REVISED REMEDIAL INVESTIGATION WORK PLAN
BROWNFIELD CLEANUP PROGRAM
GENESEE MARINA, INC.
118 PETTEN STREET
ROCHESTER, NEW YORK
SITE #C828130

Prepared For:	Genesee Marina, Inc. 118 Petten Street Rochester, New York
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1.0 INTRODUCTION

This Revised Remedial Investigation Work Plan (Work Plan) has been prepared by DAY Environmental, Inc. (DAY) on behalf of Genesee Marina, Inc., to further evaluate the nature and extent of contamination at 118 Petten Street, Rochester, New York (Site).

The Site is, or has been known as, the Riverview Yacht Basin, the Genesee Marina, and Gibbs Marina. A project locus map is attached as Figure 1. The approximate limits of the Site area are shown on Figure 2 – Site Plan Map.

The Site address was recently updated to 118 Petten Street, in the City of Rochester, Monroe County, New York, and is identified as part of SBL #61.300-0001-008.0 on City of Rochester tax maps. The Site has also been known as 00 Petten Street and 18 Petten Street Extension.

The Site is located in an urban setting and consists of approximately 25 acres, with an estimated 2,500 feet of frontage along the western shore of the Genesee River south of the Port of Rochester. The Site is improved with a marina known as Gibbs Marina. The marina includes multiple buildings, many of which are in poor condition, and more than 200 boat slips, some of which are not usable. There are two boat ramps located along the riverfront. The Site also contains asphalt and gravel roadways and parking areas, woods, and both federally and New York State Department of Environmental Conservation (DEC) regulated wetlands.

In May 2005, the Site property was subdivided into two lots to allow development of the Genesee Riverway Trail by the City on Lot #1, as shown on the filed Subdivision Map (See Figure 2). For purposes of this Work Plan, the Site is defined as Lot #2 as shown on the Subdivision Map. The Site is currently bounded to the west by Lot #1, which is now owned by the City. An active railroad spur owned by New York Central Lines LLC is located on the west side of Lot #1. The Site is bounded to the north by land (vacant) owned by the City, to the east by the Genesee River and to the south by land (vacant) owned by the City. Residential properties are located across the Genesee River and on the opposite side of the railroad spur to the west.

This Work Plan presents the approach, procedures, and scope of work for the proposed Remedial Investigation of the Site. Implementation of this Work Plan will allow for further evaluation of the environmental impacts to surface soil, subsurface soil, and groundwater quality associated with the marina use and former historical uses of the Site. In addition, other environmental media at the Site including surface water (river water) and sediment (river sediment) will be evaluated.

2.0 SITE BACKGROUND, PREVIOUS INVESTIGATIONS & PHYSICAL SETTING

2.1 Site Background

The Site has been operated commercially as a marina including boat slips, a boat repair shop, storage for boats and boat parts, and a retail boat refueling facility from approximately 1947 to the present. The Site has multiple areas that were used for waste disposal, consisting of construction and demolition debris and dredge spoils. The Site also contains offices, a shop, and a parking area for the *Spirit of Rochester* cruise boat, which ceased operations in 2003. Historic petroleum releases have occurred at the Site in the refueling area and the parking lot area. Drums that contain chemicals associated with marina operations, portable gasoline tanks, aboveground storage tanks (ASTs), and underground storage tanks (USTs) are also located at the Site. The Site is a registered bulk petroleum facility with three registered fuel tanks located at the refueling area. The Site has three septic systems, and sanitary/storm sewers are not present at the Site.

A portion of the Site was used as a railroad yard by the New York Central Railroad prior to the marina operation. Railroad spurs traversed the northern portion of the Site from approximately 1918 to 1978. The railroad spur along the western property boundary is still active. In the area formerly used as a railroad yard, the fill material contains railroad cinder and slag mixed with naturally occurring debris.

The Site is a Monroe County Environmental Management Council (EMC) Waste Disposal Site (number RO-109). The Site was used for the disposal of construction and demolition (C&D) debris from the 1960's to recently. The dumping observed by Monroe County also included dredge spoils.

These commercial uses suggest a possibility that historic on-site operations impacted the soil and groundwater quality at the Site. In addition, previous site investigations have revealed impact to soil and groundwater at the Site.

2.2 Previous Site Investigations

Three previous environmental site assessments and investigations, performed by Stantec Consulting Group Inc. (Stantec), were conducted on the Site and include: a Phase I Environmental Site Assessment (ESA), a Limited Phase II Site Assessment reported with the Phase I ESA, and a Phase II Site Assessment. These investigations are collectively referred to as previous investigations in this Work Plan. The Phase I ESA and Limited Phase II investigations were reported in June 2004. The Phase II Site Assessment reported in October 2004 was conducted at recognized environmental condition (REC) locations identified in Stantec's June 2004 Phase l ESA. DAY understands that a geotechnical report was also completed by Stantec; however, this report has not been reviewed by DAY. Stantec's project work and reports were performed on behalf of the City of Rochester, Division of Environmental Quality.

The results of previous investigations indicate detection of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and heavy metals in soil and groundwater samples. Waste disposal fill areas and storage tank locations were confirmed and non-compliance issues were also detailed. A summary of the relevant findings from these environmental reports that pertain to the

Site are presented below. The background information from the previous reports has been used by DAY to select some of the proposed locations for the surface and subsurface explorations detailed in this Work Plan. Other areas of the Site were not investigated during the previous investigations; therefore; proposed exploration locations have also been selected by DAY with respect to land use, former tank locations, and the extent of the Site.

2.2.1 Stantec Phase I and Limited Phase II Environmental Site Assessment (Stantec June 2004 Report)

The Stantec June 2004 Phase I and Limited Phase II ESA presented the conclusions relevant to the Site that are summarized below. Refer to the Stantec June 2004 Report for completed documentation and the locations of investigation and sample locations.

- On May 21, 2004 Stantec visited the subject property; however, at this time access to the interior portions of the two residential houses (Building Nos. 3 and 8) located at the Site, the Spirit of Rochester building (Building No. 9), and the leased sheds located at several docks were not made available. Visual observations were also limited at the time of the property visit due to the thick vegetative cover consisting of trees and brush, which may have precluded field observations of staining, dead or distressed vegetation, or other potential Site contamination concerns.
- The United States Fish and Wildlife Service (USFWS) National Wetlands Inventory designated the southern portion of the Site as a federally regulated wetland. The Rochester East Quadrangle indicates that the inlets are designated as a Riverine Lower Perennial Open Water Permanent Excavated (R20WHx) wetland and the southern portion of the Site is designated as a Palustrine Emergent Narrow-leaved Persistent Semipermanent (PEM5F) wetland. The New York State Department of Environmental Conservation (DEC) Freshwater Wetlands Map indicates that the southeastern portion of the Site is designated as a DEC regulated wetland (RH-9).
- Documentation received from Monroe County Department of Health (MCDOH), in the form of a letter dated November 28, 2000, from the DEC indicated based on an inspection of the Site on November 8, 2000, the DEC believes that the Site is operating as a conditionally exempt generator of hazardous waste. During the preparation of Stantec's June 2004 Report, the Site was not listed as a RCRA hazardous waste generator.

2.2.2 Stantec Phase II Environmental Site Assessment (Stantec October 2004 Report)

The report revealed several recognized environmental conditions associated with the subject property and included recommendations for Phase II investigations, remedial measures and regulatory compliance. The proposed scope of work for this investigation addressed the following recommendations from the Phase I and Limited Phase II ESA summary:

RCRA Hazardous Waste Generator Status
It was recommended that the Genesee Marina be notified that their facility was not in compliance with the EPA RCRA hazardous waste generator requirements.

Monitoring Well Plate
One of the Underground Storage Tank (UST) fill ports was covered with a monitoring well plate, and it was recommended that the monitoring well plate be replaced with an appropriate fill port cover.

Aboveground Storage Tanks (AST) and Portable Gasoline Tanks

It was recommended the tanks and their contents be properly removed and disposed of in accordance with applicable regulations, if the twenty-six (26) ASTs, the ten (10) 25-50-gallon portable gasoline tanks and the three (3) pump dispensers are not going to be used on-site. The tanks should be equipped with secondary containment and overfill prevention equipment, if the tank use on-site is to continue in the future.

Bird Droppings

It was recommended that the contractor be advised, if disturbance of the interiors of Building Nos. 5 and 7B and the debris located there, of the presence of bird droppings on the floors of these buildings so that any necessary precautionary measures can be taken to minimize potential exposure.

DEC Petroleum Bulk Storage (PBS) Regulations

It was recommended that the Genesee Marina be notified that their facility was not in compliance with the DEC's Petroleum Bulk Storage Tank regulation requirements, and that necessary registration paperwork should be prepared by the Genesee Marina facility to bring it into compliance with DEC's Petroleum Bulk Storage Tank regulations under 6 NYCRR Parts 612-614.

City representatives indicated that their in-house staff would address inaccessible structures and the investigation of suspect asbestos containing building materials should they pursue further activities at the site. Therefore, Stantec's investigation did not address the following investigation related recommendation:

Asbestos Containing Building Materials (ACBS)

It was recommended, if removal, demolition or maintenance of suspect ACBMs was planned, that the materials be sampled and analyzed for asbestos content at that time. If they are asbestos-containing (greater than one percent asbestos), or if they are assumed to be asbestos-containing, then abatement of these materials (repair, enclosure, encapsulation, or removal and disposal) prior to disturbance should be supervised by a licensed asbestos contractor in accordance with state and federal regulations in effect at that time.

Inaccessible Structures

It was recommended that access be obtained to Building Nos. 3, 8 and 9 to evaluate the potential presence of recognized environmental conditions.

Phase II ESA Recommendations

Based on the findings of the Phase I and Limited Phase II ESA, the recommendations listed below were developed, and the initial investigative portions of these recommendations were addressed by Stantec's Phase II ESA:

Spirit of Rochester Refueling Area and Parking Lot

Based on the MCDOH documentation reviewed (Hazardous Material Log Sheet dated August 15, 1988), it was recommended that an investigation be conducted in the vicinity of the Spirit of

Rochester refueling area and parking lot to determine if the soil and/or groundwater in these areas have been impacted from historic releases.

Former Underground Storage Tanks (USTs)

Three (3) composite soil samples were collected as part of the former UST removal. DEC guidance requires collection of discrete grab samples from all four sides of an excavation plus the bottom; and neither soil nor groundwater analytical results were available for review at the time the Stantec Report was prepared. Therefore, it was recommended that a subsurface investigation (i.e. soil boring with sampling and analysis, and groundwater monitoring well installation with sampling and analysis) be performed in the vicinity of the former UST area to investigate potential impacts to the underlying soils and/or groundwater.

Given that the quantity of contaminated soil from the former UST excavation that was reportedly bio-remediated and spread on-site is unknown, the location where this material was disposed is unknown, and results from the bio-remediated soil were not available at the time the Stantec Report was prepared, it was recommended that the location of the remediated soil from the former UST tank excavation that was spread on-site by Mr. Suhr be determined and an investigation be conducted in this area or in the vicinity of this area to determine potential impacts from the former UST area soil spreading activities.

Existing Underground Storage Tanks (USTs)

Given that Lt. Lill, City of Rochester Fire Marshal, had issued orders requiring the existing USTs be removed and given that these tanks were in violation of the NYS Fire Code and City of Rochester Fire Prevention Code, it was recommended that the three (3) 4,000-gallon USTs be removed in accordance with federal, state and local regulations. At the time of UST removal, an investigation should be performed in accordance with federal UST regulations and DEC guidance to determine if a release has impacted soil, groundwater, sediments, and/or the Genesee River. Note, the activities described above were not performed as part of the Stantec Phase II ESA.

Prior to the UST removal, it was recommended that a subsurface investigation be performed in the vicinity of the USTs to investigate the possibility of historic discharges of petroleum products to the soils and/or groundwater.

550-Gallon Underground Storage Tanks Filled with K-Crete

Given that three (3) 550-gallon USTs were closed in place by Genesee Marina, the location of these tanks was unknown, and no soil or groundwater investigations were performed in conjunction with the tank closures, it was recommended that a geophysical survey be performed to determine the location of these tanks. Once the location of the tanks is determined, it was recommended that a subsurface investigation (i.e. soil boring with sampling and analysis, and groundwater monitoring well installation with sampling and analysis) be performed in the vicinity of these tanks to investigate the possibility of historic discharges of petroleum products to soils and/or groundwater.

Floor Drain

It was recommended that the discharge of petroleum products to the floor drain inside Building No. 7A be stopped. It was also recommended that the floor drain inside Building No. 7A be properly cleaned and the contents of the drain be removed and properly disposed. After the floor drain has been cleaned, it was recommended that the location of the final discharge point of the floor drain be determined. If it is determined that the floor drain discharges to the surface or sub-surface, then the floor drain should either be permanently decommissioned or covered with approved drain covers (i.e., SpilMagnet®, Jomac®) and re-routed to the appropriate sewer system in conformance with any applicable permits. In addition, if it is confirmed that the floor drain discharges to the ground subsurface or sub-surface, it was recommended that a subsurface investigation be performed in the vicinity of the discharge location to evaluate potential impacts to the on-site soil and groundwater.

Illegal Dumping/On-site Fill Material/Black Granular Material Observed

Given that the subject property is a confirmed EMC Waste Disposal Site and a sample of black granular material (SS-4) contained elevated concentrations of metals that exceed DEC TAGM 4046 recommended soil cleanup objectives, it was recommended that a site-wide investigation (i.e. test pit program and/or drilling with sampling and analysis) of the on-site fill materials and the black granular material be conducted in order to further delineate the lateral and vertical extent of fill materials.

Dredge Spoils

Based on documentation provided by the MCDOH and given that the subject property is a confirmed EMC Waste Disposal Site, it was recommended that the disposal location of dredge spoils be identified and investigated to evaluate the possibility of soil and/or groundwater impacts from the historic disposal of dredge spoils on-site.

Former On-site Railroad Activities

Given that railroad spurs traversed the northern portion of the subject property from at least 1918 to at least 1978, it was recommended that a soil sampling program be conducted in this area to evaluate the potential presence of residual railroad related impacts (i.e. ballast; spills from railroad activities).

Aboveground Storage Tanks and Portable Gasoline Tanks

In conjunction with removal or retrofitting of the ASTs and portable gasoline tanks, it was recommended that a subsurface investigation be performed to investigate the possibility of historic discharges of hazardous materials or petroleum products to the underlying soils and/or groundwater.

On-site Septic Systems

Given that there are reportedly four (4) septic systems on-site, several complaints have been reported to the DEC and the MCDOH regarding sewage backup and sewage discharge into the Genesee River, and the possibility that hazardous materials and/or petroleum products were discharged to the septic systems, it was recommended that a subsurface investigation (i.e. soil boring with sampling and analysis, and groundwater monitoring well installation with sampling and analysis) be performed in the vicinity of the septic systems to investigate the possibility of historic discharges of hazardous materials or petroleum products to the underlying soils and/or groundwater.

Waste Disposal Areas

It was recommended that the contents of the various disposal areas located on the subject property (Disposal Areas A, B, C, D, E, F, G, and H) be properly removed and disposed in accordance with applicable regulations. In conjunction with, or prior to the removal of the various disposal areas, it was recommended that a subsurface investigation (i.e., test pit investigation and/or drilling program) be conducted in the disposal areas or in their vicinity to determine potential impacts from the disposal activities.

Limited Phase II ESA

Based on the analytical results from the limited Phase II ESA program, remediation was recommended in the areas of SS-2, SS-3, SS-4, FD-1 and SED-1. However prior to remediation, in order to further delineate the lateral and vertical extent of the contamination, additional sampling for SVBN TICs is recommended in the SS-3 and SS-4 sample collection areas; additional sampling for metals (in particular cadmium, chromium, mercury and lead) was recommended in the SS-4, SS-5 and SED-1 sample collection areas; and additional sampling for TPH was recommended in the SS-2, SS-3, FD-1 and SED-1 sample collection areas.

Historical/Current Activities in Building Nos. 6, 7A and 7B

Based on the historical presence of a boat repair shop and the observations made by Stantec on May 21, 2004 in Building Nos. 6, 7A and 7B, there is a potential that releases from the repair operations may have impacted the site. Therefore, it was recommended that a subsurface investigation be performed inside and outside Building Nos. 6, 7A and 7B to evaluate potential impacts from historic on-site operations.

Areas of Concern (AOCs)

To assist in the development of the scope of work for the Phase II ESA, the findings and implementation of the associated recommendations from the Phase I were grouped into the following six geographically based Areas of Concern (AOCs):

- AOC–1 including Waste Disposal Area “B” and Black Granular Material;
- AOC–2 including Waste Disposal Area “C”, Building Nos. 7A and 7B and Floor Drain;
- AOC–3 including Waste Disposal Area “D” and Septic System near “D”;
- AOC–4 including Waste Disposal Areas “E”, “F” and “G” and Dredge Spoils;
- AOC–5 including Former and Existing UST Areas, Building No. 6 and Septic System near Existing USTs; and
- AOC–6 including Waste Disposal Area “A”, the Spirit of Rochester Refueling Area and Parking Lot and Former On-site Railroad Activities

These AOCs are depicted on Figure 3 – Stantec Figure #7: Exceedances of Recommended Cleanup Objectives and Figure 4 – Stantec Figure #9: Exceedances of Class GA Groundwater Standards. The AOC designations generally served as the basis for the scope of the Phase II ESA described below. These AOC’s will be used for the proposed Remedial Investigation that is detailed in this Work Plan.

DAY has also designated the other portions of the Site that require investigation as Area 7 through Area 11, see Figure 5 – Proposed Surface Soil, Surface Water, and Sediment Sample Location Map.

Findings

The Stantec October 2004 Phase II ESA revealed the following evidence of recognized environmental conditions in connection with the subject property at that time.

AOC #1 - Waste Disposal Area B and Black Granular Material (sand blasting media)

AOC #1 is located in the north central portion of the site. It was used for boat and boat part storage. The subsurface is characterized by fill materials containing construction and demolition (C&D) debris ranging from 8 to 14 ft in thickness and is underlain by very soft brown silty peat over very soft gray silt.

The soil analytical program in this area revealed the following: 1) RCRA metals, including arsenic, barium, chromium, lead, and mercury, were present above NYSDEC TAGM 4046 Recommended Soil Cleanup Objectives (RSCOs) either in black granular fill (SS-4), beneath batteries (SS-5), or in TP-17; and 2) SVOCs were present above their respective RSCOs in test pits TP-15 and TP-13.

The AOC #1 groundwater analytical program revealed the presence of naphthalene in excess of its respective Groundwater Quality Standard (GWQS) at MW-36. The source of the Naphthalene was suspected to have originated from the fill materials in this area.

AOC #2 - Waste Disposal Area C, Buildings 7A and 7B, and Floor Drains

AOC #2 included the main office and shop areas (Buildings 7A and 7B), and also adjacent debris storage located in the central portion of the site. The subsurface is characterized by fill materials containing construction and demolition (C&D) debris ranging from 7 to 8 ft. in thickness and is underlain by very soft brown silty peat over very soft gray silt.

The soil analytical program in this area revealed the following: 1) SVOC TICs are present above RSCOs in the sediments in the shop area; and 2) SVOC TICs are present above RSCOs in the floor drain in building 7A.

The groundwater analytical program did not identify groundwater concerns in AOC #2.

AOC #3 - Waste Disposal Area D and Septic System near Area D

AOC #3 is located in the west central portion of the site and is used for boat and debris storage/staging. The subsurface is characterized by fill materials containing construction and demolition (C&D) debris ranging from 7 to 20 ft. in thickness and is underlain by very soft brown silty peat over very soft gray silt.

The soil analytical program in this area revealed the following: 1) the presence of methylene chloride in the soil at test pit TP-11A above its RSCO; 2) the RCRA metal mercury above RSCO at soil boring SB-24; and 3) SVOCs above RSCOs in test pit TP-11A and boring SB-24.

The AOC #3 groundwater analytical program revealed the presence of carbon disulfide, in excess of its GWQS at MW-23. The source of the carbon disulfide in this AOC is unknown. However, carbon disulfide was reported to be present in the fill material located in AOC #1 and AOC #6.

AOC #4 - Waste Disposal Areas E, F, G, and Dredge Spoils

AOC #4 is located in the southern portion of the site and is used as a staging area by Dissen & Juhn Marine, a contractor, and as a boat and debris storage area by the marina. The subsurface is characterized by fill materials containing construction and demolition (C&D) debris ranging from 4 to 16 ft. in thickness, and is underlain by very soft brown silty peat over very soft gray silt.

The soil analytical program in this area revealed the following: 1) methylene chloride and/or acetone were present in the soils at test pits TP-1 and TP-3 above their respective RSCOs; 2) the presence of RCRA metals, including arsenic and/or mercury, above RSCOs in test pit TP-1 and boring SB-32; 3) SVOCs were present above RSCOs in TP-1; and 4) the presence of TPH above the NYSDEC suggested clean-up level of 500,000 ppb in SB-32. The fill materials in this area are believed to be the source of these findings.

The groundwater analytical program did not identify groundwater concerns in AOC #4.

AOC #5 - Former and Existing UST Areas, Building 6 and the Septic System near the Existing USTs

AOC #5 located in the central portion of the site and was used for storage (including Building #6 and the Quonset hut) and for boat re-fueling. The subsurface is characterized by fill materials containing construction and demolition (C&D) debris ranging from 4 to 11.5 ft. in thickness. The fill thins to the east toward the river and is underlain by very soft brown silty peat over very soft gray silt.

A geophysical survey revealed an anomaly along the east wall of building 6 which was interpreted to represent the suspected location of the closed in place underground storage tanks (USTs). This area was investigated as part of the test pit program. TP-20 contained black stained soil with a petroleum odor but did not contain RSCO exceedances.

The soil analytical program in adjacent borings revealed the presence of SVOCs and RCRA metals, including arsenic and lead, above RSCOs in SB-16 and SB-19, respectively. The source of the SVOC exceedances is suspected to be the former USTs located near SB-16.

The AOC #5 groundwater analytical program revealed the following: 1) the presence of petroleum based VOCs in both MW-16 and MW-22; and 2) the presence of one SVOC (naphthalene) and one RCRA metal (arsenic) in the groundwater at MW-16. As stated above MW-16 is located near the former USTs, while MW-22 is located down gradient of the current

USTs. The former or current USTs are the suspected source of the VOC and SVOC contaminants.

AOC # 6 - Waste Disposal Area "A", the Spirit of Rochester Area and Parking Lot and Former On-site Railroad Activities

AOC #6 is located at the northern end of the site and is used for boat trailer storage and vehicle parking for the Spirit of Rochester cruise boat. The Spirit of Rochester office and gift shop are located in the area which was previously used as a former railroad yard. The subsurface is characterized by fill materials containing railroad cinder and slag with some re-worked native materials ranging from 2 to 12 ft. in thickness. The fill thins to the east towards the river and is underlain by very soft brown silty peat over very soft gray sandy clay and silt.

The soil analytical program in this area revealed the following: 1) the presence of methylene chloride at soil boring GP-7 above its RSCO; 2) the presence of RCRA metals, including arsenic, and/or mercury, above RSCOs in test pit TP-19 and/or soil boring GP-2; and 3) SVOCs above RSCOs in soil boring GP-5. The fill materials in this area are believed to be the source of these findings. The groundwater analytical program did not identify groundwater concerns in AOC #6.

The surface soil and subsurface soil sample locations, from previous investigations, with concentrations of chemical compounds that exceed NYSDEC TAGM 4046 RSCOs are presented on Figure 3. The locations of groundwater samples, from previous investigations, that exceed groundwater quality standards are presented on Figure 4.

2.3 Physical Setting

The Site consists of approximately 25 acres that includes an active marina, parking areas, and vacant land. The parcel is known as 118 Petten Street (Tax I.D. No. 061.300-0001-008) located in the City of Rochester, Monroe County, New York. The Site is zoned Harbor Town-Village District (H-V). The Site area is known as the Gibbs Marine, Riverview Yacht Basin and the Genesee Marina.

2.3.1 Geology

Site Soils

There are two (2) general subsurface areas that were revealed by test pit excavation and soil borings conducted in previous investigations. Both areas are characterized by miscellaneous fill underlain by native soils. The fill materials across the entire Site range in thickness from two (2) to twenty (20) feet.

The largest area of fill covers the central and southern portions of the site. This fill area extends south from the southern border of the former railroad yard. In this area the fill consists of construction and demolition (C&D) debris and is underlain by native materials. The thickness of the C&D fill ranged from approximately four (4) feet to twenty (20) feet. The average thickness of the C&D fill was approximately eight (8) feet. The C&D fill is very heterogeneous with materials ranging from bricks, concrete, wood, metal, and other building materials to creosote soaked timbers and boat parts.

The smaller fill area is the former railroad yard located in the northern portion of the site. The fill in this area ranges in thickness from two (2) to twelve (12) feet, with an average thickness of 8.5 feet. The fill is characterized by cinder and slag with some re-worked native materials.

Brown silty peat underlain by gray clay and silt characterizes the native materials under the central and southern fill area. In the northern portion of the site, the peat layer is absent and the fill is in direct contact with the gray sandy clay and silt.

Site Bedrock

The depth to the top of bedrock varies from approximately 66 feet to approximately 102 feet below ground surface at the Site (Stantec 2004). The bedrock surface was encountered during a limited geotechnical evaluation (Stantec 2004 Report). Stantec completed a geotechnical investigation report that documents the bedrock encountered.

3.0 PRELIMINARY EVALUATION OF CONTAMINANTS OF CONCERN AND POTENTIAL MIGRATION PATHWAYS

Contaminants of Concern (COC)

Previous Site historic uses and operations involving: land filling activities (waste disposal), marina operations, petroleum releases, and bulk petroleum storage have impacted the subsurface soil and overburden groundwater at the Site based on the laboratory analytical soil and groundwater results from the previous investigations. The contaminants of concern (COCs) are based on the laboratory analytical results from environmental media sampled during previous investigations that include: volatile organic compounds (VOCs - petroleum chemical compounds and solvents), semi-volatile organic compounds (SVOC's – petroleum chemical compounds), and metals (heavy metals). Additional sample collection and laboratory analysis will be conducted for the contaminants of concern during the BCP Remedial Investigation. Polychlorinated bi-phenols (PCB's) were not detected in environmental samples from previous investigations and are not considered a contaminant of concern. However, the previous investigations were limited to specific areas at the site and BCP requirements require complete Site characterization. Therefore, sample collection and laboratory analysis for PCB's and pesticides will be conducted as part of the proposed Remedial Investigation for the BCP detailed in this work plan.

Potential Routes of Migration

The VOC chemical compounds detected in soil and groundwater samples from previous investigations include petroleum chemical compounds (gasoline) and solvents. The SVOC chemical compounds detected include petroleum chemical compounds (diesel and oils & grease). The potential routes of migration for VOC and SVOC contaminants may include the following:

- Volatilization directly from the ground surface into the air;
- Migration horizontally and vertically through the overburden soil;
- Migration vertically into the overburden groundwater; and
- Migration horizontally in the overburden groundwater with discharge to surface water (Genesee River);
- Migration vertically from surface water to sediment (river sediment).

Metals were detected in soil and groundwater samples from previous investigations that include heavy metals (arsenic, lead, chromium, and mercury). The potential routes of migration for metals (heavy metals) may include the following:

- Migration horizontally by means of overland flow (surface run-off);
- Migration vertically into the overburden groundwater;

- Migration vertically from subsurface soils to overburden groundwater;
- Migration horizontally from overburden groundwater to surface water (Genesee River);
- Migration vertically from surface water to sediments (river sediment).

Additional information is required to evaluate the potential for migration of contaminants of concern (COC) at the Site via the various pathways listed above. The potential migration of COCs may also impact potential off-site receptors. General assumptions can be made based on the physical properties of COCs, Site uses, subsurface conditions, Site setting and existing information. Historic spills and releases of COC may result in potential leaching into the subsurface media and discharge to the Genesee River (surface water) and underlying river sediments. Although some breakdown of COCs may occur in the subsurface and surface water over time, the remaining chemical compounds and metals may migrate vertically through the soils and impact overburden groundwater and river sediments. Therefore, the following environmental media will be sampled: surface soil, sediment, subsurface soil, and overburden groundwater. In addition, the potential migration pathways will be evaluated using exploration techniques that include: collection of environmental samples, soil borings, well installations, test pit excavations, and field observations.

4.0 WORK PLAN RATIONALE

This section presents the requirements for additional data and scope of work to further evaluate the nature and extent of VOCs, SVOCs, and heavy metals (the COCs) on the Site. As stated previously, PCBs were not detected during previous investigations; however, they will be evaluated during this Remedial Investigation (RI) due to the substantial extent of former waste disposal at the Site and BCP project requirements. In addition, pesticides and cyanide will be included in the sampling to meet the BCP requirements for this RI. The data requirements identified have been developed based on the current understanding of the historical Site uses and previous soil and groundwater sample results. This section also presents the work plan approach for future implementation of the BCP Remedial Investigation, in general accordance with DER–10 NYSDEC guidance methods and procedures.

