

Appendix C: U.S. EPA 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 HgI₂ 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.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	Cert. Conc.	Meas. Conc.	%Rec.	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.

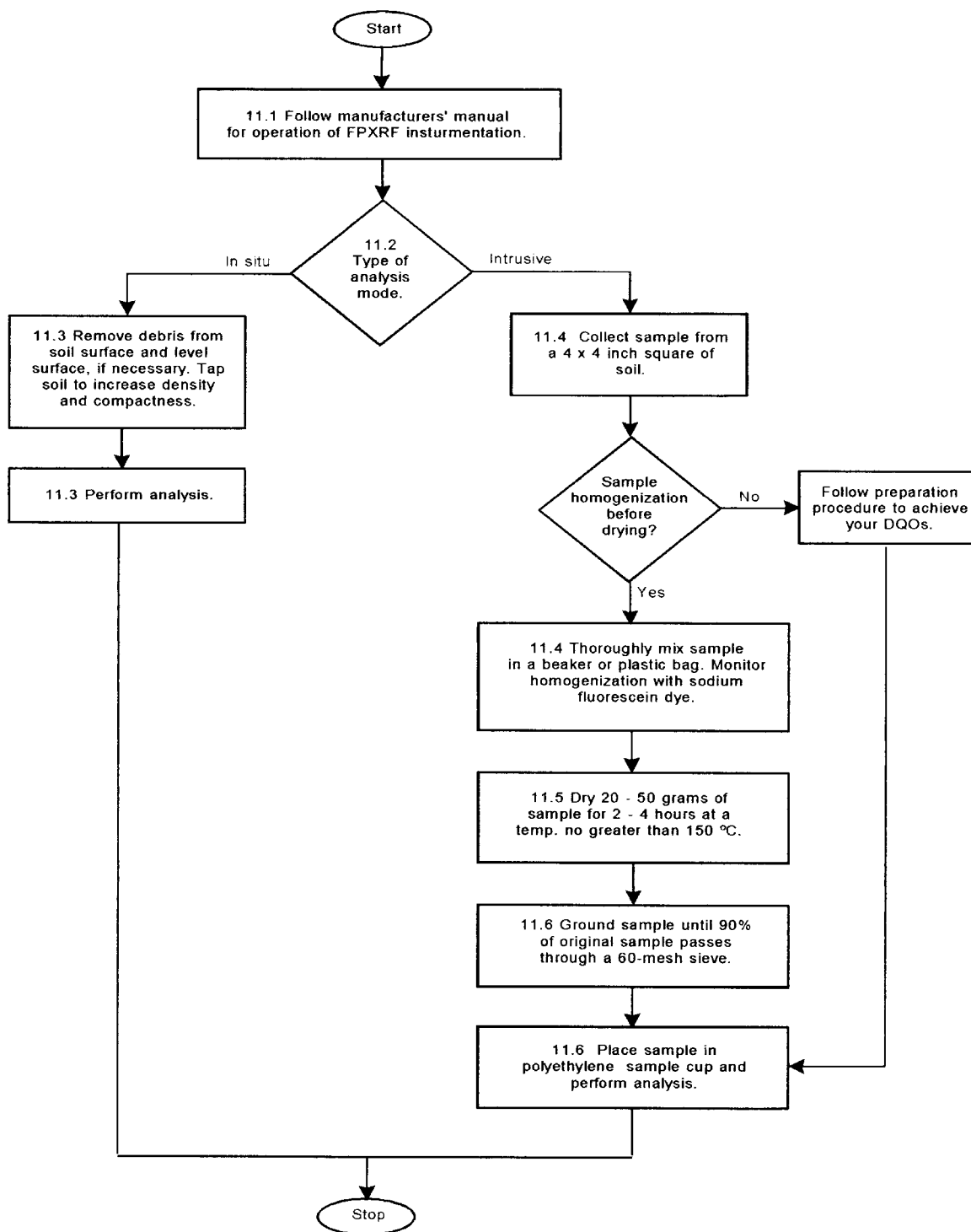
¹ Log-transformed data

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



Appendix D: Standard Operating Procedures

STANDARD OPERATING PROCEDURE

AQUATIC SEDIMENT SAMPLING

SOP NUMBER: ENV 3.8

REVISION DATE: 5/25/2012

SCHEDULED REVIEW DATE: 5/25/2017

Contents

1	Scope and Application.....	1
2	Definitions and Acronyms.....	1
3	Procedure Summary	1
4	Cautions	2
5	Equipment and Supplies	3
6	Procedures	4
6.1	Hand Sediment Sampling.....	4
6.2	Grab Sediment Sampling	5
6.3	Core Sediment Sampling	7
7	Quality Assurance/Quality Control.....	9
8	Health and Safety	10
9	Special Project Requirements.....	10

None of the information contained in this Ecology and Environment, Inc. (E & E) publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use in connection with any method, apparatus, or product covered by letters patent, nor as ensuring anyone against liability for infringement of letters patent.

Anyone wishing to use this E & E publication should first seek permission from the company. Every effort has been made by E & E to ensure the accuracy and reliability of the information contained in the document; however, the company makes no representations, warranty, or guarantee in connection with this E & E publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use; for any violation of any federal, state, or municipal regulation with which this E & E publication may conflict; or for the infringement of any patent resulting from the use of the E & E publication.

10 **References..... 10**

1 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures utilized by E & E samplers for collecting representative sediment samples from beneath aquatic environments. The purpose of sediment sampling may range from simple reconnaissance to complex sampling programs. This SOP can be followed for all routine sample collection activities which may include: visual or other observations, in situ or ex situ field measurements (monitoring), or sample collection for biological, chemical, geological, radiological or physical analysis. Site-specific sampling procedures vary depending on the data quality objectives (DQOs) identified in program/project planning documents.

E & E routinely utilizes three types of sediment collection procedures, grab sampling, hand sampling, and coring. Sediment coring can be done by hand or by a contracted driller or vibracore company. For the purposes of this SOP, sediments are those mineral and organic materials situated beneath an aqueous layer. The water may be static, as in lakes, ponds, and impoundments; or flowing, as in rivers and streams.

Procedures for collecting soil samples for volatile organic compound (VOC) analyses are presented in the E & E VOC Soil and Sediment Sampling SOP ENV 25.

Procedures for sample handling are defined in E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16. Site-specific sample handling procedures are dependent on the project DQOs.

Procedures for equipment decontamination are defined in E & E Sampling Equipment Decontamination SOP ENV 3.15. Site-specific equipment decontamination procedures are dependent on the project DQOs.

This aquatic sediment sampling SOP is intended for use by personnel who have knowledge, training and experience in the field sediment sampling activities being conducted.

2 Definitions and Acronyms

cm	centimeters
DQO	data quality objectives
E & E	Ecology and Environment, Inc.
SOP	Standard Operating Procedure

3 Procedure Summary

Hand sampling is generally utilized to collect shallow sediment samples from along freshwater and marine shorelines or wetlands. Grab sampling, as routinely performed by E & E personnel, is conducted by using small vessels/floating platforms or stationary structures (e.g., bridges) above water to collect samples. Corers may be used to collect surface and shallow subsurface sediment along freshwater or marine shorelines, wetlands, or from floating platforms or stationary structures.

Hand sampling is utilized for aquatic surface sediment collection from wetlands; shallow lakes/ponds, shallow, low velocity streams/rivers; and marine intertidal zones. Pre-cleaned spoons, trowels, or other types of scoops are used to collect shallow (usually less than 10

centimeters [cm] deep) sediment samples. Sediment is collected manually from hand dug excavations. The depth interval of sediment collection is identified in the project planning documents.

A modified Van Veen, Ponar, Ekman or equivalent dredge is used for grab aquatic sediment sampling. Pre-cleaned dredges are used to mechanically collect the grab shallow surface sediment samples. Aliquots of sediment are collected by hand from within the body of the dredge. The depth interval of sediment collection is defined based on the type of dredge selected and is usually about 15 cm. The depth of penetration will depend on the type of sediment. The selection of the appropriate dredge should be identified in the project planning documents. In deeper waters, dredges can be used can be deployed from a boat or floating platform using a wench. This work is typically contracted.

Pre-cleaned hand corers or augers are used for shore-based core sample collection. The core tube/auger is advanced into the sediment to the pre-determined depth identified in the project planning documents. For small vessels/floating platforms or above water stationary structures a pre-cleaned gravity corer is used. As with the hand corers/augers, the depth of sediment penetration into the sediment, together with sample handling procedures, is identified in the project planning documents. In some cases, corers may include a liner on the interior of the core tube. Sediment cores may be sectioned to provide vertical profiles of sediment characteristics.

Volatile organic and sulfide samples are collected immediately after sample retrieval, regardless of the sampling procedure used. If multiple samples are required to provide the sample volume identified in the project planning documents, then samples must be thoroughly homogenized prior to collection of aliquots for testing.

4 Cautions

This SOP is applicable to routine E & E aquatic sediment sampling and is limited to relatively shallow sediment sampling depths. Hand sampling is generally limited to the upper 10 cm of sediment. Grab sampling may extend to about 15 cm below the sediment surface. Corers used in this SOP are generally effective only to a maximum depth of 100 cm below the sediment surface. The depth of sample collection will be limited if bottom sediment is sandy, clayey or rocky.

Sampling for some projects, such as dredging activities, usually requires deeper sediment sample collection and more sophisticated equipment (e.g., box corers or vibracorers). These are not activities typically contracted to a driller or vibracore operator and sample collection procedures using such equipment should be described in project planning documents. Sample sectioning and sub-sampling procedures described for hand core samples also are applicable to cores collected by a contractor.

Van Veen and Ponar grab samplers are designed for use in soft sediments. Other types of sampling devices may be required for use in clayey, sandy or rocky environments. Corers may work better than grabs in clayey or sandy substrates. Bottom dredges (not routinely used by E & E) may be required for sampling rocky substrates.

Because the sampling devices specified within this SOP provide limited sample volumes, multiple samples may be required to meet project DQOs. Sample compositing and homogenization should be addressed in the project planning documents. Sample aliquots for volatile organics, sulfide, or similar analytes should be collected as soon as possible after collection and prior to homogenization. Field personnel must maintain an awareness of the sediment sample volume collected versus the volume required to meet program/project DQOs.

Maintaining sample integrity requires selecting a sediment sampler that meets the project DQOs. Carefully following procedures should minimize the disruption of the sediment structure and subsequent changes in physiochemical and biological characteristics.

In flowing water, sediment samples should be collected moving from downstream to upstream. At sites with known or suspected contamination, samples should be collected moving from least contaminated area to most contaminated area.

Re-use of equipment may be unavoidable given size and cost. Decontamination should be matched to DQOs.

Experience has shown that real-world conditions (e.g., variable bottom conditions such as the presence of rocks or wood waste) may lead to unacceptable sediment sample recoveries and multiple attempts to collect sediment samples will be required at some locations.

Standard measures, such as the use of disposable gloves, that meet project DQOs, should be used to avoid cross contamination of samples.

As with all intrusive sampling work, project planning should address the potential for encountering subsurface “utilities” and the measures to be taken to avoid problems in the field.

5 Equipment and Supplies

The equipment and supplies required for field work depend on the program/project DQOs. The following is a general list of equipment and supplies. A detailed list of equipment and supplies should be prepared based on the project planning documents. In general, the use of dedicated or disposal equipment is preferred but equipment may be re-used after thorough decontamination between sample locations (refer to E & E Sampling Equipment Decontamination SOP ENV 3.15).

