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Evaluation of Background Metal Concentrations for Shallow Groundwater in Alberta

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1.0 INTRODUCTION

Millennium EMS Solutions Ltd. (MEMS) was retained by Petroleum Technology Alliance Canada (PTAC) to develop a database of background concentrations for metals in shallow groundwater in Alberta. The database will aid industry and consultants to understand the typical ranges of background concentrations of metals in Alberta shallow groundwater and provide context for situations when metal concentrations in groundwater samples exceed generic guideline values. Groundwater in unconsolidated material within 20 metres of ground surface was considered to be shallow. Metals occur naturally in Alberta groundwater but can also be present as a result of contamination. In Alberta, the generic Tier 1 Soil and Groundwater Remediation Guidelines (AEP 2016) are a screening tool used in the evaluation of whether metal concentrations at a site are a result of contamination. The metals considered in this document are the seventeen metals included under the "metals" heading in tables in the Alberta Tier 1 guidelines document. Metals that are considered "major ions" such as sodium, calcium and magnesium are not included. The seventeen metals considered in this document are as follows:

- Aluminum;
- Antimony;
- Arsenic;
- Barium;
- Boron;
- Cadmium;
- Chromium;
- Copper;
- Iron;
- Lead;
- Manganese;
- Mercury;
- Nickel;
- Selenium;
- Silver;
- Uranium; and
- Zinc.

It is not uncommon for background metal concentrations in Alberta groundwater to exceed Tier 1 guideline values. In some instances, this situation can be reconciled by collecting site-specific background data; however, collecting sufficient data to get meaningful values for background levels can be challenging at some sites. The current work will provide a useful tool in evaluating such situations and may facilitate a determination of whether a particular Tier 1 exceedance is likely to be related to background conditions.

2.0 OBJECTIVES AND SCOPE OF WORK

The overall objective of this project is to develop distributions for the natural concentration of background metals in shallow Alberta groundwater.

It has been suggested that releases of produced water containing high concentrations of sodium could potentially mobilize other metals by cation exchange. An additional project objective was added to investigate this question by seeking any correlations between metal concentrations in shallow groundwater and produced water releases.

The scope of work for this project included the following tasks:

- identify a population of analytical data for shallow groundwater and incorporate into a database;
- consult with different analytical laboratories to determine protocols used for the analysis of metals in groundwater samples and identify whether differences in analytical protocols could affect data quality and consistency;
- develop and apply techniques for screening out non-background data points that are or may be affected by anthropogenic impacts;
- generate distributions and related statistics on background metal concentrations;
- develop correlations between metals and chloride concentrations for the full dataset; and
- generate a report summarizing the findings.

3.0 METHODOLOGY

3.1 Description of the Database

The initial dataset consisted of metal concentrations in groundwater samples from environmental impact assessments, environmental site assessments, groundwater monitoring, and remediation and reclamation activities in Alberta. The dataset is stored in an SQL server ESdat database. At the time of analysis, the database contained data sampled between April 1988 and July 2016.

Metals data within the database were primarily received from five laboratories in Alberta, including Access Analytical Laboratories Inc., AGAT Laboratories, ALS Environmental, Exova and Maxxam Analytics. Current protocols for the analysis of trace metals in groundwater samples by the five laboratories were evaluated to determine whether different analytical protocols could significantly affect data quality and consistency between laboratories. Other than for mercury, iron and manganese, all five laboratories used EPA methods 200.8 or 6020 for determining dissolved metal concentrations in groundwater, both methods use inductively coupled plasma-mass spectrometry (ICP-MS). For iron and manganese analysis, the analytical methods used by the five laboratories included EPA 6010 B or SM 3120 B, both of which use inductively coupled plasma-atomic emission spectrometry (ICP-AES). Based on the use of similar analytical methods by the different laboratories, large differences in data quality are not expected between the five laboratories for the parameters mentioned above.