4.1 Identification of Data Requirements

An evaluation of environmental media with respect to volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and heavy metals detected in previous samples collected from the Site, was conducted. Based on BCP requirements, the project data requirements will also include laboratory analysis for cyanide, PCBs, and pesticides. Environmental media samples will be collected as described below in Sections 6.1.2.1 to 6.1.2.7; from 75 surface soil and near surface soil samples, six (6) sediment samples (10 samples were collected on September 7 & 8, 2005 at five (5) locations by the property lessee), three (3) surface water samples, subsurface soil samples from 40 test pit locations, subsurface soil samples from 25 test borings, groundwater samples from 10 proposed new groundwater monitoring wells, and groundwater samples from 15 existing monitoring wells. Surface soil and subsurface soil samples (boring and test pit soil samples) will be field screened using PID and XRF technology. The field screening results will determine which samples will be collected for off-site laboratory analysis. The samples selected for off-site laboratory analysis will be biased towards those samples which have the highest elevated field screening results and with concurrence with the on-site NYSDEC representative. In addition to elevated field screening results, the samples collected will also be biased towards stained soil areas, stressed vegetation, as well as on past and present uses of the sample area. At a minimum, one surface/near-surface soil, soil boring sample, and test pitting sample will be collected from each area of concern at the Site. More soil samples may be collected where elevated field screening results in borings and test pits indicate multiple intervals of potentially contaminated soil to delineate the Site. Table 1 provides a Summary of Sampling and Analysis Requirements for this project.

4.2 Work Plan Approach and Other Project Plans

The approach of this Work Plan is to present the methods and procedures for the proposed investigations on the Site in general accordance with NYSDEC DER-10 guidance requirements. The Work Plan focuses on data requirements and exploration techniques at locations of environmental concern based on historical Site uses and operations. Data requirements are proposed to supplement the data from previous investigations, investigate areas that have not been characterized, and complete the investigation requirements for the BCP. Therefore, site investigation activities proposed in the sections of this Work Plan were developed to present investigative methods and procedures for addressing each of the identified data requirements based on the previous Site investigations and BCP requirements.

Investigation activities will include: collection of and field screening of 75 surface soil and near surface soil samples, and subsequent selection and analysis of 30 surface soil samples from these locations; collection and analysis of three (3) surface water samples; collection and analysis of six (6) sediment samples; collection and field screening of subsurface soil samples from 40 test pit locations, and subsequent laboratory analysis of 20 subsurface soil samples from these locations; collection and field screening of subsurface soil samples from 25 test borings, and subsequent laboratory analysis of 15 subsurface soil samples from these locations; collection and analysis of groundwater samples from the 10 proposed monitoring wells and the 15 existing monitoring wells. These combined proposed investigations total 99 analytical laboratory samples from 174 test locations. The investigation locations are Site wide in designated Areas of Concern (AOCs #1 through #6) and other Areas (Areas #7 through #11). The observations and laboratory results from the proposed sampling locations will be used to evaluate the nature and extent of contaminants of concern in environmental Site media. The results of the RI will be summarized in a Remedial Investigation Report (RI Report) for the proposed investigation. These results may also be used in an evaluation of potential migration pathways, in a qualitative risk assessment, and in a Fish & Wildlife assessment.

Health and Safety Plan (HASP)

A Site specific health and safety plan (HASP) and Community Air Monitoring Plan (CAMP) are required for BCP project work. A HASP that includes a CAMP has been prepared for this project and will be submitted under separated cover. The HASP will be maintained on-site during the field investigation activities. A DAY representative will act as the on-site health and safety coordinator. The health and safety coordinator will also monitor the site conditions in accordance with the provisions of the HASP and CAMP.

Citizens Participation Plan (CPP)

A Citizen Participation Plan (CPP) is part of the project requirements for the BCP. The CPP provides details for citizen involvement during the BCP project work. Citizen participation provides an opportunity for the NYSDEC/Health departments and the participant to obtain information from the public that may assist the participant with information to present or address during BCP project work.

The primary objective of citizen participation is aimed at increasing public understanding of the investigation (and subsequent remediation) project work process. The CPP purpose is to keep the public informed of the activities at the Site. This is achieved through periodic activities such as public meetings and fact sheet mailings.

A CPP has been developed by Knauf Shaw LLP under the BCP and was presented under separate cover for Genesee Marina, Inc. NYSDEC is committed to informing and involving the public concerning the investigation and remediation of the Site. The CPP describes the public information and involvement program that will be carried out with assistance from Genesee Marina, Inc. who has applied and been accepted to participate in the BCP. The CPP also identifies NYSDEC project contact(s) to whom the public may address questions or request information about the Site. The locations of the Site's document repositories are also identified in the CPP. The document repositories provide convenient access to important project documents and the brownfield site contact list for public review and comment.

Quality Assurance Project Plan (QAPP)

A quality assurance project plan (QAPP) is required for the BCP project work and describes the policies, organizations, project activities, and quality assurance and quality control (QA/QC) protocols necessary to meet the objectives of the BCP. A detailed project description including the overall project objectives, site background and setting, and an initial evaluation of the site conditions, is presented in Sections 1, 2, 3, 4, and 5 of this Work Plan. Sampling procedures, sample custody, and analytical procedures are addressed in Section 6. The overall objective of this QAPP is to provide a mechanism for control and evaluation of the quality of data to be acquired throughout the course of the Remedial Investigation for the Site.

Project Personnel

The environmental project personnel are presented on the Project Organization Chart attached in Appendix A.

Site Signage Requirement

DAY understands that the NYSDEC requires a sign at sites where remedial activities are being performed under the BCP. When future remedial activities are scheduled, a sign will be conspicuously posted at the Site prior to the start of remedial site work. An example of the proposed signage is included as Appendix B. The erected sign will reflect the actual holders of the positions indicated on the sign at the time the sign is installed.

5.0 REMEDIAL SITE INVESTIGATION TASKS

This section describes the proposed tasks to be implemented as part of the proposed remedial investigation of the Site. The tasks to be performed as part of the remedial investigation are described in the following sections of this Work Plan.

Task 1 – Preliminary Evaluation of Potential Environmental Concerns

This task was performed during the review of existing data during preparation of this work plan. A summary of the results of the preliminary evaluation of potential Environmental Concerns is presented in Sections 1 through 3 of this Work Plan and the distribution of contaminants of concern (COC) that exceed NYSDEC standards is shown on Figures 3 and Figure 4 for soil and groundwater, respectively. A total of six (6) areas of concern (AOCs – designated AOC #1 through AOC #6), five (5) other areas (designated Areas #7 through #11), have been identified during the preliminary evaluation of potential environmental concerns.

Task 2 – Project Planning

The activities associated with this task involve the evaluation of the data generated during Task 1, preparation of this Work Plan, preparation of a Health & Safety Plan, preparation of a Citizen Participation Plan, and field sampling requirements. This task also involves the identification of the scope of work for the tasks and associated schedule to be performed throughout the Remedial Investigation. The schedule for calendar dates to implement the proposed Remedial Investigation may be modified upon NYSDEC approval of the Work Plan.

Task 3 –Remedial Investigation of the Site and Potential off-Site Locations

This task will involve the implementation of the Remedial Investigation activities as presented in Section 6.1 of this Work Plan. These investigation activities will include, soil borings, surface soil sampling, test pit explorations, overburden monitoring well installation, sediment sampling, surface water sampling, and groundwater sampling from proposed monitoring wells and existing monitoring wells.

Prior to the commencement of subsurface exploration field work, an underground utility stakeout will be conducted to minimize the potential for the disturbance of utilities during project subsurface work.

Task 4 – Remedial Investigation Data Analysis

This task will involve the evaluation of the results of the Remedial Investigation. The purpose of this task is to determine if investigation (characterization) of the Site has been completed to allow for the preparation of a qualitative risk assessment (Task 5), Fish & Wildlife Assessment (Task 6), and preliminary evaluation of remedial alternatives. In the event that the investigation results do not complete the Site characterization and off-Site evaluation requirements, recommendations for additional investigation will be provided in a subsequent work plan document.

Surface soil and subsurface soil sample analytical results may be compared to Soil Cleanup Objectives (SCGs) referenced in NYSDEC 6 NYCRR §375.6 dated December 14, 2006, and/or other appropriate and relevant criteria. Sediment samples will be compared to NYSDEC Technical Guidance of Screening Contaminated Sediments updated January 1999. Surface water and groundwater sample analytical results will be compared to groundwater standards and guidance values referenced in NYSDEC TOGS 1.1.1 data source 1998 and amended by NYSDEC Table 1, dated August 1, 2001.

If VOCs are detected in the soil and/or groundwater samples which exceed the appropriate standards, criteria, or guidance concentrations, a vapor intrusion work plan will be developed and submitted to the NYSDEC, NYSDOH, and MCDOH for review and approval. Subsequent to approval, the vapor intrusion investigation will be conducted.

Task 5 – Qualitative Risk Assessment

A qualitative exposure assessment consists of characterizing the exposure setting (including the physical environment and potentially exposed human populations), identifying exposure pathways, evaluating contaminant fate and transport. An exposure pathway describes the means by which an individual may be exposed to contaminants originating from a site. An exposure pathway has five elements: (1) a contaminant source; (2) contaminant release and transport mechanisms; (3) a point of exposure; (4) a route of exposure; and (5) a receptor population.

The source of contamination is the source of contaminant release to the environment (any waste disposal area or point of discharge); if the original source is unknown, it is the environmental medium (e.g. surface soil, surface water, sediments, air) at the point of exposure. Contaminant release and transport mechanisms carry contaminants from the source to points where people may be exposed. The exposure point is a location where actual or potential human contact with a contaminated medium may occur. The route of exposure is the manner in which a contaminant actually enters or contacts the body (i.e., ingestion, inhalation, dermal absorption). The receptor population is the people who are or may be exposed to contaminants at a point of exposure.

An exposure pathway is complete when all five elements of an exposure pathway are documented; a potential exposure pathway exists when any one or more of the five elements comprising an exposure pathway is not documented. An exposure pathway may be eliminated from further evaluation when any one of the five elements comprising an exposure pathway has not existed in the past, does not exist in the present, and will never exist in the future.

To perform a qualitative exposure assessment, site conditions are characterized to evaluate whether a site poses an existing or potential hazard to the exposed or potentially exposed population. Site characterization involves a review of sampling data for environmental media (e.g., soil, surface water, groundwater, air), both on-site and off-site, and an evaluation of the physical conditions of the contaminant sources or physical hazards near the site which may pose an additional health risk to the community.

Task 6 – Fish and Wildlife Assessment

The NYSDEC has requested a Fish and Wildlife Analysis (step l through step ll B) in accordance with the NYSDEC's Fish and Wildlife Impact Analysis for Inactive Hazardous Waste Sites, October 1994. The procedures outlined in Step I of the Fish and Wildlife Analysis (FWIA) document are entitled "Site Description." Step I is subdivided into four (4) specific tasks: A - Site Maps, B – Description of Fish and Wildlife Resources, C – Description of Fish and Wildlife Resource Value, and D – Identification of Applicable Fish and Wildlife Regulatory Criteria. The procedures outlined in Step II of the FWIA document are titled "Contaminant-Specific Impact Assessment." Step II is also subdivided and DAY proposes that subsections A and B of Step II be completed for this Site as an initial assessment. Step II subsection A indicates the need for a pathway analysis including Site fish and wildlife resources as well as potential pathways of contaminant migration and exposure. Subsection B of Step II is titled "Criteria-Specific Analysis" and includes the comparison of Site-specific contaminant levels with numerical criteria to provide an assessment of potential impact. Completion of the remaining tasks for a complete Fish and Wildlife Assessment will be evaluated upon the results of the proposed work.

Laboratory samples submitted for this project work will include three (3) surface water samples from approximately 20 to 25 feet from the Genesee River shore (e.g. near the end of existing boat docks, where available). The surface water samples will be collected at three (3) locations where river sediment samples are proposed. Surface water and sediment samples will be collected from the locations shown on Figure 5. These samples will be analyzed for Target Compound List (TCL), VOCs plus Tentatively Identified Compounds (TICs), TCL SVOCs plus TICs, TAL metals plus cyanide, pesticides, and PCBs. In addition, each sediment sample will be tested for total organic carbon and each surface water sample for hardness. Sediment samples will be compared to criteria referenced in the NYSDEC Technical Guidance for Screening Contaminated Sediments dated January 1999. The surface water samples will be compared to Surface Water Standards and Guidance Values referenced in TOGS 1.1.1.

Task 7–Remedial Investigation Report

The results of the remedial investigation will be presented to the participant, the NYSDEC, the NYSDOH, and the MCDOH in a RI Report. The report will document the fieldwork, an evaluation of analytical results in the context of previous Site data/off-Site data, and recommendations for additional investigations or assessments, if required. The report will also include figures and summary tables of analytical results and project data.

The RI Report will be prepared in accordance with Section 3.14 of DER-10 and Section 3.10 of the BCP Guidance. The supporting documentation will also include a table of PID measurements, field screening results, site photographs, updated site figures, well development and sampling logs, test boring logs, test pit logs, and a Data Usability Summary Report (DUSR). The DUSR will be prepared using Appendix 2B of DER-10. The results of the RI Report will be summarized as part of this task. The report will include the following:

- Documentation of the observations and investigation activities performed.

- Evaluation of the distribution of contaminants detected.

- Tabulated summaries of soil and groundwater sample, field screening data, and analytical laboratory data.

- Figure presentations that include horizontal and vertical distribution of constituents in the environmental media at the Site.

- Recommendations for any further investigation activities necessary to complete characterization of the Site or provide recommendations for preliminary selection of remedial alternatives.

Supporting documentation will be provided as appendices to this report. These appendices will include test pit logs, test boring logs, well construction diagrams (i.e., well completion reports), laboratory analytical reports, chain of custody, and other supporting documentation referenced above.

6.0 FIELD SAMPLING PLAN (FSP) AND ANALYSIS REQUIREMENTS

The field sampling and analysis requirements have been proposed to provide the methods by which the remedial investigation sample activities will be performed. The field sampling and analysis sections below provide methods and procedures for field sampling activities, laboratory analytical methods, and data evaluation procedures. These methods and procedures will be implemented to provide the data necessary to meet the overall sampling objectives of this investigation.

Components of field activities outlined in this work plan include elements of the Triad approach in order to streamline the site investigation process at the Site without compromising data quality and reliability. This project will use real-time field screening technologies to achieve more timely and cost-effective site characterization. The Triad approach seeks to recognize and manage the uncertainties involved in generating representative data from heterogeneous environmental matrices. The real-time field screening results will assist in determining samples to be analyzed by a laboratory, and can subsequently be correlated to the analytical laboratory test results to assist in developing conclusions on contaminant distribution at the Site.

6.1 Field Sample Plan Requirements

6.1.1 Sampling Objectives

The sampling objectives for the Remedial Investigation are to:

- Provide data necessary to further evaluate the nature and extent of environmental media associated with the historical uses and operations at the Site.

- Provide initial quality data from sediment and surface water sample points at the Site.

- Provide data to be used for a qualitative risk assessment and a Fish and Wildlife Assessment.

6.1.2 Sample Locations and Frequency

To meet the objectives stated above, the sampling program to be implemented will include the collection of sediment samples and surface water samples. In addition, surface soil samples and subsurface soil samples will be collected from test borings (soil borings) and test pits. Groundwater samples will also be collected from proposed and existing groundwater monitoring wells. The proposed surface soil, sediment and surface water sample locations are presented on Figure 5 (Proposed Surface Soil, Surface Water and Sediment Sample Location Map). The test pit, test boring, and monitoring well locations are presented on Figure 6 (Proposed Test Pit and Monitoring Well Locations).

6.1.2.1 Surface Soil Samples and Near Surface Soil Samples

Surface soil is present on many parts of the Site. However, since the date of completion of the previous investigations performed by Stantec, many areas of the Site where surface soil was present have been covered with a layer of gravel. For the purposes of this work plan, these former surface soil layers that are covered with gravel are considered to be subsurface soil samples referred to in this work plan as "near-surface soils."

Surface soils and near-surface soils will be collected at 75 proposed locations to further evaluate the surface soil and near-surface soil conditions at the Site and to evaluate surface soil conditions at locations that have not yet been investigated. The proposed surface soil and near-surface soil sample locations are shown on Figure 5. Based on a cursory site visit conducted during the development of this work plan, it is anticipated that approximately 28 of these locations are covered by gravel and will result in the collection of near-surface soil samples. The sample locations may be adjusted in the field with NYSDEC concurrence to nearby areas that appear stained or devoid of vegetation, or to nearby areas that are not covered with gravel.

Surface soil samples will be collected from a 0 to 2 inch depth interval. Initially, any vegetation will be removed with a dedicated disposable plastic trowel and placed to the side of the test location. The plastic trowel will then be used to collect the surface soil sample from the 0 to 2 inch depth interval.

At near-surface soil sample locations, the gravel layer will first be removed using a pick-axe and/or shovel down to the former surface soil layer and the gravel will be placed to the side of the test location. The soil directly beneath the gravel will then be collected from a 0 to 2 inch depth interval using a dedicated disposable plastic trowel.

Portions of the samples will then be placed directly into laboratory-supplied glassware for possible laboratory analysis. To the extent practicable based on visual and olfactory observations, the portions placed in laboratory-supplied glassware will consist of the most contaminated section of the sample. Other portions of the samples will be placed in Ziploc®-type plastic baggies that will subsequently be field screened in accordance with the standard operating procedure (SOP) included in Appendix C**.** The laboratory containers and baggies for each sample location will be labeled and placed in a cooler maintained at or below 4ºC.

Re-usable sample equipment, such as the pick-axe and shovel will be decontaminated in accordance with one of the methods outlined in Section 6.3.

With input from the NYSDEC Site representative, a minimum 30 soil samples collected from surface soil test locations or near-surface soil test locations (i.e., test locations where the former surface soil layer is currently covered by a layer of gravel) will be selected for analytical laboratory testing. It is anticipated that the samples will be from locations with the greatest field evidence of environmental impact (i.e., based on visual or olfactory observations and field screening results using the PID, FID, and/or XRF), and also from locations with lower field evidence of impact for the purposes of spatial distribution across the Site and delineation/confirmation. In addition, at least one surface soil sample or near-surface soil sample from each area of concern will be selected for analytical laboratory testing.

The selected soil samples will be submitted for laboratory analysis in accordance with the laboratory-testing program included as Table 1. As shown, 15 of the soil samples will be analyzed for full TCL/TAL parameters including cyanide. Since the Triad approach field screening is to be performed on each surface soil samples and near-surface soil samples, the remaining 15 samples will only be analyzed for TCL SVOCs plus TICs using ASP Method OLM04.2, and TAL Metals plus Cyanide using ASP Method ILM04.1, which provides additional analytical results for confirmation and correlation of the field screening results.

6.1.2.2 Investigations of Floor Drains, Septic Systems and Swales

The Site's floor drains, collection systems and swales and/or culverts will be investigated for potential contamination, as well as determining the points of discharge. Based on information presented in Stantec's Phase I and Phase II investigations, the following drains and swales will require additional investigation: The floor drain in Building 7A, the roof drain that discharged to the Genesee River located adjacent to Building 7A, and the drainage swale located behind the large blue building (Building 6) that is believed to discharge to a marina inlet that is connected to the Genesee River.

In addition to the drains and swales, the below grade septic systems will be investigated to the extent feasible. There are three septic systems on Site, reportedly located adjacent to buildings 2, 7A, and 9, which need to be located and investigated. A fourth septic system was reported adjacent to Building 3 in Stantec's June 2004 Phase I report; however, this system is no longer on the property after its subdivision into Lots 1 and 2. The investigation of these areas will be completed in general accordance with Section 3.9 of DER-10. This may require the cleaning of the existing floor drains and piping to allow investigation. If there are any existing direct discharges to the environment from failing septic systems or drains, the discharges will be ceased and the discharge pathway will be terminated. If the septic systems are to be retained, the septic systems will be repaired or replaced by Genesee Marina, Inc. as needed, in order to ensure that they are in operational compliance with the applicable Monroe County Department of Health codes.

6.1.2.3 Sediment Samples

In September of 2006, 10 sediment samples (2 samples from each of 5 locations designated GM-SED-1 to GM-SED-5) were collected by the current tenant of the Site, Gibbs Marina. The locations of GM-SED-1 through GM-SED-5 are shown on Figure 5. Based on the collection of the September 2006 samples, six (6) additional sediment samples will be collected from the Site. Proposed locations for these six (6) sediment samples are presented on Figure 5. Sediment samples will be collected in general accordance with USEPA SOP# 2016 dated November 17, 1994, Sediment Sampling Procedures. A copy of SOP #2016 is included as Appendix D. The samples will be submitted for laboratory analysis in accordance with the laboratory-testing program included as Table 1. The laboratory results will be compared to NYSDEC Technical Guidance of Screening Contaminated Sediments, dated November 22, 1993 with updates through January 1999. Re-usable sampling equipment will be decontaminated in accordance with one of the methods outlined in Section 6.3.

6.1.2.4 Surface Water Samples

Three (3) surface water samples will be collected from the Genesee River along the river shoreline adjacent to the Site. Proposed locations for surface water samples are presented on Figure 5. The surface water samples will be collected prior to the sediment samples by lowering an inverted one liter amber glass laboratory prepared sample bottle (containing no preservatives) into the standing water approximately one foot, then slowly righting the container to allow it to fill. The water will then be transferred from the non-preserved container to the various laboratory sample containers to be filled. A new amber bottle will be used at each sample location. The method described above is a standard industry method for obtaining grab surface water samples. In conjunction with sampling, field parameters (pH, temperature, and conductivity) will be measured. The samples will be submitted for laboratory analysis in accordance with the laboratory-testing program included as Table 1. The laboratory results will be compared to NYSDEC TOGS 1.1.1 Surface Water Standards and Guidance Values.

6.1.2.5 Test Pit Excavations and Subsurface Soil Sampling from Test Pits

Forty test pits will be excavated with a backhoe to further evaluate the nature and extent of the fill materials present on the Site. The proposed locations of 36 of these test pits are shown on Figure 6. DAY will hold four (4) test pit locations in “reserve” for possible investigation of the drains, septic systems, or to fill in data gaps. Upon completion, the test pits will be backfilled with the excavated material, tamped in place and roughly graded to prevent water ponding on the ground surface. Re-usable excavating and sampling equipment (e.g., backhoe bucket) will be decontaminated in accordance with one of the methods outlined in Section 6.3.

As part of the test-pitting program, grab samples will be biased towards visually contaminated areas and will be collected immediately from the walls/floor of test pits when their depth is less than three feet below the ground surface, or from near the teeth of the backhoe bucket. Portions of these grab samples will be screened in the field for the presence of VOCs and metals as described in Appendix C (i.e., with a PID, FID and XRF analyzer).

With input from the NYSDEC Site representative, a minimum of 20 subsurface soil samples collected from test pit locations will be selected for analytical laboratory testing. It is anticipated that the samples will be from locations with the greatest field evidence of environmental impact (i.e., based on visual or olfactory observations and field screening results using the PID, FID and/or XRF), and also from locations with lower field evidence of impact for the purposes of spatial distribution across the Site and delineation/confirmation. In addition, at least one sub surface soil sample from each new area of concern will be selected for analytical laboratory testing. In instances when a soil sample is to be selected for analysis from a test pit location that does not exhibit visual, olfactory or field screening evidence of contamination, the soil sample obtained from that test pit that is closest to the top of the water table (as determined during excavation of the test pit) will be submitted for the analytical laboratory testing.

The selected soil samples will be submitted for laboratory analysis in accordance with the laboratory-testing program included as Table 1. As shown, 10 of the soil samples will be analyzed for full TCL/TAL parameters including cyanide. Since the Triad approach field screening is to be performed on each subsurface soil sample, the remaining 10 samples will only be analyzed for TCL SVOCs plus TICs using ASP Method OLM04.2, and TAL Metals plus CN using ASP Method ILM04.1, which provides additional analytical results for confirmation and correlation of the field screening results.

In addition, subsurface conditions at each test pit will be documented in the field, including a photographic log. Pertinent information will be recorded on test pit logs, which will include:

- Date, sample identification (if collected), location and project identification;
- Name of individual preparing the log;
- Name of subcontractor;
- Equipment used;
- Sequential stratigraphic boundaries;
- Size of test pit area (depth, width, and length);
- Field observations; and
- PID and XRF screening results.

6.1.2.6 Subsurface Soil Sampling From Test Borings

DAY proposes the installation of 25 test borings at the Site. The locations of these borings are:

- One boring in each of the "new areas" Areas 7,8,9, and 11 (See figure 6);
- Two borings in "new area" 10 (See Figure 6)
- Two borings in the swale/ditch area located west and southwest of Building 6/- "blue building" (See Figure 6);
- Three borings inside Building 6/ "blue building" (See Figure 6) with approval from the NYSDEC representative, these borings may be moved to areas inside the building that may show evidence of surficial staining;
- Two borings between Buildings 1 and 8 (See Figure 6);
- Two borings within the footprints of former Buildings 7a and 7b (i.e., within the concrete slab area north of Building 6/"blue building") (See Figure 6);
- The ten remaining borings will be used to fill in data gaps based on Stantec's previous studies and the results of the surface soil, near surface soil and test pit sampling programs. (Note: these borings are not depicted on Figure 6)

Of the 25 test borings being installed, ten (10) test soil borings will be completed into groundwater monitoring wells (refer to Section 6.1.2.7). Locations of the test borings/wells not shown on Figure 6 will be approved by the NYSDEC site representative.

Due to the heterogeneity of the fill material, the borings will be installed using 4 ¼" hollow stem augers at each test boring location. Continuous split spoon samples, driven by a 140-pound hammer free-falling 30 inches, will be collected ahead of the augers in general conformance with American Society for Testing and Materials (ASTM) D1586-99. A copy of ASTM D1586-99 is included as Appendix E. Portions of the split spoon samples will be field-screened in accordance with the SOP provided in Appendix C. Other portions of the split spoon samples will be transferred to laboratory containers for possible analysis. The target depths for the proposed borings has been assumed to be 20 feet bgs, however, final determination of boring depth will be determined made by DAY's field representative in consultation with the NYSDEC site representative and based on field conditions at the time of the investigation. Re-useable drilling and sampling equipment (e.g., split spoons, augers, and drilling rods) will be decontaminated in accordance with one of the methods outlined in Section 6.3.

With input from the NYSDEC Site representative, a minimum 15 subsurface soil samples collected from test boring locations will be selected for analytical laboratory testing. It is anticipated that the samples will be from locations with the greatest field evidence of environmental impact (i.e., based on visual or olfactory observations and field screening results using the PID, FID and/or XRF), and also from locations with lower field evidence of impact for the purposes of spatial distribution across the Site and delineation/confirmation. In instances when a soil sample is to be selected for analysis from a test boring location that does not exhibit visual, olfactory or field screening evidence of contamination, the soil sample will be collected from the interval that is closest to the top of the water table (as determined during advancement of the boring) will be submitted for the analytical laboratory testing.

The selected soil samples will be submitted for laboratory analysis in accordance with the laboratory-testing program included as Table 1. As shown, five (5) of the soil samples will be analyzed for full TCL/TAL parameters including cyanide. Since the Triad approach field screening was performed on each subsurface soil sample, the remaining 10 samples will only be analyzed for TCL VOCs plus TICs and TCL SVOCs plus TICs using ASP Method OLM04.2, and TAL Metals plus CN using ASP Method ILM04.1, which provides additional analytical results for confirmation and correlation of the field screening results.

In addition, subsurface conditions at each test boring will be documented in the field. Pertinent information will be recorded on test boring logs, which will include:

- Date, boring/well identification, and project identification;
- Name of individual preparing the log;
- Name of drilling contractor;
- Drill make and model;
- Identification of alternative drilling methods used and justification thereof;
- Depths recorded in feet and fractions thereof (tenths of inches) referenced to ground surface;
- The length of the sample interval and the percentage of the sample recovered;
- The depth of the first encountered water table, along with the method of determination, referenced to ground surface;
- Drilling and borehole characteristics;
- Sequential stratigraphic boundaries;
- Well specifications (materials; screened interval; amount of Portland cement, bentonite and water used to mix grout; etc.); and

- Field screening results in accordance with the Field Screening SOP, provided in Appendix C.

Drill cuttings from each test boring will be placed on polyethylene sheeting adjacent to each test boring as they are generated. If no evidence of potential impacts is observed during the field screening as described in Appendix C for a test boring, then the test boring will be backfilled with the cuttings generated during the completion of that test boring. Test borings will not be backfilled with cuttings generated from other test borings. Non-impacted cuttings from test borings that are converted to monitoring wells, or non-impacted cuttings that can not be returned to the generating test boring will be containerized and temporarily staged on-site in secured and labeled 55-gallon drums. If evidence of potential impacts are observed during field screening, the drill cuttings will be transferred from the polyethylene sheeting and stored on-site in secured labeled 55-gallon drums. Drummed materials will subsequently be characterized and disposed in accordance with applicable regulations. Boreholes that appear impacted, based on field screening which are not completed with a monitoring well will be grouted to the ground surface.

