



## **Quality Assurance Project and Sampling and Analysis Plan**

**NCHRP 25-54:** *Field Testing of BMPs Using Granulated Ferric Oxide Media to Remove Dissolved Metals in Roadway Stormwater Runoff*

Prepared for  
The Transportation Research Board, National Cooperative Highway  
Research Program

May 2017

Quality Assurance Project and  
Sampling and Analysis Plan  
NCHRP 25-54: Field Testing of BMPs Using Granulated Ferric Oxide  
Media to Remove Dissolved Metals in Roadway Stormwater Runoff

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## Contents

1.0	Project Organization .....	1-1
2.0	Background and Problem Definition.....	2-1
2.1	Background .....	2-1
2.2	Study Sites.....	2-1
2.2.1	Highway 36/61.....	2-1
2.2.2	Woodlyn Avenue .....	2-5
2.3	Study Objectives.....	2-8
3.0	Project and Task Description.....	3-1
3.1	Monitoring and Reporting Schedule .....	3-1
3.2	Monitoring Parameters.....	3-1
3.3	Site Preparation .....	3-1
4.0	Data Quality Objectives.....	4-1
4.1	Measurement Quality Objectives.....	4-1
4.1.1	Precision.....	4-1
4.1.2	Accuracy.....	4-2
4.1.3	Representativeness .....	4-2
4.1.4	Completeness.....	4-3
4.1.5	Comparability.....	4-3
4.1.6	Sensitivity.....	4-3
5.0	Training .....	5-1
6.0	Sampling Design.....	6-1
6.1	General Design.....	6-1
6.2	Inlet and Outlet Monitoring Configuration .....	6-1
6.2.1	Highway 36/61.....	6-1
6.2.2	Woodlynn Avenue.....	6-3
6.3	Level Sensor and In-Situ Probe Placement.....	6-4

6.4	Sample Collection .....	6-4
6.5	Autosampler Triggering and Storm Event Collection .....	6-5
6.5.1	Highway 36/61.....	6-5
6.5.2	Woodlynn Avenue.....	6-5
6.6	Telemetry and Continuous Data Recording and Presentation.....	6-5
7.0	Field Instrument and Equipment Testing, Inspection, and Maintenance.....	7-1
7.1	List of Field Supplies and Materials.....	7-1
7.2	List of field equipment .....	7-2
7.3	Equipment Testing.....	7-2
7.4	Inspection and Maintenance .....	7-4
8.0	Instrument and Equipment Calibration.....	8-1
9.0	Sampling, Handling and Processing Methods.....	9-1
9.1	Field Processing of Samples.....	9-1
9.2	Sample Preparation at the Barr Engineering Laboratory.....	9-2
9.3	Analytical Laboratories.....	9-3
9.4	Clean-Hands Dirty Hands Method .....	9-3
9.5	Bottle Washing Procedure .....	9-4
10.0	Holding Times, Bottles, and Analytical Methods .....	10-1
11.0	Data Management .....	11-1
11.1	Field Data Management .....	11-1
11.2	Laboratory Data Management.....	11-1
12.0	Assessment .....	12-1
13.0	Data Review, Verification, and Validation.....	13-1
13.1	Field data verification .....	13-1
13.2	Laboratory data verification .....	13-1
14.0	Statistical Analysis Approach .....	14-1
15.0	References.....	15-1

## List of Tables

Table 1-1	Project Contact Information.....	1-2
Table 4-1	Laboratory Limits: Accuracy, Precision, RLs.....	4-4
Table 10-1	Water Sample Methods, Containers, and Holding Times .....	10-1

## List of Figures

Figure 1-1	Project Organization.....	1-3
Figure 2-1	Highway 36/61 Above Ground Vault-Type Ferric Oxide-Sand Filter NCHRP 25-54 .....	2-3
Figure 2-2	Edited Design Drawing of the Highway 36/61 above Ground Vault-Type Ferric Oxide-Sand Filter.....	2-4
Figure 2-3	Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter NCHRP 25-24.....	2-6
Figure 2-4	Edited Design Drawing of the Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter. LS=level sensor .....	2-7
Figure 2-5	Outlet Configuration, Sampling and Flow Monitoring Locations of the Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter .....	2-7
Figure 6-1	The Existing and Proposed Configuration of the NE Inlet Manhole (called NW1 on the plan drawings) of the Highway 36/61 Site.....	6-2

## List of Attachments

Attachment A	Barr's routine level data evaluation SOPs
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## 1.0 Project Organization

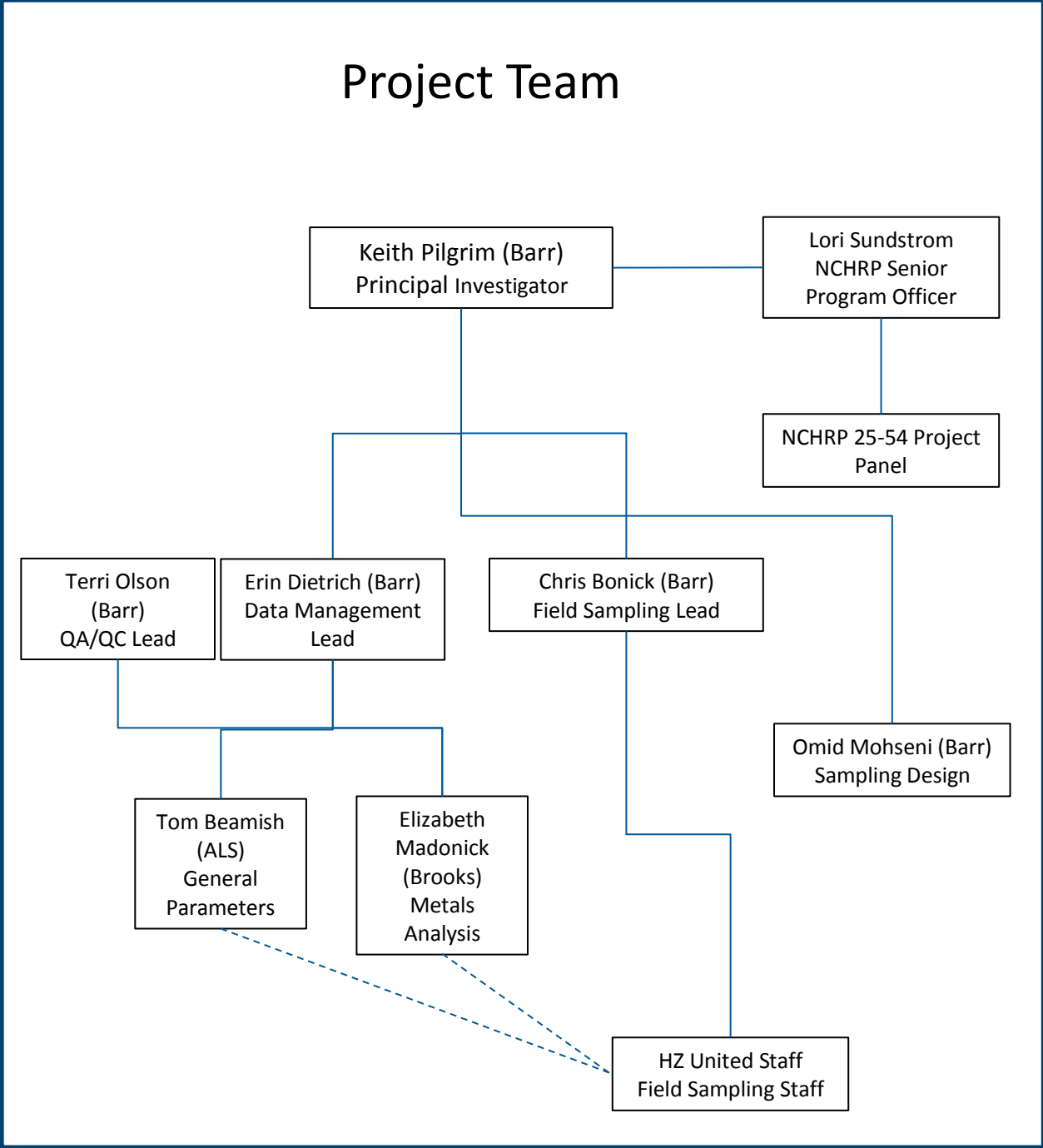
The primary activity for the field monitoring phase of NCHRP 25-54 will be the installation, maintenance, and operation of equipment for monitoring two ferric-oxide sand filters. Samples will also be collected and analyzed for analytes identified in Section 3.2. Several organizations and staff will be involved throughout this project. The overall project organization is provided on Figure 1-1 and details of staff roles are described below:

- **Lori Sundstrom** is the NCHRP program officer and is responsible for overall project administration, communication with the lead investigator, and acts as the liaison for the project Panel and the lead investigator.
- **Keith Pilgrim** (Barr Engineering Co.) is the lead investigator and is responsible for the overall study design and execution, project management, and serves as the overall coordinator of Barr Engineering Co. (Barr) staff, HZ United staff (the subcontractor), and the analytical laboratories (Brooks Applied Labs (Brooks) and ALS Environmental (ALS)).
- **Chris Bonick** (Barr) is the lead for the field monitoring and sampling program. Chris is responsible for preparation and testing of the field equipment prior to deployment, deploying the monitoring equipment, developing protocols for equipment operation, testing and field sampling, coordinating with other Barr staff with respect to equipment operation, training HZ United staff on the use, inspection and maintenance of the equipment, and training HZ United staff on proper sampling technique and recordkeeping.
- **Omid Mohseni** (Barr) is the lead for hydrology and hydraulics and for the design of equipment installation, sample collection design, and development of hydrology and hydraulics models to determine sample triggering and pacing.
- **HZ United Field Monitoring Staff:** There will be two HZ United staff responsible for daily field operations: Oskar Duva and Cody Krier. These staff will assist with equipment deployment, equipment preparation, operation and maintenance, recordkeeping, sample collection, processing, and submittal to the analytical laboratories.
- **Erin Dietrich** (Barr) is the lead for data management. Data generated from submitted samples will be processed by the data management group under the supervision of Erin.
- **Terri Olson** (Barr) is responsible for data quality review, evaluation, reporting, and laboratory communication.
- **Elizabeth Madonick** (Brooks) is the Brooks project manager and will be the primary contact of Terri Olson and Erin Dietrich with respect to data submittal, and the HZ United field staff with respect to sample submission.

- **Tom Beamish** (ALS) is the ALS project manager and will be the primary contact of Terri Olson and Erin Dietrich with respect to data submittal, and the HZ United field staff with respect to sample submission.

**Table 1-1 Project Contact Information**

Contact	Organization	Role	Office Phone	Cell Phone (if applicable)	email
Lori Sundstrom	NCHRP	Program Officer	202-334-3034		lsundstrom@nas.edu
Keith Pilgrim	Barr Engineering Co.	Principal Investigator	612-229-8092	612-229-8092	kpilgrim@barr.com
Chris Bonick	Barr Engineering Co.	Lead Field Monitoring	952-832-2760	612-812-1800	cbonick@barr.com
Omid Mohseni	Barr Engineering Co.	Sampling Design	952-832-2665	612-708-4855	omohseni@barr.com
Erin Dietrich	Barr Engineering Co.	Lead Data Management	952-832-2972		edietrich@barr.com
Terri Olson	Barr Engineering Co.	Lead Data QA/QC	952-842-3578		tolson@barr.com
Oskar Duva	HZ United	Field Monitoring	763-551-3699	267-679-2482	oskar.duva@hzunited.com
Cody Krier	HZ United	Field Monitoring	763-551-3699	651-263-7941	cody.krier@hzunited.com
Elizabeth Madonick	Brooks Applied Labs	Lab Contact-Metals	206-632-6206, ext. 141		Elizabeth@brooksapplied.com
Tom Beamish	ALS Environmental	Lab Contact-Standard Parameters	616-738-7318		Tom.Beamish@ALSGlobal.com



**Figure 1-1 Project Organization**

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## 2.0 Background and Problem Definition

### 2.1 Background

Dissolved metals in roadway stormwater runoff can exceed water quality standards. The state departments of transportation (state DOTs) in many parts of the country are being required to reduce the concentrations of these pollutants. *NCHRP Report 767: "Measuring and Removing Dissolved Metals from Stormwater in Highly Urbanized Areas"* (NCHRP Report 767), evaluated a variety of media for removing dissolved metals (primarily copper and zinc) from roadway stormwater runoff. The research concluded that granulated ferric oxide was able to remove dissolved copper and zinc under controlled conditions. This study focused on the equilibrium sorption capacity of ferric oxide for dissolved copper and zinc and was able to define the maximum sorption capacity of granulated ferric oxide to remove these metals over time. However, full-scale treatment systems with ferric oxide will not experience ideal (e.g., pH, ionic strength, and no competing ligands) or equilibrium conditions but will experience non-steady state inputs of stormwater with a range of contact times, influent metals concentrations, and potential removal rates. NCHRP Report 767 concluded that stormwater best management practices (BMPs) that use ferric oxide should be field tested to evaluate the capacity of this material to remove metals in a full-scale treatment cell.

This current study includes monitoring (flow, general chemistry, and metals) at two existing full-scale stormwater runoff treatment cells that include mixtures of ferric oxide and sand as the treatment media. These systems are described in detail below. The purpose of monitoring is to evaluate the capacity of these systems to remove dissolved metals from actual runoff, to better understand the factors that affect treatment effectiveness, and provide cost benefit and design guidance.

### 2.2 Study Sites

There are two study sites: (1) **Woodlynn Avenue**, a swale-type BMP that treats nearly 100 percent impervious parking lot runoff from a mall in Maplewood Minnesota; and (2) **Highway 36/61**, an above-ground vault-type BMP that treats runoff from the interchange of Highway 36 and Highway 61.

