17.0 Sampling of Surface Water and Water-Formed Deposits

17.1 Introduction

FDGTI field personnel must often collect samples from in or around open areas containing or having once contained water (e.g., streams, lakes, waste water lagoons, open sumps, etc.), and from streams of discharge water (e.g., from a groundwater treatment system). Samples will consist of either water or water-formed deposits. The samples are collected to establish the chemical and/or biological quality of the water or water-formed deposit either in selected areas or for an entire volume of water (e.g., in sumps and tanks). The following definitions apply:

water-formed deposit - any accumulation of insoluble material derived from water or formed by the reaction of water upon surfaces in contact with the water. Deposits can be classified as *scale, sludge, corrosion products, or biological deposit*.

scale - a deposit formed from solution directly in place upon a surface which is usually crystalline and dense, frequently laminated, and occasionally columnar in structure.

sludge - a water-formed sedimentary deposit which may include all suspended solids carried by the water and trace elements which were in solution in the water.

corrosion products - a result of chemical and electro-chemical reaction between a metal and its environment, which usually consists of insoluble material deposited on or near the corroded area, but may be deposited a considerable distance from the point at which the metal in undergoing attack.

biological deposit - water-formed deposit of organisms or the products of their life processes, usually composed of deposits of gelatinous or filamentous nature.

For the purpose of this document, water-formed deposits will also include sediments deposited by and/or underlying a body of water.

Special care must be taken to ensure that the collected sample is representative of the water or deposit at that location and that the sample is not altered or contaminated by the sampling and handling procedure.

17.2 Purpose

The purpose of this document is to present standard procedures relating to the sampling of surface waters, discharge streams from water treatment systems, and water-formed deposits. This SOP will discuss various sampling methods, QA/QC sampling protocol, proper packaging and preservation procedure, considerations regarding the transport of samples, necessary documentation procedure and standard decontamination procedure. Not all sampling methods are discussed in this document. Other sampling methods are presented in ASTM Standards listed in the references, below.

This SOP is based on ASTM Standards, and is intended to be general. State or local regulations may take precedence over this procedure and should be documented accordingly. Refer to the specific sampling plan developed for each individual site for specific instruction.

17.3 References

The following ASTM Standards were consulted in the preparation of this SOP:

D 140-93 Practice for Sampling Bituminous Materials
D 887-82(94) Practices for Sampling Water-Formed Deposits
D 3213-91 Practices for Handling, Storing, and Preparing Soft Marine Soils
D 3325-90 Practice for Preservation of Waterborne Oil Samples
D 3370-82 Practices for Sampling Water
D 3694-93 Practices for Preparation of Sample Containers and for Preservation of Organic Constituents
D 3976-92 Practice for Preparation of Sediment Samples for Chemical Analysis
D 4348-84(89) Practice for Collecting Benthic Microinvertebrates with the Holme (Scoop) Grab Sampler
D 4387-84(89) Guide for Selecting Grab Sampling Devices for Collecting Benthic Microinvertebrates
D 4411-93 Guide for Sampling Fluvial Sediment in Motion
D 4489-85(90) Practice for Sampling of Waterborne Oils
D 4547-91 Practice for Sampling Waste and Soils for Volatile Organics
D 4687-87 Guide for General Planning of Waste Sampling
D 4823-88 Guide for Core Sampling Submerged, Unconsolidated Sediments
D 4840-88(93) Practice for Sampling Chain of Custody Procedures
D 4841-88(93) Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents
D 4979-89 Test Method for Physical Description Screening Analysis in Waste
D 5012-89(94) Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition
D 5013-89(93) Practices for Sampling Wastes from Pipes and other Point Discharges
D 5088-90 Practice for Decontamination of Field Equipment Used at Nonradioactive Waste Sites
D 5358-93 Practice for Sampling with a Dipper or Pond Sampler
D 5451-93 Practice for Sampling Using a Trier Sampler
D 5495-94 Practice for Sampling with a Composite Liquid Waste Sampler (COLIWASA)
E 1391-94 Guide for Collection, Storage, Characterization, and Manipulation of Sediments for Toxicological Testing
F 1084-90 Guide for Sampling Oil/Water Mixtures for Oil Spill Recovery Equipment

Note: an ASTM serial designation in bold type denotes a major reference used in the preparation of this SOP. Non-bold serial designations denote references useful in obtaining additional information pertinent to the subject matter.

17.4 Equipment

The following equipment should be taken to the site by the field scientist or technician for conducting surface water and/or water-formed deposit sampling:

- a field instrument for screening volatile organic vapors,
- a polyethylene squirt bottle of dilute hydrochloric (HCL) acid,
- a polyethylene squire bottle of dilute nitric acid, if appropriate,
- narrow range pH paper (1.0 - 2.5 pH range),

- field meter(s) which read temperature, pH, electrical conductivity,
- a dissolved oxygen meter, if appropriate,
- plastic bags,
- sample labels,
- a cooler with ice or frozen cold packs,
- a bailer or other sampling device for collecting sample,
- bailer string, if appropriate,
- a clean knife,
- clean rags or paper towels,
- non-phosphate detergent,
- a 10% nitric or hydrochloric acid wash, if appropriate,
- methanol, if appropriate,
- deionized water,
- 3 to 4 wash buckets,
- a trash bag to collect debris,
- splash protection (disposable gloves and other personal protection equipment as necessary),
- blank monitoring/sampling record forms,
- the project field log book,
- a site plan showing sampling locations,
- a clipboard,
- waterproof ink pens,
- a waterproof ink marking pen,
- copies of previous analytical data, if available.
- blank chain of custody records, and
- the site sampling plan.