6.1.2.7 Groundwater Sampling from Monitoring Wells

Ten new groundwater monitoring wells will be installed within 10 of the new test borings described in Section 6.1.2.6. At least one new well will be installed in each of the “new areas” (Areas 7,8,9,10,11 as shown on Figure 6) and five (5) new wells will be installed to fill in data gaps based on Stantec’s previous studies and the results of the surface soil, near surface soil, and test pit sampling programs and test boring field screening. (The locations of these five wells will be approved by the NYSDEC representative.). The NYSDEC site representative will be consulted regarding the proposed locations of these 10 wells. Ultimately, groundwater samples will be collected from these 10 new wells and 15 existing Stantec wells (i.e., total of 25 wells) and analyzed as described in this work plan.

The wells will be constructed of 2-inch diameter, Schedule-40 PVC with ten-foot long, 0.010-inch slot well screens. The wells are anticipated to straddle the apparent top of the water table and extend to a total depth of 20 feet below the ground surface; however, final determination of well depth will be made by DAY’s field representative in consultation with the NYSDEC site representative. The wells will be completed with a sand pack that consists of fine sand extending approximately six inches below and 24 inches above each well screen. The sand packs will be capped with a two-foot bentonite seal, and then grouted to the surface. The wells will be completed with either a protective casing or a flush mounted road box depending on location. A well construction diagram (i.e., well completion report) will be developed for each new well. Two groundwater sampling events will be conducted (i.e., one event during a seasonal high groundwater table and one event during a seasonal low groundwater table.)

At least one week following installation, the monitoring wells will be developed prior to sampling by utilizing either a new dedicated disposable bailer with dedicated cord and/or a pump and dedicated disposable tubing. No fluids will be added to the wells during development, and non-dedicated well development equipment will be decontaminated prior to development of each well. The development procedure will be as follows:

- Obtain pre-development static water level readings;
- Calculate water/sediment volume in the well;
- Obtain initial field water quality measurements (e.g., pH, conductance, turbidity, temperature);
- Select development method and set up equipment depending on method used;
- Alternate water agitation methods (e.g., moving a bailer or pump tubing up and down inside the screened interval) and water removal methods (e.g., pumping or bailing) in order to suspend and remove solids from the well;
- Obtain field water quality measurements for every two to five gallons of water removed. Record water quantities and rates removed;
- Stop development when water quality criteria listed below have been met;
- Obtain post-development water level readings; and
- Document development procedures, measurements, quantities, etc.

To the extent feasible, development will continue until the following criteria are achieved:

- Water is clear and free of sediment and turbidity is less than 50 NTU;
- Monitoring parameters have stabilized (i.e., parameters are ±10%); and/or
- A minimum of five well volumes has been removed.

The field measurement data will be presented on Monitoring Well Development Logs.

A minimum of two (2) weeks after well development, the first of the two (2) groundwater sampling events will be conducted. The 25 groundwater samples from new and existing monitoring wells will be analyzed as outlined in Table 1. Groundwater samples will be collected starting with the wells considered least impacted, followed by those considered most impacted. The order of sample volume collection will be VOCs, SVOCs, metals, cyanide and PCBs/pesticides.

Low-flow purging and sampling procedures will be used to collect the groundwater samples. These procedures are generally based on ASTM D6771-02, “Standard Practice for Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations” (copy attached as Appendix F) and are outlined below:

- In order to minimize the potential re-suspension of solids in the bottom of the well, well depths will not be measured prior to or during low-flow purging and sampling. Well depth information will be obtained from: 1) measurements collected during well development; 2) well logs; or 3) measurements after sampling is completed.

- Prior to purging and sampling, static water level measurements will be taken from each well using a Heron Model HO1.L oil/water interface probe or similar instrument. DAY will also look for light non-aqueous phase liquid (LNAPL) by using visual observations and the Heron oil/water interface probe or similar instrument at each well location. DAY will document the results of this work in the field.

- A portable bladder pump connected to new disposable polyethylene tubing will be lowered and positioned at or slightly above the mid-point of the well screen when the screened interval is set in relatively homogeneous material. When the screened interval is set in heterogeneous materials, the pump will be positioned adjacent to the zone of highest hydraulic conductivity (as defined by geologic samples). Care will be taken to install and lower the bladder pump slowly in order to minimize disturbance of the water column.

- The pump will be connected to a control box that is operated on compressed gas (nitrogen, air, etc.) and is capable of varying pumping rates. An in-line flow-through cell attached to a Horiba U-22 water quality meter (or similar equipment) will be connected to the bladder pump effluent tubing to measure water quality data.

- The pump will be started at a low pumping rate of 100 ml/min or less (for pumps that can not achieve a flow rate this low, the pump will be started at the lowest pump rate possible). The water level in the well will be measured and the pump rate will be adjusted (i.e., increased or decreased) until the drawdown is stabilized. In order to establish the optimum flow-rate for purging and sampling, the water level in the well will be measured on a periodic basis (i.e., every one or two minutes) using an electronic water level meter or the Heron Model HO1.L oil/water interface meter (or equivalent). The pumping rate will not exceed 500ml/min during purging. When the water level in the well has stabilized (i.e., use goal of < 0.33 ft of constant drawdown), the water level measurements will be collected less frequently.

- While purging the well at the stabilized water level, water quality indicator parameters will be monitored on a three to five minute basis with a Horiba U-22 water quality meter (or similar equipment). Water quality indicator parameters will be considered stabilized after three consecutive readings for each of the following parameters are generally achieved:

    - pH (± 0.1);
    - specific conductance (± 3%);
    - dissolved oxygen (± 10 %);
    - oxidation-reduction potential (± 10 mV);
    - temperature (± 3%); and
    - turbidity (± 10%, when turbidity is greater than 10 NTUs)

- Following stabilization of the water quality parameters, the flow-through cell will be disconnected and a groundwater sample will be collected from the bladder pump effluent tubing. The pumping rate during sampling will remain at the established purging rate or it may be adjusted downward to minimize aeration, bubble formation, or turbulent filling of sample containers. A pumping rate below 250 ml/min will be used when collecting volatile organic compound (VOC) samples. The proposed analytical laboratory testing program for Round 1 groundwater samples is identified in Table 1.

- To minimize the potential for re-suspension of solids in the bottom of the well, DAY will look for dense non-aqueous phase liquid (DNAPL) subsequent to purging and sampling at each well location by using visual observations of a sample collected from the bottom of the groundwater well and/or the Heron oil/water interface probe (or equivalent). DAY will document the results of this work in the field.

The procedures and equipment used during the low-flow purging and groundwater sampling, the field measurement data will be documented in the field and recorded on a Monitoring Well Sampling Log.

Any changes in technique shall be approved by the NYSDEC site representative.

Prior to use and between wells, the portable bladder pump and any other reusable equipment (e.g., support cable) that come in contact with groundwater will be decontaminated using the following procedures:

- A wash in a mixture of potable water and Alconox®-type soap;
- Rinse the pump until soap is no longer visible;
- Rinse the pump with distilled water, allow to air dry or dry with a paper towel.

Purge water generated during well development and well sampling will be contained and temporarily staged on-site in secure 55-gallon drums. Once properly characterized, the purge water will be disposed of in accordance with applicable regulations.

A New York State Licensed Surveyor will measure to within 0.01 ft the top of riser and ground surface elevations for new and existing monitoring wells using the NGVD ’88 coordinate system. The horizontal data will be surveyed in meters using the NAD ’83 UTM Zone 18 coordinate system. During each sampling event, static groundwater level measurements will be collected from each monitoring well using an electronic static water level meter or an oil/water interface meter. Groundwater elevations will be calculated, and a potentiometric groundwater map will be prepared illustrating the approximate groundwater elevations and groundwater flow direction(s) for each groundwater sampling event. The Surfer 8 software program by Golden Software, Inc. will be used to assist in developing each groundwater potentiometric map.

6.1.3 Sample Designations

Each of the environmental media samples collected during the implementation of the remedial investigation will be given a unique sample identification name, as the sample name. The sample name will include an identifier for the Genesee Marina (GM) Site, sample location, and sample depth interval for soil samples. For example, a soil sample collected from a depth of 1.5 to 2.0 feet in Test Boring TB-101 at the Site would be given the designation GM-TB101 (1.5 - 2.0). Groundwater samples collected will be labeled similarly with the addition of the date, so monitoring well MW-1 sampled in March 2007 would be given the designation GM-MW1-3/07. In order to differentiate between surface soil and near surface soil test locations, surface soil samples will be designated as SS-x and near-surface soil samples will be designated as NSS-x. For example, surface soil sample collected at location 5 would be given the designation SS-5, while a near surface soil sample collected at location 6 would be designated NSS-6.

6.1.4 Sample Handling and Analysis

Each sample will be collected, handled, and stored as if it were to be analyzed, even though only selected soil samples will be submitted for laboratory analysis. The split-spoon soil sampler will be opened and a representative soil sample of the depth interval sampled will be placed directly into a laboratory-provided sample container.

Immediately after collection, each soil sample will be labeled with the following information and placed in a cooler to be held at a temperature of approximately 4°C until delivery to the laboratory:

- sample designation;
- sampling location;
- job number;
- date;
- time; and
- initials of person collecting sample.

Each sample will be tracked by means of a Chain-of-Custody form that will be initiated at the time of sample collection and will be maintained with the sample until delivery to the laboratory.

Laboratory analytical services associated with this program have not been determined as of the writing of this Work Plan. The selected laboratory will be NYSDOH ELAP certified. The environmental media samples will be analyzed as specified in Table 1 according to protocols described in the June 2000, New York State Analytical Services Program. The laboratory analytical data package will be a Category B deliverable.

6.2 Quality Assurance Samples

6.2.1 General

QA/QC samples will be prepared by the laboratory and collected in the field as part of the sampling requirements and data validation program. Two types of field QA/QC samples will be prepared or collected: trip blanks and duplicate samples. The QA/QC samples are discussed in more detail below.

6.2.2 Trip Blanks

The primary purpose of a trip blank is to detect additional sources of contamination that may potentially influence compound detection and concentration values reported in actual samples both quantitatively and qualitatively. Trip blanks serve as a mechanism of control on sample bottle preparation and blank water quality as well as sample handling. The trip blank travels to the Site with the empty sample containers and back from the Site with the collected samples in an effort to simulate sample handling controls. Contaminated trip blanks may indicate inadequate bottle cleaning or that the water used to prepare the blank was of questionable quality. The following have been identified as potential sources of contamination for trip blanks:

- laboratory reagent water;
- sample containers;
- cross-contamination in shipment;
- ambient air or contact with analytical instrumentation during preparation and analysis of the laboratory; and
- laboratory reagents used in analytical procedures.

A trip blank consists of a set of sample containers filled at the laboratory with laboratory demonstrated analyte-free water. This water must originate from one common source and physical location within the laboratory, and must be the same water as the method blank water used by the laboratory performing the analysis. Trip blanks should be handled, transported, and analyzed in the same manner as the samples acquired that day, except that the sample containers themselves are not opened in the field. Rather, they must travel with the sample collector. Individual sample matrices and associated blanks must be packaged in separate sample shuttles prior to shipment back to the lab. Trip blanks must return to the lab with the same set of bottles they accompanied to the field.

Trip blanks will be prepared and analyzed at a rate of one shipment of liquid matrix samples. The trip blanks will be analyzed only for volatile organic parameters specified for the environmental samples collected that day.

6.2.3 Duplicate Samples

Collection of an aqueous or soil duplicate sample provides for the evaluation of the laboratory's performance by comparing analytical results of two samples from the same location. Collection of a duplicate of water sample will be performed by alternately filling sample containers from the same sampling device for each parameter. Collection of duplicate soil samples will be accomplished by splitting soil samples in half and filling sample containers. Groundwater samples for volatile organics analysis from monitoring wells will be the first set of containers filled for the sample set. The duplicate sample may also be designated for the matrix spike/matrix spike duplicate sample for laboratory ASP protocol.

6.2.4 Matrix Spike/Matrix Spike Duplicate Samples

One Matrix Spike/Matrix Spike Duplicate (MS/MSD) will be tested for each 20 samples of each matrix (i.e., soil, groundwater, etc.) that is shipped within each seven-day period. The MS/MSD will include the same parameters as that of the field samples.

6.2.5 Field Equipment Procedures and Preventative Maintenance

Prior to the initiation of the remedial investigation, a preventive maintenance and calibration of equipment will be implemented to assure proper operation of field instruments. Members of the field team will be familiar with the maintenance, calibration, and operation of field equipment. The field equipment will be used according to manufacturer instructions.

6.2.6 Data Validation

Laboratory analytical data generated through the implementation of this investigation will be submitted for data validation in accordance with NYSDEC guidance for completion of a data usability summary report (DUSR).

A data usability summary report (DUSR) will be submitted to the NYSDEC based on the results of the data usability project work. This report will be in accordance with the NYSDEC guidelines of the "Guidance for the Development of Data Usability Summary Reports."

6.3 Equipment Decontamination Procedures

It is anticipated that many of the materials used to assist in obtaining samples will be disposable one-time use materials (e.g., sampling containers, plastic trowels, bailers, rope, pump tubing, latex gloves). However, decontamination of re-useable field equipment will be conducted to ensure that the data collected (i.e., analytical laboratory data and field screening data) is acceptable. When equipment must be re-used (e.g., static water level indicator, split spoon samplers, hollow stem augers, drilling rods, bladder pump, pick-axe, shovel, etc.), it will be decontaminated by at least one of the following methods:

- Steam clean the equipment; or

- Rough wash in tap water; wash in mixture of tap water and Alconox-type soap; double rinse with de-ionized or distilled water; and air dry and/or dry with clean paper towel.

In order to reduce the potential for cross-contamination of samples during this project, re-useable field instrumentation, sampling equipment, heavy equipment, drilling equipment, etc. must arrive on-site in clean condition and must also leave the Site in clean condition. Equipment that arrives on-site and is not clean will not be allowed on-site.

The effectiveness of the equipment decontamination will be evaluated via analytical laboratory testing of field blanks (e.g., rinsate samples).

Decontamination liquids and disposable equipment and PPE will be containerized, temporarily staged on-site (preferably inside a building). These materials will subsequently be characterized and disposed in accordance with applicable regulations.

7.0 SCHEDULE

The overall schedule to implement the Remedial Investigation detailed within this Work Plan Draft is anticipated to require a total of 20 to 24 weeks from receipt of NYSDEC approval of the Work Plan. This schedule includes: two (2) weeks for mobilization of the field program, five (5) to seven (7) weeks for completion of the field investigation activities, eight (8) weeks for laboratory analysis and data validation, and four (4) to six (6) weeks for evaluation of the results and report preparation. DAY employees will follow the Health and Safety Plan that will be submitted to the appropriate agencies prior to the implementation of the work detailed in this work plan.

8.0 REFERENCES

New York State Department of Environmental Conservation Draft Brownfield Cleanup Program Guide, May 2004

New York State Department of Environmental Conservation Draft DER-10 Technical Guidance for Site Investigation and Remediation

NYSDEC 6 NYCRR Subpart 375 Environmental Remediation Program, December 2006

Draft Remedial Investigation Work Plan; New York State Title 14 Brownfield Cleanup Program
Genesee Marina, Inc. 118 Petten Street Rochester, NY
Prepared for: Genesee Marina, Inc. 118 Petten Street Rochester, NY
Prepared by: GeoQuest Environmental, Inc 1134 Titus Ave Rochester, NY

Phase I and Limited Phase II Environmental Site Assessment
Genesee Marina 18 Petten Street Rochester, New York June 2004
Prepared for: City of Rochester Division of Environmental Quality
30 Church Street, Room 300B
Rochester, New York 14614-1278
Prepared by: Stantec 85 Metro Park
Rochester, New York 14623

Phase II Environmental Site Assessment
18 Petten Street Extension
Genesee Marina Rochester, New York
October 2004 (Draft)
Prepared for: City of Rochester Division of Environmental Quality
30 Church Street, Room 300B
Rochester, New York 14614-1278
Prepared by: Stantec 85 Metro Park
Rochester, New York 14623

EPA Sediment Sampling – SOP#: 2016
Date: 11/17/94
REV. #:0.0

ASTM STANDARD D1586-99: Standard Test Method for Penetration Test and Split Barrel Sampling of Soil

ASTM STANDARD D6771-02: Low-Flow Purging and Sampling for Wells and Devices Used for Ground Water Quality Investigations

TABLE

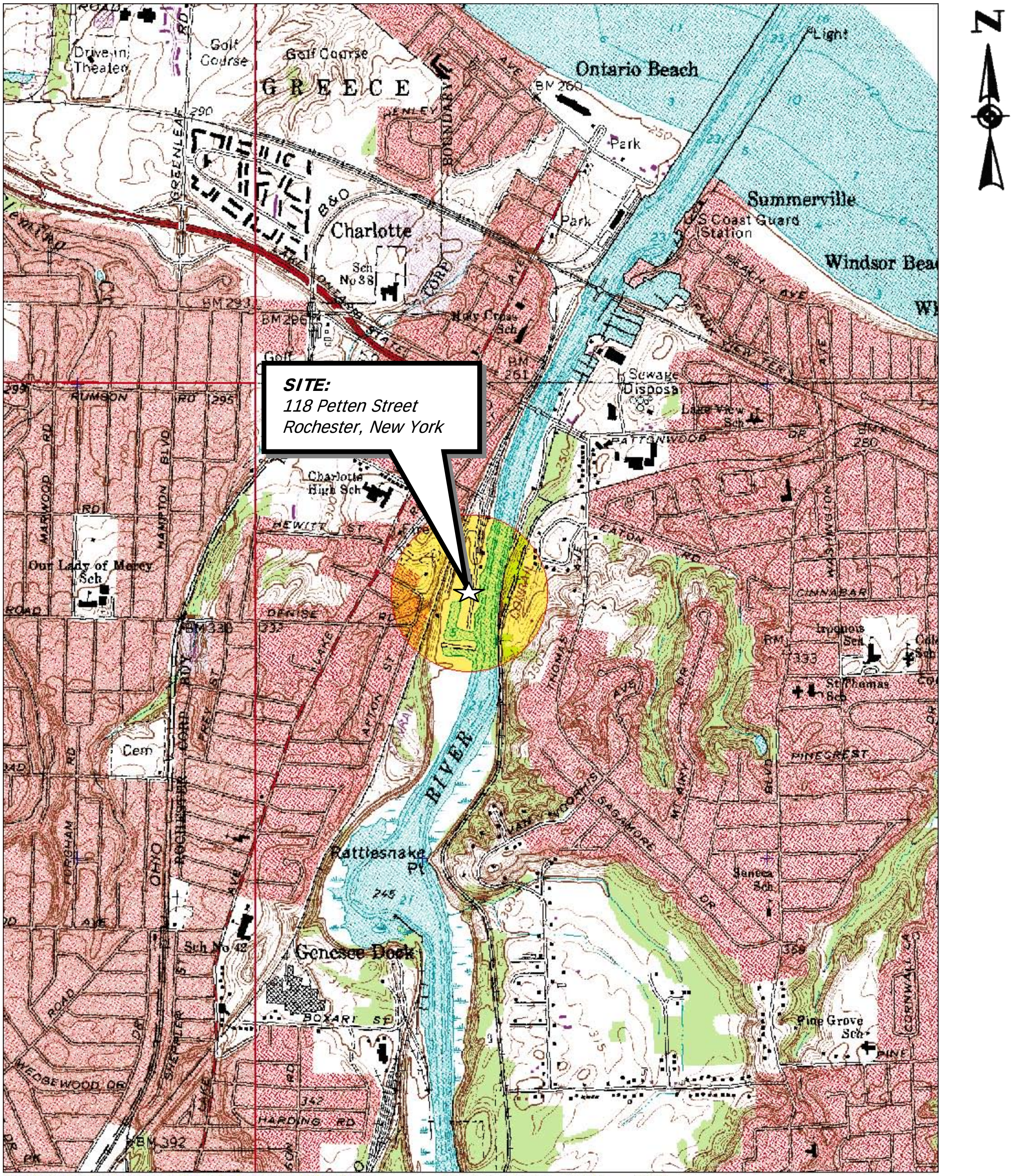
TABLE 1
SUMMARY OF SAMPLING AND ANALYSIS REQUIREMENTS
Remedial Investigation Work Plan
Genesee Marina
118 Petten Street, Rochester, New York

Number of Locations	Number of Environmental Media Samples for Laboratory Analysis	Laboratory Analysis	Number of QA/ QC Samples
69	15 Surface Soil Samples	Full TCL/TAL plus CN	1 Duplicate sample 1 MS/MSD sample
	15 Surface Soil Samples	TCL SVOCs plus TICs by OLM 4.2, TAL Metals plus CN by ILM 4.1	1 Duplicate sample 1 MS/MSD sample
6	6 Sediment Samples	Full TCL/TAL plus CN, Total Organic Carbon	1 Duplicate sample 1 MS/MSD sample
3	3 Surface Water Samples	Full TCL/TAL plus CN, Hardness	
40	10 Subsurface Samples (from test pits)	Full TCL/TAL plus CN	1 Duplicate sample 1MS/MSD sample
	10 Subsurface Samples (from test pits)	TCL SVOCs plus TICs by OLM 4.2, TAL Metals plus CN by ILM 4.1	
20	5 Subsurface Samples (from test borings)	Full TCL/TAL plus CN	1 Duplicate sample 1 MS/MSD sample
	10 Subsurface Samples (from test borings)	TCL VOCs plus TICs and TCL SVOCs plus TICs by OLM 04.2, TAL Metals plus CN by ILM 04.1	
25(2)	25 Groundwater Samples	Full TCL/TAL plus CN	1 Duplicate sample 2 MS/MSD samples 2 Trip Blanks (VOCs only)
TOTAL Locations: 163	**Total Samples Submitted: 99**		**Total QA/QC Samples: 22**

Notes:

1. Full TCL/TAL plus CN = TCL VOCs plus TICs, TCL SVOCs plus TICs, Pesticides and PCBs by ASP Method OLM04.2; and TAL Metals plus CN by ASP Method ILM04.1.
2. Quantity represents one groundwater round, two are proposed. Analytical requirements will be re-evaluated after the first round.

FIGURES



3-D TopoQuads Copyright © 1999 DeLorme Yarmouth, ME 04096 Source Data: USGS

550 ft Scale: 1 : 19,200 Detail: 14-0 Datum: WGS84

Drawing Produced From: 3-D TopoQuads, DeLorme Map Co., referencing USGS quad maps Rochester East and West (NY) 1995. Site Lat/Long: N43^{o} 14.57' – W77^{o} 36.87'

DATE
9/5/2007

DRAWN BY
CPS

SCALE
1” = 2000’

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

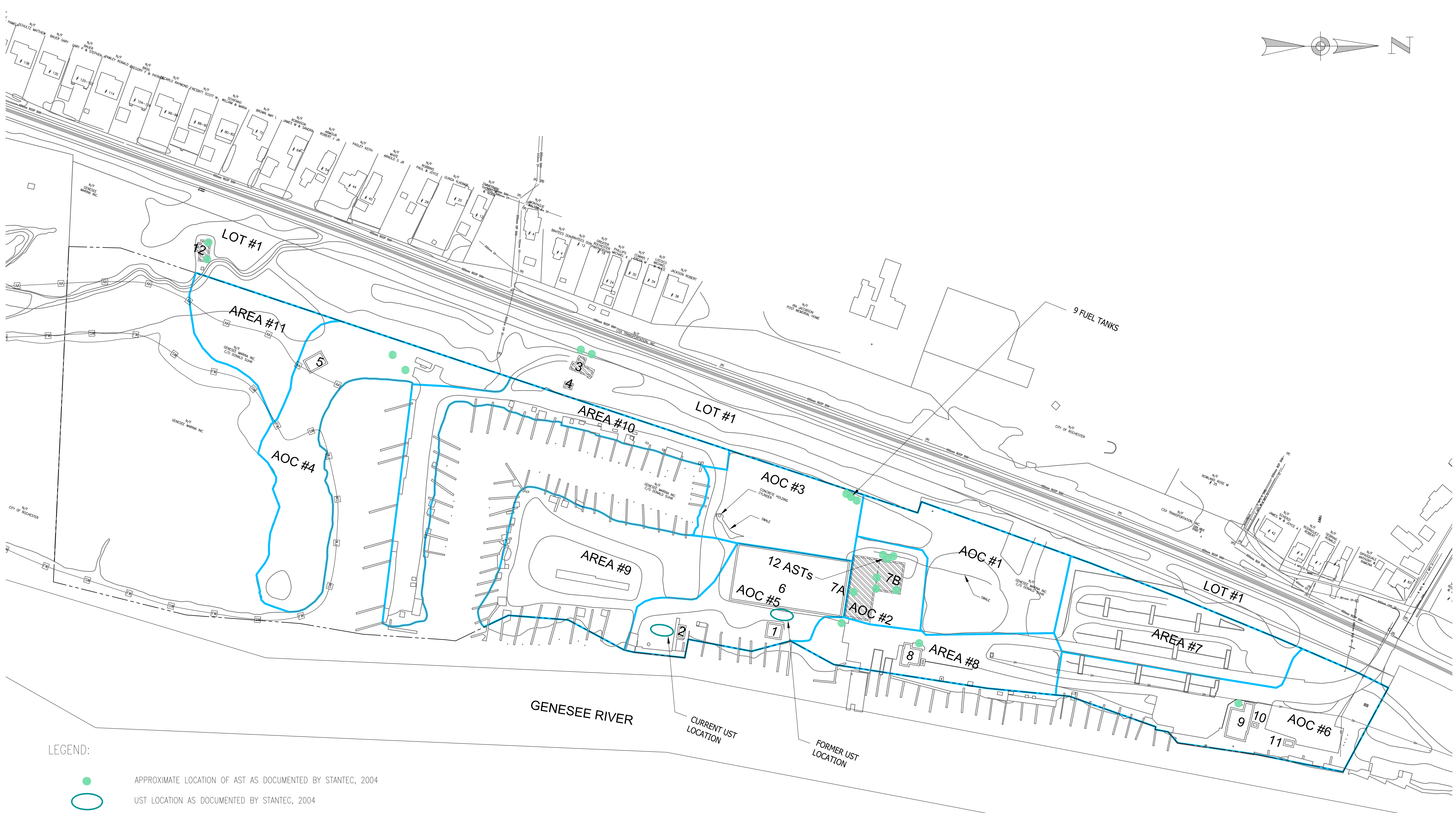
PROJECT TITLE
118 PETTEN STREET
ROCHESTER, NEW YORK

REMEDIAL INVESTIGATION WORKPLAN

DRAWING TITLE
PROJECT LOCUS MAP

PROJECT NO.
3903S-06

FIGURE 1



LEGEND:

●	APPROXIMATE LOCATION OF AST AS DOCUMENTED BY STANTEC, 2004
⬭	UST LOCATION AS DOCUMENTED BY STANTEC, 2004
— - —	APPROXIMATE PROPERTY LINE
—	AOC/AREA BOUNDARY LINE
▨	DEMOLISHED BUILDINGS SINCE STANTEC 10/2004 REPORT
6	EXISTING BUILDINGS, BUILDING NUMBER AS IDENTIFIED BY STANTEC, 2004
SW — FW	STATE AND FEDERAL WETLANDS
AA — AA	WETLANDS 100' BUFFER AREA

0' 100' 200' 300'

BUILDING KEY:

1	QUANSET HUT (STORAGE SHED)
2	FORMER FRAMED WOODEN SHED (GAS SALES OFFICE)
3	FORMER RESIDENTIAL HOME
4	FORMER SHED FOR BUILDING 3
5	STORAGE SHED
6	LARGE METAL STORAGE SHED (BLUE BUILDING)
7A	FORMER OFFICE AND SERVICE BUILDING
7B	FORMER STORAGE BUILDING
8	RESIDENTIAL HOUSE / GIBBS MARINA OFFICE
9	SPIRIT OF ROCHESTER OFFICE
10	SHED
11	SHED
12	FOUNDATION OF FORMER HOUSE

NOTES:

1. BASE MAP PROVIDED BY DRAWINGS CREATED BY STANTEC CONSULTING GROUP, INC. AS REPORTED IN STANTEC'S OCTOBER 2004 PHASE II ESA REPORT
2. LOCATIONS OF SAMPLES COLLECTED ARE APPROXIMATE
3. SAMPLE LOCATIONS ARE BASED ON THE FIELD GPS SURVEY PERFORMED ON AUGUST 25, 2004 BY STANTEC, USING A TRIMBLE GEO XT GPS SYSTEM
4. CONCRETE HOLDING CYLINDER IN AOC #3 WAS IDENTIFIED IN STANTEC'S JUNE 2004 PHASE I AND LIMITED PHASE II ESA REPORT

ABBREVIATIONS:

AOC – AREA OF CONCERN

AST – ABOVE-GROUND STORAGE TANK

UST – UNDERGROUND STORAGE TANK

PROJECT MANAGER	DATE
DJG	01-2007
DRAWN BY	DATE DRAWN
CPS	01-2007
CHECKED BY	DATE
DJG	01-2007
APPROVED BY	DATE
DJG	01-2007
SCALE	DATE ISSUED
1" = 100'	04-11-2007

DAY ENVIRONMENTAL, INC.
DRAWING ALTERATION
THIS DOCUMENT MAY NOT BE ALTERED WITHOUT THE PERMISSION OF DAY ENVIRONMENTAL, INC.

