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Groundwater Metals Potentially Associated with Oilfield Wellsites

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1.0 INTRODUCTION

This report was funded by Petroleum Technology Alliance Canada (PTAC) under project # 16-SGRC-02. It builds upon research from a former PTAC Project, 13-AU-SGRC-04 (MEMS, 2015), and the reader is referred to that report for additional supporting detail.

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. Some of these metals may be present in significant concentrations in oilfield drilling fluids or in produced formation waters. Oilfield drilling fluids may remain on site after well drilling is complete, and accidental releases of produced formation waters may occur. Accordingly, metals that are typically present at higher concentrations in oilfield drilling fluids or in produced formation waters are more likely to result in anthropogenic increases in metal concentrations in shallow wellsite groundwater than other metals. In addition, certain metals may be mobilized into groundwater as a natural by-product of the biodegradation of hydrocarbons or other organic chemicals that may be present on an oilfield wellsite as a result of anthropogenic activities. This summary report identifies groundwater metals that have a plausible source related to anthropogenic activities at oilfield wellsites.

A concentration of a metal in shallow groundwater that exceeds the Tier 1 groundwater guideline does not necessarily imply an anthropogenic source. For many metals, the natural range of background concentrations in shallow groundwater exceeds the Tier 1 groundwater guideline value. A related PTAC project, # 16-SGRC-05, being completed by Millennium EMS Solutions Ltd. (MEMS, 2017), is currently developing statistical distributions for natural concentrations of trace metals in shallow Alberta groundwater, and will be helpful in distinguishing anthropogenic from natural influences on groundwater metals concentrations.

1.1 Objectives and Scope of Work

The overall objective of this project is to summarize, with rationale, a list of metals in groundwater most likely to be associated with anthropogenic activities at oilfield wellsites.

The scope of work of this project relates to conventional oil and gas wellsites in Alberta and takes as its starting point the list of trace metals for which Alberta Tier 1 groundwater guidelines have been published. The highly soluble metals in Groups I and II of the periodic table commonly considered to be “major ions” in groundwater (sodium, potassium, calcium and magnesium) are not included. Scope items are as follows:

- Determine which of the metals could be present in significant concentrations in drilling fluids.

- Determine which of the metals 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.
- List the metals deemed to be potentially associated with oilfield wellsites and provide a brief rationale for each included metal.
- 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 conventional 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 and analysis 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 #16-SGRC-02. Thanks to Ayan Chakraborty the CAPP project sponsor for liaison with industry contacts and technical input to the project.

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. MEMS (2015) completed a detailed survey of the trace metal composition of drilling mud components.

2.2 Methodology

A screening methodology was developed in PTAC (2015) to identify metals with the potential to be of concern in relation to a drilling mud source. This methodology can be summarized as follows. The trace metal composition of 314 drilling mud components was reviewed. The highest concentration of each metal in any drilling mud component was noted. Then the ratio of this maximum concentration to the corresponding Alberta Tier 1 soil remediation guideline was calculated.

Metals with a ratio less than 1 were not considered further, since all drilling mud components would meet Tier 1 soil remediation guidelines. Metals with a ratio between 1 and 10 were only retained if the drilling mud component(s) in question could potentially compose a significant proportion of an overall drilling mud. This would include components such as weighting agents and viscosifiers. Many drilling mud components, such as corrosion inhibitors and many others, only ever form a minor proportion of the overall drilling mud. Metals with a ratio greater than 10 were included.

2.3 Conclusions

Metals that were retained as being of potential concern 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.

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. 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).

3.2 Potential Metal Mobilization by Saline Produced Water

Concerns have been raised that the potential exists for metals to be mobilized when saline produced waters are released to the environment. One possible mechanism for this would be ion exchange. Metal cations sorbed to the charged surfaces of clay minerals could be replaced by sodium ions and other cations that are present in high concentrations in the produced water. A parallel project, MEMS (2017) investigated this potential issue by looking for correlation between chloride concentrations and the concentrations of other metals in a large dataset of shallow groundwater data from Alberta. The higher chloride concentrations in this dataset would reflect impacts from produced water releases with associated high sodium concentrations. Minor correlations were found for some of the metals identified in Section 3.4 as potentially present in formations waters. These correlations were interpreted as related to the metal being present in the formation water , rather than any release of metal by ion exchange. No correlations were found between chloride and any of the other metals investigated in this report, and accordingly the release of metals ions into groundwater by ion exchange driven by produced water released does not appear to be a concern.

3.3 Methodology

MEMS (2015) conducted an extensive survey of available data on trace metal concentrations in formation waters of the Western Canada Sedimentary Basin, and found very little published data.

In the absence of a better dataset of metals concentrations in formation water from the Western Canada Sedimentary Basin, MEMS (2015) developed 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.

The rationale for the first criterion is based in part on Bernatsky (1998) and others who indicate that sea water is an important precursor of most formation waters. Evaporation of seawater prior to formation deposition or dissolution of evaporates post deposition can account for formation waters that are more saline. The most saline brines are approximately 10 times as saline as modern seawater, so metals that have seawater concentrations less than 10% of Tier 1 groundwater guideline values are highly unlikely to be of any concern.

MEMS (2015) calculated the ratio between modern seawater concentrations and Tier 1 groundwater guideline values, and determined that these ratios for sodium and chloride were orders of magnitude higher than for any of the trace metals. This confirms common experience of produced water releases in that they can generally be adequately managed based on sodium and chloride concentrations, with any considerations from trace metals being relatively minor.

Further discussion of the details of this methodology is included in MEMS (2015).

