SAMPLING AND ANALYSIS PLAN AND FUNDAMENTAL QUALITY ASSURANCE PROJECT PLAN

FORMER NODULAR FACILITY, SAGINAW, MI

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1.0 INTRODUCTION

On behalf of Revitalizing Auto Communities Environmental Response (RACER) Trust, the Sampling and Analysis Plan (SAP) presented herein has been prepared for the proposed sampling program for the Former Nodular Iron Wastewater Ponds/Basins at the Nodular Facility, in Saginaw, Michigan. This SAP describes the specific field a sampling activities, chemical analyses, and quality assurance procedures that will be conducted during the characterization study.

1.1 PURPOSE AND ORGANIZATION OF PLAN

The purpose of the SAP is to provide the protocols for a characterization study of the Former Nodular Iron Wastewater Ponds/Basins at the Nodular Facility to be conducted at the Site over a 1-year period. The characterization study is required to gain a more thorough understanding of the quality of water and sediment in the ponds for the purpose of obtaining an NPDES permit for the discharge of pond water and, if necessary, evaluate remedial alternatives to address any issues identified. The SAP is organized as follows:

Section 1.0 - Presents a general introduction to the Site and the purpose and organization of the SAP

Section 2.0 - Presents a description of the sampling and analysis activities for the 1-year characterization study

Section 3.0 - Presents a description of the sample collection procedures and equipment decontamination procedures

Section 4.0 - Presents a description of sample handling, documentation and shipment

Section 5.0 - Presents a description of the analytical methods and quality assurance/quality control (QA/QC) procedures for the one-year characterization study

Section 6.0 - Presents a description of the project schedule

Section 7.0 - Presents a description of the reporting that will be completed following the analysis of collected samples

This SAP contains the specific technical approaches to collect data of sufficient quantity and quality to develop an appropriate approach to close the basins as well as obtain necessary permits for the discharge of water.

2.0 SAMPLING AND ANALYSIS ACTIVITIES

Pond water/sediment characterization sampling will be undertaken at the 12 locations identified on Figure 2.1. At each location a sample will be collected of the surface water, of water at the midpoint of the water column for the purpose of evaluating stratification in the water column, and of the sediment. The study will monitor target analyte list (TAL) metals, polychlorinated biphenyls (PCBs), total organic carbon (TOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), pH, temperature, cyanide (total for sediment and amenable for water), formaldehyde, phenol, oil and grease, ammonia, and nitrate. The parameters were selected based on historical operations and previous sample results. The sediment samples will also be analyzed for acid volatile sulfide/simultaneously-extracted metals(AVS/SEM), grain size analysis, in-situ moisture, and consolidation testing. Twelve of the 24 water samples will be analyzed for N15 isotope. The N15 isotope analysis is being conducted to determine whether ammonia, if any, is natural (waste) or manufactured (fertilizer) since ammonia has been reported in historical samples. The mid water column depth interval was selected for analysis of the N15 isotope since ammonia close to the water surface can be volatilized or oxidized. Provided that the concentration of ammonia is greater than 0.05mg/L in the water samples, the N15 isotope analysis will be performed using the nitrogen isotopes in ammonia as describe in Appendix A. However, if the concentration of ammonia is below 0.05 mg/L, the N15 isotope testing will be performed on nitrate, as describe in Appendix B. The results will be used to determine if the ammonia is from on-site or off-site sources. Table 2.1 presents a summary of the sampling and analysis program.

The average abundance of ^{15}N in air is 0.366 percent. Fertilizer produced from atmospheric nitrogen has a delta ^{15}N of +/- 3‰ while animal manure delta ^{15}N values are between +10 and +25‰. The delta ^{15}N values obtained from the isotope analysis will be compared to these ranges in order to determine the source of the nitrogen. The standard operating procedure for the AVS/SEM testing can be seen in Appendix C.

Following the characterization sampling proposed above and to ensure that the water quality remains suitable for discharge, additional water samples will be collected from the three select locations presented in Figure 2.1. Samples will be collected of the surface water, and of the water at midpoint of the water column, and just above the sediment. All samples will be analyzed for the parameters presented in Table 2.1. Sample collection will be performed in the fall, winter and the spring. This combined with the initial characterization covering the summer season will provide any seasonal variability.

3.0 SAMPLE COLLECTION PROCEDURES

The following sections detail the sampling procedures.

3.1 POND WATER/SEDIMENT SAMPLING

Pond water/sediment sampling will be collected from the locations identified on Figure 2.1 using the procedures specified below:

1. A new pair of disposable nitrile gloves (or equivalent) will be donned for each set of samples collected at each location.
2. The pond water surface samples will be collected by submerging one of the large sampling bottles (without preservatives) and filling the laboratory supplied containers in order of decreasing analyte volatility using techniques that minimize sample agitation.
3. The pond water mid-column sample will be collected using a peristaltic pump. The pump will be run in reverse (forcing air out of the tubing), to avoid contact with water not at the desired sampling depth, as the tubing is lowered to the midpoint of the water column (determined in step 2). Once the midpoint of the water column is reached the pump will be run forward at a rate of 400 mL/min for a few minutes before collecting the sample. The pond water mid-column sample will be collected through the tubing directly into laboratory-supplied containers in order of decreasing analyte volatility using techniques that minimize sample agitation.
4. Obtain field measurements for pH and temperature for each water sample collect.
5. Measure the depth to sediment at each location using survey rod or secchi disk and approximate the depth of soft sediment.
6. The environmental sediment samples will be collected using a sediment auger which is equipped with a disposable lexan tube that the samples are augured into. A slide-hammer sediment sampler will be used to collect geotechnical samples. This method uses a disposable lexan tube that is hammered into the sediment. The sediment will be placed into laboratory-supplied containers.
7. All locations will be marked with a gallon jug upon completion of the tests, the jugs will be anchored into the sediment should it be required that additional samples be taken from these same locations.

3.2 POND WATER/SEDIMENT SAMPLING EQUIPMENT DECONTAMINATION PROTOCOLS

To prevent cross-contamination from occurring between locations during sampling, the pump, sediment auger and slide-hammer sediment sampler will be thoroughly decontaminated between sample locations. Additionally, the sampler will be rinsed thoroughly in the pond water and dried off between individual samples. The decontamination procedure will consist of the following steps:

1. Scrub sampling equipment using a standard brush and a solution of tap water and Alconox®
2. Rinse sampling equipment with regular tap water and shake off excess water
3. Rinse equipment with distilled water and allow equipment to air dry

Fluids used for cleaning will not be recycled. All wash water, rinse water, and decontamination fluids will be stored in containers on Site pending final disposal.

3.3 SURVEYING

A survey will also be conducted of the pond areas with a survey grade GPS unit to determine sediment thickness and define the topography of the pond bottom.

4.0 SAMPLE HANDLING AND DOCUMENTATION

Sample handling procedures (including container, preservation, holding time, packaging, and shipping requirements), and field documentation requirements are provided in the following subsections. A summary of the pond water/sediment characterization study is presented in Table 2.1.

4.1 SAMPLE HANDLING

Laboratory-supplied, pre-cleaned sample containers will be used to collect all samples. Sample containers, preservation, holding time periods, packaging, and shipping requirements are presented in Table 4.1. All samples will be identified using a unique sample identification number. The sample numbering system has been designed to uniquely identify every sample from each sampling program and event. This numbering system consists of the sample matrix code, sample collection date, initials of sampler, and sequential number beginning with 001 for each sampling event.

An example of the sample numbering system follows:

MC-58502-mmddyy-XX-001

Where:

MC (Matrix Code) = –SW – Surface Water

58502 = CRA Project Number

mmddyy = Date in month/day/year

XX = Samplers first and last initials

001 = Sequential number for event

Field quality control (QC) samples that will be collected during the project include equipment blank, field duplicate, trip blank, and matrix spike/matrix spike duplicate (MS/MSD) samples. Equipment blank and field duplicate samples will be submitted blindly to the laboratory and will be identified using the sample numbering system identified above. Samples designated for MS/MSD analysis will be identified as such in the remarks column of the chain-of-custody form.

Samples will be placed in shipping coolers containing bagged, cubed ice following collection. The samples will be shipped to the laboratory via an overnight courier service, generally on the day they are collected or the next business day.

4.2 FIELD DOCUMENTATION

4.2.1 FIELD LOGBOOKS

Logbooks will be used to record field data collection activities. Entries into field logbooks will be described in as much detail as possible to ensure that a particular situation could be reconstructed solely from logbook entries. Field logbooks will be bound field survey books or notebooks with consecutively numbered pages.

The title page of each logbook will contain the following information:

1. Person to whom or task for which the logbook is assigned
2. Project number
3. Project name
4. The starting date for entries into the logbook
5. The ending date for entries into the logbook

Entries into the logbook will contain a variety of information. At the beginning of each day's logbook entry, the date, start time, weather, names of all sampling team members present, and the signature of the person making the entry will be entered. The names of individuals visiting the site or field sampling team and the purpose of their visit will also be recorded in the field logbook.

All field measurements obtained and samples collected will be recorded. All logbook entries will be made in ink, signed, and dated with no erasures. If an incorrect logbook entry is made, the incorrect information will be crossed out with a single strike mark that is initialed and dated by the person making the erroneous entry. The correct information will be entered into the logbook adjacent to the original entry.

Whenever a sample is collected or a measurement is made, a detailed description of the location will be recorded in the logbook. Photographs taken at a location, if any, will also be noted in the logbook. All equipment used to obtain field measurements will be recorded in the field logbook. In addition, the calibration data for all field measurement equipment will be recorded in the field logbook or on standard field forms.

Samples will be collected following the sampling procedures described in Section 3.1. The equipment used to collect samples, date and time of sample collection, and sample description/location will be recorded in the field logbook. Each sample will be uniquely identified using the sample numbering system described in Section 4.1.

4.2.2 SAMPLE CUSTODY PROCEDURES

Chain of custody is the sequence of possession of an item. An item (such as a sample) is considered to be in custody if the item is in actual possession of a person, the item is in the view of the person after being in his/her actual possession, or the item was in a person's physical possession but was placed in a secure area by that person.

The sample packaging and shipping procedures summarized below will ensure that the samples arrive at the laboratory with the chain of custody intact:

1. The field sampler is personally responsible for the care and custody of the samples until they are transferred to another person or the laboratory. As few people as possible will handle the samples.
2. All sample containers will be identified by using sample labels that include the date of collection, unique sample number, and analyses to be performed.
3. Sample labels will be completed for each sample using waterproof ink.
4. Samples will be placed in coolers containing ice after collection.
5. Samples will be accompanied by a properly completed chain-of-custody form. An example chain-of-custody form is provided in Appendix D. The sample identification numbers will be listed on the chain-of-custody form. When transferring the possession of samples, the individuals relinquishing and receiving the samples will sign and record the date and time on the form. The chain-of-custody form documents sample custody transfers from the sampler to another person, to the laboratory, or to/from a secure storage area.
6. All sample shipments will be accompanied by the chain-of-custody form identifying its contents. The chain-of-custody form is a four-part carbonless-copy form. The form is completed by the sampling team, which, after signing and relinquishing custody to the shipper, retains the bottom (goldenrod) copy. The shipper, if different than the sampling team members, retains the pink copy after relinquishing custody to the laboratory. The yellow copy is retained by the laboratory. The fully executed top (white) copy is returned as part of the data deliverables package.
7. Samples will be properly packaged for shipment (see Table 4.1) and dispatched to the project laboratory for analysis with a separate signed chain-of-custody

form enclosed in each shipping cooler. Shipping coolers will be secured with custody tape for shipment to the laboratory. The custody tape is then covered with clear plastic tape to prevent accidental damage to the custody tape.

