



## Appendix E

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### Data Validation Review

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## QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

In order to minimize the risks associated with cross-contamination, bias between sample locations, and to provide assurance that the data were acceptable for use, quality assurance/quality control measures were implemented throughout all phases of the program (e.g., field work, laboratory analysis, and report preparation). Examples of these measures are described below.

- Locations of the grab water samples collected during the 2014 sampling campaigns can be reference in **Figures 7 and 8**.
- Grab water samples were collected in accordance with:
  - The SOP for Surface Water Sampling, which was included in Appendix C of the Work Plan (MWH, 2013b);
  - The QAPP (MWH, 2013); and,
  - The CCME Protocols Manual for Water Quality Sampling in Canada (CCME, 2011).
- Sterile laboratory-supplied sample containers with appropriate preservatives were used for sampling. Containers were pre-labelled prior to sample collection.
- New 45-micron filters were used at each location that required dissolved analysis.
- Correct preservatives were added to the samples requiring preservation.
- Clean nitrile gloves were used during the field program and replaced frequently at every sample collection point.
- At each sample location, field parameters were measured using a calibrated YSI 556 or Pro Plus incorporated 6-Series Multi-parameter Water Quality Sonde to obtain values for pH, specific conductivity, temperature, total dissolved solids (TDS), salinity, dissolved oxygen (DO), oxidation/reduction potential (ORP). Turbidity was measured using a LaMotte 2020we portable turbidity meter.
- All instrumentation was calibrated in the field per manufacturers recommended specifications.
- An appropriately accredited/certified laboratory was used to conduct analytical testing.
- All samples were stored in ice-packed coolers during transportation to the laboratory and delivered under Chain-of-Custody.
- Trip blanks, blind field blanks and blind duplicate water samples were obtained each day and submitted with the location samples. The results of the blanks and duplicates are discussed in the sections below.
  - Field blank results indicate the possible contamination of samples due to ambient conditions at the site. Methylene chloride is a commonly used laboratory solvent and may be due to use in the laboratory even though not detected in the associated method blank. Metals are ubiquitous and many analytes are naturally occurring at the site. Detections in an associated sample within five times the concentration of the field blank may be due to site contamination.
- A Relative Percent Difference (RPD) within 25% was utilized as the limit for representativeness. When analytical values are less than five (5) times the detection limit (DL) or very low concentrations, RPD values can be disproportionate and

inapplicable for validation. RPD values which exceed 25% and 5 times detection limit are flagged in **Table 3**.

- Laboratory does some or all of the following based on the method being analyzed: method blank (MB) to determine potential laboratory contamination, laboratory control standard (LCS) or certified reference material (CRM) to determine if calibration is valid and standard is still reliable and as a check for matrix spike (MS) since there is no matrix interference, laboratory duplicate (LD) to check sample handling and matrix, MS to check for potential matrix effects on analytes.
- Analytical results and QA/QC reports were reviewed for completion, outliers, concerns and QA/QC comments. Any identified concerns were discussed with the laboratory and results were verified.

## 1.1 Assessment Limitations

Due to the challenges associated with the remote locations and safety concerns of working near water, surface water quality samples were collected depending on access options. Sampling was conducted by landing a helicopter near the sampling location and walking to the water body for sample collection. These samples were obtained close to the edges of the water bodies.

*Note: QA/QC criteria vary by method. Only site specific QA/QC are discussed.*

## 1.2 Surface Water Quality – Parameter Specific QA/QC Reviews

### 1.2.1 Routine Parameters

The data validation review of routine parameters can be found in the QA/QC Summary (**Table 1**). All cooler temperatures met acceptance criterion on receipt at the laboratory. Specific conductance and pH do not have temperature requirements. All other analytes have temperature requirements.

Some short holding time parameters <10 days did not meet holding times. This is due to shipping timeframes and reliance on air transportation cargo from Norman Wells where passengers receive higher priority than cargo. Additionally, the laboratory states that regulatory hold times for nitrate and nitrite in Alberta are prescribed at 48 hours. This guideline dictates that all nitrate and nitrite water samples had exceeded their hold times upon arrival from Norman Wells, but were analyzed anyway.

