



Occurrence and source of geogenic arsenic in groundwater from the Cold Lake-Beaver River Basin, Alberta

Michael C. Moncur, S. Jean Birks, Emily Taylor, John J. Gibson
Alberta Innovates-Technology Futures

Dogan Paktunc
CANMET Mining and Mineral Sciences Laboratory

Brent Welsh
Alberta Energy Regulator

Carol J. Ptacek
University of Waterloo

Summary

Elevated arsenic concentrations have been observed in shallow groundwater in the Cold Lake-Beaver River Basin (CLBR) of Alberta. The geology of this area includes up to 200 m of unconsolidated glacial deposits, with six regional interglacial sand and gravel aquifers, underlain by marine shale. Arsenic concentrations in unconsolidated sediment samples ranged between 1 to 17 ppm. Mineralogical characterization of the sediment samples revealed the presence of fresh framboidal pyrite in the deeper unweathered sediments with variable As contents of up to 1800 ppm. In contrast, the weathered sediments did not contain framboidal pyrite, but exhibited spheroidal Fe oxyhydroxide grains with elevated As concentrations, interpreted as pseudomorphs after pyrite. X-ray absorption near edge spectroscopy (XANES) indicated that the weathered sediments are dominated by As(V) species having spectral features similar to those of goethite or ferrihydrite with adsorbed As, suggesting that Fe oxyhydroxides are the dominant As carriers. XANES spectra collected from the unweathered sediment samples indicated the presence of a reduced As species characteristic of arsenopyrite and arsenian pyrite. A survey of over 800 water wells, isolated from industrial activity, were sampled for As and found that 50% of the wells contained As concentrations exceeding drinking water guidelines of $10 \mu\text{g L}^{-1}$. Higher As concentrations in groundwater were associated with increasing depth and reducing conditions, circumneutral pH and lower concentrations of SO_4 . Speciation modelling showed that the majority of groundwater samples were undersaturated with respect to ferrihydrite, suggesting that reductive dissolution of Fe oxyhydroxides, likely formed during glaciation, may be the source of some As in deeper groundwater, whereas sulfide oxidation of pyrite during weathering is the likely source of As released to shallow aquifers. Understanding the distribution and form of As present naturally in the CLBR aquifer basins is important for managing water resources to minimize the potential health risks of As exposure.

Introduction

The CLBR basin is located in east-central Alberta, approximately 400 km northeast of Calgary (Figure 1). The basin spans portions of Athabasca and Cold Lake Oil Sands regions. Surface water and groundwater in the CLBR basin is used for a variety of activities including domestic, municipal, industrial and agricultural use and recreation (AENV, 2006). The general stratigraphy beneath the CLBR basin is comprised of 25 to 225 m of unconsolidated sediments with the basal deposits composed of Neogene sands and gravel overlain by Quaternary glacial deposits. Within the drift sediments, twelve distinct hydrostratic units have been identified as regional aquifers and aquitards. These sediments unconformably rest on bedrock comprised mainly of a thick Cretaceous shale aquitard that is also the caprock for underlying Grand Rapids, Clearwater and McMurray Formations that are exploited for gas, heavy oil, and bitumen production in the area. Refer to Andriashek and Fenton (1989), Andriashek (2003) and Parks et al. (2005) for a detailed description of the geology.

Elevated As concentration in groundwater have been reported by a number of investigations in the CLBR basin (Nriagu, 1998; AHW, 2000; Stein et al., 2000; Lemay et al., 2005; AHW, 2014; Javed et al., 2014). The main objective of this investigation was to integrate existing and newly collected As groundwater data from across CLBR basin to understand processes controlling the spatial distribution of As concentrations. A secondary objective was to determine sources and potential controls of As mobility in groundwater using mineralogical analyses of aquifer sediments and applying geochemical modeling.

