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Groundwater Metals Associated with Oilfield Wellsites Information Letter

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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 have historically often tracked a large number of individual metals. Only a subset of the metals typically analyzed have a likely anthropogenic source at conventional oil and gas wellsites. This Best Management Practices (BMP) document identifies metals with a likely anthropogenic source at conventional oil and gas wellsites to allow analytical efforts to be focused on these metals.

Potential sources of anthropogenic metals contamination at conventional oil and gas wellsites include drilling mud that remains on site at the conclusion of drilling activities, produced formation water that may be released, or metals that may be mobilized as a result of the degradation of organic co-contaminants. This document discusses these various sources, identifies the metals in the environment that could potentially come from each, and uses this information to support a list of potential anthropogenic metals at oil and gas wellsites.

The range of background concentrations of metals in unimpacted shallow groundwater in Alberta often overlaps the Tier 1 guideline values. Resources are indicated in this document where additional information can be found on the typical ranges of metal concentrations in shallow Alberta groundwater.

The term "metals" in this document excludes the soluble metals sodium, potassium, calcium and magnesium that are often referred to as "major ions".

2.0 DENTIFICATION OF RELEVANT METALS

2.1 Metals in Drilling Fluids

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 metals present in drilling fluid eventually reaching shallow groundwater. MEMS (2015) completed a detailed survey of the trace metal composition of drilling mud components.

Many drilling mud components are sourced from natural products or minerals, and as such may contain trace amounts of a wide range of metals in addition to their primary components. It was necessary to distinguish between metals only present at trace concentrations and metals that could be present at high enough concentrations in one or more drilling mud components to have a potentially significant effect on groundwater. A screening methodology was used to achieve this based on a comparison between the maximum concentration in any drill mud component and the corresponding Alberta Tier 1 soil remediation guideline. Full details are provided in MEMS (2015).

Metals that were retained as being of potential concern in relation to drilling fluids include:

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

Note that not all of these metals would necessarily be of concern in any given drilling mud. Inclusion in this list simply implies that these metals are present at a high enough concentration in some drilling mud components that they cannot be excluded.

2.2 Metals in Produced Formation Waters

Hydrocarbons are produced from a wide range of formations in the Western Canada Sedimentary Basin. 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 at oilfield wellsites.

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).

MEMS (2015) concluded that data on metals concentrations in the formation waters of the Western Canada Sedimentary Basin, are typically not available in the published literature. MEMS (2015) developed a screening methodology to identify metals of potential concern in situations where formation water is released based on available published data supplemented by an analysis based on the ratios of the concentrations of metals in modern seawater to Tier 1 groundwater guidelines. That screening methodology (see MEMS, 2015 for full details) was adopted here.

Metals that were retained as being of potential concern in relation to releases of produced water include:

- arsenic;
- boron; and
- selenium.

2.3 Metals Released *via* Biodegradation of Organic Chemicals

Organic chemicals, including petroleum hydrocarbons and other organic 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. 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 should be noted that in such cases, the increase of these dissolved metal species in groundwater does not imply the anthropogenic addition of metals directly, but rather the mobilization of metals that are already present in immobile forms in the formation. Additionally, it should be noted that

these redox changes are reversible. As soon as the groundwater in question encounters more oxidizing conditions, insoluble iron (III) and insoluble manganese (IV) will tend to precipitate, thus reducing the concentrations of soluble iron (II) and soluble manganese (II).

However, in spite of the comments in the previous paragraph, it is clear that upstream oil and gas activities can result in temporary increases in the concentrations of dissolved iron and manganese in groundwater, and that these metals should be included in the list of groundwater metals potentially associated with oilfield wellsites.

2.4 Summary of Associated Metals

Based on information in Sections 2, 3, and 4 of this document, the metals identified as being potentially associated with oilfield wellsites at concentrations that could be significant for groundwater are summarized below in Table 1 together with an indication of which of the considerations noted in previous sections are relevant for each.

Table 1 Criteria for Associating Metals with Oilfield Wellsites

Metal	Potentially Associated with Drilling Fluid? [a]	Potentially Associated with Produced Water? [b]	Potentially Associated with Hydrocarbon Degradation? [c]
Arsenic		✓	
Barium	✓		
Boron	✓	✓	
Chromium	✓		
Copper	✓		
Iron			✓
Manganese			✓
Nickel	✓		
Selenium	✓	✓	
Zinc	✓		

Notes:
a: See Section 2.1
b: See Section 2.2
c: See Section 2.3

A more detailed assessment of each metal is available in MEMS (2015).

3.0 RATIONALE AND APPLICATION

3.1 Rationale for a Reduced Analytical Suite

Tier 1 groundwater guidelines for many metals are set at levels within the range of natural background conditions in shallow groundwater in Alberta (see PTAC project 16-SGRC-05; MEMS, 2017). For this reason, false positives are a common occurrence when comparing analytical data for metal concentrations in shallow groundwater in Alberta with Tier 1 guideline values. Having a large number of false positive guideline exceedances in a dataset is not helpful, as it tends to distract the focus of the analysis away from any real guideline exceedances. Thus, the rationale for using the reduced analytical suite developed in this document is to reduce the number of false positive guideline exceedances, and to focus analytical attention on a smaller number of metals that have a plausible source in the situation under consideration

3.2 Application at Upstream Wellsites

The list of metals indicated in Tables 1 and 2 is the appropriate suite of analytes to include when metals are being analyzed in groundwater at sites that meet the following condition:

- The site is a conventional oil and gas wellsite.

Note that any non-standard activities conducted at a wellsite that involved the use of other metals would trigger the requirements to include the additional relevant metals in the analytical suite.

3.3 Applicability to Other Facilities

Additional considerations will apply to other oil and gas sites including gas plants, batteries, thermal facilities and other facilities as these sites can have a wider range of activities occurring. The analysis presented in this document does not consider the wider range of activities that can take place at such sites and therefore does not provide stand-alone guidance for sites other than conventional oil and gas wellsites. However, the information presented in this document and in the reference sources on which this document is based may form part of the rationale for a similar approach at other types of site. Such an approach would consider all relevant activities at the site in question.

4.0 SUMMARY

This document developed an analytical suite of metals relevant to oilfield wellsites. The approach 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/or formation waters to be of concern were identified. Metals that could potentially be released into shallow groundwater as a by-product of the biodegradation of organic compounds were also considered.

A total of 10 metals were identified as having the potential for significantly elevated groundwater concentrations resulting from anthropogenic activities at oilfield wellsites. These metals are summarized in Table 2.

Table 2 Summary of Metals Potentially Associated with Oilfield Wellsites

Arsenic	Iron
Barium	Manganese
Boron	Nickel
Chromium	Selenium
Copper	Zinc

The metals listed in Table 2 are an appropriate analytical suite at oilfield wellsites where metals are analyzed in groundwater.

5.0 REFERENCES

AEP (Alberta Environment and Parks, 2016. Alberta Tier 1 Soil and Groundwater Remediation Guidelines. Land and Policy Branch, Policy and Planning Division. 197 pp.

MEMS (Millennium EMS Solutions Ltd.) 2015. Development of a Reduced Analytical Suite of Upstream Oilfield Metals for Groundwater Monitoring. Report prepared for Petroleum Technology Alliance Canada (PTAC) under Project # 13-AU-SGRC-04. Dated October 2015. Available at www.ptac.org.

MEMS (Millennium EMS Solutions Ltd.) 2017. Evaluation of Background Metals Concentrations in Shallow Alberta Groundwater. Report prepared for Petroleum Technology Alliance Canada (PTAC) under Project # 16-SGRC-05.