17.5 Preparation for sampling

Prior to commencement of sampling, the following preparations must be completed:

Pre-determine the sampling strategy, including the location of sampling points for which analytes, and a QA/QC sampling plan. This should be contained in a written work plan that has been approved by the customer..

Prepare a site plan showing the sampling locations, if necessary.

Notify the laboratory to schedule analyses and order glassware, blanks, etc. from them (see Section 17.9.1, below).

Notify appropriate site personnel (e.g., station manager) several days prior to visiting the site.

prepare equipment to take to the site (see Section 17.4, above), and coordinate rental equipment and items that will be supplied by others (i.e., the lab).

Set up field notes in advance, including pre-printed forms such as the chain of custody, and a scheme for logging essential field data in an orderly fashion. Pre-determine a sample labeling system, including QA/QC samples.

Prepare sample containers (including preservatives and field blanks as necessary) and labels in advance, if possible.

Assure that all items that will be used for sampling such as sampling devices and sample containers are sterilized or have been decontaminated prior to collecting the first sample.

Assure that selected sampling equipment is chemically compatible with the expected contaminants and contaminant analyses (i.e., don't plastic sample bottles for collecting samples for analysis of petroleum hydrocarbons).

17.6 Water Sampling

17.6.1 General

The goal of sampling is to obtain for analysis a portion of the main body or stream of water that is truly representative. The most critical factors necessary to achieve this are:
points of sampling,
time of sampling,
frequency of sampling, and
maintenance of integrity of the sample prior to analysis.

Homogeneity is frequently lacking in a water body or water stream, necessitating multiple-point sampling. A totally representative sample should not be an absolute prerequisite to the selection of a sampling point. Most samples collected from a single point (either time or place) in a system must be recognized to be nonrepresentative to some degree. Therefore it becomes important to recognize the degree of representation in the sample.

There are three general categories of surface water sampling:

1. grab sampling,
2. composite sampling, and
3. continual sampling.

Grab sampling is by far the most common type of sampling performed on surface waters and water streams. It represents the conditions existing only at the point and time of sampling. Composite sampling is done by combining individual grab samples into one sample. Continual sampling is performed using a delivery valve or pump that collects a sample continuously over a given time duration. Each of these sampling categories is discussed in detail, below.

The following rules are applicable to all sampling procedures:

The samples must represent the conditions existing at the point taken.

The samples must be of sufficient volume and must be taken frequently enough to permit reproducibility of testing requisite for the desired objective, as conditioned by the method of analysis employed.

The samples must be collected, packed, shipped, and manipulated prior to analysis in a manner that safeguards against change in the particular constituents or properties to be examined.

The sampling of high purity water requires special consideration. Contact with any material other than the original container subjects the sample to possible contamination or alteration. This includes contact with air.

17.6.2 Grab Sampling

This procedure is applicable to sampling water from sources such as wells, rivers, streams, lakes, oceans, reservoirs, pipelines and conduits, processing tanks and vats, ponds, towers, and filters at atmospheric or higher pressures for chemical, physical, bacteriological, or radiological analyses. Grab sampling is the only procedure suitable for bacteriological analyses and some radiological test procedures.

Frequency and duration of sampling:

Large bodies of water such as lakes may be sampled at infrequent intervals such as bi-weekly or monthly, sufficient to cover seasonal changes. When sampling near the shore of such a water body, or when sampling smaller water bodies such as streams, more frequent samples, daily for instance, may need to be taken to provide more exact knowledge of the variations in composition of the water. The greater the variations or cycles of pollution, or the closer the surveillance of a water body must be, the more frequent the sampling should be.

Water that is undergoing treatment must be sampled with such frequency that adequate control is assured. The interval between samples is directly related to the rate at which critical characteristics can reach intolerable limits. The frequency of sampling a discharge water stream from a treatment system is generally based on calculations involving the proven treatment efficiency of the treatment system, the concentration of contaminants in the water to be treated, the volume of water to be treated over a specific time interval, and the maximum allowable discharge limits of the contaminants of concern. Regulatory agencies often dictate the required sampling frequency.

Particulate Matter:

Normally, samples should be taken without separation of particulate matter. If constituents are present in colloidal or flocculent suspension, take the sample so they are present in representative proportion.

Volume of Sample:

Consult the specific method of analysis for any given constituent to determine the volume of sample required. Frequently the required volume will vary with concentration level of any given constituent. The minimum volume collected should be 3 to 4 times the minimum needed for analysis.

Point of Sampling:

For open bodies of water, choose the point of sampling so that a representative sample of water is obtained. Avoid surface scum. In bodies of water such as a small stream where the water is mixed so as to approach uniformity, a sample can be taken at any point in the cross-section. In larger water bodies such as large rivers where water is not

likely to be uniformly mixed, more samples are desirable and are usually taken at a number of points at the surface across the entire width at a number of depths at each point. The samples can then be composited or analyzed separately.

Allow sufficient distance downstream from a suspect source with respect to stream flow to permit thorough mixing. When open water bodies are sampled, avoid nonrepresentative areas such as those created by inlet streams, stagnant areas, or abrupt changes in shorelines, unless the intent is to determine the effect of such local conditions.

Choose sampling points in treatment systems, pipelines, conduits, tanks, vats, filters, etc. with regard to the piping and configuration of the individual piece of equipment containing the water to be tested, the character and changes between the inlet and outlet water, and rate of passage through the equipment. Take care a representative sample is collected by allowing mixing to take place. A suitable sample site may be available in piping immediately downstream from a valve or fitting causing turbulent flow.

Sample Containers:

Use only sample containers that are pre-cleaned and pre-sterilized by the manufacturer or the laboratory and are made of materials that will not contaminate or react with the sample. Check with the laboratory in advance concerning the proper containers for proposed analyses.