- Stainless-steel or Teflon™ spoons, trowels, or scoops. Other construction material may be acceptable depending upon the program/project planning documents and DQOs;
- Stainless-steel mixing bowls. Other bowl construction material may be acceptable depending upon the program/project planning documents and DQOs;
- Ekman grab(s);
- Modified Van Veen or Ponar grab sampler(s);
- Hand-driven auger(s), split core sampler(s), and multistage core sampler(s);
- Liners and/or catchers for augers or core samplers as specified in the project planning documents;
- Gravity corer(s) with weights, cutting edges, core catchers, end caps;
- Pipe cutter(s), stainless steel knives(s);
- Winch with hydrowire (power supply, e.g., generator if necessary). A hand operated winch may be used;
- Nylon line;
- Siphon (short length of Teflon or inert tubing);
- Core extruder;
- Connectors (e.g., Brummell hooks or shackles); and

- Ancillary equipment and supplies (e.g., meter stick or tape measure, aluminum foil, plastic sheeting, disposable gloves).

Supporting equipment and supplies also may be required to address the following:

- Field logbooks and supplies (Refer to project planning documents and the E & E Field Activity Logbooks SOP DOC 2.1 for details)
- Decontamination equipment and supplies (Refer to project planning documents and E & E Sampling Equipment Decontamination SOP ENV 3.15 for details)
- Sample containers, preservatives, and shipping equipment and supplies (Refer to project planning documents and the E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16 for details)
- Waste handling supplies (Refer to project planning documents and E & E Handling Investigation-Derived Wastes SOP ENV 3.26 for details)

6 Procedures

E & E staff will use the following procedures for completing sediment sampling:

- Review relevant project planning documents, e.g., work plan, sampling and analysis plan, quality assurance project plan, health and safety plan, etc.
- Select the sampling procedure(s) that meet project DQOs.
- Refer to the E & E Field Activity Logbooks SOP DOC 2.1 for guidance on the types of information that should be recorded for each sample.
- Refer to the E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16 for guidance on how samples should be labeled, packaged, and shipped.

6.1 Hand Sediment Sampling

The following procedures are used for collecting sediment samples using hand tools. Wetlands, lakes/ponds, low-flow streams, and (with a tide that meets project DQOs) marine intertidal sediment samples may be collected by hand.

- Excavate shallow sediment with pre-cleaned spoons, trowels, or scoops.
- Minimize sediment disturbance.
- Identify sample collection intervals in the project planning documents. In general, the maximum depth of sample collection is 10 cm or less, although deeper sampling may be possible if the matrix is sufficiently stable for an excavation to remain open.
- Sampling device components that come into contact with the sediment samples should be constructed of stainless steel or Teflon™. Other materials may be appropriate if they meet project DQOs.
- Collect sufficient sample volume to meet the DQOs identified in the project planning documents
- Place aliquots to be analyzed for volatile organic analytes and/or sulfides directly into sample containers (i.e., prior to homogenation).
- Empty hand-collected samples into a pre-cleaned stainless steel bowl (or other type as specified in the project planning documents)

- If multiple hand collected samples are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization
- Homogenize the sample(s) as thoroughly as possible
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused sediment to the excavation when sampling is complete.

6.2 Grab Sediment Sampling

The following procedures are used for collecting sediment samples using a stainless steel Ekman dredge. Other Ekman construction materials may be appropriate if they meet project DQOs.

- Clean the Ekman grab prior to use.
- Open and lock the grab jaws
- Slowly lower the grab into the sediment
- Using whatever trip mechanism is associated with the grab, close the jaws.
- Retrieve the grab
- Empty the grab into a stainless steel bowl (or other type as specified in the project planning documents)
- Immediately collect volatile organic analyte and sulfide samples.
- If multiple Ekman grabs are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization
- Homogenize the sample as thoroughly as possible
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused sediment to the water when sampling is complete if allowed in the project planning documents.

The following procedures are used for collecting sediment samples using a grab sampling device such as a Ponar grab sampler.

- Grab sampling may be conducted from small vessels/floating platforms or stationary structures (e.g., bridges) above water. Refer to project planning documents for guidance related to sampling from small vessels.
- A pre-cleaned, modified 0.1-m² stainless steel Van Veen grab sampler is the preferred grab sampler for routine sediment collection.
- Ponar grab samplers are similar in design and operation to Van Veen samplers and may also be used. The maximum depth of sediment penetration that can be expected is about 15 cm, less in clayey, sandy or rocky environments. Van Veen and Ponar grabs may not be the most appropriate sampling devices for such matrices.
- Open and lock the grab jaws
- Remove the safety pin only after the grab is clear of the sampling platform

- Slowly lower the grab using a power winch-hydrowire, or by hand line to avoid a pressure wave
- The speed of descent should be about 1-foot per second within 1 meter from the bottom
- Once the grab reaches the bottom, the sampler will be “tripped”.
- Raise the grab slowly to allow proper jaw closure.
- Retrieve the grab. Do not exceed a 4-foot per second ascent speed to avoid disturbing the sample.
- Secure the grab on the sampling platform
- Open the upper sample access door(s) and evaluate the sample for acceptability
- The following criteria must be met for the sample to be acceptable
 - Sampler jaws should be closed (no rocks, sticks, or other materials should be trapped in the jaws since this would allow for sample washout from the grab)
 - Sampler must not be overfilled (overfilling could result in sample loss)
 - Overlying water is present (indicating sample integrity)
 - Sediment surface appears relatively undisturbed
 - The sediment surface should be even and roughly parallel to the top of the grab
 - Desired sample depth was achieved (ideally at least 1 cm of sediment should remain at the bottom of the sampler after the upper layer(s) have been sampled)
- Siphon off overlying water (turbid water may be allowed to settle for a short period)
- Immediately collect volatile organic analyte and sulfide samples.
- Depending on the project DQOs, the entire sample may be transferred to a stainless-steel mixing bowl for homogenization and collection of sample aliquots.
- The sediment within grab also may be subsampled. Avoid taking sediment that has come in direct contact with the grab sampler.
- Pre-cleaned stainless steel or Teflon™ spoons, spatulas, or other scoops may be used to collect sediment from within the grab. Other scoop construction materials may be appropriate if they meet project DQOs.
- Place sediment into stainless steel mixing bowl (or other type as specified in the project planning documents)
- If multiple Van Veen grabs (or subsections from within multiple grabs) are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization
- Homogenize the sample as thoroughly as possible
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused sediment to the water when sampling is complete if allowed in the project planning documents.

6.3 Core Sediment Sampling

The following procedures are used for collecting sediment samples using a sediment hand core. The subsampling and sectioning procedure also is applicable to core samples collected by a contractor with vibracore. Specific procedures for collection of vibracore samples by a contractor should be included in the project planning documents.

Manual core sediment sampling may be conducted in wetlands, lakes/ponds, low-flow streams, and with a tide that meets project DQOs, the marine intertidal zone. Mechanical core sediment sampling also may be conducted from small vessels/floating platforms or stationary structures (e.g., bridges) above water. Refer to project planning documents for guidance related to sampling from small vessels. Core sampling is recommended if accurate resolution of sample depths is a DQO

There are a variety of manual sediment core sampling devices available for collecting virtually undisturbed sediment core samples. Augers, split core samplers, and multistage core samplers may be used with or without liners that are used to avoid contact between the sediment and the corer. While there are many types of mechanical coring devices, E & E routinely uses only gravity corers. Gravity corers may or may not include a liner.

The following procedures are used for collecting sediment samples using a coring device.

- Pre-clean the coring equipment. See E & E Sampling Equipment Decontamination SOP ENV 3.15 for decontamination procedures.
- Before deployment, visually inspect the sediment retainer (core catcher) to verify the seal should be sufficient to prevent loss of core sediment.
- If hand coring drive the pre-cleaned manual corer into the sediment and retrieve by hand. Hand coring will generally be limited to 2-inch diameter - 1 meter long samples.
- If using a winch from a sampling platform modify the procedure as follows:
 - Adjust the depth of penetration by adding or removing weights from the top of the corer.
 - Slowly lower the corer using a power winch to prevent the core tube from swinging. The corer should enter the bottom vertically.
 - The corer should be allowed to free-fall from 5 to 10 meters above the bottom
 - Once the corer has penetrated the sediment (based on visual changes in wire strain), the winch should be braked.
 - Use the winch to extract the corer (Considerable strain on the hydrowire can occur when a core tube is embedded in sediment. Use a steady continuous pull to lift the coring device). Do not exceed a 4-foot per second ascent speed to avoid disturbing the sample.
- Bring the corer out of the water and place onto the shore or sampling platform.
- Note if there is sample leakage at the cutter end.
- Sediment cores should be capped and stored upright if not sampled immediately. In general though cores should be split as soon as possible following collection.
- After allowing the surface sediment to settle, siphon off the surface water from the top of the core tube.

- Evaluate compaction (core length versus depth of penetration [based on sediment traces on the outside of the core tube]).
- The following criteria must be met for the sample to be acceptable.
 - Core catcher should be closed (no rocks, sticks, or other materials should be trapped in the catcher)
 - Core tube must not be overfilled (overfilling could result in sample loss)
 - Overlying water is present (indicating sample integrity)
 - Desired sample depth was achieved
- Sediment cores should be extruded or split as soon as possible following collection.
 - Decant water from the top of core barrel or drill a small opening above the sediment line to allow the surface water to drain.
 - Place core barrel or liner on clean surface
 - Carefully remove end caps or catchers
 - For transverse sectioning, beginning at the sediment surface, measure and mark the sample sections on the outside of the liner
 - Cut the liner with a manual pipe cutter or core liner and core with a decontaminated saw blade into marked sections.
 - Extrude the sediment from the cut segments of the liner. If necessary use a plunger cover with aluminum foil to aid in extruding the core.
 - For some geotechnical sampling the sediment may need to remain in the core liner and be cap and sealed.
 - Empty the core segment into a stainless steel bowl (or other type as specified in the project planning documents).
 - Record observations of the sediment types.
 - Immediately collect volatile organic analyte and sulfide samples.
 - For longitudinal sectioning, open the split tube or use a knife to cut the liner and expose the upper half of the sediment cylinder.
 - Beginning at the sediment surface, measure and mark the sample sections using a tape measure set aside the core.
 - Record observations of the sediment types.
 - Immediately collect volatile organic analyte and sulfide samples.
 - Scope the core segment into a stainless steel bowl (or other type as specified in the project planning documents).
- If multiple core segments are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization.
- Homogenize the sample as thoroughly as possible.
- Decant any excess water. Sediment samples should have greater than 30% solids and greater than 50% is preferred.

- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused sediment to the water when sampling is complete if allowed in the project planning documents.

In very shallow water and soft sediment, the coring procedure can be modified to use only the core liner as follows. This procedure is only recommended for composite samples of the entire sediment depth.

- Drive the core liner into an undisturbed sediment area by hand.
- Once the liner is driven into the sediment, surface water is added to the top of the liner to create suction.
- Pull the core liner out of the sediment and place in the stainless steel bowl.
- Measure the sediment length and gently decant the water from the top of liner while holding the liner over the bowl.
- Once the suction is released the sediment should extrude into the bowl.
- Homogenize and sample as described above.

7 Quality Assurance/Quality Control

Prior to initiating field work, the project planning documents should be reviewed by field personnel to identify sampling procedure(s) that will most likely provide sediment samples that meet project DQOs.