8. If the samples are sent by common carrier, a bill of lading will be used and copies will be retained as permanent documentation. Commercial carriers are not required to sign the chain-of-custody form as long as the form is sealed inside the sample cooler and the custody tape remains intact.

9. If samples are not shipped to the laboratory the same day the samples are collected in the field, additional ice will be placed in the coolers, the coolers will be sealed and kept in a designated secure area until they are shipped to the laboratory as described above.

5.0 ANALYTICAL METHODS AND QUALITY CONTROL SAMPLES

TestAmerica will be the primary laboratory supporting the environmental sample analysis for this project utilizing their facilities in North Canton, Ohio (TA-NC) and Pittsburgh, Pennsylvania (TA-PT) for the analysis of PCB, TAL metals, AVS/SEM, TOC, nitrate, ammonia and pH. The ^{15}N isotope analysis will be completed by Colorado Plateau Stable Isotope Laboratory at Northern Arizona University in Flagstaff, Arizona. The sediment geophysical characterization will be completed by Inspecsol in Toronto, Ontario.

5.1 LABORATORY ANALYTICAL METHODS

Pond water and sediment samples will be analyzed for specified chemical constituents off Site by the project laboratory. The methods that will be used for sample analysis are presented in Table 5.1. Specific analytes and targeted quantitation limits for chemical constituents are presented in Table 5.2.

5.2 QUALITY ASSURANCE/QUALITY CONTROL PROCEDURES

5.2.1 FIELD QUALITY ASSURANCE/QUALITY CONTROL

Field QA/QC requirements for field-portable instruments include analyzing reference standards for instrument calibration and for routine calibration checks. Field QC samples collected during field sampling include equipment blank samples to determine the existence and magnitude of sample contamination resulting from ambient conditions or sampling procedures, and field duplicate samples to assess the overall precision of the sampling and analysis events. Additionally, pond water samples will be designated as MS/MSD samples for assessment of laboratory QC procedures. The specific QC samples and collection frequency are summarized in Table 2.1.

Equipment blank samples will be collected at a frequency of 1 per 20 or fewer sampling equipment decontamination procedures. Equipment blank samples will be collected by routing laboratory-provided deionized water through decontaminated sampling equipment. Equipment blank samples will be analyzed to check procedural contamination and/or ambient conditions and/or sample container contamination at the Site that may cause sample contamination. Equipment/Field blank samples will not be required for samples collected using pre-cleaned or pre-cleaned, disposable sampling equipment.

Field duplicate samples collected at a minimum frequency of 1 per 20 investigative samples. Field duplicate samples will be analyzed to assess the precision of the field sample collection procedures.

Additional sample volume will be provided to the laboratory (as necessary) for MS/MSD analyses. The data from MS/MSD analyses provide an indication of the precision and accuracy of the analytical method relative to the sample matrix. Samples for MS/MSD analysis will be designated at a minimum frequency of 1 per 20 or fewer samples.

5.2.2 LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

Laboratory QC requirements for the analysis of pond water and sediment samples analyzing method blanks, initial calibration verification standards, continuing calibration verification standards, surrogate standards, MS/MSD samples, and laboratory Control Samples (LCS). The analysis frequency for these QC samples is identified in the applicable laboratory SOP. The acceptance criteria for these QC checks will be consistent with the analytical methods provided in Table 5.1 and applicable laboratory SOP.

5.2.3 LABORATORY REPORT DELIVERABLES

Laboratory reports for samples collected will consist of the following data deliverables:

1. Case Narrative
    - i) Date of issuance
    - ii) Project name and number
    - iii) Any deviations from intended analytical strategy
    - iv) Condition of samples "as received"
    - v) Discussion of whether or not sample holding times were met
    - vi) Discussion of technical problems or other observations that may have created analytical difficulties
    - vii) Discussion of any laboratory quality control checks that failed to meet project criteria

2. Chemistry Data Package

- i) Dates of sample collection, receipt, preparation, and analysis
- ii) Cross-reference of laboratory to project sample identification numbers
- iii) Description of data qualifiers used
- iv) Methods of sample preparation and analysis
- v) Sample results in tabular format
- vi) Method blank data, LCS data, duplicate sample data, MS/MSD data, surrogate compound spike data
- vii) Fully executed chain-of-custody document

5.2.4 DATA REVIEW AND VALIDATION

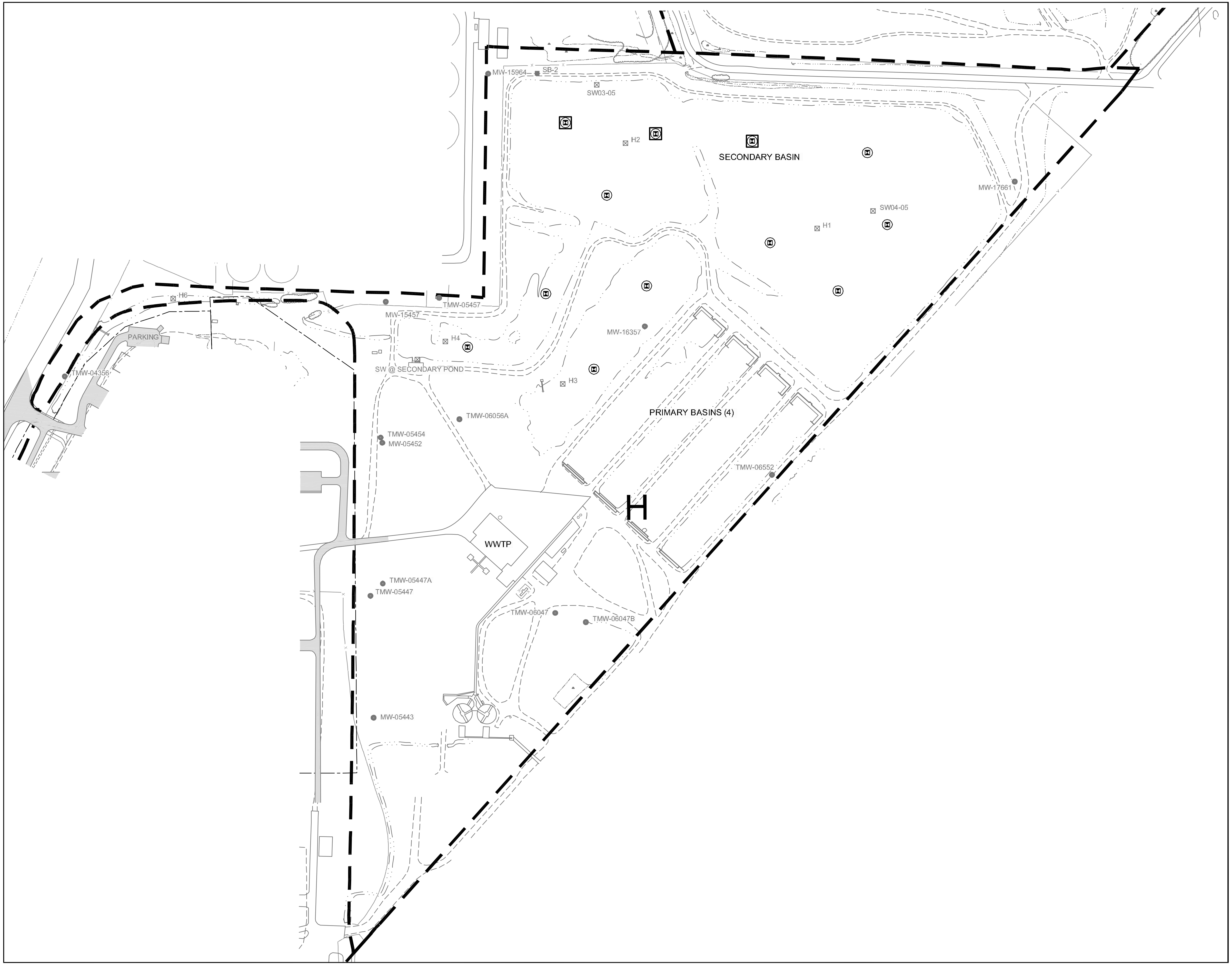
Upon receipt of the final data packages from the project laboratory the data will be reviewed and validated. The data review will evaluate the final analytical results, holding time period compliance, equipment blank sample data, field duplicate sample data, method blank data, LCS data, laboratory duplicate data, surrogate compound spike data, and MS/MSD sample data. Validation of the data will consist of evaluating the QA/QC data based on the applicable review criteria specified in "USEPA Contract Laboratory Program National Functional Guidelines for Organic Data Review", dated October 1999 and "USEPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review", dated February 1994. The results of the data review and validation process will be documented in memoranda that identify all limitations on the usability of the analytical data.

6.0 SCHEDULE

The initial pond water/sediment characterization sampling will be completed within the first 2 weeks of July 2011. The sample analysis will be competed by August 5, 2011 and the data validation will be completed by August 19, 2011. The data will be submitted to U.S. EPA by August 31, 2011. For subsequent sampling events, the data will be submitted approximately 6 weeks after completion of the field work.

7.0 REPORTING

A memorandum or letter report, providing the results of the pond water/sediment characterization study, will be prepared after each sampling event following receipt of all final analytical reports and completion of the data validation.

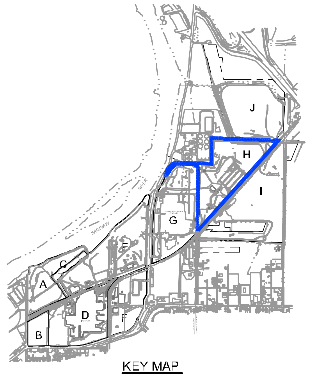


N

0 75 150 ft

LEGEND

A – –	INVESTIGATIVE UNIT BOUNDARY AND IDENTIFIER
●	MONITORING WELL LOCATION
☒	SURFACE WATER SAMPLE LOCATION
⊠	PROPOSED SEDIMENT/WATER SAMPLE LOCATION
☐	FOLLOW-UP WATER SAMPLE LOCATION



KEY MAP

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

MOTORS LIQUIDATION COMPANY

SAGINAW, MICHIGAN

PROPOSED SAMPLE LOCATIONS

CONESTOGA-ROVERS & ASSOCIATES

Source Reference:
MICHIGAN STATE PLANE SOUTH, NAD 83 USING INTERNATIONAL FEET, NGVD 88
TOPO - SANBORN, 1996

Project Manager: I.R.	Reviewed By: M.T.	Date: JUNE 2011	
Scale: 1" = 200'	Project Nº: 58502-T02	Report Nº: 004	Drawing Nº: figure 2.1

TABLE 2.1

SUMMARY OF SAMPLING AND ANALYSIS PROGRAM
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

					Quality Control Samples			
Investigation Activity	*Sample Matrix*	*Field Parameters*	*Laboratory Parameters*	*Investigative Samples*	*Equipment Blanks (1)*	*Field Duplicates*	*MS/MSD (2)*	*Total*
Pond/Basin Surface Water	Surface Water	pH/Temperature	PCB, TAL Metals, Amenable Cyanide TOC, Ammonia, Nitrate, pH, BOD, COD, HEM, Formaldehyde, Total Phenolics	24	0	2	2	28
			N15 (Ammonia)	12	0	1	1	14
Pond/Basin Surface Sediment	Sediment	None	PCB, TAL Metals, Total Cyanide, TOC, Ammonia, Nitrate, pH, AVS/SEM	12	1	1	1	15
Pond/Basin Geotechnical Sediment	Sediment	None	Grain Size Analysis, in-situ moisture, consolidation testing	12	0	0	0	12
Ongoing Pond Sampling (3 quarterly events - Fall/Winter/Spring)	Surface Water	pH/Temperature	PCB, TAL Metals, Amenable Cyanide TOC, Ammonia, Nitrate, pH	9	0	1	1	11

Notes:

(1) - Equipment / Field blank samples will not be required if dedicated or disposable sampling equipment is used.