#### 2.2.1 Highway 36/61

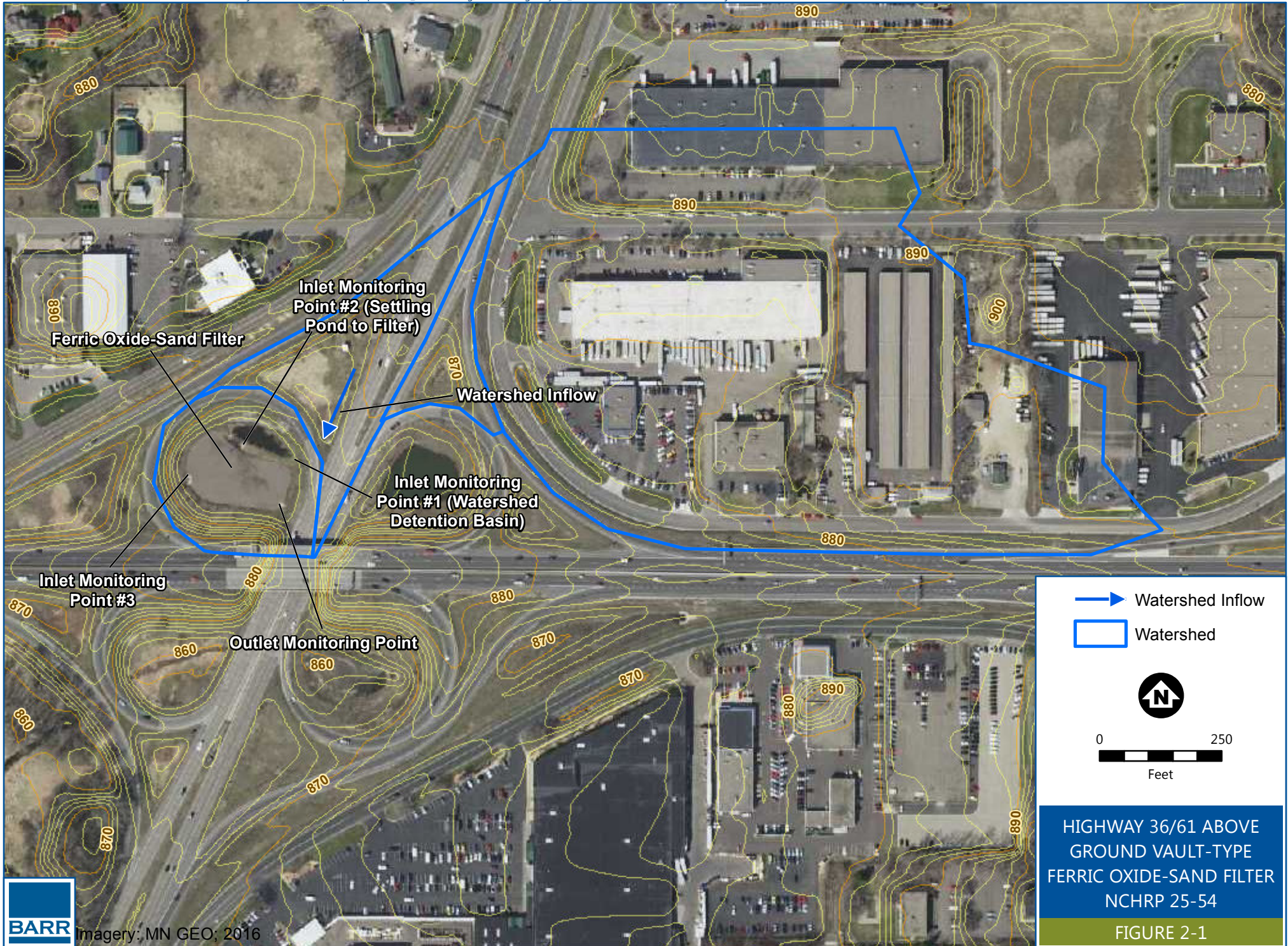
The ferric oxide-sand filter at the Highway 36/61 interchange is built within the northeast cloverleaf of the Highway 36/61 interchange (Figure 2-1). This system has been operational for about 3 years. The approximately 20 acre, and highly impervious, watershed tributary to the sand filter consists of commercial and industrial areas, as well as highways. The surface area of the filter is approximately 0.5 acres. There is one primary inlet with a sluiceway weir and a concrete bypass weir, and one small inlet that drains the upper half of an off-ramp of Highway 61. The primary inlet originates from a vegetated swale that leads to the weir control structure. Shown on Figure 2-2 (see Figure 6.1 for detail of the manhole structure) is the direction of flow at the main inlet which then directs flow to a pretreatment basin while the overflows (green arrow) bypass the system entirely. The outlet of the pretreatment basin flows to the surface of the filter near the north end of the filter. The small inlet can be seen at the



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northwest end of the ferric oxide filter. Monitoring will be conducted at the two inlets as well as at the inflow point from the pre-treatment basin to the sand filter (total of three inlet monitoring points). Details are provided in Section 6.0 regarding the location and configuration of inlet monitoring.

There are perforated under-drains in the filter bed (about 12-18 inches below the filter bed surface) that travel along the length of the bed and collect treated water and feed a header that then flows to a manhole (manhole location on Figure 2-2); the red arrow is from the filter bed). This pipe (red arrow) is where water samples and flow will be measured.



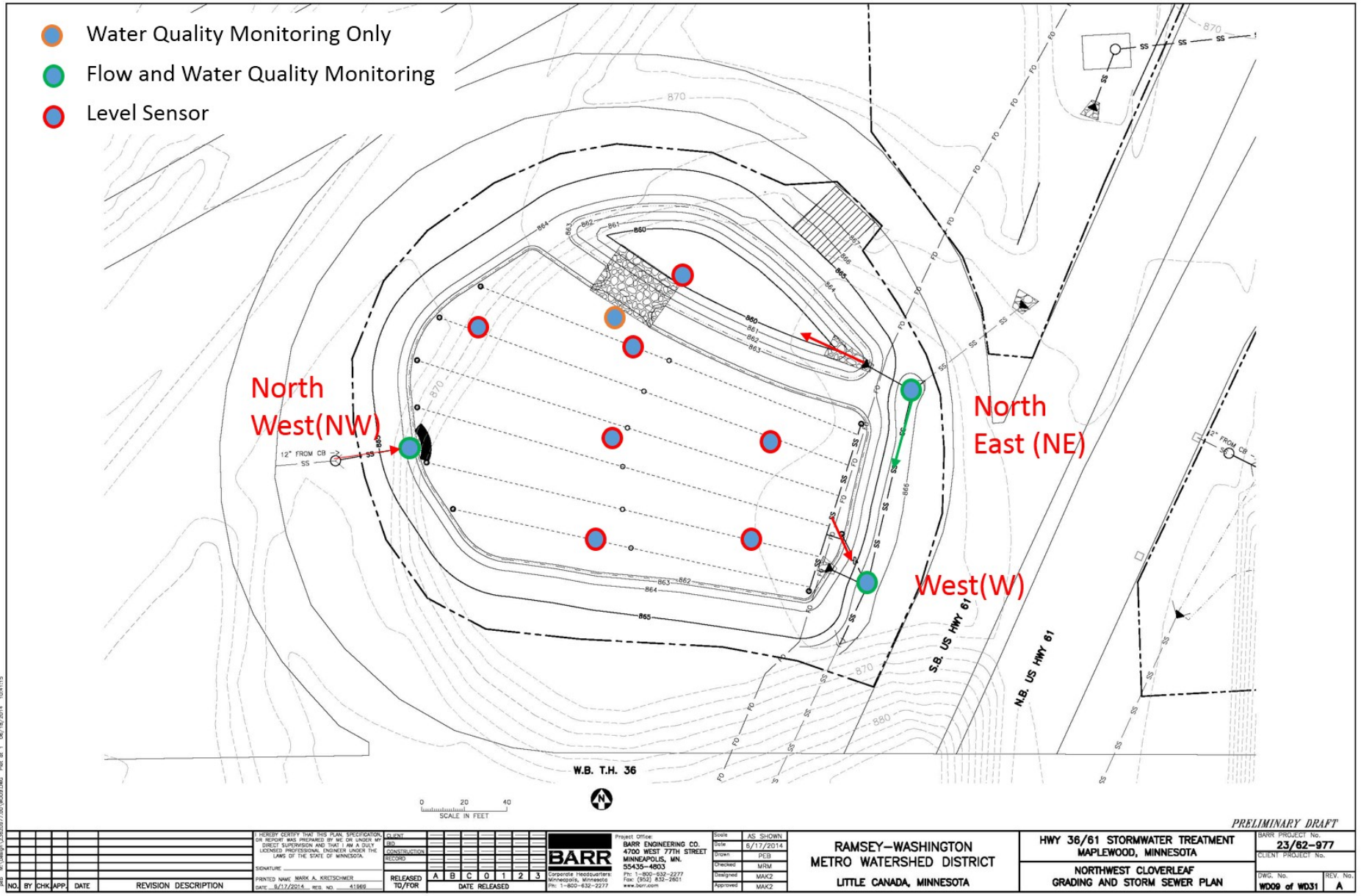


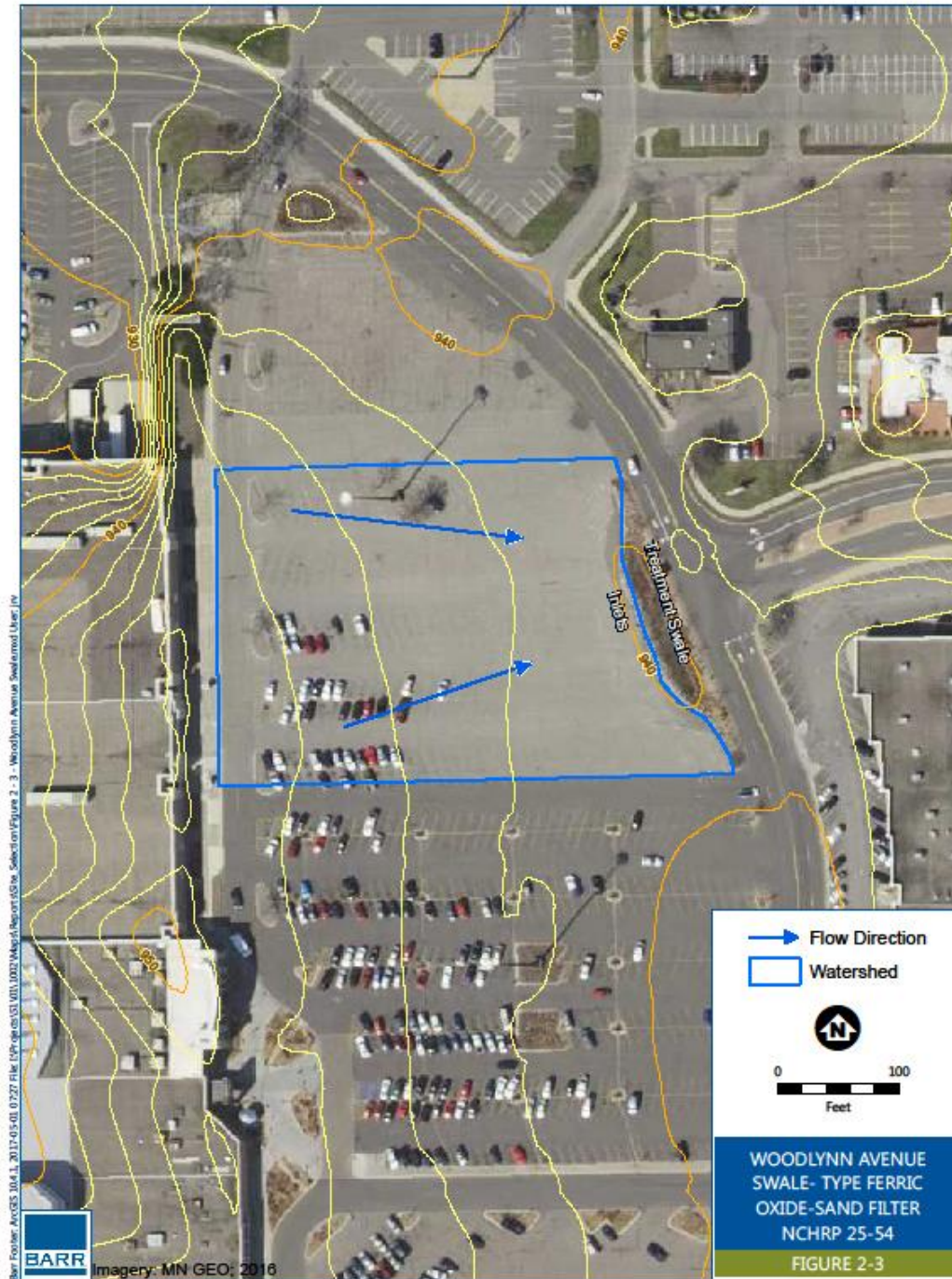
Figure 2-2 Edited Design Drawing of the Highway 36/61 above Ground Vault-Type Ferric Oxide-Sand Filter

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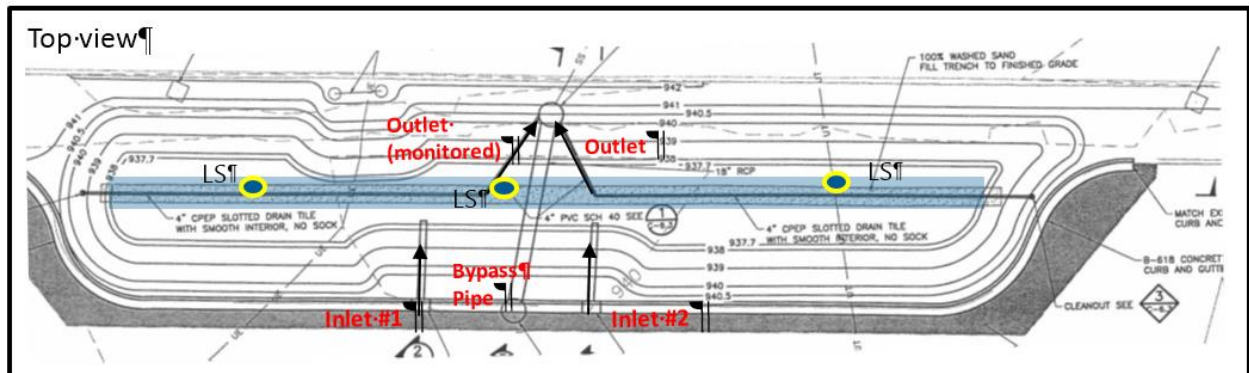
### **2.2.2 Woodlyn Avenue**

The Woodlynn ferric oxide-sand filter receives runoff from a 1.817-acre parking lot that is nearly 100 percent impervious. An aerial photo of this site is shown below on Figure 2-3 outlining the watershed, the drainage direction, and the treatment swale bed. The treatment swale has an area of approximately 0.16 acres with an effective treatment area of approximately 250 square feet.

Figure 2-3 Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter NCHRP 25-24

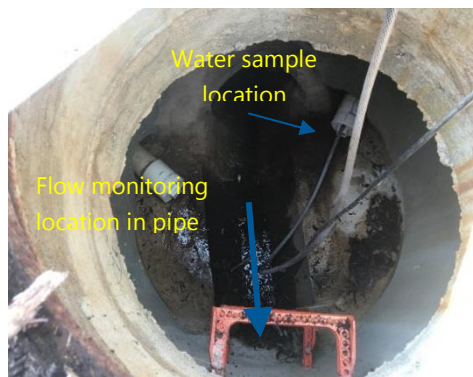


The design of the swale is shown on Figure 2-4 below. The highlighted and filled-in polygon in the design drawing shows the trench area with the mixture of ferric oxide and sand where water infiltrates through the media and into a French drain. There are two monitored inlets to the treatment swale. The swale has storage capacity and during a storm event it fills. When the swale fills above its capacity (approximately 0.9-inch storm event or greater), it overflows and backs up into the parking lot and then enters another inlet that feeds the bypass pipe (no treatment). The outlets consist of extensions from the French drain and hence convey filtered and treated water to an outlet pipe that leaves the system.



**Figure 2-4 Edited Design Drawing of the Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter. LS=level sensor**

Autosamplers will be placed at both inlet pipes for water sample collection (samples from the two inlets will be combined) and flow will be measured at the two inlets and the bypass. Water will be sampled at the outlet at one arm (see Figure 2-5). Flow will be monitored in the outlet pipe. Monitoring details are provided in Section 6.0.



