepresentative material, such as twigs, leaves, roots, insects, asphalt, and rock should be removed. The sample should be homogenized (see Sec. 7.3.3) and then a representative portion ground with a mortar and pestle or other mechanical means, prior to passing through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.3.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 g of the dried, sieved sample on a piece of kraft or butcher paper about 1.5 by 1.5 feet in size. Each corner of the paper should be lifted alternately, rolling the soil over on itself and toward the opposite corner. The soil should be rolled on itself 20 times. Approximately 5 g of the sample should then be removed and placed in a sample cup for FPXRF analysis. The rest of the prepared sample should be sent off site for ICP or AA analysis. The method use for confirmatory analysis should meet the data quality objectives of the project.

7.4 Blank samples -- The blank samples should be from a "clean" quartz or silicon dioxide matrix that is free of any analytes at concentrations above the established lower limit of detection. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.5 Standard reference materials -- Standard reference materials (SRMs) are standards containing certified amounts of metals in soil or sediment. These standards are used for accuracy and performance checks of FPXRF analyses. SRMs can be obtained from the National Institute of Standards and Technology (NIST), the U.S. Geological Survey (USGS), the Canadian National Research Council, and the national bureau of standards in foreign nations. Pertinent NIST SRMs for FPXRF analysis include 2704, Buffalo River Sediment; 2709, San Joaquin Soil; and 2710 and 2711, Montana Soil. These SRMs contain soil or sediment from actual sites that has been analyzed using independent inorganic analytical methods by many different laboratories. When these SRMs are unavailable, alternate standards may be used (e.g., NIST 2702).

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

Sample handling and preservation procedures used in FPXRF analyses should follow the guidelines in Chapter Three, "Inorganic Analytes."

9.0 QUALITY CONTROL

9.1 Follow the manufacturer's instructions for the quality control procedures specific to use of the testing product. Refer to Chapter One for additional guidance on quality assurance (QA) and quality control (QC) protocols. Any effort involving the collection of analytical data should include development of a structured and systematic planning document, such as a Quality Assurance Project Plan (QAPP) or a Sampling and Analysis Plan (SAP), which translates project objectives and specifications into directions for those that will implement the project and assess the results.

9.2 Energy calibration check -- To determine whether an FPXRF instrument is operating within resolution and stability tolerances, an energy calibration check should be run. The energy calibration check determines whether the characteristic x-ray lines are shifting,

which would indicate drift within the instrument. As discussed in Sec. 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (more than 10 °F).

9.2.1 The energy calibration check should be run at a frequency consistent with manufacturer's recommendations. Generally, this would be at the beginning of each working day, after the batteries are changed or the instrument is shut off, at the end of each working day, and at any other time when the instrument operator believes that drift is occurring during analysis. A pure element such as iron, manganese, copper, or lead is often used for the energy calibration check. A manufacturer-recommended count time per source should be used for the check.

9.2.2 The instrument manufacturer's manual specifies the channel or kiloelectron volt level at which a pure element peak should appear and the expected intensity of the peak. The intensity and channel number of the pure element as measured using the source should be checked and compared to the manufacturer's recommendation. If the energy calibration check does not meet the manufacturer's criteria, then the pure element sample should be repositioned and reanalyzed. If the criteria are still not met, then an energy calibration should be performed as described in the manufacturer's manual. With some FPXRF instruments, once a spectrum is acquired from the energy calibration check, the peak can be optimized and realigned to the manufacturer's specifications using their software.

9.3 Blank samples -- Two types of blank samples should be analyzed for FPXRF analysis, specifically, instrument blanks and method blanks.

9.3.1 An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a polytetrafluoroethylene (PTFE) block, a quartz block, "clean" sand, or lithium carbonate. This instrument blank should be analyzed on each working day before and after analyses are conducted and once per every twenty samples. An instrument blank should also be analyzed whenever contamination is suspected by the analyst. The frequency of analysis will vary with the data quality objectives of the project. A manufacturer-recommended count time per source should be used for the blank analysis. No element concentrations above the established lower limit of detection should be found in the instrument blank. If concentrations exceed these limits, then the probe window and the check sample should be checked for contamination. If contamination is not a problem, then the instrument must be "zeroed" by following the manufacturer's instructions.

9.3.2 A method blank is used to monitor for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same preparation procedure as the samples. A method blank must be analyzed at least daily. The frequency of analysis will depend on the data quality objectives of the project. If the method blank does not contain the target analyte at a level that interferes with the project-specific data quality objectives then the method blank would be considered acceptable. In the absence of project-specific data quality objectives, if the blank is less than the lowest level of detection or less than 10% of the lowest sample concentration for the analyte, whichever is greater, then the method blank would be considered acceptable. If the method blank cannot be considered acceptable, the cause of the problem must be identified, and all samples analyzed with the method blank must be reanalyzed.

9.4 Calibration verification checks -- A calibration verification check sample is used to check the accuracy of the instrument and to assess the stability and consistency of the analysis for the analytes of interest. A check sample should be analyzed at the beginning of each working day, during active sample analyses, and at the end of each working day. The frequency of calibration checks during active analysis will depend on the data quality objectives of the project. The check sample should be a well characterized soil sample from the site that is representative of site samples in terms of particle size and degree of homogeneity and that contains contaminants at concentrations near the action levels. If a site-specific sample is not available, then an NIST or other SRM that contains the analytes of interest can be used to verify the accuracy of the instrument. The measured value for each target analyte should be within ± 20 percent (%D) of the true value for the calibration verification check to be acceptable. If a measured value falls outside this range, then the check sample should be reanalyzed. If the value continues to fall outside the acceptance range, the instrument should be recalibrated, and the batch of samples analyzed before the unacceptable calibration verification check must be reanalyzed.