The program/project manager should identify personnel for the field team who have knowledge, training and experience in the field sediment sampling activities being conducted. One member of the field team should be designated as the lead for sediment sampling and will be responsible, with support from other field personnel, for implementing the procedures in this SOP. The program/project manager should also identify additional personnel, if necessary, to complete ancillary procedures (e.g., field logbook documentation, equipment decontamination, sample shipment, and waste disposal).

The sediment sampling lead should prepare a detailed equipment checklist before entering the field and verify that sufficient and appropriate equipment and supplies are taken into the field.

Guidelines for accepting a sediment grab or core are noted within the sampling procedures. Unacceptable samples should be discarded.

Volatile organic analyte and sulfide samples should always be collected prior to homogenization.

Quality assurance/quality control samples (e.g., co-located samples) are collected according to the site quality assurance project plan. Field duplicates are collected from one location and treated as separate samples. Field duplicates are typically collected after the samples have been homogenized. Collocated samples are generally collected from nearby locations and are collected as completely separate samples.

In cases where multiple hand-collected samples; grabs; or cores are required to generate an adequate sample volume, homogenization is important. Field personnel should collect sample aliquots only after mixing has produced sediment with textural and color homogeneity.

In flowing water, sediment samples should be collected moving from downstream to upstream. At sites with known or suspected contamination, samples should be collected moving from least contaminated area to most contaminated area.

8 Health and Safety

Prior to entering the field, all field personnel should formally acknowledge that they have read and understand the project specific health and safety plan.

Hazards associated with wetlands work should be clear (e.g., engulfment and snakes) and proper precautions noted.

Ekman, Van Veen, and Ponar sampling apparatus are inherently dangerous pieces of heavy equipment which a high “pinch” potential. Care should be taken at all times when handling such equipment, not just during sample collection.

Grab samplers and coring devices are difficult to handle on small vessel decks and floating platforms. Care should be taken whenever handling heavy equipment. Be sure sampling devices are well-secured when not in active use.

Hazardous preservatives (e.g., acids, solvents, and formalin) should be properly handled and stored.

Work aboard small vessels and floating platforms should conform to good safe boating practices, coast guard (or other competent authority) guidance/regulations, and the boat operators standard operating procedures.

9 Special Project Requirements

Project or program-specific requirements that modify this procedure should be entered in this section and included with the project planning documents.

10 References

The following list sources of technical information on sediment sampling.

American Society for Testing and Materials, 1993, ASTM Standards on Aquatic Toxicology and Hazard Evaluation, Philadelphia, PA, ASTM Publication Code Number (PCN): 03-547093-16.

British Columbia Field Sampling Manual for Continuous Monitoring and the Collection of Air, Air-Emission, Water, Wastewater, Soil, Sediment, and Biological Samples, 2003 Edition, Prepared and published by: Water, Air and Climate Change Branch Ministry of Water, Land and Air Protection Province of British Columbia, January 2003

Burton, G. Allen, 1992, Sediment Toxicity Assessment, Chelsea, MI.

Collection and Preparation of Bottom Sediment samples for Analysis of Radionuclides and Trace Elements, IAEA-TECDOC-1360, International Atomic Energy Agency, July 2003

Commonwealth of Virginia, Department of Environmental Quality, November 2010, Standard Operating Procedures Manual for the Department of Environmental Quality Water Monitoring and Assessment Program, Revision No. 18.

- Comprehensive Everglades Restoration Plan, 2009 Quality Assurance Systems Requirements (QASR) manual. http://www.evergladesplan.org/pm/program_docs/qasr.aspx
- Great Lakes National Program Office, 1985, Methods Manual for Bottom Sediment Sample Collection, United States Environmental Protection Agency, Chicago, Illinois, EPA-905/5-85-004.
- Handbook for Sediment Quality Assessment, Commonwealth Scientific and Industrial Research Organisation (CSIRO), 2005
- Manual for Collection, Storage and Manipulation of Sediments for Chemical and Toxicological Analyses: Technical Manual, U.S. EPA, Office of Water, EPA-823-B-01-002, October 2001
- Municipal Environmental Research Laboratory, 1980, Samplers and Sampling Procedures for Hazardous Waste Streams, United States Environmental Protection Agency, Cincinnati, Ohio EPA-600/280-018.
- National Coastal Condition Assessment Field Operations Manual, U.S. EPA, Office of Water, EPA-841-R-09-003, April 23, 2010
- Navy Environmental Compliance Sampling and Field Testing Procedures Manual, NAVSEA T0300-AZ-PRO-010
- Pacific Northwest Laboratories, 1987, Guidance for Sampling of and Analyzing for Organic Contaminants in Sediments, United States Environmental Protection Agency, Criteria and Standards Division, Richland, Washington.
- QA/QC Guidance for Sampling and Analysis of Sediments, Water, and Tissues for Dredged Material Evaluations Chemical Evaluations, U.S. EPA, Office of Water, EPA-823-B-95-001, April 1995
- Recommended Guidelines for Sampling Marine Sediment, Water Column, and Tissue in Puget Sound, prepared by Puget Sound Water Quality Action Team for U.S. EPA, Region 10, April 1997
- State of Ohio Environmental Protection Agency, November 2001, Sediment Sampling Guide and Methodologies
- Texas Commission on Environmental Quality, October 2008, Surface Quality Monitoring Procedures, Volume 1, RG-415
- United Nations Environment Programme, Mediterranean Action Plan, Manual on sediment Sampling and Analysis, UNEP(DEPI)/MED WG.321/Inf.4, 7 November 2007
- United States Department of Commerce, National Technical Information Service, 1985, Sediment Sampling Quality Assurance User's Guide, Nevada University, Las Vegas, NV.

END OF SOP

STANDARD OPERATING PROCEDURE

SURFACE WATER SAMPLING

SOP NUMBER: ENV 3.12

REVISION DATE: 6/1/2012

SCHEDULED REVIEW DATE: 6/1/2017

Contents

1	Scope and Application.....	1
2	Definitions and Acronyms.....	1
3	Procedure Summary	1
4	Cautions.....	2
5	Equipment and Supplies	2
6	Procedures	3
6.1	Sampling Considerations	3
6.2	Manual Sample Collection.....	4
6.2.1	Direct Method	4
6.2.2	Intermediate Sampler	4
6.3	Sample Collection at Depth.....	5
6.3.1	Kemmerer Bottle, Niskin Bottle, or Van Doren Sampler.....	5
6.3.2	Bacon Bomb.....	5
6.3.3	Pump and Tubing	6

None of the information contained in this Ecology and Environment, Inc. (E & E) publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use in connection with any method, apparatus, or product covered by letters patent, nor as ensuring anyone against liability for infringement of letters patent.

Anyone wishing to use this E & E publication should first seek permission from the company. Every effort has been made by E & E to ensure the accuracy and reliability of the information contained in the document; however, the company makes no representations, warranty, or guarantee in connection with this E & E publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use; for any violation of any federal, state, or municipal regulation with which this E & E publication may conflict; or for the infringement of any patent resulting from the use of the E & E publication.

6.4 Composite Sample Collection 6

6.5 Collection of Field Measured Water-Quality Parameters 6

7 Quality Assurance (QA) / Quality Control (QC) 7

8 Health and Safety 8

9 Special Project Requirements..... 8

10 References 8

1 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures utilized by E & E samplers for collecting representative aqueous samples from streams, rivers, lakes, ponds, lagoons, and surface impoundments both at the surface and at various depths in the water column. This SOP can be followed for all routine sample collection activities which may include: field measurements (monitoring) or sample collection for biological, chemical, radiological or physical analysis. Site-specific sampling procedures vary depending on the data quality objectives (DQOs) identified in program/project planning documents. The SOP may be adapted for collection of non-aqueous samples.

E & E routinely utilizes surface water collection procedures that vary depending on whether surface or near surface samples are needed or samples are collected at discrete depths. Surface water samples can be collected as manual or automated composite samples. Surface water sampling is can be done by hand from a small boat or shoreline in shallower locations or by a contracted survey company for deeper waters. Surface water samples may be static, as in lakes, ponds, and impoundments; or flowing, as in rivers and streams. Surface water samples also may be collected from pipes or outfalls.

Procedures for sample handling are defined in E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16. Site-specific sample handling procedures are dependent on the project DQOs.

Procedures for equipment decontamination are defined in E & E Sampling Equipment Decontamination SOP ENV 3.15. Site-specific equipment decontamination procedures are dependent on the project DQOs.

This surface water sampling SOP is intended for use by personnel who have knowledge, training and experience in the field sampling activities being conducted.

2 Definitions and Acronyms

E & E	Ecology and Environment, Inc.
GPS	Global Positioning System
PTFE	Polytetrafluoroethylene or Teflon™
PVC	Polyvinyl chloride
RSC	Regional safety coordinator
SOP	Standard Operating Procedure
VOCs	Volatile organic compounds

3 Procedure Summary

Sampling situations vary widely and therefore, no universal sampling procedure can be recommended. A sampling plan must be completed before any sampling operation is attempted. The sampling plan should include objectives of the study, the number and type of samples required to meet these objectives, and procedures to collect these samples based on site characteristics. A general discussion of sampling considerations is included in this SOP.

Grab sampling of both aqueous and nonaqueous liquids from the sources mentioned above can be accomplished near the surface using manual sample collection procedures or at depth using several types of samplers. Compositing of aqueous samples may be done over time or based on flow using automated or manual techniques. Compositing is over required to meet regulatory permit requirements. A general discussion of compositing methods is provided in this SOP, but specific procedures should be determined based on site-specific DQOs.

generally accomplished through the use of one of the following:

- Kemmerer bottle,
- Van Doren sampler,
- Bacon bomb,
- Dip sampler,
- Automated composite sampler,
- Direct method, or
- Field measured water-quality parameters

These sampling techniques will allow for the collection of representative samples from the majority of surface water types and impoundments encountered.

4 Cautions

In flowing water, surface water samples should be collected moving from downstream to upstream. Sampling equipment and personnel should always be downstream of the sample location. If using motorized water craft insure the sample location is upstream of the craft and the motor is downwind or away from the sample. If sediment sampling is being completed at the same location, always collect water samples first.

Because the sampling devices specified within this SOP provide limited sample volumes, multiple samples may be required to meet project DQOs. Sample compositing and homogenization should be addressed in the project planning documents. Sample aliquots for volatile organics, sulfide, or similar analytes should be collected as soon as possible after collection and prior to homogenization. Surface water samples are often chemically preserved depending on the sample test. Preservation should be done as soon as possible and should always be checked in the field prior to shipping to the laboratory. Composite sample programs need to account for chemical preservation requirements. Field personnel must maintain an awareness of the sample volume collected versus the volume required to meet program/project DQOs.

Standard measures, such as the use of disposable gloves, that meet project DQOs, should be used to avoid cross contamination of samples.

5 Equipment and Supplies

The equipment and supplies required for field work depend on the program/project DQOs. The following is a general list of equipment and supplies. A detailed list of equipment and supplies should be prepared based on the project planning documents. In general, the use of dedicated or disposal equipment is preferred but equipment may be re-used after thorough decontamination between sample locations (refer to E & E Sampling Equipment Decontamination SOP ENV 3.15).

