



# Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada



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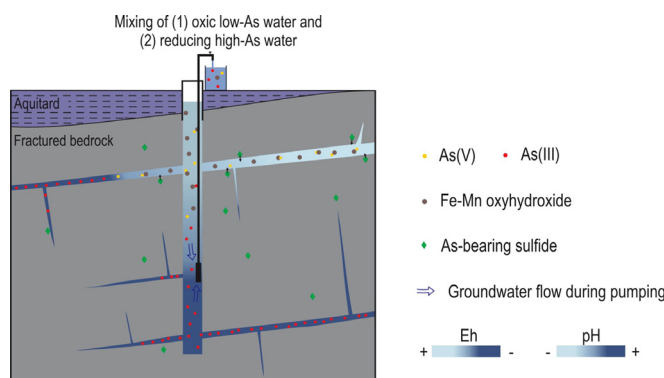
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## HIGHLIGHTS

- High As concentrations (> 10 ppb) were measured in private bedrock wells
- The oxidation of As-bearing sulfides is the primary source of As in groundwater
- As(III) was the major As species in bedrock well waters
- As in bedrock wells originates from reducing chemically evolved groundwater
- Private well users are exposed to high As concentrations

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 4 July 2016

Received in revised form 30 August 2016

Accepted 30 August 2016

Available online xxxx

Editor: D. Barcelo

### Keywords:

Arsenic  
Speciation  
Fractured bedrock aquifer  
Private wells  
Groundwater quality  
Abitibi-Témiscamingue

## ABSTRACT

High arsenic concentrations occur in groundwater collected from a fractured crystalline bedrock aquifer in western Quebec (Canada). Sampling and analysis of water from 59 private wells reveal that more than half of the bedrock wells exceed the Canadian guideline value of 10 µg/l for arsenic, whereas shallow wells in unconsolidated surficial deposits are not affected by the contamination. The weathering of arsenic-bearing sulfides present along the mineralized fault zone is considered to be the primary source of arsenic in groundwater. High-arsenic wells are generally characterized by mildly reducing conditions ( $E_h < 250$  mV), weak alkaline conditions ( $pH > 7.4$ ), low Ca/Na ratios, elevated dissolved Fe and Mn concentrations and high proportions of As(III). Private bedrock wells are open boreholes that likely receive groundwater from multiple contributing fractures. Hence, it is proposed that dissolved arsenic is mainly derived from the contribution to the well discharge of reducing and alkaline geochemically evolved groundwater that contains arsenic as As(III). Geochemically evolved groundwater provides favorable conditions to release arsenic by reductive dissolution of iron and manganese oxyhydroxides and alkaline desorption from mineral surfaces. Thus, high-arsenic wells would contain a high proportion of geochemically evolved groundwater, while oxidizing low-pH recharge water causes dilution and sequestration of arsenic. In relation with the chemical evolution of groundwater along the flow path, most contaminated wells are located in confined areas whereas most of the wells located in unconfined recharge areas are not contaminated. The occurrence of boreholes with high dissolved arsenic as As(V) and oxidizing conditions is attributed to extensive sulfide oxidation and alkaline desorption. This work shows that the determination of arsenic speciation provides a valuable tool to investigate the behavior of arsenic in bedrock groundwater.

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## 1. Introduction

The occurrence of geogenic arsenic (As) in groundwater is of major concern in fractured crystalline bedrock aquifers, in particular for residents of rural regions that rely on private bedrock wells for their domestic water supply (Ryan et al., 2013; Zheng and Ayotte, 2015). Long-term exposure to arsenic through drinking water is known to cause multiple adverse health effects including diabetes; peripheral neuropathy; cardiovascular diseases; and skin, lung, bladder and kidney cancers (Ravenscroft et al., 2009; WHO, 2011). Arsenic is generally considered to be primarily released into bedrock groundwater through the oxidation of sulfide minerals such as arsenian pyrite and arsenopyrite (e. g. Kim et al., 2012; Ryan et al., 2013). However, under oxidizing and near-neutral conditions, dissolved arsenic tends to be sequestered in secondary minerals, in particular by adsorption onto iron and manganese oxyhydroxides as well as clay minerals (Boyle et al., 1998; Yang et al., 2015). In contrast, arsenic is readily released from these secondary phases under reducing and alkaline conditions owing to the reductive dissolution of metal oxyhydroxides (Lipfert et al., 2006; Yang et al., 2015) and the desorption from mineral surfaces (Ayotte et al., 2003; Boyle et al., 1998), respectively. In relation to this, high arsenic concentrations have been commonly measured in bedrock wells under mildly reducing and weakly alkaline conditions (Kim et al., 2012; Ryan et al., 2013). However, the specific processes controlling dissolved arsenic concentrations in boreholes are still unclear, mostly owing to the complexity of groundwater flow which can receive water from multiple discrete fractures with contrasting chemistry and redox status (Harte et al., 2012; Shapiro, 2002; Yang et al., 2015). Therefore, since most studies of arsenic in bedrock groundwater are based on well water samples, the understanding of the mechanisms of arsenic mobilization and the distribution of dissolved arsenic in fractured bedrock aquifers remains challenging. In particular, little is known about the influence of the hydrogeological conditions on dissolved arsenic in bedrock groundwater. Moreover, knowledge on arsenic speciation in groundwater remains very limited (Sorg et al., 2014), particularly in fractured bedrock aquifers. Yet, the speciation is important because the toxicity and mobility of arsenic are dependent on its chemical form (Sorg et al., 2014; Watts et al., 2010). In natural groundwater, arsenic predominantly occurs in inorganic form either as arsenate ( $\text{As(V)}$ ) under oxidizing conditions, in the form of monovalent  $\text{H}_2\text{AsO}_4^-$  and divalent  $\text{HAsO}_4^{2-}$ , or as arsenite ( $\text{As(III)}$ ) under more reducing conditions, in the form of uncharged  $\text{H}_2\text{AsO}_3$  at pH less than about 9.2 (Sharma and Sohn, 2009). Arsenic can also occur in organic form, most commonly monomethylated acids (MMA) and dimethylated acids (DMA), as a result of methylation reactions catalyzed by microbial activities (Maguffin et al., 2015; Ravenscroft et al., 2009). However, very few investigations have considered the occurrence of organic species of arsenic in groundwater. Inorganic species are generally recognized as more toxic than organic species, in particular  $\text{As(III)}$  (Sharma and Sohn, 2009). Owing to its neutral charge below pH 9.2,  $\text{As(III)}$  is regarded as more mobile than  $\text{As(V)}$  except under weak alkaline conditions (Sharma and Sohn, 2009). The difficulty of acquiring data is likely responsible for the lack of information on arsenic speciation. In fact, field separation procedures are generally required for determining arsenic speciation in groundwater since there is currently no universal preservation method to prevent changes in arsenic species that may occur between sampling and laboratory analysis, particularly in water containing iron and manganese (Bednar et al., 2004; Sorg et al., 2014).