For mercury analysis, the analytical methods used by the five laboratories included the following: SM 3112B, EPA 245.7 or EPA 1631. Method SM 3112B, uses manual cold vapour atomic absorption spectroscopy (CVAAS) to measure mercury concentrations (Smith 2008). For the EPA methods, EPA 245.7 uses cold vapour atomic fluorescence spectroscopy (CVAFS) and EPA 1631 uses purge and trap CVAFS to measure mercury concentrations (Smith 2008). The method calibration range for SM 3112B is the most limited of the three methods at approximately 0.001 to 0.005 mg/L. This range is above the Tier 1 guideline of 5×10^{-6} mg/L. The operating range for EPA method 245.7 is approximately 5×10^{-6} mg/L to 1×10^{-4} mg/L. EPA method 1631 has the lowest detection limit of the three methods of approximately 5×10^{-7} mg/L, with an upper limit of 1×10^{-4} mg/L. Of the three methods, EPA 1631 is the only analytical method with a detection limit below the Tier 1 guideline.

Based on the different methods used for mercury analysis by the five labs, variable detection limits are expected in the dataset. Generally, the method of choice for mercury analysis should be based on the detection limit required and the purpose of the assessment. For example, if mercury concentration is required for a risk assessment, a method with a low detection limit may be more useful than a method with a higher detection limit which yields a high non-detect value. Additionally, methods for mercury analysis with detection limits above the Tier 1 guideline may not be useful when comparing non-detect values to the Tier 1 guideline.

3.2 Data Screening Methods

Two groups of data screening processes were used to remove data points not related to background conditions. The first group of processes involved steps that could be applied to the dataset as a whole, removing unsuitable data points based on metadata contained in the database, such as location, lithology and concentrations of other chemicals. This group of processes is referred to herein as global screening. A second group of processes, referred to herein as site-specific screening,

involved looking at the site setting of selected key data points to ensure that they were genuine background values. These two groups of processes are described in more detail below.

3.2.1 Global Screening Methods

Global screening of the full groundwater dataset was performed using the steps described below. Monitoring wells meeting any of the following conditions were screened out of the database:

- groundwater analytical results from sites outside Alberta;
- anomalous data (*e.g.,* data entered as a concentration range);
- data with no dissolved metals concentrations;
- data associated with a chloride concentration of greater than 100 mg/L (assumed to indicate anthropogenic impact);
- data associated with detectable benzene, ethylbenzene, xylenes, F1 or F2 hydrocarbon fractions (assumed to indicate anthropogenic impact). Toluene was not used for screening out data since it may also be elevated due to naturally occurring organic matter;
- data associated with detectable concentrations of sulfolane and naphthenic acid, which were assumed to indicate anthropogenic impact;
- data associated with barium concentrations in exceedance of 1 mg/L since barium is a common component of drilling mud and, thus, a common contaminant at oil and gas sites. The screening value of 1 mg/L was derived based on background groundwater values reported previously (Alberta Health 2014, Fitzgerald 2001) and is consistent with the Tier 1 guideline for barium in groundwater (AEP 2016);
- data outside the pH range of 6.5 to 9.0. The Tier 1 pH range for groundwater is between 6.5 and 8.5; however, a review of literature showed only 63.3 to 77% of data from domestic water wells in Alberta fall within the Tier 1 range of 6.5 to 8.5 (Fitzgerald et al. 2001, Alberta Health 2014). In comparison, 98.8 % of domestic water wells fall within the range of 6.5 to 9.0 (Alberta Health 2014);
- data associated with sulphur storage sites. The mobilization of metals from soil due to acidification from sulphuric acid at sulphur storage sites is well documented;
- data associated with SAGD (steam assisted gravity drainage) plant sites. The thermal mobilization of metals due to elevated temperatures used for the SAGD process is well documented;
- data associated with nitrate concentrations greater than 3 mg/L. The range of nitrate concentrations in the full dataset range from non-detect (<0.003 to <0.25) to 1,240 mg/L. The screening value of 3 mg/L was used based on Fitzgerald *et al.* (2001) and Madison and Brunett (1985) who note that groundwater samples with nitrate concentrations above 3 mg/L are likely

anthropogenic. This value is consistent with the Tier 1 guideline for nitrate in groundwater (AEP 2016).

The following data were retained in the database for screened-in samples:

- analytical data for dissolved metals;
- analytical data for all other available parameters;
- sample identification;
- sample location; and
- sample date.