9.5 Precision measurements -- The precision of the method is monitored by analyzing a sample with low, moderate, or high concentrations of target analytes. The frequency of precision measurements will depend on the data quality objectives for the data. A minimum of one precision sample should be run per day. Each precision sample should be analyzed 7 times in replicate. It is recommended that precision measurements be obtained for samples with varying concentration ranges to assess the effect of concentration on method precision. Determining method precision for analytes at concentrations near the site action levels can be extremely important if the FPXRF results are to be used in an enforcement action; therefore, selection of at least one sample with target analyte concentrations at or near the site action levels or levels of concern is recommended. A precision sample is analyzed by the instrument for the same field analysis time as used for other project samples. The relative standard deviation (RSD) of the sample mean is used to assess method precision. For FPXRF data to be considered adequately precise, the RSD should not be greater than 20 percent with the exception of chromium. RSD values for chromium should not be greater than 30 percent. If both in situ and intrusive analytical techniques are used during the course of one day, it is recommended that separate precision calculations be performed for each analysis type.

The equation for calculating RSD is as follows:

$$\text{RSD} = (\text{SD}/\text{Mean Concentration}) \times 100$$

where:

RSD = Relative standard deviation for the precision measurement for the analyte
SD = Standard deviation of the concentration for the analyte
Mean concentration = Mean concentration for the analyte

The precision or reproducibility of a measurement will improve with increasing count time, however, increasing the count time by a factor of 4 will provide only 2 times better precision, so there is a point of diminishing return. Increasing the count time also improves the sensitivity, but decreases sample throughput.

9.6 The lower limits of detection should be established from actual measured performance based on spike recoveries in the matrix of concern or from acceptable method performance on a certified reference material of the appropriate matrix and within the appropriate calibration range for the application. This is considered the best estimate of the true method sensitivity as opposed to a statistical determination based on the standard deviation of

replicate analyses of a low-concentration sample. While the statistical approach demonstrates the potential data variability for a given sample matrix at one point in time, it does not represent what can be detected or most importantly the lowest concentration that can be calibrated. For this reason the sensitivity should be established as the lowest point of detection based on acceptable target analyte recovery in the desired sample matrix.

9.7 Confirmatory samples -- The comparability of the FPXRF analysis is determined by submitting FPXRF-analyzed samples for analysis at a laboratory. The method of confirmatory analysis must meet the project and XRF measurement data quality objectives. The confirmatory samples must be splits of the well homogenized sample material. In some cases the prepared sample cups can be submitted. A minimum of 1 sample for each 20 FPXRF-analyzed samples should be submitted for confirmatory analysis. This frequency will depend on project-specific data quality objectives. The confirmatory analyses can also be used to verify the quality of the FPXRF data. The confirmatory samples should be selected from the lower, middle, and upper range of concentrations measured by the FPXRF. They should also include samples with analyte concentrations at or near the site action levels. The results of the confirmatory analysis and FPXRF analyses should be evaluated with a least squares linear regression analysis. If the measured concentrations span more than one order of magnitude, the data should be log-transformed to standardize variance which is proportional to the magnitude of measurement. The correlation coefficient (r) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r is 0.9 or greater and inferential statistics indicate the FPXRF data and the confirmatory data are statistically equivalent at a 99 percent confidence level, the data could potentially meet definitive level data criteria.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Instrument calibration -- Instrument calibration procedures vary among FPXRF instruments. Users of this method should follow the calibration procedures outlined in the operator's manual for each specific FPXRF instrument. Generally, however, three types of calibration procedures exist for FPXRF instruments, namely: FP calibration, empirical calibration, and the Compton peak ratio or normalization method. These three types of calibration are discussed below.

10.2 Fundamental parameters calibration -- FP calibration procedures are extremely variable. An FP calibration provides the analyst with a "standardless" calibration. The advantages of FP calibrations over empirical calibrations include the following:

- No previously collected site-specific samples are necessary, although site-specific samples with confirmed and validated analytical results for all elements present could be used.
- Cost is reduced because fewer confirmatory laboratory results or calibration standards are necessary.

However, the analyst should be aware of the limitations imposed on FP calibration by particle size and matrix effects. These limitations can be minimized by adhering to the preparation procedure described in Sec. 7.3. The two FP calibration processes discussed below are based on an effective energy FP routine and a back scatter with FP (BFP) routine. Each FPXRF FP calibration process is based on a different iterative algorithmic method. The calibration procedure for each routine is explained in detail in the manufacturer's user manual for each FPXRF instrument; in addition, training courses are offered for each instrument.

10.2.1 Effective energy FP calibration -- The effective energy FP calibration is performed by the manufacturer before an instrument is sent to the analyst. Although SSCS can be used, the calibration relies on pure element standards or SRMs such as those obtained from NIST for the FP calibration. The effective energy routine relies on the spectrometer response to pure elements and FP iterative algorithms to compensate for various matrix effects.

Alpha coefficients are calculated using a variation of the Sherman equation, which calculates theoretical intensities from the measurement of pure element samples. These coefficients indicate the quantitative effect of each matrix element on an analyte's measured x-ray intensity. Next, the Lachance Traill algorithm is solved as a set of simultaneous equations based on the theoretical intensities. The alpha coefficients are then downloaded into the specific instrument.

The working effective energy FP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of sampling. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. A manufacturer-recommended count time per source should be used for the calibration check. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A percent difference (%D) is then calculated for each target analyte. The %D should be within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line or the y-intercept value for the analyte. The SRM or SSCS is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

The equation to calibrate %D is as follows:

$$\%D = ((C_s - C_k) / C_k) \times 100$$

where:

%D = Percent difference

C_k = Certified concentration of standard sample

C_s = Measured concentration of standard sample

10.2.2 BFP calibration -- BFP calibration relies on the ability of the liquid nitrogen-cooled, Si(Li) solid-state detector to separate the coherent (Compton) and incoherent (Rayleigh) backscatter peaks of primary radiation. These peak intensities are known to be a function of sample composition, and the ratio of the Compton to Rayleigh peak is a function of the mass absorption of the sample. The calibration procedure is explained in detail in the instrument manufacturer's manual. Following is a general description of the BFP calibration procedure.