	REVISIONS	DATE	BY
7			
6			
5			
4			
3			
2			
1			

day
DAY ENVIRONMENTAL, INC.
ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
GENESEE MARINA
118 PETTEN STREET
ROCHESTER, NEW YORK
REMEDIAL INVESTIGATION WORKPLAN

DRAWING TITLE
SITE PLAN

PROJECT NO.
3903S-06

DRAWING NO.
FIGURE 2

Reference Files Attached:
REF1: Fig 7 Sample Location Exceedances in Soil.dwg
REF2:
REF3:
REF4:
REF5:
REF6:
REF7:
REF8:
REF9:
REF10:

File Name: Drawings\GenMarina\3903S-06\Site Plan DEC
Layout Name: Layout 2
Time Plotted: Wed Apr 11 11:15 2007
Pen Setting File: GenMarina.ctb

ANSI "D" (22x34)
DayEnv_AnsiD

FIGURE 3
Stantec Figure #7
Exceedences of Recommended Soil Cleanup Objectives (RSCOs)

Plotting Parameters
Plotted By: acummings
Dwg File: U:\190500123\civil\Fig 7 SAMPLE LOCATION EXCEEDANCES IN SOIL.dwg
Plotted: Jun 01, 2005 – 3:23pm

Profile: <<Unnamed Profile>>
Node: CUMMINGSA

LEGEND:

●	APPROXIMATE LOCATION OF AST	⊕	MONITORING WELL
—	SUBJECT PROPERTY LINE	▚	TEST PIT
—	AOC BOUNDARY LINE	○	SURFACE SOIL/SEDIMENT SAMPLE
		⌖	SOIL BORING W/ GEOPROBE
		⌖	SOIL BORING W/ HSA

0 100 200 300
APPROXIMATE SCALE IN FEET

NOTES:

1) LOCATIONS OF SAMPLES COLLECTED ARE APPROXIMATE.

2) SAMPLE LOCATIONS ARE BASED ON THE FIELD GPS SURVEY PERFORMED ON AUGUST 25, 2004, BY STANTEC, USING A TRIMBLE GEO XT GPS SYSTEM.

SOIL: SAMPLE LOCATIONS WITH COMPOUNDS IN EXCEEDANCE OF RSCOs

🟡 VOCs:
- AOC #3: TP-11A
- AOC #4: TP-1, TP-3
- AOC #6: GP-7

🟠 SVOCs:
- AOC #1: TP-13, TP-15
- AOC #2: FD, SED
- AOC #3: TP-11A, SB-24
- AOC #4: TP-1
- AOC #6: GP-5

🔴 METALS:
- AOC #1: SS-4, SS-5, TP-17
- AOC #2: SED
- AOC #3: TP-8, SB-24
- AOC #4: TP-1, SB-28, SB-32
- AOC #5: SB-19
- AOC #6: TP-19, GP-2

DAY ENVIRONMENTAL FIGURE 3

INCLUDED FOR DAY WORKPLAN
NO MAP REVISIONS

REVISIONS	DATE	BY
6		
5		
4		
3		
2		
1		
0		

PROJECT ENGINEER/ARCHITECT
D. GNAGE
PROJECT MANAGER
M. STORONSKY
DRAWN BY
A. CUMMINGS, E.I.T.
FIRST ISSUE DATE
AUGUST 2004
SCALE
AS SHOWN

STANTEC CONSULTING GROUP, INC.
85 Metro Park
Rochester, N.Y. 14623-2674
Tel:(585) 475-1440
Fax: (585) 272-1814
www.stantec.com
Stantec

PROJECT
GENESEE MARINA
18 PETTEN STREET EXTENSION
CITY OF ROCHESTER, NY

TITLE OF DRAWING
EXCEEDANCES OF RECOMMENDED SOIL CLEANUP OBJECTIVES (RSCOs)

PROJECT NO.
190500156
DRAWING NO.
FIG. 7
SHEET OF

FIGURE 4
Stantec Figure #9
Exceedences of Class GA Groundwater Standards

Plotting Parameters
Plotted By: acummings
Dwg File: U:\190500123\civil\Fig 9 SAMPLE LOCATION EXCEEDANCES IN GW.dwg
Plotted: Jun 01, 2005 – 3:25pm

Profile: <<Unnamed Profile>>
Node: CUMMINGSA

LEGEND:

● APPROXIMATE LOCATION OF AST

— SUBJECT PROPERTY LINE

— AOC BOUNDARY LINE

MONITORING WELL

TEST PIT

○ SURFACE SOIL/SEDIMENT SAMPLE

⊕ SOIL BORING W/ GEOPROBE

⊕ SOIL BORING W/ HSA

0 100 200 300

APPROXIMATE SCALE IN FEET

NOTES:

1) LOCATIONS OF SAMPLES COLLECTED ARE APPROXIMATE.

2) SAMPLE LOCATIONS ARE BASED ON THE FIELD GPS SURVEY PERFORMED ON AUGUST 25, 2004, BY STANTEC, USING A TRIMBLE GEO XT GPS SYSTEM.

GROUNDWATER: SAMPLE LOCATIONS WITH COMPOUNDS IN EXCEEDANCE OF CLASS GA STANDARDS

🟡 VOCs:
AOC #1: MW-36
AOC #3: MW-23
AOC #5: MW-16, MW-22

🟠 SVOCs:
AOC #5: MW-16

🔴 METALS:
AOC #5: MW-16

DAY ENVIRONMENTAL FIGURE 4

INCLUDED FOR DAY WORKPLAN
NO MAP REVISION

6	5	4	3	2	1	0

REVISIONS DATE BY

PROJECT ENGINEER/ARCHITECT
D. GNAGE
PROJECT MANAGER
M. STORONSKY
DRAWN BY
A. CUMMINGS, E.I.T.
SCALE
AS SHOWN
FIRST ISSUE DATE
AUGUST 2004

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PROJECT
GENESEE MARINA
18 PETTEN STREET EXTENSION
CITY OF ROCHESTER, NY

TITLE OF DRAWING
EXCEEDANCES OF CLASS GA GROUNDWATER STANDARDS

PROJECT NO.
190500156
DRAWING NO.
FIG. 9
SHEET OF

LEGEND:

●	APPROXIMATE LOCATION OF AST AS DOCUMENTED BY STANTEC, 2004
⬭	UST LOCATION AS DOCUMENTED BY STANTEC, 2004
—·—	APPROXIMATE PROPERTY LINE
—	AOC/AREA BOUNDARY LINE
▨	DEMOLISHED BUILDINGS SINCE STANTEC 10/2004 REPORT
6	EXISTING BUILDINGS, BUILDING NUMBER AS IDENTIFIED BY STANTEC, 2004
SW FW	STATE AND FEDERAL WETLANDS
AA AA	WETLANDS 100' BUFFER AREA
▲	PROPOSED SURFACE SOIL/NEAR SURFACE SOIL SAMPLE LOCATION
●	PROPOSED SEDIMENT SAMPLE LOCATION
⊗	PROPOSED SURFACE WATER SAMPLE LOCATION
MW-15	EXISTING MONITORING WELL INSTALLED BY STANTEC
TP-14	PREVIOUS TEST PIT INSTALLED BY STANTEC
GM-SS-1-5/21/04 ○	PREVIOUS SURFACE SOIL/SEDIMENT SAMPLE INSTALLED BY STANTEC
GP-4 ⊕	PREVIOUS SOIL BORING W/GEOPROBE INSTALLED BY STANTEC
SB-14 ⊕	PREVIOUS SOIL BORING W/HSA INSTALLED BY STANTEC
GM-SED-1 ●	PREVIOUS SEDIMENT SAMPLE BY GIBBS MARINA

0' 100' 200' 300'

NOTES:

1. BASE MAP PROVIDED BY DRAWINGS CREATED BY STANTEC CONSULTING GROUP, INC. AS REPORTED IN STANTEC'S OCTOBER 2004 PHASE II ESA REPORT
2. LOCATIONS OF SAMPLES COLLECTED ARE APPROXIMATE
3. SAMPLE LOCATIONS ARE BASED ON THE FIELD GPS SURVEY PERFORMED ON AUGUST 25, 2004 BY STANTEC, USING A TRIMBLE GEO XT GPS SYSTEM
4. CONCRETE HOLDING CYLINDER IN AOC #3 WAS IDENTIFIED IN STANTEC'S JUNE 2004 PHASE I AND LIMITED PHASE II ESA REPORT

ABBREVIATIONS:

AOC – AREA OF CONCERN

AST – ABOVE-GROUND STORAGE TANK

UST – UNDERGROUND STORAGE TANK

PROJECT MANAGER	DATE	DRAWN BY	DATE DRAWN	CHECKED BY	DATE	APPROVED BY	DATE	SCALE	DATE ISSUED
DJG	01-2007	CPS	01-2007	DJG	01-2007	DJG	01-2007	1" = 100'	04-11-2007

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ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
GENESEE MARINA
118 PETTEN STREET
ROCHESTER, NEW YORK

REMEDIAL INVESTIGATION WORKPLAN

DRAWING TITLE
PROPOSED SURFACE SOIL / NEAR SURFACE SOIL,
SURFACE WATER AND SEDIMENT SAMPLE LOCATION MAP

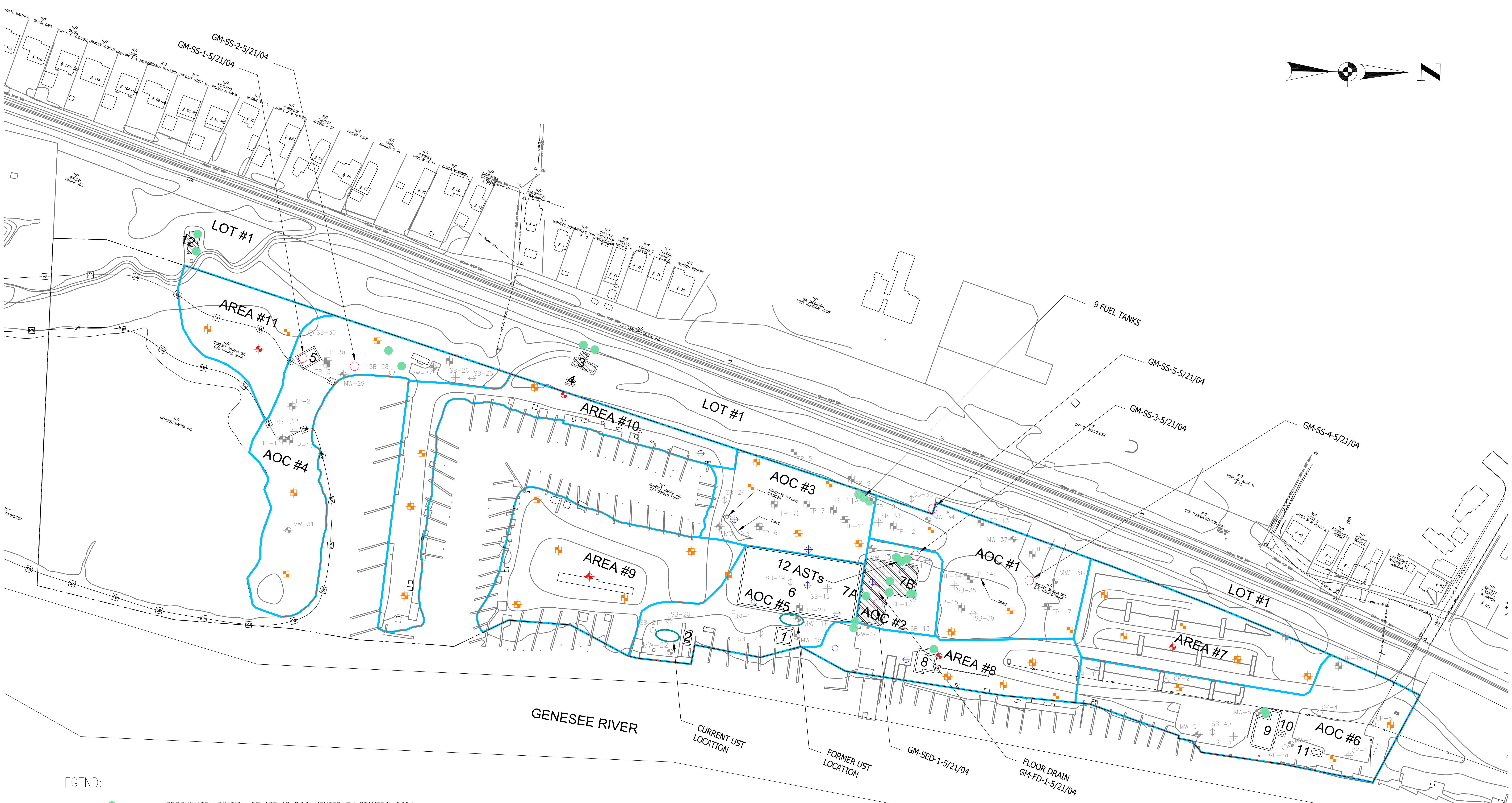
PROJECT NO.
3903S-06

DRAWING NO.
FIGURE 5

Reference Files Attached:
REF1: Fig 7 Sample Location Exceedances in Soil.dwg
REF2:
REF3:
REF4:
REF5:
REF6:
REF7:
REF8:
REF9:
REF10:

File Name: Drawings\GenMarina\3903S-06\Surface Soil Samples – DEC
Layout Name: Layout 2
Time Plotted: Tues Jun 26 16:10 2007
Pen Setting File: GenMarina.ctb

ANSI "D" (22x34)
DayEnv_AnsiD



LEGEND:

●	APPROXIMATE LOCATION OF AST AS DOCUMENTED BY STANTEC, 2004
⬭	UST LOCATION AS DOCUMENTED BY STANTEC, 2004
— - —	APPROXIMATE PROPERTY LINE
—	AOC/AREA BOUNDARY LINE
▨	DEMOLISHED BUILDINGS SINCE STANTEC 10/2004 REPORT
6	EXISTING BUILDINGS, BUILDING NUMBER AS IDENTIFIED BY STANTEC, 2004
SW FW	STATE AND FEDERAL WETLANDS
AA AA	WETLANDS 100' BUFFER AREA
⌖	PROPOSED TEST BORING LOCATION
⌖	PROPOSED TEST BORING/MONITORING WELL LOCATION
⌖	PROPOSED TEST PIT LOCATION
SB-14 ⌖	PREVIOUS SOIL BORING W/HSA INSTALLED BY STANTEC
GP-4 ⌖	PREVIOUS SOIL BORING W/GEOPROBE INSTALLED BY STANTEC
GM-SS-1-5/21/04 ○	PREVIOUS SURFACE SOIL/SEDIMENT SAMPLE INSTALLED BY STANTEC
MW-15 ⌖	EXISTING MONITORING WELL INSTALLED BY STANTEC
TP-14 ⌖	PREVIOUS TEST PIT INSTALLED BY STANTEC

NOTES:

1. BASE MAP PROVIDED BY DRAWINGS CREATED BY STANTEC CONSULTING GROUP, INC. AS REPORTED IN STANTEC'S OCTOBER 2004 PHASE II ESA REPORT
2. LOCATIONS OF SAMPLES COLLECTED ARE APPROXIMATE
3. SAMPLE LOCATIONS ARE BASED ON THE FIELD GPS SURVEY PERFORMED ON AUGUST 25, 2004 BY STANTEC, USING A TRIMBLE GEO XT GPS SYSTEM
4. CONCRETE HOLDING CYLINDER IN AOC #3 WAS IDENTIFIED IN STANTEC'S JUNE 2004 PHASE I AND LIMITED PHASE II ESA REPORT

ABBREVIATIONS:

AOC - AREA OF CONCERN

AST - ABOVE-GROUND STORAGE TANK

UST - UNDERGROUND STORAGE TANK

0' 100' 200' 300'

Reference Files Attached:
REF1: Fig 7 Sample Location Exceedances in Soil.dwg
REF2:
REF3:
REF4:
REF5:
REF6:
REF7:
REF8:
REF9:
REF10:

File Name: Drawings\GenMarina\3903S-06\TP_MW_TB - DEC
Layout Name: Layout 2
Time Plotted: Wed Apr 11 12:30 2007
Pen Setting File: GenMarina.ctb

ANSI "D" (22x34)
DayEnv_AnsiD

PROJECT MANAGER	DATE
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CHECKED BY DJG	DATE 01-2007
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SCALE 1" = 100'	DATE ISSUED 04-11-2007

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ENVIRONMENTAL CONSULTANTS
ROCHESTER, NEW YORK 14614-1008
NEW YORK, NEW YORK 10165-1617

PROJECT TITLE
GENESEE MARINA
118 PETTEN STREET EXTENSION
ROCHESTER, NEW YORK

REMEDIAL INVESTIGATION WORKPLAN

DRAWING TITLE
PROPOSED TEST PIT, TEST BORING AND MONITORING WELL LOCATIONS

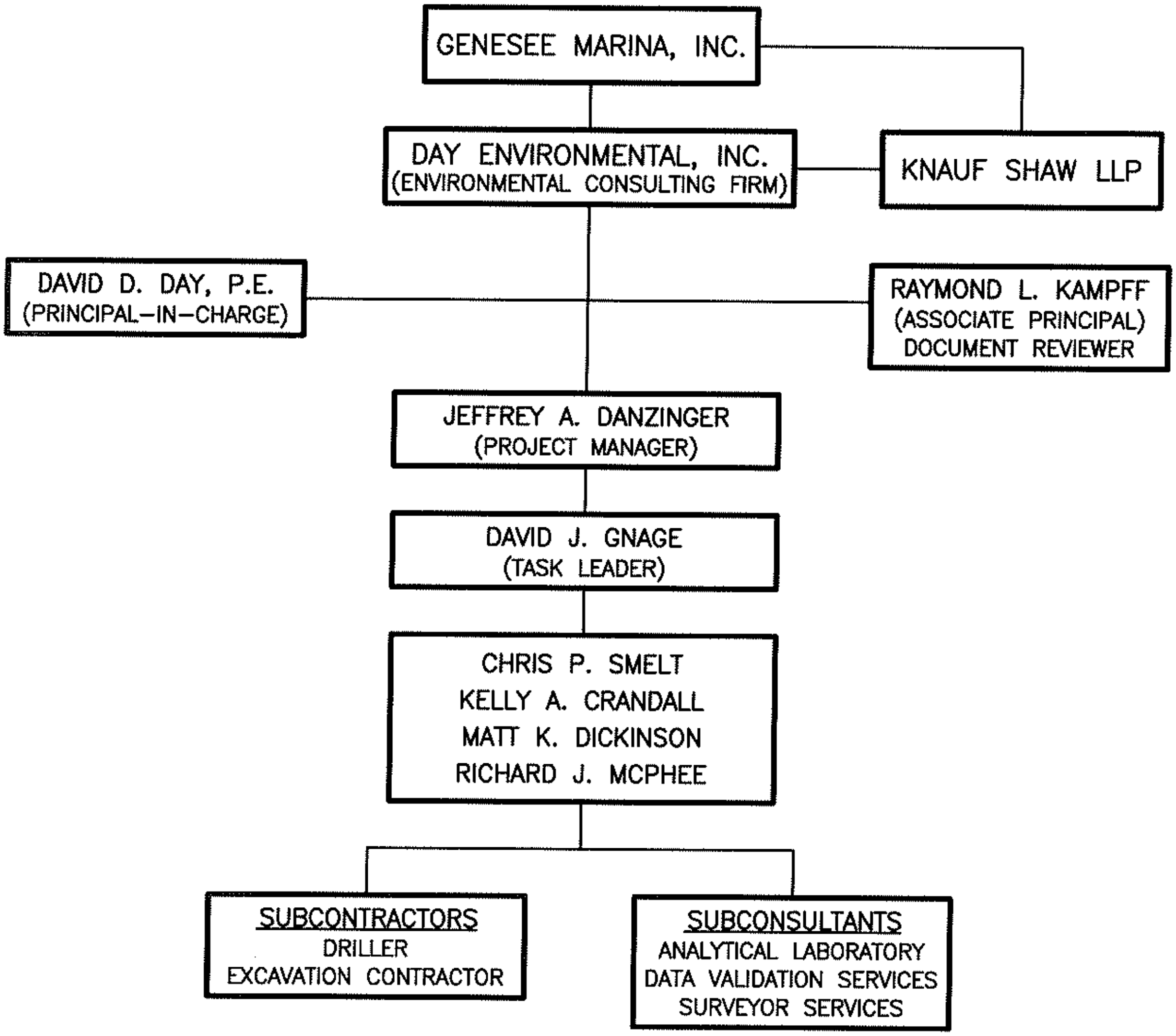
PROJECT NO.
3903S-06

DRAWING NO.
FIGURE 6

APPENDIX A

DAY Environmental, Inc.
April 5, 2007

DAY ENVIRONMENTAL, INC.
ORGANIZATIONAL CHART
BROWNFIELD CLEANUP PROGRAM
GENESEE MARINA, INC.
SITE #C828130
118 PETTEN STREET, ROCHESTER, NY



Drawings\GenMarina\3903S\Organizational Chart.dwg
Thur Apr 5 8:10 2007

APPENDIX B

Brownfield Cleanup Program

Genesee Marina, Inc.
C828130
Genesee Marina, Inc.

Eliot Spitzer, Governor
Denise M. Sheehan, Commissioner
Robert J. Duffy, Mayor

Transform the Past.... Build for the Future

APPENDIX C

Soil Sample Field Screening
Standard Operating Procedure (SOP)

As a Triad approach component for this investigation project, portions of the soil samples that are collected from surface soil, near-surface soil (i.e., former surface soil layer currently covered by gravel), test boring and test pit locations will be real-time field screened in order to achieve a more timely and cost-effective site characterization. The portions of the soil samples that are placed in sealable Ziploc®-type plastic baggies will be field screened the same day they are collected using the following protocol:

- The sample will be agitated and homogenized for at least 30 seconds and allowed to equilibrate for at least three minutes.

- The ambient headspace air inside the baggie above the soil sample will be screened for total VOC vapors with a RAE Systems MiniRAE 2000 photoionization detector (PID) equipped with a 11.7 eV lamp (or equivalent) and a Photovac MicroFID flame ionization detector (FID), or equivalent. The sampling ports for the PID and FID will be placed in the ambient air headspace inside the bag by opening a corner of the "locked" portion of the bag. The PID and FID will monitor air inside the baggie for a period of at least 15 seconds and the peak readings measured will be recorded on a log sheet or log book.

- The soil sample will then be further prepared removing debris, such as rocks, pebbles, leaves, vegetation, and roots) and further discrete homogenization. This sample preparation is in accordance with the USEPA CLU-IN "*In Situ Prepared*" XRF sample protocol (copy attached). In addition, samples with high moisture content (i.e., moisture content greater than about 20%) will either be air-dried on discrete disposable paper towels, or be dried in a toaster oven. The sample will then be field-screened for metals using an Innov-X Systems, Inc. Model Alpha 4000 X-ray fluorescence (XRF) analyzer (or equivalent) that is set up for soil screening and is equipped with "LEAP Technology." [Note: If a toaster oven is to be used to dry a sample, a separate un-dried portion of that sample must first be XRF screened for mercury since heating in the toaster oven may volatilize the mercury.] The Alpha 4000 XRF unit utilizes an X-ray tube and does not require licensing or special shipping. The field personnel utilizing the XRF analyzer will be manufacturer trained. The XRF analyzer can measure Pb, Cr, Hg, Cd, Sb, Ti, Mn, Fe, Ni, Cu, Zn, Sn, Ag, As, Se, Ba, Co, Zr, Rb, W, Br, and Tl. Detection limits can be found at Innov-X Systems, Inc. website (http://www.innov-x-sys.com/products/detect). Prior to conducting field screening, the actual analytes from this list to be reported will be approved by the NYSDEC. The XRF analyzer will be mounted to a bench-top analysis test stand/enclosure. The closed sample baggie will be placed inside the bench-top analysis test stand/enclosure. The XRF analyzer will be activated for a test period of 120 seconds, unless otherwise approved by the NYSDEC field representative. The Hewlett Packard (HP) IPAQ pocket personal computer (PC) that is part of the XRF analyzer will be used to record the results for each sample. The XRF screening portion of this SOP is based on implementation of various components of EPA Method 6200 (copy attached), which can be further referred to as deemed appropriate.

- The sample will also be observed and documented regarding its composition and any evidence of staining, unusual odors, etc.

CLU-IN

EPA United States Environmental Protection Agency

Technology Innovation Program

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Characterization and Monitoring

Technology Tools

> Technology Descriptions and Selection Tools

Select a Technology | Field Analytic Technologies Index | Ask an Expert | Problem Solver

The information on this page is provided for reference purposes and originally appeared on the Field Analytic Technologies Encyclopedia (FATE) web site, which was discontinued in July 2006.

Although the information provided here was accurate and current when first created, it is now outdated. EPA's Technology Innovation Program is in the process of updating these pages, and this note will be removed from these pages once they have been updated.

X-ray Fluorescence

Description

Field-portable, handheld device for simultaneously measuring a number of metals in various media.

Typical Uses

Energy dispersive X-ray fluorescence (EDXRF) is a method of detecting metals and other elements, such as arsenic and selenium, in soil and sediment. Some of the primary elements of environmental concern that EDXRF can identify are arsenic, barium, cadmium, chromium, copper, lead, mercury, selenium, silver, and zinc. Field-portable X-ray fluorescence (FPXRF) units that run on battery power and use a radioactive source were developed for use in analysis for lead-based paint and now are accepted as a stand-alone technique for lead analysis. In response to the growing need for field analysis of metals at hazardous waste sites, many of these FPXRF units have been adapted for use in the environmental field. The field-rugged units use analytical techniques that have been developed for analysis of numerous environmental contaminants in soils. They provide data in the field that can be used to identify and characterize contaminated sites and guide remedial work, among other applications.

More recently, FPXRF analyzers have been used to detect metals in water. The water samples must be filtered and concentrated with an ion exchange membrane to achieve detection limits in the low parts per billion (ppb) range lower than applicable maximum contaminant levels (MCL). Many manufacturers of FPXRF units currently are conducting research to refine the procedures for preparation of water samples to make FPXRF analysis a practical field analytical technique for metals in water.

Theory of Operation

FPXRF instruments were developed as an effective and nondestructive tool for measuring lead in paint and in house dust. Most homes constructed or painted before 1976 contain lead-based paint, which is one of the most common sources of lead ingested by children. In response, the U.S. Department of Housing and Urban Development (HUD) set guidelines for the inspection and abatement of contamination in public housing developments at which lead paint had been used. HUD considers any paint surface with a lead content greater than 1 milligram per square centimeter (mg/cm^2) to be a lead-based paint surface. FPXRF units were designed to detect lead in paint at levels at or lower than that level. Air filters are used to measure concentrations of metals in household dust. When the volume of air that has passed through the air filter is measured, a conversion can be made to determine the concentrations of metals suspended as particulates in the air. Although the technique was developed for homes in which contamination with lead is suspected, it also has been applied in monitoring air emissions from industrial processes or from remediation processes conducted at a hazardous waste site.

One of the advantages of EDXRF analysis is that it can be used not only to detect lead, but also to detect and measure many elements simultaneously. Generally, EDXRF units can detect and quantify elements from atomic number 16 (sulfur) through 92 (uranium). There are two types of EDXRF units: bench-top units that use an X-ray tube source and FPXRF analyzers that use a radioisotope as a source of X-rays. Instruments that use X-ray tubes as sources commonly are not used in the field because of the larger power requirements for the X-ray tube and the added weight of the instrument. Use of a radioactive source eliminates the need for a fixed power source for an X-ray tube, making the FPXRF unit truly portable.

In FPXRF analysis, a process known as the photoelectric effect is used in analyzing samples. Fluorescent X-rays are produced by exposing a sample to an X-ray source that has an excitation energy similar to, but greater than, the binding energy of the inner-shell electrons of the elements in the sample. Some of the source X-rays will be scattered, but a portion will be absorbed by the elements in the sample. Because of their higher energy level, they will cause ejection of the inner-shell electrons. The electron vacancies that result will be filled by electrons cascading in from outer electron shells. However, since electrons in outer shells have higher energy states than the inner-shell electrons they are replacing, the outer shell electrons must give off energy as they cascade down. The energy is given off in the form of X-rays, and the phenomenon is referred to as X-ray fluorescence (click to view a schematic diagram of the X-ray fluorescence process). Because every element has a different electron shell configuration, each element emits a unique X-ray at a set energy level or wavelength that is characteristic of that element. The elements present in a sample can be identified by observing the energy level of the characteristic X-rays, while the intensity of the X-rays is proportional to the concentration and can be used to perform quantitative analysis. In other words, qualitative analysis is performed by observing the energy of the characteristic X-rays. A quantitative analysis is performed by measuring the intensity of the X-ray.

The emissions of characteristic X-rays from three electron shells commonly are involved in FPXRF analysis: the K, L, and M shells. A typical emission pattern, or emission spectrum, for a given element has several peaks generated from the emission of X-rays from those shells.