3.2.2 Site Specific Screening Methods

Site specific screening of groundwater data was completed for the database following the global screening steps (Section 3.2.1). The site specific screening was performed as follows:

- The data remaining after the global screening steps were completed were used to generate an interim histogram for each metal using the data analysis tool in Excel and automatic bin size generation.
- The histograms were used to identify high outliers, with any data separated by more than two empty bins being flagged as potential outliers.
- Groundwater data for each metal were sorted from lowest to highest concentration.
- A detailed review was performed for each metal starting at the highest concentration (including flagged outliers). The review identified any possible remaining concerns for anthropogenic influence for a given sample location. If a given datapoint was questionable, it was rejected and consideration given to the next highest point in the dataset. This process was continued until a maximum background concentration could be identified with high confidence. Once a maximum background concentration was identified with high confidence, a detailed review was not performed on the remaining (lower) background data. The sources of information used to perform the detailed review included borehole logs, site diagrams, summary tables and report text.

Data points considered in the site-specific screening step are summarized for each metal in Appendix B, where the rationale for including or rejecting each value is provided.

Any metals data not consistent with a background location or associated with wells completed within bedrock were screened out of the database. For wells with multiple sampling events, if any of the events suggested the well could have been affected by anthropogenic impacts, the data for that well was screened out of the database.

The site-specific screening step ensured that the maximum value in the background distribution for each metal could be identified as a genuine background concentration with a high degree of confidence.

3.2.3 Statistical Methods

In order to facilitate the calculation of statistical parameters (including mean, median, 25th percentile, 75th percentile, 95th percentile, minimum and maximum concentrations) non-detect data (below reported detection limit [RDL]) was substituted with ½ RDL.

4.0 RESULTS

The full dataset, before screening, consisted of 25,982 unique groundwater samples. Once potentially impacted samples had been removed *via* the global screening steps, 835 unique samples remained. A summary of the reduction in available data points from the various global screening steps is provided in Table 1 below.

Table 1 Summary of Global Screening Steps

Screening Step	Number of Data Points	Number of Sites
Number of results for groundwater monitoring wells	25,982	198
Number of results for dissolved metal concentrations	5,758	89
Number of results remaining after samples with chloride concentrations greater than 100 mg/L were screened out	4,474	82
Number of results remaining after samples with detectable benzene, ethylbenzene, xylenes, F1 and F2 hydrocarbon concentrations were screened out	4,038	82
Number of results remaining after samples with detectable naphthenic acid or sulfolane were screened out	3,837	82
Number of results remaining after samples with barium concentrations greater 1 mg/L were screened out	3,155	78
Number of results remaining after samples with pH <6.5 and >9.0 were screened out	3,051	77
Number of results remaining after sulphur storage sites were screened out	2,974	75
Number of samples remaining after samples associated with SAGD sites were screened out	914	53
Number of samples remaining after samples with nitrate concentrations greater than 3 mg/L were screened out	835	42

Once the global screening steps were completed, the remaining data was screened using the site specific screening steps (Section 3.2.2). The highest concentration of each metal was examined in the remaining dataset and samples that could not unequivocally be associated with background conditions were rejected until a maximum background value could be identified. The number of background samples identified in the dataset following the site specific screening steps ranged from 412 to 815 for the different metals.

Summary statistics for 15 of the 17 Tier 1 metals, following the global and site specific screening steps, are presented in Appendix C; and selected key values for these metals are summarized in Table 2 below. Summary statistics are not presented for barium since a barium concentration of 1 mg/L was used as a screen to remove groundwater samples assumed to include drilling mud (Section 3.2.1). Summary statistics are also not presented for mercury since all background mercury samples were below detection limits. The maximum background metal concentration identified for each metal after global and site specific screening of the database is discussed below for each of the 16 metals (including mercury, excluding barium).