3.4 Conclusions

Using the methodology summarized in Section 3.2 and explained in detail in MEMS (2015), the following list of Tier 1 metals are assessed as potentially significant in produced formation water releases:

- arsenic;
- boron;
- cadmium; and,
- selenium.

4.0 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 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 the list of groundwater metals potentially associated with oilfield wellsites.

5.0 METAL BY METAL ASSESSMENT

In this section, metals identified in Sections 2 to 4 are assessed in turn. For each metal, the assessment considers whether significantly elevated groundwater concentrations could reasonably be expected to occur as a result of anthropogenic activities at oilfield wellsites. Where this is the case, the metal is included in the list of groundwater metals potentially associated with oilfield wellsites.

5.1 Arsenic

Arsenic was not identified as being present in drilling fluids at concentrations of concern (Section 2). Arsenic has been measured in formation waters at concentrations well above the Tier 1 groundwater guideline (MEMS, 2015; summarized in 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 (MEMS, 2015). Overall, the possibility of arsenic entering shallow groundwater as a result of releases of produced formations waters cannot be excluded, and arsenic is retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.2 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 is retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.3 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 (MEMS, 2015; summarized in Section 3), and is present in modern seawater at concentrations above Tier 1 groundwater guideline values (MEMS, 2015). For all these reasons, boron is retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.4 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, data included in MEMS (2015) indicate that the background concentration of cadmium in shallow groundwater can be 2-3 orders of magnitude above the range of Tier 1 groundwater guideline values. Accordingly, 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 useful to include cadmium in the list of groundwater metals potentially associated with oilfield wellsites.

5.5 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 is therefore retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.6 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 is therefore retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.7 Iron

Iron is a major component of mafic minerals and comprises approximately 6% of crustal materials (MEMS, 2015). 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 is therefore retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.8 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 is therefore retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.9 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 is retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.10 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 is retained in the list of groundwater metals potentially associated with oilfield wellsites.

5.11 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 is therefore retained in the list of groundwater metals potentially associated with oilfield wellsites.

6.0 BACKGROUND CONCENTRATIONS

Section 5 identified groundwater metals that are most likely to be associated with oilfield wellsites. However, a groundwater concentration of one of these metals on an oilfield wellsite that exceeds the Tier 1 groundwater guideline should not be assumed to reflect anthropogenic impact until the issue of the range of background concentrations of the metal in question has been considered.

MEMS (2015) conducted a brief survey of background concentrations of metals in shallow Alberta groundwater, and compared the results with the Tier 1 guideline. The work done in that report can be used to provide a very approximate, qualitative measure of the likelihood that a groundwater metal concentration which exceeds the Tier 1 guideline is a false positive. The following scale is used here. For metals where MEMS (2015) indicates that the mean background concentration exceeds the

Tier 1 guideline value, the chance of a false positive guideline exceedance is considered to be extremely likely. If the 95th percentile (but not the mean) background concentration exceeds the Tier 1 guideline value, the chance of a false positive guideline exceedance is considered to be moderately likely. If the maximum (but not the mean) background concentration exceeds the Tier 1 guideline value, the chance of a false positive guideline exceedance is considered to be possible. Based on the above qualitative scale, the likelihood for a false positive exceedance of a Tier 1 groundwater guidance can be evaluated as follows for each of the metals identified in Section 5.

Likelihood of a False Positive Guideline Exceedance:

Extremely Likely:

- iron;
- manganese; and,
- selenium.

Moderately Likely:

- arsenic;
- boron;
- copper;
- nickel; and,
- zinc.

Possible:

- barium; and,
- chromium.

Note that the above scale is intended only to point out that background concentrations may exceed Tier 1 groundwater guidelines for all these metals, and to give some indication of the relative likelihood of this occurring for the different metals. For a more quantitative assessment of background metal concentrations in groundwater, the reader is directed to a parallel project, MEMS (2017), currently in progress which provides quantitative analysis and statistical metrics on the background concentrations of metals in shallow Alberta groundwater, and draws on a much larger dataset than was available to this project.

7.0 SUMMARY

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/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. The potential issue of the mobilization of metals into groundwater as a result of a release of saline produced water and the associated ion exchange of metal ions from clay surfaces was investigated but shown not to be a concern.

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 1.

Table 1 Groundwater Metals Potentially Associated with Oilfield Wellsites

Arsenic	Iron
Barium	Manganese
Boron	Nickel
Chromium	Selenium
Copper	Zinc

The reader is cautioned that the presence of any one of these metals in shallow groundwater at an oilfield wellsite at a concentration above the Tier 1 guideline does not necessarily imply an anthropogenic source, since background concentrations of these metals frequently exceed Tier 1 guideline values. Some qualitative information relating to this issue was summarized in this report, but the reader is directed to a parallel project MEMS (2017) for more quantitative information on the range of background metal concentrations in shallow groundwater.

8.0 CLOSURE

This research project was conducted for Petroleum Technology Alliance Canada (PTAC) and is based on generally accepted risk assessment practices, and data available in the literature and provided by others. The work is based on conditions that vary with oilfield techniques and practices and with spatial location and therefore inevitably involves approximations and generalizations. The work represents MEMS professional opinion on the groundwater metals most likely to be associated with the normal range of activities undertaken at oilfield wellsites. The research work was conducted in accordance with the project objectives and scope of work indicated in Section 1 of the document.

Third parties may rely upon the information contained within this report to the extent that such reliance is expressly within the project objectives and scope of work as presented herein, and only if such third parties first return an executed copy of the Millennium Third Party Reliance Agreement (Appendix A) and agree to be bound by the terms and conditions of the Millennium Third Party Reliance Agreement.

Yours truly,

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