UNIVERSITÉ DU QUÉBEC EN ABITIBI-TÉMISCAMINGUE

ORIGINE ET DISTRIBUTION DE L'ARSENIC DANS L'EAU SOUTERRAINE DE L'AQUIFÈRE ROCHEUX FRACTURÉ DU BOUCLIER CANADIEN EN ABITIBI-TÉMISCAMINGUE

THÈSE
PRÉSENTÉE
COMME EXIGENCE PARTIELLE
DU DOCTORAT EN SCIENCES DE L'ENVIRONNEMENT

PAR
RAPHAËL BONDU

MAI 2017

AVANT-PROPOS

Cette thèse de doctorat, présentée dans le cadre du doctorat en sciences de l'environnement de l'Université du Québec à Montréal offert en association avec l'Université du Québec en Abitibi-Témiscamingue, est organisée autour des 3 articles suivants :

Bondu, R., Cloutier, V., Benzaazoua, M., Rosa, E., & Bouzahzah H. (2017). The role of sulfide minerals in arsenic contamination of bedrock groundwater in western Quebec, Canada. En préparation.

Bondu, R., Cloutier, V., Rosa, E., & Benzaazoua, M. (2017). Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada. Science of the Total Environment, 574, 509-519.

Bondu, R., Cloutier, V., Rosa, E., & Benzaazoua, M. (2016). A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. Water, Air, & Soil Pollution, 227(9), 296.

Les articles sont rédigés en anglais, selon les standards de publication des revues internationales, alors que le reste de la thèse est rédigé en français.

L'élaboration de la méthodologie, la collecte, l'analyse et l'interprétation des données, ainsi que la rédaction ont été principalement réalisées par le premier auteur de ces 3 articles. La contribution de Vincent Cloutier, directeur de recherche, a concerné le financement du projet, le support dans l'élaboration de la méthodologie et la rédaction des 3 articles, ainsi que la collecte, l'analyse et l'interprétation des données pour les articles 1 et 2. L'apport d'Eric Rosa, co-directeur de recherche, a porté sur la collecte, l'analyse et l'interprétation des données, ainsi que la rédaction de l'article 1 ; l'analyse et l'interprétation des données, ainsi que la rédaction de l'article 2 ; et l'élaboration de la méthodologie et la rédaction de l'article 3. Le support de Mostafa Benzaazoua, co-directeur de recherche, a porté sur la rédaction des 3 articles, ainsi que l'élaboration de la méthodologie, la collecte, l'analyse et l'interprétation des données de l'article 1. La contribution de Hassan Bouzahzah, agent de recherche à l'UQAT, a concerné l'élaboration de la méthodologie, la collecte et l'analyse des données de l'article 1.

REMERCIEMENTS

Ce travail de doctorat n'aurait évidemment pas pu être réalisé sans le soutien de nombreuses personnes. Je tiens tout d'abord à remercier mes encadrants, à commencer par Vincent Cloutier, directeur de recherche et instigateur de ce projet, pour son encadrement dynamique, positif et ses choix toujours judicieux. Je remercie Eric Rosa, co-directeur de recherche arrivé en cours de route, qui a su apporter un excellent soutien scientifique, de par ses commentaires constructifs et sa disponibilité. Merci à Mostafa Benzaazoua, co-directeur de recherche depuis le campus de Rouyn-Noranda, pour son encadrement efficace et son expertise indispensable en minéralogie. Je remercie toute l'équipe du Groupe de recherche sur l'eau souterraine (GRES) du campus d'Amos pour le soutien et les conseils tout au long de la thèse, en particulier Daniel Blanchette, Simon Nadeau, Magalie Roy et Nathalie Rey. Je tiens également à remercier Marc Paquin, chimiste à l'Institut de recherche en mines et en environnement (IRME), pour sa collaboration et son travail de développement des méthodes d'analyse. Je remercie Jean Goutier, géologue au Ministère de l'Énergie et des Ressources naturelles, pour son apport dans le comité d'encadrement et les discussions enrichissantes sur la géologie régionale. Je remercie Florent Barbecot, professeur à l'Université du Québec à Montréal, pour sa contribution au sein du comité d'encadrement. Je remercie également Carmen Mihaela Neculita, Alain Rouleau et Peter Crowley Ryan pour leur contribution dans le jury de thèse. Un grand merci à Danièle Laporte et Ann Gervais pour leur dynamisme et pour tous les services rendus.

Je remercie ici toutes les personnes qui ont contribué à l'élaboration du chapitre 2. Merci à Sébastien Vigneau, Patrick Lavoie et Daniel Bernard d'Hecla Québec pour leur accueil et leur aide précieuse dans la sélection des échantillons, Rémy Bilodeau de Technominex pour son aide dans le transfert des échantillons de roche

et Benoît Plante pour ses conseils sur les essais en laboratoire. Je tiens à remercier le personnel disponible et efficace de l'Unité de recherche et de service en technologie minérale (URSTM) qui a participé aux travaux de laboratoire. Un grand merci à Alain Perreault et Mathieu Villeneuve pour leur excellent travail dans le suivi des cellules humides, ainsi qu'à Mélinda Gervais, Mélanie Bélanger, Amélie Cyr et Annie-Claude Drouin pour les analyses chimiques. Je remercie enfin Simon Nadeau, Daniel Blanchette et Marika Labbé pour leur support lors des travaux de terrain.

Concernant l'élaboration du chapitre 3, je tiens à remercier Frédéric Bilodeau, de l'Agence de la Santé et des Services Sociaux de l'Abitibi-Témiscamingue, pour le transfert des données relatives à la contamination des puits individuels dans la région. Merci à Jean Goutier pour ses précisions sur la géologie du secteur d'étude et à Yacouba Fomba pour son aide précieuse durant la campagne d'échantillonnage. Enfin, je remercie Pooneh Golestani pour sa révision de l'anglais scientifique.

Pour le reste, je remercie Emeline pour sa patience et son soutien de tous les instants, ma maman Marie-Claude pour m'avoir inculqué la curiosité et le plaisir d'apprendre, et ma sœur Aurore pour sa générosité et toutes ses attentions.

TABLE DES MATIÈRES

LISTE DES FIGURES

LISTE DES TABLEAUX

RÉSUMÉ

L'arsenic (As) est un des contaminants naturels de l'eau souterraine les plus problématiques à l'échelle mondiale. Dans les aquifères rocheux fracturés, les concentrations naturelles en arsenic dans l'eau souterraine peuvent dépasser la recommandation de 10 µg/l de l'Organisation Mondiale de la Santé. L'exposition à l'arsenic via la consommation d'eau issue de puits domestiques peut entraîner divers problèmes de santé incluant cancers, troubles cardiovasculaires ou encore diabètes. L'objectif de cette thèse de doctorat est d'améliorer les connaissances sur l'origine et la distribution de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés, en s'appuyant sur le cas de la contamination de l'aquifère rocheux du Bouclier canadien dans la région de l'Abitibi-Témiscamingue (Province de Québec, Canada). Pour ce faire, ce travail de recherche se base sur une démarche pluridisciplinaire incluant approche conceptuelle, investigations de terrain et de laboratoire ainsi que travaux de modélisation. L'introduction (chapitre 1) présente la problématique de la contamination naturelle à l'arsenic dans les aquifères rocheux ainsi que les objectifs et la méthodologie de recherche. La libération d'arsenic à partir de l'altération des minéraux sulfurés est généralement considérée comme la source primaire principale d'arsenic dans l'eau souterraine. Dans le chapitre 2, les résultats d'investigations minéralogiques, d'essais de laboratoire et d'analyses d'eau souterraine dans une zone minéralisée confirment cette hypothèse et montrent par ailleurs que la libération d'arsenic est en partie déterminée par la susceptibilité des sulfures par rapport à l'altération. L'oxydation de la gersdorffite (NiAsS), minéral du groupe de la cobaltite, libère davantage d'arsenic que l'oxydation de l'arsénopyrite (FeAsS), l'un des minéraux d'arsenic les plus courants. Ces résultats suggèrent que la minéralogie des sources primaires d'arsenic pourrait avoir un impact significatif sur les concentrations en arsenic dans des zones où l'oxydation des sulfures constitue un mécanisme important de mobilisation. Néanmoins, ce travail montre que la concentration d'arsenic dans l'eau souterraine ne dépend pas uniquement de la libération d'arsenic à partir des minéraux sulfurés, mais aussi de sa mobilité dans l'eau souterraine qui est elle-même fonction des conditions géochimiques dans l'aquifère. Dans le chapitre 3, des investigations hydrochimiques dans les puits domestiques d'un secteur contaminé de la région suggèrent que les fortes concentrations en arsenic sont majoritairement associées à des eaux souterraines géochimiquement évoluées caractérisées par des conditions réductrices et alcalines. La spéciation de l'arsenic est dominée par l'arsénite (As(III)), l'espèce la plus toxique d'arsenic, alors que des espèces organiques méthylées sont présentes à des concentrations relativement faibles mais néanmoins détectables. L'arsenic apparaît comme étant essentiellement mobilisé par un processus à deux étapes mettant en jeu (1) l'altération des minéraux sulfurés dans la partie oxydante de l'aquifère, suivie par (2) la dissolution dans la partie plus réductrice de l'aquifère des oxyhydroxides de fer et de manganèse qui sont considérés comme les principaux minéraux secondaires d'arsenic. En lien avec l'évolution géochimique de l'eau souterraine, les concentrations élevées d'arsenic sont généralement observées dans les zones captives de l'aquifère situées dans la partie aval des systèmes d'écoulement. À l'inverse, les eaux souterraines des zones de recharge libres contiennent en général de faibles concentrations d'arsenic, à l'exception de celles associées à l'oxydation des sulfures. L'écoulement de l'eau souterraine apparaît donc être un facteur déterminant dans la mobilisation de l'arsenic dans les aquifères rocheux. En ce sens, le chapitre 4 examine l'impact des modifications des conditions hydrologiques sur les concentrations en arsenic en contexte de changements climatiques. Lors des épisodes plus fréquents de sécheresse extrême, il se pourrait que la baisse des niveaux piézométriques accélère l'oxydation des sulfures dans la zone non saturée, et que la baisse des débits renforce la présence d'eau géochimiquement évoluée favorable à la mobilisation de l'arsenic dans la zone saturée. Dans certains cas, la mobilisation de l'arsenic pourrait également être indirectement affectée par des changements dans les activités humaines, notamment ceux favorisant l'extraction et la pollution des eaux souterraines. Comme détaillé en conclusion (chapitre 5), les résultats issus de cette thèse fournissent de nouvelles informations essentielles à la compréhension des mécanismes contrôlant les concentrations en arsenic dans l'eau des aquifères rocheux fracturés. Les principales retombées de cette recherche pour la société concernent la gestion des problématiques associées à la présence d'arsenic dans les captages destinés à l'approvisionnement en eau potable. La qualité de l'eau est une question centrale dans les aquifères rocheux fracturés qui constituent une source d'eau de plus en plus utilisée par les sociétés à travers le monde.