**Figure 2-5 Outlet Configuration, Sampling and Flow Monitoring Locations of the Woodlynn Avenue Swale-Type Ferric Oxide-Sand Filter**

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## 2.3 Study Objectives

The overall objective of the stormwater monitoring phase of this study is to develop a high-quality data set that characterizes the inlet and outlet concentrations of dissolved metals, particulate metals, and other general chemical and physical parameters for the ferric oxide-sand filters identified above. Several task level objectives are listed below:

- **Water balance:** Collect data to develop a detailed water balance for each storm event and between storm events such that the mass of metals loaded to the ferric oxide-sand filter can be accurately compared to the mass of metals leaving the system through the treatment cell outlet. This task consists of three sub-tasks below.
  - **Flow:** Continuously measure surface water inflows to and outflows from the treatment systems to less than 5 percent error.
  - **Level:** Install level sensors in each ferric oxide-filter to the degree necessary such that the total fraction of the filter bed (e.g., volume) that is in contact with stormwater can be assessed throughout each storm event. Level sensor accuracy should be +/- 0.1 inch.
  - **Rain gauge:** Install, calibrate, and properly maintain a rain gauge at the Highway 36/61 site with a range of 5 inches per hour, an accuracy of 1 percent at rates up to 1 inch per hour and precision of 0.01-inch increments. An existing rain gauge is maintained at the Woodlynn Avenue site.
- **Low level metals:** Analyze dissolved and total metals to reporting limits that are below 1 part per billion for most metals, except for iron which is 6.0 µg/L and zinc which is 3.0 µg/L. Brooks has been chosen for metals analysis.
- **In-situ chemistry:** Collect high precision and reliable pH, dissolved oxygen, and temperature data at one location within the ferric oxide-sand filter bed. Maintain and calibrate these probes to the frequency needed such that the data are available for each storm event. The dissolved oxygen sensor should have an accuracy of +/- 2 percent and the pH sensor an accuracy of +/- 0.2 pH units.
- **Recordkeeping:** Use best practices with respect to recordkeeping (field notebook, chains-of-custody (COC)), maintain records during the course of the project, and use methods that minimize error. All field data will be maintained on the Barr network and direct data deliveries from the analytical laboratories will be maintained in Barr's Laboratory Management Information System to minimize data management error.
- **Statistical significance:** Collect a number of storm event samples such that tests of statistical significance can have the statistical power to minimize Type II error.

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- **Data quality measurements:** Collect field samples (duplicates and equipment blanks) and laboratory QA/QC measurement (e.g., laboratory blanks and spiked recoveries) to provide the necessary inputs for a data quality evaluation (see Section 13.0).
  - **Minimize contamination:** Minimize or, if possible, eliminate contamination by using clean metals approaches for sample collection.



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## 3.0 Project and Task Description

### 3.1 Monitoring and Reporting Schedule

The monitoring program is planned to be a 2-year program, starting the first year from May 2017 through the fall of 2017 (likely November 2017 depending upon the weather). Equipment testing, maintenance, and calibration will begin in early to mid-April 2017. Equipment will be deployed in late April 2017. The second year will begin in spring of 2018 to capture salt-impacted runoff. The duration of second year monitoring will be determined after the first year is complete, and a statistical assessment has been conducted using the 2017 data set to identify the number of samples needed in 2018 for statistical power (see Section 14.0).

Monitoring for chemistry will be storm event based while other equipment measurements (e.g., flow, pH, precipitation) will be continuous. The sampling design and protocols are discussed in Section 6.0. Reporting will be quarterly with an interim report after the first year of monitoring and a draft report after the second year of monitoring.

### 3.2 Monitoring Parameters

The following metals (dissolved and total) will be analyzed for each stormwater sample that is collected: copper, zinc, lead, nickel, chromium, iron, and arsenic. Other analytical parameters that will be measured for each storm event include dissolved organic carbon, TSS, VSS, alkalinity (total and bicarbonate), hardness, and chloride. Stormwater samples, after collection and processing for analytes, will be measured for dissolved oxygen, pH, specific conductance, and temperature.

### 3.3 Site Preparation

Site preparation began in early 2017 with the clean out of the treatment system inlets. Site preparation in the spring of 2017 will consist of:

- Construction and placement of observation wells (PVC pipe with a screen) for the level sensors.
- Installation of a weir at the Highway 36/61 primary inflow.
- Construction and installation of specialized multi-port samplers with a winged arm at the inlet and outlet of both sites.
- Development of a sampling trough at the Highway 36/61 site. The trough will be placed between the pre-treatment basin and the ferric oxide-sand filter.
- Installation of the rainfall tipping bucket at the Highway 36/61 site.
- Installation of the sampling equipment shelters.
- Installation of the Campbell Scientific data acquisition equipment and the autosamplers.

## 4.0 Data Quality Objectives

Data quality objectives (DQOs) are qualitative and quantitative statements that clarify project objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support decisions. The DQOs for the project are to develop and implement procedures for field sampling, chain-of-custody and note taking, laboratory analysis and electronically gathered field measurements which include level, pH, and dissolved oxygen, and reporting that will provide the level of data required for determining the characteristics of the stormwater.

### 4.1 Measurement Quality Objectives

Measurement quality objectives (MQOs) are statements that support the project DQOs and contain specific units of measure that are directly compared to data. The purpose of this section is to address the MQOs for the six data quality indicators (precision, accuracy, representativeness, completeness, comparability, and sensitivity), along with the means by which they are measured to monitor compliance with the project needs.

#### 4.1.1 Precision

Precision measures the reproducibility of a measurement under a given set of conditions. Precision of field sampling will be assessed by comparing the analytical results between field duplicate samples. A field duplicate sample is a second aliquot of a sample generated in the field that, when collected, processed, and analyzed by the same organization, provides precision information for the entire measurement system including: sample acquisition, sample constituent heterogeneity, handling, shipping, storage, preparation, and analysis. Field duplicate samples will be submitted to the laboratory as blind (masked) samples. The relative percent difference (%RPD) will be calculated using the equation below for each pair of duplicate analyses where both results are greater than five times the reporting limit (RL).

$$\%RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

Where: S = First sample value (original value)

D = Second sample value (duplicate value)

Field duplicate samples will be collected and sent to the laboratory at a frequency of one per twenty field samples, with a minimum of one per sampling event alternating between the locations (e.g., 1st event Highway 36/61, 2nd event Woodlynn Avenue, 3rd event Highway 36/61, etc.). RPDs  $\leq$  30% will be considered acceptable (when both the native and field duplicate sample concentrations are greater than five times the RL). RPDs above 30% for water samples will result in corrective actions or qualification by the QA/QC Lead. These corrective actions are discussed in Section 12.0 of this document.

Precision in the laboratory is assessed through the calculation of RPDs for laboratory control samples/laboratory control sample duplicates (LCS/LCSD), matrix spike/matrix spike duplicates (MS/MSD),

and/or laboratory duplicates. The laboratories' precision criteria are in the laboratory reports and in Table 4-1.

### 4.1.2 Accuracy

For the analytical results, accuracy is evaluated as the degree of agreement between an observed value and an accepted reference value and measures bias in a measurement system. Accuracy will be addressed by calibrating field and laboratory instruments, and by analyzing LCS and/or MS samples. The recovery limits for accuracy are expressed in terms of acceptable % recovery of a known quantity and are listed in Table 4-1. The percent recovery (%R) for spiked samples will be calculated using the following equation (for LCS and other laboratory-prepared samples, B is zero):

$$\%R = \frac{A - B}{C} \times 100$$

Where:        A =     The analyte concentration determined from the analysis of the spiked sample  
               B =     The background level determined by a separate analysis of the unspiked sample  
               C =     The amount of the spike added

For the field gathered electronic measurements of oxygen, pH, level, and precipitation, accuracy will be judged using calibration standards (or staff gauge for level) and comparison to manufacturer-identified accuracy: pH: accuracy of ±0.1 percent over full range (pH of 0 to 14 s.u.), dissolved oxygen: ± 2 percent, level ±1 cm, precipitation is ±1 percent at rates up to 1 in./h.

Corrective action for pH and dissolved oxygen is recalibration of the probe or replacement of the probe if the probe cannot hold calibration. For level it may be replacement of the sensor if the staff gauge measured level is greater than twice the expected precision of 1 cm.

### 4.1.3 Representativeness

Representativeness is defined as the degree to which data accurately and precisely represents a characteristic of a population, a parameter variation at a sampling point, a process condition, or an environmental condition. Representativeness is a qualitative parameter that is dependent upon the proper design of the sampling program and proper laboratory protocols. The sampling network was designed to provide samples representative of site conditions. During development of the sampling program, consideration was given to past waste disposal practices, past operations, existing analytical data, physical setting, and constraints inherent in the monitoring program. The representativeness criteria will be satisfied by following this sampling plan and by the use of proper sampling techniques and appropriate analytical procedures. This will be assessed on this project through the use of MS, MSDs, equipment blank, and field duplicate samples. The equipment blank and field duplicate samples will be collected at a frequency of one per sampling event alternating between the locations (e.g., 1<sup>st</sup> event Highway 36/61, 2<sup>nd</sup> event Woodlynn Avenue, 3<sup>rd</sup> event Highway 36/61, etc.).

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#### 4.1.4 Completeness

Completeness is a measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under normal conditions. Rejected data, or sampling points that do not yield a usable sample count against the percent completeness. Field completeness goals for this project is greater than 90 percent. It is expected that the laboratories will provide data meeting QC acceptance criteria for 90 percent or more of all samples tested. Following completion of analytical testing, completeness will be calculated as a percent using the following equation:

$$\text{Completeness (\%)} = \frac{\text{Number of valid data}}{\text{Number of targeted data}} \times 100$$

$$\text{Data} = \# \text{ of samples} \times \# \text{ of parameters per sample}$$

#### 4.1.5 Comparability

Comparability is defined as the confidence with which one set of data can be compared with another. The extent to which existing and planned analytical data will be comparable depends on the similarity of: sampling methods, sample preparative procedures, analytical methods and holding times. Comparability will be satisfied by ensuring that this document and proper and consistent sampling techniques are followed. This will be accomplished by the project team and measured with the use of quality control samples as well as adherence to the laboratory and field SOPs.

#### 4.1.6 Sensitivity

Sensitivity expresses the methodology's and laboratory's ability to meet the RLs as shown in Table 4-1.

**Table 4-1 Laboratory Limits: Accuracy, Precision, RLs**

Test Method	Analyte	RL	Units	LCS Low (%)	LCS High (%)	MS/MSD Low (%)	MS/MSD High (%)	RPD (%)
<b>Metals</b>								
EPA 1638 Mod	Arsenic	0.080	µg/L	75	125	75	125	20
EPA 1638 Mod	Chromium	0.15	µg/L	75	125	75	125	20
EPA 1638 Mod	Copper	0.30	µg/L	75	125	75	125	20
EPA 1638 Mod	Iron	6.0	µg/L	75	125	75	125	20
EPA 1638 Mod	Lead	0.030	µg/L	75	125	75	125	20
EPA 1638 Mod	Nickel	0.24	µg/L	75	125	75	125	20
EPA 1638 Mod	Zinc	3.0	µg/L	75	125	75	125	20
Metals RPD Note: results $\leq 5 \times$ RL will use $\pm$ RL instead of the 20% RPD								
<b>General Parameters</b>								
SM2540 D-97	Total Suspended Solids (TSS)	0.6	mg/L	80	115	--	--	5
SM2540 E-97	Volatile Suspended Solids (VSS)	0.6	mg/L	--	--	--	--	5
SM5310C-00	Organic Carbon, Dissolved (DOC)	0.5	mg/L	80	120	75	125	20
SM2320 B-97	Alkalinity, Total (as CaCO <sub>3</sub> )	10	mg/L	90	106	--	--	20
SM2320 B-97	Alkalinity, Bicarbonate (as CaCO <sub>3</sub> )	10	mg/L	--	--	--	--	20
SM4500-Cl E-97	Chloride	1	mg/L	80	120	75	125	25
SM2340 C-97	Total Hardness (as CaCO <sub>3</sub> )	5	mg/L	95	107	--	--	20

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## 5.0 Training

Chris Bonick of Barr will be the field sampling lead, and with support from the Barr Data Management Group and QA/QC Group, will be responsible for training the HZ United field staff with respect to several project functions. As part of the training, an SOP will be created as a joint effort between Barr and HZ United staff for each study site and for laboratory procedures, which will describe proper execution of these functions. These SOPs will be completed prior to commencement of monitoring. We consider these SOPs to be “living documents” that will be updated during the course of the monitoring program. We (Barr and HZ United) will develop a checklist for the field staff. The project functions included in the training and SOP’s will be as following:

### **For the Highway 36/61 Site:**

- Safely accessing the study site, including use of cones, strobe lights, hi-visibility vests, permit possession, etc.
- General site inspection.
- Downloading and reviewing data from the Campbell Scientific data logger using the Campbell Loggernet software and/or the Vista Data Vision software. Data stored on this datalogger will include flow into and out of the sand filter, rainfall, water level in the pretreatment basin and sand filter, and pH in the sand filter.
- Operation and maintenance of the autosamplers.
- Handling of autosampler bottles, transferring samples to laboratory bottles, and preparation of the samples for lab delivery.
- Downloading and reviewing data from the HOBO Water Level and HOBO Dissolved Oxygen Data Loggers.
- Field probe and device calibration, maintenance, and operation. Field probes and devices include the pH probe, dissolved oxygen probe, rain gage, water level sensors, weirs, and flow meter.
- Documentation of work in a field notebook.

### **For the Woodlynn Avenue Site:**

- Safely accessing the study site, including use of cones, strobe lights, hi-visibility vests, etc.
- General site inspection.
- Downloading and reviewing data from the Isco flow meter modules/autosamplers. Data stored on the Isco instruments will include flow into and out of the sand filter and bypass flow.
- Operation and maintenance of the autosamplers.

- 
- Handling of autosampler bottles, transferring samples to laboratory bottles, and preparation of the samples for lab delivery.
  - Flow meter maintenance and operation.
  - Documentation of work in a field notebook.

**For laboratory procedures:**

- Laboratory safety.
- Autosampler bottle washing procedure.
- Laboratory data management protocols.
- Recordkeeping and sample submittal.

Training is expected to begin in April 2017 at Barr Engineering Co. A representative from Barr will train HZ United staff on COC documentation, sample submittal, and data tracking.

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## 6.0 Sampling Design

### 6.1 General Design

The ferric oxide-sand filter study sites with inflows and outflows were identified in Section 2.2. To determine the dissolved metals removal performance of these treatment systems, autosamplers will be used to take water samples at the inlets and outlet (monitoring parameters in Section 3.2). Removal performance being judged as the difference between the inlet and outlet concentration and calculated mass (see Section 14.0 on statistical analysis). Sample collection will be triggered by inflows at the start of storm event (see Section 6.5). Flow monitoring will be at the inlets and the outlet (see Section 6.2). A tipping bucket rain gauge (with telemetry) will be installed at the Highway 36/61 site and an existing tipping bucket rain gauge will be operated and maintained by the Ramsey-Washington Metro Watershed District at the Woodlynn Avenue site.

Measurements will also be taken in the ferric-oxide sand filter bed to better understand those factors that affect treatment performance. Levels sensors as well as pH and dissolved oxygen probes (Section 6.3) will be placed to identify the volume of the filter bed that is inundated during each storm and the general chemistry of the water in the filter bed during the storm event.