System Components

A FPXRF system has two basic components: the radioisotope source and the detector. The source irradiates the sample to produce characteristic X-rays, as described above. The detector measures both the energy of the characteristic X-rays that are emitted and their intensity to identify and quantify the elements present in the sample. The following sections describe each of the components in greater detail.

Radioisotope Sources

An X-ray source will excite characteristic X-rays from an element only if the source energy is greater than the binding energy, or absorption edge energy, of the electrons in a given electron shell. A given individual source can analyze only certain elements. Analysis is more sensitive for an element with an absorption edge energy similar to, but less than, the excitation energy of the source. For example, when using a cadmium-109 (C-109) source, FPXRF would exhibit more sensitivity to zirconium, which has a K shell energy of 15.7 kiloelectron volts (keV), than for chromium, which has a K shell energy of 5.41 keV.

The radioisotope sources that are becoming standard in FPXRF units are Fe-55, Cd-109, and Am-241. Elements that those sources commonly analyze include:

- Fe-55: sulfur (S), potassium (K), calcium (Ca), titanium (Ti), and chromium (Cr)
- Cd-109: vanadium (V), Cr, manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), strontium (Sr), zirconium (Zr), molybdenum (Mo), mercury (Hg), lead (Pb), rubidium (Rb), and uranium (U)
- Am-241: cadmium (Cd), tin (Sn), antimony (Sb), barium (Ba), and silver (Ag)

Because individual sources by nature reliably analyze only a limited number of sources, FPXRF instruments that use more than one source have been developed, allowing them to analyze a greater number and range of elements. Typical arrangements of such multisource instruments include Cd-109 and Am- 241 or Fe-55, Cd-109, and Am-241.

X-ray Tube Sources

Miniature x-ray tube sources are now being employed by a number of vendors. The advantage of the x-ray tube sources is that it does not require licensing or special shipping, as do XRF units employing radioactive sources. These units usually have a low-power hot-filament cathode x-ray tube. The transmission anode operates at a high enough energy range (~35 keV) in order to simultaneously excite a large range of elements (k through u). Interferences and sensitivity problems associated with high energy sources are corrected using sophisticated software built into the XRF unit.

Detectors

Two basic types of detectors are used in FPXRF units: gas-filled and solid-state. Each detector has its advantages and limitations and is better suited to some applications than to others.

Common solid-state detectors include Si(Li), HgI_2, and silicon pin diode. Among those detectors, the Si(Li) is capable of the highest resolution but is quite temperature-sensitive and will register signal "noise" if not cooled sufficiently. The Si(Li) has a resolution of 170 electron volts (eV) if cooled to at least −90°C, either with liquid nitrogen or by thermoelectric cooling that uses the Peltier effect. The HgI_2 detector can operate at a moderately subambient temperature and is cooled by use of the Peltier effect. It has a resolution of 270 to 300 eV. The silicon pin diode detector operates near ambient temperatures and is cooled only slightly by use of the Peltier effect. It has a resolution of 250 eV.

Some elements produce peaks that are near each other in the spectrum, while very high concentrations of one element may produce a peak that overwhelms the peaks of other elements that are present at lower concentrations. The higher the resolution, the better the detector is able to separate characteristic peaks. The XRF operator must be careful to select an FPXRF unit that has sufficient resolution to satisfy the data quality needs of the project. The following link provides an illustration of this concept by providing the resolution differences among some common XRF detectors. Resolution is discussed in greater detail in a later section.

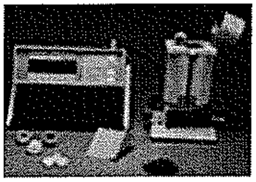
Mode of Operation

The radioisotope source or sources are housed in a metal turret, with additional lead shielding inside the probe. To perform an analysis, a sample is positioned in front of the plastic film measurement window of the probe and measurement of the sample is initiated, usually by depressing a trigger or start button. Doing so exposes the sample to the source radiation. For units that use multiple sources, after the sample has been exposed to one source, the turret is rotated to expose it to the next source. The length of time the sample actually is exposed to each source is referred to as the count time. The sample is exposed to the radioactive source for a number of seconds. Fluorescent and backscattered X-rays from the sample reenter the analyzer through the window and are counted by the instrument's detector. X-rays emitted by the sample at each energy level are called "counts". The detector records the counts, measures the energy of each X-ray and builds a spectrum of analyte peaks on a multichannel analyzer (MCA). The unit's software integrates the peaks to produce a readout of concentrations of analytes, and, usually, the standard deviation for each analyte. Numerous sample results and spectra can be stored for later viewing, downloading into a computer, or printing. Some units also allow the operator to recall previous results and even to view their spectra. At the completion of the exposure time, the instrument software statistically computes a concentration from the readings collected from each energy level along the spectrum. Count times are not to be confused with the total analytical time, which includes all of the analytical functions, such as rotation of the source into position, and processing of the results by the instrument software, in addition to the count time of each source.

Count times from 30 seconds per source to as long as 200 seconds per source can be employed, depending on the data quality needs of the project. As count times increase, the detector collects a larger number of X-rays from the sample, including more X-rays from elements that are present at comparatively lower concentrations. For that reason, the longer the count time, the lower the detection limits; typically, quadrupling the count time will cut the detection limit in half. For example, if a 50-second count time yields a detection limit of 100 parts per million (ppm) for a given element, increasing the count time to 200 seconds will lower the detection limit to approximately 50 PPM Using the instrument's software, the operator can select the appropriate count times.

An FPXRF detector can be operated in the in situ or the intrusive mode. Count times of 30 to 60 seconds per source are common for in situ analysis, while count times for intrusive analysis may be as long as 200 seconds per source. The particular requirements of the job, such as the required detection limits or data sample precision, and the purpose of sampling–for field screening or for definitive analysis–will determine which mode is appropriate and what count times are needed. Descriptions of each mode follow.

In situ analysis refers to the rapid screening of soils in place. For in situ operation, the window of the probe is placed in direct contact with the surface to be analyzed, and a trigger is pulled, much as one would fire a gun. Because analyses in this mode typically are completed very quickly (in less than one minute) and sample heterogeneity of the samples sometimes is a concern, it is recommended that three to four measurements be taken in a small area and the values be averaged to determine the concentrations of metals. Intrusive analysis used to ensure greater precision when lower detection limits are needed. Those goals are achieved through more extensive sample preparation and longer analysis times to reduce heterogeneity among samples and increase the sensitivity of the instrument, respectively. For intrusive operation, a sample is collected, prepared (usually by homogenizing, drying, grinding, and sieving), and placed in a 31- or 40-millimeter (mm) polyethylene sample cup that has a transparent Mylar window. The sample cup is placed over the probe window (some units provide a safety cover for intrusive analysis) and analyzed. Some FPXRF instruments can analyze samples in either mode, while others have only one mode of operation.Standard Operating Procedures (SOPs)



- Spectrace 9000XMET 920
- XMET 880

While a clear distinction is made here between in situ analysis and fully intrusive analysis, sample analysis is in reality a continuum. Thorough homogenization will improve the precision and accuracy of the analysis dramatically; an "in situ prepared" sample can be collected, homogenized, and analyzed right next to the sample location (possibly right through a plastic bag used for homogenization). Drying the sample also may improve the results significantly, and, depending on the project's data quality objectives, homogenization and drying may be all the preparation required for an intrusive analysis. Preparation of samples is discussed in greater detail in a later section.

Target Analytes

The target analytes are metals and other nonmetallic elements, such as arsenic and selenium.

Performance Specs

Performance specifications include information about interferences, detection limits, calibration, sample preparation, quality control, and precision and accuracy.

Interferences

There are a number of factors known as interferences that can affect the detection and quantification of elements in a sample. Some interferences can be inherent in the method of analysis, while others are the result of the instrument's setup, such as calibration methods. Other interferences may arise from outside sources, such as the sample matrix (for example, soils and sediment). Some factors can be prevented or minimized through careful preparation and sample design; others are natural effects that must be taken into consideration. To produce useful data, it is important that the analyst understand the interferences. Their effects and the procedures used to evaluate them are described below.

Matrix Effects
Matrix effects can cause a great deal of variation in sample analyses. Physical matrix effects result from variations in the physical character of the sample soils, such as particle size, uniformity, homogeneity, and condition of the surface. The FPXRF demonstration conducted under the Superfund Innovative Technology Evaluation (SITE) program provided convincing evidence that the heterogeneity of the sample generally has the greatest effect on comparability with confirmatory samples. Every effort should be made to homogenize soil samples thoroughly before analysis. One way to reduce particle size effects is to grind and sieve all soil samples to a uniform particle size.

Moisture Effects
Moisture content above 20 percent may cause problems, since moisture alters the soil matrix for which the FPXRF has been calibrated. This problem can be minimized by drying, preferably in a convection or toaster oven. Drying by microwave can increase variability between the FPXRF data and confirmatory data and can cause arcing if fragments of metal are present in the sample.

Sampling Effects

In environmental samples, typical X-ray penetration depths range from 0.1 millimeter (mm) to 1 mm. 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. Maintaining a consistent distance between the window and the sample minimizes that problem. For best results, the window of the probe should be in direct contact with the sample.

Chemistry Effects

Chemical matrix effects also can occur as X-ray absorption and enhancement phenomena. For example, iron tends to absorb copper X-rays, while chromium actually will be enhanced in the presence of iron. The effects can be corrected mathematically through the FPXRF instrument's software.

Detector Resolution Effects

The resolution of the detector may cause problems in analyzing some elements. If the energy difference between the characteristic X-rays of two elements (as measured in eV) is less than the resolution of the detector in eVs, the detector will not be able to resolve the peaks. In other words, if two peaks are 240 eVs apart, but the resolution of the detector is 270 eV, the detector will have difficulty in differentiating those peaks. A common example is the overlap of the arsenic K peak with the lead L peak. With the use of mathematical corrections that subtract the lead interference, lead can be measured from the lead L peak and arsenic still can be measured from the arsenic K peak. However, concentrations of arsenic cannot be calculated efficiently for samples that have lead to arsenic ratios of 10 to 1 or more, because the lead peak will overwhelm the arsenic peak completely.

Detection Limits

An FPXRF operator must consider two types of detection limits: instrument detection limits (DL) and method detection limits (MDL). A DL is the absolute threshold concentration of a given element that a particular instrument can resolve, as determined by the standard deviation (SD) of an individual analytical result. DLs of 10 to 100 PPM are typical for soil samples, although DLs may be higher for elements like chromium and cadmium that have characteristic X-ray peaks far removed from the energy level of the sources typically used.

MDLs depend on the analytical method (such as preparation and analysis times) and may be higher than DLs. The results of replicate measurements of a low-concentration sample can be used to generate an average site-specific MDL. The MDL is defined as three times the SD of the results for a replicate analysis of a low-concentration sample. With the exception of chromium which has a MDL as high as 900 milligram per kilogram (mg/kg) depending the instrument being used, the MDLs for most analytes are in the range of 40 to 200 mg/kg.

Click to view a comparison of method detection limits for six commercial FPXRF instruments.

Calibration

FPXRF units are calibrated by any of several methods. The methods will vary according to the make of the unit and the use to which the data are to be put, such as for screening or for definitive analysis. Basically, there are two types of calibration, although there is some overlap between two.

Fundamental Parameters Calibration

The fundamental parameters (FP) calibration is a "standardless" calibration. Rather than calibrating a unit's calibration curve by measuring its response to standards that contain analytes of known concentrations, FP calibration relies on the known physics of the spectrometer's response to pure elements to set the calibration. Built-in mathematical algorithms are used to adjust the calibration for analysis of soil samples and to compensate for the effects of the soil matrix. The FP calibration is performed by the manufacturer, but the analyst can adjust the calibration curves (slope and y-intercept) on the bases of results of analyses of check samples, such as standard reference materials (SRM), which are analyzed in the field.

Empirical Calibration

In performing an empirical calibration, a number of actual samples, such as site-specific calibration standards (SSCS), are used, and the instrument's measurement of the concentrations of known analytes in the samples are measured. Empirical calibration is effective because the samples used closely match the sample matrix. SSCSs are well-prepared samples collected from the site of interest in which the concentrations of analytes have been determined by inductively coupled plasma (ICP), atomic absorption (AA), or other methods approved by the US Environmental

Protection Agency (EPA). The standards should contain all the analytes of interest and interfering analytes. Manufacturers recommend that 10 to 20 calibration samples be used to generate a calibration curve.

Compton Normalization

The Compton normalization method incorporates elements of both empirical and FP calibration. A single, well-characterized standard, such as an SRM or a SSCS, is analyzed, and the data are normalized 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 intensity of the Compton peak changes as various matrices affect the way in which source radiation is scattered. For that reason, normalizing to the Compton peak can reduce problems with matrix effects that vary among samples. Compton normalization is similar to the use of internal standards in analysis for organic analytes.

Sample Preparation

Procedures for sample preparation for in situ and intrusive analysis vary considerably, since the two methods serve completely different purposes. Sample preparation for in situ analysis is fairly straightforward, while sample preparation for intrusive analysis can be fairly complicated, depending on the data quality required.

In situ or "point-and-shoot" analysis requires little sample preparation.

- First, any unrepresentative debris, such as rocks, pebbles, leaves, vegetation, roots, and so forth, should be removed from the surface of the soil.
- Second, the surface must be smooth, so that the probe window makes good contact with the soil surface.
- Last, the surface of the soil should not be saturated to the point that ponded water is present.

For an "in situ prepared" sample:

- Soil from the sampling point is collected, and all unrepresentative debris, such as rocks, pebbles, leaves, vegetation, roots, and so forth, is removed.
- The soil is thoroughly homogenized.
- The sample probe is placed directly on the soil for analysis, as with a true in situ sample, or the sample can be analyzed directly through a plastic bag used for homogenization.

For intrusive analysis, the sample first must be collected and then prepared for analysis in a sample cup. Some or all of the following steps are necessary, depending on the data quality needed:

- The most important preparation step is thorough homogenization. Mixing the sample in a plastic bag works well.
- Any large unrepresentative debris should be removed from the sample.
- If the sample contains more than 20 percent moisture, the sample should be dried, preferably in a convection or toaster oven. Drying in a microwave oven is discouraged because doing so can increase the variability of results and arcing can occur when metal fragments are present in the sample.
- If a high degree of precision is required, the sample should be passed through a sieve. If the sample is not wet (has a moisture content of less than 20 percent) and is not high in clay content, the sample can be sieved in the field before it is placed in a container. Otherwise, the sample is ground with a mortar and pestle and passed through a 40- or 60-mesh sieve after drying.
- Finally, the sample is placed in a 31- or 40-mm polyethylene cup and covered with Mylar film.

Quality Control

Ensuring that the data generated by FPXRF analysis are of a known quality is vital to ensuring the usefulness of those data, regardless of their purpose. Quality control (QC) measures take several forms and can be performed in the field, during sample analysis, and after sample data have been collected. The amount and type of QC necessary will depend on the project's data quality objectives. A much higher degree of QC is necessary to produce defensible, definitive data, but analytical results from intrusive analysis have been demonstrated to compare favorably with results obtained through traditional laboratory methods, given that sample preparation has been thorough and QC adequate. By nature, results obtained in situ are of lower quality because of the lack of sample preparation, but, with the use of proper QC, in situ data can be corrected. A typical QC program would include the following measures:

- An energy calibration check sample at least twice daily

- An instrument blank for every 20 environmental samples
- A method blank for every 20 samples
- A calibration verification check sample for every 20 samples
- A precision sample for every 20 environmental samples.
- A confirmatory sample for every 10 environmental samples

Each of the measures identified above is discussed in detail below.

Energy calibration check samples are used to test FP calibrations. A check sample consists of a pure element, such as iron, lead, or copper, and is analyzed to determine whether the characteristic X-ray lines are shifting, which would indicate drift in the detector. The check also serves as a gain check in the event that ambient temperatures are fluctuating significantly (more than 10 to 20° F). The energy calibration check should be run at a frequency consistent with the manufacturer's recommendations. Generally, the check would be performed at the beginning of each working day, after the batteries have been changed or the instrument shut off, at the end of each working day, and at any other time at which the instrument operator believes that drift is occurring during analysis.

Two types of blanks can be used during FPXRF analysis. The first is an instrument blank, which is used to verify that there is no contamination in the spectrometer or on the probe window. The instrument blank can be silicon dioxide, a Teflon block, or a quartz block. The instrument blank should be analyzed a minimum of once daily, preferably once for every 20 samples, and should not contain any target analytes at levels higher than the MDL. The second type of blank is a method blank. The method blank is used to monitor sampling and analysis methods for laboratory-induced contaminants or interferences. The method blank can be "clean" silica sand or lithium carbonate that undergoes the same sample preparation procedures as the environmental samples. The method blank should be analyzed with the same frequency as the instrument blank and should not contain any target analytes at levels higher than the MDL.

Precision and Accuracy

Calibration verification check samples are used to check the accuracy of the instrument and assess the stability and consistency of the analysis of the target analytes. Accuracy is a measure of the instrument's ability to measure the "true" concentration of an element in a sample. The check sample can be an SSCS or an SRM, such as the National Institute of Standards and Technology (NIST) SRMs, that contains the target analytes, preferably at concentrations near any action levels for the site. The check sample should be run at the beginning and the end of each day or for every 20 environmental samples. The percent difference (%D) between the true value and the measured value should be less than 20 percent.

Instrument precision refers to an instrument's ability to produce the same result for a number of measurements of the same sample. The precision of FPXRF measurements is monitored by performing several analyses of samples that contain low, medium, and high concentrations of target analytes. It is especially important to know the precision of the instrument in measuring concentrations that are similar to action levels, because precision is dependent on analyte concentrations of analytes: as the concentration increases, the precision increases. A minimum of one precision sample should be run per day by conducting from 7 to 10 replicate measurements of the sample. The precision is assessed by calculating a relative standard deviation (RSD) of the replicate measurements for the analyte. The RSD values should be less than 20 percent for most analytes, except chromium, for which the value should be less than 30 percent.

Click to see a comparison of instrument precision.

Click to view the percent recovery by the FPXRF instrument for a number of metals in performance evaluations and standard reference materials.

Click to view the performance of an FPXRF instrument during the analysis of commercial performance evaluation (PE) samples. PE samples are commercially available standards containing certified concentrations of various target analytes.

Confirmatory samples are collected from the same sample material that is analyzed on site, but are sent to an off-site laboratory for formal analysis. The results of the on-site analysis are compared with the results of the off-site analysis to determine whether they are comparable within the acceptable range. The acceptable range is determined by the analytical method, if applicable, or by the user. The purpose of a confirmatory sample is to judge the accuracy of the data obtained by analysis on site and to allow corrections, if necessary. One confirmatory sample usually is submitted for every 10 to 20 samples analyzed on site, depending on the nature of the job.

Advantages

Most instruments weigh less than 30 pounds and can be operated using battery power for 8 to 10 hours.

A sample can be analyzed in less than five minutes. Throughput is a measure of the maximum rate of analysis that realistically can be obtained when using an instrument. That measure includes not only analytical time, but all sample preparation, QC, and data processing necessary to produce useable results. Throughput usually is expressed in samples per hour or samples per day. A throughput of 50 to 100 samples a day typically can be achieved for intrusive analysis, and as many as 150 samples per day can be analyzed in situ.

Analyses of as many as 35 elements can be performed simultaneously in a single analysis.

The sample is not destroyed during preparation or analysis; therefore, it is possible to perform replicate analyses on a sample and send the same sample for confirmatory analysis, so that comparability studies can be performed. The sample also can be archived for later use as a soil standard.

Because no solvents or acids are used for sample extraction, no waste is generated; disposal costs therefore are eliminated.

Operators usually can be trained in one or two days. The software is menu-driven. No data manipulation is required. Instruments are marketed for use by general scientists.

Little or no sample preparation is required; therefore, sample throughput is enhanced and time and money are saved.

Limitations

Detection limits for chromium are 200 mg/kg or higher. Action levels for some elements, such as arsenic or cadmium, may be lower than the detection limits of XRF.

Concentrations of elements in different types of soil or matrices might change, causing interferences--for example, between arsenic and lead. Site-specific calibration standards can compensate for some of those effects.

It is difficult to obtain soil standards. One of the best sources is SRMs from NIST. Those standards cost from $200 to $500 each.

A specific license is required to operate some FPXRF instruments. The total cost of attending a radiation safety course, obtaining the necessary paperwork, and paying the fee for the license can range from $500 to $1,000.

The Cd-109 source should be replaced every two years. The cost of replacement is approximately $4,000 to $5,000.

Any instrument that has a Si(Li) detector will require liquid nitrogen and a dewar (aluminum container) to hold the liquid nitrogen. This requirement adds the time and cost of obtaining and handling liquid nitrogen to cool an instrument with a Si(Li) detector before analysis can be performed.

Cost Data

XRF costs vary significantly. Instrument design and accessories affect instrument prices. Manufacturers listed below should be contacted directly for cost information.

Additional Resources

Comparing Field Portable X-Ray Fluorescence (XRF) To Laboratory Analysis Of Heavy Metals In Soil

Niton User's Guide Version 5.0

On-site Analysis of Metals in Liquids

Sample Handling Strategies for Accurate Lead-in-Soil Measurements in the Field and Laboratory

Vendor/Instrument Information

HNU Systems, Inc.	SEFA-P Analyzer	ET✓ PDF
Scitech Corporation	AP Spectrum Analyzer	ET✓ PDF
TN Spectrace	TN Pb Analyzer	ET✓ PDF

Verification/Evaluation Reports

Verification of the performance of site characterization and field analytical technologies is conducted through a variety of programs. Evaluation and verification reports from EPA's Superfund Innovative Technologies Evaluation (SITE) Measuring and Monitoring Program, EPA's Environmental Technology Verification Program (ETV) program, along with links to certification statements from California EPA's (CalEPA) California Environmental Technology Certification Program, are provided below.

Superfund Innovative Technologies Evaluation (SITE) Measuring and Monitoring Program
The SITE Demonstration Program encourages the development and implementation of innovative treatment technologies for (1) remediation of hazardous waste sites and (2) monitoring and measurement. In the SITE Demonstration Program, the technology is field-tested on hazardous waste materials. Engineering and cost data on the innovative technologies are gathered so that potential users can assess the technology's applicability to a particular site. Data collected during the field demonstration are used to assess the performance of the technology, the potential need for pre- and post-treatment processing of the waste, applicable types of wastes and waste matrices, potential operating problems, and approximate capital and operating costs.

See ETV reports below

EPA's Environmental Technology Verification (ETV) Program
EPA's Environmental Technology Verification (ETV) Program verifies the performance of innovative technologies. ETV was created to substantially accelerate the entrance of new environmental technologies into the domestic and international marketplaces. ETV verifies commercialized, private sector technologies. After the technology has been tested, the companies will receive a verification report that they can use in marketing their products. The results of the testing also are available on the Internet. The following reports from the ETV program are available for x-ray fluorescence:

- HNU Systems SEFA-P was verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.
- The Metorex X-MET 920-P and 940Field Portable X-ray Fluorescence Analyzer was verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.

- The Metorex X-MET 920-MP Fluorescence Analyzer was verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.
- The Niton XL Spectrum Analyzer was verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.
- The Scitec MAP Spectrum Analyzer was verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.
- The Spectrace TN 9000 and TN Pb Field Portable X-ray Fluorescence Analyzers were verified for detection and measurement of a series of inorganic analytes in soil. The primary target analytes were arsenic, barium, chromium, copper, lead, and zinc; nickel, iron, cadmium, and antimony were secondary analytes. The verification documents available consist of a verification report.

California EPA's California Environmental Technology Certification Program

CalEPA's environmental technology certification program is a voluntary program that provides participating technology developers, manufacturers, and vendors an independent, recognized third-party evaluation of the performance of new and mature environmental technologies. Developers and manufacturers define quantitative performance claims for their technologies and provide supporting documentation; CalEPA reviews that information and, when necessary, conducts additional testing to verify the claims. The technologies, equipment, and products that are proven to work as claimed are given official state certification. The certification program is voluntary and self-supporting. Companies participating in the program pay the costs of the evaluation and certification of their technologies.

Technologies that have been certified through this program are listed below. Links are provided to the web sites that provide the Certified Environmental Technology Transfer Advisory and Certification Notice for the technologies.

No reports available for this technology

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http://www.clu-in.org/char/technologies/xrf.cfm
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METHOD 6200

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

1.0 SCOPE AND APPLICATION

1.1 This method is applicable to the in situ and intrusive analysis of the 26 analytes listed in Table 1 for soil and sediment samples. Some common elements are not listed in Table 1 because they are considered "light" elements that cannot be detected by field portable x-ray fluorescence (FPXRF). They are: lithium, beryllium, sodium, magnesium, aluminum, silicon, and phosphorus. Most of the analytes listed in Table 1 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.

1.2 Detection limits depend on several factors, 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. General instrument detection limits for analytes of interest in environmental applications are shown in Table 1. These detection limits apply to a clean matrix of quartz sand (silicon dioxide) free of interelement spectral interferences using long (600-second) count times. These detection limits are given for guidance only and will vary depending on the sample matrix, which instrument is used, and operating conditions. A discussion of field performance-based detection limits is presented in Section 13.4 of this method. The clean matrix and field performance-based detection limits should be used for general planning purposes, and a third detection limit discussed, based on the standard deviation around single measurements, should be used in assessing data quality. This detection limit is discussed in Sections 9.7 and 11.3.

1.3 Use of this method is restricted to personnel either trained and knowledgeable in the operation of an XRF instrument or under the supervision of a trained and knowledgeable individual. This method is a screening method to be used with confirmatory analysis using EPA-approved methods. This method's main strength is as a rapid field screening procedure. The method detection limits (MDL) of FPXRF are above the toxicity characteristic regulatory level for most RCRA analytes. If the precision, accuracy, and detection limits of FPXRF meet the data quality objectives (DQOs) of your project, then XRF is a fast, powerful, cost effective technology for site characterization.

2.0 SUMMARY OF METHOD

2.1 The FPXRF technologies described in this method use sealed radioisotope sources to irradiate samples with x-rays. X-ray tubes are used to irradiate samples in the laboratory and are beginning to be incorporated into field portable instruments. When a sample is irradiated with x-rays, the source x-rays may undergo either scattering or absorption by sample atoms. This later 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 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) or beta (β), 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 15.7 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: 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 standard.

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 and Chapter Three for additional definitions.

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, 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 no As being reported 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 by an EPA-approved method.

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 SW-846 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 data quality objectives.

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, the confirmatory method used was Method 3050, and the FPXRF data compared very well with regression correlation coefficients (r^2 often exceeding 0.95, except for barium and chromium. See Table 9 in Section 17.0). The critical factor is that the digestion procedure and analytical reference method used should meet the data quality objectives (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 Section 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 to 20°F. The operator should follow the manufacturer's recommendations for gain check frequency.

5.0 SAFETY

5.1 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 operators 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. Licenses for radioactive materials are of two types; (1) general license which is usually provided by the manufacturer for receiving, acquiring, owning, possessing, using, and transferring radioactive material incorporated in a device or equipment, and (2) specific license which is issued to named persons for the operation of radioactive instruments as required by local state agencies. 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. A copy of the radioactive material licenses 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. Finally, an additional hazard present with x-ray tubes is the danger of electric shock from the high voltage supply. The danger of electric shock is as substantial as the danger from radiation but is often overlooked because of its familiarity.

5.2 Radiation monitoring equipment should be used with the handling 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 should be worn in the area of most frequent 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.

5.3 Refer to Chapter Three for guidance on some proper safety protocols.

6.0 EQUIPMENT AND SUPPLIES

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: Most 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, cadmium (Cd)-109, americium (Am)-241, and curium (Cm)-244. These sources may be contained in a probe along with a window and the detector; the probe is 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. 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 required 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 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. 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 most FPXRF instruments operated in the intrusive mode, the probe is rotated so that the window faces upward. 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 Si(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 Si(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 Si(Li) detector have an internal liquid nitrogen dewar with a capacity of 0.5 to 1.0 liter. 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; Si(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 amptitudes (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 parts per million on a liquid crystal display (LCD) in the instrument. FPXRF instruments can store both spectra and from 100 to 500 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, data can be downloaded by means of an RS-232 port and cable to a PC.

6.2 Spare battery chargers.

6.3 Polyethylene sample cups: 31 millimeters (mm) 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 micrometers (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 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 required 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.

7.2 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.

7.2.1 The SSCS must be representative of the matrix to be analyzed by FPXRF. These samples must be well homogenized. A minimum of ten 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.

7.2.2 Each sample should be oven-dried for 2 to 4 hours at a temperature of less than 150°C. If mercury is to be analyzed, a separate sample portion must remain undried, 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 ground with a mortar and pestle and passed through a 60-mesh sieve. Only the coarse rock fraction should remain on the screen.

7.2.3 The sample should be homogenized by using a riffle splitter or by placing 150 to 200 grams 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 grams 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.

7.3 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 method detection limits. These samples are used to monitor for cross-contamination and laboratory-induced contaminants or interferences.