Mots clés : Arsenic, Aquifères rocheux fracturés, Interaction eau/roche, Minéraux sulfurés, Changements climatiques.

ABSTRACT

Arsenic (As) is a major naturally occurring contaminant of groundwater in the world. In particular, natural arsenic concentrations exceeding the World Health Organization guideline value of 10 µg/l may occur in groundwater from bedrock aquifers. Exposure to arsenic through the consumption of water from private domestic wells is known to cause multiple adverse health effects including cancers, cardiovascular diseases and diabetes. The overall objective of this doctoral thesis is to improve knowledge on the origin and distribution of arsenic in groundwater from fractured bedrock aquifers. For this purpose, a multidisciplinary approach including field, laboratory, conceptual and modeling investigations was performed to study the arsenic contamination of groundwater from the bedrock aquifer of the Canadian Shield in the Abitibi-Temiscamingue region (Province of Quebec, Canada). The introduction (chapter 1) presents the issue of the natural arsenic contamination in bedrock aquifers and the objectives and methods of this research. The release of arsenic from the weathering of sulfide minerals is generally considered to be the primary source of arsenic in groundwater. In chapter 2, the results of mineralogical investigations, laboratory tests and groundwater analyses in a mineralized area confirm this hypothesis and show that arsenic release may be affected by the susceptibility of sulfides to weathering. The oxidation of gersdorffite (NiAsS), a mineral of the cobaltite group, releases higher amounts of arsenic than the oxidation of arsenopyrite (FeAsS), one of the most common arsenic minerals. These findings suggest that the mineralogy of primary arsenic sources may significantly influence arsenic concentrations in areas where sulfide oxidation is an important mobilization mechanism. Nevertheless, this work shows that arsenic concentrations in groundwater are not only controlled by the release from sulfides, but also by the arsenic mobility that mainly depends on geochemical conditions in the aquifer. In chapter 3, the study of private domestic wells in a contaminated area suggests that high arsenic concentrations are generally associated with geochemically evolved groundwater characterized by reducing and alkaline conditions. The arsenic speciation is dominated by arsenite (As(III)), which is the most toxic species, while organic species are present at low but detectable concentration. Arsenic is expected to be mainly released by a two steps process involving (1) arsenic bearing sulfides weathering in the oxic/suboxic zone of the aquifer, followed later by (2) the dissolution of iron and manganese oxyhydroxides, which are considered to be the main secondary arsenic minerals, in the reducing part of the aquifer. In relation with the geochemical evolution of groundwater, high arsenic concentrations are generally observed in confined areas, in the downgradient portion of the aquifer. In contrast, unconfined recharge areas generally contain low arsenic concentrations, with the exception of those directly derived from sulfide oxidation. Therefore, groundwater flow appears to be a key factor involved in the arsenic mobilization in bedrock aquifers. In relation to this, chapter 4 presents an evaluation of the potential effects of hydrological changes on arsenic mobilization under climate change. During more frequent extreme drought periods, it is likely that the drop in water table increases the oxidation of sulfides in the unsaturated zone ; and the decrease in groundwater flow increases the occurrence of geochemically evolved groundwater favorable to the mobilization of arsenic in the saturated zone. In some cases, arsenic mobilization may also be indirectly affected by climate change through changes in human activities, particularly those causing increased groundwater withdrawals and pollution. As detailed in the conclusion (chapter 5), the results of this doctoral thesis provide essential information for the understanding of the geochemical processes controlling the mobilization of arsenic in groundwater from bedrock aquifers. The benefits to society concern the management of problems associated with the occurrence of arsenic in drinking water supplies. The water quality is a key issue in bedrock aquifers which represent a source of drinking water increasingly used across the world.

Keywords : Arsenic, Fractured bedrock aquifers, Water-rock interaction, Sulfide minerals, Climate change.

CHAPITRE 1

INTRODUCTION GÉNÉRALE

1.1 Importance de la qualité de l'eau souterraine

L'eau souterraine représente une ressource stratégique pour de nombreuses sociétés, notamment en raison de son omniprésence et de sa qualité. Elle constituerait la majeure partie de l'eau douce disponible sur Terre et à l'heure actuelle près de la moitié de la ressource en eau potable utilisée dans le monde (UNESCO, 2008; World Water Assessment Programme, 2009). L'eau souterraine exerce également des fonctions essentielles au maintien des régimes hydriques et des écosystèmes dans beaucoup de régions du monde (Treidel et al., 2012). Dans le futur, la pression sur la ressource en eau devrait continuer à s'intensifier en lien avec la croissance de la population mondiale et l'augmentation de la demande pour l'agriculture, l'accès à l'eau potable, les activités industrielles et la production d'énergie (World Water Assessment Programme, 2009). Par ailleurs, les changements climatiques devraient grandement modifier la disponibilité des ressources en eau dans le monde (Treidel et al., 2012). Comme les eaux de surface sont susceptibles d'être les premières affectées du fait de leur relation plus directe avec le climat, il est vraisemblable que notre dépendance à l'eau souterraine s'accroisse fortement à l'avenir (Kundzewicz et Doell, 2009). La disponibilité de la ressource en eau souterraine représente donc un enjeu majeur pour les sociétés. Celle-ci dépend autant de la quantité d'eau souterraine que de sa qualité, c'est-à-dire de ses caractéristiques physiques, chimiques et biologiques. La qualité peut constituer un facteur limitant d'utilisation de l'eau souterraine, en particulier pour la consommation d'eau potable ou l'irrigation des cultures (Gurdak et al., 2012). La dégradation de la qualité de l'eau souterraine peut être d'origine anthropique, comme dans le cas de contaminations liées à l'entreposage de déchets domestiques et industriels, à l'utilisation d'engrais et de pesticides, au rejet d'eaux usées, ou au déversement accidentel de produits chimiques. La qualité de l'eau peut aussi se déteriorer naturellement, en lien avec la présence de substances géogènes, tels que le fluor et certains éléments métalliques. Parmi les contaminants inorganiques naturels de l'eau souterraine, l'arsenic est sans doute celui qui pose le plus de problèmes vis-à-vis de la santé humaine à l'échelle mondiale (Ravenscroft et al., 2009).

