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Development of a Reduced Analytical Suite of Upstream Oilfield Metals for Groundwater Monitoring

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Introduction

Current analytical techniques allow for convenient and simultaneous analysis of a wide range of metals in environmental samples. Groundwater monitoring programs at upstream oil and gas wellsites in Alberta often track a large number of individual metals, many of which have no known connection to oilfield operations. Some of these metals will exceed Tier 1 groundwater guidelines from time to time as a result of natural variations in background concentrations, and potentially distract the focus of the groundwater monitoring program from the metals that could be related to wellsite operations. Potential sources of anthropogenic metals in shallow groundwater at oil and gas wellsites include disposal of drilling fluids and unintended releases of formation water. This project develops, with rationale, a reduced suite of metals relevant to groundwater monitoring at oil and gas wellsites.

Methodology

Available data were compiled on the likely range of concentrations of each to the Tier 1 metals in i) drilling fluids, ii) formation waters, and iii) unimpacted (background) shallow groundwater. Each of the Tier 1 metals was assessed relative to these data to determine whether there was sufficient justification to include it in the analytical suite for monitoring shallow groundwater at oil and gas wellsites.

Results

The recommended suite of metals for groundwater monitoring at oil and gas wellsites is summarized in Table A. Metals with Tier 1 groundwater guidelines for which it is not considered necessary to analyze include aluminum, antimony, cadmium, lead, mercury, silver, and uranium.

It should be noted that the range of shallow groundwater background concentrations for all these metals include the Tier 1 groundwater guideline. For this reason, a significant number of false positive guideline exceedances are to be expected. Consulting Figure 2 will give a qualitative sense of the likelihood of a false positive exceedance for each metal.

Table A	**Recommended Suite of Metals for Groundwater Monitoring at Oil and Gas Wellsites**
Arsenic	Iron
Barium	Manganese
Boron	Nickel
Chromium	Selenium
Copper	Zinc

1.0 INTRODUCTION

Current analytical techniques (e.g., ICP-MS) allow for convenient and simultaneous analysis of a wide range of metals in environmental samples. Perhaps for this reason, groundwater monitoring programs at upstream oil and gas wellsites in Alberta often track a large number of individual metals, many of which have no known connection to oilfield operations. Some of these metals will exceed Tier 1 groundwater guidelines from time to time as a result of natural variations in background concentrations, and potentially distract the focus of the groundwater monitoring program from the metals that could be related to wellsite operations. For convenience, the term "Tier 1 groundwater guideline" is used in this document to refer to the lowest Tier 1 guideline for any land use, i.e., the lowest value for a particular metal in Table 2 of ESRD (2014a).

Metals could potentially be released to groundwater via wellsite activities including disposal of drilling fluids, unintended release of produced formation water and degradation of released hydrocarbons or other organic chemicals. This project compiles information relevant to these activities on the seventeen metals (excluding major ions) included in the Alberta Tier 1 guidelines (Table 1), and also compiles information on background levels of the metals in shallow groundwater. The project develops, with rationale, a reduced suite of metals relevant to groundwater monitoring at oil and gas wellsites.

Table 1 Alberta Tier 1 Groundwater Metals

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

1.1 Objectives and Scope of Work

The overall objective of this project is to determine, with rationale, a reduced suite of metals relevant to groundwater monitoring at oil and gas wellsites.

The scope of work of this project relates to conventional oil and gas wellsites in Alberta and is as follows:

- Determine which of the Tier 1 metals are could be present in significant concentrations in drilling fluids.
- Determine which of the Tier 1 metals are could be present in significant concentrations in produced formation waters.
- Identify metals that could be released to shallow groundwater as a result of anaerobic biodegradation of organic chemicals.
- Summarize any other information that can put concentrations of the Tier 1 metals into context.
- Determine the typical range of background concentrations of each of the Tier 1 metals in shallow groundwater in Alberta.
- Develop a reduced suite of metals in shallow groundwater that are relevant to oil and gas wellsite operations.
- Generate a report summarizing the findings.

1.2 Applicability

The work summarized in this document is intended to apply to shallow groundwater monitoring activities at oil and gas wellsites based on typical activities that occur at such facilities. Gas plants and other upstream facilities are excluded since they may have a much wider range of activities occurring, and the information presented herein will not be sufficient to exclude the possibility of a wider range of anthropogenic metals being present in shallow groundwater. Thermal facilities are excluded since the injection of heat into the subsurface can change the geochemistry and concentrations of trace metals in shallow groundwater.