The occurrence of high arsenic concentrations in private bedrock wells has been widely reported in northeastern United States including Maine (Ayotte et al., 2003; Lipfert et al., 2006), New Hampshire (Ayotte et al., 2003; Peters and Blum, 2003) and Vermont (Ryan et al., 2013), and, to a lesser extent, in eastern Canada such as in New Brunswick (Bottomley, 1984), Nova Scotia (Grantham and Jones, 1977) and Newfoundland (Serpa et al., 2009). Although less well documented, elevated arsenic concentrations also occur in bedrock groundwater from the

Canadian Shield in the Province of Quebec, Canada. In the Abitibi-Temiscamingue region (western Quebec), private bedrock wells have been reported to contain arsenic concentrations greater than the World Health Organization and Canadian drinking water standard of  $10 \mu\text{g/l}$  (Gagnon et al., 2016; Lalonde et al., 1981; Poissant, 1997). Exposure to arsenic in drinking water is a public health concern in the Abitibi-Temiscamingue region because groundwater is the main source of domestic water for more than 70% of the population. It is estimated that about 40% of the population that relies on groundwater as a source of drinking water uses private domestic wells, the vast majority being completed in the fractured bedrock aquifer (MDDELCC, 2015). A previous study of private well users in the region (Lampron-Goulet, 2012) revealed that diabetes, personal history of diabetes, and use of oral hypoglycemic agents or insulin were associated with arsenic concentration in well water. In addition, a recent study of 153 households supplied by a private well (Gagnon et al., 2016) confirmed the association of urinary and toenail arsenic with concentration of inorganic arsenic in wells and daily well water inorganic arsenic intake. Although abandoned or active mining sites are often located in the vicinity of contaminated areas, the presence of arsenic in groundwater is generally considered to be of natural origin, associated with the occurrence of arsenic in mineralized fault zones and metasedimentary formations (Poissant, 1997). However, to date, little is known about the geochemical processes responsible for the arsenic contamination in groundwater from the crystalline bedrock aquifer of the region.

The main objective of this paper is to evaluate the mobility and speciation of naturally occurring arsenic in a fractured bedrock aquifer. The study was conducted in a small mineralized area of the Abitibi-Temiscamingue region known as a contaminated zone by the regional health agency (Poissant, 1997). Groundwater samples from private domestic wells were analyzed for major, minor, traces elements, and arsenic species using a field separation method. The influence of the sampling wells characteristics was considered in the interpretation of the collected data.

## 2. Study area

The study area covers about  $30 \text{ km}^2$  located in the Rapide-Danseur and Duparquet municipalities, in the western part of the Province of Quebec, Canada (Fig. 1). This is a rural area, sparsely populated, and mostly occupied by boreal forest, marshlands and grasslands for pasture. The topography is slightly hilly with a surface elevation ranging from 268 to 310 m above the sea level. Geologically, the study area lies on the Archean Abitibi greenstone belt in the southern part of the Superior Province of the Canadian Shield (Fig. 1 (A)). The Abitibi Subprovince is composed of volcanic and sedimentary rocks intruded by granitoids and mainly metamorphosed at the greenschist facies (Goutier and Lacroix, 1992). The volcano-sedimentary units are separated by east-west trending fault systems such as the Porcupine-Destor fault that crosses the study area (Fig. 1 (B)). In the study area, the bedrock is mainly composed of basalts from the Deguisier formation north of the Porcupine-Destor fault and from Hébécourt formation south of the fault. In the fault zone, the metasedimentary rocks essentially consist of sandstone and mudstone from the Mont-Brun and Duparquet formations (Goutier and Lacroix, 1992). The Porcupine-Destor deformation zone represents an important gold metallotect in the Abitibi Subprovince (Legault et al., 2005). To the south-west of the study area, the abandoned Beattie-Donchester gold mine operated about 10 million tonnes of ore between 1933 and 1956 (Legault et al., 2005). The extraction of the gold associated with pyrite and arsenopyrite mineralization left 140 ha of arsenic rich tailings on site (MDDELCC, 2016) (Fig. 1 (C)). In the study area, the Porcupine-Destor deformation zone mainly consists of quartz-carbonates veins with high arsenic content associated with the occurrence of arsenian pyrite and arsenopyrite (MERN, 2016). The Precambrian bedrock is largely covered by Quaternary sediments deposited during the last ice retreat

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