(2) - Matrix Spike/Matrix Spike duplicate (MS/MSD) analyses are required for samples submitted for organic and inorganic analyses are to be analyzed at a frequency of one per group of twenty (20) or fewer investigative samples for the activities detailed above.

PCB - Polychlorinated Biphenyls
TOC - Total Organic Carbon
BOD - Biochemical Oxygen Demand
COD - Chemical Oxygen demand
HEM - Hexane Extractable Material
AVS/SEM - Acid Volatile Sulfide/Simultaneously Extracted Metals

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
WATER (surface water)						
Polychlorinated Biphenyls (PCB)	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	7 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Formaldehyde	Two 1 liter amber glass bottles per analysis	Iced, 4 ± 2° C	3 days for extraction 40 days after extraction for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 1 liter plastic bottle per analysis	HNO_3 to pH < 2 Iced, 4 ± 2° C	180 days (mercury- 28 days) for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Low Level Mercury[3]	Four 40 mL teflon-lined septum vials per analysis	Iced, 4 ± 2° C	48 hours until laboratory preservation with BrCl, 28 days from collection until analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Cyanide (total and amenable)	One 250 ml plastic bottle per analysis	NaOH to pH>12 Iced, 4 ± 2° C	14 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Ammonia	One 250-ml plastic bottle per analysis	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack Bubble-wrap
Biochemical Oxygen Demand (BOD)	One 1 liter plastic bottle per analysis	Iced, 4 ± 2° C	48 hours to start analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Analyses	*Sample Containers* [1]	*Preservation*	*Maximum Holding Time from Sample Collection* [2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
WATER (surface water) Continued						
Chemical Oxygen Demand (COD)	One 250-ml plastic bottle per analysis	H_2SO_4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack Bubble-wrap
Hexane Extractable Material (HEM)	One 1 liter amber glass bottle	H2SO4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Nitrate	One 250-ml plastic bottle per analysis	Iced, 4 ± 2° C	48 hours to start analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack Bubble-wrap
pH	One 250 ml plastic bottle per analysis	Iced, 4 ± 2° C	24 hours for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Total Organic Carbon	Two 40 ml Teflon-lined septum vials per analysis	H2SO4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Total Phenolics	One 1 liter amber glass bottle per analysis	H2SO4 to pH < 2 Iced, 4 ± 2° C	28 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Nitrate - N15	One 250 ml brown plastic bottle per analysis	Iced, 4 ± 2° C	28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Analyses	*Sample Containers* [1]	*Preservation*	*Maximum Holding Time from Sample Collection* [2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
SOLID (Sediment)						
Polychlorinated Biphenyls (PCB)	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for extraction 40 days after extraction for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Metals (AVS/SEM)	One 4-ounce glass jar	Iced, 4 ± 2° C	180 days (mercury 28 days) for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Cyanide (total)	One 4-ounce glass jar	Iced, 4 ± 2° C	14 days for analysis	Fill to shoulder of jar	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Ammonia	One 4-ounce glass jar	Iced, 4 ± 2° C	7 days for extraction 28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack Bubble-wrap
Nitrate	One 4-ounce glass jar	Iced, 4 ± 2° C	7 days for extraction 28 days for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Bubble Pack Bubble-wrap
Total Organic Carbon	One 4-ounce glass jar	Iced, 4 ± 2° C	28 days for analysis	Fill completely, no air bubbles	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
pH	One 4-ounce glass jar	Iced, 4 ± 2° C	24 hours for analysis	Fill to neck of bottle	Overnight or Hand Deliver	Foam Liner or Bubble-wrap

TABLE 4.1

CONTAINER, PRESERVATION, SHIPPING AND PACKAGING REQUIREMENTS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Analyses	*Sample Containers*[1]	*Preservation*	*Maximum Holding Time from Sample Collection*[2]	*Volume of Sample*	*Shipping*	*Normal Packaging*
GEOTECHNICAL (Sediment)						
Grain Size Analysis	Air-tight Container	NA	NA	Fill completely	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
In-situ Moisture	Air-tight Container	NA	24 hours for analysis	Fill completely	Overnight or Hand Deliver	Foam Liner or Bubble-wrap
Consolidation Testing	Shelby Tube	ASTM D1587	NA	ASTM D1587	ASTM D1587	ASTM D1587

Notes:

[1] - Multiple parameters on a single sample may be combined into one single 16 ounce glass jar.

[2] - These are technical holding times, i.e., are based on time elapsed from time of sample collection.

[3] - Sample containers must be fluoropolymer or borosilicate glass.

NA - Not Applicable

ASTM - "Annual Book of ASTM Standards", American Society for Testing and Materials.

TABLE 5.1

SUMMARY OF ANALYTICAL METHODS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Parameter[1]	*Preparation Method*[2]	*Analytical Method*[2]
Surface Water Samples		
PCB	SW-846 3500C	SW-846 8082
Formaldehyde	SW-846 8315	SW-846 8315
Metals		
ICP/MS Metals	SW-846 3010A/3020A	SW-846 6020
Mercury	SW-846 7470A	SW-846 7470A
Mercury (Low Level)	EPA 1631E	EPA 1631E
Cyanide (Amenable)	SW-846 9012A	SW-846 9012A
Ammonia, Nitrogen	SM 4500 NH3	SM 4500 NH3
Biochemical Oxygen Demand (BOD)	SM 5210B	SM 5210B
Chemical Oxygen Demand (COD)	SM 5220	SM 5220
Hexane Extractable Material (HEM)	EPA 1664	EPA 1664
Nitrate, Nitrogen	SW-846 9056	SW-846 9056
Total Phenolics	EPA-WW 420.1	EPA-WW 420.1
pH	NA	EPA-WW 150.1
Total Organic Carbon	SW-846 9060	SW-846 9060
Ammonia - N15	Micro-Diffusion	Micro-Diffusion
Sediment Samples		
PCB	SW-846 3545	SW-846 8082
Metals[3]		
ICP/MS Metals	SW-846 3050B	SW-846 6020
Mercury	SW-846 7471A	SW-846 7471A
AVS/SEM	USEPA Draft	SW-846 9034/6010
Cyanide (Total)	SW-846 9012A	SW-846 9012A
Total Organic Carbon	Lloyd Khan	Lloyd Khan
Nitrate, Nitrogen	SW-846 9056	SW-846 9056
Ammonia, Nitrogen	EPA-WW 350.3	EPA-WW 350.3
pH	NA	EPA-WW 150.1

TABLE 5.1

SUMMARY OF ANALYTICAL METHODS
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Parameter [1]	*Preparation Method* [2]	*Analytical Method* [2]
Geotechnical Samples		
In-Situ Moisture	ASTM D6031	ASTM D6031
Grain Size Analysis	ASTM D422	ASTM D422
Consolidation Testing	ASTM D2435	ASTM D2435

Notes:

[1] Refer to Tables 1.2 for the compounds/elements of each parameter group.

[2] Preparation and Analytical Method References:

- SW-846 - "Test Methods for Evaluating Solid Wastes, Physical/Chemical Methods ", SW-846, 3rd Edition, and Promulgated Updates, November 1986. Actual method versions employed will include the latest promulgated version of the method adopted by the lab.
- EPA-WW - "Methods for Chemical Analysis of Water and Wastes", EPA-600/4-79-020, Revised March 1983.
- ASTM - Annual Book of ASTM Standards, American Society for Testing Materials, Section 5 and Section 11.

PCB Polychlorinated Biphenyls
AVS/ Acid Volatile Sulfide/Simultaneously Extracted Metals
NA Not Applicable

TABLE 5.2

SURFACE WATER AND SEDIMENT SAMPLE PARAMETER LIST
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

	Estimated Quantitation Limits (EQL) [1]		*Method Detection Limits (MDL)* [2]		*Rule 57 Action Levels*	
Compound	*Water (µg/L)*	*Sediment (µg/kg)*	*Water (µg/L)*	*Sediment (µg/kg)*	*Value (µg/L)*	*Standard* [3]
Polychlorinated Biphenyls (PCB) as Aroclors						
Aroclor-1016	0.2	264	0.044	21	0.000026	HCVd
Aroclor-1221	0.2	264	0.05	16	0.000026	HCVd
Aroclor-1232	0.2	264	0.1	14	0.000026	HCVd
Aroclor-1242	0.2	264	0.060	13	0.000026	HCVd
Aroclor-1248	0.2	264	0.061	17	0.000026	HCVd
Aroclor-1254	0.2	264	0.032	17	0.000026	HCVd
Aroclor-1260	0.2	264	0.038	17	0.000026	HCVd

	Estimated Quantitation Limits (EQL) [1]		*Method Detection Limits (MDL)* [2]		*Rule 57 Water Action Levels*	
Compound	*Water (µg/L)*	*Sediment (mg/kg)*	*Water (µg/L)*	*Sediment (mg/kg)*	*Value (µg/L)*	*Standard* [3]
TAL Metals						
Aluminum	50	1.0	19	0.40		
Antimony	2	0.16	0.13	0.024	1.7	HNVd
Arsenic	5	0.08	0.4	0.062	10	HNVd
Barium	100	0.8	0.19	0.071	1900	HNVd
Beryllium	1	0.16	0.2	0.043	160	HNVd
Cadmium	1	0.08	0.13	0.036	2.5	HNVd
Calcium	1000	400000	22	37	NA	NA
Chromium	5	0.4	0.71	0.2	120	HNVd
Cobalt	7	0.4	0.058	0.16	100	FCV
Copper	2	0.8	0.29	0.74	470	HNVd
Iron	50	5.0	26	0.72	NA	NA
Lead	3	0.24	0.18	0.19	14	HNVd
Magnesium	1000	100000	17	12	NA	NA
Manganese	15	0.8	0.83	0.074	1300	HNVd
Mercury	0.2	0.04	0.12	0.015	0.0013	WV
Mercury (Low Level)	0.0005	0.04	0.00012	0.015	0.0013	WV
Nickel	20	0.8	0.2	0.27	2600	HNVd
Potassium	1000	500000	1.2	5.1	NA	NA
Selenium	5	0.16	1.2	0.09	5	FCV
Silver	0.2	0.08	0.08	0.016	0.06	FCV
Sodium	1000	100000	6.9	50	NA	NA
Thallium	1	0.08	0.14	0.013	1.2	HNVd
Vanadium	4	0.8	0.44	0.12	27	FCV
Zinc	20	0.8	2.3	0.44	3300	HNVd

TABLE 5.2

SURFACE WATER AND SEDIMENT SAMPLE PARAMETER LIST
CHARACTERIZATION STUDY OF FORMER NODULAR IRON WASTEWATER PONDS/BASINS
NODULAR FACILITY
SAGINAW, MICHIGAN

Compound	*Estimated Quantitation Limits (EQL)* [1]		*Method Detection Limits (MDL)* [2]		*Rule 57 Water Action Levels*	
	Water (µg/L)	*Sediment (mg/kg)*	*Water (µg/L)*	*Sediment (mg/kg)*	*Value (µg/L)*	*Standard* [3]
AVS/SEM						
Cadmium	NA	0.08	NA	0.036	NA	NA
Copper	NA	0.8	NA	0.74	NA	NA
Lead	NA	0.24	NA	0.19	NA	NA
Mercury	NA	0.04	NA	0.015	NA	NA
Nickel	NA	0.8	NA	0.27	NA	NA
Zinc	NA	0.8	NA	0.44	NA	NA
Additional Parameters						
Cyanide (amenable)	5	NA	5	NA	5.2	FCV
Cyanide (total)	NA	0.1	NA	0.1	NA	NA
Ammonia-N	200	2.0	35	0.35	29	FCV
Biochemical Oxygen Demand	2,000	NA	2,000	NA	NA	NA
Chemical Oxygen Demand	20,000	NA	10,000	NA	NA	NA
Formaldehyde	50	NA	8.4	NA	120	FCV
Hexane Extractable Material	5,000	NA	770	NA	NA	NA
Nitrate	100	5.0	23	0.23	10000	HNVd
Total Phenolics	40	NA	7.3	NA	NA	NA
Total Organic Carbon	1	1000	0.24	NA	NA	NA
N15 Isotope	NA	NA	NA	NA	NA	NA

Notes:

[1] - Please note that these are targeted quantitation limits and are presented for guidance only. Actual quantitation limits are highly matrix dependent and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes.