Sample Collection:

Chemical and physical analyses:

When sampling streams under pressure, regulate the rate of flow in the sample line to not less than 500 mL/min after first flushing the sample line at a rate sufficiently high to remove all sediment and gas pockets. In special cases where dissolved gases are caused to be released from solution by the drop in pressure, note this on the sample label and/or in the field log.

When sampling water from cocks and valves, insert the sample line or a thoroughly washed glass tube or sulfur-free rubber tube extension of the sample line, into the sample container so that it touches the bottom. Allow a volume of water equal to at least ten times the volume of the sample container to flow into and overflow from the container before the sample is taken.

Note: if the sample is to be tested for constituents that may be adsorbed on the walls of the sample container (such as oil, grease, or PCBs) do not rinse the container and do not overflow it during sample collection.

If a preservative or additive has been added to the sample container, allow the sample to free fall into the container and do not allow it to overflow.

If contact with air would cause a change in the concentration or characteristics of a constituent to be determined, secure the sample without contact with air and completely fill the container.

Microbiological Samples:

When taking a sample from a sample line or tap, allow the water to run for at least 5 minutes or long enough to flush, with six to ten times its volume the entire part of the system that has been stagnant for 2 hours or more.

Check with the laboratory in advance regarding the sample volume and type of containers required for sample collection. In cases where the water to be sampled contains chlorine or an oxidizing agent, thiosulfate ($Na_2S_2O_3$) may need to be added to the sample.

Keep sample bottles tightly capped and protected from dirt and dust prior to collecting the sample.

To collect the sample, first put on clean disposable gloves. Remove the cap from the bottle, grasping it by the outside to avoid touching the rim or inner liner - do not lay it down. Do not rinse the bottle with the sample. Quickly hold the bottle under the flowing water to be sampled until it is about ¾-full to permit mixing by shaking prior to testing. Replace the cap and tighten. Take care that the cap does not touch the outer surface of the bottle when replacing it and that no dust blows into the bottle, insofar as possible.

COLIWASA Sampling Device:

a device known as a composite liquid waste sampler (COLIWASA) exists for obtaining a representative sample from stratified or unstratified liquids. Its most common use is for sampling containerized liquids, such as tanks, barrels, and drums. It may also be used for pools and other open bodies of stagnant liquid. The COLIWASA is used to obtain a vertical column of liquid representing an accurate cross-section of the sampled material.

Figure 17-1 shows a typical COLIWASA. The COLIWASA **should not** be used to sample flowing or moving liquids.

Use the following procedure to collect a liquid sample using a COLIWASA:

- Make certain that the device is clean and functioning properly (see Section 17.11 for decontamination procedure). It is essential that the stopper at the bottom of the sampling tube closes securely.

- Open the COLIWASA by placing the stopper mechanism in the open position.

- Lower the COLIWASA into the liquid **slowly** so that the levels of the liquid inside and outside the sampler tube remain about the same.

- Use the stopper mechanism to close the COLIWASA when it reaches the desired depth in the liquid.

- Withdraw the sampler from the liquid with one hand while wiping the sampler tube with a disposable cloth or rag with the other hand.

- Carefully discharge the sample into a suitable container by slowly opening the stopper mechanism while the lower end of the COLIWASA is positioned in the sample container.

- Seal, label and preserve the sample container according to standard protocol and log the sample into the field log (see Sections 17.9 and 17.10, below).

- Decontaminate the sampling equipment prior to collection of the next sample.

Time Interval Between Collection and Analysis of Samples:

In general, allow as short a time as possible to elapse between the collection of a sample and its analysis. Under some conditions, analysis in the field may be necessary to obtain reliable results. the actual time that may be allowed to intervene between the collection and analysis of a sample varies with the type of examination to be conducted, the character of the sample, and the time interval allowable for applying corrective treatment. Always consult with the laboratory in advance regarding specific holding and turn-around times.

Do not hold samples for microbiological analyses longer than 6 hours from time of collection to analysis (confirm this holding time with the laboratory). Consider field examination if the required holding time cannot be met.

Make the determination of dissolved gases such as oxygen, hydrogen sulfide, and carbon dioxide at the source, except that in some cases such constituents may be fixed and determined later as specified by the laboratory.

17.6.3 Composite Sampling

a composite sample can be one of three types:
composed of individual grab samples that were collected at varied time intervals from the same site,
composed of individual grab samples that were collected at various sites, or
composed of individual grab samples that combine both site and time variables.

Composite sampling is applicable for subsequent chemical and physical analyses. It may not be suitable for sample collection for radiological

examination. Composite samples **are not** suited for bacteriological examination or for purgable organics.

Sample Collection:

Composite samples may be made by mutual agreement of the interested parties (i.e., FDGTI, the customer, and the regulatory authority) by combining individual (grab) samples taken at frequent intervals or by means of automatic samplers.

Indicate whether or not the volume of sample is proportional to the rate of flow. At the end of a definite period, mix the composite sample thoroughly so that determinations on a portion of the composite sample will represent the average for the stable constituents. Variations of unstable constituents may be determined by analysis on the individual samples.

Frequency and Duration:

In sampling process waters (such as from a treatment system) collect composite samples in at least one 24-hr. period. If the process is cyclic in nature, collect samples during at least one complete process cycle, and identify this in the field log. Collect increments for composite samples at regular intervals from 15 min. to 1 hr. and in proportion to the rate of flow of the water. This may be conveniently done by taking a simple multiple of the flow rate. Choose a suitable factor to give a proper volume (about 4 litres) for the composite sample.

When samples are taken from a stream, composite samples for analysis normally consist of equal quantities of daily samples for a suitable number of consecutive days.

17.6.3 Continual Sampling

This procedure is applicable to sampling water from sources such as rivers, streams, lakes, oceans, reservoirs, pipelines and conduits, processing tanks and vats, ponds, towers and filters on a continual basis for chemical, physical or radiological analyses.