Routine parameters found above laboratory detection in field blanks for 2014 sampling events can be found in **Table 4**. Field blank results indicate the possible contamination of samples due to ambient conditions at the site. Methylene chloride is a commonly used laboratory solvent and may be due to use in the laboratory even though not detected in the associated method blank. Metals are ubiquitous and many analytes are naturally occurring at the site. Detections in an associated sample within five times the concentration of the field blank may be due to site contamination.

All MS and MB met laboratory acceptance criteria with the exception of those not evaluated due to high analyte background in the parent sample.

Ion balance results outside acceptable 70-130% range included HSKY\_014 (165%), HSKY\_016 (159%), HSKY\_081 (164%), HSKY\_008 (462%), HSKY\_042 (150%), all sampled on September 19, 2014.

### 1.2.2 Total and Dissolved Metals

Mercury and hexavalent chromium are the only metals with temperature criteria. The data validation review of total and dissolved metals can be found in the QA/QC Summary (**Table 1**).

Metals found above laboratory detection in field blanks for 2014 sampling events can be found itemized in **Table 4**.

There were numerous cases of total metals with results less than their dissolved metals counterparts (**Appendix C-2**). These results were checked and validated by the laboratory. Below is an excerpt from ALS's Quality Control Protocols (May 8, 2012) which explains why this situation can occur.

*"Total versus Dissolved Metals ("D > T" Check) – One of the most important and common relational checks we do is a check for situations where Dissolved Metal concentrations significantly exceed Total Metal concentrations. By definition, this situation should not occur. However, there are a few reasons why this can occur:*

- I. Circumstances where Dissolved Metals slightly exceed Total Metals are expected in a small percentage of samples, simply due to normal random variability. In fact, when all metals in a test sample exist in the dissolved form, we expect that Dissolved Metals measurements will numerically exceed Total Metals measurements exactly half the time (by a small margin), simply due to random chance.*
- II. Samples to be analyzed for Dissolved Metals must be filtered, which is normally done in the field. Filtration processes are a common source of low level metals contaminants. Contamination of a sample during filtration is the most common source of significant D>T issues.*
- III. Field samples for Dissolved and Total Metals are normally collected independently, so variability of the sampling process is another common cause of D > T issues."*

### 1.2.3 CCME Hydrocarbons, VOCs, and PAHs

The data validation review of CCME hydrocarbons, VOCs and PAHs can be found in the QA/QC Summary (**Table 1**). PHCs, VOCs, and/or PAHs found above laboratory detection in field blanks for 2014 sampling events can be found itemized in **Table 4**.

### 1.2.4 Glycol and Methanol

The data validation review of glycols and methanol parameters can be found in the QA/QC Summary (**Table 1**). All glycol and methanol data validation measures were met without exception in 2014.

## 1.3 Summary

Based on the QA/AC of the data collected, it has been concluded that the data is of acceptable quality.

Table 1: Summary of QA/QC Review for 2014 Data

QA/QC Methods		Criteria	Routine Parameters		Metals (Total and Dissolved)		PHCs and VOCs		PAHs		Glycol and Methanol	
			2014 June	2014 Sept	2014 June	2014 Sept	2014 June	2014 Sept	2014 June	2014 Sept	2014 June	2014 Sept
Laboratory	Did <b>sample temperature</b> upon receipt at laboratory meet the recommended criteria?	Less than 10°C	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	Did <b>holding times</b> meet recommended criteria?	Appendix G	N: See Table 2	N: See Table 2	Y	N: See Table 2	Y	Y	Y	Y	Y	Y
	Does <b>Laboratory Control Standard (LCS)/Certified Reference Material (CRM)</b> meet laboratory acceptance criteria?	Appendix G	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
	Do the <b>Matrix Spikes (MS)</b> meet laboratory acceptance criteria?	Appendix G	Y	N	Y	Y	N	Y	Y	Y	Y	Y
	Do the <b>Laboratory Duplicates (LD)</b> meet laboratory acceptance criteria?	Appendix G	N	Y	Y	Y	Y	Y	Y	Y	Y	Y
	Do all <b>surrogates</b> met laboratory acceptance criteria?	Appendix G	Shaded	Shaded	Shaded	Shaded	Y	Y	Y	Y	Y	Y
	Were all analytes below DL in the <b>Method Blanks (MB)</b> ?	Appendix G	Y	Y	Y	Y	Y	Y	Y	Y	Y	Y
Field	Are the Relative Percent Difference (RPD) below 25% and less than 5 times detection limit (DL) for <b>field duplicates</b> ?	Appendix C	N: See Table 3	N: See Table 3	N: See Table 3	N: See Table 3	Y	Y	Y	Y	Y	Y
	Were all analytes below laboratory reporting limits in the <b>field blanks</b> ?	Appendix D-X	N: See Table 4	N: See Table 4	N: See Table 4	N: See Table 4	Y	N: See Table 4	N: See Table 4	Y	Y	Y
	Were all analytes below laboratory reporting limits in the <b>trip blanks</b> ?	Appendix D-X	Shaded	Shaded	Shaded	Shaded	Y	Y	Shaded	Shaded	Shaded	Shaded