The concentrations of all detected and quantified elements are entered into the computer software system. Certified element results for an NIST SRM or confirmed and validated results for an SSCS can be used. In addition, the concentrations of oxygen and silicon must be entered; these two concentrations are not found in standard metals analyses. The manufacturer provides silicon and oxygen concentrations for typical soil types. Pure element standards are then analyzed using a manufacturer-recommended

count time per source. The results are used to calculate correction factors in order to adjust for spectrum overlap of elements.

The working BFP calibration curve must be verified before sample analysis begins on each working day, after every 20 samples are analyzed, and at the end of the analysis. This verification is performed by analyzing either an NIST SRM or an SSCS that is representative of the site-specific samples. This SRM or SSCS serves as a calibration check. The standard sample is analyzed using a manufacturer-recommended count time per source to check the calibration curve. The analyst must then adjust the y-intercept and slope of the calibration curve to best fit the known concentrations of target analytes in the SRM or SSCS.

A %D is then calculated for each target analyte. The %D should fall within ± 20 percent of the certified value for each analyte. If the %D falls outside this acceptance range, then the calibration curve should be adjusted by varying the slope of the line the y-intercept value for the analyte. The standard sample is reanalyzed until the %D falls within ± 20 percent. The group of 20 samples analyzed before an out-of-control calibration check should be reanalyzed.

10.3 Empirical calibration -- An empirical calibration can be performed with SSCS, site-typical standards, or standards prepared from metal oxides. A discussion of SSCS is included in Sec. 7.3; if no previously characterized samples exist for a specific site, site-typical standards can be used. Site-typical standards may be selected from commercially available characterized soils or from SSCS prepared for another site. The site-typical standards should closely approximate the site's soil matrix with respect to particle size distribution, mineralogy, and contaminant analytes. If neither SSCS nor site-typical standards are available, it is possible to make gravimetric standards by adding metal oxides to a "clean" sand or silicon dioxide matrix that simulates soil. Metal oxides can be purchased from various chemical vendors. If standards are made on site, a balance capable of weighing items to at least two decimal places is necessary. Concentrated ICP or AA standard solutions can also be used to make standards. These solutions are available in concentrations of 10,000 parts per million, thus only small volumes have to be added to the soil.

An empirical calibration using SSCS involves analysis of SSCS by the FPXRF instrument and by a conventional analytical method such as ICP or AA. A total acid digestion procedure should be used by the laboratory for sample preparation. Generally, a minimum of 10 and a maximum of 30 well characterized SSCS, site-typical standards, or prepared metal oxide standards are necessary to perform an adequate empirical calibration. The exact number of standards depends on the number of analytes of interest and interfering elements. Theoretically, an empirical calibration with SSCS should provide the most accurate data for a site because the calibration compensates for site-specific matrix effects.

The first step in an empirical calibration is to analyze the pure element standards for the elements of interest. This enables the instrument to set channel limits for each element for spectral deconvolution. Next the SSCS, site-typical standards, or prepared metal oxide standards are analyzed using a count time of 200 seconds per source or a count time recommended by the manufacturer. This will produce a spectrum and net intensity of each analyte in each standard. The analyte concentrations for each standard are then entered into the instrument software; these concentrations are those obtained from the laboratory, the certified results, or the gravimetrically determined concentrations of the prepared standards. This gives the instrument analyte values to regress against corresponding intensities during the modeling stage. The regression equation correlates the concentrations of an analyte with its net intensity.

The calibration equation is developed using a least squares fit regression analysis. After the regression terms to be used in the equation are defined, a mathematical equation can be developed to calculate the analyte concentration in an unknown sample. In some FPXRF instruments, the software of the instrument calculates the regression equation. The software uses calculated intercept and slope values to form a multiterm equation. In conjunction with the software in the instrument, the operator can adjust the multiterm equation to minimize interelement interferences and optimize the intensity calibration curve.

It is possible to define up to six linear or nonlinear terms in the regression equation. Terms can be added and deleted to optimize the equation. The goal is to produce an equation with the smallest regression error and the highest correlation coefficient. These values are automatically computed by the software as the regression terms are added, deleted, or modified. It is also possible to delete data points from the regression line if these points are significant outliers or if they are heavily weighing the data. Once the regression equation has been selected for an analyte, the equation can be entered into the software for quantitation of analytes in subsequent samples. For an empirical calibration to be acceptable, the regression equation for a specific analyte should have a correlation coefficient of 0.98 or greater or meet the DQOs of the project.

In an empirical calibration, one must apply the DQOs of the project and ascertain critical or action levels for the analytes of interest. It is within these concentration ranges or around these action levels that the FPXRF instrument should be calibrated most accurately. It may not be possible to develop a good regression equation over several orders of analyte concentration.

10.4 Compton normalization method -- The Compton normalization method is based on analysis of a single, certified standard and normalization for the Compton peak. The Compton peak is produced from incoherent backscattering of x-ray radiation from the excitation source and is present in the spectrum of every sample. The Compton peak intensity changes with differing matrices. Generally, matrices dominated by lighter elements produce a larger Compton peak, and those dominated by heavier elements produce a smaller Compton peak. Normalizing to the Compton peak can reduce problems with varying matrix effects among samples. Compton normalization is similar to the use of internal standards in organics analysis. The Compton normalization method may not be effective when analyte concentrations exceed a few percent.

The certified standard used for this type of calibration could be an NIST SRM such as 2710 or 2711. The SRM must be a matrix similar to the samples and must contain the analytes of interests at concentrations near those expected in the samples. First, a response factor has to be determined for each analyte. This factor is calculated by dividing the net peak intensity by the analyte concentration. The net peak intensity is gross intensity corrected for baseline reading. Concentrations of analytes in samples are then determined by multiplying the baseline corrected analyte signal intensity by the normalization factor and by the response factor. The normalization factor is the quotient of the baseline corrected Compton K_{α} peak intensity of the SRM divided by that of the samples. Depending on the FPXRF instrument used, these calculations may be done manually or by the instrument software.