1.2 L'arsenic dans l'environnement et les eaux naturelles

1.2.1 Géochimie de l'arsenic

L'arsenic (As) est un élément connu pour ses effets néfastes sur les organismes vivants et la santé humaine. C'est un métalloïde, c'est-à-dire un élément ayant des propriétés hybrides entre les métaux et les non-métaux. De numéro atomique 33, il se situe dans le groupe 15 du tableau périodique des éléments avec l'azote (N), le phosphore (P), l'antimoine (Sb) et le bismuth (Bi). Bien que l'arsenic puisse s'associer de manière covalente avec un grand nombre d'éléments, on le retrouve le plus souvent lié au soufre (S) et à l'oxygène (O) dans l'environnement (O'Day, 2006). On le rencontre essentiellement au degré d'oxydation -3, -1 , 0, +3 et +5, rarement sous sa forme élémentaire, principalement sous forme d'arsénosulfures, d'arséniures, d'arsénites et d'arséniates. Dans les arsénosulfures et les arséniures, l'arsenic se présente sous forme réduite (valence de -1 et 0), alors que dans les arsénites et les arséniates, il se présente sous forme oxydée (valence de +3 et +5, respectivement). En solution, l'arsenic est stable sous forme d'oxyanions d'arsénite (As(III)) et d'arséniate (As(V)), qui dominent en fonction des conditions d'oxydo-réduction (figure 1.1). L'arsénite apparaît comme une espèce neutre dans les conditions de pH typiques des eaux naturelles ($pK_{a1} = 9{,}2$), alors que l'arséniate a tendance à former des anions univalent ou divalent ($pK_{a1} = 2{,}3$, $pK_{a2} = 7{,}0$)(figure 1.1). Une grande variété de composés organiques methylés de l'arsenic existent comme sous produits des activités bactériennes, fongiques, et eukaryotiques. Les mieux connus sont l'acide monométhylarsonique (MMA(V)) et l'acide diméthylarsinique (DMA(V)) qui sont relativement stables dans l'environnement. À noter que dans des environnements riches en soufre, l'arsenic peut exister sous forme de thioarsenic dans lequel les atomes d'oxygène sont remplacés par des atomes de soufre (Campbell et Nordstrom, 2014).

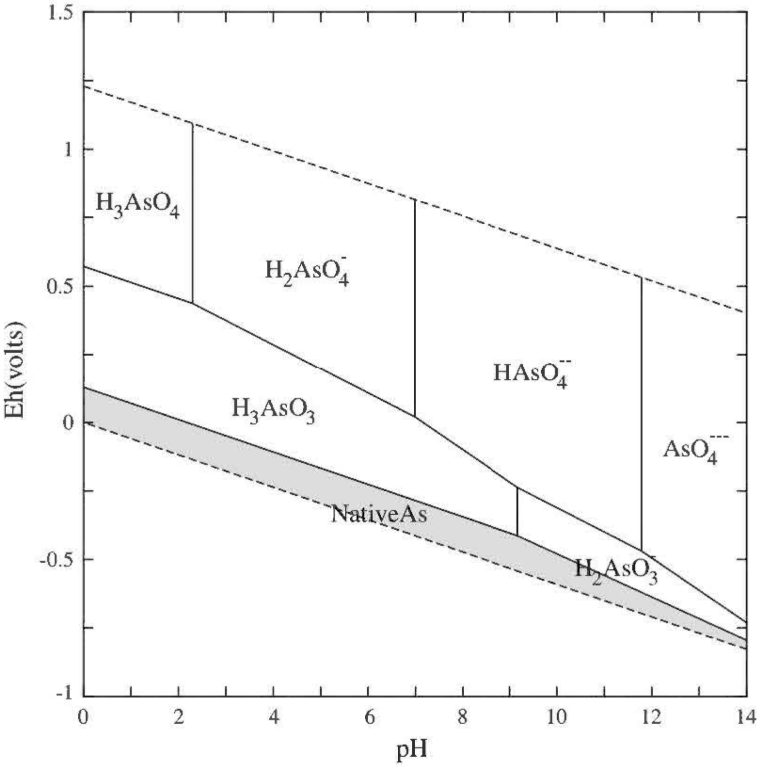

Figure 1.1. Diagramme Eh-pH pour le système As-O-H à 25 °C et 1 bar avec $\Sigma As = 10^{-6}$ M (tiré de Lu et Zhu, 2011).

1.2.2 La lithosphère, source d'arsenic dans l'environnement

Le principal réservoir d'arsenic dans l'environnement est la lithosphère. La concentration moyenne d'arsenic dans la croûte terrestre est évaluée entre 1,0 et 1,8 mg/kg (Henke, 2009), mais les teneurs en arsenic peuvent être très variables selon les environnements géologiques. L'arsenic tend à se concentrer dans les dépôts hydrothermaux généralement associés aux roches magmatiques et métamorphiques. Il peut également être abondant dans les charbons et les lignites ainsi que dans les roches sédimentaires d'origine marine formées dans des conditions réductrices comme certaines argilites (Bowell et al., 2014). L'arsenic ne se substitue pas facilement dans des minéraux abondants tels que les silicates et les carbonates, et est généralement présent dans des minéraux sulfurés et des oxydes. On dénombre actuellement dans la nature plus de 560 minéraux dans lesquels l'arsenic est présent en tant que composant principal, dont environ 58 % d'arséniates, 24 % de sulfures et sulfosels, 8 % d'oxydes et d'arsénites, le reste étant des arséniures, l'arsenic sous forme native ou dans des alliages (Majzlan et al., 2014). La plupart sont des minéraux hydrothermaux et leurs produits d'altération (Smedley et Kinniburgh, 2013). L'arsenic peut aussi se substituer au soufre et être présent à des concentrations significatives (jusqu'à 10 %) dans d'autres minéraux sulfurés tels que la pyrite, la chalcopyrite ou la galène (Smedley et Kinniburgh, 2002). À noter que dans les sédiments alluviaux, l'arsenic est généralement présent à des teneurs modérées, le plus souvent dans des oxydes de fer et dans une moindre mesure dans la pyrite framboïdale (Ravenscroft et al., 2009). Le tableau 1.1 présente une sélection de minéraux primaires et secondaires d'arsenic communs dans les dépôts hydrothermaux associés aux zones magmatiques et métamorphiques.

Tableau 1.1. Minéraux d'arsenic communs dans les dépôts hydrothermaux associés aux roches magmatiques et métamorphiques.

Minéral	Composition chimique	Groupe
Pyrite arsénifère	$Fe(S,As)_2$	Arséniosulfure
Arsénolite	As_2O_3	Arsénite
Arsénopyrite	$FeAsS$	Arséniosulfure
Cobaltite	$(Co,Fe)AsS$	Arséniosulfure
Énargite	Cu_3AsS_4	Arséniosulfure
Annabergite	$(Ni,Co)_3(AsO_4)_2 \cdot 8H_2O$	Arséniate
Gersdorffite	$NiAsS$	Arséniosulfure
Löllingite	$FeAs_2$	Arséniure
Nickéline	$NiAs$	Arséniure
Orpiment	As_2S_3	Arséniosulfure
Pharmacosidérite	$KFe_4(AsO_4)_3(OH)_4 \cdot (6\text{-}7)H_2O$	Arséniate
Réalgar	AsS (As_4S_4)	Arséniosulfure
Scorodite	$FeAsO_4 \cdot 2H_2O$	Arséniate

1.2.3 L'arsenic dans les eaux naturelles et ses impacts sur la santé humaine

La présence d'arsenic dans les eaux naturelles est dans la majorité des cas d'origine géogène, bien que localement de fortes concentrations en arsenic peuvent être liées à des pollutions industrielles (Chatterjee et al., 1993), des activités minières (Williams, 2001) ou plus rarement à des pesticides et herbicides (Peryea et Creger, 1994) et des additifs pour l'alimentation animale (D'Angelo et al., 2012). En général, les eaux de surface contiennent naturellement peu d'arsenic. En revanche, les eaux souterraines peuvent contenir des concentrations significatives d'arsenic géogène du fait de l'influence des interactions eau/roche sur leur composition chimique et des conditions géochimiques favorables à la mobilisation de l'arsenic dans les aquifères (Smedley et Kinniburgh, 2013; Campbell et Nordstrom, 2014). Les concentrations d'arsenic dans les eaux souterraines peuvent atteindre plusieurs milligrammes par litre (mg/l), alors qu'elles dépassent rarement quelques microgrammes par litre (µg/l) dans les eaux de surface. L'arsenic est probablement unique, y compris parmi les éléments qui apparaissent sous forme d'oxyanions tels que le sélénium (Se), l'antimoine (Sb), le chrome (Cr), le vanadium (V) ou le molybdène (Mo), par sa capacité à être mobilisé dans des gammes de pH typiques des eaux naturelles (6,5 à 8,5), et dans des conditions réductrices comme oxydantes (Smedley et Kinniburgh, 2002). L'arsenic représente ainsi une sérieuse menace pour la santé humaine lorsque de l'eau souterraine contaminée est utilisée comme source d'eau potable ou comme eau d'irrigation pour les cultures (Ravenscroft et al., 2009). On estime qu'actuellement plus de 200 millions de personnes dans le monde consomment de l'eau souterraine dépassant la recommandation de 10 µg/l de l'Organisation Mondiale de la Santé (Naujokas et al., 2013). La plupart des personnes affectées se situent dans les bassins alluviaux et deltas asiatiques, notamment au Bangladesh, en Inde, en Chine ou encore au Vietnam (Nickson et al., 2000; Berg et al., 2001; Rodríguez-Lado et al., 2013). L'ingestion d'arsenic par la consommation d'eau et de nourriture contaminées peut être à l'origine de nombreux problèmes de santé tels que des cancers de la peau, du foie, des reins ou de la vessie, des diabètes, des troubles cardiovasculaires, neurologiques ou encore reproductifs (Ravenscroft et al., 2009; Naujokas et al., 2013).