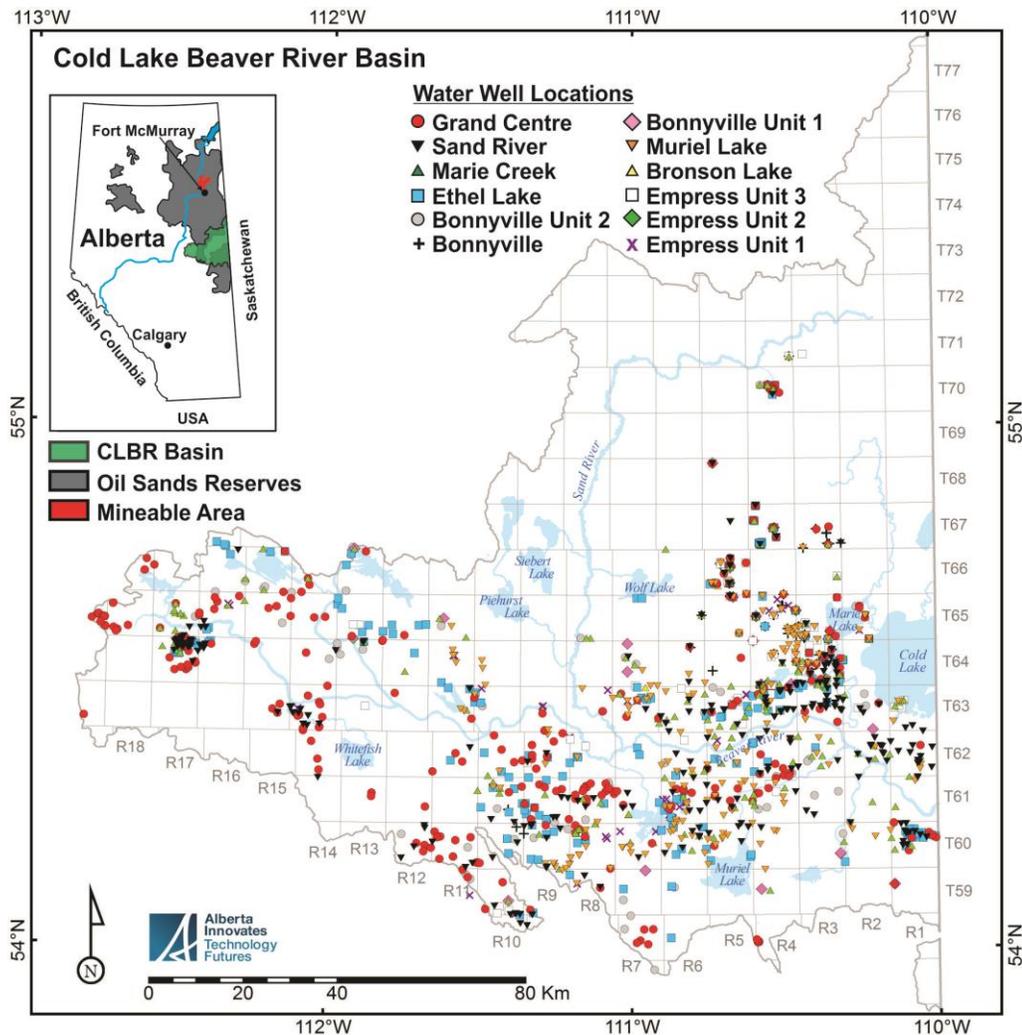


Figure 1. Map showing location of water wells sampled for this study, with symbols differentiated by geological formations. The formations are ordered from shallowest (Grand Centre) to deepest (Empress Unit 1). Location of the CLBR basin and extent of oil sands deposits is shown in inset.

Methods

Groundwater geochemistry data for this study was provided by Alberta Environment and Sustainable Resource Development, Alberta Water Well Information Database, Alberta Health and Wellness, Beaver River Watershed Alliance, industry studies, and a number of wells sampled by Alberta Innovates – Technology Futures. Refer to Moncur et al. (2015) for a detailed description of methods.

Results

The mean concentration of As in groundwater from all glaciofluvial formations was $15 \mu\text{g L}^{-1}$, with 50% of wells exceeding the Canadian Drinking Water Guideline of $10 \mu\text{g L}^{-1}$. Groundwater As concentrations were

lowest in the upper Grand Centre Formation with only 17 % of the wells exceeding $10 \mu\text{g L}^{-1}$, whereas in the deeper Empress 3 Formation, concentrations were highest with 70 % of the wells exceeding $10 \mu\text{g L}^{-1}$ (Moncur et al., 2015). In general, As concentrations increased with depth within the glaciofluvial formations (Figure 2). Within the underlying shale bedrock units, all wells sampled had As concentrations below $10 \mu\text{g L}^{-1}$. The spatial distribution of As concentrations in groundwater across the CLBR was highly variable with no obvious distribution pattern. The spatial variability of As concentration is consistent with the findings of previous studies in the CLBR (Lemay et al., 2005) and in other locations with elevated As (eg. Reimann et al., 2009; Huang et al., 2014) which show a high degree of spatial heterogeneity in As distributions in groundwater. The heterogeneous nature of glacially deposited sediments likely influences the random distribution of As concentrations in groundwater within the CLBR basin.