1.3 Acknowledgements

This work was made possible by funding from Petroleum Technology Alliance Canada (PTAC) under project number #13-AU-SGRC-04. Thanks to James Agate, the CAPP project sponsor for liaison with industry contacts and other important contributions to the project. Thanks also to Marquis Alliance for providing chemical analysis of the metals content of a wide range of drilling mud components.

2.0 METALS IN DRILLING FLUIDS

2.1 Introduction

Drilling fluids, also known as drilling muds, are synthetic fluids that are circulated down the drill string and back up the wellbore annulus during drilling operations. They serve a range of functions, including the following:

- Bringing drill cuttings to the surface and suspending them when drilling is paused;
- Creating sufficient hydrostatic pressure to contain formation fluids (oil and gas) within the formation;
- Preventing the swelling of unstable clay minerals in shale formations;
- Sealing porous formations;
- Cooling and lubricating the drill bit;
- Inhibiting corrosion; and,
- Inhibiting biofouling.

Typically a drilling fluid will be tailored to a particular well to account for formation type, well depth, formation fluid pressure, and other well-specific conditions. Drilling fluids therefore vary from well to well, and may comprise a wide range of possible ingredients.

Once the well has been completed, current and historical practices often involve the spent drilling fluid remaining on site either mixed with surrounding soil and buried, or via a number of other allowable practices. This raises the possibility of any trace metals present in drilling fluid eventually reaching shallow groundwater. For this reason, a survey of the trace metal composition of drilling mud components was carried out.

Chemical analysis of the metals content of a total of 314 drilling mud components was kindly provided for review by Marquis Alliance. The data are proprietary, however, permission was granted to present the data in summary form.

2.2 Approach

The approach to summarizing the trace metal composition of drilling mud components was as follows. Firstly, for each trace metal, the highest concentration of the metal in any drilling mud component was noted. Then this maximum concentration was compared to the Tier 1 soil remediation guideline for that trace metal, and a ratio calculated (Table 2).

Ratios less than 1.0 (mercury, silver and uranium, Table 2) indicated situations where no drilling mud component analyzed had a concentration exceeding the Tier 1 soil remediation guideline. Disposal of

drilling mud will therefore not result in soil concentrations in the receiving environment exceeding Tier 1 values.

Ratios between 1 and 10 (antimony, arsenic, cadmium, lead) were given additional consideration. For each component where the ratio of maximum concentration to Tier 1 soil guideline was between 1 and 10, an assessment was made of the way in which that drilling mud component would be used. A few drilling mud components, including weighting agents (e.g. barite) and viscosifiers (e.g., bentonite) can comprise a significant proportion of an overall drilling mud. However, most components (e.g., corrosion inhibitors, deflocculants, sulphide scavengers and many more) only ever form a minor part of an overall drilling mud. None of the drilling mud components that had metal ratios in the range 1 to 10 would comprise more than 10% of a drilling mud, and therefore disposal of drilling mud will therefore not result in soil concentrations in the receiving environment exceeding Tier 1 values for these metals.

Ratios between above 10 (barium, boron, chromium, copper, nickel, selenium, zinc, Table 2) indicate situations where disposal of drilling mud could potentially result in soil concentrations in the receiving environment exceeding Tier 1 values.

Maximum concentrations and ratios are summarized in Table 2. Table 3 indicates for each metal the type of component that has the highest concentration of a given metal.

2.3 Conclusions

Metals that are not a concern, either because the maximum concentration is less than the Tier 1 soil guideline or the maximum concentration is less than 10x the Tier 1 soil guideline and the product would only be used as <10% of a drilling mud system include:

- Antimony;
- Arsenic;
- Cadmium;
- Lead;
- Mercury;
- Silver; and,
- Uranium.

Metals that are a potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline include :

- Barium;

- Boron;
- Chromium;
- Copper;
- Nickel;
- Selenium; and,
- Zinc.