[2] - Method Detection Limits (MDL) are also presented for guidance only. Actual MDLs will vary depending on sample specific preparation factors. The MDLs are also highly matrix dependant and may be elevated due to matrix effects, QA/QC problems and high concentrations of target and non-target analytes. Laboratory MDLs are updated on a periodic basis and the MDLs in effect when the samples are analyzed will be used for reporting purposes.

[3] - HCVd = HCV-Human Cancer Value-Drink
HNVd = Human Noncancer Value-Drink
FCV = Final Chronic Value
WV = Wildlife Value

[4] - Values in red are the lowest specified value by Rule 57, excluding calculations involving hardness.

APPENDIX A

SAMPLING, PRESERVATION, AND SHIPPING PROTOCOL FOR δ^{15} N-NH_4 ANALYSIS BY THE MICRO-DIFFUSION METHOD

Sampling, Preservation, and Shipping Protocol for δ^{15}N-NH4 Analysis by the Micro-Diffusion Method

Benjamin Moan
Northern Arizona University
Colorado Plateau Stable Isotope Laboratory
(updated 14Jun10)

Background

The analytical procedure for analyzing δ^{15}N-NH4 involves converting all of the NH4 to ammonia gas, driving the gas into the container headspace, and diffusion of the ammonia through a Teflon membrane onto an acidified filter disk as NH4+. The sample concentrations of N-NH4 must be determined before δ^{15}N analysis. We target 40 µg of N per sample, so enough sample material must be sent to achieve this. For quality control, we analyze each sample in triplicate, so the volume sent must take this into consideration (120 µg of N-NH4 must be sent at a minimum). Applicable sample matrices are water or salt extracts. For extracts, the type and concentration of salt must be provided.

Sample Requirements

Concentration:	Samples must contain a minimum of 0.05 mg N-NH4/L. Note that this is mg N/L, not mg/L of the entire ion. If the concentrations are unknown, we will need to analyze the samples on our Lachat Quikchem colorimetry system. Please visit our website for concentration analysis pricing. If the concentrations are known, please include these data with the samples.
Volume:	We need a total N mass of 120 µg from NH4, so the minimum volume will depend on the sample concentration. We cannot analyze volumes >1L, so 3 L total is the maximum per sample volume that we can accept. For higher concentrations, please send smaller volumes as freezer space is limited.
Matrix:	The matrix may be water or a salt extract solution such as 2M KCl. Samples must be filtered through a 0.45 µm (micron) nylon filter. For extracts, please provide us with information regarding the type and amount of salt used for each sample. Please freeze the samples and keep them frozen until shipment. We cannot accept samples preserved with any acid or other agent. Frozen samples can be stored indefinitely. For KCl or other salt extracts, please follow your own laboratory procedure for extracting NH4+.
Shipping:	Samples should be kept frozen until shipment and shipped frozen in an ice-chest with cold packs. Overnight shipping

is preferable, but 3 or 5 day shipping may work for samples originally stored below -40 C and shipped with cold packs. We can accept samples shipped on dry ice only if declared and all proper shipping and labeling protocols are followed. Please contact your institution's regulatory compliance department and courier service prior to shipping with dry ice, and please inform us as well. We recommend Nalgene bottles for collection, storage, and shipping of samples. Specimen cups are notoriously leaky as the samples start to thaw in shipment and are not recommended.

Water Sampling and Storage

Labs may follow their own water collection protocol, provided that any samples submitted are filtered and unpreserved, but frozen. The following protocol may be used to collect natural water samples.

Materials:

- 1 L Nalgene bottles
- Smaller Nalgene bottles if it is known that the ion concentrations are high
- B-D 60 ml syringe
- Millipore Filtration apparatus
- 0.45 µm Nylon membrane filters (Whatman, 47 mm, Cat no. 7404-004)
- Ice-chest with ice or cold packs.

Water Collection (General Procedure):

1. Rinse 1.0 L Nalgene 5 times with water from desired sample location.
2. Fill 1.0 L Nalgene with water sample at desired depth and screw the cap on the water sample. Bring sample to a place on-site where filtration can be done.
3. Rinse the collecting syringe and filter housing at least 3 times with the water from the 1.0 L Nalgene.
4. Rinse each of the smaller vials with small amount of filtered sample water from the 1.0 L bottle. The size of the container needed will depend on the required volume for analysis. NH4+ concentrations are unknown or expected to be low (<0.10 mg N/L), collect at 3 Liters of each sample.
5. On-site, filter water from the 1.0 L sample into the sample Nalgene vials. Always use a new filter on samples from different sites.
6. Make sure that the lids are on tight and transport the samples on ice to the laboratory.
7. Freeze the samples immediately upon return to the lab and keep them frozen until shipping or analysis.
8. If you would like to have our lab analyze for NH4+ concentrations, please collect and ship a separate 60 ml Nalgene for each sample. The filtration and preservation procedure is identical to that for isotope analysis.

APPENDIX B

SAMPLING, PRESERVATION, AND SHIPPING PROTOCOL FOR δ^{15} N-NO_3 AND δ^{18} O-NO_3 ANALYSIS BY THE N_2O-DENITRIFIER METHOD

Sampling, Preservation, and Shipping Protocol for δ^{15}N-NO_3 and δ^{18}O-NO_3 Analysis by the N_2O-Denitrifier Method

Benjamin Moan
Northern Arizona University
Colorado Plateau Stable Isotope Laboratory
(updated April 22, 2010)

Background

Nitrate (NO_3) in water samples or salt extracts is converted to N_2O gas by bacteria that lack the enzyme to reduce it to N_2 gas. N_2O can then be analyzed with an isotope ratio mass spec (IRMS) to determine δ^{15}N and δ^{18}O values of nitrate. *P. aureofaciens* is used for most analyses, but *P. chlororaphis* may be substituted in some cases (e.g., ^{15}N-enriched samples or salt extracts where only δ^{15}N is needed). Precision, reported as one standard deviation, is $\leq 0.30‰$ for δ^{15}N and $\leq 0.60‰$ for δ^{18}O. We can only analyze NO_3 by this method, not NH_4.

Sample Requirements

Concentration:	The minimum concentration of nitrate for routine analysis is 0.07 mg/L as N. Samples below this concentration can be analyzed, but isotopic precision may not be as good due to smaller-than optimal peak sizes. Concentration data must be submitted with the samples. If concentration is unknown, we can analyze the samples on our Lachat Quikchem colorimetry system for an additional cost. Please visit our website for pricing.
Volume:	25–50 ml is sufficient for isotope analysis if the nitrate concentration of the samples is known. 50–100 ml is necessary if we need to analyze for nitrate concentration. If concentration analysis is required, it is preferable that two separate vials, each with about 50 ml, are shipped for each sample. That will allow us to keep the isotope sample frozen while we analyze for concentration. Please do not send samples in containers larger than 250 ml as freezer storage space is limited.
Preservation:	The samples should be filtered through 0.45 µm (micron) nylon filters to remove suspended solids and some of the natural bacteria. Samples with suspended solids or sediments in the vial cannot be accepted. Samples must be free of any acid or other preservative as it may kill the microbes. Samples should be frozen as soon as possible after collection and filtering and kept frozen until shipment. They can be stored frozen indefinitely.

1M KCl Extracts: As of April 22, 2010, the following salt concentrations have been confirmed as acceptable for this analysis: 1M KCl samples with nitrate concentrations of 0.07 mg N/L or higher, and 2M KCl with nitrate concentrations of 0.14 mg N/L or higher . Please follow your own protocol for extracting NO_3 from soil using 1M or 2M KCl. The samples should be free of suspended solids and sediment, and should be frozen as soon as possible after filtering. Even high grade KCl may contain nitrate contamination. To correct for this:

- Make one large batch of 1M or 2M KCl for all of the samples that you wish to extract.
- Include 1 L from the same batch of 1M or 2M KCl with the shipment of samples so that we can make blanks and standards to correct for nitrate contamination. It is important that this comes from your lab as the KCl in our lab may not have the same degree of contamination. If you are shipping more than 100 samples, include an additional L of 1M or 2M KCl for every 100 samples.
- If we will be analyzing for nitrate concentrations, please double the volume of 1M or 2M KCl that you send.

Shipping: Samples should be kept frozen until shipment and shipped frozen in an ice-chest with cold packs. Overnight shipping is preferable, but 3 or 5 day shipping may work for samples originally stored below 40 C and shipped with cold packs. We can accept samples shipped on dry ice only if declared and all proper shipping and labeling protocols are followed. Please contact your institution's regulatory compliance department and courier prior to shipping with dry ice, and please inform us as well. We recommend Nalgene bottles for collection, storage, and shipping of samples. Specimen cups are notoriously leaky as the samples start to thaw in shipment and are not recommended.

Water Sampling and Storage

Labs may follow their own water collection protocol, provided that any samples submitted are filtered and unpreserved, but frozen. The following protocol may be used to collect natural water samples.

Materials:

- 60 ml Nalgene bottles, 2 per sample
- B-D 60 ml syringe
- Millipore Filtration apparatus

- 0.45 µm Nylon membrane filters (Whatman, 47 mm, Cat no. 7404-004), at least one per sample.
- Ice-chest with ice or cold packs.

Water Collection (General Procedure):

1. Rinse the collecting syringe and filter housing at least 3 times with the water from each location before and between sampling.
2. Rinse the two 60 ml Nalgene bottles for that sample site with about 15 ml of filtered water and discard.
3. Filter about 45-50 ml of water into each 60 ml Nalgene. Be sure to leave some headspace for expansion during freezing. You may need to change the filter half way through collection if the water is very dirty. Otherwise change the filter between sample sites.
4. Make sure that the lids are on tight and transport the samples on ice to the laboratory.
5. Freeze the samples immediately upon return to the lab and keep them frozen until shipping or analysis.
6. The first vial is used for nitrate concentration analysis and does not need to be submitted to our lab if you will be performing this analysis. The second vial is for nitrate isotope analysis.