### 6.2 Inlet and Outlet Monitoring Configuration

#### 6.2.1 Highway 36/61

Flow monitoring will be conducted using weirs and level sensors or area velocity (AV) flow meters. Figure 2-2 shows the layout of the Highway 36/61 site. Flows will be measured at three locations:

1. The northeast (NE) inlet manhole.
2. The west (W) inlet manhole.
3. The outlet.

Water sampling will be conducted at four locations:

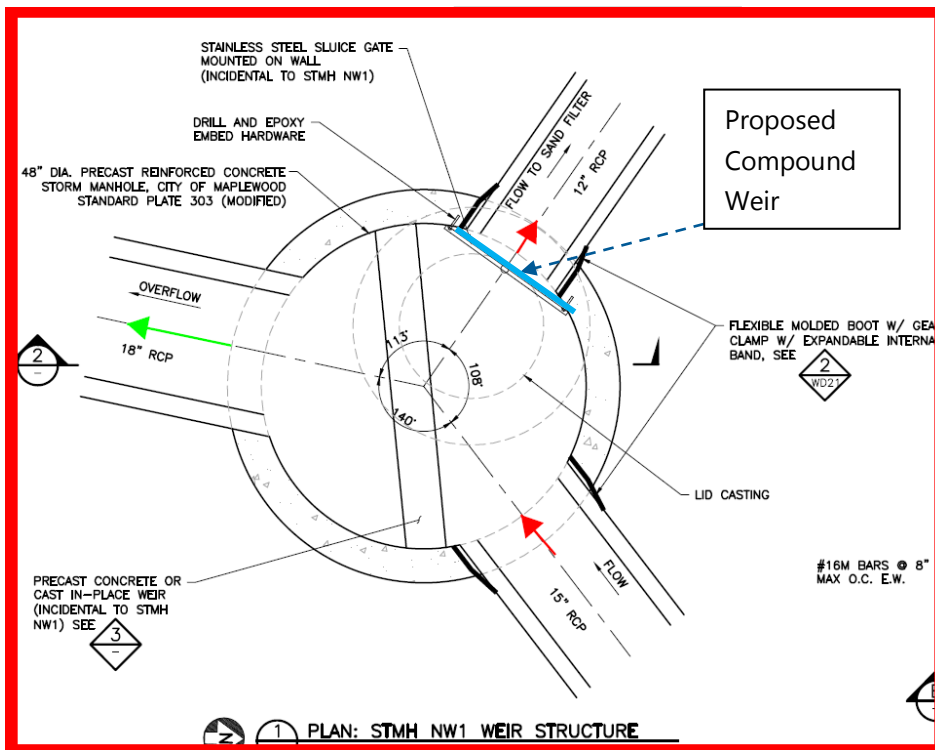
1. The northeast (NE) inlet manhole.
2. The west (W) inlet manhole.
3. The point where flows from the pretreatment basin inlet to the pond. Water monitoring will be triggered by flows at the NE inlet manhole.
4. The outlet.

Water monitoring at the NE inlet manhole is somewhat redundant considering that the same water will be sampled again at the monitoring point identified in #3 above. However, this is necessary since there is a pre-treatment basin between the two sampling locations and it is not known what effect that basin may have on sample chemistry. Sampling at the monitoring point #3 could be complicated by the lack of a defined sampling pipe at this location. Hence, the sampling is designed to be redundant.



At the NE manhole there is an existing (Figure 6-1) rectangular sharp-crested weir with a crest length of about 15 inches. Based on the hydrologic analysis of the drainage area and flow duration analysis of the past 50 years, the inflow is less than 1 cubic foot per second (cfs) during 90% of wet days, and less than 4 cfs during 99% of wet days. To accurately measure inflow into the Highway 36/61 site, the existing weir will be replaced with a compound weir, with a maximum capacity of 3 cfs. The excess flow will be diverted into the 18-inch overflow pipe (Figure 6-1 see green arrow). The compound weir with a pressure transducer has an accuracy of 5 percent. The accuracy increases to about 0.2 percent for flows from 0.3 to 1.0 cfs. An additional pressure transducer will be installed downstream of the weir to measure the flow rate when the weir is submerged. A thin plate will be installed on the cast-in place weir to convert the overflow weir into a sharp-crested weir. The flow over the concrete cast-in place weir (with a thin plate in place) into the 18-inch RCP pipe (i.e., the overflow) will be estimated by the compound weir pressure transducer treating it as a sharp-crested weir.

It should be noted that water sampling (e.g., the inlet tube of the autosampler) will be conducted upstream of the weir in the manhole to facilitate sample collection of low flows as well as high flows. This manhole has been cleaned of sand and small gravel.



**Figure 6-1 The Existing and Proposed Configuration of the NE Inlet Manhole (called NW1 on the plan drawings) of the Highway 36/61 Site**

For the manhole inlet (see location of manhole on Figure 2-2), a 90-degree V-notch weir will be installed in the manhole. Since the 12-inch pipe downstream of the manhole has a steep slope, the V-notch weir will never be submerged. Sampling will be conducted downstream of the V-notch weir.

For measuring outflows at the Highway 36/61 site (see Figure 2-5), the West (W) manhole does not have a sump and a weir becomes impractical because it will flood the filter thereby affecting treatment. Therefore, an area velocity (AV) flow meter will be installed inside the 24-inch RCP. Since outflow from the filter may be clear and free of solids, plates will be installed at the bottom of the pipe to generate microbubbles in the flow stream. To optimize the generation of microbubbles and to determine the accuracy of the AV flow meter, an AV flow meter is being tested at the Saint Anthony Falls Laboratory using this configuration. The plates and possible small tubes attached to the plates will be optimized in the laboratory before the field installation. During the laboratory testing of the AV flow meter, the accuracy of the flow meter will be determined at different flow rates. After the completion of monitoring, the AV flow meter will be tested in the laboratory to determine if the accuracy of the flow meter has changed and by how much. Water monitoring will be in the outlet pipe that leads from the treatment cell to the West (W) manhole. This will contain only treated ferric oxide-sand filter water during storm events.

### **6.2.2 Woodlynn Avenue**

Figure 2-4 shows the layout of the Woodlynn Avenue site. Flows will be measured at three locations:

1. Inlet #1 (see Figure 2-4).
2. Inlet #2 (see Figure 2-4).
3. The overflow inlet (see Figure 2-4).
4. The outlet (see Figure 2-3 for the flow monitoring and water sampling locations).

Water sampling will be conducted at three locations:

1. Inlet #1 (see Figure 2-4).
2. Inlet #2 (see Figure 2-4).
3. The outlet (see Figure 2-3 for the flow monitoring and water sampling locations).

For the Woodlynn Avenue filter, AV flow meters were previously installed at both inlets, the overflow inlet, and the outlet. The relationship between rainfall depth and runoff volume (e.g., inflows to the filter) is known. In 2015 and 2016, storm event sampling was triggered when the level in the inlet pipe was approximately 1 inch (note that there are two inlet pipes). This corresponds to 0.25-inch rainfall depth for a 1-hour duration storm. Hence, rainfall events of approximately 0.25 inches or larger will be considered to be potentially sampleable events.

At the filter outlet, the AV flow meter may not provide accurate results because of solids-free water coming out of the filter. Therefore, the method devised to generate microbubbles for the outlet of the Highway 36/61 site will also be implemented for the outlet of the Woodlynn Avenue site.

The volume of the Woodlynn Avenue filter as a function of the depth above the filter bed is known. Hence level sensors placed in the filter bed will provide estimates of water depth in the filter bed as well as the depth of water above the filter. This will enable calculation of water volume in the filter over the course of

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the storm event. Flows through the outlet can be calculated as the difference between inlet flow and the change in bed volume over the storm event. Hence, the level sensors will provide an additional check on the accuracy of the AV meters at the filter outlet.

### 6.3 Level Sensor and In-Situ Probe Placement

Three level sensors (with integrated temperature sensors) will be placed in the Woodlynn Avenue ferric oxide-sand filter (see Figure 2-4 for the location of the level sensors-LS) and total of 6 level sensors (see Figure 2-2 for placement location) will be placed in the Highway 36/61 ferric oxide-sand filter. The level sensors at the Woodlynn Avenue site can be used to calculate the fraction of the filter bed inundated during the storm event as well as serve as a check on outlet flows (see discussion above).

The level sensors in the Highway 36/62 ferric oxide-sand filter will be used to calculate the fraction of the filter bed that provides treatment during a given storm event. The level sensor in the pre-treatment basin will be used to quantify the relationship between water levels in the basin and water levels in the sand filter.

The in-situ probes for pH and dissolved oxygen will be placed in the center of the treatment cell at near the bottom of the filter bed at the Woodlynn Avenue site while at the Highway 36/61 site the probes will be near the inlet from the pre-treatment basin.

### 6.4 Sample Collection

Two types of water samples will be collected in 2017: (1) flow weighted composite samples where individual sample bottles are filled according to the volume of water that passes the sampling and flow monitoring location and the bottles are composited (using a churn type sample splitter) during sample processing (e.g., event mean concentrations); and (2) discrete, flow-paced water samples where each bottle that is collected is considered to be a separate sample and is processed separately. The discrete water samples (#2 above) will provide some understanding of the relationship between changing chemistry, contact time, and performance throughout the event. Details regarding the handling and processing of water samples is described in Section 9.0.

When a storm event is complete (or before the first storm event of the year), the sampling crew will bring a new acid-washed bottle set and replace it for the sample bottles that have been filled during the storm event. The filled bottles will be capped (acid washed caps) and returned to the Barr laboratory for processing. An equipment blank sample will then be collected by pouring ultrapure laboratory water into a clean autosampler bottle that has been placed into the autosampler. This sample will be collected and also returned to the laboratory. For dissolved constituents, the sample will be filtered and then processed as an equipment and filter blank. For constituents measured as total only, the sample will not be filtered prior to processing as an equipment blank. One duplicate sample will also be collected per storm event. The equipment blank and field duplicates samples will be alternated between the locations (e.g., 1<sup>st</sup> event Highway 36/61, 2<sup>nd</sup> event Woodlynn Avenue, 3<sup>rd</sup> event Highway 36/61, etc.).

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After samples have been processed in the Barr laboratory and prepared for delivery to the analytical laboratories, an aliquot of sampled water will be measured with a YSI multiprobe meter for pH, dissolved oxygen, specific conductance, and temperature.

## **6.5 Autosampler Triggering and Storm Event Collection**

### **6.5.1 Highway 36/61**

An XP-SWMM model of the drainage areas of NE and W manholes of the Highway 36/61 site was developed and flows into the filter were estimated for a period of 50 years. The model was run as a continuous runoff model. The simulated flows were used to develop flow duration curves for both inlet locations into the Highway 36/61 site. For the NE manhole, 50 percent of the wet period (flow through the inlet) exhibits flows higher than 0.02 cfs (3,900 GPD), and during 25 percent of the wet period, flow exceeds 0.2 cfs (39,000 GPD). Note that these flows are for the entire duration of the storm period and there is storage upstream of the sand filter. On average there have been 22 storm events per year with peak flows in excess of 0.2 cfs (the range is between 12 to 29 events per year). For this analysis, storms were considered to be separate when there was no inflow for a minimum of 6 hours. However, separating storm events by 6 hours is not practical for this study. As a result, an average of 22 storm events per year with a 6-hour non-storm period will be more like six or seven storms with peak flows in excess of 0.2 cfs (meaning, it can be expected that a minimum of six or seven events will be captured if the inter-storm event period can be expected to be 6 hours or greater). In order to capture a minimum of six or seven storm events during the monitoring period, autosamplers will be set to trigger when the head over the crest of the weirs exceeds 1.75 inches, which corresponds to 0.02 cfs flow over the weir. The triggering flow is set about 10 percent of peak to ensure that the first flush is properly captured by the autosamplers. It should be noted that the intake for sample collection will be above the weir.

For the W inlet, the autosampler will be set to trigger when the head over the crest of the V-notch weir exceeds 1 inch.

A 0.2 cfs flow in the outlet pipe corresponds to a flow depth of approximately 1 inch. It is important to note that the flow hydrograph in the outlet pipe will be relatively flat, i.e., the rising limb increases slowly and the falling limb drops slowly, and therefore, a peak inflow of 0.2 cfs will result in a significantly smaller peak outflow. The triggering depth for sampling outflow will be refined after the first storm.

### **6.5.2 Woodlynn Avenue**

Please see text in Section 6.2.2.

## **6.6 Telemetry and Continuous Data Recording and Presentation**

Telemetry will be used for autosampler control, monitoring flow, as well as monitoring precipitation in real time. Alarms will be developed using a program called Vista Data Vision that also presents graphs of the data and autosampler activity in a web browser. This allows all parties to monitor the progress of a storm event and also know if the autosampler is functioning and when it is done sampling. Telemetry also

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provides a mean to periodically download and record data for storage on the Barr Engineering network. This will minimize data loss and error.

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## 7.0 Field Instrument and Equipment Testing, Inspection, and Maintenance

### 7.1 List of Field Supplies and Materials

Below is a list of field supplies and materials and supplies for the laboratory per sampling event:

- Laboratory supplied sample bottles, a total of 7 sets per storm event with composite sampling. Each bottle set will consist of:
  - One (1) General unpreserved (TSS, VSS, alkalinity (total and bicarbonate), chloride);
  - Two (2) nitric acid preserved (dissolved and total metals);
  - One (1) sulfuric acid preserved (DOC);
  - One (1) nitric acid preserved (total hardness).
- Laboratory supplied sample bottles for duplicate and blank samples, a total of 2 sets per storm event with composite sampling. Each bottle set will consist of:
  - One (1) General unpreserved (TSS, VSS, alkalinity (total and bicarbonate), chloride);
  - Two (2) nitric acid preserved (dissolved and total metals);
  - One (1) sulfuric acid preserved (DOC);
  - One (1) nitric acid preserved (total hardness).
- Sample bottle labels
- COC sheets
- 4 Bags of ice in a cooler
- Field notebook
- Laptop computer
- HOBO Optic Base Station (data transfer unit for the HOBO Data Loggers)
- Connection cables for downloading data from Isco and Campbell equipment
- Acid washed caps (48)
- Replacement set (24 in a set) of acid washed one liter sample bottles for each autosampler
- Safety cone (3 ft)
- Safety vests
- Strobe lights
- MNDOT permit
- Nitrile gloves
- 6 liters of ultrapure distilled water for equipment blank
- Churn type sample splitter
- 4 Millipore single use 0.45 um filters (Stericup Vacuum Filter Units)
- Paper towels
- Replacement desiccant for monitoring equipment
- Field ruler (for verification/calibration of water level sensors)
- Handheld water quality meter (for verification/calibration of pH and DO probes)
- Hip-boots or chest waders

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- Manhole cover remover
  - Digital camera
  - Keys for enclosure locks

## 7.2 List of field equipment

List of field equipment includes:

### For the Highway 36/61 site:

- Seven (7) Water level sensors (5 HOBO U20L-004, and Two (2) Pressure transducers or ultrasonic sensors) with stilling wells
- Four (4) Autosamplers with batteries, in-take tubing, sample bottles, sampler control cables
- An area velocity meter and Three (3) Campbell Scientific water level sensors (Campbell CS451 Pressure Transducers) for use with the weirs for flow measurement
- Two (2) Weirs (supplier to be determined)
- pH probe (Campbell Scientific CS526 pH Probe)
- Dissolved oxygen probe (HOBO DO Data Logger U26-001)
- Tipping bucket rain gauge (Texas Electronics 525-L Rain Gage with 6-in. Orifice)
- CR1000 Campbell Datalogger with battery
- Weather-proof enclosures with locks
- Solar panel
- RAVENXTV Cellular modem with antenna (telemetry unit)

### For the Woodlynn Ave. site:

- Three (3) Isco autosamplers with batteries, in-take tubing, sample bottles, sampler control cables
- Four (4) 2150 Isco AV Flow Meter Module
- Weather-proof enclosures with locks

## 7.3 Equipment Testing

Prior to installation of field equipment, it will be bench tested to ensure it is working properly. The following tests will be performed:

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### **Campbell Scientific CR1000 Datalogger**

- CRBasic program will be written, uploaded to the datalogger, and tested to check that the datalogger is communicating with all sensors and autosamplers.
- Test data will be downloaded to check that they are being properly stored and at the desired interval (test will be conducted over a period of at least 24 hours).