Apparatus:

Continual-sampling apparatus shall consist of:

- a delivery valve or pump;
- a piping system;
- a flow regulation system; and
- a waste disposal system.

Frequency and Duration of Sampling:

Sampling is essentially on a continuous basis. Intermittent operation is possible, though seldom used, through use of sample by-pass equipment.

Single Sample for Multipoint Sampling

When simultaneous samples from several locations are required, water is drawn continually from each individual source proportionate to flow and mixed into a single sample.

Particulate Matter:

The size, quantity and, in some cases, type of particulate matter often accounts for one or more of the variables to be measured and, in other cases, introduces errors in the analysis if they are disturbed. The water delivery system shall flow fast enough to keep the heavier particles in suspension, and the system volume shall be large enough to prevent undesirable filter action through restrictions.

The sampling system should be sized to maintain a Reynolds number of approximately 4,000 to assure turbulent flow.

Sample Collection:

Because pumps employing suction principles disturb the gas-liquid balance, use a submersible-type pump for pumping samples from open bodies of water whenever the measurements to be made concern dissolved gases such as oxygen or carbon dioxide. Pumps, screens, valves, and piping must be selected of corrosion-resistant material to prevent sample contamination from corrosion products and to prevent undue maintenance.

The debris screens employed around the pump intake shall be of sufficient size to preclude a significant pressure drop developing across the screen in the event of partial clogging. The piping system between the pump and the sample container shall be designed so that the pump is operating against the lowest practical head. The piping system shall be constructed with a continual rise in elevation from the pump to the point of delivery without reverse bends in which sediment and algae can accumulate.

17.7 Sampling of Water-Formed Deposits

17.7.1 General

The goal of sampling of water-formed deposits is to obtain for analysis a portion of the whole that is representative. The most critical factors are the selection of sampling areas and number of samples, the method used for sampling, and the maintenance of the integrity of the sample prior to analysis.

17.7.2 Site Selection

Site selection for sampling sediments or other bottom deposits beneath large bodies of water should consider the location of pollution loadings and hydrological flow patterns. The site selection may also meed to be of a random or stratified random nature, depending on the study objectives. Sediment/sludge variability must be considered since most bottom deposits are very heterogeneous in nature. A preliminary view of background data may therefore be required to determine accurately the appropriate number of sediment replicates to collect.

17.7.3 Removal of Foreign Material

Sediments and other water-formed deposits such as sludges are inherently heterogeneous in nature in that they contain occluded water in varying and unpredictable amounts and may contain foreign objects or material not ordinarily considered as sediment, the inclusion of which would result in inaccurate analysis. Standard methods for separating foreign objects to facilitate homogenization will minimize errors due to poor mixing and inclusion of extraneous material. Standard field methods include the following:

- The analytical sample is arbitrarily defined as that which passes a 10-mesh (approximately 2-mm openings) sieve. The purpose of this is to provide a basis for discrimination of the sediment/sludge and foreign objects or materials. For convenience in the field, this distinction can be estimated by eye, and the sample does not need to be physically sieved.

- Avoid collecting foreign objects such as stones, twigs, leaves, trash, etc. as part of the packaged sample. Remove these objects, if possible, manually as the sample is packaged. minimize agitation of samples that will be analyzed for volatile components.

  Note: always wear clean, protective gloves while sampling and do not allow sediments, sludges or other materials that may contain contaminants or sharp objects to contact your skin.

17.7.4 Loss of Volatiles

Loss of volatile organics during sample collection, handling and shipment affects the concentrations detected by the laboratory. The principle mechanisms of loss are volatilization of the compounds and biodegradation. Follow proper handling and preservation protocol to minimize loss of volatiles (see Section 17.9, below).

17.7.5 Sampling Submerged Deposits

Table 1, attached, presents a summary of advantages and disadvantages of the various collection methods that can be used to collect submerged deposits. All sampling methods disturb the sediment integrity to a degree. It is important to obtain sediments with as little disruption as possible. Core sampling is preferred above other methods for this reason.

a number of coring devices exist for collecting sediment and other deposits from the bottom of water bodies. These devices include various types of open-barrel and piston samplers. a comprehensive discussion of the pros and cons of a number of submerged deposit samplers is presented in ASTM Standard D 4823 (see also ASTM Standard E 1391 for a comprehensive discussion on the sampling of submerged sediments). Many of the principles pertaining to handling and packaging of core samples collected using such devices is the same as those for collecting soil samples using a split-barrel sampler (See SOP No. 12).

17.8 QA/QC Sampling

A project's QA/QC sampling protocol is pre-determined during work scope preparation, and will depend on a number of factors including project goals, level of detail, and cost constraints. The customer may already have a specific protocol for QA/QC sampling which may or may not include all of the samples recommended below. However, QA/QC sampling is essential to lending validity to the sampling program and analytical results. The QA/QC protocol presented here is taken from relevant ASTM standards and so is considered the industry standard protocol. State or local regulations may require a protocol that differs from the one presented here. If the customer's requested QA/QC sampling protocol varies significantly from either the state/local protocol or the one presented here (whichever is relevant to the project), the project manager should inform the customer of this discrepancy and advise him/her of the potential consequences.

Four types of quality control samples relate to the quality assurance of field sampling:

1. Field blanks,
2. Split samples,
3. Field rinsates, and
4. Field spikes.

The selection of the types of quality control samples to be used should be made prior to the sampling event and included in the site sampling plan.

17.8.1 Field Blanks

Field blanks are samples prepared in the laboratory using reagent water or other blank matrix and sent with the sampling team. These samples are exposed to the sampling environment and returned with the samples to the laboratory for analysis. The purpose of the field blank is to verify that none of the analytes of interest measured in the field samples resulted from contamination of the samples during sampling.