APPENDIX C

AVS-SEM STANDARD OPERATING PROCEDURES

Title: Acid Volatile Sulfides (AVS) and Simultaneously Extracted Metals (SEM) in Sediment

Approvals (Signature/Date):

Michael P. Wesoloski	9/30/2010		10/1/2010
Mike Wesoloski Technical Specialist	Date	Steve Jackson Health & Safety Manager / Coordinator	Date
Nasreen K. DeRubeis	11/05/10	Deborah Lowe	11/10/10
Nasreen DeRubeis Quality Assurance Manager	Date	Deborah Lowe Laboratory Director	Date

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1. SCOPE AND APPLICATION

1.1. This method describes the procedure for the determination of acid volatile sulfides (AVS) and for metals that are solubilized during the acidification step (Simultaneously Extracted Metals, SEM). The conditions used have been reported to measure amorphous or moderately crystalline monosulfides. As a precipitant of toxic heavy metals, sulfide is important in controlling the bioavailability of metals in anoxic sediments. If the molar ratio of toxic metals measured by SEM to AVS exceeds one, the metals are potentially bioavailable. Because the relative amounts of AVS and SEM are important in the prediction of potential metal bioavailability, it is important to use the SEM procedure for sample preparation for metal analysis. This uses the same conditions for release of both sulfide and metal from the sediment and thus provides the most predictive means of assessing the amount of metal associated with the sulfide.

1.2. Method 9034 is used to quantify the concentration of sulfide and Method 6010B is used to quantify the concentration of the routine SEM metals (arsenic, cadmium, chromium, copper, lead, nickel, silver and zinc). If mercury is requested as a SEM, Method 7470A is used for quantification. Reporting limits are listed in Attachment 1.

2. SUMMARY OF METHOD

2.1. The AVS in the sample is first converted to hydrogen sulfide (H2S) by acidification with hydrochloric acid at room temperature. The H2S is then purged from the sample and trapped. The amount of sulfide that is trapped is then determined titrimetrically following Method 9034. The SEM are metals liberated from the sediment during the acidification. These are determined following Method 6010B after filtration of the sample (plus 7470A if mercury is required).

3. DEFINITIONS

3.1. Acid Volatile Sulfides (AVS): Amorphous, moderately crystalline monosulfides, and other sulfides that form hydrogen sulfide under the conditions of this test.

3.2. Simultaneously Extracted Metals (SEM): Metals which form less soluble sulfides than do iron or manganese, and which are at least partially soluble under the conditions of this test. The routine SEMs are cadmium, copper, lead, nickel, and zinc. Mercury may also be determined on a project specific basis.

3.3. ICV: Initial Calibration Verification: An undistilled standard prepared by adding 1 mL of a 1000 ppm (or standardized concentration) sodium sulfide standard (different source than the standard used for the LCS and MS/MSD) to 50 mL of reagent water (20 ppm concentration).

3.4. ICB: Initial Calibration Blank: undistilled blank consisting of 50 mL of reagent water.

3.5. PBW: Prep Blank Water or Method Blank.

3.6. CCV: Continuing Calibration Verification: preparation is the same as the ICV.

3.7. CCB: Continued Calibration Blank: preparation is the same as the ICB.

3.8. LCS: Laboratory Control Sample.

4. INTERFERENCES

4.1. Oxygen in the reagents and apparatus is the primary interference reported. Samples must be taken with minimum aeration to avoid volatilization of sulfide or reaction with oxygen, which oxidizes sulfide to sulfur compounds that are not detected. Use deoxygenated, deionized water and reagents.

4.2. Reduced sulfur compounds, such as sulfite and hydrosulfite, may decompose in acid and form sulfur dioxide. This gas may carry over to the zinc acetate solutions and subsequently react with iodine during the titration, thus causing a positive bias to the results.

4.3. The iodometric method suffers interference from reducing substances that react with iodine, including thiosulfate, sulfite, and various organic compounds.

4.4. The pH of the sample after the addition of the acid and during the purge process must be below 3.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Hydrogen sulfide (H_2S) gas is generated by the addition of sulfuric acid. Inhalation of H_2S gas can cause headache, dizziness, nausea and unconsciousness and potentially death.

5.2. Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Hydrochloric Acid	Corrosive Poison	5 ppm-Ceiling	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Iodine	Poison Corrosive Oxidizer	0.1 ppm-Ceiling	Vapors severely irritate and can burn the mucous membranes and respiratory tract. Liquid contact may cause blistering burns, irritation, and pain. Vapors may be severely irritating to the skin. Vapors are severely irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Potassium Dichromate	Oxidizer Corrosive Carcinogen	0.1 Mg/M3 TWA as CrO3	Extremely destructive to tissues of the mucous membranes and upper respiratory tract. May cause ulceration and perforation of the nasal septum. Symptoms of redness, pain, and severe burn can occur. Dusts and strong solutions may cause severe irritation. Contact can cause blurred vision, redness, pain and severe tissue burns. May cause corneal injury or blindness.
Sodium Hydroxide	Corrosive	2 Mg/M3-Ceiling	Severe irritant. Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat or runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes, and with greater exposures it can cause burns that may result in permanent impairment of vision, even blindness.
Sodium Sulfide	Corrosive	10 ppm-TWA 15 ppm-STEL	Will form Hydrogen Sulfide (HS) gas if combined with strong acids. Inhalation of HS gas may be fatal. Symptoms include painful conjunctivitis, headache, nausea, dizziness, coughing and, in extreme cases, pulmonary edema and possible death. Irritant. Contact with skin can produce serious caustic burns with painful inflammation and possible destruction of tissue. Inflammation, tearing and pain may be expected. Severe contact can cause destruction of tissue.
Sulfuric Acid	Corrosive Oxidizer Dehydrator Poison Carcinogen	1 Mg/M3-TWA	Inhalation produces damaging effects on the mucous membranes and upper respiratory tract. Symptoms may include irritation of the nose, throat, and labored breathing. Symptoms of redness, pain, and severe burn can occur. Contact can cause blurred vision, redness, pain and severe tissue burns. Can cause blindness.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

5.3. Procedures shall be carried out in a manner that protects the health and safety of all TestAmerica associates.

5.4. Eye protection that satisfies ANSI Z87.1 (as per the Chemical Hygiene Plan), laboratory coat, and appropriate gloves must be worn while samples, standards, solvents, and reagents are being handled. Disposable gloves that have been contaminated will be removed and discarded; other gloves will be cleaned immediately.

5.5. The health and safety hazards of many of the chemicals used in this procedure have not been fully defined. Additional health and safety information can be obtained from the Material Safety Data Sheets (MSDS) maintained in the laboratory.

5.6. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore, unless they are known to be non-hazardous, all samples must be opened, transferred and prepared in a fume hood, or under other means of mechanical ventilation. Solvent and waste containers will be kept closed unless transfers are being made.

5.7. The preparation of standards and reagents will be conducted in a fume hood with the sash closed as far as the operation will permit.

5.8. All work must be stopped in the event of a known or potential compromise to the health and safety of a TestAmerica associate. The situation must be reported **immediately** to a laboratory supervisor or a TestAmerica Emergency Coordinator.

6. EQUIPMENT AND SUPPLIES

6.1. Instrumentation

6.1.1. Not Applicable.

6.2. Supplies

6.2.1. Boiling tube.

6.2.2. Inlet adapter.

6.2.3. Dropping funnel.

6.2.4. Gas inlet.

6.2.5. Impinged bubbler.

6.2.6. Fritted bubbler.

6.2.7. Bubbler vessels.

6.2.8. WestClips®

6.2.9. Gas line “T” connector.

6.2.10. Class A Volumetric flasks, pipettes, and burettes.

6.2.11. High purity nitrogen gas.

6.2.12. Regulator.

6.2.13. 100 mL and 300 mL graduated disposable flasks.

6.2.14. 100 mL disposable beaker

6.2.15. Hot plate stirrer.

6.2.16. 50mL burette.

6.2.17. Parafilm

6.2.18. Filtering apparatus and 0.45 µm filter membrane.

7. REAGENTS AND STANDARDS

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

7.2. Reagent water (Super Q/DI Water). All references to water in this method refer to reagent water.

7.3. Zinc acetate for the scrubber. Zinc acetate solution (approximately 0.5M). Dissolve about 110g zinc acetate dihydrate in 200mL of reagent water. Add 1mL hydrochloric acid (concentrated), to prevent precipitation of zinc hydroxide. Dilute to 1L.

7.4. Acid to acidify the sample. 6 M Hydrochloric acid, 1:1 HCl:reagent water. Purge with nitrogen for at least 30 minutes prior to use.

7.5. 1:4 Sulfuric Acid (H2SO4): Carefully add 250 mls of concentrated sulfuric acid to a 1 liter volumetric flask containing at least 500 mls of reagent water. Bring up to volume.

7.6. UHP/zero grade nitrogen gas. Gas chromatographic grade with two-stage regulator.

7.7. Starch indicator. 0.5%. Purchased.

7.8. 0.0250N $Na_2S_2O_3$. Purchased.

7.9. 0.025N Iodine. Purchased.

7.10. 1000ppm Sodium sulfide prepared by adding 3.75g $Na_2S{\bullet}9H_20$ to 500mL reagent water. May be commercially available.

8. SAMPLE COLLECTION, PRESERVATION, SHIPMENT AND STORAGE

8.1. Samples must be cooled to 4°C and stored headspace free. Typically a separate 4 oz jar is filled specifically for this test.

8.2. The acidification of the sample (H_2S generation) and sulfide determination must be performed within 14 days from the date of collection. The routine SEMs are stable up to six months after sample collection (28 days for mercury, if required).

8.3. If after distillation, the AVS distillate can not be immediately titrated it may be stored at $\leq$ 6°C for up to 24 hours before final titration provided the 7 day holding time is not exceeded.

9. QUALITY CONTROL

9.1. Sample QC

9.1.1. A Laboratory Control Sample (LCS) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) LCS and metals (SEM) LCS is performed.

9.1.1.1. The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.1.2. A matrix spike and a matrix spike duplicate (MS/MSD) must be analyzed with each batch of 20 or fewer samples. A separate sulfide (AVS) MS/MSD and metals (SEM) MS/MSD is performed.

9.1.2.1. The percent recovery for matrix spike and matrix spike duplicate should be ± 25 percent. If this criterion is not met, evaluate method process. If no errors are found, document in a Non-Conformance Memo (NCM).

9.1.2.2. The relative percent difference (RPD) between the MS and MSD must be within ± 20 percent. If this criterion is not met, then repeat the analysis once. The results with the better RPD will be reported. If the results for the reanalysis are the same as the original analysis, then report the original analysis.

9.1.3. A method blank must be analyzed with each batch of 20 samples or fewer processed at the same time. The prep blank (or method blank) can be used as the ICB if it meets the ICB acceptance criteria. The processing of a method blank will assure non-contamination of the reagents. The ICB result must be less than the Reporting Limit. The method blank result must be less than two times the Reporting Limit, otherwise all samples must be reprepared and reanalyzed. If this is not possible due to limited sample quantity (or there is no sample left) the corresponding samples will be flagged and the PM will be notified. If repreparation and reanalysis happen to be outside holding time, then approval from the client must be obtained before any reanalysis is performed.

9.2. Instrument QC

9.2.1. A sulfide run will consist of the following sequence: ICV, ICB, and up to 10 samples followed by a CCV and a CCB. See the appropriate metals SOP for the SEM analyses.