### **RAVENXTV Cellular Modem (telemetry)**

- Using the vendor-supplied software, proper settings will be made to allow for compatibility with the CR1000 Datalogger.
- A dynamic IP address will be installed in the cellular modem.
- Modem will be wired to the datalogger and remote connection will be attempted to verify that it is functioning correctly.

### **Campbell CS451 Pressure Transducer Water Level Sensors/Ultrasonic Water Level Sensors**

- Sensors will be wired to the CR1000 Datalogger and placed in (pressure transducers) or above (ultrasonics) a bucket of water.
- A manual water depth measurement will be taken with a ruler and compared to readings on the datalogger to verify accuracy.

### **HOBO Water Level Data Loggers**

- Loggers will be programmed using the HOBOWare Pro software and deployed in a bucket of water.
- A manual water depth measurement will be taken with a ruler and compared to the logger readings to verify accuracy.
- Test data will be downloaded using the HOBO Optic Base Station and reviewed to check that level data are being properly stored and at the desired interval (test will be conducted over a period of at least 24 hours).

### **Area-velocity Flow Meters**

- A-V flow meters will be wired to their respective controllers (CR1000 Datalogger for Hwy. 36/61 Site and Isco 2150 Flow Modules for Woodlynn Ave Site) and placed in a bucket of water to verify zero-velocity point.

### **Texas Electronics TE525 Rain Gage**

- Rain gage will be wired to the CR1000 Datalogger and the tipping bucket mechanism will be toggled to verify pulse signal.

### **Campbell CS526 pH Probe**

- pH Probe will be wired to the CR1000 Datalogger and placed in a container with a known pH standard to verify accuracy.



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### **HOBO DO Data Logger**

- DO logger will be programmed using the HOBOWare Pro software and placed in a bucket of water with known DO concentration to verify accuracy.

### **Autosamplers**

- Autosamplers will be programmed and the intake tubing will be placed in a bucket of water.
- Peristaltic pumps and sample volume accuracy will be tested.
- For the autosamplers at the Highway 36/61 site, they will be wired to the CR1000 Datalogger using the Sample Control Cable and the trigger pulse will be tested.

## **7.4 Inspection and Maintenance**

After installation of field equipment, it should be inspected periodically and maintained in good working condition. Inspection tasks will include the following:

1. During field visits the weirs, area-velocity sensors, water level sensors, and rain gage should be inspected for debris or sediment buildup that may interfere with accurate measurements. Any debris or sediment should be cleared away, if present.
2. Desiccant indicators for the samplers, datalogger, and sensors should be inspected and desiccant replaced if needed.
3. pH Probe readings will be verified with a handheld pH meter and calibrated if drifting has occurred.
4. DO probe readings will be verified with a handheld DO probe and calibrated if drift has occurred.
5. Water level in the stilling wells and pretreatment basin at the Highway 36/61 Site should be measured manually and compared to the water level sensor readings to verify their accuracy.
6. After sampling, the autosampler bottles should be checked for proper filling. If bottles are filling unevenly or excessive water is spilling into the base, the sample volume should be recalibrated and the distribution arm inspected.
7. Power supply should be monitored and batteries replaced when necessary.

These items will be included in the field SOP's for each study site. As previously stated, the development of SOPs will be part of the training process for the HZ United staff and will be considered to be "living documents" with frequent updates.

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## 8.0 Instrument and Equipment Calibration

Instruments and equipment will be calibrated per the instructions in the operation manuals provided by the vendors. Relevant pages in the manuals will be referenced in the field SOP's. As previously stated, the development of SOPs will be part of the training process for the HZ United staff and will be considered to be "living documents" with frequent updates.

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## 9.0 Sampling, Handling and Processing Methods

This section focuses on the water sample collection, handling, processing, and submission to the analytical laboratory.

### 9.1 Field Processing of Samples

The following procedures will be followed in sequence after the sampling crew has arrived on site at the end of a storm event.

- Upon arrival at the site, the sampling crew will take note of the site for any issues such as clogged sampler hoses and obstructed flow meters. Notes will be taken throughout sample collection, including date, time, sampling crew name, weather, general site conditions, number of samples collected, observation of the sample condition (e.g., turbid, clear, etc.), extent that the sample bottles have been filled, and any other notable observations.
- The autosampler bottle record will be checked to evaluate the storm for any sampling issues such as a missed bottle. If there is a missed bottle or sampling issue, the sampling crew will first discuss this with Chris Bonick and then Keith Pilgrim (if Chris is not available). Samples will be collected regardless of the error unless no stormwater had been collected.
- The top of the autosampler will be removed from for the field box leaving the bottle carriage in the field box. One field staff will put on nitrile gloves and will cap each bottle (pre-numbered from 1 to 24) with an acid washed cap. Once the bottles are capped, the entire bottle carriage will be removed and placed in the vehicle and 2 bags of ice (double bagged) will be placed in the middle of the sampling carriage. These samples will be returned to the Barr Engineering Co. laboratory for processing.
- Before new bottles are placed in the autosampler, an equipment blank will be taken. All staff will be wearing clean nitrile gloves (double gloved such that one pair can be removed if necessary). Blank collection consists of pouring ultrapure laboratory water (supplied by Brooks Labs) into a clean autosampler bottle.
- "Dirty Hands" staff will operate the autosampler and perform all moving of equipment. For the blank collection, the "Clean Hands" staff will simply cap the bottle and remove the bottle and place into a plastic bag.
- New bottles are placed in the sampling box with the caps on. Clean hands removes the caps and the top of the autosampler is put in place. The autosampler is turned on and programmed to collect the next storm event.

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## 9.2 Sample Preparation at the Barr Engineering Laboratory

The following procedures will be followed in sequence after the sampling crew has returned with samples to the Barr Engineering Co. Laboratory.

- The sample bottles are placed on the counter in the Barr Engineering Co. Laboratory, wiped off if necessary and then composited using an acid washed 14-liter churn-type (Zoro # G843435) sample splitter. The entire contents of each sample bottle will be poured into the churn splitter. Prior to pouring, the bottle will be mixed but not too vigorously to avoid changing the chemistry of the water (e.g., cause the pH to rise and cause metal precipitation). If the total sample volume is greater than 14 liters, compositing will be conducted twice with equal-proportion sample transfer using a clean graduated cylinder. The dirty hands staff conducts all activities except for analytical laboratory bottle handling.
- The following is the filtering procedure for dissolved metals and dissolved organic carbon. As part of the sample splitting and preparation process, a sample is collected in a 1-liter labeled bottle and set aside for filtration. Single use filtration units (0.45 um-Millipore Stericup) will be used to filter the sample for dissolved metals and dissolved organic carbon analyses. Filtering will be done in the Barr Engineering Co. laboratory. The Millipore filter is a complete unit with a sample well, filter, and collection well. The dirty hands operator will conduct all of the equipment moving and operation and filtration unit preparation. Clean hands will pour the sample into the filtration unit (outer gloves removed after this is complete). Once filtration is complete, clean hands will then take the cap off the laboratory sample bottle, hold the laboratory bottle in one hand and the cap in the other. Dirty hands will pour the contents of the filtered sample into the bottle. The bottle will be placed into a plastic bag by clean hands (plastic bag held by dirty hands on the outside of the bag) and then directly into the cooler.
- Bottles from the analytical laboratories will be pre-labeled and placed on the clean counter for filling. Once filled directly from the sample splitter, the chain of custody (COC) should be completed with each line of the COC corresponding to one sample. COCs (one for each laboratory) will include the date, time, sample location, and analytic parameters for each sample. When handling bottles, staff will ensure that clean gloves are being used. Samples will be placed in a clean cooler with a copy of the COC placed in the cooler in a plastic bag and with ice to keep the sample cool. The analytical laboratories are identified in Section 9.3.

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## 9.3 Analytical Laboratories

Samples for total and dissolved metals will be sent to the following address:

Attention Sample Receiving  
Brooks Applied Labs  
18804 North Creek Pkwy #100  
Bothell, WA 98011

The project reference number assigned by Brooks for this project is BAR-MN003V.

Samples for all the other analytes will be sent to:

Attention Sample Receiving  
ALS  
3352 128<sup>th</sup> Avenue  
Holland, MI 49424

The project reference number assigned by ALS for this project is 51011002.

## 9.4 Clean-Hands Dirty Hands Method

The “Clean Hand/Dirty Hands” procedure (US EPA Method 1669) was identified Section 9.2 for the particular procedure that it was being applied. Herein is a brief discussion of the overall approach and principle of the method.

Water sample collection and processing is conducted with two staff. One staff is designated as “dirty hands” and the other is designated as “clean hands.”

The dirty hands staff conducts work where there is reduced opportunity to directly contaminate the sample but also there is greater contact with sources of potential contamination. This may involve equipment and material handling, bottle retrieval that involves contacting the outside of a potentially dirty bottle, note taking, or in some cases it involves holding clean items such as a sampling bag on the outside of the bag for the clean hands staff to deposit a clean sample bottle. The dirty hands staff wears nitrile gloves to remain as clean as possible. It is recommended that the dirty hands staff wear two pairs of powder free nitrile gloves such that dirty gloves can be removed and hence a clean pair is available underneath if needed. Clean suits are not necessary for this project.

The role of the clean hands staff is to handle the clean laboratory sample bottles and caps, the clean caps of the autosampler bottles, and pack the clean sample bottle into a clean bag for delivery to the analytical laboratory. In the case of the sample splitter (as noted in Section 9.2), the dirty hands staff will open the sampling spigot while clean hands holds the sample bottle and cap. When conducting sample filtration (as noted in Section 9.2), clean hands will hold the clean Millipore filtration unit. Dirty hands will pour the sample into the filter and clean hands will hold the sample bottle and cap while dirty hands pours the filtered sample into the clean laboratory bottle. It is recommended that dirty hands removes the outer gloves prior to handling and pouring the filtered water.

Both staff need to be aware that all materials can be a source of contamination.

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## 9.5 Bottle Washing Procedure

The 1-liter autosampler bottles will be acid washed in preparation of stormwater sample collection. Prior to conducting the washing the following safety equipment is required: laboratory coat, nitrile gloves, rubber gloves, and safety goggles.

For the first time that the sample bottles are used the following washing sequence will be conducted:

- Use Liquinox (phosphate free) detergent to scrub and clean the sample bottle.
- Filling the sample bottle to the top, rinse 3 times with ultrapure laboratory water.
- Add a 500 mL aliquot of 1% HCl solution to the bottle and cap the bottle. The bottle will be gently inverted several times for approximately 1 minute and then the acid is transferred to the next bottle. After 24 bottles have been cleaned with 500 mL HCl solution, discard properly the HCl and get a new 500 mL HCl solution for the next set of 24 bottles.
- Rinse the bottle 3 times with 1 liter of ultrapure laboratory water.
- Place the bottle inverted on a drying rack (wipe down the drying rack prior to use).

After the sample bottles have been used in the field, the following washing sequence will be conducted:

- Filling the sample bottle to the top, rinse 2 times with ultrapure laboratory water.
- Add a 500 mL aliquot of 1% HCl solution to the bottle and cap the bottle. The bottle will be gently inverted several times for approximately 1 minute and then the acid is transferred to the next bottle. After 24 bottles have been cleaned with 500 mL HCl solution, discard properly the HCl and get a new 500 mL HCl solution for the next set of 24 bottles.
- Rinse the bottle 3 times with 1 liter of ultrapure laboratory water.
- Place the bottle inverted on a drying rack (wipe down the drying rack prior to use).

## 10.0 Holding Times, Bottles, and Analytical Methods

The holding times, bottles, and analytical methods are provided in the table below.

**Table 10-1 Water Sample Methods, Containers, and Holding Times**

Parameter	Laboratory	Method	Container Preservation	Holding Time
Total Metals	Brooks	EPA 1638 Mod (ICP-MS)	125-mL polyethylene HNO <sub>3</sub> , pH < 2	6 Months
Dissolved Metals ^	Brooks	EPA 1638 Mod (ICP-MS)	125-mL polyethylene HNO <sub>3</sub> , pH < 2	6 Months
Total Suspended Solids (TSS)	ALS	SM2540 D-97	1 L polyethylene Cool ≤ 6 °C	7 Days
Volatile Suspended Solids (VSS)	ALS	SM2540 E-97		7 Days
Alkalinity, Total (as CaCO <sub>3</sub> )	ALS	SM2320 B-97		14 Days
Alkalinity, Bicarbonate (as CaCO <sub>3</sub> )	ALS	SM2320 B-97		14 Days
Chloride	ALS	SM4500-Cl E-97		28 Days
Organic Carbon, Dissolved (DOC) ^	ALS	SM5310C-00	125-mL glass/plastic H <sub>2</sub> SO <sub>4</sub> , pH < 2; Cool ≤ 6 °C	28 Days
Total Hardness	ALS	SM2340 C-97	250-mL polyethylene HNO <sub>3</sub> , pH < 2	6 months

^ Filtered at the Barr Engineering laboratory.

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## 11.0 Data Management

### 11.1 Field Data Management

Field staff will manage raw data during field activities. Data will be recorded on the appropriate field forms or in field logbooks. Field staff will provide the data collected in the field to the Data Management team in order to maintain results.

As appropriate, the Data Management team will transfer the data to electronic formats such as Microsoft® Excel, Microsoft® Access, EQUIS, or other database management systems to better organize and track incoming data and to identify any data gaps. The Data Management team will verify the field data for completeness. Any issues in field QA/QC will be brought to the attention of the QA/QC Lead.

### 11.2 Laboratory Data Management

The analytical laboratory project manager (Brooks Labs and ALS) will be responsible for the coordination of laboratory data management. Each laboratory has documented procedures for data review and data reporting. The laboratory will provide the analytical results in a laboratory report and an electronic data deliverable (EDD) in Barr EQUIS specifications. The analytical data report will include sample results, method blank results, accuracy and precision data, definition of lab applied qualifiers, and a laboratory narrative describing any out of control analyses.

As appropriate, Barr's Data Management staff will upload the EDD from the laboratory into EQUIS and review the data against Barr's specifications for accuracy. Further, Barr's Data Management team will verify the electronic data for completeness and accuracy, specifically validating the normal, duplicate, and blank sample results and data matches the laboratory report. After Barr QA/QC review (Section 13.0), Barr-specific qualifiers will be applied to the data in EQUIS. The data, including QA/QC results, will become part of the project files and will be maintained by Barr's data management group. Barr will review laboratory data in accordance with accepted statistical methodologies (see Section 14.0).



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## 12.0 Assessment

The analytical results will be compared to the project quality objectives that are summarized in Section 4.0. The data reconciliation process may involve multiple steps depending on the results of the initial QA review. Data that has been qualified (by the laboratory or by Barr) will be assessed for the particular circumstances surrounding the sample. Corrective actions may include resampling and/or reanalysis of the sample. The laboratory limits may be elevated due to dilutions or matrix interferences, affecting the sensitivity of the analysis. In these cases, the necessity of the non-detect data to decision-making will be evaluated and potential corrective actions may include using the qualified data or resampling.

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## 13.0 Data Review, Verification, and Validation

Data verification (data review) is defined as an evaluation of performance against predetermined requirements such as an analytical method, SOP, or Quality Assurance Manual. It is performed during or at the end of field or laboratory data collection activities. The goal of data verification is to ensure and document that the reported results reflect what was actually done. Data validation is the evaluation of the technical usability of the data. It focuses on the particular data needs for a project as defined in project-specific documentation (e.g., SAP or QAPP). Data validation begins with the outputs from data verification. Data review and validation will be performed as presented below.