- Sampling equipment needed for collecting surface water samples, as specified in the work plan, may include:
 - Kemmerer bottle,
 - Van Doren sampler,
 - Bacon bomb,
 - Dip sampler,
 - Automated composite sampler, and
 - Multi-analyte programmable data logger (for field measured water-quality parameters);
- Nylon rope or steel cable, for raising and lowering sampler line and messengers;
- Survey stakes, flags, or buoys and anchors; and
- Ancillary equipment and supplies (e.g., meter stick or tape measure, aluminum foil, plastic sheeting, disposable gloves).

Supporting equipment and supplies also may be required to address the following:

- Field logbooks and supplies (Refer to project planning documents and the E & E Field Activity Logbooks SOP DOC 2.1 for details)
- Decontamination equipment and supplies (Refer to project planning documents and E & E Sampling Equipment Decontamination SOP ENV 3.15 for details)
- Sample containers, preservatives, and shipping equipment and supplies (Refer to project planning documents and the E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16 for details)
- Waste handling supplies (Refer to project planning documents and E & E Handling Investigation-Derived Wastes SOP ENV 3.26 for details)

6 Procedures

6.1 Sampling Considerations

In order to collect a representative sample, the hydrology and morphology of a stream or impoundment should be determined prior to sampling. This will aid in determining the presence of phases or layers in lagoons or impoundments, flow patterns in streams, and appropriate sample locations and depths. Additional information can be found in the references.

Prior to the initiation of any sampling operation, the immediate area should be checked for radioactivity, VOCs, photoionization potential, airborne dust, and explosivity, as required by the Site Safety Plan. In addition, if co-collection of surface water and sediment samples is indicated per the work plan, the surface water samples should be collected before any sediment samples to avoid substrate cross-contamination.

Generally, the deciding factors in the selection of a sampling device for surface water sampling are:

- Depth and flow of surface water body,
- Location from where the sample will be collected, and
- Depth at which the sample(s) is to be collected.

The sampling device must be constructed of the appropriate materials. Samplers constructed of glass, stainless steel, polyvinyl chloride (PVC), or polytetrafluoroethylene (PTFE or Teflon™) should be used, depending on the types of analyses to be performed (e.g., samples to be analyzed for metals should not be collected in metallic containers).

Sampling of outfalls for regulatory programs such as State or National Pollutant Discharge Elimination System (SPDES or NPDES) permits should follow the specific requirements for that program. This SOP provides only general guidance on the outfall sampling.

Some water quality parameters require that samples be filtered prior to sample analysis. Filtering should be performed in the field prior to sample preservation using one 0.45-micrometer (μm) membrane filter per sample. Several water quality parameters also have very short holding times prior to sample analysis. Consideration for use of a local laboratory may be needed to meet these holding times.

6.2 Manual Sample Collection

6.2.1 Direct Method

For streams, rivers, lakes, and other surface waters, the direct method may be utilized to collect grab water samples with the first 12 inches from the surface. This method is not to be used for sampling lagoons or other impoundments where contact with contaminants is a concern.

Using adequate protective clothing (e.g., gloves and hip waders), access the sampling station by appropriate means (wading or boat). For shallow stream stations, collect the sample under the water surface, pointing the sample container upstream. The container must also be upstream of the collector. Avoid disturbing the substrate. For lakes and other impoundments, collect the sample under the water surface, avoiding surface debris and the boat wake.

Samples can be collected directly into the sample container or in a sample container connected to pole. It is best to use samples containers that are not pre-preserved if possible.

- For unpreserved containers, remove the lid and invert the sample jar and lower the container beneath the surface. If surface debris or film is present, the container lid can be removed once the underwater if possible. Tilt the container in the direction of water flow and allow the container to fill and then quickly return to the surface. Discard a small portion of sample to allow for expansion and add the correct preservative. Invert the container to mix. Check preservation by pouring a small portion of sample into the lid or another clean container. Secure the cap, label and immediately cool.
- For preserved containers, leave the container lid on until the container is submerged. Slowly open the container in an upright position and allow container to almost fill. Close the container and follow similar steps to check sample preservation.

6.2.2 Intermediate Sampler

A grab sample also can be collected using an intermediate container such as a clean sample container or bucket. All intermediate containers should be rinsed with surface water and the water discard downstream of the location. The intermediate container should be filled by following the direct sampling method. Once the intermediate container is filled, minimize agitation, and then carefully fill the sample containers.

A dip sampler is useful for situations in which a sample is to be recovered from an outfall pipe, such as through a storm sewer grating or along a lagoon bank where direct accessibility is

limited. The long handle on such a device allows access from a discrete location. The procedure is as follows:

- Assemble the device in accordance with the manufacturer's instructions,
- Extend the device to the sample location, rinse with site water and collect the sample, and
- Retrieve the sampler and fill the sample containers leaving a little headspace for all non-volatile samples.

Check sample container preservation as noted above.

6.3 Sample Collection at Depth

6.3.1 Kemmerer Bottle, Niskin Bottle, or Van Doren Sampler

A Kemmerer bottle or a Van Doren sampler may be used in most situations where site access is from a boat or structure such as a bridge or pier, and where samples at depth are required. Sampling procedures are as follows:

- Using a properly decontaminated Kemmerer bottle and rinse with site water. Set the sampling device so that the sampling end pieces are pulled away from the sampling tube, allowing the substance to pass through this tube;
- Measure the depth of water column to verify sample can be collected at the specified water depth. Mark the line incrementally to appropriate sample depth;
- Slowly lower the preset sampling device to the predetermined depth. Avoid bottom disturbance;
- When the Kemmerer bottle is at the required depth, send down the messenger, closing the sampling device;
- Retrieve the sampler slowly; and
- Transfer the sample to the sample container.

Kemmerer and Van Doren samplers constructed of plastic and rubber cannot be used for volatile and extractable organic sampling. Stainless steel, Teflon™ or Teflon™-coated Models for these sampling devices are available and acceptable for all analyte groups without restriction.

6.3.2 Bacon Bomb

A bacon bomb sampler has a check valve that is opened and closed with a separate trigger line. It is often used to sample tanks and non-aqueous samples. This type of sampler also may be used in situations similar to those outlined for the Kemmerer bottle. Sampling procedures are as follows:

- Mark the lead line the same as the other depth samplers;
- Lower the bacon bomb sampler carefully to the desired depth, allowing the line for the trigger to remain slack at all times. When the desired depth is reached, pull the trigger line until taut; and
- Release the trigger line and retrieve the sampler. Transfer the sample to the sample container by pulling on the trigger;

- Retrieve the sampler slowly; and
- Transfer the sample to the sample container.

6.3.3 Pump and Tubing

Samples can be collected at depth using pump and tubing appropriate to the analytical parameters and sample depth. A peristaltic pump with Teflon tubing would be used in most situations. Sampling procedures are as follows:

- Assemble the pump, tubing, and power source;
- Attach the tubing to pole or rod that is mark with the require sample depth;
- If the pump method is being used to collect grab samples, then tubing should be lowered at least 6 inches below the surface;
- Lower the rod or tubing carefully to the desired depth;
- Pump surface water through the tubing to thoroughly flush the system prior to collecting samples (use at least at 3 tubing volumes if possible);
- Set the pumping rate to allow the sample containers to fill without splashing or overfilling; and
- Fill the sample containers without touching the tubing to the container and leaving a little headspace for all non-volatile samples.

Check sample container preservation as noted above.

6.4 Composite Sample Collection

Compositing can be done to collect time weighted or flow proportion samples when required to be representative of the site conditions or to meet permit conditions. Samples can be collected manually or with automatic samplers. Use automatic samplers when a location is to be sampled at frequent intervals or when a continuous sample is required over a long time period. Composite samplers can be used to collect time composite or flow samples. Use appropriate equipment and tubing, depending on the analyte collection. Automated samplers are often used for outfall or discharge sample collection. Flow measurements are typically required for composite. The most common flow measurement devices are flumes or weirs in which flow is calculated based on depth through a known area using a specific geometric relationship.

Composite surface sampling is not considered a routine procedure because of the variety of sites requirements, equipment, and regulatory requirements. The procedures and rationale for composite sampling should be specified in the project planning documents. A variety of references are included in this SOP. Special consideration for the collection of volatile samples and water quality parameters with short holding times need to be part of the planning documents.

6.5 Collection of Field Measured Water-Quality Parameters

Field-measured water-quality parameters (such as temperature, dissolved oxygen, pH, specific conductance, or turbidity) may need to be measured as specified in the project planning documents. These parameters can be measured in the field, as a grab sample, using a multi-analyte programmable data logger (Hydrolab® or equivalent) or as a flow through cell using a YSI meter or equivalent. There are a variety of water-quality data loggers/meters are available

that measure the water-quality parameters identified above. Field personnel should be familiar with the instrument and its user's manual. Steps to consider for the use of these instruments are:

- a. Calibrate the Hydrolab® or equivalent instrument used to measure water-quality parameters in accordance with the instruments' manufacturer recommendations by following the calibration procedures specified in the instruction manual.
- b. Collect field-measured water quality parameters from the same location and depth as the sample location for laboratory analysis.
- c. Collect field measurements in-situ by deploying the data logger to the desired sample location.
- d. Allow a one- to two-minute equilibration period following deployment of the data logger.
- e. Record the measurements in the field logbook.

7 Quality Assurance (QA) / Quality Control (QC)

Prior to initiating field work, the project planning documents should be reviewed by field personnel to identify sampling procedure(s) that will most likely provide surface water samples that meet project DQOs.

The program/project manager should identify personnel for the field team who have knowledge, training and experience in the surface water sampling activities being conducted. One member of the field team should be designated as the lead for surface water sampling and will be responsible, with support from other field personnel, for implementing the procedures in this SOP. The program/project manager should also identify additional personnel, if necessary, to complete ancillary procedures (e.g., field logbook documentation, equipment decontamination, sample shipment, and waste disposal).

The surface water sampling lead should prepare a detailed equipment checklist before entering the field and verify that sufficient and appropriate equipment and supplies are taken into the field.

Collecting representative samples for surface water is an important quality consideration. Many parameters such as flow, depth, biological impacts, and rainfall impacts need to be considered in establishing the sampling protocol. Surface water quality criteria are often very low values that are difficult to achieve with routine analytical procedures.

Volatile organic analyte samples should always be collected prior to homogenization.

Chemical preservation and field filtering are critical components of sample quality that need to be addressed in the project planning documents.

Quality assurance/quality control samples (e.g., co-located samples) are collected according to the site quality assurance project plan. Field duplicates are collected from one location and treated as separate samples. Field duplicates are typically collected after the samples have been homogenized. Field blanks should be processed at the site location to account for atmospheric site conditions.

In flowing water, sediment samples should be collected moving from downstream to upstream. At sites with known or suspected contamination, samples should be collected moving from least contaminated area to most contaminated area.

8 Health and Safety

Prior to entering the field, all field personnel should formally acknowledge that they have read and understand the project specific health and safety plan.

Hazards associated with wetlands work should be clear (e.g., engulfment and snakes) and proper precautions noted.

When sampling lagoons or surface impoundments contain known or suspected hazardous substances, adequate precautions must be taken to ensure the safety of sampling personnel. The sampling team member collecting the sample should not get too close to the edge of the impoundment, where bank failure may cause him/her to lose their balance. The person performing the sampling should be on a lifeline and wearing adequate protective equipment.

Hazardous preservatives (e.g., acids, solvents, and formalin) should be properly handled and stored.

Work aboard small vessels and floating platforms should conform to good safe boating practices, coast guard (or other competent authority) guidance/regulations, and the boat operators standard operating procedures.

9 Special Project Requirements

Project or program-specific requirements that modify this procedure should be entered in this section and included with the project planning documents.