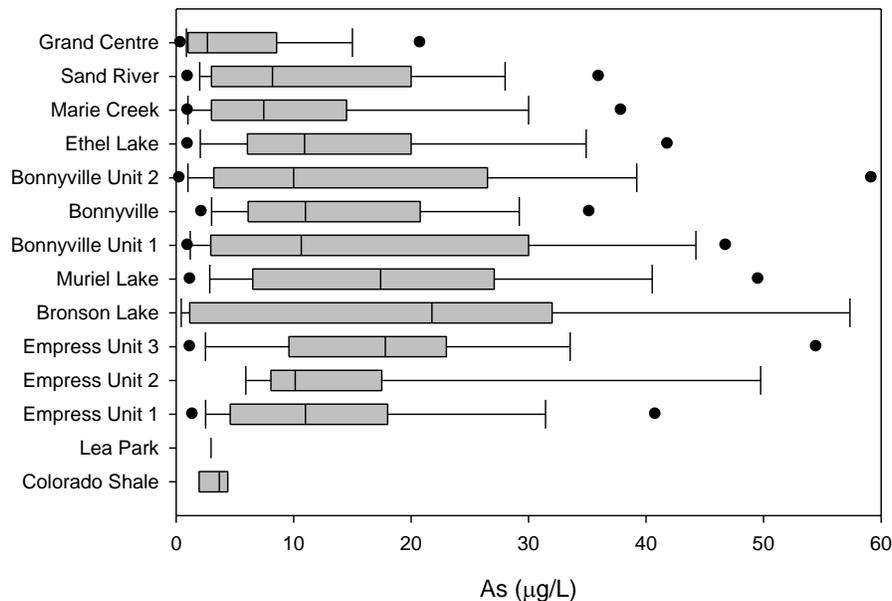


Figure 2. Box-whisker plot showing As concentrations in groundwater from 816 wells in the CLBR basin. Formations are arranged in increasing depth with Grand Centre representing the shallowest.

Across CLBR basin, As concentrations in glaciofluvial sediment ranged from 1 to 17 ppm, averaging 6 ppm (Andriashek, 2000; Moncur et al., 2010; Moncur et al., 2015). In the deeper unweathered sediments, mineralogical characterization revealed the presence of fresh framboidal pyrite with an average As concentration of 530 ppm, with values up to 1840 ppm (Moncur et al., 2015). In contrast, framboidal pyrite was absent in the weathered sediments, but exhibited spheroidal Fe oxyhydroxide with elevated As concentrations, interpreted to be an oxidation product of former framboidal pyrite grains. X-ray absorption fine structure spectroscopy experiments indicated that the weathered sediments were dominated by As(V) species having spectral features similar to those of goethite or ferrihydrite with adsorbed As, suggesting that Fe oxyhydroxides were the dominant As carriers. In contrast, XANES spectra collected on unweathered sediment samples showed the presence of a reduced As species As(-I) distinctive of arsenopyrite and arsenian pyrite. Least-squares fitting of the XANES spectra with arsenopyrite and goethite model compounds indicate the proportion of As(-I) species make up 17 to 26 % of the total As in the unoxidized sediments, suggesting that Fe reduction of Fe oxyhydroxides could be the main source of As to the groundwater, consistent with observations by Javed et al. (2015). Speciation modelling calculations showed that groundwater from 72 % of the wells were at saturation or undersaturated with respect to ferrihydrite. These calculations are consistent with the XANES results suggesting that the primary mechanism for As release from the unweathered sediments is the reductive dissolution of Fe oxyhydroxide minerals. Within the near-surface sediments, mineralogical analyses indicated that the oxidation of framboidal pyrite during weathering may be the source of As released to shallow aquifers whereas

reductive dissolution of Fe oxyhydroxide minerals may be the source in deeper reduced aquifers in the CLBR region.

Conclusions

Glaciofluvial aquifers of the CLBR basin contained widespread elevated As concentrations in groundwater with 50 % of the wells exceeding 10 µg/L. The distribution of As did not show any obvious spatial pattern or trend along groundwater flow paths. Speciation of the As found that arsenite, the more mobile and toxic form was dominant in most of the groundwater. The highest concentrations of As were associated with reducing conditions, circumneutral pH and lower concentrations of Fe and SO₄. Speciation modeling showed that the majority of groundwater samples were undersaturated with respect to Fe oxyhydroxide minerals. Within the near-surface weathered sediments, mineralogical analyses indicate that the oxidation of frambroidal pyrite during weathering may be the source of As released to shallow aquifers in this region. In the unweathered deeper sediments below the water table, reduction of Fe oxyhydroxides is likely the main source of As to the groundwater.