The sampling plan should normally include a minimum of **one field blank for each procedure for each sampling event**. These samples can be submitted blind to the laboratory to challenge their analytical system or can be shipped with the instruction to hold them unless there is a reason to suspect sample contamination. The submission of blind field blanks would normally be reserved for those situations where the competency of the analytical laboratory was unproven.

17.8.2 Split Samples

Split samples are used to challenge the analytical laboratory

perfor mance . Split sampl es are also used when two differe nt parties are sampli ng the same site and verific ation of analyti cal results is neces sary. A split sampl e is prepar ed by

A water sample that is to be split for non-volatile analysis should be placed in a large container and stirred or swirled to ensure thorough mixing of the medium prior to subsampling. For samples that will be analyzed for volatile constituents, discharge the water directly from the sampling bailer (or pump) directly into the two (or more) sets of sample containers by discharging a small portion to one container, then the next, then the next, and so on, until all containers are full.

Homogenous split samples of solids cannot be prepared for samples that will be analyzed for volatile organics. In such a case, the split will consist of packaging two “side-by-side” portions of undisturbed sample (e.g., two adjacent sections of a sample core). For all other samples, a sufficient quantity of the solid material is collected and mixed sufficiently with clean utensils to assure that stratification of analytes is avoided, and subsampled.

Split samples are treated as separate study samples and are submitted to the analytical laboratory without distinguishing identification (i.e., label each sample so as not to indicate that it is a split). Split samples are an indication of the precision of the analytical procedures.

Where feasible, each sampling event should include a minimum of **one split sample for each type of media or location sampled**. Where the data are intended for demonstration of data quality to an outside agency, splits should be included at a greater frequency, **up to 10% of the total number of samples collected**.

17.8.3 Field Rinsates

Field rinsates are samples collected in the field by filling a sample collection vessel that has just been decontaminated (such as a sample bailer and bottom-discharge device) with reagent water or other blank matrix, and then transferring this water to the proper sample bottles. The purpose of a field rinsate is to ensure that sampling equipment cleaned in the field is not cross contaminating samples through improper cleaning techniques. These types of samples should be taken **at least once for each procedure for each sampling event when field cleaning is performed**. If only one such sample is taken it should be collected just prior to the last sample.

17.8.4 Field Spikes

Field spikes are samples collected in the field and spiked with compounds of interest or related compounds. These samples are used to check on the potential for loss of analyte on shipping and for recovery of analytes from a particular medium. The field spike is prepared by adding a known amount of the spiking material to a known amount of the matrix and mixing thoroughly prior to closing and sealing the sample container.

Field spikes are normally not required but may be desired where preservation techniques are in question and the integrity of analytes at the laboratory is not known, when there is a question concerning matrix effects, and when the results from the analytical laboratory for a particular analyte or class of analytes are in question.

Field spikes should be submitted blind to the laboratory in the same manner as outlined for the split samples. These samples should be carried through all stages of the sampling and sample handling process as the actual study samples to ensure that they truly indicate the integrity of the samples collected.

17.8.5 QA/QC Samples for Decontamination Procedure

It is important to document the effectiveness of the decontamination procedure (see Section 17.10, below). Therefore the project's QA/QC program should include provisions for the collection of samples to evaluate the completeness of the decontamination procedure. This could include:

Collection of rinse or wipe samples before the initial equipment decontamination prior to its use for sampling to establish a base line level of contaminants residing on or in the equipment;

Collection of final rinse or wipe samples after equipment decontamination following its use; and

The frequency of sampling to demonstrate the completeness of equipment decontamination is dependent upon objectives of the project as they relate to QA/QC. At a minimum it is recommended after every ten decontamination washings.

17.9 Preserving and Transporting Samples

Complete and unequivocal preservation of samples is practically impossible. At best, preservation techniques only retard the chemical and biological changes that inevitably continue after the sample is removed from the source. Therefore, insuring the timely analysis of a sample should be one of the foremost considerations in the sampling plan schedule.

ASTM Standards D 3694 and D 4448 contain detailed discussions and summary tables regarding sample preservation practices and holding times. The most common preservation practices used by FDGTI are detailed in Section 17.9.2, below.

17.9.1 Laboratory Notification

Prior to scheduled sample collection, the sample shipment and analysis requirements must be discussed with the laboratory. The exact requirements for the volumes of sample needed and the number and type of containers to use may vary from laboratory to laboratory. This will depend on the specific analyses to be performed, the concentration levels of interest, and the individual laboratory protocols. Turnaround time, holding time, report contents and pricing requirements must be discussed with the laboratory prior to sample shipment.

Notify the laboratory in advance of any laboratory blanks or sample containers that must be supplied by the laboratory. Confirm the minimum amount of sample required for specific analyses, types of containers, preservatives, etc. prior to sample collection.

17.9.2 Sample Preservation

Methods of preservation are intended to retard biological action, retard hydrolysis of chemical compounds and complexes, and reduce the volatility of constituents. Preservation methods are generally limited to pH control, chemical addition, refrigeration and freezing. For water samples, **immediate** refrigeration is often the best preservation technique available.

Some water samples require the addition of preservatives in the sample container (usually acid) while others do not. Sample containers must be tightly sealed to prevent the escape of vapors or introduction of vapors to the sample, and they should be subjected to minimal disturbance (i.e., agitation) after collection, particularly if the samples will be analyzed for volatile contaminants. Upon collection, the handling of each sample should be minimized. All collected samples should be immediately placed into a secure, light-proof storage container which is kept out of direct sun and away from any source of excessive heat or potential contaminated vapors (e.g. car exhaust). **Do not** place collected product samples into the same storage container as water samples.