1.2.4 L'arsenic dans l'eau souterraine des aquifères rocheux fracturés et cas de l'Abitibi-Témiscamingue

La contamination naturelle des eaux souterraines à l'arsenic se produit dans des contextes géologiques variés, incluant des bassins alluviaux, des sédiments éoliens, et des roches fracturées du socle cristallin. Bien que les cas de contamination les plus problématiques se situent dans des aquifères alluviaux de régions densément peuplées en Asie, la majorité des problèmes de contamination à l'arsenic dans le monde sont associés à des aquifères rocheux (Ravenscroft et al., 2009). Les aqui-

Figure 1.2. Localisation de l'Abitibi-Témiscamingue au sein du Bouclier canadien.

fères rocheux fracturés désignent des milieux de faible perméabilité matricielle, dans lesquels l'eau s'écoule principalement dans les ouvertures des factures au sein de roches cristallines telles que des roches métamorphiques, magmatiques, volcaniques ou sédimentaires. Le plus souvent, les problèmes de contamination surgissent dans des roches métamorphisées jusqu'au faciès des schistes verts ayant subi des phénomènes d'altération hydrothermale. C'est le cas dans la région de l'Abitibi-Témiscamingue au Québec (Canada) qui chevauche la sous-province de l'Abitibi, la plus grande ceinture de roches vertes archéennes du monde, au sein de la province du Supérieur dans le Bouclier canadien (figure 1.2). La sous-province de l'Abitibi est essentiellement formée de bandes de roches métavolcaniques et métasédimentaires orientées est-ouest et recoupées par des intrusions de granitoïdes (Hocq et Verpaelst, 1994). La contamination des eaux souterraines touche des secteurs minéralisés du socle rocheux à proximité des zones de failles et en association avec des roches métasédimentaires (Poissant, 1997). Dans les secteurs ruraux, la présence d'arsenic dans l'eau souterraine constitue une problématique sanitaire majeure, du fait de la consommation d'eau souterraine issue de puits individuels pour l'alimentation en eau potable.

1.3 La problématique de la mobilisation et de la distribution de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés

1.3.1 État des connaissances

Dans les aquifères rocheux fracturés, la mobilisation de l'arsenic, c'est-à-dire le passage de l'arsenic sous forme dissoute dans l'eau souterraine, peut être causée par différents mécanismes géochimiques (figure 1.3). L'arsenic est majoritairement présent dans le socle rocheux sous forme de minéraux sulfurés, qui ne sont stables qu'en conditions réductrices. En présence d'oxygène, l'altération des minéraux sulfurés libère de l'arsenic dans l'eau souterraine. L'oxydation des sulfures peut constituer le principal mécanisme de mobilisation dans le cas où des quantités importantes de minéraux sulfurés riches en arsenic sont exposés à des conditions oxydantes. Les sulfures sont toutefois susceptibles de s'altérer lentement dans l'eau souterraine et, dans bien des cas, la séquestration par sorption ou co-précipitation dans des minéraux secondaires peut limiter les concentrations en arsenic. La séquestration de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés est principalement attribuée à des phénomènes de sorption sur des oxyhydroxydes métalliques, en particulier de fer (Fe) et de manganèse (Mn), et sur des minéraux argileux (e.g. Boyle et al., 1998; Foley et Ayuso, 2008; Smedley et al., 2007). L'arsenic peut aussi se lier de manière covalente au sein de minéraux secondaires, principalement des arséniates tels que la scorodite, l'annabergite ou la pharmacosidérite (tableau 1.1). La formation et le comportement des minéraux secondaires sont fortement dépendants des conditions géochimiques dans l'aquifère. Ainsi, la dissolution des oxyhydroxydes de Fe et de Mn riches en arsenic en conditions réductrices peut constituer le principal processus à l'origine de la mobilisation de

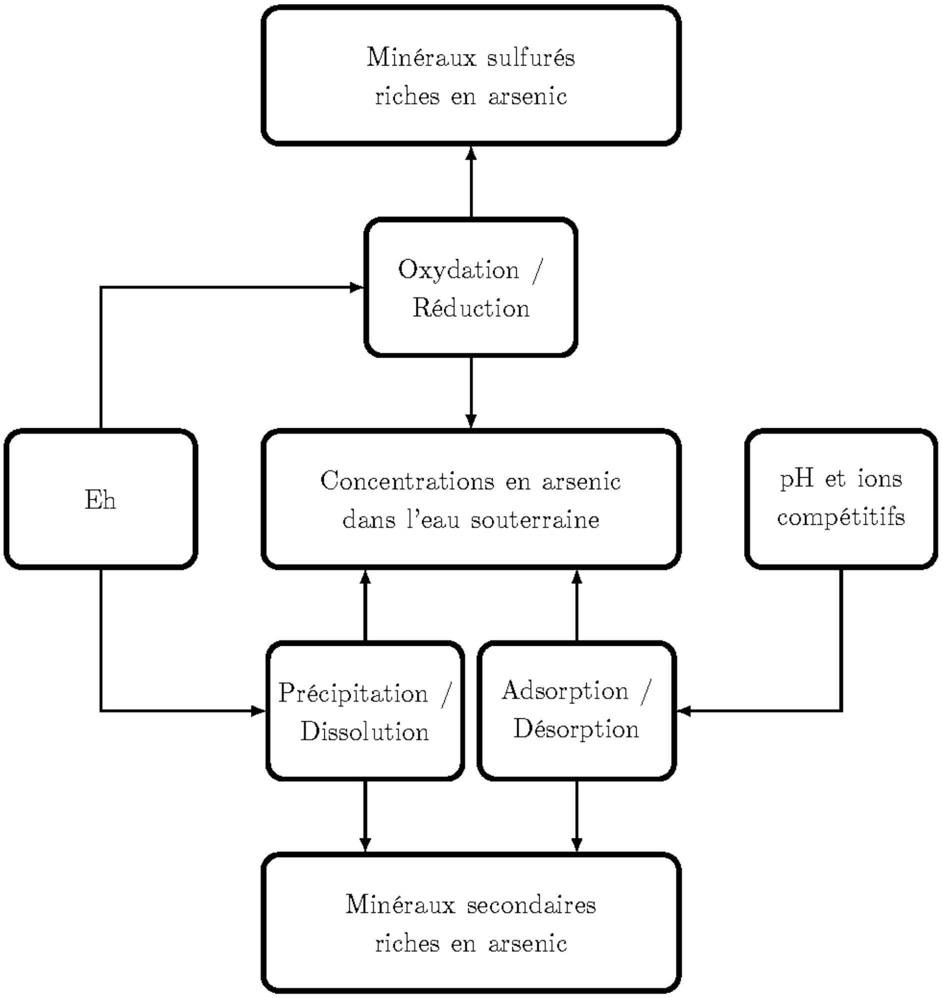

Figure 1.3. Mobilité de l'arsenic dans l'eau souterraine d'un aquifère rocheux fracturé (modifié de Bondu et al., 2016).

l'arsenic dans l'eau souterraine (e.g. Lipfert et al., 2006; Yang et al., 2015). Par ailleurs, à un pH supérieur à 7,5 - 8, les surfaces minérales des principaux minéraux adsorbants sont chargées négativement et les oxyanions d'arsenic ont tendance à être désorbés. Dans les aquifères fracturés, comme les conditions sont généralement faiblement alcalines en lien avec l'hydrolyse des silicates et la dissolution des carbonates, la désorption alcaline pourrait jouer un rôle dans la mobilisation de l'arsenic (e.g. Boyle et al., 1998; Ayotte et al., 2003; Peters et Blum, 2003).

Dans le cas de la dissolution réductrice des oxyhydroxydes métalliques et de la désorption alcaline, l'oxydation des sulfures est la source primaire d'arsenic mais les principaux mécanismes de mobilisation sont associés à des sources secondaires.