Understanding the distribution and species of As present naturally in aquifer material and groundwater in the CLBR basin is important for managing regional water resources, including the location of domestic water wells to minimize the potential health risks of As exposure. Industrial activity in the CLBR area includes in situ development and the results of this study contribute towards better understanding of baseline water quality across the region as well as the processes that can result in the release of As and other metals during thermal operations. Identifying which aquifers contain As bearing minerals can be used to identify those with greatest risks for thermal mobilization of As and where to focus on-site groundwater monitoring.

Acknowledgements

Funding for this project was provided by Alberta Health and Wellness, Alberta Environment, Beaver River Watershed Alliance and Alberta Innovates – Technology Futures. We thank Joe Prusak, Debora Mooney, Don Jones, Yves Thibault, and Kent Richardson for their advice and technical assistance. The XAFS experiments were performed at the PNC/XOR beamline, Advanced Photon Source, Argonne National Laboratory which is supported by the US Department of Energy under Contracts W-31-109-Eng-38 (APS) and DE-FG03-97ER45628 (PNC-CAT). The XAFS experiments were also supported by the Natural Sciences and Engineering Research Council of Canada through an MRS grant.

References

- AENV (Alberta Environment), 2006. Cold Lake-Beaver River Basin, groundwater quality, state of the basin report. Alberta Environment Publication Number T/848.
- AHW (Alberta Health and Wellness), 2000. Arsenic in groundwater from domestic wells in three areas of northern Alberta. Health Surveillance Report, ISBN (0-7785-0708-4).
- AHW (Alberta Health and Wellness), 2014. Domestic well water quality in the Beaver River Basin 2009, drinking water quality and human health assessment. Alberta Domestic Well Water Quality and Assessment Program. ISBN (978-0-7785-8281-6).
- Andriashek, L.D., Fenton, M.M., 1989. Quaternary Stratigraphy and Surficial Geology of the Sand River Area. Alberta Research Council, NTS 73L, Bulletin 57.
- Andriashek, L.D., 2000. Geochemistry of selected glacial and bedrock geologic units, Cold Lake Area, Alberta. Alberta Geological Survey Earth Sciences Report 2000-10.
- Andriashek, L.D., 2003. Quaternary Geological Setting of the Athabasca Oil Sands (In Situ) Area, Northeast Alberta. Alberta Geological Survey Earth Sciences Report 2002-03.

- Huang, S., Liu, C., Wang, Y., Zhan, H., 2014. Multivariate analysis of the heterogeneous geochemical processes controlling arsenic enrichment in a shallow groundwater system. *Journal of environmental science and health. Part A, Toxic/hazardous substances & environmental engineering* 49, 478-489.
- Javed, M.B., Kachanoski, G., Siddique, T., 2014. Arsenic fractionation and mineralogical characterization of sediments in the Cold Lake area of Alberta, Canada. *Science of the Total Environment*, 500-501, 181-190.
- Lemay, T., Parks, K., Andriashek, L.D., Michael, K., Jean, G., Kempin, E. Stewart, S., 2005. Regional groundwater quality appraisal, Cold Lake-Beaver River drainage basin, Alberta. Alberta Geological Survey Special Report 73.
- Moncur, M.C., 2010. Uranium anomalies in shallow groundwater near Bonnyville, Alberta. *Water for Life: Knowledge and Research Series*. ISBN: 978-0-7785-9952-4.
- Moncur, M.C., Paktunc, D., Birks, S.J., Ptacek, C.J., Welsh, B., Thibault, Y., 2015. Source and distribution of naturally occurring arsenic in groundwater from Alberta's Southern Oil Sands Regions. *Applied Geochemistry* 62, 171-185.
- Nriagu, J.O., 1998. Arsenic in groundwater in the Cold Lake area. *Sessional Paper* 560199.
- Parks, K., Andriashek, L.D., Michael, K., Lemay, T., Stewart, S., Jean, G., Kempin, E., 2005. Regional groundwater resource appraisal, Cold Lake-Beaver River drainage basin, Alberta. Alberta Geological Survey Special Report 74.
- Reimann, C., Matschullat, J., Birke, M., Salminen, R., 2009. Arsenic distribution in the environment: the effects of scale. *Applied Geochemistry* 24, 1147-1167.
- Stein, R., Dudas, M., Klebek, M., 2000. Occurrence of arsenic in groundwater near Cold Lake, Alberta. Alberta Environment.