All samples must be kept chilled to at least 4^{o} C (39^{o} F). To assure this, the samples, when being placed in the storage container (usually a cooler), should be packed in (i.e., surrounded by) ice or cold packs. Do not just place the samples on top of the ice as they may not stay cold enough. Also, assure that the sample integrity will not suffer from becoming wet from the ice or cold packs (i.e., labels or tape coming off). If necessary, place sample containers into individual sealable plastic bags as an extra protective measure.

Acidification of Organic Compounds in Water Samples:

At the start of each sampling round, the amount of acid required to

Prior to sample collection, put 2 to 10 drops of 15% to 25% dilute hydrochloric acid (HCL) into a 40-ml trial (practice) sampling vial (larger sampling containers will require more acid) and fill the vial with water from the source (do not allow the container to overflow). Determine the pH of the water in the vial using pH paper. If the pH is higher than 2, repeat the procedure using more drops of acid in the vial. Repeat until the pH of the water in the sample vial is just less than 2. Note the amount of acid required to lower the pH of the volume of water in the sampling vial. Discard the practice acidified sample in a disposal container.

Once the amount of acid required to reach a pH of 2 is known, the acid can be routinely added to each sample container directly. The water to be analyzed is added to vial or container containing the appropriate amount of acid. More frequent pH analysis may be required depending on chemical usage at a particular site or if significantly different hydrogeochemical environments exist at a site.

The volume of acid required depends on acid normality (concentration) and water pH. Therefore, note that the amount of acid required is site specific and should be noted in the field log.

The above procedure is valid for acidifying samples for EPA 601/8010, 602/8020, and 624/8240 analyses.

Do not acidify EPA 625/8270 samples. **Do not** acidify separate phase product samples.

Acidification of Metals in water Samples:

Use dilute nitric acid (HNO_3) to preserve water samples for metals analysis. Using nitric acid instead of HCl, follow the procedure for acidification of organic compounds, above, to lower the pH of the sample to 2.

17.9.3 Sample Packaging

Water samples and samples of water-formed deposits will be packaged into sample containers for shipment to the appropriate laboratory. The method of sample handling and containment is dependent on the method to be used in the laboratory for analysis of specified physical or chemical parameters. The following general rules apply to the preservation of the validity of a sample: the sampling procedure should be completed in a minimum amount of time, with the least possible handling of the sample before it is sealed in a container;

If possible, the sample should be physically inspected and its characteristics (color, sediment content, odor) documented;
All packaged samples should be placed immediately into a secure, storage container that is out of direct sunlight, away from heat-generating sources and away from potential sources of cross-contamination such as car exhaust;
all samples must be immediately placed on ice or other cooling source that will sustain a temperature no greater than 4^{o} C (39^{o} F); and
Place 40-ml sample vials and 1-liter bottles into the cooler in clean foam sponges in a standing position. If foam sponges are not available, place sets of vials (three or four) into a small plastic bag, close the bag, then wrap duct tape tightly around the packaged vials before placing them in the cooler. **Do not** place product samples in the same cooler as water samples. The 1-liter bottles can be wrapped in plastic bubble wrap to avoid breakage. Stand them up and pack them tightly to prevent their moving around in the cooler. Make sure to drain all water from cooler before shipping samples.

17.9.4 Sample Labeling

Identify each collected and packaged sample by attaching a water-proof tag or label to the container prior to sampling or immediately thereafter. Tags or labels must be completed using permanent, waterproof ink. They should be protected against detachment from the individual sample containers if they get wet. Each tag or label must include, at a minimum, the following information:
a sample number that uniquely identifies that sample (as pre-determined and documented in the sampling plan);
company name (i.e., FDGTI);
the FDGTI project number;
the project name or site name;
the name, signature or initials of the person who collected the sample;
date and time of sample collection; and
preservative added.

If space exists on the tag or label, the requested analysis should also be recorded (this is important if the sample is collected into several different containers each having unique preservatives for specific laboratory analyses).
Additional information that should be recorded at the time of sample labeling (either in the field notes or on the COC) includes:
source of sample;
point of sampling (designated in sufficient detail to enable anyone to collect a second sample from the identical spot from which the first sample was taken);
temperature and rate of flow of the fluid in the equipment from which the sample was taken;
temperature of sample when collected;
results of field tests made on the sample;
observations and remarks pertinent to the sample collection; and
storage temperature if the sample is stored in a refrigerator.

17.9.5 Transporting Samples

When transporting samples from the site to either the office or the laboratory, they must be kept inside a secure storage container at all times the inside of which, if necessary, is kept chilled. The storage container should not be

subjected to excessive heat or potential sources of contamination (e.g.,, car exhaust). **Do not store or transport samples in the trunk of a car**.

Shipment and receipt of samples must be coordinated with the laboratory to minimize time in transit. Samples should ideally arrive at the laboratory within one day after they are shipped (or sooner for microbiological samples) and be constantly maintained at about 4 degrees C during shipment.

If samples are relinquished by the sampler to another person for transport to the laboratory, proper chain of custody transfer documentation must be followed (see Section 17.10, below). **Custody of the samples should only be transferred to persons who are qualified to handle or transport them** (i.e., FDGTI technical personnel, certified couriers, or laboratory personnel).

Some samples (notably, product samples) are legally classified as hazardous substances because of the contaminants they contain, and as such they are under the control of federal regulations that govern the transport and handling of hazardous materials. It is the responsibility of FDGTI personnel to be aware of all regulations regarding the transport of samples containing specific contaminants and to conform to those regulations. If in doubt as to the legality of shipping a batch of samples, consult the FDGTI legal department **before arranging shipment**.