Table 2 Drilling Mud Components – Maximum Trace Metal Concentrations and Ratio to Tier 1 Soil Guidelines

Metal	Maximum Concentration	Tier 1 Soil Guideline	Ratio
	(mg/kg)	(mg/kg)	
Aluminum	no data	-	-
Antimony	64.2	20	3.2
Arsenic	96.3	17	5.7
Barium	19200	750	26
Boron	1940	2	970
Cadmium	9.32	1.4	6.7
Chromium	1360	64	21
Copper	15333	63	240
Iron	no data	-	-
Lead	102	70	1.5
Manganese	no data	-	-
Mercury	1.76	6.6	0.3
Nickel	46636	50	930
Selenium	16.2	1	16
Silver	12.2	20	0.6
Uranium	9.9	23	0.4
Zinc	561000	200	2,800

Notes:
"Maximum concentration" is the concentration in the drilling mud component that has the highest concentration of that metal
"Ratio" is maximum concentration/Tier 1 soil guideline

Table 3 Drilling Mud Components with Highest Metals Concentrations	
Metal	**Product Type**
Aluminum	Sulphide scavenger
Antimony	Lost circulation additive
Arsenic	Lost circulation additive
Barium	Weighting agent
Boron	Deflocculant
Cadmium	Deflocculant
Chromium	Mica
Copper	Deflocculant
Iron	no data
Lead	Drilling system
Manganese	no data
Mercury	nr
Nickel	Deflocculant
Selenium	Impurity in KCl
Silver	nr
Uranium	nr
Zinc	Sulphide scavenger

Notes:
nr = not relevant: maximum concentration is below Tier 1 soil guideline value

3.0 METALS IN PRODUCED FORMATION WATERS

3.1 Introduction

Hydrocarbons are produced from a wide range of formations in the Western Canada Sedimentary Basin. The formations from which most of the production is extracted range in age from Cambrian to Cretaceous (Mossop and Shetson, 1994; Hay, 1994; Bernatsky, 1998). Producing oil and/or gas wells yield variable proportions of formation water in addition to the hydrocarbons. Unintended releases of these produced formation waters can occur at wellsites, and therefore an understanding of the chemistry of these waters can be important to an understanding of potential for anthropogenic trace metals appearing in shallow groundwater.

Mesozoic formation waters in the Western Canada Sedimentary Basin are typically moderately saline (TDS approximately 10,000 to 20,000 mg/L), while paleozoic formation waters are often highly saline or brines (TDS 70,000 to 210,000 mg/L). Mean formation water salinity for nine primary oilfield hydrologic units in Saskatchewan are summarized in Table 4.

Table 4 Formation Water Salinity – Western Canada Sedimentary Basin in Saskatchewan

Hydrologic Unit	Period	Average TDS (mg/L)	n	Salinity Classification
Upper Cretaceous	Cretaceous	11,393	159	Saline
Mannville Group	Cretaceous	15,913	385	Saline
Jurassic	Jurassic	13,387	309	Saline
Madison Group	Carboniferous	114,182	968	Brine
Saskatchewan Group	Devonian	77,720	245	Saline
Manitoba Group	Devonian	132,378	64	Brine
Elk Point Group	Devonian	201,259	83	Brine
Silurian	Silurian	207,533	42	Brine
Deadwood	Cambrian	147,451	55	Brine

Source: Bernatsky (1998)

Most formation waters are predominantly sodium chloride, with minor calcium, potassium, sulphate and bicarbonate (Bernatsky, 1998).

3.2 Available Data

Very limited published information is available concerning trace metal concentrations for formation waters in the Western Canada Sedimentary Basin. Enquires and requests to industry members for unpublished information did not yield any data.

Hitchon et al. (1977) indicate that the mean and maximum boron concentration in Alberta Mesozoic formation waters are 15.7 mg/L and 86 mg/L, respectively, while the mean and maximum boron

concentration in Alberta Paleozoic formation waters are 101 mg/L and 920 mg/L, respectively. These values are approximately 3x to 180x the Canadian drinking water guideline for boron (5 mg/L).

Smedley and Kinniburgh (2002) report one instance of an arsenic concentration of 0.23 mg/L in a sodium bicarbonate formation water from a 1,000 m deep oilfield well in Alberta (formation not specified). This is 23x the Canadian drinking water guideline for arsenic (0.01 mg/L).

Additional data on the concentration of trace metals in formation waters of the Western Canada Sedimentary Basin were not found.