9.2.2. This can be followed by up to 10 more samples, followed by a CCV and CCB.

9.2.3. Repeat 9.2.1 and 9.2.2 sequence for additional samples.

9.2.4. The following QC requirements must be met for the sulfide (AVS) analyses:

9.2.4.1. The ICV must be within ± 15 percent. If this criterion is not met, then recalibrate and reanalyze the samples. The LCS can be used as an ICV if it meets the ICV acceptance criteria of 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

9.2.4.2. The CCV must be within ± 15 percent. If this criterion is not met, then reanalyze the samples with a valid CCV. If the analysis sequence shows ICV, ICB, and 10 samples followed by CCV, CCB, and this CCV fails, then all those 10 samples must be reanalyzed. If with the above sequence 10 additional samples are analyzed following a CCV and a CCB and this second CCV fails, then all the samples up to the last acceptable CCV must be reanalyzed. The CCB criteria are the same as ICB.

9.3. All quality control data must be maintained and available for reference or inspection for a period of three years. This method is restricted to use by or under supervision of experienced analysts.

9.4. All sample preparation and analysis information will be documented on laboratory bench sheets, computer printouts, standard logbooks, etc. All the documents associated with an analysis will be forwarded for reporting and for inclusion in the project files.

10. PROCEDURE

10.1. Sample Preparation

10.1.1. Place the boiling tube containing approximately 10 grams of sample (record to the nearest 0.1 grams) and 50 mL of reagent water in the heater block (used as a holder only) and assemble the acid soluble sulfide distillation apparatus as shown in Figure 1. The sample can be weighed on a 2” x 2” piece of Parafilm and placed into the boiling tube.

10.1.2. Spike the sulfide (AVS) LCS, MS, and MSD with 1 mL of the 1000 ppm sodium sulfide solution (7.11) which is equivalent to 100 mg/Kg in a 10 gram sample. Spike the metals (SEM) LCS, MS, and MSD with 2.5 mLs of the metals ICP MS solution. If mercury is required, a mercury spike will need to be added to the LCS, MS, and MSD.

10.1.3. Place 2.0mL of 0.5M zinc acetate solution and 20.0mL of deionized water in each of two bubbler vessels. Place an impinged bubbler in the first (front) and second (back) vessel, and seal them with size 24/40 WestClips®. The sealed vessels and impingers function as the gas scrubbers. Connect the first scrubber to the inlet adapter and place the second bubbler vessel in the bubbler vessel rack. Connect the two impingers in series using Tygon® tubing.

10.1.4. Close stopcock of dropping funnel. Place 20 mL of the nitrogen purged 6 M hydrochloric acid in the dropping funnel.

10.1.5. Connect a high-purity (GC grade) nitrogen gas source to the main inlet of the gas manifold of the aluminum heater block as specified in the Heater Block Operation Manual. Use a two-stage gas tank regulator and set the pressure into the gas manifold to 20psi.

10.1.6. Connect a black gas line from each gas manifold valve to a “T” connector and a tygon gas line from the “T” to each of the two gas inlets of the apparatus. One at the top of the dropping funnel and one at the inlet adapter as shown in Figure 1.

10.1.7. Purge assembled apparatus with high-purity nitrogen for 10 minutes to remove atmospheric oxygen from the apparatus and contained solutions. During purge, adjust nitrogen flow such that 2-3 bubbles per second exit the base of the inlet adapter.

10.1.8. Open stopcock of dropping funnel and allow all of the 6M hydrochloric acid to drip into the boiling tube. Once dropping funnel is empty, close the stopcock to ensure sample is not lost into the funnel.

10.1.9. Purge the sample for 1 hour at room temperature. After the 1 hour purging period, remove the bubbler vessels. Turn off the nitrogen flow. Carefully combine the gas scrubber solutions in a 100 mL graduated disposable flask. Do not shake or mix solutions to avoid loss of sulfide. Bring up to 50 mL with reagent water. Determine the concentration of acid volatile sulfide in the zinc acetate gas scrubber solutions by using the Titrimetric-iodine method (9034)—proceed to Section 10.3.

10.1.10. After the generation of sulfide has been completed, the sediment suspension remaining in the boiling tube is filtered through a 0.45 μm membrane filter. The pH of the solution is determined using narrow range pH strips to verify that the pH is less than 3. If the pH is not less than 3, the group supervisor and QA Manager should be consulted. Document all actions in a Nonconformance Memo (NCM). The solution is brought up to a final volume of 250 mL in a 300 mL graduated disposable flask. This solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

10.2. Calibration

NOTE: All periodic standardizations of titrants can be found in the Wet Chemistry standardization logbook. Daily standardizations are found on the bench worksheet.

10.2.1. Stock sulfide standard is titrated daily before each distillation of sample sets. The stock standard must be reprepared every week.

10.2.2. Sodium thiosulfate (0.0250N) standardization—performed daily.

10.2.2.1. Use 0.0250 N Biiodate titrant: dissolve 0.8124g potassium biiodate (dried 2 hours) in Super-Q water and dilute to 1 L.

10.2.2.2. Place 2g KI in 250mL beaker and add 100mL Super-Q water and stir. Add 10mL 1:4 H_2SO_4 and 10mL biiodate.

10.2.2.3. Place in the dark for 5 minutes. Dilute to 150mL and add starch indicator (Section 7.8)

10.2.2.4. Titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Repeat procedure two additional times. Determine the normality of the $Na_2S_2O_3$ as follows:

$$N\ Na_2S_2O_3 = \frac{10\text{ mL biiodate} \times 0.025\text{ N biiodate}}{\text{mL } Na_2S_2O_3\text{ titrant}}$$

10.2.3. Iodine standardization: performed daily

10.2.3.1. Place 20mL .0250N iodine in Erlenmeyer flask. Add 2mL 6 N HCl.

10.2.3.2. Titrate with $Na_2\ S_2O_3$ (7.9) to a pale yellow color.

10.2.3.3. Add starch indicator (7.8) and titrate with $Na_2S_2O_3$ (7.9) to clear endpoint. Determine the normality of the iodine (I) as follows:

$$N\ I = \frac{NNa_2S_2O_3 \times \text{mL } Na_2S_2O_3\text{ titrant}}{\text{mL I solution}}$$

10.3. Sample Analysis

10.3.1. Pipette a known amount of standardized 0.025N iodine solution in a 100mL disposable beaker, adding an amount in excess of that needed to oxidize the sulfide.

10.3.2. Add 2mL of 6N HCl to the iodine.

10.3.3. Pour the gas scrubbing solutions obtained in Section 10.1.9 into the flask. If at any point in transferring the zinc acetate solution, the amber color of the iodine disappears or fades to yellow, more 0.025N iodine must be added. This additional amount must be added to the amount from Section 10.3.1 for calculations. Record the total volume of standardized 0.025N iodine solution used.

10.3.4. Titrate the solution in the flask with standard 0.025N sodium thiosulfate solution until the amber color fades to yellow. Add enough starch indicator for the solution to turn dark blue and titrate until the blue disappears. Record the volume of titrant used.

10.3.5. For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

11. CALCULATIONS / DATA REDUCTION

11.1. One mL of 0.0250 N standard iodine solution reacts with 0.4mg sulfide present in titration vessel.

11.2. AVS mg/Kg-dry =

$$\text{AVS mg/Kg-dry} = \frac{[(A \times B) - (C \times D)] \times 16000}{E \times F}$$

A = mL of iodine solution
B = N of iodine solution
C = mL of $Na_2S_2O_3$ solution
D = N of $Na_2S_2O_3$ solution
E = weight of sample (grams or mls)
F = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.3. To convert the AVS concentration from mg/Kg-dry to μmoles/gram-dry, divide by 32.066 (molecular weight of sulfur).

11.4. Enter the completed data work sheet into computer program, sulfide analysis worksheet, for final results.

11.5. For each SEM, first determine concentration in mg/Kg-dry as follows:

$$\text{SEM mg/Kg-dry} = \frac{A \times B}{C \times D}$$

A = conc. of metal in solution as determined by 6010B or 7470A (mg/L)
B = final volume of solution in liters—typically 0.25 liters.
C = weight of sample in Kg.
D = Percent solids as decimal fraction (i.e., 50% solid is 0.50)

11.6. To convert the concentration of each SEM from mg/Kg-dry to µmoles/gram-dry, divide by the molecular weight of that metal (cadmium = 112.411; copper = 63.546; lead = 207.2; mercury = 200.59; nickel = 58.69; and zinc = 65.39).

11.7. Calculate the Total SEM molar concentration of the sample by summing each of the individual SEM concentrations in units of µmoles/gram-dry. If any one of the SEMs is not detected (ND), it is considered a zero (0) in the summation.

11.8. Calculate the molar ratio of SEM over AVS as follows:

SEM/AVS = A/B

A = Total SEM molar concentration (µmoles/gram-dry).
B = AVS molar concentration (µmoles/gram-dry).

Note: If AVS is not detected (ND), the molar ratio cannot be determined.

11.9. Matrix Spike percent recovery:

$$Theoretical\ Spike\ Conc. = \frac{\begin{pmatrix} Spike \\ Conc. \end{pmatrix} \times \begin{pmatrix} Vol.\ of \\ Spike\ Added \end{pmatrix}}{Final\ Vol.\ Spiked}$$

$$\%\ \mathrm{Re}cov ery = \frac{\begin{pmatrix} Final \\ Spike + Sample \end{pmatrix} - Sample\ \mathrm{Re}sult \begin{pmatrix} \frac{Vol.\ Sample \\ Spiked}{Final\ Vol. \\ Spiked} \end{pmatrix}}{Theoretical\ Spike\ Conc.} \times 100$$

12. METHOD PERFORMANCE

12.1. Method Detection Limit Study (MDL)

12.1.1. Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

12.1.2. Method Detection Limit (MDL) for Metals - An MDL must be determined for each analyte/matrix prior to the analysis of any samples. Either an annual MDL study or quarterly MDL Verification can be done. The MDL is determined using seven replicates of reagent water, spiked with all the analytes of interest that have been carried through the entire analytical procedure. MDLs must be determined in accordance with 40 CFR Part 136 Appendix B requirements as detailed in SOP: PT-QA-007. The spike level must be between the calculated MDL and 10X the MDL to be valid. The result of the MDL determination must be below the TestAmerica reporting limit.

12.2. Demonstration of Capabilities

12.2.1. Prior to analysis of any samples using this SOP, the following requirements must be met: Initial Demonstration Study: This requires the analysis of four QC check samples. The QC check sample is a well-characterized, laboratory-generated sample used to monitor method performance, which should contain the analyte(s) of interest. The results of the initial demonstration study must be acceptable before analysis of samples under this SOP may begin. Four aliquots of the check sample (LCS) are prepared and analyzed using the procedures detailed in this SOP. Acceptance criteria for the LCS are given in Section 9.1.1.1.

12.3. Training Qualifications

12.3.1. The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. The group/team leader must document the training and PE performance and submit the results to the QA Manager for inclusion in associate training files.

13. POLLUTION CONTROL

13.1. It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for “Waste Management and Pollution Prevention.”

13.2. This method does not contain any specific modifications that serve to minimize or prevent pollution.

14. WASTE MANAGEMENT

14.1. Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP PT-HS-001. The following waste streams are produced when this method is carried out.

14.1.1. Acidic waste generated by sample titration. This waste is collected in a waste container identified as “Acid Waste”, Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.1.2. Unused sample distillate. This waste is collected in a waste container identified as “Acid Waste”, Waste #33. This waste is neutralized to a final pH between 6 and 9 and discharged down into a lab sink.

14.2. Waste generated in the procedure will be segregated, and disposed according to the facility hazardous waste procedures. The Environmental Health and Safety Coordinator should be contracted if additional information is required.

15. REFERENCES

15.1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, 3rd ed.; U.S. EPA. Office of Solid Waste and Emergency Response. U.S. Government Printing Office: Washington, DC, 1997; SW-846.