Du point de vue de la distribution spatiale des concentrations en arsenic, certaines études suggèrent que les eaux souterraines sont de plus en plus favorables à la mobilisation de l'arsenic avec leur évolution géochimique le long des chemins d'écoulement, alors que le potentiel d'oxydo-réduction diminue et que le pH augmente en lien avec les interactions eau/roche (Lipfert et al., 2006; Ryan et al., 2013). Les rares travaux portant sur la variabilité temporelle de l'arsenic dans les aquifères rocheux fracturés semblent indiquer que dans la plupart des cas les concentrations sont assez stables dans le temps, bien que dans certains cas ces dernières peuvent varier de manière très significative (Ayotte et al., 2015).

1.3.2 Lacunes scientifiques actuelles

À l'heure actuelle, il existe de nombreuses lacunes de connaissance sur la contamination naturelle à l'arsenic dans les aquifères rocheux fracturés. La spéciation de l'arsenic a encore été peu étudiée et la répartition des espèces d'arsenic dans l'eau souterraine est mal connue (Sorg et al., 2014), notamment les espèces organiques. Cela est en grande partie lié à la difficulté d'acquérir des données de spéciation fiables. Par ailleurs, les auteurs ne s'accordent pas toujours sur les mécanismes de mobilisation (Ayotte et al., 2003; Lipfert et al., 2006; Verplanck et al., 2008), bien qu'évidemment ceux-ci peuvent varier selon les aquifères. Peu de choses sont connues sur la libération d'arsenic à partir des sources primaires, notamment en relation avec la minéralogie et les conditions géochimiques dans l'aquifère. La contribution de l'oxydation des minéraux sulfurés est encore mal évaluée par rapport aux autres mécanismes de mobilisation qui impliquent des sources secondaires. L'hétérogénéité du milieu et le mélange d'eaux souterraines en provenance de différents systèmes de fractures compliquent grandement l'évaluation des mécanismes de mobilisation (Yang et al., 2015). D'une manière générale, il existe peu de connaissances sur les variations spatiales des concentrations en arsenic et des mécanismes de mobilisation. Ceux-ci sont pourtant susceptibles de varier significativement dans des environnements aussi hétérogènes que les milieux fracturés, en lien avec les variations dans la répartition des sources primaires et dans les conditions hydrogéologiques (O'Shea et al., 2015). En outre, les variations temporelles des concentrations en arsenic sont encore méconnues, alors que ces dernières pourraient être affectées par des changements de conditions hydrologiques et de niveaux d'eau souterraine. Cela pourrait avoir son importance en contexte de changement climatique, alors que l'impact des variations du climat sur la qualité de l'eau souterraine reste une question peu abordée et pourtant fondamentale. Enfin, du point de vue géographique, de nombreuses études ont été menées au Nord-Est des États-Unis (e.g. Ayotte et al., 2003; Lipfert et al., 2006; Ryan et al., 2013; Yang et al., 2015) mais relativement peu à l'Est du Canada, bien que de multiples cas de contamination à l'arsenic dans les aquifères rocheux fracturés y ont été répertoriés (Nouvelle-Écosse, Nouveau-Brunswick, Labrador, Québec). C'est notamment le cas dans la région de l'Abitibi-Témiscamingue au Québec où peu de choses sont connues sur l'origine et la distribution de l'arsenic dans les eaux souterraines du socle rocheux.

1.3.3 Objectifs de recherche

L'objectif général de cette thèse de doctorat est d'améliorer les connaissances portant sur la contamination naturelle des eaux souterraines à l'arsenic dans les aquifères rocheux fracturés. Pour répondre à cet objectif, ce travail de recherche aborde trois grands thèmes complémentaires qui se répartissent en chapitres rédigés sous forme d'articles scientifiques.

Le chapitre 2 étudie la question de la libération de l'arsenic à partir de l'altération des minéraux sulfurés. Les objectifs spécifiques associés à l'étude d'un aquifère rocheux en zone minéralisée riche en sulfures sont les suivants :

1) identifier les minéraux primaires d'arsenic ;
2) évaluer la libération d'arsenic en solution à partir de ces minéraux ;
3) déterminer les mécanismes responsables de la mobilisation de l'arsenic dans l'eau souterraine.

Le chapitre 3 s'intéresse à la forme chimique et au comportement de l'arsenic une fois libéré dans l'eau souterraine. Il a pour objectifs spécifiques, dans une zone d'étude connue par la direction de santé publique pour la contamination de nombreux puits domestiques :

1) de déterminer la spéciation de l'arsenic dans l'eau souterraine ;
2) d'évaluer les facteurs qui contrôlent la mobilité de l'arsenic dans l'aquifère ;
3) d'évaluer l'influence des conditions hydrogéologiques sur les concentrations en arsenic ;
4) d'identifier les processus contrôlant les concentrations et la spéciation de l'arsenic dans les puits domestiques.

Finalement, le chapitre 4 s'intéresse aux changements dans les mécanismes à l'origine de la contamination naturelle à l'arsenic sous l'impact des changements climatiques. Pour ce faire, il propose, à partir d'une approche conceptuelle basée sur une revue de littérature :

1) d'évaluer des impacts potentiels des changements dans l'hydrodynamique souterraine sur la géochimie de l'arsenic ;
2) de mettre en avant des stratégies d'acquisition de données pour palier au manque de connaissance sur le sujet.

1.3.4 Démarche scientifique et méthodologie

La démarche scientifique adoptée dans les chapitres 2 et 3 se base sur la collecte et l'interprétation de données géochimiques. Le chapitre 2, qui vise à caractériser les interactions entre les minéraux primaires d'arsenic et l'eau souterraine, se situe à la frontière entre l'hydrogéologie, la géochimie et la minéralogie. Trois forages dans le socle rocheux font l'objet d'une étude pluridisciplinaire incluant des analyses d'échantillons d'eau souterraine et de carottes de roche, ainsi que des essais de lixiviation en laboratoire. Les forages étudiés se situent en zone minéralisée, sur le site d'exploration minière d'Heva-Hosco (Hecla Québec). La sélection des forages est réalisée en tenant compte de la possibilité d'échantillonner de l'eau souterraine (forages non scellés), de la disponibilité de carottes de roche, et des caractéristiques lithologiques en particulier la présence de roches susceptibles de contenir des teneurs élévées d'arsenic. La collecte des données sur la chimie de l'eau souterraine est effectuée par l'échantillonnage et l'analyse de l'eau des forages. Les analyses minéralogiques et les essais de lixiviation sont réalisés à partir de carottes de roche collectées par Hecla Québec lors de la campagne de forage. Les analyses des carottes de forage incluent la détermination de la composition chimique (« XRF » ou spectrométrie de fluorescence des rayons X et digestion acide) ainsi que l'identification des principaux minéraux (« XRD » ou diffractométrie de rayons X) et des minéraux riches en arsenic (« MEB-EDS » ou microscopie électronique à balayage équipé pour l'analyse dispersive en énergie et « EPMA-WDS » ou microsonde électronique équipé pour l'analyse dispersive en longueur d'onde). Les analyses chimiques de l'eau souterraine et des lixiviats incluent la mesure des paramètres physico-chimiques (température, pH, Eh, conductivité électrique spécifique), la détermination des concentrations des anions majeurs (« IC » ou chromatographie ionique), des cations majeurs (« ICP-AES » ou spectroscopie d'émission atomique à plasma à couplage inductif) et des éléments traces métalliques (« ICP-MS » ou spectroscopie de masse à plasma à couplage inductif). La modélisation géochimique (spéciation et saturation) est effectuée à partir des données de composition chimique de l'eau souterraine et des lixiviats en utilisant le logicel PHREEQC (Parkhurst et Appelo, 1999).

Dans le chapitre 3, la collecte des données hydrogéochimiques est effectuée dans des puits individuels en collaboration avec les habitants des municipalités de Rapide-Danseur et de Duparquet. Les informations relatives aux puits et à l'utilisation de l'eau souterraine sont collectées auprès des propriétaires. La mesure des paramètres physico-chimiques et la séparation des espèces d'arsenic sont réalisées sur le terrain. Les éléments dissous sont analysés selon le même protocole que pour le chapitre 2. Les informations sur la géologie du socle rocheux sont basées sur les données du Ministère de l'Énergie et des Ressources Naturelles (MERN, 2016), alors que les informations sur les dépôts de surface et les contextes hydrogéologiques sont tirées des travaux du Groupe de recherche sur l'eau souterraine (GRES) de l'UQAT (Cloutier et al., 2015). Les données sont analysées et interprétées en faisant usage des statistiques descriptives, de la modélisation géochimique, et de représentations graphiques spécifiques.

Contrairement aux chapitres 2 et 3, la démarche scientifique du chapitre 4 est davantage déductive. La première partie consiste en une revue de littérature de la contamination à l'arsenic des eaux souterraines dans les aquifères rocheux fracturés. Elle sert de socle à une seconde partie conceptuelle qui, en considérant les dernières prévisions climatiques du Groupe d'experts intergouvernemental sur l'évolution du climat (Intergovernmental Panel on Climate Change, 2014), tente d'apporter des éléments de réponse sur l'évolution des concentrations en arsenic sous les conditions climatiques futures. Le développement s'appuie en grande partie sur des graphiques conceptuels et schématiques qui illustrent et synthétisent les arguments présentés.