Legend:

- Y Meets criteria
- N Does not meet criteria
- Shaded Not Applicable

**Table 2: Summary Holding Time Exceedances**

Parameter	Holding Time	Recommended Holding Time	Sample Location
<i>June 2014</i>			
Nitrate, Nitrite	46 – 77 hours	48 hours (AB)	ALL SAMPLES
Hexavalent Chromium	70 – 77 hours	24 hours	HSKY_011, HSKY_035, HSKY_037, HSKY_080, HSKY_017, HSKY_019, HSKY_038, HSKY_005, HSKY_015, HSKY_036, HSKY_018, HSKY_003, HSKY_043, HSKY_070
Routine	70 – 77 hours	48 hours	HSKY_011, HSKY_035, HSKY_037, HSKY_080, HSKY_017, HSKY_019, HSKY_038, HSKY_005, HSKY_015, HSKY_036, HSKY_018, HSKY_003, HSKY_043, HSKY_070
Turbidity	70 – 77 hours	48 hours	HSKY_011, HSKY_035, HSKY_037, HSKY_080, HSKY_017, HSKY_019, HSKY_038, HSKY_005, HSKY_015, HSKY_036, HSKY_018, HSKY_003, HSKY_043, HSKY_070
<i>September 2014</i>			
Nitrate, Nitrite	94 – 103 hours	48 hours (AB)	ALL SAMPLES
Hexavalent Chromium	94 – 103 hours	24 hours	HSKY_025, HSKY_037, HSKY_017, HSKY_080, HSKY_019, HSKY_028, HSKY_026, HSKY_039, HSKY_036, HSKY_018, HSKY_027, HSKY_003, HSKY_029, HSKY_070, HSKY_043, HSKY_013, HSKY_032, HSKY_071, HSKY_011, HSKY_035, HSKY_014, HSKY_002, HSKY_016, HSKY_081, HSKY_023, HSKY_009, HSKY_008, HSKY_015, HSKY_042, HSKY_033, HSKY_001b, HSKY_072, HSKY_038, HSKY_005, HSKY_006, HSKY_007, HSKY_030, HSKY_040, HSKY_031, HSKY_082,
Turbidity	94 – 101 hours	48 hours	HSKY_043, HSKY_013, HSKY_032, HSKY_071, HSKY_011, HSKY_035, HSKY_014, HSKY_002, HSKY_016, HSKY_081, HSKY_023, HSKY_009, HSKY_008, HSKY_015, HSKY_042, HSKY_033

Samples within the 080's range are field duplicates.  
 Samples within the 070's range are field blanks.