3.3 Approach

Bernatsky (1998) indicates that sea water is an important precursor of most formation waters. The mean concentrations of selected major ions and Tier 1 metals in modern sea water are summarized in Table 5. Modern seawater has a salinity of approximately 35 parts per thousand (ppt). The upper limit of salinity for brines is approximately 359 ppt (the salinity of a saturated sodium chloride solution). Brines are produced by the evaporation of sea water or the dissolution of evaporites (which in turn are produced by the evaporation of seawater). If the simplistic assumption is made that the Tier 1 metals are concentrated during these processes to the same extent as the major ions and the overall salinity, then it is possible to make a very rough estimate of the maximum concentration of Tier 1 metals in brines by multiplying the sea water concentrations by 359/35 (column 2 in Table 5). However, this simplistic analysis does not account for mean seawater concentrations changing over geological time and changes in concentration due to chemical and diagenetic changes. Comparison of the concentrations in column 2 of Table 5 with the limited available metals data available from formation water analyses summarized in Section 3.2 suggests that the processes actually occurring are more complicated than those assumed in this simplistic analysis.

For practical purposes, though, it is noted that releases of produced water are normally easily identified by a sodium chloride signature. A quick examination of the data in Table 5 show that concentrations of sodium and chloride in modern seawater exceed Tier 1 guideline values by a factor of approximately 50 to 200, while of the Tier 1 metals, only boron exceeds its Tier 1 guideline value (by a factor of ~10). This confirms the practical experience of managing produced water releases in Alberta, that the releases can generally be managed on the basis of sodium and chloride concentrations, with boron as a more minor concern, and other Tier 1 metals rarely being significant in relation to the major ion salinity.

In the absence of a better dataset of metals concentrations in formation water from the Western Canada Sedimentary Basin, it is proposed to use the following criteria. Tier 1 metals considered to be potentially significant in produced water are those with:

1. mean concentrations in modern sea water that are at least 10% of the Tier 1 groundwater guideline; or,
2. any metals with literature data for formation water concentrations from the Western Canada Sedimentary Basin that exceed Tier 1 guideline values.

3.4 Conclusions

Using the approach indicated in Section 3.3, and the data in Table 5 results in the following list of Tier 1 metals that are potentially significant in produced formation water releases:

- Arsenic;
- Boron;
- Cadmium; and,
- Selenium.

Table 5 Mean Modern Seawater Concentrations and Extrapolated Maximum Brine Concentrations for Selected Major Ions and Tier 1 Metals			
Metal	**Mean Seawater Concentration [a] (mg/L)**	**Extrapolated Maximum Brine Concentration [b] (mg/L)**	**Tier 1 Groundwater Guideline (mg/L)**
Selected Major Ions			
Sodium	11,071	113,560	200
Magnesium	425	4,357	-
Calcium	1,325	13,593	-
Potassium	410	4,209	-
Chloride	19,917	204,292	100
Sulphate	2,767	28,383	500
Bicarbonate	141	1,449	-
Tier 1 Metals			
Aluminum	5.6E-05	5.70E-04	0.05 [c]
Antimony	2.0E-04	2.06E-03	0.006
Arsenic	1.8E-03	1.82E-02	0.005
Barium	1.6E-02	1.59E-01	1
Boron	4.6E+00	4.75E+01	0.5
Cadmium	6.9E-05	7.12E-04	0.00016 [d]
Chromium	2.1E-04	2.20E-03	0.0089
Copper	2.0E-04	2.01E-03	0.007
Iron	2.9E-05	2.95E-04	0.3
Lead	2.1E-06	2.19E-05	0.0032 [d]
Manganese	1.7E-05	1.74E-04	0.05
Mercury	2.1E-07	2.12E-06	0.000005
Nickel	4.8E-04	4.96E-03	0.052 [d]
Selenium	1.4E-04	1.42E-03	0.001
Silver	2.2E-06	2.28E-05	0.0001
Uranium	3.0E-03	3.0E-02	0.015
Zinc	3.4E-04	3.45E-03	0.03

Notes:
a. Bruland and Lohan (2004); Emsley (2001).
b. See text
c. For pH >= 6.5
d. Evaluated at a hardness of 100 mg/L and 400 mg/L

4.0 METALS RELEASED VIA BIODEGRADATION OF ORGANIC CHEMICALS

Organic chemicals, including petroleum hydrocarbons and organic process chemicals may be released into the subsurface as a result of upstream oil and gas activities. Many of these chemicals degrade quite readily in subsurface soils and groundwater (e.g., ESRD, 2014a). Based on thermodynamic considerations, biodegradation will typically take place initially using any dissolved oxygen as the terminal electron acceptor (TEA). As the dissolved oxygen becomes depleted, biodegradation may proceed using a series of increasingly less thermodynamically favoured TEAs. These include nitrate, iron (III), manganese (IV), sulphate and carbon dioxide.