11.0 PROCEDURE

11.1 Operation of the various FPXRF instruments will vary according to the manufacturers' protocols. Before operating any FPXRF instrument, one should consult the manufacturer's manual. Most manufacturers recommend that their instruments be allowed to warm up for 15 to 30 minutes before analysis of samples. This will help alleviate drift or energy calibration problems later during analysis.

11.2 Each FPXRF instrument should be operated according to the manufacturer's recommendations. There are two modes in which FPXRF instruments can be operated: in situ and intrusive. The in situ mode involves analysis of an undisturbed soil sediment or sample. Intrusive analysis involves collection and preparation of a soil or sediment sample before analysis. Some FPXRF instruments can operate in both modes of analysis, while others are designed to operate in only one mode. The two modes of analysis are discussed below.

11.3 For in situ analysis, remove any large or nonrepresentative debris from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Also, the soil surface must be as smooth as possible so that the probe window will have good contact with the surface. This may require some leveling of the surface with a stainless-steel trowel. During the study conducted to provide example performance data for this method, this modest amount of sample preparation was found to take less than 5 min per sample location. The last requirement is that the soil or sediment not be saturated with water. Manufacturers state that their FPXRF instruments will perform adequately for soils with moisture contents of 5 to 20 percent but will not perform well for saturated soils, especially if ponded water exists on the surface. Another recommended technique for in situ analysis is to tamp the soil to increase soil density and compactness for better repeatability and representativeness. This condition is especially important for heavy element analysis, such as barium. Source count times for in situ analysis usually range from 30 to 120 seconds, but source count times will vary among instruments and depending on the desired method sensitivity. Due to the heterogeneous nature of the soil sample, in situ analysis can provide only "screening" type data.

11.4 For intrusive analysis of surface or sediment, it is recommended that a sample be collected from a 4- by 4-inch square that is 1 inch deep. This will produce a soil sample of approximately 375 g or 250 cm³, which is enough soil to fill an 8-ounce jar. However, the exact dimensions and sample depth should take into consideration the heterogeneous deposition of contaminants and will ultimately depend on the desired project-specific data quality objectives. The sample should be homogenized, dried, and ground before analysis. The sample can be homogenized before or after drying. The homogenization technique to be used after drying is discussed in Sec. 4.2. If the sample is homogenized before drying, it should be thoroughly mixed in a beaker or similar container, or if the sample is moist and has a high clay content, it can be kneaded in a plastic bag. One way to monitor homogenization when the sample is kneaded in a plastic bag is to add sodium fluorescein dye to the sample. After the moist sample has been homogenized, it is examined under an ultraviolet light to assess the distribution of sodium fluorescein throughout the sample. If the fluorescent dye is evenly distributed in the sample, homogenization is considered complete; if the dye is not evenly distributed, mixing should continue until the sample has been thoroughly homogenized. During the study conducted to provide data for this method, the time necessary for homogenization procedure using the fluorescein dye ranged from 3 to 5 min per sample. As demonstrated in Secs. 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, the direct analysis through the plastic bag is possible without the more labor intensive steps of drying, grinding, and sieving given in Secs. 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps should be followed.

11.5 Once the soil or sediment sample has been homogenized, it should be dried. This can be accomplished with a toaster oven or convection oven. A small aliquot of the sample (20 to 50 g) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hr in the convection or toaster oven at a temperature not greater than 150 °C. Samples may also be air dried under ambient temperature conditions using a 10- to 20-g portion. Regardless of what drying mechanism is used, the drying process is considered complete when a constant sample weight can be obtained. Care should be taken to avoid sample cross-contamination and these measures can be evaluated by including an appropriate method blank sample along with any sample preparation process.

CAUTION: Microwave drying is not a recommended procedure. Field studies have shown that microwave drying can increase variability between the FPXRF data and confirmatory analysis. High levels of metals in a sample can cause arcing in the microwave oven, and sometimes slag forms in the sample. Microwave oven drying can also melt plastic containers used to hold the sample.

11.6 The homogenized dried sample material should be ground with a mortar and pestle and passed through a 60-mesh sieve to achieve a uniform particle size. Sample grinding should continue until at least 90 percent of the original sample passes through the sieve. The grinding step normally takes an average of 10 min per sample. An aliquot of the sieved sample should then be placed in a 31.0-mm polyethylene sample cup (or equivalent) for analysis. The sample cup should be one-half to three-quarters full at a minimum. The sample cup should be covered with a 2.5 μm Mylar (or equivalent) film for analysis. The rest of the soil sample should be placed in a jar, labeled, and archived for possible confirmation analysis. All equipment including the mortar, pestle, and sieves must be thoroughly cleaned so that any cross-contamination is below the established lower limit of detection of the procedure or DQOs of the analysis. If all recommended sample preparation steps are followed, there is a high probability the desired laboratory data quality may be obtained.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in ppm and can be downloaded to a personal computer, which can be used to provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation. See the manufacturer's instructions regarding data analysis and calculations.

13.0 METHOD PERFORMANCE

13.1 Performance data and related information are provided in SW-846 methods only as examples and guidance. The data do not represent required performance criteria for users of the methods. Instead, performance criteria should be developed on a project-specific basis, and the laboratory should establish in-house QC performance criteria for the application of this method. These performance data are not intended to be and must not be used as absolute QC acceptance criteria for purposes of laboratory accreditation.