7.4 Standard Reference Materials: Standard reference materials (SRM) 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.

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 Refer to Chapter One for additional guidance on quality assurance protocols. All field data sheets and quality control data should be maintained for reference or inspection.

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 Section 4.10, this check also serves as a gain check in the event that ambient temperatures are fluctuating greatly (> 10 to 20°F).

The energy calibration check should be run at a frequency consistent with manufacturers 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.

9.2.1 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 radioactive 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: instrument blanks and method blanks. An instrument blank is used to verify that no contamination exists in the spectrometer or on the probe window.

9.3.1 The instrument blank can be silicon dioxide, a Teflon 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 method detection limits 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. To be acceptable, a method blank must not contain any analyte at a concentration above its method detection limit. If an analyte's concentration exceeds its method detection limit, 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.

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 detection limit, but decreases sample throughput.

9.6 Detection Limits: Results for replicate analyses of a low-concentration sample, SSCS, or SRM can be used to generate an average site-specific method detection and quantitation limits. In this case, the method detection limit is defined as 3 times the standard deviation of the results for the low-concentration samples and the method quantitation limit is defined as 10 times the standard deviation of the same results. Another means of determining method detection and quantitation limits involves use of counting statistics. In FPXRF analysis, the standard deviation from counting statistics is defined as $\text{SD} = (N)^{1/2}$, where SD is the standard deviation for a target analyte peak and N is the net counts for the peak of the analyte of interest (i.e., gross counts minus background under the peak). Three times this standard deviation would be the method detection limit and 10 times this standard deviation would be the method quantitation limit. If both of the above mentioned approaches are used to calculate method detection limits, the larger of the standard deviations should be used to provide the more conservative detection limits.

This SD based detection limit criteria must be used by the operator to evaluate each measurement for its useability. A measurement above the average calculated or manufacturer's detection limit, but smaller than three times its associated SD, should not be used as a quantitative measurement. Conversely, if the measurement is below the average calculated or manufacturer's detection limit, but greater than three times its associated SD. It should be coded as an estimated value.

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 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^2) for the results should be 0.7 or greater for the FPXRF data to be considered screening level data. If the r^2 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: 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 required, 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 required.

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 Section 7.2. 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 Section 7.2; 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 required. 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 required to perform an adequate empirical calibration. The number of required 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 interference. 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 on in 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, one requirement is that any large or nonrepresentative debris be removed from the soil surface before analysis. This debris includes rocks, pebbles, leaves, vegetation, roots, and concrete. Another requirement is that the soil surface 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 data for this method, this modest amount of sample preparation was found to take less than 5 minutes 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 required detection limits.

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 grams or 250 cm^3, which is enough soil to fill an 8-ounce jar. 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 Section 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 homogenization procedure using the fluorescein dye required 3 to 5 minutes per sample. As demonstrated in Sections 13.5 and 13.7, homogenization has the greatest impact on the reduction of sampling variability. It produces little or no contamination. Often, it can be used without the more labor intensive steps of drying, grinding, and sieving given in Sections 11.5 and 11.6. Of course, to achieve the best data quality possible all four steps must 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 grams) is placed in a suitable container for drying. The sample should be dried for 2 to 4 hours in the convection or toaster oven at a temperature not greater than 150°C. 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 minutes 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 MDLs of the procedure or DQOs of the analysis.

12.0 DATA ANALYSIS AND CALCULATIONS

Most FPXRF instruments have software capable of storing all analytical results and spectra. The results are displayed in parts per million and can be downloaded to a PC, which can provide a hard copy printout. Individual measurements that are smaller than three times their associated SD should not be used for quantitation.

13.0 METHOD PERFORMANCE

13.1 This section discusses four performance factors, field-based method detection limits, precision, accuracy, and comparability to EPA-approved methods. The numbers presented in Tables 4 through 9 were generated from data obtained from six FPXRF instruments. 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.

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

13.3 All data presented in Tables 4 through 9 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.

13.4 Field-Based Method Detection Limits: The field-based method detection limits are presented in Table 4. The field-based method detection limits were determined by collecting ten replicate measurements on site-specific soil samples with metals concentrations 2 to 5 times the expected method detection limits. Based on these ten replicate measurements, a standard deviation on the replicate analysis was calculated. The method detection limits presented in Table 4 are defined as 3 times the standard deviation for each analyte.

The field-based method detection limits were generated by using the count times discussed earlier in this section. All the field-based method detection limits were calculated for soil samples that had been dried and ground and placed in a sample cup with the exception of the MAP Spectrum Analyzer. This instrument can only be operated in the in situ mode, meaning the samples were moist and not ground.

Some of the analytes such as cadmium, mercury, silver, selenium, and thorium were not detected or only detected at very low concentrations such that a field-based method detection limit could not be determined. These analytes are not presented in Table 4. Other analytes such as calcium, iron, potassium, and titanium were only found at high concentrations (thousands of mg/kg) so that reasonable method detection limits could not be calculated. These analytes also are not presented in Table 4.

13.5 Precision Measurements: The precision data is presented in Table 5. 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 5 is an average RSD for the precision samples that had analyte concentrations at 5 to 10 times the MDL 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 5. Some analytes such as cadmium, nickel, and tin were only detected at concentrations near the MDLs so that an RSD value calculated at 5 to 10 times the MDL 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 6 shows these results. The additional nine soil samples were comprised of three from each texture and had analyte concentrations ranging from near the detection limit of 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 6 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 6 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 versus 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 7 presents a summary of this data. With the exception of cadmium, chromium, and nickel, the values presented in Table 7 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 7. 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 7.

Table 8 provides a more detailed summary of accuracy data for one FPXRF instrument (TN 9000) for the 9 soil SRMs and 4 sediment SRMs. Table 8 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 9. Similar trends in the data were seen for all instruments.

Table 9 shows the regression parameters for the whole data set, broken out by soil type, and by preparation method. 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--in situ, sample collected and homogenized; preparation 3--intrusive, with sample in a sample cup but sample still wet and not ground; and preparation 4--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 9 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 9 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.

Section 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 required to dry and grind the sample for small improvements in comparability. Homogenization requires 3 to 5 minutes. Drying the sample requires one to two hours. Grinding and sieving requires another 10 to 15 minutes per sample. Lastly, when grinding and sieving is conducted, time must 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 Hewitt, A.D. 1994. "Screening for Metals by X-ray Fluorescence Spectrometry/Response Factor/Compton K_α Peak Normalization Analysis." *American Environmental Laboratory.* Pages 24-32.

13.8.2 Piorek, S., and J.R. Pasmore. 1993. "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. Volume 2, Pages 1135-1151.

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 Street N.W., Washington D.C. 20036, (202) 872-4477.

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. 1994. Energy Dispersive X-ray Fluorescence Spectrometry: An Introduction.

3. TN Spectrace. Spectrace 9000 Field Portable/Benchtop XRF Training and Applications Manual.

4. Unpublished SITE data, recieved from PRC Environment Management, Inc.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

The pages to follow contain Tables 1 through 9 and a method procedure flow diagram.

TABLE 1
INTERFERENCE FREE DETECTION LIMITS

Analyte	Chemical Abstract Series Number	Detection Limit 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: References 1, 2, and 3

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	458	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: Reference 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: Reference 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
FIELD-BASED METHOD DETECTION LIMITS (mg/kg)[a]

Analyte	Instrument					
	TN 9000	TN Lead Analyzer	X-MET 920 (SiLi Detector)	X-MET 920 (Gas-Filled Detector)	XL Spectrum Analyzer	MAP Spectrum Analyzer
Antimony	55	NR	NR	NR	NR	NR
Arsenic	60	50	55	50	110	225
Barium	60	NR	30	400	NR	NR
Chromium	200	460	210	110	900	NR
Cobalt	330	NR	NR	NR	NR	NR
Copper	85	115	75	100	125	525
Lead	45	40	45	100	75	165
Manganese	240	340	NR	NR	NR	NR
Molybdenum	25	NR	NR	NR	30	NR
Nickel	100	NR	NA	NA	NA	NR
Rubidium	30	NR	NR	NR	45	NR
Strontium	35	NR	NR	NR	40	NR
Tin	85	NR	NR	NR	NR	NR
Zinc	80	95	70	NA	110	NA
Zirconium	40	NR	NR	NR	25	NR

Source: Reference 4

[a] MDLs are related to the total number of counts taken. See Section 13.3 for count times used to generate this table.

NR Not reported.

NA Not applicable; analyte was reported but was not at high enough concentrations for method detection limit to be determined.

TABLE 5
PRECISION

Analyte	Average Relative Standard Deviation for Each Instrument at 5 to 10 Times the MDL					
	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

Source: Reference 4

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

NR Not reported.

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

TABLE 6
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

Source: Reference 4

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

ND Not detected.

NR Not reported.

TABLE 7
ACCURACY

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: Reference 4

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 8
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: Reference 4

[a] All concentrations in milligrams per kilogram.
%Rec. Percent recovery.
ND Not detected.
NA Not applicable.
-- No data.

TABLE 9
REGRESSION PARAMETERS FOR COMPARABILITY[1]

	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

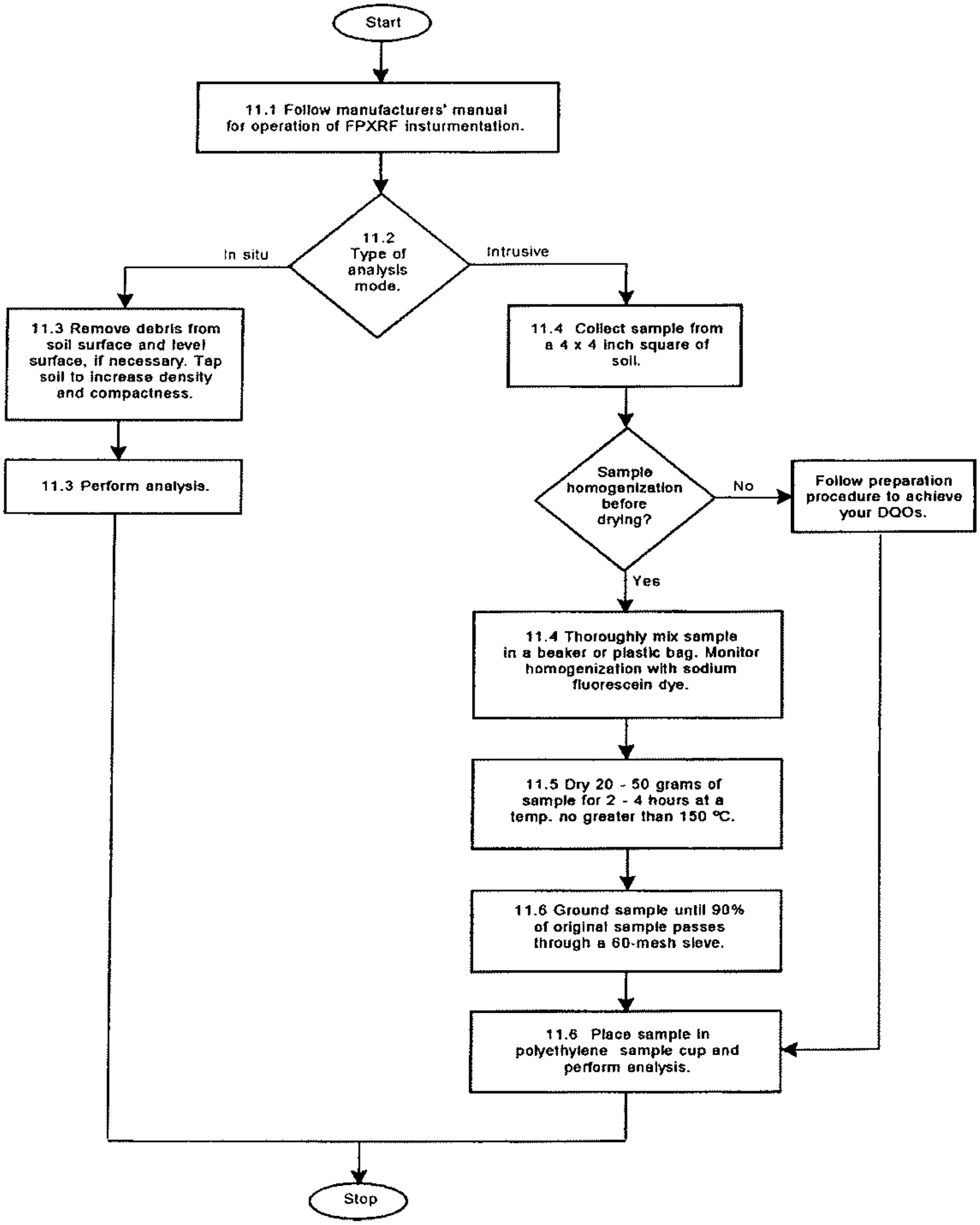
	Lead				Zinc				Chromium			
	n	r^2	Int.	Slope	n	r^2	Int.	Slope	n	r^2	Int.	Slope
All Data	1205	0.92	1.66	0.95	1103	0.89	1.86	0.95	280	0.70	64.6	0.42
Soil 1	357	0.94	1.41	0.96	329	0.93	1.78	0.93	—	—	—	—
Soil 2	451	0.93	1.62	0.97	423	0.85	2.57	0.90	—	—	—	—
Soil 3	397	0.90	2.40	0.90	351	0.90	1.70	0.98	186	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: Reference 4

[1] Log-transformed data
n Number of data points
r^2 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

SEDIMENT SAMPLING

SOP#: 2016
DATE: 11/17/94
REV. #: 0.0

1.0 SCOPE AND APPLICATION

This standard operating procedure (SOP) is applicable to the collection of representative sediment samples. Analysis of sediment may be biological, chemical, or physical in nature and may be used to determine the following:

- toxicity;
- biological availability and effects of contaminants;
- benthic biota;
- extent and magnitude of contamination;
- contaminant migration pathways and source;
- fate of contaminants;
- grain size distribution.

The methodologies discussed in this SOP are applicable to the sampling of sediment in both flowing and standing water. They are generic in nature and may be modified in whole or part to meet the handling and analytical requirements of the contaminants of concern, as well as the constraints presented by site conditions and equipment limitations. However, if modifications occur, they should be documented in a site or personal logbook and discussed in reports summarizing field activities and analytical results.

For the purposes of this procedure, sediments are those mineral and organic materials situated beneath an aqueous layer. The aqueous layer may be either static, as in lakes, ponds, and impoundments; or flowing, as in rivers and streams.

Mention of trade names or commercial products does not constitute U.S. EPA endorsement or recommendation for use.

2.0 METHOD SUMMARY

Sediment samples may be collected using a variety of methods and equipment, depending on the depth of the aqueous layer, the portion of the sediment profile required (surface vs. subsurface), the type of sample required (disturbed vs. undisturbed), contaminants present, and sediment type.

Sediment is collected from beneath an aqueous layer either directly, using a hand held device such as a shovel, trowel, or auger; or indirectly, using a remotely activated device such as an Ekman or Ponar dredge. Following collection, sediment is transferred from the sampling device to a sample container of appropriate size and construction for the analyses requested. If composite sampling techniques are employed, multiple grabs are placed into a container constructed of inert material, homogenized, and transferred to sample containers appropriate for the analyses requested. The homogenization procedure should not be used if sample analysis includes volatile organics; in this case, sediment, or multiple grabs of sediment, should be transferred directly from the sample collection device or homogenization container to the sample container.

3.0 SAMPLE PRESERVATION, CONTAINERS, HANDLING AND STORAGE

1. Chemical preservation of solids is generally not recommended. Cooling to 4°C is usually the best approach, supplemented by the appropriate holding time for the analyses requested.

2. Wide mouth glass containers with Teflon lined caps are utilized for sediment samples. The sample volume is a function of the analytical requirements and will be specified in the Work Plan.

3. If analysis of sediment from a discrete depth or location is desired, sediment is transferred directly from the sampling device to a labeled sample container(s) of appropriate size and construction for the analyses

requested. Transfer is accomplished with a stainless steel or plastic lab spoon or equivalent.

4. If composite sampling techniques or multiple grabs are employed, equal portions of sediment from each location are deposited into a stainless steel, plastic, or other appropriate composition (e.g., Teflon) containers. The sediment is homogenized thoroughly to obtain a composite representative of the area sampled. The composite sediment sample is transferred to a labeled container(s) of appropriate size and construction for the analyses requested. Transfer of sediment is accomplished with a stainless steel or plastic lab spoon or equivalent. Samples for volatile organic analysis must be transferred directly from the sample collection device or pooled from multiple areas in the homogenization container prior to mixing. This is done to minimize loss of contaminant due to volatilization during homogenization.

5. All sampling devices should be decontaminated, then wrapped in aluminum foil. The sampling device should remain in this wrapping until it is needed. Each sampling device should be used for only one sample. Disposable sampling devices for sediment are generally impractical due to cost and the large number of sediment samples which may be required. Sampling devices should be cleaned in the field using the decontamination procedure described in the Sampling Equipment Decontamination SOP.

4.0 INTERFERENCES AND POTENTIAL PROBLEMS

Substrate particle size and organic matter content are a direct consequence of the flow characteristics of a waterbody. Contaminants are more likely to be concentrated in sediments typified by fine particle size and a high organic matter content. This type of sediment is most likely to be collected from depositional zones. In contrast, coarse sediments with low organic matter content do not typically concentrate pollutants and are generally found in erosional zones. The selection of a sampling location can, therefore, greatly influence the analytical results and should be justified and specified in the Work Plan.

5.0 EQUIPMENT/APPARATUS

Equipment needed for collection of sediment samples may include:

- Maps/plot plan
- Safety equipment
- Compass
- Tape measure
- Survey stakes, flags, or buoys and anchors
- Camera and film
- Stainless steel, plastic, or other appropriate composition bucket
- 4-oz., 8-oz., and one-quart wide mouth jars w/Teflon lined lids
- Ziploc plastic bags
- Logbook
- Sample jar labels
- Chain of Custody records, field data sheets
- Cooler(s)
- Ice
- Decontamination supplies/equipment
- Spade or shovel
- Spatula
- Scoop
- Trowel
- Bucket auger
- Tube auger
- Extension rods
- "T" handle
- Sediment coring device (tube, drive head, eggshell check value, nosecone, acetate tube, extension rods, "T" handle)
- Ponar dredge
- Ekman dredge
- Nylon rope or steel cable
- Messenger device

6.0 REAGENTS

Reagents are not used for preservation of sediment samples. Decontamination solutions are specified in the Sampling Equipment Decontamination SOP.

7.0 PROCEDURES

7.1 Preparation

1. Determine the objective(s) and extent of the sampling effort. The sampling methods to be employed, and the types and amounts of equipment and supplies required will be a function of site characteristics and objectives of the study.
2. Obtain the necessary sampling and monitoring equipment.
3. Prepare schedules, and coordinate with staff, client, and regulatory agencies, if appropriate.
4. Decontaminate or preclean equipment, and ensure that it is in working order.
5. Perform a general site survey prior to site entry in accordance with the site specific Health and Safety Plan.
6. Use stakes, flagging, or buoys to identify and mark all sampling locations. Specific site factors including flow regime, basin morphometry, sediment characteristics, depth of overlying aqueous layer, contaminant source, and extent and nature of contamination should be considered when selecting sample locations. If required, the proposed locations may be adjusted based on site access, property boundaries, and surface obstructions.

7.2 Sample Collection

Selection of a sampling device is most often contingent upon: (1) the depth of water at the sampling location, and (2) the physical characteristics of the sediment to be sampled. The following procedures may be utilized:

7.2.1 Sampling Surface Sediment with a Trowel or Scoop from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 12 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with tools such as spades, shovels, trowels, and scoops. Although this method can be used to collect both unconsolidated/consolidated sediment, it is limited somewhat by the depth and movement of the aqueous layer. Deep and rapidly flowing water render this method less accurate than others discussed below. However, representative samples can be collected with this procedure in shallow sluggish water provided care is demonstrated by the sample team member. A stainless steel or plastic sampling implement will suffice in most applications. Care should be exercised to avoid the use of devices plated with chrome or other materials; plating is particularly common with garden trowels.

The following procedure will be used to collect sediment with a scoop, shovel, or trowel:

1. Using a decontaminated sampling implement, remove the desired thickness and volume of sediment from the sampling area.
2. Transfer the sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.
3. Surface water should be decanted from the sample or homogenization container prior to sealing or transfer; care should be taken to retain the fine sediment fraction during this procedure.

7.2.2 Sampling Surface Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of surface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of bucket auger or tube auger, a series of extensions, and a "T" handle (Figure 1, Appendix A). The use of additional extensions in conjunction with a bucket auger can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. However, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger or tube auger is driven into the sediment and used to extract a core. The various depths represented by the core are homogenized or a subsample of the core is taken from the appropriate depth.

The following procedure will be used to collect sediment samples with a bucket auger or tube auger:

1. An acetate core may be inserted into the bucket auger or tube auger prior to sampling if characteristics of the sediments or waterbody warrant. By using this technique, an intact core can be extracted.
2. Attach the auger head to the required length of extensions, then attach the "T" handle to the upper extension.
3. Clear the area to be sampled of any surface debris.
4. Insert the bucket auger or tube auger into the sediment at a 0° to 20° angle from vertical. This orientation minimizes spillage of the sample from the sampler upon extraction from the sediment and water.
5. Rotate the auger to cut a core of sediment.
6. Slowly withdraw the auger; if using a tube auger, make sure that the slot is facing upward.
7. Transfer the sample or a specified aliquot of sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

7.2.3 Sampling Deep Sediment with a Bucket Auger or Tube Auger from Beneath a Shallow Aqueous Layer

For the purpose of this method, deep sediment is considered to range from six to greater than 18 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches. Collection of deep sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a bucket auger, a tube auger, a series of extensions and a "T" handle. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to five feet or more. However, water clarity must be high enough to permit the sampler to directly observe the sampling operation. In addition, sample handling and manipulation increases in difficulty with increasing depth of water. The bucket auger is used to bore a hole to the upper range of the desired sampling depth and then withdrawn. The tube auger is then lowered down the borehole, and driven into the sediment to the lower range of the desired sampling depth. The tube is then withdrawn and the sample recovered from the tube. This method can be used to collect firmly consolidated sediments, but is somewhat limited by the depth of the aqueous layer, and the integrity of the initial borehole.

The following procedure will be used to collect deep sediment samples with a bucket auger and a tube auger:

1. Attach the bucket auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.
2. Clear the area to be sampled of any surface debris.
3. Begin augering, periodically removing any accumulated sediment (i.e., cuttings) from the auger bucket. Cuttings should be disposed of far enough from the sampling area to minimize cross contamination of various depths.
4. After reaching the upper range of the desired depth, slowly and carefully remove bucket auger from the boring.
5. Attach the tube auger bit to the required lengths of extensions, then attach the "T" handle to the upper extension.
6. Carefully lower tube auger down borehole using care to avoid making contact with the borehole sides and, thus, cross contaminating the sample. Gradually force tube auger into sediment to the lower range of the desired sampling depth. Hammering of the tube auger to facilitate coring should be avoided as the vibrations may cause the boring walls

to collapse.

7. Remove tube auger from the borehole, again taking care to avoid making contact with the borehole sides and, thus, cross contaminating the sample.

8. Discard the top of core (approximately 1 inch); as this represents material collected by the tube auger before penetration to the layer of concern.

9. Transfer sample into an appropriate sample or homogenization container. Ensure that non-dedicated containers have been adequately decontaminated.

7.2.4 Sampling Surface Sediment with an Ekman or Ponar Dredge from Beneath a Shallow or Deep Aqueous Layer

For the purpose of this method, surface sediment is considered to range from 0 to six inches in depth. Collection of surface sediment can be accomplished with a system consisting of a remotely activated device (dredge) and a deployment system. This technique consists of lowering a sampling device (dredge) to the surface of the sediment by use of a rope, cable, or extended handle. The mechanism is activated, and the device entraps sediment in spring loaded or lever operated jaws.

An Ekman dredge is a lightweight sediment sampling device with spring activated jaws. It is used to collect moderately consolidated, fine textured sediment. The following procedure will be used for collecting sediment with an Ekman dredge (Figure 2, Appendix A):

Attach a sturdy nylon rope or stainless steel cable through the hole on the top of the bracket, or secure the extension handle to the bracket with machine bolts.

2. Attach springs to both sides of the jaws. Fix the jaws so that they are in open position by placing trip cables over the release studs. Ensure that the hinged doors on the dredge top are free to open.

3. Lower the sampler to a point 4 to 6 inches above the sediment surface.

4. Drop the sampler to the sediment.

5. Trigger the jaw release mechanism by lowering a messenger down the line, or by depressing the button on the upper end of the extension handle.

6. Raise the sampler and slowly decant any free liquid through the top of the sampler. Care should be taken to retain the fine sediment fraction during this procedure.

7. Open the dredge jaws and transfer the sample into a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment grabs until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

A Ponar dredge is a heavyweight sediment sampling device with weighted jaws that are lever or spring activated. It is used to collect consolidated fine to coarse textured sediment. The following procedure will be used for collecting sediment with a Ponar dredge (Figure 3, Appendix A):

1. Attach a sturdy nylon rope or steel cable to the ring provided on top of the dredge.

2. Arrange the Ponar dredge with the jaws in the open position, setting the trip bar so the sampler remains open when lifted from the top. If the dredge is so equipped, place the spring loaded pin into the aligned holes in the trip bar.

3. Slowly lower the sampler to a point approximately two inches above the sediment.

4. Drop the sampler to the sediment. Slack on

the line will release the trip bar or spring loaded pin; pull up sharply on the line closing the dredge.

5. Raise the dredge to the surface and slowly decant any free liquid through the screens on top of the dredge. Care should be taken to retain the fine sediment fraction during this operation.

6. Open the dredge and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenized and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

7.2.5 Sampling Subsurface Sediment with a Coring Device from Beneath a Shallow Aqueous Layer

For purposes of this method, subsurface sediment is considered to range from 6 to 24 inches in depth and a shallow aqueous layer is considered to range from 0 to 24 inches in depth. Collection of subsurface sediment from beneath a shallow aqueous layer can be accomplished with a system consisting of a tube sampler, acetate tube, eggshell check valve, nosecone, extensions, and "T" handle, or drivehead. The use of additional extensions can increase the depth of water from which sediment can be collected from 24 inches to 10 feet or more. This sampler may be used with either a drive hammer for firm sediment, or a "T" handle for soft sediment. However, sample handling and manipulation increases in difficulty with increasing depth of water.

The following procedure describes the use of a sample coring device (Figure 4, Appendix A) used to collect subsurface sediments.

1. Assemble the coring device by inserting the acetate core into the sampling tube.

2. Insert the "egg shell" check valve into the lower end of the sampling tube with the convex surface positioned inside the acetate core.

3. Screw the nosecone onto the lower end of the sampling tube, securing the acetate tube and eggshell check valve.

4. Screw the handle onto the upper end of the sampling tube and add extension rods as needed.

5. Place the sampler in a perpendicular position on the sediment to be sampled.

6. If the "T" handle is used, place downward pressure on the device until the desired depth is reached. After the desired depth is reached, rotate the sampler to shear off the core at the bottom. Slowly withdraw the sampler from the sediment and proceed to Step 15.

7. If the drive hammer is selected, insert the tapered handle (drive head) of the drive hammer through the drive head.

8. Drive the sampler into the sediment to the desired depth.

9. Record the length of the tube that penetrated the sample material, and the number of blows required to obtain this depth.

10. Remove the drive hammer and fit the keyhole-like opening on the flat side of the hammer onto the drive head. In this position, the hammer serves as a handle for the sampler.

11. Rotate the sampler to shear off the core at the bottom.

12. Lower the sampler handle (hammer) until it just clears the two ear-like protrusions on the drive head, and rotate about 90°.

13. Slowly withdraw the sampler from the sediment. If the drivehead was used, pull the hammer upwards and dislodge the sampler from the sediment.

14. Carefully remove the coring device from the water.

15. Unscrew the nosecone and remove the eggshell check valve.

16. Slide the acetate core out of the sampler tube. Decant surface water, using care to retain the fine sediment fraction. If head space is present in the upper end, a hacksaw may be used to shear the acetate tube off at the sediment surface. The acetate core may then be capped at both ends. Indicate on the acetate tube the appropriate orientation of the sediment core using a waterproof marker. The sample may be used in this fashion, or the contents transferred to a sample or homogenization container.

17. Open the acetate tube and transfer the sediment to a stainless steel, plastic or other appropriate composition (e.g., Teflon) container. Ensure that non-dedicated containers have been adequately decontaminated. If necessary, continue to collect additional sediment until sufficient material has been secured to fulfill analytical requirements. Thoroughly homogenize and then transfer sediment to sample containers appropriate for the analyses requested. Samples for volatile organic analysis must be collected directly from the bucket before homogenization to minimize volatilization of contaminants.

8.0 CALCULATIONS

This section is not applicable to this SOP.

9.0 QUALITY ASSURANCE/ QUALITY CONTROL

There are no specific quality assurance (QA) activities which apply to the implementation of these procedures. However, the following QA procedures apply:

1. All data must be documented on field data sheets or within site logbooks.

2. All instrumentation must be operated in accordance with operating instructions as supplied by the manufacturer, unless otherwise specified in the work plan. Equipment checkout and calibration activities must occur prior to sampling/operation, and they must be documented.