10 References

Commonwealth of Virginia, Department of Environmental Quality, November 2010, Standard Operating Procedures Manual for the Department of Environmental Quality Water Monitoring and Assessment Program, Revision No. 18.

Comprehensive Everglades Restoration Plan, 2009 Quality Assurance Systems Requirements (QASR) manual. http://www.evergladesplan.org/pm/program_docs/qasr.aspx

U.S. Environmental Protection Agency, 1992, *NPDES Stormwater Sampling Guidance*, EPA 833-B-92-001, July 1992, Washington, DC.

U.S. Geological Survey, 1977, *National Handbook on Recommended Methods for Water Data Acquisition, Office of Water Data Coordination, Reston, Virginia.*

U.S. Geological Survey, variously dated, *National field manual for the collection of water-quality data*: U.S. Geological Survey Techniques of Water-Resources Investigations, book 9, chaps. A1-A9, available online at <http://pubs.water.usgs.gov/twri9A>

END OF SOP

STANDARD OPERATING PROCEDURE
SURFACE and SHALLOW SUBSURFACE SOIL SAMPLING
SOP NUMBER: ENV 3.13

REVISION DATE: 5/25/2012

SCHEDULED REVIEW DATE: 5/26/2017

Contents

1	Scope and Application.....	1
2	Definitions and Acronyms.....	1
3	Procedure Summary	1
4	Cautions.....	2
5	Equipment and Supplies	3
6	Procedures	4
6.1	Hand Scoop Surface and Subsurface Soil Sampling	4
6.2	Subsurface Soil Sampling with a Soil Core Samplers.....	4
6.3	Subsurface Soil Sampling with Bucket Augers	6
6.4	Subsurface Soil Sampling with Continuous Flight Augers	6
7	Quality Assurance/Quality Control.....	7
8	Health and Safety	8
9	Special Project Requirements.....	8
10	References	8

None of the information contained in this Ecology and Environment, Inc. (E & E) publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use in connection with any method, apparatus, or product covered by letters patent, nor as ensuring anyone against liability for infringement of letters patent.

Anyone wishing to use this E & E publication should first seek permission from the company. Every effort has been made by E & E to ensure the accuracy and reliability of the information contained in the document; however, the company makes no representations, warranty, or guarantee in connection with this E & E publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use; for any violation of any federal, state, or municipal regulation with which this E & E publication may conflict; or for the infringement of any patent resulting from the use of the E & E publication.

1 Scope and Application

This Standard Operating Procedure (SOP) describes the procedures utilized by E & E for collecting surface and shallow subsurface environmental soil samples. The purpose of soil sampling may range from simple reconnaissance to complex sampling programs. This SOP can be followed for all routine sample collection activities which may include: visual or other observations, in situ or ex situ field measurements (monitoring), or sample collection for biological, chemical, geological, radiological or physical analysis. Site-specific sampling procedures vary depending on the data quality objectives (DQOs) identified in program/project planning documents.

E & E routinely utilizes three types of surface and shallow subsurface environmental soil collection procedures, hand scoop, hand coring, and hand auger. Powered hand augers are sometimes used and the procedure is addressed in this SOP. The definition of the depth of a “surface” soil sample is dependent on the program/project specific DQOs; and may be driven by regulatory, risk-based or other considerations. Hand sampling is generally limited to no more than three feet (one meter) below ground surface. The site-specific depth interval of soil collection is identified in the project planning documents.

Procedures for collecting soil samples for volatile organic compound (VOC) analyses are presented in the E & E VOC Soil and Sediment Sampling SOP ENV 25.

Procedures for collecting “deeper” subsurface soil samples (using back hoes, drill rigs and direct push equipment) are presented in the E & E Borehole Installation Methods SOP GEO 4.7.

Procedures for sample handling are defined in E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16. Site-specific sample handling procedures are dependent on the project DQOs.

Procedures for equipment decontamination are defined in E & E Sampling Equipment Decontamination SOP ENV 3.15. Site-specific equipment decontamination procedures are dependent on the project DQOs.

This surface and shallow subsurface soil sampling SOP is intended for use by personnel who have knowledge, training and experience in the field soil sampling activities being conducted.

2 Definitions and Acronyms

cm	centimeter
DQO	Data Quality Objective
E & E	Ecology and Environment, Inc.
SHASP	Site Specific Health and Safety Plan
SOP	Standard Operating Procedure
VOC	Volatile Organic Compound

3 Procedure Summary

Pre-cleaned spoons, trowels, or other types of scoops are used to collect shallow (usually less than 6 inches [15 cm] deep) soil samples using a hand scoop procedure. Shallow subsurface

soil is collected manually using scoops from the sides of hand dug excavations. Pre-cleaned hand soil core samplers and/or bucket augers are used for collecting relatively undisturbed shallow (usually no deeper than 3 feet [1 meter]) subsurface soil samples. The corer barrel/bucket auger is advanced into the soil to the pre-determined depth identified in the project planning documents. In some cases, corers may include a liner on the interior of the core barrel. Soil cores may be sectioned to provide vertical profiles of soil characteristics.

Disturbed soil samples are collected directly from the auger when continuous flight (screw) augers are used

Unless otherwise specified, surface soil scoop aliquots are combined, homogenized and then placed in appropriate sample containers. Volatile organic and sulfide samples are collected immediately after sample retrieval, regardless of the sampling procedure used. VOC samples are not homogenized (see E & E VOC Soil and Sediment Sampling SOP ENV 25) If multiple samples are required to provide the sample volume identified in the project planning documents, then samples are thoroughly homogenized prior to collection of aliquots for testing.

4 Cautions

This SOP is applicable to routine E & E surface and shallow subsurface soil sampling and is limited to relatively shallow soil sampling depths. Hand augers and corers used in this SOP are generally effective only to a maximum depth of 3 feet (1 meter) below the soil surface. The depth of sample collection will be limited if soil is sandy, clayey or rocky. Grass, roots, or other natural or anthropogenic materials may not be considered part to the soil sample.

Because the sampling devices specified within this SOP provide limited sample volumes, multiple samples may be required to collect sufficient volume for sample analysis. Samples from multiple locations also may be collected and composited to provide a sample representative of a larger area. Sample compositing and homogenization should be addressed in the project planning documents. If a compositing scheme is employed and an area(s) is not visually consistent with other areas, then observations should be noted in the field log and a course of action determined based on the program/project DQOs. Samples for volatile organics, sulfide, or similar analyses are normally collected as discrete aliquots and should be containerized as soon as possible after collection and prior to compositing and homogenization. Field personnel must maintain an awareness of the soil sample volume collected versus the volume required to meet program/project DQOs.

Maintaining sample integrity requires selecting a soil sampling device and procedure that meets project DQOs. Carefully following procedures minimizes the disruption of the soil structure and subsequent changes in physiochemical and biological characteristics.

Continuous flight augers are satisfactory for use when a composite of the soil column is desired.

If a powered auger is used, if possible, position the power unit downwind of the sample location to avoid fumes from fuel used to power the unit.

At sites with known or suspected contamination, based on the data available, samples are collected moving from least to most contaminated soil.

Re-use of equipment may be unavoidable given size and cost. Decontamination matched to DQOs is specified in the project planning documents.

Experience has shown that real-world conditions (e.g., variable soil conditions such as the presence of rocks or trash) may lead to unacceptable soil sample recoveries and multiple attempts to collect soil samples will be required at some locations.

Abandon auger and/or core holes according to applicable regulations. Generally, shallow holes can simply be backfilled with the removed soil material.

Standard measures, such as the use of disposable gloves, that meet project DQOs, are used to avoid cross contamination of samples.

As with all intrusive sampling work, project planning should address the potential for encountering subsurface “utilities” and the measures to be taken to avoid problems in the field.

5 Equipment and Supplies

The equipment and supplies required for field work depend on the program/project DQOs. The following is a general list of equipment and supplies. A detailed list of equipment and supplies should be prepared based on the project planning documents. In general, the use of dedicated or disposal equipment is preferred but equipment may be re-used after thorough decontamination between sample locations (refer to E & E Sampling Equipment Decontamination SOP ENV 3.15).

- Stainless-steel or Teflon™ spoons, trowels, or scoops. Other construction material may be acceptable depending upon the program/project planning documents and DQOs
- Stainless-steel mixing bowls. Other bowl construction material may be acceptable depending upon the program/project planning documents and DQOs
- Hand-driven bucket/continuous flight auger(s), split core sampler(s), and single or multistage core sampler(s)
- Rubber mallet or T-bar to help drive hand augers
- Powered auger(s)
- Spade(s) and/or shovel(s)
- Liners and/or catchers for augers or core samplers as specified in the project planning documents
- Pipe cutter(s), stainless steel knives(s), or power saw to cut liners
- Survey stakes or flags to mark locations
- Ancillary equipment and supplies, e.g., meter stick or tape measure, aluminum foil, plastic sheeting, disposable gloves

Supporting equipment and supplies also may be required to address the following:

- Field logbooks and supplies (Refer to project planning documents and the E & E Field Activity Logbooks SOP DOC 2.1 for details)
- Decontamination equipment and supplies (Refer to project planning documents and E & E Sampling Equipment Decontamination SOP ENV 3.15 for details)
- Sample containers, preservatives, and shipping equipment and supplies (Refer to project planning documents and the E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16 for details)
- Waste handling supplies (Refer to project planning documents and E & E Handling Investigation-Derived Wastes SOP ENV 3.26 for details)

6 Procedures

E & E staff will use the following procedures for completing soil sampling:

- Review relevant project planning documents, e.g., work plan, sampling and analysis plan, quality assurance project plan, health and safety plan, etc.
- Select the sampling procedure(s) that meet project DQOs.
- Refer to the E & E Field Activity Logbooks SOP DOC 2.1 for guidance on the types of information that should be recorded for each sample.
- Refer to the E & E Environmental Sample Handling, Packaging and Shipping SOP ENV 3.16 for guidance on how samples should be labeled, packaged, and shipped.

6.1 Hand Scoop Surface and Subsurface Soil Sampling

- Surface and shallow subsurface soil samples may be collected by hand using scoops.
- Pre-cleaned spoons, trowels, or scoops are used to excavate shallow soil.
- Sample collection intervals are identified in the project planning documents.
- Clear the area to be sampled of surface debris (e.g., twigs, rocks, and litter).
- Carefully remove the top layer of soil to the desired sample depth with a pre-cleaned tool.
- When sampling from the sides or bottom of an excavation, use a pre-cleaned, scoop, spoon, or trowel to remove and discard the thin layer of soil from the area that came into contact with the shovel or spade.
- Collect sufficient sample volume to meet the DQOs identified in the project planning documents
- Place aliquots to be analyzed for volatile organic analytes and/or sulfides directly into sample containers (i.e., prior to homogenization). Procedures for collecting soil samples for VOC analyses are presented in the (see E & E VOC Soil and Sediment Sampling SOP ENV 25).
- Empty hand-collected samples into a pre-cleaned stainless steel bowl (or other type as specified in the project planning documents).
- If multiple hand collected samples are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization.
- Homogenize the sample(s) as thoroughly as possible.
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused soil to the excavation, level the area, replace grass turf as necessary.

6.2 Subsurface Soil Sampling with a Soil Core Samplers

This system consists of pre-cleaned corer barrels (with liners and liner caps, as appropriate), caps, core tips, and slide hammer. The dimensions of the core barrel define the volume and depth interval of possible sample collection. Core sampling is recommended if accurate resolution of sample depths is a DQO. Hand coring will generally be limited to 2-inch diameter – 3 foot (1 meter) long samples.