15.2. Allen, H.E. and F. Gongmin et al. 1991. Determination of Acid Volatile Sulfide and Simultaneously Extractable Metals in Sediment, April 1991 (Draft Analytical Method for the Determination of Acid Volatile Sulfide in Sediment, U.S. EPA Office of Water and Office of Science and Technology, Health and Ecological Criteria Division, Washington, D.C., August 1991.

15.3. SOP PT-MT-001, Inductively Coupled Plasma-Atomic Emission Spectroscopy, Spectrometric Method for Trace Element Analyses, SW-846 Method 6010B, 6010C and EPA Method 200.7, current revision.

15.4. SOP PT-MT-005, Preparation and Analysis of Mercury in Aqueous Samples by Cold Vapor Atomic Absorption, SW-846 7470A and MCAWW 245.1, current revision.

15.5. SOP PT-WC-010, Total Sulfide as Acid Soluble Sulfide, Method 9030B/9034, SM 20th Ed. 4500S-$^{2-}$F and EPA Method 376.1, current revision.

15.6. SOP PT-QA-007, Detection Limits, current revision.

15.7. SOP PT-QA-003, Glassware Clean-up for Organic/Inorganic Procedures, current version.

15.8. SOP PT-QA-006, Procurement of Standards and Materials; Labeling and Traceability, current version.

15.9. SOP PT-QA-008, Thermometer Calibration and Temperature Monitoring, current version.

15.10. SOP PT-QA-011, Data Recording Requirements, current version.

15.11. SOP PT-QA-012, Selection and Calibration of Balances and Weights, current version.

15.12. SOP PT-QA-016, Nonconformance & Corrective Action System, current version.

15.13. SOP PT-QA-021, Quality Assurance Program, current version.

15.14. SOP PT-QA-022, Equipment Maintenance, current version.

15.15. SOP PT-QA-027, Sample Receiving and Chain of Custody, current version.

15.16. PT-LQAM, current version.

16. METHOD MODIFICATIONS

16.1. Not applicable.

17. ATTACHMENTS

17.1. Figure 1 – Acid Volatile Sulfide generation apparatus.

17.2. Attachment 1 – SEM and AVS Reporting Limits. MDLs listed in the two attachments for metals and sulfide are subject to change.

18. REVISION HISTORY

18.1. Revision 1, 5/16/08.

18.1.1. Renamed SOP as PT-WC-008.

18.1.2. Changed laboratory name to TestAmerica.

18.1.3. Updated SOP format to match corporate SOP format.

18.1.4. Corrected some typographical errors and several Section references that were incorrect.

18.1.5. Revised section 9.1.1.1: The LCS and ICV are the same standard. Therefore the ICV/LCS acceptance criteria are 85 to 115 percent. If the LCS is not used as the ICV, then the LCS must meet a 75 to 125 percent recovery criterion.

18.1.6. Added to Section 12.1.1: Method Detection Limit (MDL) for Titrimetric Procedures - The detection limit for titrimetric procedures can be defined by the smallest amount of reagent that can be added during a titration to cause a chemical change. This is typically determined by the smallest size of the drop that can be produced on a particular burette or other titrating device. Drop size can be estimated by averaging the size of several (5 to 10 is a good number) repeated drops. The detection limit can then be calculated based on the titrant concentration, the sample size, and the minimum drop size.

18.1.7. Modified Section 12.1.2 to add either annual MDL Study or quarterly MDL Verification can be done for metals..

18.1.8. All revisions are highlighted throughout the SOP.

18.2. Revision 2

18.2.1. Updated SOP reference numbers throughout the SOP.

18.2.2. Added TestAmerica Pittsburgh's SOP References in section 15.

18.3. Revision 3

18.3.1. Section 1.2, added As, Cr and Ag for ICP. Added: Reporting limits are in Attachment 1.

18.3.2. Formaldehyde is not used in executing this SOP, thus references to formaldehyde in sections 4.2, the Table under 5.2, 7.3 and 10.1.3.

18.3.3. Section 8.3 was added to clarify that a distillate will be refrigerated no more than 24 hours before final titration provide the 7 day holding time is still met.

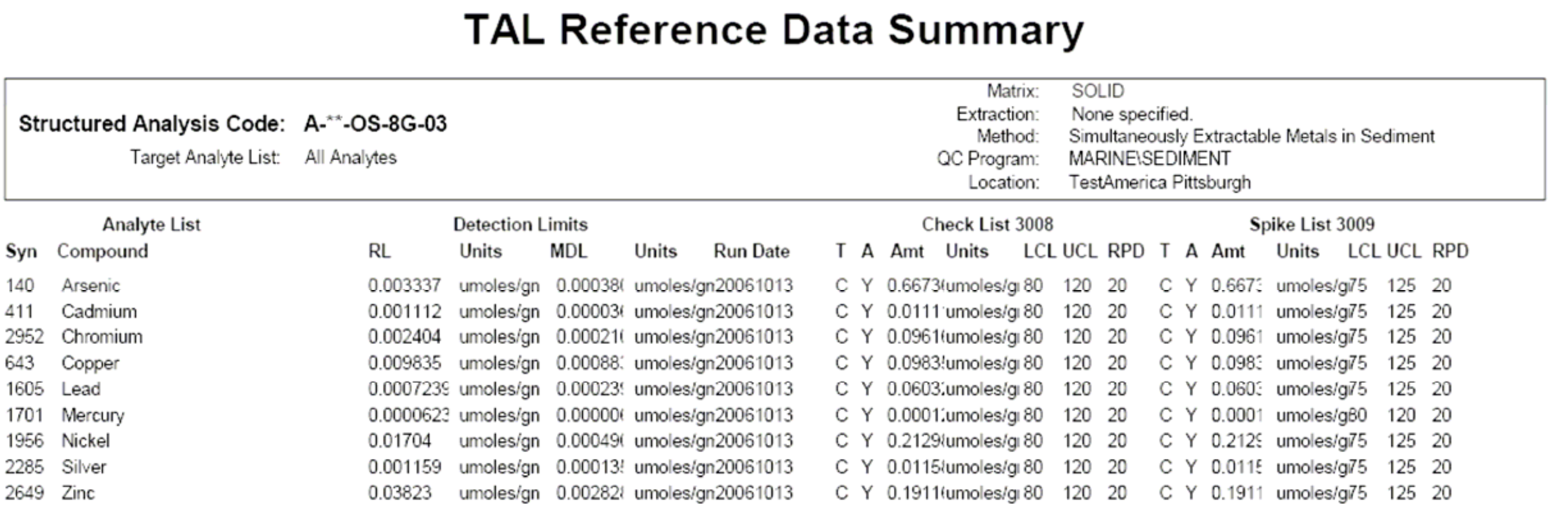
18.3.4. In section 10.1.1, corrected the volume of reagent water added to the heater block from 100 ml to 50 ml.

18.3.5. Added section 10.3.5: For metals, the solution is analyzed directly by ICP for the routine SEMs (see SOP PT-MT-001). If mercury is required, an aliquot of this solution is prepared following Method 7470A and analyzed by CVAA (see SOP PT-MT-005).

18.3.6. In section 11.2, correct variable E to read weight of sample (grams or mLs).

18.3.7. In Section 15 References/Cross-References, references were added to all pertinent QA SOP's and the PT-LQAM.

Attachment 1 – Reporting Limits



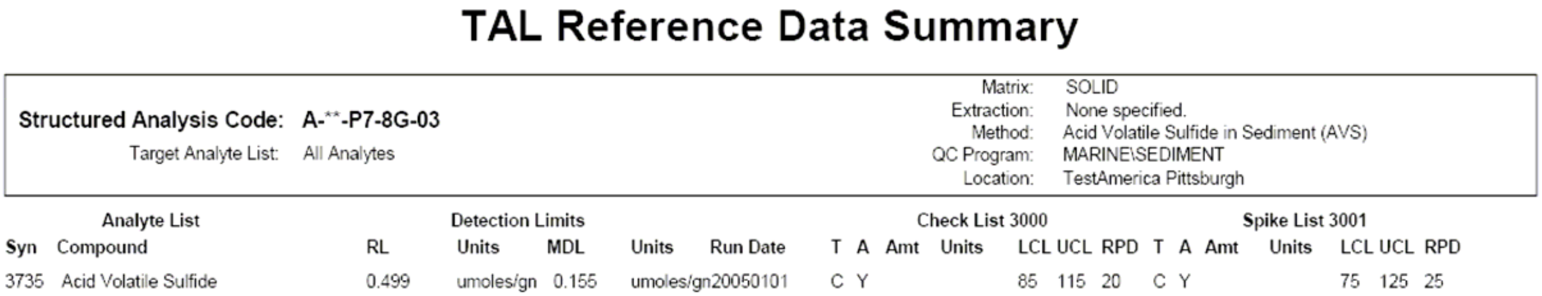
TAL Reference Data Summary

Structured Analysis Code: **A-**-OS-8G-03**
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Simultaneously Extractable Metals in Sediment
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List		Detection Limits					Check List 3008							Spike List 3009						
Syn	Compound	RL	Units	MDL	Units	Run Date	T	A	Amt	Units	LCL	UCL	RPD	T	A	Amt	Units	LCL	UCL	RPD
140	Arsenic	0.003337	umoles/gn	0.00038	umoles/gn	20061013	C	Y	0.6673	umoles/g	80	120	20	C	Y	0.667	umoles/g	75	125	20
411	Cadmium	0.001112	umoles/gn	0.00003	umoles/gn	20061013	C	Y	0.0111	umoles/g	80	120	20	C	Y	0.0111	umoles/g	75	125	20
2952	Chromium	0.002404	umoles/gn	0.00021	umoles/gn	20061013	C	Y	0.0961	umoles/g	80	120	20	C	Y	0.0961	umoles/g	75	125	20
643	Copper	0.009835	umoles/gn	0.00088	umoles/gn	20061013	C	Y	0.0983	umoles/g	80	120	20	C	Y	0.098	umoles/g	75	125	20
1605	Lead	0.000723	umoles/gn	0.00023	umoles/gn	20061013	C	Y	0.0603	umoles/g	80	120	20	C	Y	0.060	umoles/g	75	125	20
1701	Mercury	0.000062	umoles/gn	0.00000	umoles/gn	20061013	C	Y	0.0001	umoles/g	80	120	20	C	Y	0.0001	umoles/g	80	120	20
1956	Nickel	0.01704	umoles/gn	0.00049	umoles/gn	20061013	C	Y	0.2129	umoles/g	80	120	20	C	Y	0.212	umoles/g	75	125	20
2285	Silver	0.001159	umoles/gn	0.00013	umoles/gn	20061013	C	Y	0.0115	umoles/g	80	120	20	C	Y	0.011	umoles/g	75	125	20
2649	Zinc	0.03823	umoles/gn	0.00282	umoles/gn	20061013	C	Y	0.1911	umoles/g	80	120	20	C	Y	0.1911	umoles/g	75	125	20

Attachment 1 – Cont.