10.0 DATA VALIDATION

This section is not applicable to this SOP.

11.0 HEALTH AND SAFETY

When working with potentially hazardous materials, follow U.S. EPA/OSHA and Corporate health and safety procedures.

More specifically, when sampling sediment from waterbodies, physical hazards must be identified and adequate precautions must be taken to ensure the safety of the sampling team. The team member collecting the sample should not get too close to the edge of the waterbody, where bank failure may cause loss of balance. To prevent this, the person performing the sampling should be on a lifeline, and be wearing adequate protective equipment. If sampling from a vessel is determined to be necessary, appropriate protective measures must be implemented.

12.0 REFERENCES

Mason, B.J., Preparation of Soil Sampling Protocol: Technique and Strategies. 1983 EPA-600/4-83-020.

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

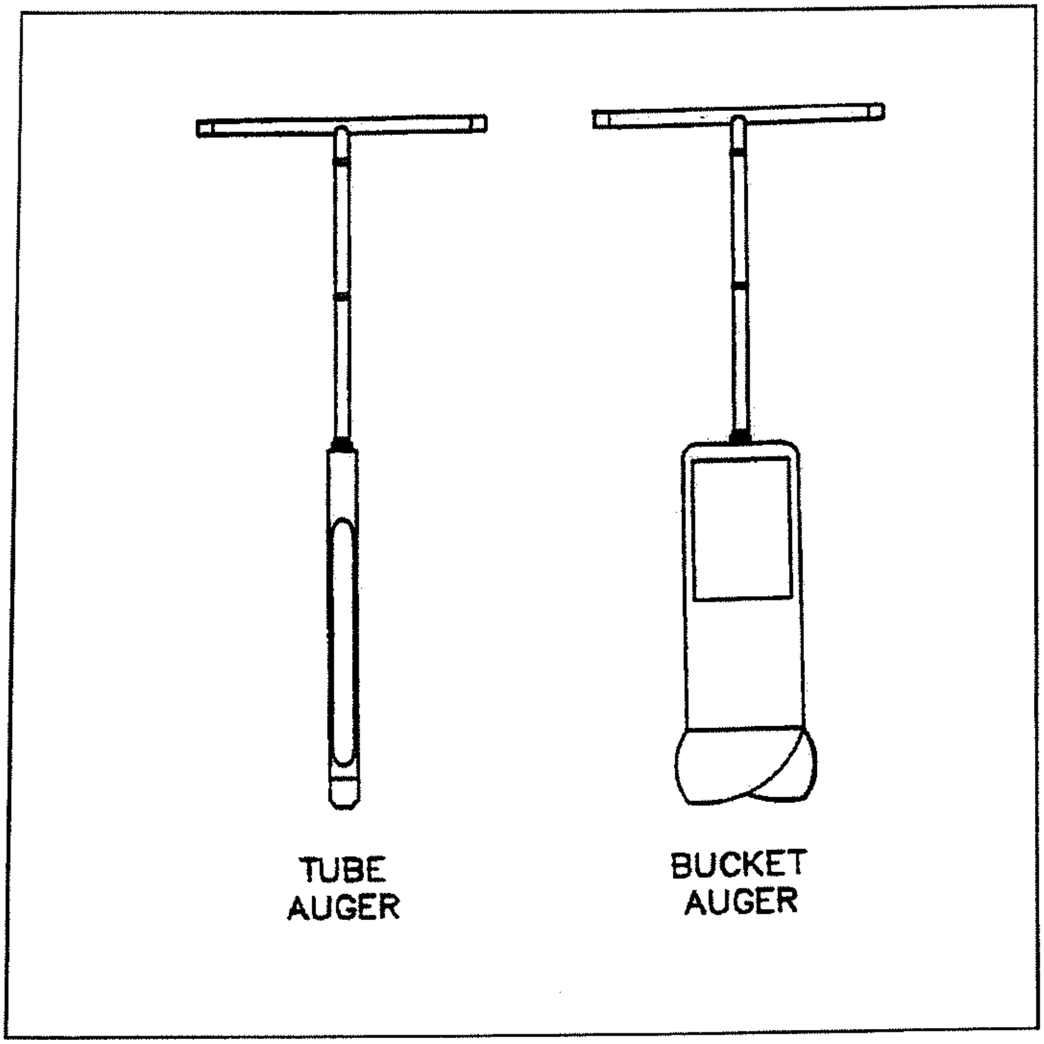
U.S. EPA. Characterization of Hazardous Waste Sites - A Methods Manual: Volume II. Available Sampling Methods, Second Edition. 1984 EPA-600/4-84-076.

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

APPENDIX A

Figures

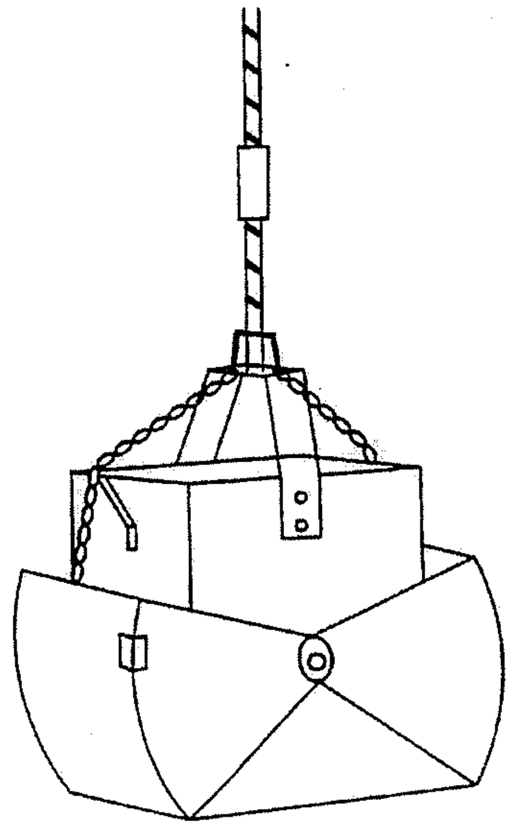
FIGURE 1. Sampling Auger



APPENDIX A (Cont'd)

Figures

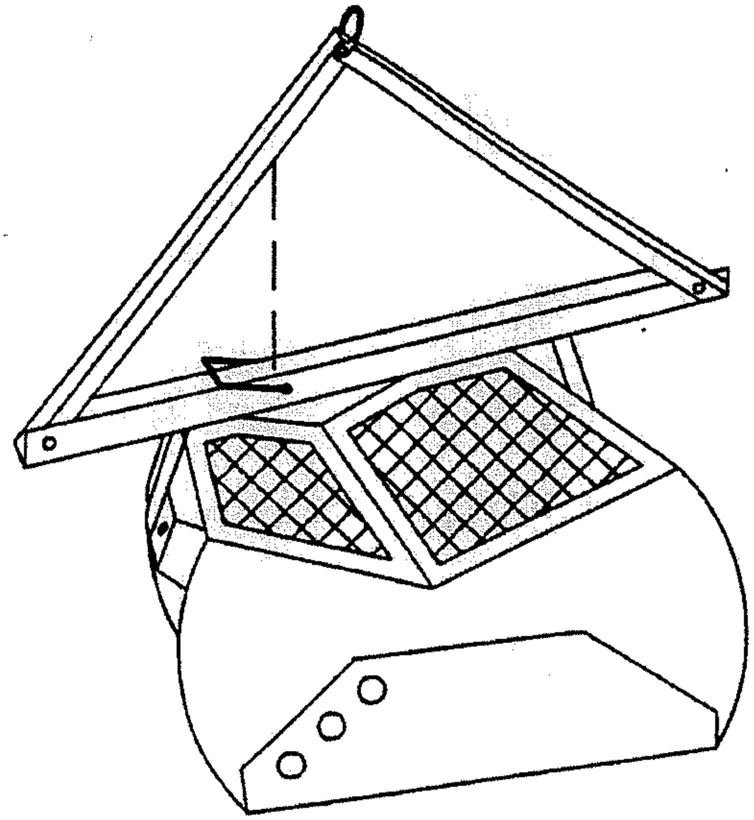
FIGURE 2. Ekman Dredge



APPENDIX A (Cont'd)

Figures

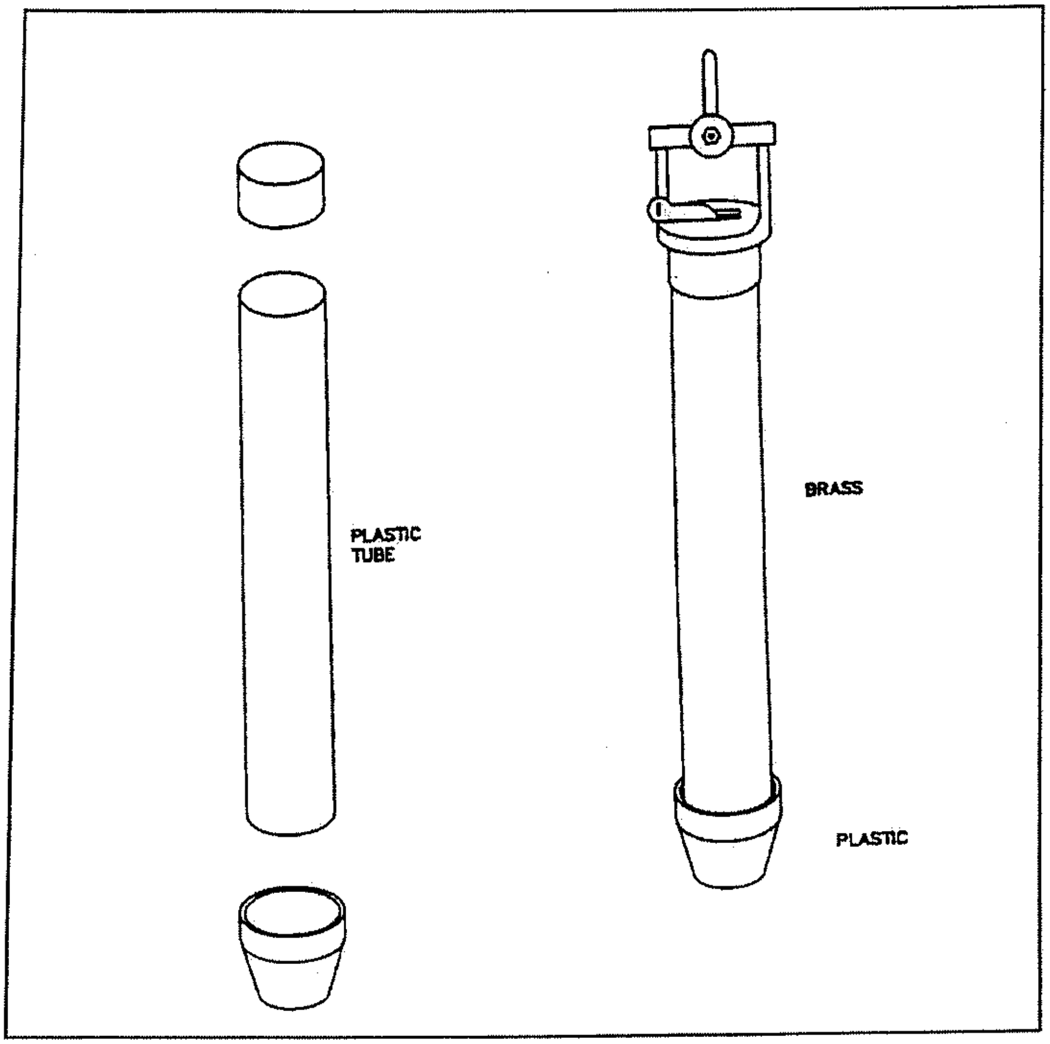
FIGURE 3. Ponar Dredge



APPENDIX A (Cont'd)

Figures

FIGURE 4. Sample Coring Device



APPENDIX E

Designation: D 1586 – 99

AMERICAN SOCIETY FOR TESTING AND MATERIALS
100 Barr Harbor Dr., West Conshohocken, PA 19428
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Standard Test Method for Penetration Test and Split-Barrel Sampling of Soils[1]

This standard is issued under the fixed designation D 1586; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This standard has been approved for use by agencies of the Department of Defense.

1. Scope *

1.1 This test method describes the procedure, generally known as the Standard Penetration Test (SPT), for driving a split-barrel sampler to obtain a representative soil sample and a measure of the resistance of the soil to penetration of the sampler.

1.2 *This standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For a specific precautionary statement, see 5.4.1.

1.3 The values stated in inch-pound units are to be regarded as the standard.

NOTE 1—Practice D 6066 can be used when testing loose sands below the water table for liquefaction studies or when a higher level of care is required when drilling these soils. This practice provides information on drilling methods, equipment variables, energy corrections, and blow-count normalization.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2487 Practice for Classification of Soils for Engineering Purposes (Unified Soil Classification System)[2]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[2]

D 4220 Practices for Preserving and Transporting Soil Samples[2]

D 4633 Test Method for Stress Wave Energy Measurement for Dynamic Penetrometer Testing Systems[2]

D 6066 Practice for Determining the Normalized Penetration Resistance Testing of Sands for Evaluation of Liquefaction Potential[3]

3. Terminology

3.1 *Definitions of Terms Specific to This Standard:*

3.1.1 *anvil*—that portion of the drive-weight assembly which the hammer strikes and through which the hammer energy passes into the drill rods.

3.1.2 *cathead*—the rotating drum or windlass in the rope-cathead lift system around which the operator wraps a rope to lift and drop the hammer by successively tightening and loosening the rope turns around the drum.

3.1.3 *drill rods*—rods used to transmit downward force and torque to the drill bit while drilling a borehole.

3.1.4 *drive-weight assembly*—a device consisting of the hammer, hammer fall guide, the anvil, and any hammer drop system.

3.1.5 *hammer*—that portion of the drive-weight assembly consisting of the 140 ± 2 lb (63.5 ± 1 kg) impact weight which is successively lifted and dropped to provide the energy that accomplishes the sampling and penetration.

3.1.6 *hammer drop system*—that portion of the drive-weight assembly by which the operator accomplishes the lifting and dropping of the hammer to produce the blow.

3.1.7 *hammer fall guide*—that part of the drive-weight assembly used to guide the fall of the hammer.

3.1.8 *N-value*—the blowcount representation of the penetration resistance of the soil. The N-value, reported in blows per foot, equals the sum of the number of blows required to drive the sampler over the depth interval of 6 to 18 in. (150 to 450 mm) (see 7.3).

3.1.9 ΔN—the number of blows obtained from each of the 6-in. (150-mm) intervals of sampler penetration (see 7.3).

3.1.10 *number of rope turns*—the total contact angle between the rope and the cathead at the beginning of the operator's rope slackening to drop the hammer, divided by 360° (see Fig. 1).

3.1.11 *sampling rods*—rods that connect the drive-weight assembly to the sampler. Drill rods are often used for this purpose.

3.1.12 *SPT*—abbreviation for standard penetration test, a term by which engineers commonly refer to this method.

4. Significance and Use

4.1 This test method provides a soil sample for identification purposes and for laboratory tests appropriate for soil obtained from a sampler that may produce large shear strain disturbance in the sample.

4.2 This test method is used extensively in a great variety of geotechnical exploration projects. Many local correlations and

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[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.02 on Sampling and Related Field Testing for Soil Investigations.

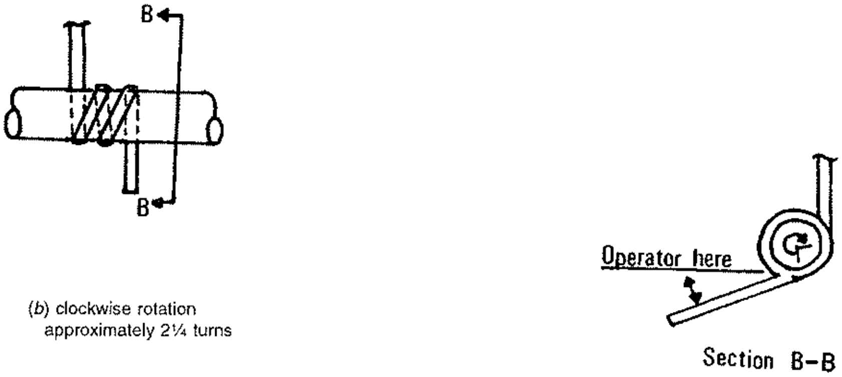
Current edition approved Jan. 10, 1999. Published March 1999. Originally published as D 1586 – 58 T. Last previous edition D 1586 – 98.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 04.09.

***A Summary of Changes section appears at the end of this standard.**

(*a*) counterclockwise rotation approximately 1¾turns



(*b*) clockwise rotation approximately 2¼ turns

FIG. 1 Definitions of the Number of Rope Turns and the Angle for (*a*) Counterclockwise Rotation and (*b*) Clockwise Rotation of the Cathead

widely published correlations which relate SPT blowcount, or *N*-value, and the engineering behavior of earthworks and foundations are available.

5. Apparatus

5.1 *Drilling Equipment*—Any drilling equipment that provides at the time of sampling a suitably clean open hole before insertion of the sampler and ensures that the penetration test is performed on undisturbed soil shall be acceptable. The following pieces of equipment have proven to be suitable for advancing a borehole in some subsurface conditions.

5.1.1 *Drag, Chopping, and Fishtail Bits*, less than 6.5 in. (162 mm) and greater than 2.2 in. (56 mm) in diameter may be used in conjuction with open-hole rotary drilling or casing-advancement drilling methods. To avoid disturbance of the underlying soil, bottom discharge bits are not permitted; only side discharge bits are permitted.

5.1.2 *Roller-Cone Bits*, less than 6.5 in. (162 mm) and greater than 2.2 in. (56 mm) in diameter may be used in conjunction with open-hole rotary drilling or casing-advancement drilling methods if the drilling fluid discharge is deflected.

5.1.3 *Hollow-Stem Continuous Flight Augers*, with or without a center bit assembly, may be used to drill the boring. The inside diameter of the hollow-stem augers shall be less than 6.5 in. (162 mm) and greater than 2.2 in. (56 mm).

5.1.4 *Solid, Continuous Flight, Bucket and Hand Augers*, less than 6.5 in. (162 mm) and greater than 2.2 in. (56 mm) in diameter may be used if the soil on the side of the boring does not cave onto the sampler or sampling rods during sampling.

5.2 *Sampling Rods*—Flush-joint steel drill rods shall be used to connect the split-barrel sampler to the drive-weight assembly. The sampling rod shall have a stiffness (moment of inertia) equal to or greater than that of parallel wall "A" rod (a steel rod which has an outside diameter of 1⅝ in. (41.2 mm) and an inside diameter of 1⅛ in. (28.5 mm).

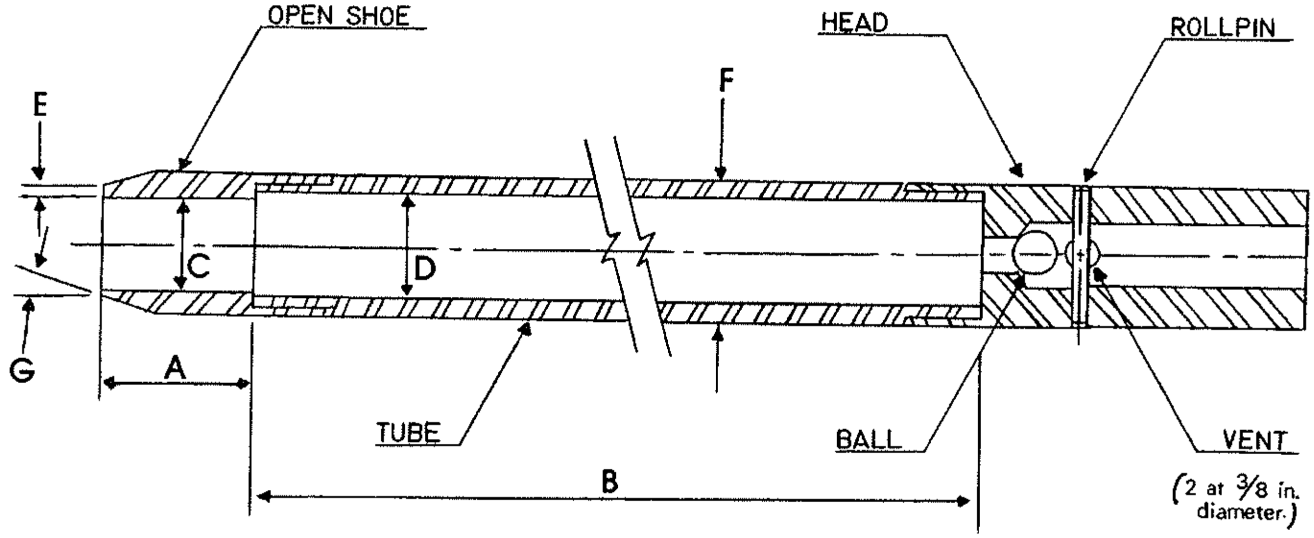
NOTE 2—Recent research and comparative testing indicates the type rod used, with stiffness ranging from "A" size rod to "N" size rod, will usually have a negligible effect on the *N*-values to depths of at least 100 ft (30 m).

5.3 *Split-Barrel Sampler*—The sampler shall be constructed with the dimensions indicated in Fig. 2. The driving shoe shall be of hardened steel and shall be replaced or repaired when it becomes dented or distorted. The use of liners to produce a constant inside diameter of 1⅜ in. (35 mm) is permitted, but shall be noted on the penetration record if used. The use of a sample retainer basket is permitted, and should also be noted on the penetration record if used.

NOTE 3—Both theory and available test data suggest that *N*-values may increase between 10 to 30 % when liners are used.

5.4 *Drive-Weight Assembly*:

5.4.1 *Hammer and Anvil*—The hammer shall weigh 140 ± 2 lb (63.5 ± 1 kg) and shall be a solid rigid metallic mass. The hammer shall strike the anvil and make steel on steel contact when it is dropped. A hammer fall guide permitting a free fall



A = 1.0 to 2.0 in. (25 to 50 mm)
B = 18.0 to 30.0 in. (0.457 to 0.762 m)
C = 1.375± 0.005 in. (34.93 ± 0.13 mm)
D = 1.50 ± 0.05 - 0.00 in. (38.1 ± 1.3 - 0.0 mm)
E = 0.10 ± 0.02 in. (2.54 ± 0.25 mm)
F = 2.00 ± 0.05 - 0.00 in. (50.8 ± 1.3 - 0.0 mm)
G = 16.0° to 23.0°

The 1½ in. (38 mm) inside diameter split barrel may be used with a 16-gage wall thickness split liner. The penetrating end of the drive shoe may be slightly rounded. Metal or plastic retainers may be used to retain soil samples.

FIG. 2 Split-Barrel Sampler

shall be used. Hammers used with the cathead and rope method shall have an unimpeded overlift capacity of at least 4 in. (100 mm). For safety reasons, the use of a hammer assembly with an internal anvil is encouraged.

NOTE 4—It is suggested that the hammer fall guide be permanently marked to enable the operator or inspector to judge the hammer drop height.

5.4.2 *Hammer Drop System*—Rope-cathead, trip, semi-automatic, or automatic hammer drop systems may be used, providing the lifting apparatus will not cause penetration of the sampler while re-engaging and lifting the hammer.

5.5 *Accessory Equipment*—Accessories such as labels, sample containers, data sheets, and groundwater level measuring devices shall be provided in accordance with the requirements of the project and other ASTM standards.

6. Drilling Procedure

6.1 The boring shall be advanced incrementally to permit intermittent or continuous sampling. Test intervals and locations are normally stipulated by the project engineer or geologist. Typically, the intervals selected are 5 ft (1.5 mm) or less in homogeneous strata with test and sampling locations at every change of strata.

6.2 Any drilling procedure that provides a suitably clean and stable hole before insertion of the sampler and assures that the penetration test is performed on essentially undisturbed soil shall be acceptable. Each of the following procedures have proven to be acceptable for some subsurface conditions. The subsurface conditions anticipated should be considered when selecting the drilling method to be used.

6.2.1 Open-hole rotary drilling method.

6.2.2 Continuous flight hollow-stem auger method.

6.2.3 Wash boring method.

6.2.4 Continuous flight solid auger method.

6.3 Several drilling methods produce unacceptable borings. The process of jetting through an open tube sampler and then sampling when the desired depth is reached shall not be permitted. The continuous flight solid auger method shall not be used for advancing the boring below a water table or below the upper confining bed of a confined non-cohesive stratum that is under artesian pressure. Casing may not be advanced below the sampling elevation prior to sampling. Advancing a boring with bottom discharge bits is not permissible. It is not permissible to advance the boring for subsequent insertion of the sampler solely by means of previous sampling with the SPT sampler.

6.4 The drilling fluid level within the boring or hollow-stem augers shall be maintained at or above the in situ groundwater level at all times during drilling, removal of drill rods, and sampling.

7. Sampling and Testing Procedure

7.1 After the boring has been advanced to the desired sampling elevation and excessive cuttings have been removed, prepare for the test with the following sequence of operations.

7.1.1 Attach the split-barrel sampler to the sampling rods and lower into the borehole. Do not allow the sampler to drop onto the soil to be sampled.

7.1.2 Position the hammer above and attach the anvil to the top of the sampling rods. This may be done before the sampling rods and sampler are lowered into the borehole.

7.1.3 Rest the dead weight of the sampler, rods, anvil, and drive weight on the bottom of the boring and apply a seating blow. If excessive cuttings are encountered at the bottom of the boring, remove the sampler and sampling rods from the boring and remove the cuttings.

7.1.4 Mark the drill rods in three successive 6-in. (0.15-m) increments so that the advance of the sampler under the impact of the hammer can be easily observed for each 6-in. (0.15-m) increment.

7.2 Drive the sampler with blows from the 140-lb (63.5-kg) hammer and count the number of blows applied in each 6-in. (0.15-m) increment until one of the following occurs:

7.2.1 A total of 50 blows have been applied during any one of the three 6-in. (0.15-m) increments described in 7.1.4.

7.2.2 A total of 100 blows have been applied.

7.2.3 There is no observed advance of the sampler during the application of 10 successive blows of the hammer.

7.2.4 The sampler is advanced the complete 18 in. (0.45 m) without the limiting blow counts occurring as described in 7.2.1, 7.2.2, or 7.2.3.

7.3 Record the number of blows required to effect each 6 in. (0.15 m) of penetration or fraction thereof. The first 6 in. is considered to be a seating drive. The sum of the number of blows required for the second and third 6 in. of penetration is termed the "standard penetration resistance," or the "*N*-value." If the sampler is driven less than 18 in. (0.45 m), as permitted in 7.2.1, 7.2.2, or 7.2.3, the number of blows per each complete 6-in. (0.15-m) increment and per each partial increment shall be recorded on the boring log. For partial increments, the depth of penetration shall be reported to the nearest 1 in. (25 mm), in addition to the number of blows. If the sampler advances below the bottom of the boring under the static weight of the drill rods or the weight of the drill rods plus the static weight of the hammer, this information should be noted on the boring log.

7.4 The raising and dropping of the 140-lb (63.5-kg) hammer shall be accomplished using either of the following two methods:

7.4.1 By using a trip, automatic, or semi-automatic hammer drop system which lifts the 140-lb (63.5-kg) hammer and allows it to drop 30 ± 1.0 in. (0.76 m ± 25 mm) unimpeded.

7.4.2 By using a cathead to pull a rope attached to the hammer. When the cathead and rope method is used the system and operation shall conform to the following:

7.4.2.1 The cathead shall be essentially free of rust, oil, or grease and have a diameter in the range of 6 to 10 in. (150 to 250 mm).

7.4.2.2 The cathead should be operated at a minimum speed of rotation of 100 RPM, or the approximate speed of rotation shall be reported on the boring log.

7.4.2.3 No more than 2¼ rope turns on the cathead may be used during the performance of the penetration test, as shown in Fig. 1.

NOTE 5—The operator should generally use either 1¾ or 2¼ rope turns, depending upon whether or not the rope comes off the top (1¾ turns) or the bottom (2¼ turns) of the cathead. It is generally known and accepted that 2¾or more rope turns considerably impedes the fall of the hammer and should not be used to perform the test. The cathead rope should be maintained in a relatively dry, clean, and unfrayed condition.

7.4.2.4 For each hammer blow, a 30-in. (0.76-m) lift and drop shall be employed by the operator. The operation of pulling and throwing the rope shall be performed rhythmically without holding the rope at the top of the stroke.

7.5 Bring the sampler to the surface and open. Record the percent recovery or the length of sample recovered. Describe the soil samples recovered as to composition, color, stratification, and condition, then place one or more representative portions of the sample into sealable moisture-proof containers (jars) without ramming or distorting any apparent stratification. Seal each container to prevent evaporation of soil moisture. Affix labels to the containers bearing job designation, boring number, sample depth, and the blow count per 6-in. (0.15-m) increment. Protect the samples against extreme temperature changes. If there is a soil change within the sampler, make a jar for each stratum and note its location in the sampler barrel.