CHAPITRE 2

THE ROLE OF SULFIDE MINERALS IN ARSENIC CONTAMINATION OF BEDROCK GROUNDWATER IN WESTERN QUEBEC, CANADA

Bondu, R., Cloutier, V., Benzaazoua, M., Rosa, E., Bouzahzah H.. Sources of arsenic in bedrock groundwater from a mineralized area in the Canadian Shield, Quebec, Canada. En préparation.

Résumé

Les minéraux primaires d'arsenic et leur lien avec la mobilisation de l'arsenic dans l'eau souterraine sont examinés dans une zone minéralisée du Bouclier canadien (Province de Québec, Canada). Des échantillons de carottes de forage et d'eau souterraine ont été prélevés dans trois forages d'exploration minière creusés dans l'aquifère rocheux fracturé. L'analyse minéralogique des carottes de forage indique que l'arsenic est principalement présent dans l'arsénopyrite (FeAsS) et la gersdorffite (NiAsS). Les essais de lixiviation suggèrent que la libération d'arsenic en conditions oxydantes et faiblement alcalines dépend essentiellement de la minéralogie de l'arsenic. Le taux d'oxydation élevé de la gersdorffite est vraisemblablement à l'origine de la libération importante d'arsenic à partir des échantillons de roche riches en gersdorffite par rapport aux échantillons riches en arsénopyrite. Les résultats des analyses d'eau souterraine montrent que les forages sont contaminés à l'arsenic, avec des concentrations allant de 110 à 460 µg/l. Cependant, l'altération locale de la gersdorffite n'est pas considérée comme une source importante d'arsenic dans l'eau souterraine. La composition de l'eau souterraine suggère que l'arsenic est libéré via la dissolution réductrice des oxyhydroxides de fer et de manganèse dans l'aquifère rocheux captif. En outre, l'écoulement de l'eau souterraine en provenance des zones enrichies en gersdorffite ne devrait pas contribuer significativement à l'écoulement d'eau dans le forage. La libération initiale d'arsenic via l'oxydation des sulfures en conditions oxydantes, sa séquestration dans des oxyhydroxides métalliques et des minéraux argileux, son transport dans l'eau souterraine à travers le réseau de fractures, et sa (re)mobilisation par la dissolution réductrice des oxyhydroxides de fer et de manganèse sont proposés comme étant les principaux processus responsables des teneurs élevées d'arsenic dans l'eau des forages. Davantage d'information est nécessaire concernant la libération d'arsenic à partir des minéraux sulfurés et son implication pour la contamination naturelle de l'eau souterraine.

Mots-clés

Arsenic, Oxydation des sulfures, Aquifères rocheux fracturés, Contamination de l'eau souterraine, Minéralogie de l'arsenic, Essais de lixiviation.

Abstract

The primary arsenic-bearing minerals and their relation to the mobilization of arsenic in groundwater were investigated in a mineralized area of the Canadian Shield (Province of Quebec, Canada). Bedrock core and groundwater samples were collected from three mining exploration boreholes completed in the fractured bedrock aquifer. Mineralogical analyses of core samples indicate that arsenic is mainly present in arsenopyrite (FeAsS) and gersdorffite (NiAsS). Core leaching experiments show that the release of arsenic in oxidizing and weak alkaline water largely depends on the mineralogy of arsenic. The high oxidation rate of gersdorffite is thought to explain the large amounts of arsenic released from the gersdorffite-rich rock samples compared to the arsenopyrite-rich samples. The results of groundwater analyses show that the boreholes are contaminated by arsenic at concentrations ranging from 110 to 460 µg/l. However, the local weathering of gersdorffite is not expected to be a major source of arsenic in groundwater. The groundwater composition suggests that dissolved arsenic is related to the reductive dissolution of Fe and Mn oxyhydroxides in the confined bedrock aquifer. In addition, the groundwater flow from the gersdorffite-rich zones is not expected to significantly contribute to the well discharge. It is proposed that the primary release of arsenic through sulfide oxidation under oxidizing conditions, the sequestration by sorption onto Fe-Mn oxyhydroxides and clay minerals, the transport in groundwater through fractures, and the (re)mobilization by reductive dissolution are the dominant processes responsible for the high arsenic concentrations in the boreholes. Additional information is needed regarding the leaching behavior of arsenic from sulfide minerals and its implication for the natural contamination of groundwater.

Keywords

Arsenic, Sulfide oxidation, Fractured bedrock aquifers, Groundwater contamination, Arsenic mineralogy, Leaching experiments.

2.1 Introduction

Arsenic (As) is probably the most serious naturally occurring contaminant in groundwater worldwide. The use of arsenic-contaminated groundwater for drinking and irrigation is a major public health concern in many countries (Ravenscroft et al., 2009). Arsenic exposure through drinking water and food is known to cause multiple adverse effects on human health including skin, lung, liver, bladder and kidney cancers, diabetes, cardiovascular, neurological and reproductive alterations (Ravenscroft et al., 2009; WHO, 2011). The large majority of arsenic contamination problems are associated with geogenic sources, although locally the mobilization of As may be caused, or exacerbated, by anthropogenic activities such as mining, fossil-fuel combustion and use of synthetic arsenical compounds (Smedley and Kinniburgh, 2013). Arsenic is generally present at low concentration in the earth's crust (around 1.0-1.8 mg/kg on average; Henke, 2009), but can occur at very high concentration in hydrothermal ore deposits (Bowell et al., 2014). More than 560 minerals containing arsenic as an essential structural constituent are known in the environment, most of them being ore minerals and their alteration products (Smedley and Kinniburgh, 2013; Majzlan et al., 2014). In hydrothermal deposits, arsenic primarily occurs in sulfide minerals including arsenic sulfides such as arsenian pyrite ($Fe(S,As)_2$), orpiment (As_2S_3) and realgar (As_4S_4); arsenides such as nickeline (NiAs) and löllingite ($FeAs_2$); sulfarsenides such as arsenopyrite (FeAsS), cobaltite (CoAsS) and gersdorffite (NiAsS); and sulfosalts such as enargite (Cu_3AsS_4). Sulfide minerals are stable under reducing conditions but may readily decompose if natural processes or anthropogenic activities, such as mining, exposed them to oxygen and water (Henke, 2009; Lengke et al., 2009). The natural contamination of groundwater by arsenic has been extensively reported in areas of sulfide mineralization, in particular in the northeastern United States (e.g. Ayotte et al., 2003; Lipfert et al., 2006; Foley and Ayuso, 2008) and, to a lesser extent, in eastern Canada (e.g. Bottomley, 1984; Bondu et al., 2017). The weathering of As-bearing sulfide minerals is generally considered to be the primary source of arsenic in groundwater from mineralized bedrock (e.g. Foley and Ayuso, 2008; Verplanck et al., 2008). However, the implication of sulfide oxidation in the arsenic contamination of bedrock groundwater remains unclear. The oxidation of sulfides is known to be influenced by the redox conditions, pH, temperature, presence of water, microbiological activity and dissolution rate of minerals that mostly depends on the crystal structure and chemistry as well as the surface area exposed to weathering (Lottermoser, 2003; Chandra and Gerson, 2010). Although the most common sulfide minerals reported to be responsible for arsenic release in bedrock groundwater are arsenopyrite and arsenian pyrite, the contribution of other intimately associated As-bearing sulfides including Fe-sulfide, Co-arsenide, and Ni-arsenide minerals may also be significant (Foley and Ayuso, 2008). The As-bearing sulfides have different dissolution rates that may affect the leaching of arsenic in the environment (Lengke et al., 2009; Chopard et al., 2015). Yet, the properties of As-bearing sulfides are rarely invoked to explain the arsenic concentration in groundwater. Moreover, the contribution of sulfide oxidation to arsenic mobilization is not well known, in particular with respect to processes affecting the mobility of arsenic in groundwater such as reductive dissolution of metal oxyhydroxides and alkaline desorption from mineral surfaces. The influence of hydrogeological conditions on sulfide oxidation is also poorly understood although it may significantly affect the spatial distribution of arsenic concentrations in bedrock aquifers (Bondu et al., 2016).