4.1 Aluminum

A maximum background dissolved aluminum concentration in groundwater of 3.04 mg/L and a 95th percentile value of 0.305 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline range of 0.023 to 0.1 mg/L (pH dependent) for agricultural and other land uses. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background near the southwestern boundary of the site and approximately 200 m upgradient of the nearest area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened from 3.0 to 6.0 metres below ground surface (m bgs) in silty clay and clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum aluminum concentration was identified was 3 mg/L. A deeper well at the same location, screened between 14.5 to 16.0 m bgs in silty clay and clay till, had a maximum aluminum concentration of 1.0 mg/L and a maximum chloride concentration of 14 mg/L. Based on low chloride concentrations and no other evidence of impacts, there is a high level of confidence that the aluminum concentration of 3.04 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of aluminum concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.2 Antimony

A maximum background dissolved antimony concentration in groundwater of <0.005 mg/L was identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The detection limit of 0.005 mg/L is below the Tier 1 guideline of 0.006 mg/L for agricultural and other land uses.

A histogram and statistics illustrating the distribution of antimony concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.3 Arsenic

A maximum background dissolved arsenic concentration in groundwater of 0.037 mg/L and a 95th percentile value of 0.0093 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples impacted, or potentially impacted by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.005 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location northeast of a pipeline release and approximately 100 m cross-gradient from the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 8.5 to 10 m bgs in silty clay soil. Lateral delineation to below Tier 1 levels was obtained between this well and the localized hydrocarbon and salt impacts at the release location. The maximum chloride concentration measured at the monitoring well where the maximum arsenic concentration was identified was 3 mg/L. A shallower well at the same location, screened between 3.0 to 4.5 m bgs in sand, had a maximum arsenic concentration of 0.000142 mg/L and a maximum chloride concentration of 9 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the arsenic concentration of 0.037 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of arsenic concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.4 Boron

A maximum background dissolved boron concentration in groundwater of 0.50 mg/L and a 95th percentile value of 0.35 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are below the Tier 1 guideline of 1 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location south of a wellsite, approximately 100 m upgradient of the nearest identified area with anthropogenic impacts

exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 10.5 to 12.0 m bgs in clayey silt. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater salt impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum boron concentration was identified was 3 mg/L. A shallower well at the same location, screened between 4.0 to 5.5 m bgs in silt, had a maximum boron concentration of 0.03 mg/L and a maximum chloride concentration of <1 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the boron concentration of 0.5 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of boron concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.5 Cadmium

A maximum background dissolved cadmium concentration in groundwater of 0.00158 mg/L and a 95th percentile value of 0.000696 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline range of 0.00004 to 0.00037 mg/L (hardness dependent) for agricultural and other land uses. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background near the southwestern boundary of the site and approximately 100 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 18.5 and 20.0 m bgs in silty clay and clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum cadmium concentration was identified was 14 mg/L. A shallower well at the same location, screened between 3.0 to 6.0 m bgs in silty clay and clay till, had a maximum cadmium concentration of 0.00138 mg/L and a maximum chloride concentration of 12 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the cadmium concentration of 0.00158 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of cadmium concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.6 Chromium

A maximum background dissolved chromium concentration in groundwater of 0.0070 mg/L and a 95th percentile value of 0.0025 mg/L (unspeciated chromium, insufficient data were available for trivalent and hexavalent chromium) were identified from the database, once the global and site-

specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum value is above the Tier 1 guideline of 0.0049 mg/L (for trivalent chromium) for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location south of a pipeline-right-of-way and approximately 100 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 10.5 to 12 m bgs in clay till. Lateral delineation was obtained between this well and localized groundwater salinity impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum chromium concentration was identified was 5 mg/L. A shallower monitoring well at the same location, screened from 3.0 to 4.5 m bgs in clay till, had a maximum chromium concentration of <0.001 mg/L and a maximum chloride concentration of 5 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the chromium concentration of 0.0070 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of chromium concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.7 Copper

A maximum background dissolved copper concentration in groundwater of 0.020 mg/L and a 95th percentile value of 0.0061 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum value was above the Tier 1 guideline of 0.007 mg/L for agricultural and other land uses and the 95th percentile was just below the Tier 1 guideline. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background approximately 50 m cross-gradient from the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 3.0 to 4.5 m bgs within silty clay/silty sand. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum copper concentration was 3 mg/L. A deeper well at the same location, screened between 14.5 to 16.0 m bgs in silty clay and clay till, had a maximum copper concentration of 0.0060 mg/L and a maximum chloride concentration of 14 mg/L. Based on low chloride concentrations and no other evidence of impacts, there is a high level of confidence that the copper concentration of 0.020 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of copper concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.8 Iron