13.2 The sections to follow discuss three performance evaluation factors; namely, precision, accuracy, and comparability. The example data presented in Tables 4 through 8 were generated from results obtained from six FPXRF instruments (see Sec. 13.3). The soil samples analyzed by the six FPXRF instruments were collected from two sites in the United States. The soil samples contained several of the target analytes at concentrations ranging from "nondetect" to tens of thousands of mg/kg. These data are provided for guidance purposes only.

13.3 The six FPXRF instruments included the TN 9000 and TN Lead Analyzer manufactured by TN Spectrace; the X-MET 920 with a SiLi detector and X-MET 920 with a gas-filled proportional detector manufactured by Metorex, Inc.; the XL Spectrum Analyzer manufactured by Niton; and the MAP Spectrum Analyzer manufactured by Scitec. The TN 9000 and TN Lead Analyzer both have a HgI_2 detector. The TN 9000 utilized an Fe-55, Cd-109, and Am-241 source. The TN Lead Analyzer had only a Cd-109 source. The X-Met 920 with the SiLi detector had a Cd-109 and Am-241 source. The X-MET 920 with the gas-filled proportional detector had only a Cd-109 source. The XL Spectrum Analyzer utilized a silicon pin-diode

detector and a Cd-109 source. The MAP Spectrum Analyzer utilized a solid-state silicon detector and a Cd-109 source.

13.4 All example data presented in Tables 4 through 8 were generated using the following calibrations and source count times. The TN 9000 and TN Lead Analyzer were calibrated using fundamental parameters using NIST SRM 2710 as a calibration check sample. The TN 9000 was operated using 100, 60, and 60 second count times for the Cd-109, Fe-55, and Am-241 sources, respectively. The TN Lead analyzer was operated using a 60 second count time for the Cd-109 source. The X-MET 920 with the Si(Li) detector was calibrated using fundamental parameters and one well characterized site-specific soil standard as a calibration check. It used 140 and 100 second count times for the Cd-109 and Am-241 sources, respectively. The X-MET 920 with the gas-filled proportional detector was calibrated empirically using between 10 and 20 well characterized site-specific soil standards. It used 120 second times for the Cd-109 source. The XL Spectrum Analyzer utilized NIST SRM 2710 for calibration and the Compton peak normalization procedure for quantitation based on 60 second count times for the Cd-109 source. The MAP Spectrum Analyzer was internally calibrated by the manufacturer. The calibration was checked using a well-characterized site-specific soil standard. It used 240 second times for the Cd-109 source.

13.5 Precision measurements -- The example precision data are presented in Table 4. These data are provided for guidance purposes only. Each of the six FPXRF instruments performed 10 replicate measurements on 12 soil samples that had analyte concentrations ranging from "nondetects" to thousands of mg/kg. Each of the 12 soil samples underwent 4 different preparation techniques from in situ (no preparation) to dried and ground in a sample cup. Therefore, there were 48 precision data points for five of the instruments and 24 precision points for the MAP Spectrum Analyzer. The replicate measurements were taken using the source count times discussed at the beginning of this section.

For each detectable analyte in each precision sample a mean concentration, standard deviation, and RSD was calculated for each analyte. The data presented in Table 4 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the lower limit of detection for that analyte for each instrument. Some analytes such as mercury, selenium, silver, and thorium were not detected in any of the precision samples so these analytes are not listed in Table 4. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the lower limit of detection so that an RSD value calculated at 5 to 10 times this limit was not possible.

One FPXRF instrument collected replicate measurements on an additional nine soil samples to provide a better assessment of the effect of sample preparation on precision. Table 5 shows these results. These data are provided for guidance purposes only. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the lower limit of detection for the FPXRF analyzer to thousands of mg/kg. The FPXRF analyzer only collected replicate measurements from three of the preparation methods; no measurements were collected from the in situ homogenized samples. The FPXRF analyzer conducted five replicate measurements of the in situ field samples by taking measurements at five different points within the 4-inch by 4-inch sample square. Ten replicate measurements were collected for both the intrusive undried and unground and intrusive dried and ground samples contained in cups. The cups were shaken between each replicate measurement.

Table 5 shows that the precision dramatically improved from the in situ to the intrusive measurements. In general there was a slight improvement in precision when the sample was dried and ground. Two factors caused the precision for the in situ measurements to be poorer. The major factor is soil heterogeneity. By moving the probe within the 4-inch by 4-inch square,

measurements of different soil samples were actually taking place within the square. Table 5 illustrates the dominant effect of soil heterogeneity. It overwhelmed instrument precision when the FPXRF analyzer was used in this mode. The second factor that caused the RSD values to be higher for the in situ measurements is the fact that only five instead of ten replicates were taken. A lesser number of measurements caused the standard deviation to be larger which in turn elevated the RSD values.

13.6 Accuracy measurements -- Five of the FPXRF instruments (not including the MAP Spectrum Analyzer) analyzed 18 SRMs using the source count times and calibration methods given at the beginning of this section. The 18 SRMs included 9 soil SRMs, 4 stream or river sediment SRMs, 2 sludge SRMs, and 3 ash SRMs. Each of the SRMs contained known concentrations of certain target analytes. A percent recovery was calculated for each analyte in each SRM for each FPXRF instrument. Table 6 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 6 were generated from the 13 soil and sediment SRMs only. The 2 sludge and 3 ash SRMs were included for cadmium, chromium, and nickel because of the low or nondetectable concentrations of these three analytes in the soil and sediment SRMs.

Only 12 analytes are presented in Table 6. These are the analytes that are of environmental concern and provided a significant number of detections in the SRMs for an accuracy assessment. No data is presented for the X-MET 920 with the gas-filled proportional detector. This FPXRF instrument was calibrated empirically using site-specific soil samples. The percent recovery values from this instrument were very sporadic and the data did not lend itself to presentation in Table 6.

Table 7 provides a more detailed summary of accuracy data for one particular FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. These data are provided for guidance purposes only. Table 7 shows the certified value, measured value, and percent recovery for five analytes. These analytes were chosen because they are of environmental concern and were most prevalently certified for in the SRM and detected by the FPXRF instrument. The first nine SRMs are soil and the last 4 SRMs are sediment. Percent recoveries for the four NIST SRMs were often between 90 and 110 percent for all analytes.

