



Arsenic fractionation and mineralogical characterization of sediments in the Cold Lake area of Alberta, Canada



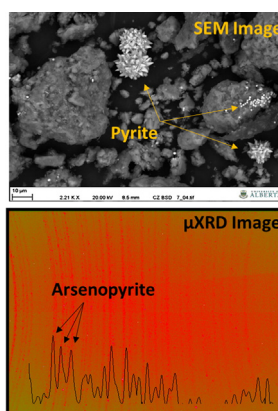
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HIGHLIGHTS

- High arsenic was found in sediments derived from shale.
- Arsenic was mainly found in exchangeable and sulfide bound phases.
- Pyrite and arsenopyrite minerals were found in high arsenic sediments.
- Sulfide minerals in the sediments could be the potential source of groundwater As.

GRAPHICAL ABSTRACT



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ABSTRACT

Elevated arsenic ($\text{As} > 0.01 \text{ mg L}^{-1}$) in some domestic well water in the Cold Lake area of Alberta, Canada is of great concern for public health. To determine possible sources of groundwater As, sediments ($n = 135$) collected from five different locations (up to $\sim 300 \text{ m}$ depth) in the area were characterized. Total As concentrations in the sediments varied from ~ 1 to 35 mg kg^{-1} . Sediments derived from shale contained high As ($\sim 13 \text{ mg kg}^{-1}$; $n = 14$), particularly the shale of Lea Park formation where maximum average As was $\sim 32 \text{ mg kg}^{-1}$ ($n = 2$). Unoxidized sediments of Grand Centre ($24.9 \pm 4.2 \text{ mg kg}^{-1}$ As) and Bonnyville ($19.9 \pm 1.8 \text{ mg kg}^{-1}$ As) formations also contained high As. Sequential extraction procedure (SEP) revealed the dominance of exchangeable and specifically adsorbed As (6 to 46% of total As) in the sediments of varying As concentrations (0.8 to 35.4 mg kg^{-1} As). The high As sediments ($> 7 \text{ mg kg}^{-1}$ As) also contained significant amount of sulfide bound As (11 to 34% of total As), while low As ($< 7 \text{ mg kg}^{-1}$ As) sediments had crystalline oxide minerals bound As (25 to 75% of total As) as major phases. X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses confirmed the presence of pyrite, and μ -XRD analysis signaled the presence of arsenopyrite in sediments containing $\sim 20 \text{ mg kg}^{-1}$ As. X-ray absorption near edge structure (XANES) spectroscopy analysis suggested dominance of arsenite (As(III) ; ~ 60 to 90% of total As) in all the sediments. These findings may help to devise strategies to investigate mechanisms of As release into the groundwater.

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1. Introduction

Arsenic (As) is a ubiquitous metalloid with some of its chemical forms being extremely toxic. It has received global attention in recent years for its groundwater contamination and subsequent serious health effects. It is estimated that 40 to 100 million people in the world are at risk of consuming As contaminated water (Páez-Espino et al., 2009; van Halem et al., 2009; de Mora et al., 2011). The biggest poisoning outbreak of the 20th century is also attributed to As contaminated groundwater in Bangladesh, where 30 to 77 million people are at risk due to excessive As in drinking water (Smith et al., 2000; van Halem et al., 2009). In Alberta (Canada), relatively high As concentrations have been found in the groundwater particularly in the Lakeland health region including Cold Lake area (Health Surveillance, 2000; Fitzgerald et al., 2001) where ~50% of drinking water wells contained As that exceeded the maximum acceptable concentration (As 0.01 mg L⁻¹; Health Canada, 2006). Generally, high levels of As in groundwater (a source of drinking water) are attributed to the sulfide-rich high As aquifers (Wang and Mulligan, 2006).

It is agreed that As in groundwater usually originates geogenically from sediments (Nickson et al., 2000). Arsenic is naturally enriched in shale containing pyrite (FeS₂, which is considered the principal carrier of As in rocks) and other minerals such as arsenopyrite (FeAsS), enargite (Cu₃AsS₄), scorodite (FeAsO₄·2H₂O) and annabergite [(Ni)₃(AsO₄)₂] (Boyle and Jonasson, 1973). Weathering and biological transformation of these As containing minerals under natural conditions can mobilize As from soil and sediment to the aquatic environment (Smedley and Kinniburgh, 2002; Muloin and Dudas, 2005). Alberta Health and Wellness (Health Surveillance, 2000) and Alberta Environment and Water Communications (Moncur, 2011) conducted studies in eastern Alberta and correlated naturally occurring higher groundwater As concentration with bedrock geological formations containing marine shale. Marine shale inclusions or enrichment within Quaternary (glacial) sediments are one of the important sources of groundwater As (Andriashok, 2000).