A maximum background dissolved iron concentration in groundwater of 58.8 mg/L and a 95th percentile value of 21.4 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.3 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background approximately 100 m cross-gradient of a pipeline release and the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 3.0 to 4.5 m bgs in silty clay. Lateral delineation to below Tier 1 levels was obtained between this well and the localized salt and hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum iron concentration was identified was <1 mg/L. A deeper well at the same location, screened between 6.0 to 7.5 m bgs in silty clay, had a maximum iron concentration of 41.4 mg/L and a maximum chloride concentration of 1 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the iron concentration of 58.8 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of iron concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.9 Lead

A maximum background dissolved lead concentration in groundwater of 0.0154 mg/L and a 95th percentile value of 0.0025 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected or potentially affected by anthropogenic impacts (see Appendix B). The maximum value is above the Tier 1 guideline range of 0.001 to 0.007 mg/L (hardness dependent) for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location south of a pipeline-right-of-way and approximately 100 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 10.5 to 12 m bgs in clay till. Lateral delineation was obtained between this well and localized groundwater salinity impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum lead concentration was identified was 5 mg/L. A shallower monitoring well at the same location, screened from 3.0 to 4.5 m bgs in clay till, had a maximum lead concentration of <0.001 mg/L and a maximum chloride concentration of 5 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the lead concentration of 0.0154 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of lead concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.10 Manganese

A maximum background dissolved manganese concentration in groundwater of 4.12 mg/L and a 95th percentile value of 2.34 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.05 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location north of a wellsite, approximately 100 m cross-gradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 4.0 to 5.5 m bgs in silty soil. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater salt impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum manganese concentration was identified was 2 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the manganese concentration of 4.12 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of manganese concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.11 Mercury

A maximum background dissolved mercury concentration in groundwater of <0.0001 mg/L was identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The detection limit of 0.0001 mg/L is above the Tier 1 guideline for total mercury of 0.000005 mg/L for agricultural and other land uses.

A histogram and statistics illustrating the distribution of mercury concentrations in background shallow groundwater in Alberta are not provided since all background mercury concentrations present in the database are below their RDLs. The RDLs for mercury in the screened data ranged from 0.000002 mg/L to 0.0001 mg/L.

4.12 Nickel

A maximum background dissolved nickel concentration in groundwater of 0.060 mg/L and a 95th percentile value of 0.025 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum value of 0.060 mg/L is above the lower limit of the hardness

dependent Tier 1 guideline range of 0.037 to 1.52 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background near the southwestern boundary of the site and approximately 200 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 3.0 to 6.0 m bgs in silty clay and clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum nickel concentration was identified was 3 mg/L. A deeper well at the same location, screened between 14.5 to 16.0 m bgs in silty clay and clay till, had a maximum nickel concentration of 0.021 mg/L and a maximum chloride concentration of 14 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the nickel concentration of 0.060 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of nickel concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.13 Selenium

A maximum background dissolved selenium concentration in groundwater of 0.011 mg/L and a 95th percentile value of 0.003 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.001 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in the M.D. of Greenview No. 16. This sample was obtained from a location south of a pipeline-right-of-way and approximately 100 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 10.5 to 12 m bgs in clay till. Lateral delineation was obtained between this well and localized groundwater salinity impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum selenium concentration was identified was 5 mg/L. A shallower monitoring well at the same location, screened from 3.0 to 4.5 m bgs in clay till, had a maximum selenium concentration of 0.002 mg/L and a maximum chloride concentration of 5 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the selenium concentration of 0.011 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of selenium concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.14 Silver