For information about legal requirements for packaging and shipping petroleum oils and other hazardous materials, refer to U.S. Postal Service Publication 52, “Acceptance of Hazardous, Restricted, or Perishable Matter,” the Domestic Mail Manual, Part 124, “Nonmailable Matter - Articles and Substances; Special Mailing Rules,” and the packaging requirements listed in the Domestic Mail Manual, part 121.

17.10 Chain of Custody Procedures

17.10.1 Importance

The purpose of chain of custody (COC) procedures is to permit traceability from the time samples are collected until all data has been generated. The procedures are intended to document sample possession from the time of collection and disposal. This practice provides documentation during each step, that is, during shipping, storage, and during the process of analysis. A COC is necessary if there is any possibility that analytical data or conclusions based upon analytical data will be used in litigation. This possibility is assumed to exist on **every** FDGTI project. Therefore sampling COC procedures **must** be followed during every sampling event, and the information contained on the COC must accurately represent the sample collection information and the associated analytical requests.

17.10.2 Field Custody Procedures

As few people as possible should handle samples.

The field sampler is personally responsible for the care and custody of the samples collected until they are properly transferred.

Labels or tags should be firmly attached to the sample containers and made of waterproof paper. Use waterproof ink to label the sample.

The field supervisor (i.e., the lead FDGTI person on site) determines whether custody procedures are being followed during the field work and decides if additional samples are required (the project manager must be notified immediately if the pre-planned sampling protocol is to be changed).

17.10.3 Chain of Custody Record

A blank copy of a typical COC record is included as Figure 17-2, attached. All laboratories and some customers furnish blank COC records, and they are all essentially the same as the one shown in Figure 17-2. All information listed below that is required to be recorded must be recorded on the COC form. If a place does not exist on the form for the recording of any of the required information, then that information should be recorded in an existing “comments” or “remarks” section on the record or, at least, in the project field notes. A completed example of a completed COC for is presented as Figure 17-3 for reference.

As with all other field data, COC information should be recorded when the sampling is taking place. **Record all COC sampling data while on site.** Any errors on COC documents should be corrected by drawing a single line through the error. The error and the correction should be initialed and dated. If uncorrected errors are noted by the laboratory staff, the corrections must be made in writing by the project manager and submitted to the laboratory. These documents will also become part of the project file and must be dated and signed by the project manager.

The COC record accompanies the samples. When transferring possession of samples, the individuals relinquishing, the shipper, and the receiver of the samples are to sign, date, and note the time on the record. This record documents sample custody transfer from the sampler, often through another person, to the analyst in a laboratory. Document any opening or closing of sample storage containers (i.e., coolers) on the COC record.

17.10.4 Required Information

The following instructions describe the information required on the COC record. The numbers correspond to sections on the blank COC record shown in Figure 17-2, attached.

(1) *Project Manager*: Print the name of the project manager or the name of the person who should receive the laboratory report. **Note:** - the example COC does not have a space for recording the name of the company (i.e., FDGTI). Therefore, the company name should follow the project manager’s name in this section.

(2) *Address*: Enter the address of the project manager or the address of the person who should receive the report.

(3) *Project #*: Enter the FDGTI project number.

(4) *Phone #*: Enter the telephone number where the project manager or other contact person can be reached.

(5) *Fax #*: Enter the facsimile telephone number where preliminary laboratory results should be sent.

(6) *Site Location*: Enter the city and state where samples were collected.

(7) *Project Name*: Enter the name of the project.

(8) *Sampler Name*: Print sampler's name and the sampler should initial any existing statement regarding field sampling procedures.

(9) *Field Sample ID*: Enter one sample ID per line per matrix. Print the ID which will identify the sample, it should be identical to the sample ID on that sample's label. The ID must be limited to 8 characters.

(10) *Source of Sample*: This information is optional and is used to describe where the sample was taken from (e.g., "lagoon" or "sump").

(11) *Lab #*: For Lab Use Only. Do not write in this space.

(12) *# Containers*: Enter the total number of containers, regardless of analysis or preservation type, for the sample ID listed on that line.

(13) *Matrix*: Put a check in the appropriate box to describe the sample matrix. If the matrix is "Other" specify what it is in the *Remarks* section.

(14) *Method Preserved*: Put the number of containers in the box which describes the type of preservation used. If ice is used, put a check in that box. Describe "Other" types of preservation in the *Remarks* section.

(15) *Sampling Date*: Enter the date (month, day, year) the sample was collected.

(16) *Sampling Time*: Enter the time (military) the sample was collected.

(17) *Analysis Request*: Choose a method by putting a check in the box(es) in the appropriate column(s). Most COCs list the most common methods requested plus have several blank columns where you can request analytical methods that are not already listed by writing the method(s) in the heading (note the three blank columns on the attached record). Contact the laboratory's customer service if you have any questions regarding the type of method to choose or to schedule special analysis requests.

(18) *Special Handling*: Request special handling of the analysis and report by putting a check in the appropriate box(es). If you have been given a quote number, it should be recorded in this section.

(19) *Special Detection Limits*: Specify special detection limits if they are required. For example, if your sample is from a municipal water supply you may need to specify drinking water detection limits.

(20) *Special Reporting Requirements*: Specify any special reporting requirements.

(21) *Remarks*: Any additional information regarding samples, analyses requested, or special considerations must be noted here. Samples which are known to be highly contaminated can be noted in this section. Enter the method of shipment, courier's name(s) and other pertinent shipping information in this section. Additional project identifiers should be specified in this section (site location, site number, code, etc.).

(22) *Lab Use Only/Storage Location/Lot #/Work Order #*: Do not write in this space.

(23) *Relinquished by Sampler*: To be signed by the sampler at the time the samples are relinquished by the sampler to the carrier for shipment, or to any other authorized person.