There are a variety of manual soil core sampling devices available for collecting undisturbed soil core samples. Split core, single core, and multistage core samplers may be used with or without liners that are used to avoid contact between the soil and the corer.

The following procedures are used for collecting soil samples with the soil core sampler:

- Assemble the soil core sampler based on manufacturer instructions and project DQOs (e.g., using a liner and/or catcher).
- Clear the area to be sampled of surface debris (e.g., twigs, rocks, and litter).
- Using the slide hammer or sledge hammer or pounding sleeve, begin driving the pre-cleaned corer into the soil until the desired upper sampling depth is reached.
- Carefully retrieve the corer from the boring.
- Decontamination or replace the core barrel with a pre-cleaned core barrel and resume coring. See E & E Sampling Equipment Decontamination SOP ENV 3.15 for decontamination procedures.
- Soil cores should be extruded or split as soon as possible following collection.
 - Place core barrel or liner on clean surface
 - Carefully remove end caps and/or catchers
 - Evaluate compaction (core length versus depth of penetration)
 - For transverse sectioning, beginning at the soil surface, measure and mark the sample sections on the outside of the liner
 - Cut the liner with a manual pipe cutter or core liner and core with a decontaminated saw blade into marked sections.
 - Extrude the soil from the cut segments of the liner. If necessary use a plunger cover with aluminum foil to aid in extruding the core.
 - Empty the core segment into a stainless steel bowl (or other type as specified in the project planning documents).
 - Record observations of the soil types.
 - Immediately collect volatile organic analyte and sulfide samples.
 - For longitudinal sectioning, open the split tube or use a knife to cut the liner and expose the upper half of the soil cylinder.
 - Beginning at the soil surface, measure and mark the sample sections using a tape measure set aside the core.
 - Record observations of the soil types.
 - Immediately collect volatile organic analyte and sulfide samples.
 - Scope the core segment into a stainless steel bowl (or other type as specified in the project planning documents).
- If multiple core segments are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization
- Homogenize the sample as thoroughly as possible

- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- Return unused soil to the boring, level the area, replace grass turf as necessary.

6.3 Subsurface Soil Sampling with Bucket Augers

This system consists of pre-cleaned bucket augers, a series of extensions, and a T-handle. The dimensions of the bucket define the volume and depth interval of possible sample collection. The following procedures are used for collecting soil samples with the bucket auger:

- Attach the bucket auger bit to a drill rod extension, and attach T-handle to the drill rod.
- Clear the area to be sampled of surface debris (e.g., twigs, rocks, and litter).
- Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole until the desired upper sampling depth is reached.
- Decontaminate the bucket auger or replace the bucket auger with a pre-cleaned auger bucket and resume augering. After reaching the desired depth (no more than the maximum length of the auger bucket), carefully remove the auger from the boring.
- Empty bucket auger-collected samples into a pre-cleaned stainless steel bowl (or other type as specified in the project planning documents) OR use pre-cleaned scoops and carefully subsample soil from within the bucket that has not come in contact with the auger.
- Immediately collect volatile organic analyte and sulfide samples.
- If multiple bucket auger collected samples are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization.
- Homogenize the sample(s) as thoroughly as possible.
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- If another sample is to be collected in the sample hole, but at a greater depth, decontaminate or re-attach a pre-cleaned auger bucket, and follow steps above.
- Return unused soil to the excavation, level the area, replace grass turf as necessary

6.4 Subsurface Soil Sampling with Continuous Flight Augers

This system consists of pre-cleaned continuous flight augers, a series of extensions, and a T-handle. The dimensions of the flight define the volume and depth interval of possible sample collection.

When continuous flight augers are used, the sample can be collected directly off the flights. Continuous flight augers are satisfactory for use when a composite of the soil column is desired.

A powered auger may be used at this time. The following procedures are used for collecting soil samples with an auger:

- Attach the continuous flight auger to a drill rod extension, and attach T-handle to the drill rod.
- Clear the area to be sampled of surface debris (e.g., twigs, rocks, and litter).

- Begin augering, periodically removing and depositing accumulated soils onto a plastic sheet spread near the hole until the desired upper sampling depth is reached.
- Decontaminate or replace the auger flight with a pre-cleaned auger flight and resume augering. After reaching the desired depth (no more than the maximum length of the auger flight), carefully remove the auger from the boring.
- Place auger-collected samples into a pre-cleaned stainless steel bowl (or other type as specified in the project planning documents) OR use pre-cleaned scoops and carefully subsample soil from within the auger flights as it comes to the surface.
- Immediately collect volatile organic analyte and sulfide samples.
- If multiple auger flight-collected samples are necessary to collect adequate sample volume, they should all be combined in the bowl prior to homogenization
- Homogenize the sample(s) as thoroughly as possible.
- Transfer sample aliquots to appropriate sample containers and preserve as required in the project planning documents.
- If another sample is to be collected in the sample hole, but at a greater depth, decontaminate or re-attach a pre-cleaned auger flight, and follow steps above.
- Return unused soil to the excavation, level the area, replace grass turf as necessary.

7 Quality Assurance/Quality Control

Prior to initiating field work, the project planning documents (e.g., work plan, sampling and analysis plan, quality assurance project plan, SHASP, *et al*) should be reviewed by field personnel to identify sampling procedure(s) that will most likely provide surface and shallow subsurface soil samples that meet project DQOs.

The program/project manager should identify personnel for the field team who have knowledge, training and experience in the field soil sampling activities being conducted. One member of the field team should be designated as the lead for soil sampling and will be responsible, with support from other field personnel, for implementing the procedures in this SOP. The program/project manager should also identify additional personnel, if necessary, to complete ancillary procedures, e.g., field logbook documentation, equipment decontamination, sample shipment, and waste disposal.

The soil sampling lead should prepare a detailed equipment checklist before entering the field and verify that sufficient and appropriate equipment and supplies are taken into the field.

Quality assurance/quality control samples (e.g., co-located samples) are collected according to the site quality assurance project plan. Field duplicates are collected from one location and treated as separate samples. Field duplicates are typically collected after the samples have been homogenized. Collocated samples are generally collected from nearby locations and are collected as completely separate samples.

In cases where multiple hand-collected scoop, auger or core samples are required to generate an adequate sample volume, homogenization is important. Field personnel should collect sample aliquots only after mixing has produced soil with textural and color homogeneity.

At sites with known or suspected contamination, samples should be collected moving from least to most contaminated areas.

8 Health and Safety

Prior to entering the field, all field personnel formally acknowledge that they have read and understand the project specific health and safety plan.

Augers and soil core sampling apparatus are inherently dangerous pieces of heavy equipment which a high “pinch” potential. Care should be taken at all times when handling such equipment, not just during sample collection.

Prior to any subsurface work, verify that underground utilities have been located and marked.

9 Special Project Requirements

Project or program-specific requirements that modify this procedure should be entered in this section and included with the project planning documents.

10 References

The following list sources of technical information on soil sampling.

Barth, D. S. and B. J. Mason, 1984, *Soil Sampling Quality Assurance User's Guide*, EPA-600/4-84-043.

de Vera, E. R., B. P. Simmons, R. D. Stephen, and D. L. Storm, 1980, *Samplers and Sampling Procedures for Hazardous Waste Streams*, EPA-600/2-80-018.

Navy Environmental Compliance Sampling and Field Testing Procedures Manual, NAVSEA T0300-AZ-PRO-010

U.S. Environmental Protection Agency (EPA), 1985, *Characterization of Hazardous Waste Sites – A Methods Manual: Volume II, Available Sampling Methods*, (2nd ed.), 1985, EPA-600/S4-84-076.

_____, 1995, *Removal Program Representative Sampling Guidance: Volume I – Soil*, (Interim Final), EPA-9360.4-10.

_____, 1984, *Characterization of Hazardous Waste Sites – A Methods Manual: Volume I, Site Investigations*, Section 7: Environmental Monitoring Systems Laboratory, Las Vegas, Nevada, EPA/600/4-84/075.

_____, February 1989, *Methods for Evaluating the Attainment of Cleanup Standards: Volume I, Soils and Solid Media*, EPA/230/02-89/042.

_____, November 2001, *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*, USEPA Region 4

_____, 18 February 2000, U.S. EPA Environmental Response Team Standard Operating Procedures, Soil Sampling, SOP #2012

END OF SOP

STANDARD OPERATING PROCEDURE
SAMPLING EQUIPMENT DECONTAMINATION

SOP NUMBER: ENV 3.15

REVISION DATE: 5/25/2012

SCHEDULED REVIEW DATE: 5/25/2017

Contents

1	Scope and Application.....	1
2	Definitions and Acronyms.....	1
3	Procedure Summary.....	2
4	Cautions.....	2
5	Equipment and Supplies.....	2
6	Procedures.....	3
6.1	Decontamination Methods for Direct Sample Contact Equipment.....	4
6.2	Decontamination Methods for Other Equipment and Meters.....	4
6.3	Decontamination Methods for Heavy Equipment.....	5
7	Quality Assurance/Quality Control.....	5
8	Health and Safety.....	5
9	Special Project Requirements.....	6

None of the information contained in this Ecology and Environment, Inc. (E & E) publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use in connection with any method, apparatus, or product covered by letters patent, nor as ensuring anyone against liability for infringement of letters patent.

Anyone wishing to use this E & E publication should first seek permission from the company. Every effort has been made by E & E to ensure the accuracy and reliability of the information contained in the document; however, the company makes no representations, warranty, or guarantee in connection with this E & E publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use; for any violation of any federal, state, or municipal regulation with which this E & E publication may conflict; or for the infringement of any patent resulting from the use of the E & E publication.

10 **References..... 6**

1 Scope and Application

This Standard Operating Procedure (SOP) describes the routine procedures utilized by E & E personnel in the field for decontaminating sampling equipment that is not dedicated or disposal and that may have come into contact with site contaminants. It is applicable for equipment that will be re-used in the field and for equipment that will be returned to a warehouse or other storage facility prior to re-use.

Program/project specific data quality objectives (DQOs) dictate the types of sampling equipment requiring decontamination and site-specific sampling procedures should be identified in program/project planning documents. This SOP applies to equipment routinely used for:

- Water quality sampling (e.g., buckets, bailers, Kemmerers, and Niskins);
- Flow/water depth measuring (e.g., velocity meters, stream gauges, and depth sounders);
- Soil and sediment sampling (e.g., corers, augers, Van Veens, direct-push samplers, homogenization buckets, and mixing tools); and
- Miscellaneous tools (e.g., shovels, scoops, tapes/rulers/meter sticks, and cutting tools).

Decontamination is time consuming and expensive, often including analyses of field rinsates and other “blanks” to verify decontamination procedures provide equipment that meet program/project DQOs. The use of clean, dedicated, disposable equipment (e.g., Teflon or plastic bailers for groundwater sampling, aluminum bowls for soil homogenization) is preferred, whenever practicable.

This sampling equipment decontamination SOP is intended for use by personnel who have knowledge, training, and experience in the field sampling activities being conducted and who understand the importance of decontamination in meeting program/project-specific DQOs.

The SOP does not address personnel decontamination. As part of the health and safety plan, a personnel decontamination plan should be developed and set up before any personnel or equipment enters the areas of potential contamination.