Under iron-reducing conditions, insoluble iron (III) from soil minerals gets reduced to soluble iron (II) species and increases the concentration of dissolved iron in groundwater. Similarly, under manganese-reducing conditions, insoluble manganese (IV) from soil minerals gets reduced to soluble manganese (II) species and increases the concentration of dissolved manganese in groundwater. It is therefore clear that upstream oil and gas activities can result in increases in the concentrations of iron and manganese in groundwater, and that these metals should be included in any analytical suite intended for monitoring groundwater quality at upstream facilities.

5.0 ABUNDANCE OF TIER I METALS IN EARTH MATERIALS

The typical concentrations of Tier 1 metals in US soils and global crustal materials are included in Table 6 for context.

Table 6 Mean Metal Concentrations in Soils and Crustal Material

Metal	Mean Concentration in US Soils [a]	Mean Concentration in Earth's Crust [b]
	(mg/kg)	(mg/kg)
Aluminum	72,000	82,000
Antimony	2.3	0.2
Arsenic	7.2	2.1
Barium	580	340
Boron	33	8.7
Cadmium	nd	0.15
Chromium	54	140
Copper	25	68
Iron	26,000	63,000
Lead	19	10
Manganese	550	1,100
Mercury	0.089	0.067
Nickel	19	90
Selenium	0.39	0.05
Silver	nd	0.08
Uranium	2.7	1.8
Zinc	60	79

Source::

a. Shacklette and Boerngen (1984).

b. Webelements (2015)

nd = no data

6.0 BACKGROUND CONCENTRATIONS OF METALS IN SHALLOW GROUNDWATER

6.1 Rationale

Tier 1 groundwater guidelines are calculated based on standard risk-based principles including exposure rates and toxicity thresholds for a range of exposure pathways and receptors. Tier 1 groundwater guideline values for some metals can fall within the typical range for background

concentrations for shallow groundwater in Alberta. Before taking any action based on measured concentrations of metals in groundwater, it is important to be able to put those concentrations in the context of typical background values for shallow groundwater in Alberta.

6.2 Methodology

To this end, some preliminary data analysis was conducted on groundwater samples in the Millennium analytical database. Screening techniques were used to exclude samples with any indications of anthropogenic impact. Starting from the complete set of groundwater chemistry data available in March 2014, the data screening/interpretation steps were as follows.

- Samples with screened depths deeper that 10 m were excluded (this analysis is focussed on shallow groundwater).
- Samples with chloride concentration >100 mg/L were excluded (based on these samples possibly representing anthropogenic impact from a release of produced formation water).
- Samples with detectable BTEX, F1, F2, or process chemicals (methanol, amines, glycols) were excluded (based on these samples indicating anthropogenic impact).
- Metals recorded as below detection limit in a given sample were assumed to be present at the detection limit.

Statistical parameters for the distribution of background concentrations for each of the Tier 1 metals are summarized in Table 7.

The Tier 1 groundwater guidelines for metals presented in Table 7 are the lowest of the Tier 1 groundwater guidelines for any exposure pathway or land use. Note that, in the calculation of Tier 1 groundwater guidelines for metals for the aquatic life and protection of domestic use aquifer exposure pathways, no allowance is made for any attenuation that may occur between source and exposure point, and thus these Tier 1 guidelines are conservative relative to actual receptor exposure and risk.

Note also that the guidelines for cadmium, lead, and nickel are calculated as a function of hardness (ESRD, 2014a,b). Hardness data for groundwater samples were also extracted from the Millennium analytical dataset using the same screening techniques noted above. The guidelines presented in Table 7 are evaluated at a hardness of 100 mg/L (representing approximately the 5th percentile of the hardness dataset), and 400 mg/L (the greatest hardness for which guidelines are available in ESRD (2014b) and still below the mean hardness value from the dataset (630 mg/L).