The distribution and chemical association of As with different sediment constituents affect As mobility in sediment pore water and its transport to groundwater depending on the prevailing geochemical conditions. Arsenic sequestration (sorption/coprecipitation) in solid constituents, especially oxyhydroxides of iron (Fe), aluminum (Al) and manganese (Mn) is one of the most important processes that immobilize As under oxidizing conditions (Smith et al., 1998; Larios et al., 2012). Arsenic-bearing Fe oxyhydroxides may also act as a source of As during reductive dissolution under reducing conditions (Larios et al., 2012). Arsenic associated with Mn oxyhydroxides (easily reducible oxides) is relatively more labile than Fe oxyhydroxides (Tessier et al., 1979). One other major form of As is naturally occurring As-bearing sulfide minerals that are stable under reducing conditions but oxidative breakdown of these minerals can release As into the environment (Larios et al., 2012). Anthropogenic activities such as mining and smelting can enhance As release by exposing these unoxidized minerals to the atmosphere and making them vulnerable to weathering (Smedley and Kinniburgh, 2002). However, part or all of the released As may occlude in the resulting metastable secondary minerals such as FeAsO₄·2H₂O (Sadiq, 1997) and diminish the danger of groundwater contamination.

Because the source(s) responsible for As-laden groundwater in the Cold Lake area of Alberta are still unknown, this study combines sequential extraction procedure (SEP), mineralogical and spectroscopic techniques to comprehensively investigate the As distribution in surficial deposits (sediments) in the Cold Lake area. This study will provide base knowledge to further investigate geochemical processes governing As release into the groundwater.

2. Material and methods

2.1. Reagents and minerals

Trace metal grade nitric acid (HNO₃), sodium acetate (CH₃COONa; abbreviated as NaOAc), sodium phosphate (NaH₂PO₄), calcium chloride (CaCl₂), ammonium oxalate [(NH₄)₂C₂O₄·H₂O], oxalic acid (H₂C₂O₄), titanium (Ti) powder, sodium citrate (Na₃C₆H₅O₇·2H₂O), sodium bicarbonate (NaHCO₃), ethylene-diamine-tetra-acetic acid (C₁₀H₁₄N₂Na₂O₂·2H₂O; abbreviated as EDTA), acetic acid (CH₃COOH; abbreviated as HOAc) and hydrofluoric acid (HF) were purchased from Sigma-Aldrich (Ontario, Canada) to prepare the extraction solutions. All solutions were prepared using nanopure water (Barnstead nanopure, Thermo Scientific), and the pH of the extractant solution, if required, was adjusted to the desired level (as reported in Table S1) with either sodium hydroxide (NaOH) or appropriate acid (HOAc, H₂C₂O₄ or HNO₃). The reagent blanks from all the extraction solutions were also analyzed along with the experimental samples. Negligible concentrations of trace elements (As was undetectable) were found in all the blank solutions that were accounted for during calculations. All laboratory glass-and plastic-ware was cleaned by soaking in 5% (v/v) HNO₃ overnight and then repeatedly rinsed with nanopure water.

Pure phases of sodium arsenate [Na₃As(V)O₄], sodium arsenite [Na₃As(III)O₃] and arsenic oxide [As₂(III)O₃] were purchased from Sigma-Aldrich (Ontario, Canada). Natural minerals such as annabergite [Ni₃(As(V)O₄)₂], orpiment [As₂(III)S₃] and arsenopyrite [FeAs(III)S] were collected from the Mineralogy Petrology Museum in the Department of Earth and Atmospheric Sciences at the University of Alberta, Canada. These salts and minerals were used to obtain X-ray diffraction (XRD) patterns and X-ray absorption near edge structure (XANES) white line energy positions (As absorption edge energy) of arsenite (As^{III}) and arsenate (As^V) for comparison with the sediment As.

2.2. Sediment collection and their physicochemical characterization

The Alberta Geological Survey, Alberta Energy Regulator (AGS-AER) drilled surficial deposits (105 to ~300 m-thick sediments above bedrock) at eight different locations in the Cold Lake area (southeast part of the Athabasca Oil Sands) to explore the hydrogeology and hydrogeochemistry of the region. The cores were stored in wooden boxes at the AGS Mineral Core Research Facility in Edmonton, Alberta, Canada under ambient conditions. To cover a large area in the region, these already drilled cores were used for As distribution in sediments. For this study, five sediment cores (four cores drilled in 1999–2000 namely WR99-1, WEPA99-1, WEPA99-2, and WEPA00-1, and one core drilled in 2009 namely 14-01w) were selected based on stratigraphic units and their proximity to buried channel aquifers (Fig. S1A). The stratigraphy of the area consists of eight glacial and non-glacial formations (Fig. S1B), and the nature and distribution of geological sediments are well described by Andriashok (2003). Because of the lithological heterogeneity in each sediment core, sub-samples were taken along the whole core depth to represent each stratum (based on visual observation) in the cores. In addition, sub-samples were also collected from the depths that represent oxidized (brownish sediment due to Fe oxyhydroxide) and reduced [grayish sediment due to high iron sulfide (FeS)] zones as well as the zones of surficial (<75 m deep) and buried (75–150 m deep) channel aquifers to correlate sediment redox conditions with groundwater As concentration.

Sediment cores were air dried when sub-samples were taken in 2010, which might have changed the oxidation state of As in the sediments. Therefore, chemical speciation of As was not performed using these sediments. Total As concentrations determined in the sediments taken from the outer and inner portions of the cores were compared to the As concentration determined at the time of core collection by Andriashok (2003). No significant difference was found in As concentrations between the outer and inner sediments and the As determined in

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