2 Definitions and Acronyms

ASTM	American Society for Testing and Materials
De-ionized water	Purified water produced by distillation or by filtration through de-ionizing columns or other means (e.g., reverse osmosis) or some combination of treatments. Program/project DQOs establish the level of purity required (e.g., maximum level of electrical conductivity)
DQO	Data quality objective
Potable water	Tap water from a treated drinking water supply
SHASP	Site-specific Health and Safety Plan
SOP	Standard Operating Procedure
USEPA	United States Environmental Protection Agency

3 Procedure Summary

Sampling equipment decontamination procedures vary depending on the DQOs identified in the program/project planning documents. These documents address the types and degrees of contamination anticipated and identify appropriate decontamination procedures, materials, and wastes handling.

A decontamination line is set up in the contamination reduction zone, outside of the contamination “hot” zone, where personnel follow a multi-step decontamination procedure. If a formal decontamination line is established for the site, then all equipment decontamination must be completed with the “hot” zone.

This procedure can be expanded to include additional or alternate wash/rinse steps designed to remove specific target analytes/compounds, if required by site-specific work plans or as directed by a particular client.

4 Cautions

Decontamination of sampling equipment left in situ for long periods (e.g., groundwater pumps, stack samplers, continuous flow samplers) is addressed in program/project-specific planning documents.

Sites with biohazards are not considered routine operations. Biohazard site sampling equipment decontamination is addressed site-specific program/project planning documents.

Sites with explosive hazards are not considered routine operations. Explosives site sampling equipment decontamination is addressed in site-specific program/project planning documents.

Sites requiring ultra-clean sampling methods (e.g., United States Environmental Protection Agency [USEPA] Method 1669) require ultra-clean sampling equipment decontamination. Ultra-clean sampling equipment decontamination is addressed in site-specific program/project planning documents.

Decontamination of contaminated or potentially contaminated sampling equipment may generate incompatible hazardous wastes. Only compatible waste streams, as defined in the program/project planning documents are combined for disposal.

The use of distilled/deionized water commonly available from commercial vendors may be acceptable for decontamination of sampling equipment provided that it has been verified by laboratory analysis to be analyte-free distilled/deionized water. Analyte-free deionized water can be obtained from the project analytical laboratories if available. Distilled water available from local grocery stores and pharmacies is generally not acceptable for final decontamination rinses. Contaminant-free deionized water that has been stored on site should not be used without testing. Any new source of water should be tested prior to use if not certified by a vendor or laboratory.

In general, use of solvents is avoided for low level environmental analysis, but may be necessary for more contaminated areas.

5 Equipment and Supplies

Planning documents provide direction on the specific equipment and supplies, and the numbers/volumes required to meet program/project-specific DQOs. The following equipment and supplies are used for routine sampling equipment decontamination:

- Appropriate protective clothing (including safety glasses or splash shield and nitrile gloves);
- Galvanized or similar wash basins;
- Waste collection drums (if required) ;
- Plastic buckets (5-gallon);
- Long-handled brushes;
- Spray/squeeze bottles;
- Non-phosphate detergent (e.g., Liquinox™ or Alconox™);
- Pesticide grade (or equivalent) organic solvents (e.g., methanol, hexane, or other as specified in the planning documents.) if necessary based on the contaminants
- Ten percent, by volume in de-ionized water, nitric acid (ultrapure);
- Tap water;
- Deionized water (usually American Society for Testing and Materials [ASTM] Type II);
- Organic-free water;
- Plastic sheeting for ground cover;
- Paper towels;
- Trash bags;
- Aluminum foil; and
- Waste handling supplies. (Refer to project planning documents and E & E Investigation-Derived Waste SOP for details.)

Note all waters, acids and detergents should be are stored in their original containers or clearly marked clean sealable glass, plastic, or Teflon® bottles in which information from the original label has been transferred. The secondary labeling should include reagent name, source, date opened/transferred, and expiration date as well as any hazardous labels.

6 Procedures

Before entering the field personnel reviews relevant program/project planning documents (e.g., work plan, sampling and analysis plan, quality assurance project plan, health and safety plan);and select the sampling equipment decontamination procedures (e.g., organic solvent[s] to be used) that meet project DQOs.

In the field personnel should follow best practices to minimize contamination of equipment and prevent cross contamination of cleaned equipment.

- Set-up a zone that isolates areas of contamination from clean areas of the site. All equipment should be decontaminated within the contamination area.
- Employing work practices that minimize contact with hazardous or toxic substances (e.g., avoid areas of obvious contamination, avoid touching potentially contaminated materials);
- Covering monitoring and sampling equipment with plastic or other protective material;

- Use of disposable outer garments and disposable sampling equipment with proper containment of these disposable items;
- Use of disposable towels to clean the outer surfaces of sample bottles before and after sample collection; and
- Encasing the source of contaminants with plastic sheeting or overpacks.

6.1 Decontamination Methods for Direct Sample Contact Equipment

Field personnel should set-up a decontamination line that moves contaminated equipment through the decontamination process to a clean zone. At all stations in the decontamination line, contaminated and/or potentially contaminated fluids and/or wastes are collected and containerized.

Routine decontamination steps for equipment that directly contacts samples are described below.

1. Physically remove gross contamination from equipment by abrasive scraping and/or brushing.
2. Wash equipment with non-phosphate detergent (i.e., Alconox™ or Liquinox™) in tap water.
3. Rinse with tap water
4. Rinse with de-ionized water.
5. Rinse with 10% nitric acid, if specified in planning documents. Nitric acid washes are typically used for metals contamination.
6. Rinse with de-ionized water (if the acid rinse is conducted).
7. Rinse with organic solvent(s) to remove high levels of organic contamination, refer to the planning documents for the site/activity-specific solvent choice.

Use a methanol rinse to dissolve and remove soluble organic contaminants for high concentration samples.

Use a hexane rinse to dissolve waste lubricating oils, tars, and bunker fuels for high concentration samples.
8. Air drying
9. Rinse with deionized, organic-free water, usually only if alternative solvents are used.
10. Wrap sampling equipment in aluminum foil or plastic ; if it will not be used immediately. Determine the best material to wrap equipment based on site contaminants for example plastic bags should not be used is sampling for volatile and extractable organics.
11. Containerize all solvent rinsing wastes, detergent wastes and other chemical wastes requiring off-site or regulated disposal. Dispose of all wastes in conformance with applicable regulations as defined in the project planning documents.

6.2 Decontamination Methods for Other Equipment and Meters

Several types of sampling equipment such as meters, pumps and tubing that cannot be cleaned directly as described in 6.1. Consult the manufacturers guidelines before decontaminating and equipment.

General decontamination steps are described below.

1. Physically remove visible contamination from equipment by brushing the outside of the equipment or wiping with paper towel.
2. If tubing or other portions of the equipment comes into contact with the sample then pump any decontamination solvents through the equipment.
3. Rinse/or pump with tap water
4. Rinse/or pump with de-ionized water.
5. Air dry
6. Wrap sampling equipment in aluminum foil or plastic ; if it will not be used immediately. Determine the best material to wrap equipment based on site contaminants.

6.3 Decontamination Methods for Heavy Equipment

For heavy equipment, a decontamination pad should be established by the driller or subcontractor. Heavy sampling equipment (e.g., augers) decontamination may include a steam cleaning and/or high-pressure water wash step after gross contamination is removed by detergent and brushing.

7 Quality Assurance/Quality Control

Program/project planning documents define the quality assurance/quality control procedures (e.g., collection and analysis of equipment rinsate and other “blanks”) necessary to meet program/project DQOs. Typically, a field blank (equipment rinsate blank) consists of a sample of analyte-free water passed through/over a decontaminated sampling device to assess possible cross contamination from equipment to sample contamination.

8 Health and Safety

Personnel review and acknowledge that they understand the project planning documents, especially the SHASP prior to entering the field. Material Safety Data Sheets are taken into the field for hazardous materials used at a site.

Some types of sampling equipment are inherently dangerous pieces of heavy equipment with high pinch or crush potential. Proper handling procedures are followed during decontamination of heavy equipment.

Decontamination procedures may pose hazards, especially when chemical decontamination procedures, high pressure, and/or steam are used. Exposure to hazardous materials or wastes is controlled by the use of appropriate personal protective equipment and proper handling and storage of the materials/wastes, as specified in the project planning documents, especially the SHASP.

Steam cleaning - follow equipment manufacturer operating and safety guidelines.

High-pressure water cleaning - follow equipment manufacturer operating and safety guidelines.

Waste collection and disposal procedures are presented in program/project planning documents and E & E Investigation-Derived Waste SOP.

Avoiding practices that increase tendencies for hand-to-mouth contact including: eating, drinking, smoking, or using chewing tobacco is a basic procedure employed during all field activities.

9 Special Project Requirements

Special project requirements are presented in the program/project planning documents. If required, contract or other client-specific, site-specific requirements may be entered in this section.

10 References

The following list sources of technical information on decontamination procedures.

ASTM D 5088 – 02 Standard Practice for Decontamination of Field Equipment Used at Waste Sites, 2008

USEPA Environmental Response Team “Sampling Equipment Decontamination”, SOP #: 2006, REV.#:0.0, 08/11/94

USEPA Environmental Investigations Standard Operating Procedures and Quality Assurance Manual, Region 4, November 2001

USEPA Region IV, Field Equipment Cleaning and Decontamination, SESDPROC-205-R2, December 20, 2011

Navy Environmental Compliance Sampling and Field Testing Procedures Manual, NAVSEA T0300-AZ-PRO-010

END OF SOP

STANDARD OPERATING PROCEDURE
ENVIRONMENTAL SAMPLE HANDLING, PACKAGING AND
SHIPPING

SOP NUMBER: ENV 3.16

REVISION DATE: 5/25/2012

SCHEDULED REVIEW DATE: 5/25/2017

Contents

1	Scope and Application.....	1
2	Definitions and Acronyms.....	1
3	Procedure Summary	2
4	Cautions.....	2
5	Equipment and Supplies	3
6	Procedure	3
6.1	Prior to Field Activity	3
6.2	Field Sampler Support	3
6.3	Environmental Sample Packaging Procedures	3
6.4	Marking, Labeling and Shipping Procedures.....	5
7	Quality Assurance/Quality Control	5
8	Health and Safety.....	6

None of the information contained in this Ecology and Environment, Inc. (E & E) publication is to be construed as granting any right, by implication or otherwise, for the manufacture, sale, or use in connection with any method, apparatus, or product covered by letters patent, nor as ensuring anyone against liability for infringement of letters patent.

Anyone wishing to use this E & E publication should first seek permission from the company. Every effort has been made by E & E to ensure the accuracy and reliability of the information contained in the document; however, the company makes no representations, warranty, or guarantee in connection with this E & E publication and hereby expressly disclaims any liability or responsibility for loss or damage resulting from its use; for any violation of any federal, state, or municipal regulation with which this E & E publication may conflict; or for the infringement of any patent resulting from the use of the E & E publication.

9 Special Project Requirements..... 6

10 References..... 6

1 Scope and Application

This Standard Operating Procedure (SOP) describes the packing, marking, labeling, and shipping procedures routinely used by E & E field personnel to transfer environmental samples from the field to off-site laboratories. Unpreserved and/or properly preserved environmental samples include the following matrices:

- Drinking water;
- Groundwater;
- Surface water;
- Soil;
- Sediment;
- Treated municipal and industrial effluent;
- Biological specimens (i.e., non-pathogenic plant and/or animal tissue); or
- Samples not expected to be contaminated with high levels of hazardous substances.