Table 7 Background Concentrations of Metals in Groundwater - Statistics					
Metal	**Mean**	**95th Percentile**	**Maximum**	**n (number of data points)**	**Tier 1 Groundwater Guideline**
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Aluminum	**0.160**	**0.699**	**3.14**	247	0.05 [a]
Antimony	0.00066	0.00200	0.00800	112	0.006
Arsenic	0.00367	**0.0130**	**0.0350**	385	0.005
Barium	0.325	0.826	**39.9**	446	1
Boron	0.289	**1.55**	**2.14**	456	0.5
Cadmium	**0.00058**	**0.00186**	**0.0188**	190	0.00016-0.00037 [b]
Chromium	0.00313	0.00679	**0.0115**	59	0.0089
Copper	0.00605	**0.0208**	**0.210**	366	0.007
Iron	**10.9**	**19.0**	**1330**	491	0.3
Lead	0.00137	**0.00432**	**0.0220**	93	0.0032-0.007 [b]
Manganese	**1.54**	**5.25**	**150**	809	0.05
Mercury	**0.00247**	**0.0102**	**0.0390**	19	0.000005
Nickel	0.0263	**0.0600**	**0.835**	331	0.052-0.17 [b]
Selenium	**0.118**	**0.700**	**4.42**	148	0.001
Silver	0.00009	**0.00034**	**0.00069**	34	0.0001
Uranium	**0.0154**	**0.0686**	**0.310**	373	0.015
Zinc	0.0229	**0.0917**	**0.520**	303	0.03

Notes:
Values in red exceed the Tier 1 groundwater guideline (or the lower of the two values presented)

a. For pH >= 6.5
b. Evaluated at a hardness of 100 mg/L and 400 mg/L

6.3 Results

The distributions of background shallow groundwater metals concentrations are illustrated graphically in Figure 1. Figure 2 illustrates the range of background concentrations for each metal relative to the Tier 1 groundwater guideline (using the figure evaluated at a hardness of 100 mg/L for

hardness-dependant metals). Thus, in Figure 2, a value of 1.0 represents a concentration at the Tier 1 groundwater guideline (indicated by the red line), while a value of 10 represents a concentration 10x the Tier 1 guideline.

Overall, it is clear from Figure 1 that the background concentrations of all the Tier 1 metals vary over several orders of magnitude. In addition, it is clear from Figure 2 that, for all Tier 1 metals, the Tier 1 guideline lies within the range of natural variation in background conditions. Thus, when analysis of metals in shallow groundwater yields concentrations that exceed Tier 1 guideline values, this does not necessarily imply anthropogenic impact, and Figure 2 may be of value in a qualitative determination of the likelihood of a particular concentration being related to background.

7.0 METAL BY METAL ASSESSMENT

In this section, the Tier 1 metals are considered in turn to summarize the relevant information and make a determination as to whether there is good reason to include each in shallow groundwater analysis at wellsites.

7.1 Aluminum

Aluminum is a major component of aluminosilicate minerals and makes up approximately 7-8% of crustal materials and soils (Table 6). However, under normal environmental conditions it has limited solubility, and is present in modern seawater at concentrations 3 orders of magnitude below the Tier 1 guideline (Table 5), implying a low likelihood of impact from releases of formation water. The mean background concentration, of aluminium in shallow groundwater is above Tier 1 groundwater guideline values (Table 7 and Figure 2) raising the likelihood of frequent false positive detections when analyzing aluminium in shallow groundwater. For these reasons, it is not considered necessary or desirable to analyze aluminium in shallow groundwater at typical upstream oil and gas wellsites.

7.2 Antimony

Antimony was not flagged as a metal of environmental concern in drilling fluids (Section 2), and its concentration in modern seawater is 1.5 orders of magnitude below the Tier 1 guideline (Table 7), implying a low likelihood of impact from releases of formation water. For these reasons, it is not considered necessary or desirable to analyze antimony in shallow groundwater at typical upstream oil and gas wellsites.