13.7 Comparability -- Comparability refers to the confidence with which one data set can be compared to another. In this case, FPXRF data generated from a large study of six FPXRF instruments was compared to SW-846 Methods 3050 and 6010 which are the standard soil extraction for metals and analysis by inductively coupled plasma. An evaluation of comparability was conducted by using linear regression analysis. Three factors were determined using the linear regression. These factors were the y-intercept, the slope of the line, and the coefficient of determination (r^2).

As part of the comparability assessment, the effects of soil type and preparation methods were studied. Three soil types (textures) and four preparation methods were examined during the study. The preparation methods evaluated the cumulative effect of particle size, moisture, and homogenization on comparability. Due to the large volume of data produced during this study, linear regression data for six analytes from only one FPXRF instrument is presented in Table 8. Similar trends in the data were seen for all instruments. These data are provided for guidance purposes only.

Table 8 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. These data are provided for guidance purposes only. The soil types are as follows: soil 1--sand; soil 2--loam; and soil 3--silty clay. The preparation methods are as follows: preparation 1--in situ in the field; preparation 2--intrusive, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not

ground; and preparation 4—intrusive, with sample dried, ground, passed through a 40-mesh sieve, and placed in sample cup.

For arsenic, copper, lead, and zinc, the comparability to the confirmatory laboratory was excellent with r^2 values ranging from 0.80 to 0.99 for all six FPXRF instruments. The slopes of the regression lines for arsenic, copper, lead, and zinc, were generally between 0.90 and 1.00 indicating the data would need to be corrected very little or not at all to match the confirmatory laboratory data. The r^2 values and slopes of the regression lines for barium and chromium were not as good as for the other for analytes, indicating the data would have to be corrected to match the confirmatory laboratory.

Table 8 demonstrates that there was little effect of soil type on the regression parameters for any of the six analytes. The only exceptions were for barium in soil 1 and copper in soil 3. In both of these cases, however, it is actually a concentration effect and not a soil effect causing the poorer comparability. All barium and copper concentrations in soil 1 and 3, respectively, were less than 350 mg/kg.

Table 8 shows there was a preparation effect on the regression parameters for all six analytes. With the exception of chromium, the regression parameters were primarily improved going from preparation 1 to preparation 2. In this step, the sample was removed from the soil surface, all large debris was removed, and the sample was thoroughly homogenized. The additional two preparation methods did little to improve the regression parameters. This data indicates that homogenization is the most critical factor when comparing the results. It is essential that the sample sent to the confirmatory laboratory match the FPXRF sample as closely as possible.

Sec. 11.0 of this method discusses the time necessary for each of the sample preparation techniques. Based on the data quality objectives for the project, an analyst must decide if it is worth the extra time necessary to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 min. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 min per sample. Lastly, when grinding and sieving is conducted, time has to be allotted to decontaminate the mortars, pestles, and sieves. Drying and grinding the samples and decontamination procedures will often dictate that an extra person be on site so that the analyst can keep up with the sample collection crew. The cost of requiring an extra person on site to prepare samples must be balanced with the gain in data quality and sample throughput.

13.8 The following documents may provide additional guidance and insight on this method and technique:

13.8.1 A. D. Hewitt, "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_{α} Peak Normalization Analysis," American Environmental Laboratory, pp 24-32, 1994.

13.8.2 S. Piorek and J. R. Pasmore, "Standardless, In Situ Analysis of Metallic Contaminants in the Natural Environment With a PC-Based, High Resolution Portable X-Ray Analyzer," Third International Symposium on Field Screening Methods for Hazardous Waste and Toxic Chemicals, Las Vegas, Nevada, February 24-26, 1993, Vol 2, pp 1135-1151, 1993.

13.8.3 S. Shefsky, "Sample Handling Strategies for Accurate Lead-in-soil Measurements in the Field and Laboratory," *International Symposium of Field Screening Methods for Hazardous Waste and Toxic Chemicals*, Las Vegas, NV, January 29-31, 1997.

14.0 POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity and/or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult *Less is Better: Laboratory Chemical Management for Waste Reduction* available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th St., N.W. Washington, D.C. 20036, <http://www.acs.org>.

15.0 WASTE MANAGEMENT

The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management, consult *The Waste Management Manual for Laboratory Personnel* available from the American Chemical Society at the address listed in Sec. 14.2.

16.0 REFERENCES

1. Metorex, X-MET 920 User's Manual.
2. Spectrace Instruments, "Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction," 1994.
3. TN Spectrace, Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.
4. Unpublished SITE data, received from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The following pages contain the tables referenced by this method. A flow diagram of the procedure follows the tables.

TABLE 1

EXAMPLE INTERFERENCE FREE LOWER LIMITS OF DETECTION

Analyte	Chemical Abstract Series Number	Lower Limit of Detection in Quartz Sand (milligrams per kilogram)
Antimony (Sb)	7440-36-0	40
Arsenic (As)	7440-38-0	40
Barium (Ba)	7440-39-3	20
Cadmium (Cd)	7440-43-9	100
Calcium (Ca)	7440-70-2	70
Chromium (Cr)	7440-47-3	150
Cobalt (Co)	7440-48-4	60
Copper (Cu)	7440-50-8	50
Iron (Fe)	7439-89-6	60
Lead (Pb)	7439-92-1	20
Manganese (Mn)	7439-96-5	70
Mercury (Hg)	7439-97-6	30
Molybdenum (Mo)	7439-93-7	10
Nickel (Ni)	7440-02-0	50
Potassium (K)	7440-09-7	200
Rubidium (Rb)	7440-17-7	10
Selenium (Se)	7782-49-2	40
Silver (Ag)	7440-22-4	70
Strontium (Sr)	7440-24-6	10
Thallium (Tl)	7440-28-0	20
Thorium (Th)	7440-29-1	10
Tin (Sn)	7440-31-5	60
Titanium (Ti)	7440-32-6	50
Vanadium (V)	7440-62-2	50
Zinc (Zn)	7440-66-6	50
Zirconium (Zr)	7440-67-7	10

Source: Refs. 1, 2, and 3

These data are provided for guidance purposes only.