Shipping includes transport by air, rail, or motor vehicle.

Samples containing known or suspected International Air Transport Authority (IATA)-defined dangerous goods and/or United States Department of Transportation (DOT)-defined hazardous materials or which have anesthetic, noxious, or other properties that could inhibit the abilities of transporters do not meet the criteria for shipping as “environmental” samples.

This environmental sample packaging and shipping SOP is intended for use by personnel who have knowledge, training, and experience in the procedures described herein and who have received training on E & E’s On-line Hazardous Materials/Dangerous Goods Shipping Guidance Manual. Regional Hazardous Materials Transportation Coordinators (RHTCs) are available to provide technical support for environmental sample shipping.

In the event the sample material meets the established criteria of a DOT hazardous material, consult one of the RHTC personnel and follow guidelines in E & E’s Hazardous Materials/Dangerous Goods Shipping Guidance Manual (see http://www.corp.ene.com/departments/health & safety/shipping_manual.asp).

2 Definitions and Acronyms

°C	degrees Celsius
COC	Chain-of-Custody
DNAPL	dense non-aqueous phase liquid
DOT	(United States) Department of Transportation
DQO	Data Quality Objective
EPA	United States Environmental Protection Agency
IATA	International Air Transport Authority
LNAPL	light non-aqueous phase liquid
RHTC	Regional Hazardous Materials Transportation Coordinator

SHASP	Site-specific Health and Safety Plan
SOP	Standard Operating Procedure
UN	United Nations
VOA	volatile organic analysis

3 Procedure Summary

Sample packaging, marking, labeling and shipping procedures vary depending on the data quality objectives (DQOs) identified in the program/project planning documents (e.g., work plan, sampling and analysis plan, quality assurance project plan, SOPs, and site-specific health and safety plan [SHASP]). These documents address the types and degrees of contamination anticipated and identify appropriate shipping and handling procedures.

Properly identified, preserved, and sealed individual sample bottles/jars provided by field samplers are sealed in plastic bags and placed in lined shipping containers. Packing material (e.g., bubble wrap) is used reduce the risk of damage to sample bottles/jars and loss of samples during transport. Absorbent material (e.g., highly absorbent small animal bedding material made from recycled paper/wood waste) is added to the shipping container to contain spills from sample bottles/jars during transport. Double-bagged ice is added to the shipping containers as a preservative. Chain-of-custody (COC) documents are prepared and enclosed in the shipping containers. Shipping containers are marked in compliance with DOT/IATA regulations. Shipping papers (e.g., Federal Express shipping documents) are completed and attached to the shipping containers. Shipping containers are custody sealed and taped. Clients, program/project managers, shippers and laboratories already scheduled to receive samples are notified daily of impending shipments.

4 Cautions

Samples collected from sources, such as waste lagoons, drums, tanks, heavily stained soils, and groundwater contaminated with LNAPL or DNAPL, do not qualify as environmental samples.

Known or suspected samples of IATA-defined dangerous goods and/or DOT-defined hazardous materials do not meet the criteria for shipping as “environmental” samples.

Shipping of IATA dangerous goods and/or DOT hazardous materials is not covered by this SOP. Guidance on shipping dangerous goods and hazardous materials is presented in E & E’s Hazardous Materials/Dangerous Goods Shipping Guidance Manual (see http://www.corp.ene.com/departments/health_&_safety/shipping_manual.asp).

Samples preserved in accordance with United States Environmental Protection Agency (EPA) Contract Laboratory Program guidance (most current version) are routinely shipped as environmental samples.

A RHTC should be consulted prior to any biological specimen shipping.

Transboundary/International shipping requirements are presented in program/project planning documents.

Samples preserved with methanol are not shipped as environmental samples. DOT/IATA regulations apply to the shipment of methanol preserved samples.

Individual sample bottle/jar labels are the responsibility of the field samplers who verify that labels are complete and correct, and match the COC forms prior to shipment to laboratories.

Known or suspected PCB and dioxin samples require additional packaging (i.e., sealing in metal cans) and are not covered by this environmental sample packaging and shipping SOP.

It is E & E's intent to package samples so securely to prevent leakage during shipment. This is to prevent the loss of samples and the expenditure of funds for emergency responses to spills and the efforts necessary to re-obtain the sample. Liquid samples are particularly vulnerable. Because transporters (carriers) are not able to know the difference between a package leaking distilled water and a package leaking a hazardous chemical, they will react to a spill in an emergency fashion, potentially causing enormous expense to E & E for the cleanup of the sample material. Therefore, liquids are to be packed in plastic bags and absorbent/cushioning material to help prevent possibility of leaks from a package.

5 Equipment and Supplies

Coolers, sample bottles/jars, COC forms, and sample labels are typically supplied by the laboratory.

Federal Express or other shippers provide shipping forms.

Packaging material, such as plastic bags, ice, and absorbent material, are purchased locally.

E & E-purchased durable packaging equipment, such as coolers, are labeled with the applicable E & E office (or, in some cases, field office) address.

6 Procedure

6.1 Prior to Field Activity

- Program/project managers or designated personnel utilize the project planning documents to stage the equipment and supplies required to meet project DQOs.
- Labeled temperature blanks, tap water filled 40-mL volatile organic analysis (VOA) vials, are prepared for use in the field.
- The project manager or designee arranges for shipper support and coordinates with the laboratory(ies) necessary to conduct the tests needed to meet project DQOs.

6.2 Field Sampler Support

Field samplers collect samples in accordance with the program/project planning documents and provide properly identified, preserved, and sealed individual sample bottles/jars to the field personnel responsible for sample packaging, marking, labeling, and shipping.

6.3 Environmental Sample Packaging Procedures

Environmental samples are usually shipped in 80-quart solid outer shell plastic or metal coolers (although other size coolers may be used if they meet program/project needs). Disposable, pressed Styrofoam coolers are not used. Before use, shipping cooler drain holes are sealed to prevent leakage. Non-applicable labels are removed from the cooler. Marking, Labeling, and Shipping procedures are presented in Section 6.4 of this SOP.

The following steps are used for routine packaging:

- Verify that the bottle is clean and labeled;
- Verify the caps are secure cap and if necessary use fiber reinforced tape;

- Seal each sample bottle and temperature blank in a sealable plastic bag; and
- Add one temperature blank to each cooler.

When a precut foam block insert is used to prevent sample bottle breakage during shipping:

- Verify cooler has this side up labels/arrows;
- Place at least 1 inch of inert absorbent material in the bottom of the cooler;
- Line the cooler with two double-bagged plastic (e.g., large heavy-duty garbage) bags;
- Place a foam insert (with holes cut to receive the sample bottles) inside the plastic bag;
- Place the bottles upright in the holes in the foam block;
- Fill void spaces with double-bagged ice to the top of the cooler;
- Seal each plastic bag lining the cooler with tape;
- Place a COC form in a waterproof, sealable bag taped to the inside of the cooler lid;
- Place custody seals over top edge of cooler so cooler cannot be opened without breaking seals;
- Cover the custody seals with clear tape; and
- Secure the cooler with strapping tape over the hinges and around the entire cooler.

When bubble wrap or similar packing is used to prevent sample bottle breakage during shipping:

- Verify cooler has this side up labels/arrows,
- Place at least 1 inch of inert absorbent material in the bottom of the cooler,
- Line the cooler with two double-bagged plastic (e.g., large heavy-duty garbage) bags,
- Surround each bottle/jar (including the bottom) with bubble wrap, taping the wrap securely around the bottle,
- Place the bottles upright in the inner bag,
- Fill void spaces with double-bagged ice to the top of the cooler,
- Seal each plastic bag lining the cooler with tape,
- Place a COC form in a waterproof, sealable bag taped to the inside of the cooler lid, and
- Place custody seals over top edge of cooler so cooler cannot be opened without breaking seals;
- Cover the custody seals with clear tape; and
- Secure the cooler with strapping tape over the hinges and around the entire cooler.

When only absorbent material is used to prevent sample bottle breakage during shipping:

- Place at least 1 inch of inert absorbent material in the bottom of the cooler;
- Line the cooler with two double-bagged plastic (e.g., large heavy-duty garbage) bags;
- Place at least 1 inch of inert absorbent material in the bottom of the inner bag;

- Place each sample bottle upright inside the inner bag maintaining at least 3 inches between bottles;
- Fill the void spaces around the bottles with absorbent to at least half the height of the largest bottles;
- Fill void spaces with double-bagged ice to the top of the cooler;
- Seal each plastic bag lining the cooler with tape;
- Place a COC form in a waterproof, sealable bag taped to the inside of the cooler lid;
- Place custody seals over top edge of cooler so the cooler cannot be opened without breaking the seals;
- Cover the custody seals with clear tape; and
- Secure the cooler with strapping tape over the hinges and around the entire cooler.

6.4 Marking, Labeling and Shipping Procedures

Program/project planning documents provide the information necessary to initiate filling out the COC forms. Additional information is available in the site field logbook(s).

Environmental samples are shipped as nonhazardous cargo.

Outer marking and labeling on each container is compliant with requirements for the carrier that will be used requirements. Coolers have this side up or arrow labels affixed. Extraneous markings are removed.

Markings indicating ownership of the container, destination, and shipping company labels are acceptable and attached as required.

Hazardous materials/dangerous goods airbills are not used when shipping environmental samples.

Environmental sample packages generally shipped overnight by Federal Express or equivalent. Field personnel check with shippers in advance to verify both pick-up and delivery schedules; especially when weekend and/or holiday pick-up and/or delivery may be required.

7 Quality Assurance/Quality Control

Hazardous Materials/Dangerous Goods Shipping training is provided to personnel responsible for shipping environmental samples. RHTCs are available to provide technical support for environmental sample shipping.

COC forms may be completed electronically or by hand. Samples recorded on the COC form are checked against the packaged samples.

Custody seals are attached to shipping containers so the receiving laboratory may verify the temperature of the samples.

Field samplers and shipping personnel verify the samples in the cooler and the samples listed on the COC match.

Site-identifying information is not listed on samples, forms, or other documents and is not provided to the receiving laboratory(ies).

Clients, program/project managers, shippers, and laboratories already scheduled to receive samples are notified daily of impending shipments. E & E personnel verify shipping addresses and confirm the receiving facility's commitment to accept samples based on shipment dates.

Samples shipped on ice require preservation to 4°C (±2°C). Samples that arrived at the laboratory outside this range could have compromised data quality. Samples should be cooled prior to packaging and sufficient ice used to keep samples cool particularly in warm weather. If samples are being shipped for Saturday or holiday delivery, then the availability of personnel should be verified with the laboratory and the shipping documentation checked to verify the appropriate delivery date is noted. Always confirm delivery of the samples with the shipper.

8 Health and Safety

Prior to entering the field, personnel will formally acknowledge that they have read and understand the project specific health and safety plan (SHASP).

Preserved samples (e.g., samples containing acids, solvents, and formalin) will be handled in accordance with the SHASP.

Good basic lifting and handling procedures will be followed when handling filled coolers.

9 Special Project Requirements

Special project requirements may be found in the program/project planning documents.

10 References

U.S. Environmental Protection Agency (EPA). 2011. Office of Superfund Remediation and Technology Innovation, *Contract Laboratory Program Guidance for Field Samplers*, OSWER 9240.0-47 EPA 540-R-09-03, January 2011. Accessed online at: <http://www.epa.gov/superfund/programs/clp/download/sampler/CLPSamp-01-2011.pdf>.

END OF SOP