7.3 Arsenic

Arsenic was not identified as being present in drilling fluids at concentrations of concern (Section 2). However it was measured in one sample of formation water at a concentration well above the Tier 1 groundwater guideline (Section 3), and was identified as a metal with a concentration in modern sea water within an order of magnitude of the Tier 1 groundwater guideline. Overall, the possibility of

arsenic entering shallow groundwater as a result of releases of produced formations waters cannot be excluded, and therefore arsenic should be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Note, however, that a significant proportion of background shallow groundwater concentrations of arsenic exceed the Tier 1 guideline value (Figure 2) and therefore false positive exceedances are to be expected.

7.4 Barium

Barium is a ubiquitous component of drilling muds and was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Barium should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Figure 2 shows that most, but not all, measurements of barium in background shallow groundwater are below the Tier 1 guideline value, and therefore occasional false positive exceedances should be expected.

7.5 Boron

Boron was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Boron has also been measured in formation waters at concentrations that are orders of magnitude above Tier 1 groundwater guideline values (Section 3), and is present in modern seawater at concentrations above Tier 1 groundwater guideline values. For all these reasons, boron should be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Figure 2 shows that most, but not all, measurements of boron in background shallow groundwater are below the Tier 1 guideline value, and therefore occasional false positive exceedances should be expected.

7.6 Cadmium

Cadmium was not identified as being present in drilling fluids at concentrations of concern (Section 2). Release of produced formation water was identified as a possible minor consideration for this metal based on a concentration in modern sea water within an order of magnitude of the Tier 1 groundwater guideline. However, Table 7 indicates that the mean cadmium concentration in shallow background groundwater is well above the range of Tier 1 groundwater guideline values, and Figure 2 illustrates graphically that most background measurements for cadmium exceed the Tier 1 groundwater guideline value, sometimes by as much as 2-3 orders of magnitude. For these reasons, any possible effect from cadmium in released formation water is likely to be lost in the variation of background concentrations, and most Tier 1 exceedances of shallow groundwater guidelines will be false positives. For these reasons, it is not considered necessary or desirable to analyze cadmium in shallow groundwater at typical upstream oil and gas wellsites.

7.7 Chromium

Chromium was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Chromium should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Figure 2 shows that almost all measurements of chromium in background shallow groundwater are below the Tier 1 guideline value, and therefore false positive exceedances should be rare, but will occasionally occur.

7.8 Copper

Copper was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Copper should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Note, however, that a significant proportion of background shallow groundwater concentrations of copper exceed the Tier 1 guideline value (Figure 2) and therefore false positive exceedances are to be expected.

7.9 Iron

Iron is a major component of mafic minerals and comprises approximately 6% of crustal materials (Table 6). Iron was identified in Section 4 as a metal that can be mobilized in shallow groundwater as a by-product of the biodegradation of organic chemicals including crude oil that can be released at oil and gas wellsites. For this reason, increased concentrations of dissolved iron in shallow groundwater are expected at most sites with impact from hydrocarbons or other organic chemicals. Iron should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. However, Table 7 indicates that the mean iron concentration in shallow background groundwater is well above the Tier 1 groundwater guideline value, and Figure 2 illustrates graphically that background measurements for iron in shallow groundwater can exceed the Tier 1 groundwater guideline value by 2 orders of magnitude or more. For this reason, a high proportion of false positive exceedances should be expected for iron.

7.10 Lead

Lead was not flagged as a metal of environmental concern in drilling fluids (Section 2), and its concentration in modern seawater is 3+ orders of magnitude below the Tier 1 guideline (Table 5), implying a low likelihood of impact from releases of formation water. For these reasons, it is not considered necessary or desirable to analyze lead in shallow groundwater at typical upstream oil and gas wellsites.

7.11 Manganese

Manganese was identified in Section 4 as a metal that can be mobilized in shallow groundwater as a by-product of the biodegradation of organic chemicals including crude oil that can be released at oil and gas wellsites. For this reason, increased concentrations of dissolved manganese in shallow groundwater are expected at most sites with impact from hydrocarbons or other organic chemicals. Manganese should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. However, Table 7 indicates that the mean manganese concentration in shallow background groundwater is well above the Tier 1 groundwater guideline value, and Figure 2 illustrates graphically that background measurements for manganese in shallow groundwater can exceed the Tier 1 groundwater guideline value by 2 orders of magnitude or more. For this reason, a high proportion of false positive exceedances should be expected for manganese.