The arsenic contamination of groundwater is a major concern in the Abitibi-Temiscamingue region, located in the western part of the Province of Quebec, Canada (MDDELCC, 2015; Bondu et al., 2017). Private bedrock wells have been reported to exceed the Canadian drinking water standard of 10 µg/l for As in areas located in the vicinity of mineralized fault zones (Poissant, 1997; Bondu et al., 2017). The exposure to arsenic is a major public health concern in rural areas where bedrock groundwater is used as source of drinking water (Lampron-Goulet, 2012; Gagnon et al., 2016). Although mining activities are often located along the major faults, the arsenic contamination is generally considered to be of natural origin, primarily derived from the weathering of As-bearing sulfide minerals. A recent study based on the sampling of domestic wells (Bondu et al., 2017) investigated the speciation and mobility of arsenic in bedrock groundwater in the region. However, the processes associated with the release of arsenic from primary sources have not been thouroughly investigated so far. In this context, the specific objectives of this study are to (1) identify the primary As-minerals in the bedrock, (2) assess the leaching behavior of arsenic from the aquifer matrix, and (3) evaluate the geochemical processes responsible for the high As concentrations in groundwater. To that end, mineralogical investigations, leaching tests and groundwater quality analyses were conducted on rock core and groundwater samples from three boreholes located in a mineralized fault zone.

2.2 Geological and hydrogeological settings

The boreholes are located in the eastern part (Hosco sector) of the Heva-Hosco exploration property in the Joannes Township, 20 km east of the city of Rouyn-Noranda, Province of Quebec, Canada (figure 2.1). Geologically, the Heva-Hosco property is located along the Cadillac-Larder Lake fault zone (CLLFZ), at the southeastern margin of the Abitibi greenstone belt, within the Archean Superior Province of the Canadian Shield. The CLLFZ is a major east-west trending structure extending over more than 200 km long and known to be one of the most prolific structures for gold and base metals production of the Abitibi Greenstone Belt (Hocq and Verpaelst, 1994). The CLLFZ marks the boundary between the

Abitibi Subprovince (north, an area dominated by alternating strips of volcanic and metasedimentary rocks), and the Pontiac Subprovince (south, an area dominated by metasedimentary rocks) (Hocq and Verpaelst, 1994) (figure 2.1).

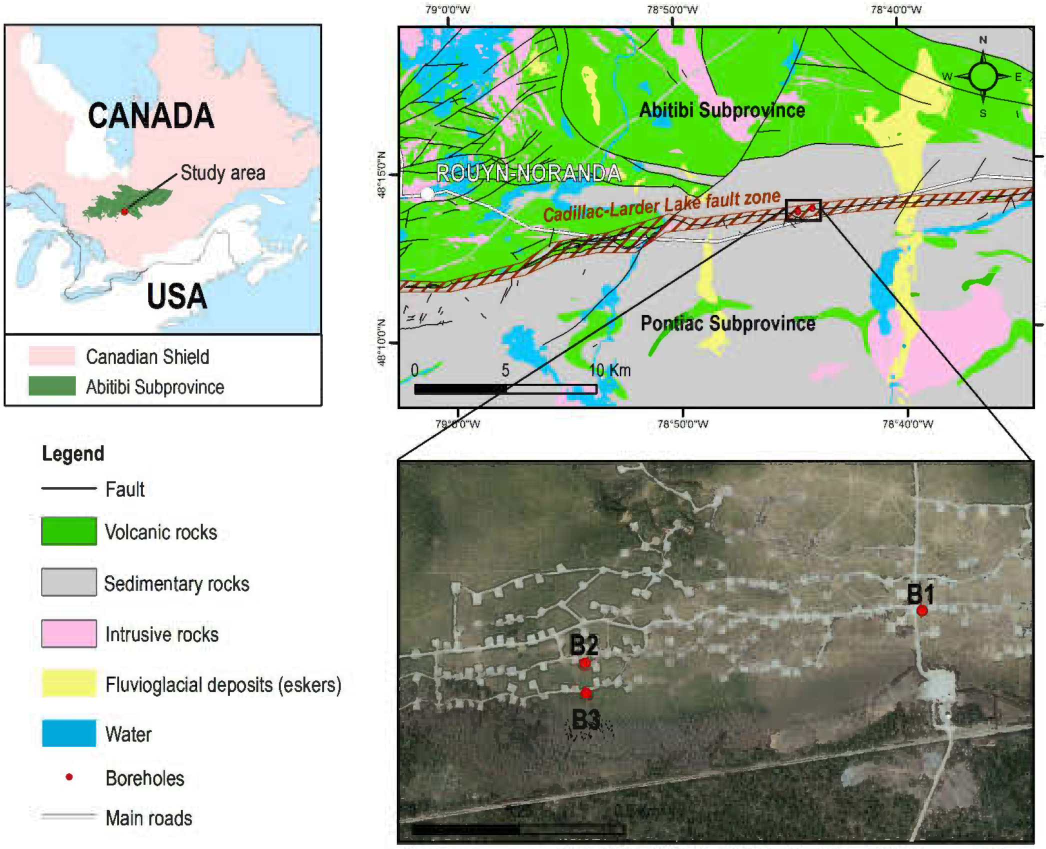

Figure 2.1. Location of the boreholes and simplified geological map of the region.

The geological information provided by the Hecla Mining Company indicates that the fault dips 55° to the north in the Heva-Hosco property and consists of a 10 to 20 meters wide brittle structure, essentially composed of chlorite schists with some minerals re-crystallized at the superior greenschist to amphibolite facies, included in a much broader ductile deformation zone. The Timiskaming sedimentary rocks are found along the fault and consist of poorly graded greywacke interbedded with polymict conglomerates. The overburden is mainly composed of peat up to 2 meters thick overlying Quaternary glaciolacustrine varved silts and clays that can exceed several tens of meters thick. The Heva-Hosco property was explored extensively and more than 1100 boreholes were drilled between 2007 and 2013.

In the Archean bedrock of the region, the groundwater flow mostly occurs within the fracture network related to the geological history, in particular the tectonic stresses and the stresses caused by the glacial-deglacial cycles (Rouleau et al., 2013). The fractured bedrock aquifer is characterized by a low primary porosity and a variable hydraulic conductivity that is mainly controlled by the presence and characteristic of fractures (Cloutier et al., 2007). A previous study by Rouleau et al. (2013) suggested that subhorizontal fractures, particularly abundant in the first 75 m, are likely to provide important pathways for groundwater flow in the bedrock of the region. In the Heva-Hosco property, pumping tests conducted by the Hecla Mining Company showed that the hydraulic conductivity of the bedrock ranges approximately from 10^{-8} to 10^{-6} m/s. Although the fault zone is highly fractured, no significant inflow from the fault was observed in the boreholes. The presence of fine minerals including talc and chlorite may contribute to clog the pores and fractures, thus limiting groundwater flow in the fault zone. In most of the area, the bedrock aquifer is confined by the overlying fluvioglacial silts and clays. The recharge mostly occurs in the unconfined bedrock area to the south, as well as in unconfined glaciofluvial deposits of pebble, sand and gravel that are located approximately 4 km east of the boreholes (figure 2.1).

2.3 Material and methods

2.3.1 Samples collection

Rock and groundwater samples were obtained from three exploratory boreholes (B1, B2 and B3) located in the Heva-Hosco property (figure 2.1). Based on the information provided by the Hecla Mining Company, the boreholes were selected according to (1) the availability of drill cores, (2) the possibility to sample groundwater (no cement grout), (3) the presence of dissolved arsenic in groundwater and (4) the occurrence of rocks that are likely to contain high arsenic contents.

Continuous bedrock core samples collected during the drilling of the boreholes were provided by the Hecla Mining Company (B1: 15-100 m, B2: 11-100 m, and B3: 12-84 m). The boreholes were drilled using a diamond drill bit of 76 mm diameter, unscreened and cased through the overburden: B1 was drilled in 2008 over 136.5 m length and with an inclination of 61.3° from the horizontal; B2 and B3 were drilled in 2010 over lengths of 145.6 m and 85 m, respectively, and both with an inclination of 45° from the horizontal.

Groundwater samples were collected from in each borehole using a *Grundfos Redi-Flo 2* submersible pump, at a pumping rate of 7 l/min. Temperature (T), specific conductance (SC), pH and redox potential (ORP) were measured in the field using a multiparameter probe (*YSI 556*). Prior to sampling, each well was purged of approximately one to two well volumes until stabilization of T, SC and pH values in order to ensure the removal of stagnant water and the sampling of water from the aquifer. The samples were collected in HDPE bottles and include for each well (1) one filtered and unacidified aliquot for alkalinity determination and anions analysis, and (2) one filtered aliquot acidified with ultra pure nitric acid for major cations and trace elements analysis. Filtration was performed in the field with 0.45 µm membrane filters using disposable plastic syringes. The samples were stored in the ice until delivery to the laboratory and stored at 4 °C until analysis.