TAL Reference Data Summary

Structured Analysis Code: **A-**-P7-8G-03**
Target Analyte List: All Analytes

Matrix: SOLID
Extraction: None specified.
Method: Acid Volatile Sulfide in Sediment (AVS)
QC Program: MARINE\SEDIMENT
Location: TestAmerica Pittsburgh

Analyte List		Detection Limits					Check List 3000							Spike List 3001						
Syn	**Compound**	**RL**	**Units**	**MDL**	**Units**	**Run Date**	**T**	**A**	**Amt**	**Units**	**LCL**	**UCL**	**RPD**	**T**	**A**	**Amt**	**Units**	**LCL**	**UCL**	**RPD**
3735	Acid Volatile Sulfide	0.499	umoles/gn	0.155	umoles/gn	20050101	C	Y			85	115	20	C	Y			75	125	25

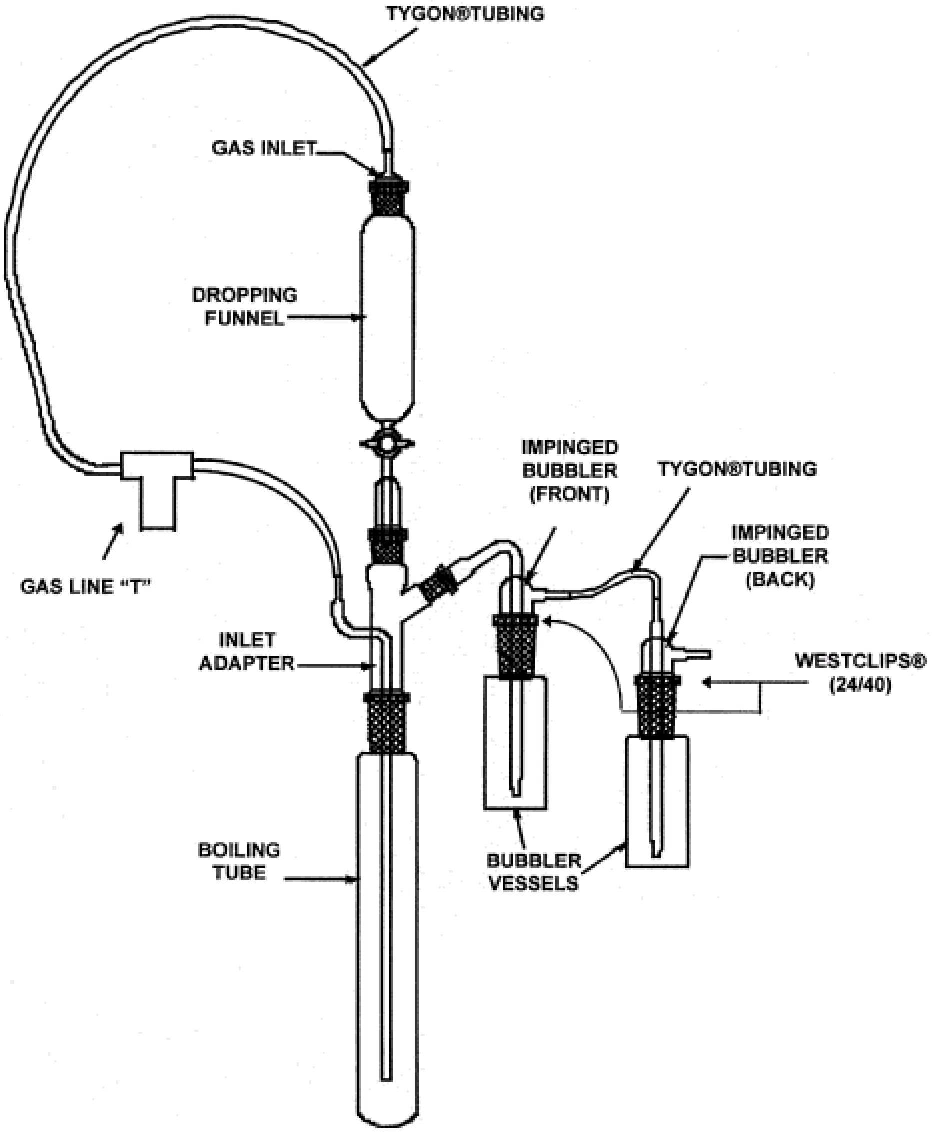
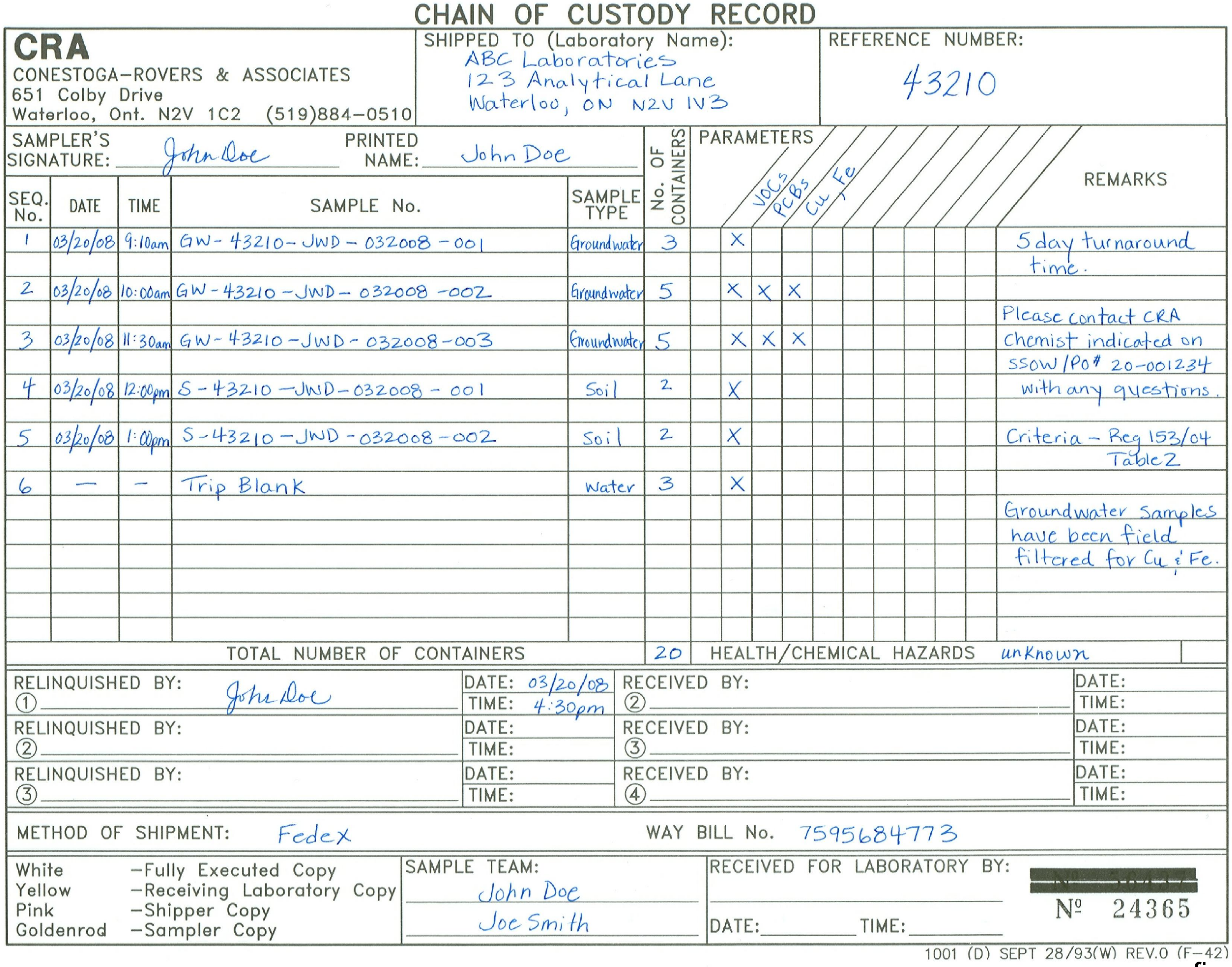


Figure 1 – Acid Volatile Sulfide generation apparatus.

APPENDIX D

TYPICAL COMPLETED CHAIN-OF-CUSTUDY FORM



CHAIN OF CUSTODY RECORD

CRA
CONESTOGA-ROVERS & ASSOCIATES
651 Colby Drive
Waterloo, Ont. N2V 1C2 (519)884-0510

SHIPPED TO (Laboratory Name):
ABC Laboratories
123 Analytical Lane
Waterloo, ON N2V 1V3

REFERENCE NUMBER: 43210

SAMPLER'S SIGNATURE: John Doe

PRINTED NAME: John Doe

SEQ. No.	DATE	TIME	SAMPLE No.	SAMPLE TYPE	No. OF CONTAINERS	PARAMETERS: VOCs	PCBs	Cu, Fe	REMARKS
1	03/20/08	9:10am	GW-43210-JWD-032008-001	Groundwater	3	X			5 day turnaround time.
2	03/20/08	10:00am	GW-43210-JWD-032008-002	Groundwater	5	X	X	X	
3	03/20/08	11:30am	GW-43210-JWD-032008-003	Groundwater	5	X	X	X	Please contact CRA chemist indicated on SSOW/PO# 20-001234 with any questions.
4	03/20/08	12:00pm	S-43210-JWD-032008-001	Soil	2	X			
5	03/20/08	1:00pm	S-43210-JWD-032008-002	Soil	2	X			Criteria – Reg 153/04 Table 2
6	–	–	Trip Blank	Water	3	X			
									Groundwater samples have been field filtered for Cu & Fe.

TOTAL NUMBER OF CONTAINERS: 20

HEALTH/CHEMICAL HAZARDS: unknown

RELINQUISHED BY: ① John Doe	DATE: 03/20/08 TIME: 4:30pm	RECEIVED BY: ②	DATE: TIME:
RELINQUISHED BY: ②	DATE: TIME:	RECEIVED BY: ③	DATE: TIME:
RELINQUISHED BY: ③	DATE: TIME:	RECEIVED BY: ④	DATE: TIME:

METHOD OF SHIPMENT: Fedex

WAY BILL No. 7595684773

White	–Fully Executed Copy
Yellow	–Receiving Laboratory Copy
Pink	–Shipper Copy
Goldenrod	–Sampler Copy

SAMPLE TEAM:
John Doe
Joe Smith

RECEIVED FOR LABORATORY BY:

DATE: TIME:

[redacted]

Nº 24365

1001 (D) SEPT 28/93(W) REV.0 (F-42)

figure 3.15

TYPICAL COMPLETED CHAIN-OF-CUSTUDY FORM

APPENDIX E

COST ESTIMATE PROPOSAL FOR SECONDARY POND AND NORTH DITCH CHARACTERIZATION

TABLE 2

COST ESTIMATE PROPOSAL
FOR SECONDARY POND AND NORTH DITCH CHARACTERIZATION
RACER NODULAR FACILITY
SAGINAW, MICHIGAN

Item	*Quantity*	*MLC Discounted Unit*	*Rate*	*Cost Estimate*
Secondary Pond and North Ditch Characterization				
Project Manager	15	hour	$127.04	$1,905.60
Project Engineer	30	hour	$85.69	$2,570.70
Field Technicians (2 men crew)	60	hour	$150.71	$9,042.60
Analytical Cost	1	lump sum	$16,200.00	$16,200.00
Chemist (lab contracting/coordination/validation)	35	hour	$98.09	$3,923.60
Geotechnical Engineer	10	hour	$127.04	$1,270.40
Database	15	hour	$69.15	$1,037.25
Word Processing	15	hour	$48.48	$727.20
Drafting	10	hour	$77.42	$774.20
Survey	1	lump sum	$7,500.00	$7,500.00
Disbursements (copies, Fed-ex, phone, field supplies, etc.)	1	lump sum	$1,500.00	$1,500.00
Geotechnical Study	1	lump sum		
			Subtotal	$46,451.55
			TOTAL COST ESTIMATE (Rounded)	$46,450.00

Notes:

Professional fees are based on the 2009 CRA fee schedule with a 17.31% discount + $3 for IT for MLC projects