### 13.1 Field data verification

Field data are reviewed by the Field Sampling Lead for completeness and transcription errors. Additionally, during preparation of the final field report, Barr technical field staff will verify their documentation for accuracy and completeness. If any errors are found, the field personnel will be contacted and corrective action will be initiated.

### 13.2 Laboratory data verification

The laboratory will review the data as described in their quality control documentation. Discrepancies from the established protocols will be qualified and/or narrated.

The Barr QA/QC Lead will conduct a systematic review of the data reported by the laboratory in accordance with Barr's routine level data evaluation SOPs in Attachment A. They are based on quality assurance elements within USEPA Contract Laboratory Program National Functional Guidelines. Data quality evaluation procedures will use the QC recovery limits in Table 4-1 and/or in the laboratory reports. The specific requirements that will be checked during data evaluation (where applicable) are:

- Holding times
- Preservation
- Blank sample data
- LCS data
- MS data
- Duplicate sample data

The data reviewer will identify any out-of-control results and data omissions and work with the laboratory to correct any data deficiencies.

The data assessment by the Barr Principal Investigator will check that the sample was collected and handled according to the established plan (this document). One hundred percent (100 percent) of the data will be reviewed. Decisions to repeat sample collection and analyses may be made by the Barr

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Principal Investigator based on the extent of the deficiencies and their importance in the overall context of the project.

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## 14.0 Statistical Analysis Approach

This section discusses options for statistical analysis of the data and evaluates the minimum number of samples required to obtain a minimum confidence level and power for conducting certain types of statistical comparisons. Specific statistical test methods will be selected after reviewing the data, and the rationale will be included in the final report. The data review will utilize exploratory and visual data evaluation tools such as charts or box plots, will include calculation of descriptive statistics and distribution and outlier testing, where appropriate.

The general objective of the statistical analyses will be to compare inlet and outlet concentrations using statistical methods to determine if the treatment results in a statistically significant reduction in concentrations. Inlet and outlet concentrations for each parameter will be compiled for each storm event. Composite sample results (e.g., the event mean concentration) from each storm event will be used so that one a minimum of one pair of data is available for each event.

Inlet and outlet concentration data may be compared either by pooling all the storm events for each data set (inlet and outlet) and comparing the mean concentrations of inlet and outlet data, or by pairing the data by each storm event and evaluating the mean difference between the inlet and outlet concentration pairs.

If the data are pooled into two groups (inlet and outlet), a two-sample test, such as a T-test (for parametric distributions) or Wilcoxon Mann-Whitney (aka Wilcoxon Rank-Sum) test (for nonparametric distributions) would be used to compare the means of the inlet and outlet data sets to assess whether the mean outlet concentration is less than the mean inlet concentration within a specified confidence level.

Null Hypothesis: The mean outlet concentration is greater or equal to the mean inlet concentration

$$H_0 : \mu_{out} \geq \mu_{in}$$

Alternative Hypothesis: the mean outlet concentration is less than the mean inlet concentration

$$H_A : \mu_{out} < \mu_{in}$$

If the inlet and outlet data are paired based on storm event, the difference between the inlet and outlet data will be computed and a one-sample test conducted to assess whether the mean difference (inlet—outlet) is greater than zero. The paired T-test (for parametric distributions) or Wilcoxon Sign Rank test (for non-parametric data set) would be used to assess whether the mean difference between the inlet and outlet data pairs is greater than zero with a specific confidence level. The paired T-test is essentially the same as conducting a one-sample T-test on the calculated differences between inlet and outlet concentrations.

Null Hypothesis: the mean difference between the inlet and outlet concentrations is less than or equal to zero

$$H_A : \mu_D \leq 0$$

Alternate Hypothesis: the mean difference between the inlet and outlet concentrations is greater than zero

$$H_0 : \mu_D > 0$$

Prior to selecting the statistical test to conduct, goodness-of-fit testing would be conducted to assess whether the data sets fit a parametric distribution (e.g., normal or lognormal) using a method such as the Shapiro Wilks test for normality. If they do not, non-parametric statistical test methods would be used.

To reduce the probability of a statistical test resulting in false conclusions, the test should have adequate power and confidence. The power or sensitivity of a binary hypothesis test is the probability that the test correctly rejects the null hypothesis ( $H_0$ ) when the alternative hypothesis ( $H_A$ ) is true. A test with a high power will have a low probability of falsely rejecting the null hypothesis (Type II errors). Power can be equivalently thought of as the probability of accepting the alternative hypothesis ( $H_1$ ) when it is true—that is, the ability of a test to detect an effect, if the effect actually exists, reducing Type II errors. Similarly, a test with a high confidence will reduce the probability of falsely accepting the null hypothesis (Type I errors).

The null hypothesis for statistical tests outlined above can be set up so that it represents the case that is believed to be true (test Form 2), or the case that is not believed to be true, but would be rejected by the test (test Form 1). The example null hypotheses shown above are based on test Form 1. The EPA suggests the following minimum values to reduce the two types of error rates (EPA, ProUCL v. 5.0 technical guidance):

- For Test Form 1, the confidence level should be at least 80% ( $\alpha = 0.20$ ) and the power should be at least 90% ( $\beta = 0.10$ ).
- For Test Form 2, the confidence level should be at least 90% ( $\alpha = 0.10$ ) and the power should be at least 80% ( $\beta = 0.20$ ).

The number of samples that should be collected in order to obtain a certain confidence level and power can be calculated for two-sample tests with the following formula (EPA, QA-G9, Box 3-14):

$$n = \frac{2(Z_{1-\alpha} + Z_{1-\beta})^2 s^2}{\Delta^2} + \frac{Z_{1-\alpha}^2}{4}$$

And for one-sample tests (EPA, QA-G9, Box 3-1):

$$n = \frac{(Z_{1-\alpha} + Z_{1-\beta})^2 s^2}{\Delta^2} + \frac{Z_{1-\alpha}^2}{2}$$

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Where

- $Z_p$  = the  $p^{\text{th}}$  percentile of the standard normal distribution;
- $\alpha$  = the probability of making a Type I error (false rejection error rate);
- $\beta$  = the probability of making a Type II error (false acceptance error rate);
- $s$  = an estimate of the standard deviation ( $s^2$  is an estimate of the variance); and
- $\Delta$  = the width of the gray region or the acceptable inaccuracy.

When the standard deviation of the data,  $s$ , is unknown, which is the case prior to sampling, the equation can be used to estimate the required number of samples by selecting an appropriate ratio between the width of the gray region ( $\Delta$ ) and  $s$ . The proposed acceptable accuracy for this project is one standard deviation. For Test Form 1, the minimum number of samples,  $n$ , where  $\Delta=s$ , for a confidence level of 80% ( $\alpha = 0.20$ ) and a power of 90% ( $\beta = 0.10$ ), is 9 for two-sample tests and 5 for one-sample tests.

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## 15.0 References

Barrett, M; Katz, L; Taylor, S; Sansalone, J, and M. Stevenson. 2014. "Measuring and Removing Dissolved Metals from Stormwater in Highly Urbanized Areas", NCHRP Report 767.

U.S. EPA. 2000. Guidance for Data Quality Assessment. Practical Methods for Data Analysis. EPA QA/G-9. QA00 UPDATE. EPA/600/R-96/084.

U.S. EPA. 2002. Guidance for Quality Assurance Project Plans. EPA QA/G-5. EPA/240/R-02/009.

U.S. EPA. 2006. Guidance on Systematic Planning Using the Data Quality Objectives Process. EPA QA/6-4. EPA/240/B-06/001.

U.S. EPA. 2013. ProUCL v. 5.0 technical guidance. EPA/600/R-07/041. September 2013.

US EPA Method 1669. Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. July 1996.

## **Attachment A**

### **Barr's Routine Level Data Evaluation SOPs**





**Compendium  
Of  
Data Quality Assessment Documentation**

## Barr DQ Assessment Definitions

**Accuracy:** Accuracy is the degree of agreement between an observed value and an accepted reference value. Accuracy measures the bias in a measurement system. Accuracy of laboratory results may be assessed using the analytical results of method blanks, field blanks, reagent/preparation blank, matrix spike/matrix spike duplicate samples and laboratory control samples. The percent recovery for (%R) matrix spikes and laboratory control samples will be calculated using the following equation:

$$\%R = \frac{SSR - SR}{SA} \times 100$$

Where: %R = % recovery  
SSR = spiked sample result  
SR = sample result  
SA = spike added to native sample

*NOTE: In the case of LCS and other laboratory-prepared samples, SR is zero.*

**Batch:** Group of samples of the same matrix prepared for single or multiple analyses that will be analyzed during one operation at a given specific time frame. Typical size is 1-20 samples.

**Blank:** A sample designed to assess specific sources of contamination.

**Calibration:** Calibration is the process of checking, adjusting or determining by comparison under specified conditions an instrument's response to standards for each target compound to be analyzed. The source and accuracy of standards used for this purpose are integral to obtaining the best quality data.

**Contamination:** A component of a sample or an extract that is not representative of the environmental source of the sample. Contamination may stem from other samples, sampling equipment, while in transit, from laboratory reagents, laboratory environment, or analytical instruments.

**Data Quality Specialist:** An individual that is part of the Data Quality group at Barr Engineering and may be referred to as a Quality Assurance Manager, Quality Assurance Officer, or Quality Manager within Quality Assurance Project Plans or other project documentation.

**Duplicate:** A second aliquot of a sample that is treated the same as the original sample in order to determine the precision of the method.

**Equipment (Rinsate) Blank:** A sample of analyte-free water collected when rinsing sampling equipment. It measures the potential for sample cross contamination due to insufficient decontamination of sampling equipment.

**Field Blank:** A sample of analyte-free water exposed to environmental conditions at the sampling site by transferring from one sample container to another or by removing the lid and exposing a container filled with analyte-free water to the atmosphere for the time equivalent necessary to fill a container. It measures the potential for sample cross contamination due to site conditions.

**Field Duplicate:** A duplicate sample generated in the field that is used to demonstrate acceptable precision and reproducibility of the field and laboratory procedures. The sample identification is typically kept blind (masked) from the laboratory.

**Holding Time:** The maximum recommended amount of time samples may be held before they are processed.

**Instrument Blank:** A blank designed to determine the level of contamination either associated with the analytical instruments, or resulting from carryover. It measures laboratory sources of contamination.

**Laboratory Control Sample (LCS) and Laboratory Control Sample Duplicate (LCSD):** A sample of analyte-free media spiked with known concentrations of target analytes that is carried through the same sample preparation and analytical procedures. LCS recoveries are used to estimate overall analytical method accuracy independent of sample matrix effects. The RPD between the LCS and LCSD is used to assess the overall analytical method precision. Also referred to as a Laboratory Fortified Blank.

**Matrix:** The predominant material of which the sample to be analyzed is composed (e.g. water, soil, sediment, etc.).

**Matrix Effect:** In general, the effect of a particular matrix on the constituents with which it contacts. Matrix effects may prevent efficient purging/extraction of target analytes, and may affect DMC and surrogate recoveries. In addition, non-target analytes may be extracted from the matrix causing interferences.

**Matrix Spike (MS) and Matrix Spike Duplicate (MSD):** A sample spiked with known concentrations of target analytes that is carried through the sample preparation and analysis procedures in order to assess the accuracy of a method in a given sample matrix. The RPD between the MS and MSD is used to assess the precision of a method in a given sample matrix. Also referred to as a Laboratory Fortified Matrix.

**Method Detection Limit (MDL):** The MDL is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. EPA procedures for determining the MDL are given at 40 CFR 136, Appendix B.

**Method Blank:** A sample of a matrix similar to the batch of associated samples (when available) that is free from the analytes of interest and is processed simultaneously with and under the same conditions as samples through all steps of the analytical procedures, and in which no target analytes or interferences are present at concentrations that impact the analytical results for sample analyses. It measures laboratory sources of contamination.

**Narrative:** The portion of the data package which includes laboratory, contact, sample number identification, and descriptive documentation of any problems encountered in processing the samples, along with corrective action taken and problem resolution.

**Precision.** Precision measures the reproducibility of measurements under a given set of conditions. Precision of analytical laboratory data may be assessed by comparing the analytical results between matrix spike/matrix spike duplicates (MS/MSD), laboratory duplicates, or masked field samples (field duplicates). Field duplicate samples, when collected, processed, and analyzed by the same organization, provide intralaboratory precision information for the entire measurement system, including: sample acquisition, sample constituent heterogeneity, handling, shipping, storage, preparation, and analysis. Field duplicate samples are submitted to the laboratory as blind or mask samples. The relative percent difference (%RPD) will be calculated using the equation below for each pair of duplicate analysis.

$$RPD = \frac{|S - D|}{(S + D)/2} \times 100$$

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Where: RPD = relative percent difference  
S = original sample result  
D = duplicate sample result

**Quality Assurance Project Plan (QAPP):** A formal document describing in comprehensive detail the necessary quality assurance (QA), quality control (QC), and other technical activities that must be implemented to ensure that the results of the work performed will satisfy the stated performance criteria.

**Reporting Limit (RL):** The RL is the lowest reported concentration, provided on the sample-analysis data report, after corrections have been made for sample dilution, sample weight, and (for soils and sediments) amount of moisture in the sample.

**Sample Delivery Group (SDG):** Identifies a group of samples for delivery, A sample delivery group is defined by the following, whichever is most frequent:

- Each set of field samples received; or
- Each 20 field samples within a sampling event; or
- Each 7 calendar day period (3 calendar day period for 7-day turnaround) during which field samples are received.

**Synthetic Precipitation Leaching Procedure (SPLP):** A test designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes. It can be used to assess the risk of groundwater contamination posed by the land application of granular solid wastes.

**Toxicity Characteristic Leaching Procedure (TCLP):** A test designed to determine whether a waste is hazardous or requires treatment to become less hazardous; also can be used to monitor treatment techniques for effectiveness.

## Barr Qualifiers/Footnotes

Qualifier	Definition
a	Estimated value, calculated using some or all values that are estimates.
b	Potential false positive value based on blank data validation procedures.
c	Coeluting compound.
e	Estimated value, exceeded the instrument calibration range.
f	Sample was collected at a flowrate exceeding the recommended rate of 200 mL/minute.
h	EPA recommended sample preservation, extraction or analysis holding time was exceeded.
i	Indeterminate value based on failure of blind duplicate data to meet quality assurance criteria.
j	Estimated detected value. The reported value is less than the stated laboratory quantitation limit but greater than the laboratory method detection limit.
p	Relative percent difference is >40% (25% CLP pesticides) between primary and confirmation GC columns.
pp	Small peak in chromatogram below method detection limit.
r	The presence of the compound is suspect based on the ID criteria of the retention time and relative retention time obtained from the examination of the chromatograms.
t	Sample positive for total coliforms but negative for <i>E. coli</i> .
v	Sample was collected under a vacuum of greater than XX inches of mercury.
*	Estimated value, QA/QC criteria not met.
**	Unusable value, QA/QC criteria not met.
AT	Sample chromatogram is noted to be atypical of a petroleum product.
EMPC	Estimated maximum possible concentration.