A maximum background dissolved silver concentration in groundwater of 0.00026 mg/L and a 95th percentile value of 0.000125 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.0001 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background near the southwestern boundary of the site and approximately 200 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 14.5 to 16.0 m bgs in silty clay and clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum silver concentration was identified was 14 mg/L. A shallower well at the same location, screened between 3.0 to 6.0 m bgs in silty clay and clay till had a maximum silver concentration of <0.00006 mg/L and a maximum chloride concentration of 3 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the silver concentration of 0.00026 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of silver concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.15 Uranium

A maximum background dissolved uranium concentration in groundwater of 0.030 mg/L and a 95th percentile value of 0.019 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum and 95th percentile values are above the Tier 1 guideline of 0.01 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located in Red Deer County. This sample was obtained from a location identified as background approximately 50 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines near a pipeline release. The sample was collected from a well which was screened between 3.5 to 5.0 m bgs in clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum uranium concentration was identified was 8 mg/L. Based on the low chloride concentration and no evidence of impacts, there is a high level of confidence that the uranium concentration of 0.030 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of uranium concentrations in background shallow groundwater in Alberta are provided in Appendix C.

4.16 Zinc

A maximum background dissolved zinc concentration in groundwater of 0.063 mg/L and a 95th percentile value of 0.025 mg/L were identified from the database, once the global and site-specific screening processes had excluded samples affected, or potentially affected by anthropogenic impacts (see Appendix B). The maximum value is above the Tier 1 guideline of 0.03 mg/L for agricultural and other land uses. The sample with the maximum confirmed background value was located at an active sour gas plant in the M.D. of Greenview No. 16. This sample was obtained from a location identified as background near the southwestern boundary of the site and approximately 200 m upgradient of the nearest identified area with anthropogenic impacts exceeding Tier 1 guidelines. The sample was collected from a well which was screened between 3.0 to 6.0 m bgs in silty clay and clay till. Lateral delineation to below Tier 1 levels was obtained between this well and the localized groundwater hydrocarbon impacts at the site. The maximum chloride concentration measured at the monitoring well where the maximum zinc concentration was identified was 3 mg/L. A deeper well at the same location, screened between 14.5 to 16.0 m bgs in silty clay and clay till, had a maximum zinc concentration of 0.025 mg/L and a maximum chloride concentration of 14 mg/L. Based on low chloride concentrations and no evidence of impacts, there is a high level of confidence that the zinc concentration of 0.063 mg/L represents background conditions.

A histogram and statistics illustrating the distribution of zinc concentrations in background shallow groundwater in Alberta are provided in Appendix C.

5.0 DISCUSSION

5.1 Provincial Coverage for Verified Background Data

The distribution of sample locations following the global and site specific screening steps is shown in Figure 1. As can be seen, the dataset provides fair provincial coverage, but is biased towards the western half of the province where much of the conventional oil and gas activity occurs.

5.2 Discussion of Findings

The starting point for this project was a database of groundwater samples from environmental site investigational and other activities across the province. Global screening steps removed any samples associated with common contaminants, as well as processes known or suspected to potentially cause metal contamination (*e.g.* thermal mobilization of metals at SAGD sites). Site specific screening steps were used to examine the highest concentrations in the remaining dataset, rejecting samples that

could not unequivocally be associated with background conditions until a maximum background value could be identified.

Statistical data for the resulting background metal distributions in shallow Alberta groundwater are summarized in Table 2 below, along with the Tier 1 guideline value for each metal. The number of data points for each metal ranged from 412 to 815. All maximum background metal concentrations identified from the database were associated with locations identified as background in their respective investigations. Maximum background metal concentrations were well below their respective Tier 1 guideline value for antimony and boron. Maximum background concentration for nickel was slightly above the lower limit of the Tier 1 guideline range of 0.037 to 1.52 mg/L, suggesting background concentrations would be below Tier 1 guidelines except occasionally for samples with low hardness values. Maximum background concentrations were above their respective Tier 1 guideline value for aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, selenium, silver, uranium and zinc. Therefore, background concentrations of these metals may exceed the Tier 1 guideline at some sites within Alberta. The maximum background concentration for mercury was below the RDL of 0.0001 mg/L; however, this detection limit is above the Tier 1 guideline for mercury.