TABLE 2

SUMMARY OF RADIOISOTOPE SOURCE CHARACTERISTICS

Source	Activity (mCi)	Half-Life (Years)	Excitation Energy (keV)	Elemental Analysis Range	
Fe-55	20-50	2.7	5.9	Sulfur to Chromium Molybdenum to Barium	K Lines L Lines
Cd-109	5-30	1.3	22.1 and 87.9	Calcium to Rhodium Tantalum to Lead Barium to Uranium	K Lines K Lines L Lines
Am-241	5-30	432	26.4 and 59.6	Copper to Thulium Tungsten to Uranium	K Lines L Lines
Cm-244	60-100	17.8	14.2	Titanium to Selenium Lanthanum to Lead	K Lines L Lines

Source: Refs. 1, 2, and 3

TABLE 3

SUMMARY OF X-RAY TUBE SOURCE CHARACTERISTICS

Anode Material	Recommended Voltage Range (kV)	K-alpha Emission (keV)	Elemental Analysis Range	
Cu	18-22	8.04	Potassium to Cobalt Silver to Gadolinium	K Lines L Lines
Mo	40-50	17.4	Cobalt to Yttrium Europium to Radon	K Lines L Lines
Ag	50-65	22.1	Zinc to Technicium Ytterbium to Neptunium	K Lines L Lines

Source: Ref. 4

Notes: The sample elements excited are chosen by taking as the lower limit the same ratio of excitation line energy to element absorption edge as in Table 2 (approximately 0.45) and the requirement that the excitation line energy be above the element absorption edge as the upper limit (L2 edges used for L lines). K-beta excitation lines were ignored.

TABLE 4

EXAMPLE PRECISION VALUES

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the Lower Limit of Detection					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	6.54	NR	NR	NR	NR	NR
Arsenic	5.33	4.11	3.23	1.91	12.47	6.68
Barium	4.02	NR	3.31	5.91	NR	NR
Cadmium	29.84 ^a	NR	24.80 ^a	NR	NR	NR
Calcium	2.16	NR	NR	NR	NR	NR
Chromium	22.25	25.78	22.72	3.91	30.25	NR
Cobalt	33.90	NR	NR	NR	NR	NR
Copper	7.03	9.11	8.49	9.12	12.77	14.86
Iron	1.78	1.67	1.55	NR	2.30	NR
Lead	6.45	5.93	5.05	7.56	6.97	12.16
Manganese	27.04	24.75	NR	NR	NR	NR
Molybdenum	6.95	NR	NR	NR	12.60	NR
Nickel	30.85 ^a	NR	24.92 ^a	20.92 ^a	NA	NR
Potassium	3.90	NR	NR	NR	NR	NR
Rubidium	13.06	NR	NR	NR	32.69 ^a	NR
Strontium	4.28	NR	NR	NR	8.86	NR
Tin	24.32 ^a	NR	NR	NR	NR	NR
Titanium	4.87	NR	NR	NR	NR	NR
Zinc	7.27	7.48	4.26	2.28	10.95	0.83
Zirconium	3.58	NR	NR	NR	6.49	NR

These data are provided for guidance purposes only.

Source: Ref. 4

^a These values are biased high because the concentration of these analytes in the soil samples was near the lower limit of detection for that particular FPXRF instrument.

NR Not reported.

NA Not applicable; analyte was reported but was below the established lower limit detection.

TABLE 5

EXAMPLES OF PRECISION AS AFFECTED BY SAMPLE PREPARATION

Analyte	Average Relative Standard Deviation for Each Preparation Method		
	In Situ-Field	Intrusive-Undried and Unground	Intrusive-Dried and Ground
Antimony	30.1	15.0	14.4
Arsenic	22.5	5.36	3.76
Barium	17.3	3.38	2.90
Cadmium ^a	41.2	30.8	28.3
Calcium	17.5	1.68	1.24
Chromium	17.6	28.5	21.9
Cobalt	28.4	31.1	28.4
Copper	26.4	10.2	7.90
Iron	10.3	1.67	1.57
Lead	25.1	8.55	6.03
Manganese	40.5	12.3	13.0
Mercury	ND	ND	ND
Molybdenum	21.6	20.1	19.2
Nickel ^a	29.8	20.4	18.2
Potassium	18.6	3.04	2.57
Rubidium	29.8	16.2	18.9
Selenium	ND	20.2	19.5
Silver ^a	31.9	31.0	29.2
Strontium	15.2	3.38	3.98
Thallium	39.0	16.0	19.5
Thorium	NR	NR	NR
Tin	ND	14.1	15.3
Titanium	13.3	4.15	3.74
Vanadium	NR	NR	NR
Zinc	26.6	13.3	11.1
Zirconium	20.2	5.63	5.18

These data are provided for guidance purposes only.

Source: Ref. 4

^a These values may be biased high because the concentration of these analytes in the soil samples was near the lower limit of detection.

ND Not detected.

NR Not reported.