**Barr Engineering Company**  
**Routine Level Quality Control Report**

**Project #** \_\_\_\_\_

**Laboratory** \_\_\_\_\_

**Lab Report #** \_\_\_\_\_

**Report Date** \_\_\_\_\_

**Holding Times Met**                      Yes              No

If no, comments \_\_\_\_\_

\_\_\_\_\_

**Temps on Receipt (°C)** \_\_\_\_\_

**Project Name** \_\_\_\_\_

**COC(s)/Event** \_\_\_\_\_

**Matrix** \_\_\_\_\_

**Review Date** \_\_\_\_\_

**Reviewed By** \_\_\_\_\_

**Posted to QC Track?**                     

**Revised Report?**                                **Rev #** \_\_\_\_\_

**Data Report Request #** \_\_\_\_\_

<b>Method Blanks</b>
<b>Field Blanks</b>
<b>Trip Blanks (VOCs Only)</b>
<b>Field Duplicates (if applicable)</b>

<b>LCS/LCSD</b>
<b>MS/MSD</b>
<b>Surrogates (if applicable)</b>
<b>Lab Duplicates (if applicable)</b>

**Additional Notes (include historical comparison, if appropriate)**

Qualifier Summary		Qualifier Changes		
Sample Name	Parameter	Added	Removed	Retained

**Additional Notes to DM**

**For DM Use Only**

Equis     Y / N	Data Tech Init:
Facility ID:	Date entered into Equis:



# Standard Operating Procedure

## Routine Level General Chemistry Data Evaluation

Revision 6

January 8, 2016

Approved By:

James Taraldsen      *James Taraldsen*      01/08/16  
Print      Technical Reviewer      Signature      Date

Terri Olson      *Terri A. Olson*      01/08/16  
Print      QA Manager      Signature      Date

Review of the SOP has been performed and the SOP still reflects current practice.

Initials: _____	Date: _____
Initials: _____	Date: _____
Initials: _____	Date: _____
Initials: _____	Date: _____



# Routine Level General Chemistry Data Evaluation

## 1.0 Scope and Applicability

This SOP is intended as a guidance document for the routine level evaluation of general chemistry data provided by laboratories to be used in Barr Engineering Company (Barr) projects.

This SOP is based on the recommendations of the associated approved analytical methods from USEPA, ASTM, and *Standard Methods for the Examination of Water and Wastewater* and applies to routine general chemistry data evaluation including a variety of approved methods not limited to the following parameters:

Alkalinity as CaCO <sub>3</sub>	Nitrate (or Nitrite) only
Ammonia, total (NH <sub>3</sub> + NH <sub>4</sub> <sup>-</sup> )	Nitrate + Nitrite
Biological Oxygen Demand (BOD)	pH – <i>in lab</i>
Chemical Oxygen Demand (COD)	Phosphorus, total
Chloride	Sulfate
Chromium VI (Hexavalent Chromium)	Sulfide
Conductance, Specific – <i>in lab</i>	Total Dissolved Solids (TDS)
Cyanide (as CN <sup>-</sup> )	Total Kjeldahl Nitrogen (TKN)
Fluoride	Total Organic Carbon (TOC)
Hardness	Total Suspended Solids (TSS)
Oil and Grease (as HEM)	

In the case of specific parameters not listed above, the guidelines within this document will provide the basis upon which to make adequate professional judgment in the evaluation of data submitted for review.

The recommended procedures in this SOP should be followed unless conditions make it impractical or inappropriate to do so. Modifications should be noted in the applicable documentation and communicated to appropriate personnel. Significant changes may result in a revision or newly created SOP.

## 2.0 Limitations

- Level IV data evaluation is not covered in this SOP and should be performed in accordance with project specific requirements.

## 3.0 Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.), or documenting the impact to the data.

The Data Quality Specialist is responsible for evaluating the data in accordance with this document, in addition to using professional judgment where necessary or appropriate. Project specific requirements, such as those specified in a Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP), may differ from these recommendations and professional judgment should be applied before qualifying any data.

## 4.0 Procedure

The Quality Assurance/Quality Control (QA/QC) data detailed below are the most typical found in a routine level laboratory report. Other QA/QC data may be provided by the laboratory within the laboratory report case narrative, data qualifiers, or cover sheet and should be evaluated using professional judgment (e.g., initial calibration, calibration verification, internal standards, post digestion, serial dilution).

Definitions to common QA/QC terms and terms used within this SOP along with a list of Barr 'Data Qualifiers/Footnotes' that may be applied during review can be found in Barr's "Compendium of Data Quality Assessment Documentation".

### 4.1 Holding Time and Preservation

The purpose of holding time and preservation evaluation is to ascertain the validity of the analytical results based on the sample condition, preservation, and time elapsed between the date of sample collection and date of analysis.

40 CFR Part 136 and the *Test Methods for Evaluating Solid Waste (SW-846)* are used as guidance for the recommended holding time and preservation acceptance criteria listed in *Table 1*.

Table 1 - Recommended Holding Times and Preservation											
Parameter (Alternate Name)	Recommended Hold Time						Preservation				
	24 Hour	48 Hour	7 Day	14 Day	28 Day	180 Day	Ice Only (< 6 °C)	HCl	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	NaOH ZnAc + NaOH
Alkalinity, as CaCO <sub>3</sub>				X			X				
Ammonia as N					X		X		X		
Biochemical Oxygen Demand (BOD)		X					X				
Chemical Oxygen Demand (COD)					X		X		X		
Chloride					X		X				
Chromium, hexavalent	X				a		X				
Conductance, specific - in lab					X		X				
Cyanide				X			X			X	
Dissolved Organic Carbon (DOC)					X		X	X <sup>c</sup>	X <sup>c</sup>		
Fluoride					X		X				
Hardness						X		X <sup>c</sup>	X <sup>c</sup>		

(Table 1 continued on next page)

Parameter (Alternate Name)	Recommended Hold Time						Preservation					
	24 Hour	48 Hour	7 Day	14 Day	28 Day	180 Day	Ice Only (< 6 °C)	HCl	HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub>	NaOH	ZnAc + NaOH
Nitrate or Nitrite		X					X					
Nitrate + Nitrite as N					X		X		X			
Oil & Grease, HEM					X		X	X <sup>c</sup>	X <sup>c</sup>			
pH <sup>b</sup> - in lab			X				X					
Phosphorus, total					X		X		X			
Sulfate					X		X					
Sulfide			X				X					X
Total Dissolved Solids (TDS)			X				X					
Total Kjeldahl Nitrogen (TKN)					X		X		X			
Total Organic Carbon (TOC)					X		X	X <sup>c</sup>	X <sup>c</sup>			
Total Suspended Solids (TSS)			X				X					

a = Per 40 CFR Part 136.3, a 28-day holding time may be achieved if the ammonium sulfate buffer solution specified in EPA Method 218.6 is used. This footnote supersedes preservation and holding time requirements in approved hexavalent chromium methods, unless this would compromise the measurement and then the method must be followed.

b = Method recommends pH should be measured in the field.; however, for confirmation measurements in the laboratory, a maximum holding time of 7 days from sample collection will be used as a guideline for qualification.

c = Either preservative may be used (pH < 2) - for hardness, HNO<sub>3</sub> only if calculated from Ca and Mg.

If samples do not meet holding time, preservation and analysis recommendations in *Table 1*, consider qualification with an "h". Other matrices, such as product samples (e.g. oil, waste rock, drill cores) may not be subjected to the same holding time recommendations.

If the sample was stored on ice upon collection and delivered to the laboratory the same day, the sample may exceed recommended temperature at the time of laboratory receipt. Professional judgment should be applied (considering temperature, matrix, magnitude of the exceedance, etc.) when evaluating the application of qualifiers when criteria are not met.

## 4.2 Blank Samples

Blank sample evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- While not required for all methods, method blanks are recommended for all but the pH analysis. Evaluation pertains to the batch of samples analyzed with the method blank.
- Field or equipment blank collection and analysis frequency is project specific. Evaluation pertains to the field samples associated with the field or equipment blank.
- Blank analyses may not have involved the same weights, volumes, or dilution factors as the associated samples. It may be easier to work with the raw data and/or convert the data to the same units for comparison purposes.

<b>Table 2 – Guidelines for Blank Contamination</b>	
<b>Sample Result</b>	<b>Recommended Action for Associated Data</b>
Non-detect	No action required
< 5x blank concentration	Qualify with 'b'
≥ 5x blank concentration	Use professional judgment

b = Reported value may be a potential false positive based on blank data evaluation procedures

Note: Other multipliers of the blank contamination may be used based on professional judgment (reporting to the MDL, common lab contaminant, etc.)

Professional judgment regarding the usability of the data should be used in cases where gross detections of target analytes are found in the blank sample. A number of factors may be considered including historical data, prior knowledge of the site conditions, target analytes involved, type of blank sample, etc. In such cases, it may be appropriate to qualify the affected data with '\*' (estimated value, QA/QC criteria not met) or '\*\*' (unusable value, QA/QC criteria not met).

#### 4.3 Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicate Samples (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. The LCS should be analyzed:

- Once every preparation batch (typically 20 or less samples of the same matrix).
- Once for each matrix.

Laboratory control samples contain a known amount of each target compound and the percent recoveries are evaluated based on the criteria within the laboratory report or project specific requirements. Percent recoveries are calculated for accuracy and the relative percent difference (RPD) is calculated for precision (when an LCSD was analyzed). Accuracy and precision equations can be found in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation".

<b>Table 3 – Guidelines for Laboratory Control Samples</b>		
<b>Criteria</b>	<b>Recommended Action for Associated Data</b>	
	<b>Detect</b>	<b>Non-Detect</b>
%R and RPD > Upper Limit	Qualify with '*'	No qualification
%R < Lower Limit	Qualify with '*' or '**', use professional judgment	
%R and RPD within Limits	No qualification	

\* = Reported value is estimated and QA/QC criteria were not met

\*\* = Reported value is unusable and QA/QC criteria were not met

#### 4.4 Laboratory Duplicate Samples

Laboratory duplicate samples are separate aliquots of field samples analyzed to demonstrate acceptable method precision by the laboratory at the time of analysis. Field blanks and proficiency testing (PT) samples should not be used for duplicate analysis. The RPDs are calculated using the equation as provided in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation" and are not calculated where data are already qualified with b, U, <, or \*\*. RPD results are dependent on the homogeneity of the samples.

Duplicates should be analyzed (whichever is more frequent):

- One from each matrix (soil or water)
- One from each SDG

The MS/MSD duplicate pairs may be substituted for laboratory duplicates.

Laboratory acceptance criteria or project specific requirement are used to evaluate RPDs. If criteria are not available, use professional judgment when considering qualification of associated results.

Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. RPDs are typically only evaluated for samples where both the native and duplicate sample concentrations are greater than five times (>5x) the RL. In cases where either of the samples (native or duplicate) is non-detect for a parameter and the other corresponding sample has detectable concentrations much greater than five times (>5x) the RL, professional judgment should be used to determine if qualification is appropriate.

<b>Table 4 – Guidelines for Laboratory Duplicates</b>	
<b>% RPD</b>	<b>Recommended Action for Associated Data</b>
RPD < Upper Limit	No action is required
RPD > Upper Limit	Both results are ≤ 5x RL, no action is required
RPD > Upper Limit	Both results are > 5x RL, consider qualifying with '**'

\* = Reported value is estimated and QA/QC criteria were not met

#### 4.5 Field Duplicate Samples

Field duplicate samples (also known as "masked" or "blind" duplicate samples) are used to demonstrate acceptable precision and reproducibility of the field and laboratory procedures. Frequency of collection is project specific. The RPDs are calculated using the equation as provided under precision in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation" and are not calculated where data is already qualified with b, U, <, or \*\*. RPD results are dependent on the homogeneity of the samples.

Acceptance criteria for field duplicate samples are subject to the professional judgment of the Data Quality Specialist but typically RPDs ≤ 30% for aqueous samples and ≤ 40% for soil and sediment samples are considered acceptable unless other project specific requirements are defined.

Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. RPDs are typically only evaluated for samples where both the native and duplicate sample

concentrations are greater than five times (>5x) the RL. In cases where either of the samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample has detectable concentrations much greater than five times (>5x) the RL, professional judgment should be used to determine if qualification is appropriate.

#### 4.6 Matrix Spikes (MS) and Matrix Spike Duplicate (MSD) Samples

Matrix spike samples contain a known amount of a target compound and provide information about the effect of each samples' matrix on the sample preparation procedures and analytical results. Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples
- 1 per preparation batch per matrix
- 1 per SDG

However, the frequency may be project specific and the documents outlining the needs of the project (SAP, QAPP, etc.) should be reviewed. In some cases, MS/MSD analysis is not required.

The percent recoveries are evaluated based on the criteria within the laboratory report or project specific requirements. If a matrix spike recovery does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added (>4x), spike recovery cannot be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

If criteria are not available, use guidance found in the NFG. Percent recoveries of matrix spike (and matrix spike duplicate) samples should be calculated using the equation provided under accuracy in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation".

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity. Professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

<b>Table 5 – Guidelines for Matrix Spikes</b>		
<b>Criteria</b>	<b>Recommended Action for Associated Data</b>	
	<b>Detect</b>	<b>Non-Detect</b>
%R and RPD > Upper Limit	Qualify with '**'	No qualification
%R < Lower Limit	Qualify with '**' or '**'', use professional judgment	
%R and RPD within Limits	No qualification	

\* = Reported value is estimated and QA/QC criteria were not met

\*\* = Reported value is unusable and QA/QC criteria were not met

While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS and MSD pairs using the equation as provided under precision in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation".

#### 4.7 Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

#### 5.0 Quality Control and Quality Assurance (QA/QC)

Depending on the project objectives, the data review may include the completion of a Routine Level Quality Control Report (see Barr's "Compendium of Data Quality Assessment Documentation") as part of the evaluation process. Within each QC data section, the reviewer should include references to whether the QC data met or exceeded the acceptance criteria. The qualifiers, added, removed, or retained, should be documented also. Where multiple qualifiers may be applicable to a sample/analyte result, professional judgment should be used to determine if all qualifiers are necessary or if one qualifier would be sufficient to represent the deviations. A statement as to whether the data are acceptable as reported or acceptable with qualification(s) should also be included. If revised reports are required and the revision affects the sample results, notification should be given to the appropriate data management personnel and/or project team members.

The Data Quality Specialist will verify that the qualifiers associated with data tables match the Routine Level Quality Control Report.

#### 6.0 Records

The Routine Level Quality Control Report should be saved to the appropriate internal Barr file and the link uploaded to the tracking system. Periodically, Data Quality staff should check for missing Routine Level Quality Control Reports in the tracking system to help maintain the most current information.

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- Routine Level Quality Control Report

Additional records information can be found in Barr's "Records Management System Manual".

#### 7.0 References

Environmental Protection Agency. *Title 40 of the Code of Federal Regulations, Part 136.3.*

Environmental Protection Agency, *National Functional Guidelines for Inorganic Superfund Data Review.*

Analytical methods listed under the 'Scope and Applicability' section of this SOP.