Table 2 Statistical Summary for Background Metal Distributions in Alberta Groundwater (mg/L)

Metal	Tier 1 Guideline	Background Metal Concentration			
		Maximum	95th Percentile	Mean	Number of samples
Aluminum	0.023 to 0.1 (varies with pH)	**3.04**	**0.305**	**0.073**	797
Antimony	0.006	<0.005	NC	NC	776
Arsenic	0.005	**0.037**	**0.0093**	0.0021	790
Boron	1	0.50	0.35	0.10	784
Cadmium	0.00004 to 0.00037 (varies with hardness)	**0.00158**	**0.00070**	**0.00015**	814
Chromium (unspeciated)	0.0049 (trivalent)	**0.007**	0.003	0.001	601
Copper	0.007	**0.020**	0.006	0.002	791
Iron	0.3	**58.8**	**21.4**	**2.8**	815
Lead	0.001 to 0.007 (varies with hardness)	**0.0154**	0.0025	0.0005	803
Manganese	0.05	**4.12**	**2.34**	**0.62**	794
Mercury	0.000005 (for total mercury)	*<0.0001*	NC	NC	412

Table 2 Statistical Summary for Background Metal Distributions in Alberta Groundwater (mg/L)

Metal	Tier 1 Guideline	Background Metal Concentration			
		Maximum	95th Percentile	Mean	Number of samples
Nickel	0.037 to 1.52 (varies with hardness)	**0.060**	0.025	0.007	800
Selenium	0.001	**0.0110**	**0.0030**	0.0008	795
Silver	0.0001	**0.00026**	**0.00013**	0.00004	796
Uranium	0.01	**0.030**	**0.019**	0.005	774
Zinc	0.03	**0.063**	0.025	0.008	790

Bolded and underlined values indicate concentrations above the Tier 1 guideline value
Italicized values indicate RDL is above the Tier 1 guideline value
NC, not calculated

Histograms and associated statistics for background metal concentrations in Alberta are shown in Appendix C. Most metals show artificially elevated frequencies in the histograms for their lowest metal concentrations due to substitution of data below the RDL with ½ RDL. As is evident from the histograms, the Tier 1 guideline is distinctly higher than the distributions of background antimony and boron concentrations. The highest background concentrations of aluminum, arsenic, cadmium, chromium, copper, iron, lead, manganese, nickel, selenium, silver, uranium and zinc exceeded their respective Tier 1 guidelines.

5.3 Comparison to Other Studies in Alberta

The Alberta Centre for Toxicology, in collaboration with Alberta Health, performed testing on more than 36,000 domestic well water samples in Alberta from 2002 to 2008, including 249 samples tested for trace elements in raw water samples (Alberta Health 2014). One of the objectives of the program was to provide baseline information on the distribution of physical and chemical properties of domestic well waters. Average well depths in the study were approximately 45 m; however, the study noted that no correlations were observed between well depth and the levels of any of the parameters examined (Alberta Health 2014). Raw water samples were collected from the kitchen tap, after purging for 5 minutes, if the water was not treated. Raw water samples were collected from the well head, after purging for 5 minutes, if a water treatment system was in place. Filtering or preservation of the raw water samples was not conducted in the field.

Maximum metal concentrations reported by the above mentioned study for domestic water wells are summarized in Table 3. The results from the current study are also included in Table 3 for reference. Both Alberta Health (2014) and the present study reported maximum metal concentrations that

exceed their respective Tier 1 guideline for aluminum, arsenic, chromium (unspeciated), copper, iron, lead, manganese, nickel and zinc. Maximum concentrations for cadmium and silver also exceeded their respective Tier 1 guideline in the present study. With the exception of iron, manganese and selenium, maximum metal concentrations reported in the current study were generally one to two orders of magnitude below those reported in the Alberta Health (2014) study. Iron, manganese and selenium concentrations were within the same order of magnitude for both studies.