TABLE 6
EXAMPLE ACCURACY VALUES

Analyte	Instrument															
	TN 9000				TN Lead Analyzer				X-MET 920 (SiLi Detector)				XL Spectrum Analyzer			
	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD	n	Range of % Rec.	Mean % Rec.	SD
Sb	2	100-149	124.3	NA	--	--	--	--	--	--	--	--	--	--	--	--
As	5	68-115	92.8	17.3	5	44-105	83.4	23.2	4	9.7-91	47.7	39.7	5	38-535	189.8	206
Ba	9	98-198	135.3	36.9	--	--	--	--	9	18-848	168.2	262	--	--	--	--
Cd	2	99-129	114.3	NA	--	--	--	--	6	81-202	110.5	45.7	--	--	--	--
Cr	2	99-178	138.4	NA	--	--	--	--	7	22-273	143.1	93.8	3	98-625	279.2	300
Cu	8	61-140	95.0	28.8	6	38-107	79.1	27.0	11	10-210	111.8	72.1	8	95-480	203.0	147
Fe	6	78-155	103.7	26.1	6	89-159	102.3	28.6	6	48-94	80.4	16.2	6	26-187	108.6	52.9
Pb	11	66-138	98.9	19.2	11	68-131	97.4	18.4	12	23-94	72.7	20.9	13	80-234	107.3	39.9
Mn	4	81-104	93.1	9.70	3	92-152	113.1	33.8	--	--	--	--	--	--	--	--
Ni	3	99-122	109.8	12.0	--	--	--	--	--	--	--	--	3	57-123	87.5	33.5
Sr	8	110-178	132.6	23.8	--	--	--	--	--	--	--	--	7	86-209	125.1	39.5
Zn	11	41-130	94.3	24.0	10	81-133	100.0	19.7	12	46-181	106.6	34.7	11	31-199	94.6	42.5

Source: Ref. 4. These data are provided for guidance purposes only.

n: Number of samples that contained a certified value for the analyte and produced a detectable concentration from the FPXRF instrument.

SD: Standard deviation; NA: Not applicable; only two data points, therefore, a SD was not calculated.

%Rec.: Percent recovery.

-- No data.

TABLE 7

EXAMPLE ACCURACY FOR TN 9000^a

Standard Reference Material	Arsenic			Barium			Copper			Lead			Zinc		
	Cert. Conc.	Meas. Conc.	%Rec.												
RTC CRM-021	24.8	ND	NA	586	1135	193.5	4792	2908	60.7	144742	149947	103.6	546	224	40.9
RTC CRM-020	397	429	92.5	22.3	ND	NA	753	583	77.4	5195	3444	66.3	3022	3916	129.6
BCR CRM 143R	--	--	--	--	--	--	131	105	80.5	180	206	114.8	1055	1043	99.0
BCR CRM 141	--	--	--	--	--	--	32.6	ND	NA	29.4	ND	NA	81.3	ND	NA
USGS GXR-2	25.0	ND	NA	2240	2946	131.5	76.0	106	140.2	690	742	107.6	530	596	112.4
USGS GXR-6	330	294	88.9	1300	2581	198.5	66.0	ND	NA	101	80.9	80.1	118	ND	NA
NIST 2711	105	104	99.3	726	801	110.3	114	ND	NA	1162	1172	100.9	350	333	94.9
NIST 2710	626	722	115.4	707	782	110.6	2950	2834	96.1	5532	5420	98.0	6952	6476	93.2
NIST 2709	17.7	ND	NA	968	950	98.1	34.6	ND	NA	18.9	ND	NA	106	98.5	93.0
NIST 2704	23.4	ND	NA	414	443	107.0	98.6	105	106.2	161	167	103.5	438	427	97.4
CNRC PACS-1	211	143	67.7	--	772	NA	452	302	66.9	404	332	82.3	824	611	74.2
SARM-51	--	--	--	335	466	139.1	268	373	139.2	5200	7199	138.4	2200	2676	121.6
SARM-52	--	--	--	410	527	128.5	219	193	88.1	1200	1107	92.2	264	215	81.4

Source: Ref. 4. These data are provided for guidance purposes only.

^a All concentrations in milligrams per kilogram.

%Rec.: Percent recovery; ND: Not detected; NA: Not applicable.

-- No data.

TABLE 8

EXAMPLE REGRESSION PARAMETERS FOR COMPARABILITY¹

	Arsenic				Barium				Copper			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	824	0.94	1.62	0.94	1255	0.71	60.3	0.54	984	0.93	2.19	0.93
Soil 1	368	0.96	1.41	0.95	393	0.05	42.6	0.11	385	0.94	1.26	0.99
Soil 2	453	0.94	1.51	0.96	462	0.56	30.2	0.66	463	0.92	2.09	0.95
Soil 3	—	—	—	—	400	0.85	44.7	0.59	136	0.46	16.60	0.57
Prep 1	207	0.87	2.69	0.85	312	0.64	53.7	0.55	256	0.87	3.89	0.87
Prep 2	208	0.97	1.38	0.95	315	0.67	64.6	0.52	246	0.96	2.04	0.93
Prep 3	204	0.96	1.20	0.99	315	0.78	64.6	0.53	236	0.97	1.45	0.99
Prep 4	205	0.96	1.45	0.98	313	0.81	58.9	0.55	246	0.96	1.99	0.96
	Lead				Zinc				Chromium			
	n	r ²	Int.	Slope	n	r ²	Int.	Slope	n	r ²	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186	0.66	38.9	0.50
Prep 1	305	0.80	2.88	0.86	286	0.79	3.16	0.87	105	0.80	66.1	0.43
Prep 2	298	0.97	1.41	0.96	272	0.95	1.86	0.93	77	0.51	81.3	0.36
Prep 3	302	0.98	1.26	0.99	274	0.93	1.32	1.00	49	0.73	53.7	0.45
Prep 4	300	0.96	1.38	1.00	271	0.94	1.41	1.01	49	0.75	31.6	0.56

Source: Ref. 4. These data are provided for guidance purposes only.

¹ Log-transformed data

n: Number of data points; r²: Coefficient of determination; Int.: Y-intercept

— No applicable data

METHOD 6200

FIELD PORTABLE X-RAY FLUORESCENCE SPECTROMETRY FOR THE DETERMINATION OF ELEMENTAL CONCENTRATIONS IN SOIL AND SEDIMENT