7.12 Mercury

Mercury was not flagged as a metal of environmental concern in drilling fluids (Section 2), and its concentration in modern seawater is 1.5 orders of magnitude below the Tier 1 guideline (Table 5), implying a low likelihood of impact from releases of formation water. For these reasons, it is not considered necessary or desirable to analyze mercury in shallow groundwater at typical upstream oil and gas wellsites.

7.13 Nickel

Nickel was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Nickel should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Note, however, that a significant proportion of background shallow groundwater concentrations of nickel exceed the Tier 1 guideline value (Figure 2) and therefore false positive exceedances are to be expected.

7.14 Selenium

Selenium was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Selenium is present in modern seawater at concentrations within an order of magnitude of Tier 1 groundwater guideline values, thus raising the possibility of significant selenium reaching shallow groundwater from a formation water release. For these reasons, selenium should be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. However, Table 7 indicates that the mean selenium concentration in shallow background groundwater is well above the Tier 1 groundwater guideline value, and Figure 2 illustrates graphically that background measurements for selenium in shallow groundwater can exceed the Tier 1 groundwater guideline value by 2 orders of

magnitude or more. For this reason, a high proportion of false positive exceedances should be expected for selenium

7.15 Silver

Silver was not flagged as a metal of environmental concern in drilling fluids (Section 2), and its concentration in modern seawater is 1.5 orders of magnitude below the Tier 1 guideline (Table 5), implying a low likelihood of impact from releases of formation water. For these reasons, it is not considered necessary or desirable to analyze silver in shallow groundwater at typical upstream oil and gas wellsites.

7.16 Uranium

Uranium was not identified in Section 2 as being present in drilling fluids at concentrations of concern. Release of produced formation water was identified as a possible consideration for this metal based on a concentration in modern sea water within an order of magnitude of the Tier 1 groundwater guideline (Section 3). However, Table 7 indicates that the mean uranium concentration in shallow background groundwater is approximately equal to the Tier 1 groundwater guideline value, and Figure 2 illustrates graphically that many background measurements for uranium can exceed the Tier 1 groundwater guideline value, sometimes by an order of magnitude or more. Any possible effect from uranium in released formation water is therefore likely to be lost in the variation of background concentrations, and most Tier 1 exceedances of shallow groundwater guidelines will likely be false positives. For these reasons, it is not considered necessary or desirable to analyze uranium in shallow groundwater at typical upstream oil and gas wellsites.

7.17 Zinc

Zinc was identified in Section 2 as a metal of potential concern due to a maximum concentration in a drilling mud component that exceeds 10x the Tier 1 soil guideline. Zinc should therefore be included in the suite of metals to be analyzed in shallow groundwater monitoring activities at oil and gas wellsites. Note, however, that a significant proportion of background shallow groundwater concentrations of arsenic exceed the Tier 1 guideline value (Figure 2) and therefore false positive exceedances are to be expected

8.0 SUMMARY

When a groundwater monitoring program calls for analysis of metals in shallow groundwater, current standard practice is to analyze for all metals that have an Alberta Tier 1 groundwater guideline. However, typically, many of the metals data that are acquired are false positive guideline exceedances, and significant time is wasted in justifying these false positives.

This project gave consideration to which metals in shallow groundwater could potentially have an anthropogenic source at a typical oil or gas wellsite. Metals that could have sufficiently high concentrations in drilling mud components and formation waters to be of concern were identified. In addition, the background concentration distribution was identified for each metal in shallow groundwater in Alberta to allow some estimate of the likelihood of false positive guideline exceedances.

The recommended suite of metals for groundwater monitoring at oil and gas wellsites is summarized in Table 8. Metals with Tier 1 groundwater guidelines for which it is not considered necessary to analyze include aluminum, antimony, cadmium, lead, mercury, silver, and uranium.

It should be noted that the range of shallow groundwater background concentrations for all these metals include the Tier 1 groundwater guideline. For this reason, a significant number of false positive guideline exceedances are to be expected. Consulting Figure 2 will give a qualitative sense of the likelihood of a false positive exceedance for each metal.

Table 8 Recommended Suite of Metals for Groundwater Monitoring at Oil and Gas Wellsites

Arsenic	Iron
Barium	Manganese
Boron	Nickel
Chromium	Selenium
Copper	Zinc

9.0 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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