## Attachment 1 Revision History

Revision Number	Date of Revision	Section	Revision Made
3.1	02/2009	Document Wide	Edits to references, formatting; minor language additions and corrections;
		IX	Changed to Section X
		Attachments	Added Attachment 3
		IX (new)	Added Table 9.
3.2	04/2011	Document Wide	Added missing analytical method references.
		Attachments	Updated Attachments to current forms.
3.3	04/2011	References	Update the reference to the current NFG Metals data validation document.
4.0	04/06/12	Document Wide	Major revision
5.0	06/17/13	Cover page	Added Calgary office
		Applicability	Added US to EPA reference
		I	Added waste rock and drill cores to examples of product sample
		III	Added LCSD information
		III, IV, V, VI	Added 'project specific requirements' as possible criteria source
		V	Added 'field and laboratory procedures' to clarify that it's not only a laboratory item
		V	Clarified field duplicate criteria as < one value and not a range
		VIII	Added statement regarding multiple qualifiers
6.0	01/07/16	Document Wide	SOP restructuring, new format

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# Standard Operating Procedure Routine Level Metals Data Evaluation

Revision 6

January 7, 2016

Approved By:

Michael Dupay                                            01/07/16  
Print      Technical Reviewer      Signature                      Date

Terri Olson                                            01/07/16  
Print      QA Manager      Signature                      Date

Review of the SOP has been performed and the SOP still reflects current practice.

Initials: _____	Date: _____
Initials: _____	Date: _____
Initials: _____	Date: _____
Initials: _____	Date: _____

# Routine Level Metals Data Evaluation

## 1.0 Scope and Applicability

This SOP is intended as a guidance document for the routine level evaluation of metals data provided by laboratories to be used in Barr Engineering Company (Barr) projects.

This SOP is based on quality assurance elements, not the specific criteria, of *USEPA Contract Laboratory Program National Functional Guidelines (NFG) for Inorganic Data* and applies to routine metals data evaluation for analyses by the following technologies:

- Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES)
  - Method examples: EPA 200.7, EPA 6010
- Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)
  - Method examples: EPA 200.8, EPA 6020
- Cold Vapor Atomic Absorption (CVAA)
  - Method examples: EPA 245.1, EPA 7470, EPA 7471, SM 3112 B
- Cold Vapor Atomic Fluorescence Spectrometry (CVAF)
  - Method examples: EPA 245.7, EPA 1631 (low-level mercury), EPA 7474
- Thermal Decomposition / Atomic Absorption Spectrophotometer
  - EPA 7473
- Graphite Furnace Atomic Absorption (GFAA)
  - Method examples: EPA 7010, SM 3113 B
- Methods above in conjunction with Toxicity Characteristic Leachate Procedure (TCLP), EPA 1311
- Methods above in conjunction with Synthetic Precipitation Leachate Procedure (SPLP), EPA 1312

In the case of specific technologies and/or methods not listed above, the guidelines within this document will provide the basis upon which to make adequate professional judgment in the evaluation of data submitted for review.

The recommended procedures in this SOP should be followed unless conditions make it impractical or inappropriate to do so. Modifications should be noted in the applicable documentation and communicated to appropriate personnel. Significant changes may result in a revision or newly created SOP.

## 2.0 Limitations

- Level IV data evaluation is not covered in this SOP and should be performed in accordance with NFG or project specific requirements.

### 3.0 Responsibilities

The laboratory is responsible for generating data from the samples submitted for analysis. In instances where QC criteria are not met for the analysis of samples, the laboratory is responsible for reanalysis of the samples, provided reanalysis is possible (considering matrix interference, holding times and sample volume, etc.), or documenting the impact to the data.

The Data Quality Specialist is responsible for evaluating the data in accordance with this document, in addition to using professional judgment where necessary or appropriate. Project specific requirements, such as those specified in a Quality Assurance Project Plan (QAPP) or Sampling and Analysis Plan (SAP), may differ from these recommendations and professional judgment should be applied before qualifying any data.

### 4.0 Procedure

The Quality Assurance/Quality Control (QA/QC) data detailed below are the most typical found in a routine level laboratory report. Other QA/QC data may be provided by the laboratory within the laboratory report case narrative, data qualifiers, or cover sheet and should be evaluated using professional judgment (e.g., initial calibration, calibration verification, internal standards, post digestion, serial dilution).

Definitions to common QA/QC terms and terms used within this SOP along with a list of Barr 'Data Qualifiers/Footnotes' that may be applied during review can be found in Barr's "Compendium of Data Quality Assessment Documentation".

#### 4.1 Holding Time and Preservation

The purpose of holding time and preservation evaluation is to ascertain the validity of the analytical results based on the sample condition, preservation, and time elapsed between the date of sample collection and date of analysis.

40 CFR Part 136 and the *Test Methods for Evaluating Solid Waste (SW-846)* are used as guidance for the recommended holding time and preservation acceptance criteria listed in *Table 1*.

Table 1 – Recommended Holding Times and Preservation				
Compound	Matrix	Temp.	Preservative	Maximum Holding Time
Mercury	Aqueous	--	HNO <sub>3</sub> < 2 pH	28 days
	Aqueous (low level)	--	Pre-tested hydrochloric acid or bromine chloride	48 hours preserve or analyze if not oxidized in sample bottle/28 days preserve if oxidized in sample bottle 90 days analysis (from collection) if preserved
	Sediment/Soil	Cool, ≤ 6 °C	Ice	28 days
	Wipe/Air	--	NA	28 days

(Table 1 continued on next page)

<b>Table 1 – Recommended Holding Times and Preservation</b>				
<b>Compound</b>	<b>Matrix</b>	<b>Temp.</b>	<b>Preservative</b>	<b>Maximum Holding Time</b>
Mercury	TCLP	--	NA	28 days TCLP Extraction/ 28 days analysis
All other metals	Aqueous	--	HNO <sub>3</sub> < 2 pH	180 days
	Sediment/Soil	Cool, ≤ 6 °C	Ice	180 days
	Wipe/Air	--	NA	180 days
	TCLP	--	NA	180 days TCLP Extraction/ 180 days analysis

Note: When analyzing boron or silica, do not collect samples in borosilicate glass bottles.

If samples do not meet holding time, preservation and analysis recommendations in *Table 1*, consider qualification with an “h”. Other matrices, such as product samples (e.g. oil, waste rock, drill cores) may not be subjected to the same holding time recommendations.

If the sample was stored on ice upon collection and delivered to the laboratory the same day, the sample may exceed recommended temperature at the time of laboratory receipt. Professional judgment should be applied (considering temperature, matrix, magnitude of the exceedance, etc.) when evaluating the application of qualifiers when criteria are not met.

#### **Special considerations for low-level mercury**

Low-level mercury must be collected directly into a specially cleaned, pretested, fluoropolymer or glass bottle using sample handling techniques specially designed for collection of mercury at trace levels and preserved with pre-tested hydrochloric acid (required for methyl mercury) or bromine chloride. Samples not collected in the correct type of container may be qualified with an “h”. These samples may be shipped unpreserved provided:

- Sample is collected in a fluoropolymer or glass bottle.
- Bottle contains no headspace and is capped tightly.
- Sample temperature was maintained at ≤ 6 °C.
- Samples are preserved or analyzed within 48 hours or oxidized in the bottle within 28 days.

## **4.2 Blank Samples**

Blank sample evaluation is conducted to determine the existence and magnitude of target analyte contamination as a result of activities in the field during collection and transport or from inter-laboratory sources.

- For each matrix, at least one method blank should be prepared and analyzed with each sample delivery group (SDG), or each batch digested (whichever is more frequent). Evaluation pertains to the batch of samples analyzed with the method blank.
- Field or equipment blank collection and analysis frequency is project specific. Evaluation pertains to the field samples associated with the field or equipment, blank.

- Blank analyses may not have involved the same weights, volumes, or dilution factors as the associated samples. It may be easier to work with the raw data and/or convert the data to the same units for comparison purposes.
- Low-level mercury method requires at least three method blanks per run per analytical batch.

<b>Table 2 – Guidelines for Blank Contamination</b>	
<b>Sample Result</b>	<b>Recommended Action for Associated Data</b>
Non-detect	No action required
< 5x blank concentration	Qualify with 'b'
≥ 5x blank concentration	Use professional judgment

b = Reported value may be a potential false positive based on blank data evaluation procedures

Note: Other multipliers of the blank contamination may be used based on professional judgment (reporting to the MDL, common lab contaminant, etc.)

Professional judgment regarding the usability of the data should be used in cases where gross detections of target analytes are found in the blank sample. A number of factors may be considered including historical data, prior knowledge of the site conditions, target analytes involved, type of blank sample, etc. In such cases, it may be appropriate to qualify the affected data with '\*' (estimated value, QA/QC criteria not met) or '\*\*' (unusable value, QA/QC criteria not met).

### 4.3 Laboratory Control Samples (LCS) and Laboratory Control Sample Duplicate Samples (LCSD)

The laboratory control sample is used to monitor the overall performance of each step during analysis, including sample preparation. The LCS should be analyzed:

- Once every preparation batch (typically 20 or less samples of the same matrix).
- Once for each matrix.
- For low-level mercury, ongoing precision and recovery (OPR) samples are run before and after each analytical batch - quality control samples (QCS) should be from a different source and analyzed once per analytical batch.

Laboratory control samples contain a known amount of each target compound and the percent recoveries are evaluated based on the criteria within the laboratory report or project specific requirements. If criteria are not available, use guidance found in the NFG. Percent recoveries are calculated for accuracy and the relative percent difference (RPD) is calculated for precision (when an LCSD was analyzed). Accuracy and precision equations can be found in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation".

<b>Table 3 – Guidelines for Laboratory Control Samples</b>		
<b>Criteria</b>	<b>Recommended Action for Associated Data</b>	
	<b>Detect</b>	<b>Non-Detect</b>
%R and RPD > Upper Limit	Qualify with '**'	No qualification
%R < Lower Limit	Qualify with '*' or '**', use professional judgment	
%R and RPD within Limits	No qualification	

\* = Reported value is estimated and QA/QC criteria were not met

\*\* = Reported value is unusable and QA/QC criteria were not met

#### 4.4 Laboratory Duplicate Samples

Laboratory duplicate samples are separate aliquots of field samples analyzed to demonstrate acceptable method precision by the laboratory at the time of analysis. Field blanks and proficiency testing (PT) samples should not be used for duplicate analysis. The RPDs are calculated using the equation as provided in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation" and are not calculated where data are already qualified with b, U, <, or \*\*. RPD results are dependent on the homogeneity of the samples.

Duplicates should be analyzed (whichever is more frequent):

- One from each matrix (soil or water)
- One from each SDG

The MS/MSD duplicate pairs may be substituted for laboratory duplicates.

Laboratory acceptance criteria or project specific requirement are used to evaluate RPDs. If criteria are not available, use guidance found in NFG or use professional judgment when considering qualification of associated results.

Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. RPDs are typically only evaluated for samples where both the native and duplicate sample concentrations are greater than five times (>5x) the RL. In cases where either of the samples (native or duplicate) is non-detect for a parameter and the other corresponding sample has detectable concentrations much greater than five times (>5x) the RL, professional judgment should be used to determine if qualification is appropriate.

<b>Table 4 – Guidelines for Laboratory Duplicates</b>	
<b>% RPD</b>	<b>Recommended Action for Associated Data</b>
RPD < Upper Limit	No action is required
RPD > Upper Limit	Both results are ≤ 5x RL, no action is required
RPD > Upper Limit	Both results are > 5x RL, consider qualifying with '**'

\* = Reported value is estimated and QA/QC criteria were not met

## 4.5 Field Duplicate Samples

Field duplicate samples (also known as “masked” or “blind” duplicate samples) are used to demonstrate acceptable precision and reproducibility of the field and laboratory procedures. Frequency of collection is project specific. The RPDs are calculated using the equation as provided under precision in ‘Definitions’ from Barr’s “Compendium of Data Quality Assessment Documentation” and are not calculated where data is already qualified with b, U, <, or \*\*. RPD results are dependent on the homogeneity of the samples.

Acceptance criteria for field duplicate samples are subject to the professional judgment of the Data Quality Specialist but typically RPDs  $\leq$  30% for aqueous samples and  $\leq$  40% for soil and sediment samples are considered acceptable unless other project specific requirements are defined.

Higher RPDs are expected when results are at or near the reporting limits and are not always indicative of poor precision. RPDs are typically only evaluated for samples where both the native and duplicate sample concentrations are greater than five times ( $>5x$ ) the RL. In cases where either of the samples (native or field duplicate) is non-detect for a parameter and the other corresponding sample has detectable concentrations much greater than five times ( $>5x$ ) the RL, professional judgment should be used to determine if qualification is appropriate.

## 4.6 Matrix Spikes (MS) and Matrix Spike Duplicate (MSD) Samples

Matrix spike samples contain a known amount of a target compound and provide information about the effect of each samples’ matrix on the sample preparation procedures and analytical results. Matrix spikes are typically analyzed at the following frequencies:

- 1 (MS/MSD pair) in every 20 samples
- 1 per preparation batch per matrix
- 1 per SDG

However, the frequency may be project specific and the documents outlining the needs of the project (SAP, QAPP, etc.) should be reviewed. In some cases, MS/MSD analysis is not required.

The percent recoveries are evaluated based on the criteria within the laboratory report or project specific requirements. If a matrix spike recovery does not meet acceptance criteria and is not associated with a project sample, no further action is required unless other systematic evidence warrants qualification.

If the native concentration of a spiked sample is significantly greater than the spike added ( $>4x$ ), spike recovery cannot be accurately evaluated, therefore the criteria do not apply. Professional judgment should be used for percent recoveries nominally outside laboratory acceptance criteria prior to qualifying data.

If criteria are not available, use guidance found in the NFG. Percent recoveries of matrix spike (and matrix spike duplicate) samples should be calculated using the equation provided under accuracy in ‘Definitions’ from Barr’s “Compendium of Data Quality Assessment Documentation”.

Solid samples may have highly variable concentrations of target analytes and percent recoveries (%R) may be influenced by the sampling precision and inherent sample homogeneity. Professional judgment should be used for difficult matrices and the acceptance criteria adjusted accordingly.

<b>Table 5 – Guidelines for Matrix Spikes</b>		
<b>Criteria</b>	<b>Recommended Action for Associated Data</b>	
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While matrix spike duplicates are not required by all methods, if results for MSD analyses are reported, evaluate the RPD for MS and MSD pairs using the equation as provided under precision in 'Definitions' from Barr's "Compendium of Data Quality Assessment Documentation".

#### 4.7 Overall Assessment

The chain-of-custody should be reviewed to determine if the laboratory report matches the requested analyses and that project specific parameters were analyzed as requested. The narrative and other supporting documentation should be evaluated to ensure that sample condition was appropriately documented by the laboratory upon receipt. If available, historical data should be used to assist with data evaluation. Any additional anomalies should be documented and evaluated, if necessary.

#### 4.8 Total vs. Dissolved

Occasionally, the measurements for dissolved metals are equivalent to or greater than the associated results reported for the total metals analysis. When this occurs, the variation between the total and dissolved results may indicate that the majority of the target metals present in the sample were in the dissolved phase and normal analytical variability may account for the difference. Professional judgment should be used to determine if the variation is significant enough to be qualified.

#### 5.0 Quality Control and Quality Assurance (QA/QC)

Depending on the project objectives, the data review may include the completion of a Routine Level Quality Control Report (see Barr's "Compendium of Data Quality Assessment Documentation") as part of the evaluation process. Within each QC data section, the reviewer should include references to whether the QC data met or exceeded the acceptance criteria. The qualifiers, added, removed, or retained, should be documented. Where multiple qualifiers may be applicable to a sample/analyte result, professional judgment should be used to determine if all qualifiers are necessary or if one qualifier would be sufficient to represent the deviations. A statement as to whether the data are acceptable as reported or acceptable with qualification(s) should also be included. If revised reports are required and the revision affects the sample results, notification should be given to the appropriate data management personnel and/or project team members.



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