8. Report

8.1 Drilling information shall be recorded in the field and shall include the following:

8.1.1 Name and location of job,

8.1.2 Names of crew,

8.1.3 Type and make of drilling machine,

8.1.4 Weather conditions,

8.1.5 Date and time of start and finish of boring,

8.1.6 Boring number and location (station and coordinates, if available and applicable),

8.1.7 Surface elevation, if available,

8.1.8 Method of advancing and cleaning the boring,

8.1.9 Method of keeping boring open,

8.1.10 Depth of water surface and drilling depth at the time of a noted loss of drilling fluid, and time and date when reading or notation was made,

8.1.11 Location of strata changes,

8.1.12 Size of casing, depth of cased portion of boring,

8.1.13 Equipment and method of driving sampler,

8.1.14 Type sampler and length and inside diameter of barrel (note use of liners),

8.1.15 Size, type, and section length of the sampling rods, and

8.1.16 Remarks.

8.2 Data obtained for each sample shall be recorded in the field and shall include the following:

8.2.1 Sample depth and, if utilized, the sample number,

8.2.2 Description of soil,

8.2.3 Strata changes within sample,

8.2.4 Sampler penetration and recovery lengths, and

8.2.5 Number of blows per 6-in. (0.15-m) or partial increment.

9. Precision and Bias

9.1 *Precision*—A valid estimate of test precision has not been determined because it is too costly to conduct the necessary inter-laboratory (field) tests. Subcommittee D18.02 welcomes proposals to allow development of a valid precision statement.

9.2 *Bias*—Because there is no reference material for this test method, there can be no bias statement.

9.3 Variations in *N*-values of 100 % or more have been observed when using different standard penetration test apparatus and drillers for adjacent borings in the same soil formation. Current opinion, based on field experience, indicates that when using the same apparatus and driller, *N*-values in the same soil can be reproduced with a coefficient of variation of about 10 %.

9.4 The use of faulty equipment, such as an extremely massive or damaged anvil, a rusty cathead, a low speed cathead, an old, oily rope, or massive or poorly lubricated rope sheaves can significantly contribute to differences in *N*-values obtained between operator-drill rig systems.

9.5 The variability in *N*-values produced by different drill rigs and operators may be reduced by measuring that part of the hammer energy delivered into the drill rods from the sampler and adjusting *N* on the basis of comparative energies. A method for energy measurement and *N*-value adjustment is given in Test Method D 4633.

10. Keywords

10.1 blow count; in-situ test; penetration resistance; split-barrel sampling; standard penetration test

SUMMARY OF CHANGES

(1) Added note to Section 1, Scope. The note refers to a related standard, Practice D 6066.

(2) Added Practice D 6066 to Section 2 on Referenced Documents.

APPENDIX F

INTERNATIONAL **Designation: D 6771 – 02**

Standard Practice for
Low-Flow Purging and Sampling for Wells and Devices Used for Ground-Water Quality Investigations[1]

1. Scope

1.1 This practice covers the method for purging and sampling wells and devices used for ground-water quality investigations and monitoring programs known as low-flow purging and sampling. This method is also known by the terms minimal drawdown purging or low-stress purging. This method could be used for other types of ground-water sampling programs but these uses are not specifically addressed in this practice.

1.2 This practice applies only to wells sampled at the wellhead.

1.3 This practice does not address sampling of wells containing either light or dense non-aqueous-phase liquids (LNAPLs or DNAPLs).

1.4 This practice offers a set of instructions for performing one or more specific operations. This document cannot replace education or experience and should be used in conjunction with professional judgment. Not all aspects of this practice may be applicable in all circumstances. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "standard" in the title means that the document has been approved through the ASTM consensus process.

1.5 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 4750 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation Well)[2]

D 5088 Practice for Decontamination of Field Equipment Used at Non-Radioactive Waste Sites[2]

D 5092 Practice for Design and Installation of Ground-Water Monitoring Wells in Aquifers[2]

D 5521 Guide for Development of Ground-Water Monitoring Wells in Granular Aquifers[2]

D 5903 Guide for Planning and Preparing for a Ground-Water Sampling Event[3]

D 6026 Practice for Using Significant Digits in Geotechnical Data[3]

D 6089 Guide for Documenting a Ground-Water Sampling Event[3]

D 6452 Guide for Purging Methods for Wells Used for Ground-Water Quality Investigations[3]

D 6517 Guide for Field Preservation of Ground-Water Samples[3]

D 6564 Guide for Field Filtration of Ground-Water Samples[3]

D 6634 Guide for the Selection of Purging and Sampling Devices for Ground-Water Monitoring Wells[3]

3. Terminology

3.1 *drawdown (low-flow purging and sampling), n*—lowering of the water level in a well caused by pumping the well.

3.2 *entrance velocity, n*—the velocity with which formation pore water passes through a well screen during pumping of the well. This velocity should be controlled (held to less than 0.10 ft/s or 3.0 cm/s) to avoid turbulent flow through the screen and to minimize or eliminate deleterious effects on water chemistry and on well construction materials.

3.3 *low flow, n*—refers to the velocity that is imparted during pumping to the formation pore water adjacent to the well screen. It does not necessarily refer to the flow rate of water discharged by a pump at the surface.

4. Summary of Practice

4.1 Low-flow purging and sampling is a method of collecting samples from a well that, unlike traditional purging methods, does not require the removal of large volumes of water from the well. Low-flow purging differs from traditional methods of purging (as described in Guide D 6452) in that its use is based on the observations of many researchers that water moving through the formation also moves through the well

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[1] This practice is under the jurisdiction of ASTM Committee D18 on Soil and Rock and is the direct responsibility of Subcommittee D18.21 on Ground-Water and Vadose Zone Investigations.

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[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 04.09.

screen. Thus, the water in the screen is representative of the formation water surrounding the screen. This assumes that the well has been properly designed, constructed, and developed as described in Practice D 5092 and Guide D 5521. In wells in which the flow through the screen or intake zone is limited by hydraulic conductivity contrasts (for example, borehole smearing, residual filter cake, filter pack grain size, or well screen open area), the head difference induced by low-flow pumping provides an exchange of water between the formation and the well. Low-flow purging involves removing water directly from the screened interval without disturbing any stagnant water above the screen. This is done by pumping the well at a low enough flow rate to maintain minimal drawdown of the water column within the well as determined through water-level measurement during pumping. The objective is to pump in a manner that minimizes stress to the ground-water system to the extent practical, taking into account site sampling objectives. Pumping at low rates, in effect, hydraulically isolates the column of stagnant water in the well and negates the need for its removal prior to sample collection. Typically, flow rates on the order of 0.1 to 0.5 L/min are used; however, this is dependent on site-specific and well-specific factors **(1)**. Some very coarse textured formations have been successfully purged and sampled in this manner at flow rates up to 1 L/min. Pumping water levels in the well and water-quality indicator parameters (such as pH, temperature, specific conductance, dissolved oxygen and redox potential) should be monitored during pumping, with stabilization indicating that purging is completed and sampling can begin. Because the flow rate used for purging is, in most cases, the same or only slightly higher than the flow rate used for sampling, and because purging and sampling are conducted as one continuous operation in the field, the process is referred to as low-flow purging and sampling.

5. Significance and Use

5.1 The objective of most ground-water sampling programs is to obtain samples that are representative of formation-quality water. Wells used in ground-water quality investigations or monitoring programs are generally purged of some amount of water in an attempt to obtain a representative sample. For traditional methods of purging (for example, well-volume purging), purging is done to minimize bias associated with stagnant water standing in the casing of the well (above the well screen), which generally does not accurately reflect ambient ground-water chemistry. To use low-flow purging and sampling, a pump intake is set within the well screen and the pump is operated at a low flow rate (generally less than or equal to the natural recovery rate of the well), minimizing drawdown in the well and thus hydraulically isolating the water in the screened zone from the water in the casing. Water pumped in this way comes directly from the screened interval of the well. This obviates the need to purge the stagnant water in the well prior to collecting samples. Access to formation-quality water is confirmed by monitoring water quality parameters to the point at which they stabilize as described in Guide D 6452.

5.2 Low-flow purging and sampling may be used in any well that can be pumped at a constant rate of 1.0 L/min or less without continuous drawdown of the water level in the well **(1)**. It is feasible to implement low-flow purging and sampling in wells in which the water level is always above the top of the well screen, and in wells that are constructed so that the water level is always within the well screen.

5.3 Low-flow purging and sampling can be used to collect samples for all categories of aqueous-phase contaminants and naturally occurring analytes, including volatile and semi-volatile organic compounds (VOCs and SVOCs), metals and other inorganics, pesticides, PCBs, other organic compounds, radionuclides and microbiological constituents. It is particularly well suited for use where it is desirable to sample aqueous-phase constituents that may sorb or partition to particulate matter. It is not applicable to sampling either light or dense non-aqueous-phase liquids (LNAPLs or DNAPLs).

6. Benefits and Limitations of Low-Flying Purging and Sampling

6.1 Purging and sampling at a low flow rate offers a number of benefits over traditional methods including:

6.1.1 Improved sample quality and reduced (or eliminated) need for sample filtration, through minimized disturbance of the well and the formation, which results in reduced artifactual sample turbidity and minimization of false positives for analytes associated with particulate matter;

6.1.2 Improved sample accuracy and precision and greatly reduced sample variability as a result of reduced stress on the formation, reduced mixing of the water column in the well and dilution of analytes, and reduced potential for sample agitation, aeration and degassing or volatilization;

6.1.3 Samples represent a smaller section or volume of the formation, representing a significant improvement in the ability to detect and resolve contaminant distributions, which may vary greatly over small distances in three-dimensional space;

6.1.4 Overall, improved sample reproducibility, especially when using dedicated pumps;

6.1.5 Improved ability to directly quantify the total mobile contaminant load (including mobile colloid-sized particulate matter) without the need for sample filtration;

6.1.6 Increased well life through reduced pumping stress on the well and formation, resulting in greatly reduced movement of fine sediment into the filter pack and well screen;

6.1.7 Greatly reduced purge-water volume, (often 90 to 95 %) resulting in significant savings of cost related to purge water handling and disposal or treatment, and reduced exposure of field personnel to potentially contaminated purge water; and

6.1.8 Reduced purging and sampling time (much reduced at sites using dedicated pumps), resulting in savings of labor cost, depending on the time required for water-quality indicator parameters to stabilize.

6.2 Though the application of low-flow purging and sampling will improve sampling results and produce significant technical and cost benefits at most sites, not all sites, and not all individual wells within a site, are well suited to this approach. Limitations of the method include the following:

6.2.1 On a practical basis, low-flow purging and sampling is generally not suitable for use in very low-yield wells (those that will not yield sufficient water without continued drawdown with pumping over time). This limitation is largely a function of the limitations of discharge rates of available pumps and the volume of the flow cell (if used) for indicator parameter measurement;

6.2.2 The need to use a variable flow-rate pump capable of pumping within the desired flow-rate range. Low-flow purging cannot be performed using grab sampling devices, such as bailers, or inertial lift devices, which severely agitate the water column in the well, resulting in significant mixing of the water column and release of considerable sediment, which shows up as increased turbidity in samples.

6.2.3 For some applications, the need to use a flow-through cell, which may increase capital costs, lead to slightly greater set-up time in the field, and add one piece of field equipment.

7. Equipment Requirements for Low-Flow Purging and Sampling

7.1 A variety of pumps capable of pumping at low flow rates may be used for low-flow purging and sampling. Continuous discharge and cyclic discharge pumps work equally well as long as the pump has adjustable flow rate controls and is capable of being run at a low enough flow rate to avoid causing continuous drawdown in the well. Because the purging and sampling processes are joined together into one continuous operation, the pump selected (see Guide D 6634) should be appropriate for use both in purging and sampling the analytes of interest. For example, if VOCs or other pressure-sensitive parameters (for example, dissolved oxygen, carbon dioxide, trace metals) are analytes of interest, peristaltic and other suction-lift pumps should be avoided because they may cause loss of VOCs, degassing and redox and pH changes **(2-5)**.

7.2 Dedicated pumps (those that are permanently installed in the well) are preferred over portable pumps because they eliminate disturbance to the water column in the well resulting in lower turbidity values, shorter purge times and lower purge volumes to achieve stabilized indicator parameter measurements. However, portable pumps can be used if care is taken to minimize disturbance to the water column during pump installation and some time is allowed prior to pump operation for any fines agitated in the water column to settle.

7.3 Grab sampling devices, such as bailers and kemmerer samplers, and inertial-lift devices, cannot be used for low-flow purging and sampling because of the disturbance they cause to the water column in the well and the attendant effects of mixing and increased sample turbidity.

7.4 A volume measuring device (for example, graduated cylinder) and a time piece capable of measuring in seconds will be necessary to calculate the flow rate from the discharge tube from the pump.

7.5 Low-flow purging and sampling requires continuous or periodic water-level measurements (see Test Method D 4750). Any water-level measurement equipment that does not disturb the water column in the well may be used, as long as it provides the accuracy required by the sampling program (generally ±0.01 ft [3 mm]).

7.6 Low-flow purging and sampling requires continuous or periodic measurement of selected water-quality indicator parameters (and, possibly, turbidity) to determine when purging is complete and sampling can commence. Continuous monitoring in a closed flow-through cell of known volume generally provides the most consistent and reliable results, especially for dissolved oxygen and redox potential, and is the preferred method of measuring indicator parameters. However, individual instruments designed to measure the most common water-quality indicator parameters (temperature, pH, and conductivity or specific conductance) may also be used. Dissolved oxygen and redox potential measurements made after the purged water is exposed to atmospheric conditions, however, will not accurately reflect in-situ conditions. All instruments used to measure indicator parameters should be properly calibrated and maintained in accordance with manufacturers' instructions at the well head at the start of each day of sampling and calibration should be checked periodically throughout the sampling event.

7.7 Other equipment and supplies that may be used in low-flow purging and sampling include those items specified by the site-specific sampling and analysis plan (for example, decontamination supplies, sample bottles, filtration media and equipment, preservation supplies, wellhead screening instruments [PID, FID, OVA, combustible gas indicators], sample shipping containers, and field documentation materials [for example, field notebook, field data sheets, chain-of-custody forms, sample bottle labels, shipping documents]).

8. Description of the Procedure

8.1 *General*:

8.1.1 "Low flow" refers to the velocity with which water enters the pump intake and that is imparted during pumping to the formation pore water adjacent to the well screen. This velocity must be minimized to preclude the entrainment of artifactual particulate matter in the water to be collected as a sample. Low-flow does not necessarily refer to the flow rate of water discharged by a pump at the surface, which can be affected by valves, restrictions in the discharge tubing or flow regulators. Some researchers refer to the method as "low-stress" purging, where "low-stress" refers to the impact of pumping the well on the formation. Water-level drawdown provides a measurable indicator of the stress on a given formation imparted by a pumping device operated at a given flow rate. The objective of low-flow purging is to pump in a manner that minimizes stress (drawdown) or disturbance to the ground-water flow system to the extent practical.

8.2 *Preparation for Low-Flow Purging and Sampling*:

8.2.1 Prior to conducting the initial sampling event, the sampling team should prepare themselves and any equipment and materials to be used in the event in accordance with Practice D 5903. Any equipment used in the sampling program that could contact the water in the well, the water collected during field parameter measurement, or the water collected as a sample should be properly cleaned before each use (see Practice D 5088). The clean equipment should not be allowed to contact the ground or other surfaces that could impart contaminants. An effort should be made to closely match the length of the tubing used for portable pumps with the depth at which the pump will be set in the well. Excess tubing can affect the temperature of the water sampled, which could affect sample chemistry (see Guide D 6634). All instrumentation used during low-flow purging and sampling must be properly calibrated. Instructions for calibration are specific to the individual instrument and manufacturers' instructions should be followed. The frequency and timing of calibration should be in accordance with the site-specific sampling and analysis plan.

8.3 *Pump Placement*:

8.3.1 In situations where a well is screened or open across a single zone of interest, and that zone is comprised of nearly homogeneous geologic materials, the pump intake should be positioned at or near the mid-point of the well screen. In this type of situation, the water that is withdrawn will likely represent the water quality of the entire screened zone, even at low-flow pumping rates. In situations in which the geology of the screened zone consists of heterogeneous materials with layers of contrasting hydraulic conductivity, the pump intake should be positioned adjacent to the zone of highest hydraulic conductivity (as defined by geologic samples). This provides the preferred flow pathway for ground water, and samples will be drawn primarily from this zone. In situations in which dissolved-phase contaminants of interest are known to concentrate near the top or bottom of the screened zone, it may be desirable to position the pump intake to target this zone.

8.3.2 Care should be taken not to position the pump intake too near the top of the screen in wells in which the water level is above the top of the screen (to avoid drawing in water from storage in the casing), or too near the bottom of the screen (to avoid mobilization and entrainment of settled solids from the bottom of the well). If screen length allows, the pump intake should be at least two feet from the top and two feet from the bottom of the screen.

8.3.3 Portable pumps can be used for low-flow purging and sampling, but the pump must be installed carefully and lowered slowly into the screened zone to minimize disturbance of the water column. Even if done with the utmost care, the installation of a portable pump will result in some mixing of the water column above the well screen with that within the screened interval, and the release of some suspended material. This usually requires pumping for a longer period of time to achieve stabilization of indicator parameters and turbidity. Ideally the pump should remain in place prior to operation until any turbidity resulting from pump installation has settled out and until horizontal flow through the well screen has been reestablished. Carefully lowering the pump intake to the appropriate position in the well screen, then completing preparation of other equipment and materials to be used in the sampling event often allows sufficient time for reduction of initial turbidity to acceptable levels. If, after the pump is started, initial turbidity readings are high (for example, >100 NTU) and reducing the pumping rate does not result in lower readings after a few minutes, it may be necessary to stop the pump and allow turbidity to settle for an hour or more. The time required for turbidity to settle is well-specific and should be determined on a well-by-well basis.

8.4 *Pumping Rate*:

8.4.1 In general, the pumping rate used during low-flow purging and sampling must be low enough to minimize mobilization and entrainment of particulate matter that is not naturally mobile (for example, artifactual particles) under ambient, non-pumping conditions and to minimize hydraulic stress on the well and the formation (for example, to minimize drawdown and to eliminate inclusion of stagnant water from the casing in the sample).

8.4.2 Because each well screen is installed in a hydraulically unique position, and because of differences in the effects that drilling and well development may have had on the borehole and adjacent formation, the hydraulic performance of each well will be different. This means that the pumping rate used for low-flow purging and sampling should be determined on a well-specific basis. It is not appropriate to assess one well in a network of wells and apply the low-flow purging and sampling techniques and rates from that one well to all of the wells in the network. If possible, the optimum pumping rate for each well should be established in advance of the initial sampling event. For newly installed wells, this can be done immediately following well development by running a short-term single well pilot test ideally using the same pump that will be used for low-flow purging and sampling. Once the optimum pumping rate is established for a given well, the same pumping rate can be used for that well for each sampling event, provided well performance does not vary over the life of the well.

8.4.3 To determine the appropriate pumping rate for any given well, the following procedure is recommended. After the pump intake is properly set in the well, the pump should be started at a low pumping rate, generally 100 mL/min or less. For pumps that cannot achieve a flow rate this low, start the pump at the lowest flow rate possible. From the time the pump is started, the water level in the well should be measured (see 8.5) to determine the amount of drawdown caused by pumping. If drawdown is rapid and continuous, the pumping rate should be lowered until drawdown decreases and stabilizes. If drawdown is very slow or imperceptible, the pumping rate may be raised slowly and adjusted to the point at which drawdown stabilizes. The maximum pumping rate used for sampling should not exceed the rate used for purging. Increases in pumping rates may induce increases in turbidity **(6-9)**.

8.5 *Drawdown and Water-Level Measurement*:

8.5.1 Prior to installing a portable pump in the well or prior to the commencement of pumping in wells in which dedicated pumps are installed, an initial water level measurement should be obtained.

8.5.2 Measurement of the water level in the well during purging, on either a continuous or periodic basis, is critical to establishing the optimum flow rate for purging and to determining the stress placed on the well by pumping. The goal is to achieve a stabilized pumping water level as quickly as possible with minimal drawdown. Continuous water-level measurements may be made using devices such as downhole pressure transducers, bubblers or acoustic tools; periodic measurements may be made with electric tapes, poppers or ploppers or other devices as described in Test Method D 4750. Measurement accuracy of the device used should be in accordance with that specified in the sampling and analysis plan (generally ±0.01 ft [3 mm]). Water-level measurements should be taken every one to two minutes to the point at which the water level in the well has stabilized, or at which drawdown ceases. Pumping rate (see 8.4) may need to be adjusted to allow the water level to stabilize.

8.5.3 After the water level in the well has stabilized, water-level measurements can be discontinued. Once the optimum pumping rate is established for the well, it may be necessary to periodically monitor the water level during subsequent purging and sampling events, more frequently if a significant difference in well performance (generally signified by an increase in drawdown over time) is noted in subsequent sampling events.

8.5.4 Several researchers have proposed limits on the amount of drawdown that should be allowed before water-level stabilization occurs, but none have provided any scientific rationale for the proposed limits. For example, Puls and Barcelona suggest a limit of less than 0.1 m (0.33 ft or about 4 in.) drawdown for all wells, conceding that this goal may be difficult to achieve under some conditions due to geologic heterogeneities within the screened interval, and may require adjustment based on site-specific conditions and personal experience **(1)**. In practical terms, allowable drawdown should never exceed the distance between the top of the well screen and the pump intake, which is normally positioned near the mid-point of the screen. To provide a safety factor, drawdown should generally not exceed 25 % of this distance to ensure that no water stored in the casing prior to purging is drawn down into the pump intake and collected as part of the sample.

8.6 *Measurement of Water Quality Indicator Parameters and Turbidity:*

8.6.1 Water-quality indicator parameters should be measured to determine when purging is complete and sampling can commence. In wells in which the pump intake is set in the screen and operated at a rate less than the natural recovery rate of the well, stabilized water chemistry indicates that formation-quality water is being pumped and, therefore, that conditions are suitable for sampling **(1)**. The water quality parameters that are most easily measured in the field and that provide evidence that formation-quality water is being provided include: pH, conductivity (or specific conductance), dissolved oxygen and oxidation-reduction potential (redox or ORP, also measured as Eh).

8.6.2 Water-quality indicator parameters can be monitored on either a continuous or periodic basis, though continuous monitoring in a closed flow-through cell provides the most consistent and reliable results, particularly for dissolved oxygen and redox potential. Indicator parameters are considered stable when three consecutive readings made several minutes apart fall within the ranges presented in Table 1.

8.6.3 While the criteria in Table 1 are reasonable criteria for many hydrogeochemical situations, it should be recognized that firm criteria may not be appropriate for other situations because of factors including variability in aquifer properties, monitoring well hydraulics, and natural spatial and temporal variation in ground-water chemistry and contaminant distribution. Therefore, the criteria in Table 1 should be compared to well-specific measurements to determine if the site-specific criteria need to be adjusted. Additionally, these criteria should be evaluated to select those that are most important and relevant to meeting the sampling objectives for the specific site. Not all criteria need to be met for all sites. Stabilization criteria that are too stringent may unnecessarily lead to the generation of large amounts of contaminated purge water without providing the benefit of ensuring that the samples are any more representative.

TABLE 1 Example Criteria for Defining Stabilization of Water-Quality Indicator Parameters

Parameter	Stabilization Criterion
pH	±0.2 pH units[A]
Conductivity	±3 % of reading
Dissolved Oxygen	±10 % of reading or ±0.2 mg/L, whichever is greater[A]
Eh or ORP	±20 mV[A]

[A] Related to the measurement accuracy of commonly available field instruments.

8.6.4 For in-line flow-through cells, the frequency of the measurements should be based on the time required to completely evacuate one volume of the cell, to ensure that independent measurements are made. For example, a 500 mL cell in a system pumped at a rate of 250 mL/min will be evacuated in 2 min so measurements should be made at least 2 min apart. It is important, therefore, that the sampling team establish the following volumes and rates in the field prior to the sampling event: (*1*) Volume of the pump and discharge tubing; (*2*) Optimum pump discharge rate; and (*3*) Volume of the flow-through cell corrected for displacement volume of the field parameter measurement instrumentation installed inside the flow-through cell. It is also important to know the manufacturer's recommendations for the amount of time to allow individual sensors being used to measure field parameters (for example, dissolved oxygen) to stabilize to ensure that representative data are being collected.

8.6.5 For wells in which dedicated pumps are used, chemical indicator parameters tend to stabilize more readily because there is minimal disturbance of the water column in the well. For wells in which portable pumps are used, the effects of pump installation on the water column usually result in the need to remove significantly more water before chemical indicator parameters (and, as noted below, turbidity) reach stabilization.

8.6.6 Though not a chemical parameter, and not indicative of when formation-quality water is being pumped, turbidity may also be a useful parameter to monitor. Turbidity is a physical parameter that provides a measure of the suspended particulate matter in the water being pumped. Turbidity may be most indicative of pumping stress on the formation. Sources of turbidity in monitoring wells can include: (*1*) Naturally occurring colloid-sized or larger solids that may be in transit through the formation; (*2*) Naturally occurring solids or artifactual solids from well drilling and installation (for example, drilling fluids, filter pack, grout) that have not been effectively removed by well development and are mobilized by agitation of the water column (that is, by bailing, by installation of a portable pump, or by overpumping the well); (*3*) Microbial growth that often occurs within monitoring wells in the presence of certain types of contaminants (that is, petroleum hydrocarbons); and (*4*) Precipitation caused by different redox conditions in the well than in the aquifer. Turbidity levels elevated above the natural formation condition can result in biased analytical results for many chemical parameters. Naturally occurring turbidity in some ground water can exceed 10 NTU **(1)** and may be unavoidable. Turbidity in a properly designed, constructed and developed well is most often a result of significant disturbance of the water column or excessive stress placed on the formation by overpumping.

8.6.7 To avoid artifacts in sample analysis, turbidity should be as low as possible when samples are collected.[4] Turbidity measurements should be taken at the same time that chemical parameter measurements are made, or, at a minimum, once when pumping is initiated and again just prior to sample collection, after indicator parameters have stabilized. The stabilization criterion for turbidity is ±10 % of the prior reading or ±1.0 NTU, whichever is greater. If turbidity values are persistently high, the pumping rate should be lowered until turbidity decreases. If high turbidity persists even after lowering the pumping rate, the pump may have to be stopped for a period of time until turbidity settles, and the purging process restarted. If this fails to solve the problem, well maintenance or redevelopment may be necessary. Difficulties with high turbidity should be identified during pilot tests prior to implementing low-flow purging or during the initial low-flow sampling event, and contingencies should be established to minimize the problem of elevated turbidity.

8.7 *Sample Collection Following Purging*:

8.7.1 After drawdown and chemical indicator parameters stabilize, sampling can begin per the site's approved sampling and analysis plan. If an in-line flow-through cell is used to continuously monitor chemical indicator parameters, it should be disconnected or bypassed during sample collection. The pumping rate may remain at the established purging rate or it may be adjusted downward to minimize aeration, bubble formation, or turbulent filling of sample bottles. For most parameters, sampling rates of less than 500 mL/min are appropriate **(1)**. Sampling rates for the most sensitive parameters (for example, VOCs) should be lower (generally less than 250 mL/min). Generally, the most sensitive parameters, or those that are of greatest interest at the site, should be sampled first; analyses that require filtration should be sampled last (1). Sample filtration (see Guide D 6564), preservation (see Guide D 6517), handling, shipping and documentation (see Guide D 6089) should be consistent with procedures documented in the approved site-specific sampling and analysis plan.

9. Reporting

9.1 The procedures and equipment used during low-flow purging and sampling must be documented in the field. Specific guidance on documenting a ground-water sampling event is provided in Guide D 6089. Field data specific to low-flow purging and sampling that should be recorded includes:

9.1.1 Equipment calibration;
9.1.2 Equipment decontamination;
9.1.3 Equipment configuration for purging and sampling;
9.1.4 Pump placement (relative to well screen position and static water level);
9.1.5 Initial static water level;
9.1.6 Initial pumping rate;
9.1.7 Drawdown measurements;
9.1.8 Stabilized pumping water level;
9.1.9 Final pumping rate;
9.1.10 Water quality indicator and turbidity measurements;
9.1.11 Times for all measurements; and
9.1.12 Sampling flow rate.

10. Keywords

10.1 ground water; ground-water monitoring; ground-water quality; ground-water sampling; indicator parameters; low-flow purging; low-stress purging; micropurging; minimal drawdown purging; purging; water quality monitoring

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[4] The primary reason for minimizing turbidity during purging and sampling is that turbidity can affect the aqueous phase concentration of the analytes of interest for both organic and inorganic analytes. The accurate analysis of aqueous-phase inorganic analytes can be affected by stripping of cations, particularly metal species, from the surface of suspended inorganic particulate matter (for example, clays) by the sample preservation process (acidification). The accurate analysis of hydrophobic organic compounds can be affected by the presence of both organic and inorganic particulate matter. In addition, analysis of aqueous-phase organic analytes can be hampered by the physical presence of suspended solids (that is, causing clogging of the nebulizer on the analytical equipment).

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