**Table 3: Summary of Duplicates – Results >5X DL & >25% RPD**

Sample Location	Parameter	Detection Limit	Unit	Normal	Field Duplicate	RPD
<i>June 2014</i>						
HSKY_031	Total suspended solids	1	mg/L	10	32	104.8%
HSKY_031	Turbidity	0.5	NTU	7.2	12.4	53.1%
HSKY_031	Aluminum (Total)	0.002	mg/L	0.188	0.511	92.4%
HSKY_031	Iron (Total)	0.1	mg/L	1.0	1.8	57.1%
HSKY_031	Zinc (Total)	0.001	mg/L	0.009	0.012	28.6%
HSKY_038	Total suspended solids	3	mg/L	69	422	143.8%
HSKY_038	Turbidity	0.5	NTU	43.8	149	109.1%
HSKY_038	Aluminum (Total)	0.002	mg/L	1.53	0.198	154.2%
HSKY_038	Iron (Total)	0.1	mg/L	2.2	3.3	40.0%
HSKY_038	Manganese (Total)	0.005	mg/L	0.038	0.090	81.3%
HSKY_038	Zinc (Total)	0.001	mg/L	0.022	0.032	37.0%
HSKY_039	Total suspended solids	3	mg/L	444	341	26.2%
HSKY_039	Turbidity	0.5	NTU	184	39.2	129.7%
HSKY_039	Zinc (Total)	0.001	mg/L	0.086	0.056	42.3%
<i>September 2014</i>						
HSKY_016	Turbidity	0.2	NTU	17.9	39.8	75.9%
HSKY_016	Aluminum (Total)	0.004	mg/L	0.68	1.48	74.1%
HSKY_016	Cadmium (Total)	0.000016	mg/L	0.000084	0.000214	87.2%
HSKY_016	Iron (Total)	0.1	mg/L	1.9	4.3	77.4%
HSKY_016	Manganese (Total)	0.005	mg/L	0.052	0.095	58.5%
HSKY_016	Silicon (Total, as Si)	0.032	mg/L	2.88	3.83	28.3%
HSKY_016	Titanium (Total)	0.001	mg/L	0.013	0.030	79.1%
HSKY_038	Ammonia (total, as N)	0.02	mg/L	0.10	0.13	26.1%
HSKY_038	Dissolved organic carbon (DOC)	1	mg/L	17	23	30.0%
HSKY_038	Total suspended solids	2	mg/L	30	491	177.0%
HSKY_038	Manganese (Total)	0.005	mg/L	0.055	0.076	32.1%

Table 4: Summary of Detections in Field Blanks

Parameter	Recovery	Date Sampled	Field Identification
<i>June 2014</i>			
Naphthalene	0.00006 mg/L	6/13/2014	HSKY_070
Naphthalene	0.00003 mg/L	6/14/2014	HSKY_071
2-Methylnaphthalene	0.00002 mg/L	6/13/2014	HSKY_070
2-Methylnaphthalene	0.00002 mg/L	6/14/2014	HSKY_071
Total Aluminum	<b>0.036 mg/L</b>	6/13/2014	HSKY_070
Total Aluminum	<b>0.016 mg/L</b>	6/14/2014	HSKY_071
Total Aluminum	0.008 mg/L	6/15/2014	HSKY_072
Total Zinc	0.007 mg/L	6/13/2014	HSKY_070
Total Zinc	0.006 mg/L	6/14/2014	HSKY_071
Total Zinc	0.013 mg/L	6/15/2014	HSKY_072
Mercury Dissolved	0.007 µg/L	6/13/2014	HSKY_070
pH	6.30	6/13/2014	HSKY_070
pH	6.15	6/14/2014	HSKY_071
pH	6.28	6/15/2014	HSKY_072
Phenols	0.033 mg/L	6/13/2014	HSKY_070
Phenols	0.002 mg/L	6/14/2014	HSKY_071
Phenols	0.005 mg/L	6/15/2014	HSKY_072
Ammonia, Total (as N)	0.02 mg/L	6/14/2014	HSKY_071
Nitrogen – Total Kjeldahl (TKN)	0.1 mg/L	6/14/2014	HSKY_071
<i>September 2014</i>			
Chloroform	0.008 mg/L	9/17/2014	HSKY_070
Chloroform	0.006 mg/L	9/19/2014	HSKY_071
Chloroform	0.006 mg/L	9/20/2014	HSKY_072
Dissolved Tin	0.0011 mg/L	9/17/2014	HSKY_070
Dissolved Organic Carbon (DOC)	2 mg/L	9/17/2013	HSKY_070
Dissolved Organic Carbon (DOC)	1 mg/L	9/19/2014	HSKY_071
Dissolved Organic Carbon (DOC)	1 mg/L	9/20/2014	HSKY_072
Total Tin	0.0004 mg/L	9/17/2014	HSKY_070
Total Aluminum	<b>0.006 mg/L</b>	9/19/2014	HSKY_071
Ammonia, Total (as N)	2.74 mg/L	9/17/2014	HSKY_070
Ammonia, Total (as N)	0.09 mg/L	9/19/2014	HSKY_071
Turbidity	0.64 NTU	9/17/2014	HSKY_070
Total Kjeldahl Nitrogen	4.2 mg/L	9/17/2014	HSKY_070
Total Kjeldahl Nitrogen	0.3 mg/L	9/19/2014	HSKY_071
Total Kjeldahl Nitrogen	0.2 mg/L	9/20/2014	HSKY_072

**Bold** = Exceedance