(24) *Relinquished by/Received by Date*: The date is entered by the relinquisher at the time custody of the samples is relinquished to another person.

(25) *Relinquished by/Received by Time*: The time is entered by the relinquisher when custody of the samples is relinquished to another person.

(26) *Received by*: To be signed by each person who receives custody of the samples prior to the laboratory taking custody.

(27) *Relinquished by*: The final acknowledgment of transferral is signed by the person who relinquishes custody of the samples to the laboratory.

(28) *Relinquished by/Received by Date*: The final date is entered by the person who relinquishes custody of the samples to the laboratory.

(29) *Relinquished by/Received by Time*: The final time is entered by the person who relinquishes custody of the samples to the laboratory.

(30) *Received by Laboratory*: To be signed by laboratory log-in person at the time of sample receipt by the laboratory.

(31) *Waybill #*: The shipping waybill number will be entered in this box at the time of receipt of the samples by the laboratory.

Reminders: To best achieve project objectives, all samples should be scheduled at least 48 hours prior to shipment. In order to insure that holding time are met, all samples should be shipped the day of collection. All changes on the chain of custody document must be initialed by the project manager or sampler.

A separate COC record must accompany each separate shipment of samples. The sample storage containers (i.e., coolers) should be padlocked or sealed with tape or other sealing material prior to shipment to the laboratory.

Alternative procedures can be used to establish a new COC form or document whenever a transfer of custody is made. In these cases, both the transferer and the transferee should keep a signed receipt of such a transfer. Note these procedures in the field log.

The original COC record must accompany each shipment to identify its contents. A copy of the COC record is retained by the FDGTI project manager. If sent by mail, register the package with return receipt requested. Freight bills, post office receipts, and bills of lading should be retained as part of the permanent documentation.

17.10.5 Sample Seals

Sample seals are sometimes used to detect unauthorized tampering of samples following collection up to the time of analysis. Use waterproof adhesive paper seals for this purpose. If a seal is used, add the date and the sealer to the COC record or on the seal itself. Each seal must be attached in such a way that it is necessary to break the seal to open the sample container. Seals must be affixed to containers before the samples leave the custody of the sampling personnel. Each split sample must have its own seal.

17.11 Decontamination of Sampling Equipment

An appropriately developed, executed and documented equipment decontamination procedure is an integral and essential part of environmental site investigations. The benefits of its use include:
minimizing the spread of contaminants within a study area and from site to site;
reducing the potential for worker exposure by means of contact with contaminated sampling equipment; and
improved data quality and reliability.

The following reagents will be used to decontaminate equipment in the field:
a non-phosphate detergent solution;
an inorganic desorbing agent consisting of a 10% nitric or hydrochloric acid solution made from reagent grade nitric or hydrochloric acid and deionized water (1% is applied to low-carbon steel equipment);
an organic desorbing agent consisting of a pesticide grade isopropanol, acetone, or methanol solvent rinse;
control rinse water, preferably from a water system of known chemical composition; and organic-free, reagent grade deionized water.

Prior to initiating a field program that will involve equipment decontamination, a site specific decontamination protocol should be prepared. Information in the protocol should include:
site location and description;
statement of the sampling program objective and desired precision and accuracy;
summary of available information regarding hydrogeology and anticipated chemistry of the materials to be sampled;
listing of the equipment to be used for water and/or sediment sampling, and materials needed for decontamination;
detailed step-by-step procedure for equipment decontamination for each piece or type of equipment to be used and procedures for rinse fluids containment and disposal as appropriate;
summary of QA/QC procedures and QA/QC samples to be collected to document decontamination completeness including specific type of chemical analyses and their detection limit; and
outline of equipment decontamination verification report.

Equipment associated with water and sediment sampling can generally be defied as sample contacting equipment, i.e., equipment that can potentially come in direct contact with the water sample that will undergo chemical or biological analyses.

The general procedure for decontaminating sampling equipment is as follows:

Wash with detergent solution, using a brush made of inert material to remove any particles or surface film.

For equipment that, because of internal mechanism or tubing cannot be adequately cleaned with a brush (e.g., sampling pumps, bailers), the decontamination solutions should be circulated through the equipment.

Rinse thoroughly with control water.

Rinse with an inorganic desorbing agent (i.e., acid rinse). This step may be deleted if the samples will not undergo inorganic chemical analysis.

Rinse with control water.

Rinse with an organic desorbing agent (i.e., solvent rinse). This step may be deleted if the samples will not undergo organic chemical analysis.

Rinse with deionized water.

Allow equipment to air dry prior to next use.

Wrap equipment for transport with inert material (aluminum foil or plastic wrap) to prevent direct contact with potentially contaminated material.

Sample containers such as jars and vials are generally assumed to be pre-sterilized by the manufacturer or supplier. This should be confirmed prior to their use. Any equipment whose cleanliness is not confirmed should be decontaminated using the above process prior to use.

Depending on site conditions, it may be appropriate to contain spent decontamination rinse fluids. If this is the case, the appropriate vessel for fluid containment (i.e., a drum approved by the Department of Transportation or similar container suitable for this purpose) should be used depending on the ultimate disposition of the material.

Depending on site conditions, it may be desirable to perform all equipment decontamination at a centralized location as opposed to the location where the equipment was used. If this is the case, care must be taken to transport the equipment to the decontamination area such that the spread of contamination is minimized.

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ATTACH TABLE 1, SUMMARY OF BOTTOM SAMPLING EQUIPMENT, HERE
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ATTACH FIG. 17-1, COLIWASA SAMPLER, HERE
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ATTACH FIG. 17-2, BLANK COC RECORD, HERE
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ATTACH FIG. 17-3, EXAMPLE OF COMPLETED COC, HERE
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