Table 3 Maximum Groundwater Metal Concentrations Reported by Alberta Health (2014) for Domestic Water Wells (mg/L)

Metal	Tier 1 Guideline	Maximum Concentration Alberta Health (2014)	Maximum Concentration Current Study
Aluminum	0.023 to 0.1 (varies with pH)	**18.2**	**3.04**
Antimony	0.006	**0.34**	<0.005
Arsenic	0.005	**0.46**	**0.037**
Boron	1	**1.64**	0.50
Cadmium	0.00004 to 0.00037 (varies with hardness)	<0.001	**0.00158**
Chromium (unspeciated)	0.0049 (trivalent)	**34.2**	**0.007**
Copper	0.007	**1.19**	**0.020**
Iron	0.3	**107**	**58.8**
Lead	0.001 to 0.007 (varies with hardness)	**0.76**	**0.0154**
Manganese	0.05	**3.23**	**4.12**
Mercury	0.000005 (for total mercury)	0.004	<0.0001
Nickel	0.037 to 1.52 (varies with hardness)	**0.13**	**0.060**
Selenium	0.001	**0.03**	0.0110
Silver	0.0001	<0.001	**0.00026**
Uranium	0.01	Not available	**0.030**
Zinc	0.03	**4.4**	**0.063**

Bolded and underlined values indicate concentrations above the Tier 1 guideline value
NC, not calculated

5.4 Correlations Between Chloride and Metal Concentrations

Produced water releases may occur at oil and gas facilities. Produced water can contain high concentrations of sodium, chloride, other major ions, and trace metals. Correlations between chloride and Tier 1 metal concentrations in groundwater were examined in the full dataset prior to screening out impacted samples. Any positive correlations would suggest that either: i) the metal is a

significant component in produced water, or ii) that high concentrations of sodium in produced water mobilized the metal via ion exchange. The results of this assessment are summarized in Appendix D. The results show a linear correlation between sodium and chloride concentrations, ($R^2 = 0.82$), as would be expected for produced water impacts. No other significant correlations were observed between chloride and Tier 1 metals for the groundwater dataset indicating that metals do not appear to be mobilized into shallow groundwater by produced water releases.

6.0 DATA GAPS AND UNCERTAINTY

Factors affecting the level of uncertainty associated with the data presented in this report are discussed below.

The dataset of background groundwater samples on which the distributions were based were comprised of approximately 412 to 815 samples for the different metals. While a greater number of samples would improve the statistical results, the number of samples available is assumed to be sufficient to include the majority of variability in shallow groundwater across the province.

The spatial coverage of samples available in this project is provided in Figure 1. Most areas of the province are represented, however the potential exists for different distributions in areas that are not represented.

Global screening methods were used in this work to reject any samples which appeared to have elevated levels of anthropogenic contaminants typically associated with oil and gas activities (including chloride, petroleum hydrocarbons and process chemicals). This step is expected to remove the majority of instances of groundwater samples impacted with anthropogenic metals on the assumption that anthropogenic metals will typically be associated with other contaminants. However, this relatively broad brush screening step will likely have removed some samples that had background concentrations of metals since the presence of chloride, petroleum hydrocarbons or process chemicals will not always be associated with anthropogenic metals.

There is a high level of confidence that the concentration identified as the maximum background groundwater value for each metal is a true background value. However, since the site-specific screening process rejected many samples based on not being able to definitively exclude the possibility of anthropogenic impact, it is likely that some samples were rejected that did in fact represent background conditions.

It was not practical within the scope of this project to make a site-specific evaluation of each of the samples included in the background dataset. Site-specific evaluation efforts were focused on identifying a maximum value that represented background conditions for each metal with a high degree of confidence. It is therefore possible that the distribution of background concentrations for

each metal contains some values that could include anthropogenic impacts. However, it is expected that the global screening steps will have eliminated the majority of these, and any impact on the distributions presented in Appendix C will be minor.

Natural background metal concentrations in groundwater can vary substantially between sites, depending largely on the nature of the geological material in contact with the groundwater. Caution should therefore be exercised when extrapolating the results described in this report to other sites. Sound professional judgement is required when evaluating whether elevated metal concentrations in groundwater are anthropogenic or natural in origin.

7.0 ACKNOWLEDGEMENTS

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8.0 CLOSURE

We trust that the information presented herein meets your requirements. Should you have any questions, please call either of the undersigned at 403.592.6180.

Yours truly,

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