2.3.2 Rock samples analysis

The chemical composition of continuous core samples was analyzed by portable X-ray fluorescence (XRF) spectroscopy (*Thermo Scientific Niton XL3t XRF analyzer*), at 1 m intervals. Based on the total As content measured by the XRF and the lithological information provided by the Hecla Mining Company, 10 core subsamples were selected for further chemical and mineralogical analysis and batch leaching tests (figure 2.2). Total chemical analyses were performed by inductively coupled plasma mass spectrometry (ICP-MS; *Agilent 7700x*) following a microwave assisted acid digestion with $HNO_3/Br_2/HF/HCl$. The major crystalline phases were identified by X-ray diffraction (XRD) using a *Bruker AXS Advance D8* with a copper anticathode scanning in the 2Θ range of 5-70° with a step of $0.02° s^{-1}$. The *Diffracplus EVA software (v. 9)* was used to identify the mineral species. The quantitative mineralogical compositions were evaluated by Rietveld refinement using the *TOPAS software (v. 2.1)* with a precision of ± 0.5-1 %. The identification of As-bearing minerals was conducted on both polished core surfaces and polished sections made of composite rock samples embedded in epoxy resin. The composite rock samples used for polished sections and humidity cell tests were prepared using four 250 g subsamples (1 kg of core) from each selected interval, crushed to less than 6.3 mm, homogenized and quartered (figure 2.2). The identification of sulfide minerals was conducted with a scanning electron microscope (SEM; *Hitachi S-3500N*) equipped with an energy dispersive spectrometer (EDS; *Oxford SDD, X-Max 20 mm*^{2}) under operating conditions of 20 kV accelerating voltage, 100 µA beam current, and 15 mm working distance.

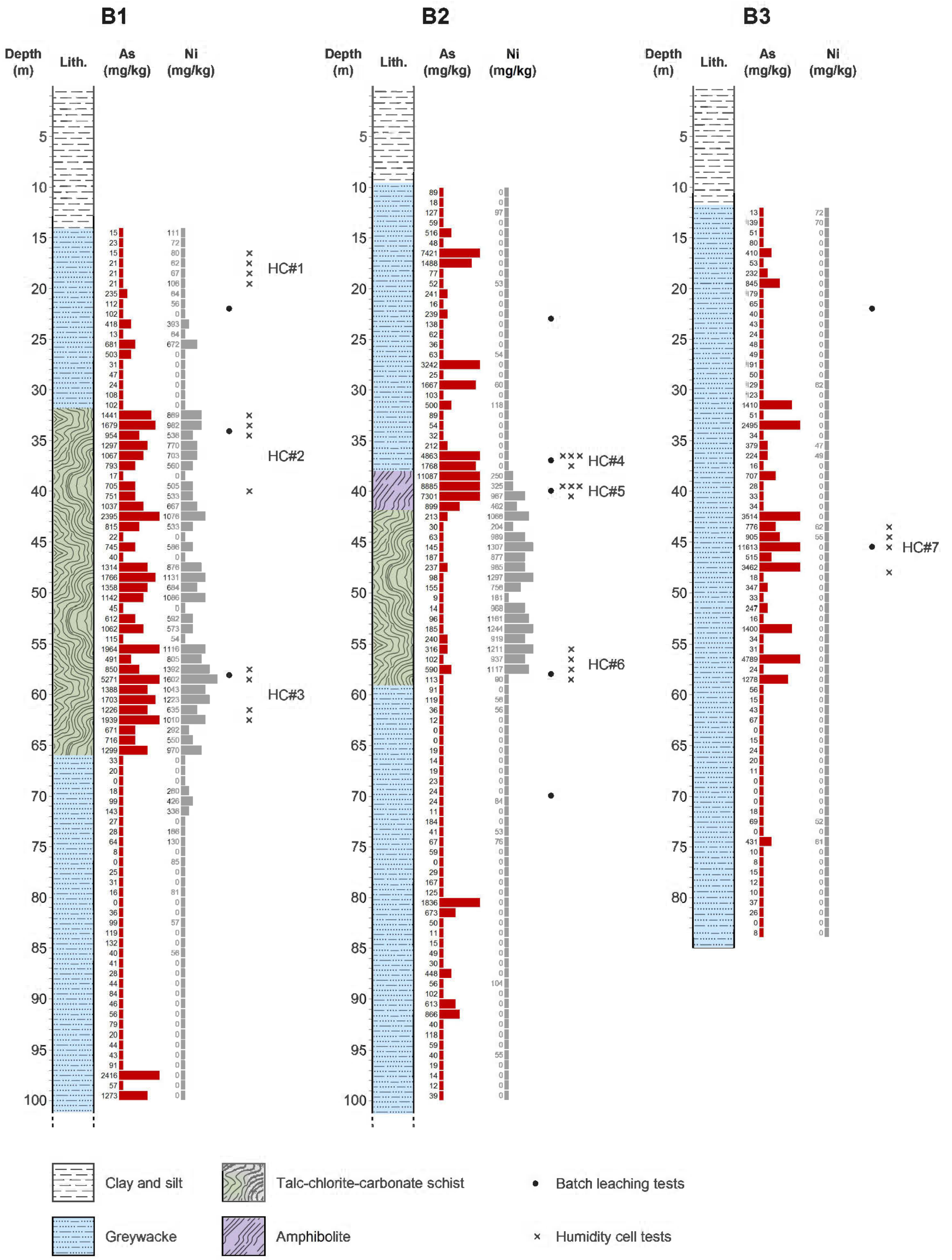

Figure 2.2. Lithology, total As and Ni contents (XRF), and location of subsamples for leaching tests and mineralogical observations in core samples of B1, B2 and B3.

Electron probe micro-analyzer (EPMA; *CAMECA SX-100*) equipped with five wavelength-dispersive spectrometers (WDS) operated at 15 kV and 20 nA was used to determine the precise chemical composition of the individual sulfides.

2.3.3 Laboratory tests

2.3.3.1 Batch leaching tests

Batch leaching tests were conducted in order to provide a first assessment of the arsenic release from core samples (figure 2.2). The batch tests were performed using solid liquid ratios of 1:4 in neutral pH water following the CTEU-9 method (CEAEQ, 2012). Forty grams of core were crushed to less than 150 µm and mixed with 160 mL deionized water adjusted at pH 7.0 ± 0.1 with 0.1 N sodium hydroxide solution. The batch leaching experiments were conducted in a closed system over seven days (168 h) at a rotation speed of 30 rpm. After 168 h, the pH, Eh and SC were measured, and the leachates were obtained by filtration using a 0.45 µm membrane filter. The leachate sample for cations and trace metals analysis was acidified to $pH < 2$ with ultrapure nitric acid to avoid metal precipitation. Chemical analyses were conducted for major cations and anions, as well as trace metals.

2.3.3.2 Humidity cell tests

Humidity cell tests were conducted to assess the leaching behavior of arsenic over time under weathering conditions similar to those occurring in the unsaturated zone. The testing was performed by placing composite core samples in plexiglass cylinders of 10.2 cm inside diameter by 20.3 cm height, following the ASTM D5744-13 protocol (Plante et al., 2011; ASTM, 2013). The cells were subjected to 25 weathering cycles of one week, each cycle composed of 3 days of dry ambient air, followed by 3 days of water-saturated air, and by flushing on the 7th day by inundation and soaking for 4 h with 1 L deionized water. The flush promoted the removal of leachable mineral dissolution products produced from the previous week's weathering cycle (ASTM, 2013). Measurements of pH, Eh and SC were performed after the flush. The leachates were filtered at 0.45 µm, cations and trace metals samples were acidified to $pH < 2$ with ultrapure nitric acid, and analyzed for major, minor and trace metals including As.

2.3.4 Chemical analysis

Chemical analyses were conducted to determine the composition of groundwater, batch and humidity cell leachates. Alkalinity (as $CaCO_3$) was determined by titration with sulfuric acid to pH 4.5 using an automatic titrator (*Metrohm Titrino Plus 870 KF*). Major anions (SO_4^{2-}, Cl^-, NO_3^-, F^- and Br^-) were measured by ion chromatography (*Metrohm 881 Compact IC Pro*). Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and silica (Si) were determined by inductively-coupled plasma atomic-emission spectroscopy (ICP-AES; *Perkin Elmer Optima 3100 RL*). Minor and trace elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Ti, U, V, Zn) were measured by inductively-coupled plasma mass spectrometry (ICP-MS; *Agilent 7700x*) according to the standard procedure MA. 200 - Mét. 1.2 of the province of Quebec's Ministry of the Environment (CEAEQ, 2014). Calibration standard solutions were prepared from a certified stock standard solution of 10,000 mg/l As (SCP Science). Quality-control procedures included the analysis of a CEAEQ standard reference sample, blanks and duplicate samples, as well as calculation of charge balances (within ± 10 %). The WATEQ4F thermodynamic database of the PHREEQC program (Parkhurst and Appelo, 1999) was used for the calculation of saturation indices (SI) in leachates and groundwater.

2.4 Results

2.4.1 Arsenic content and mineralogy in bedrock cores

The lithology and total As and Ni contents in B1, B2 and B3 cores are presented in figure 2.2. The XRD analysis indicated that the greywacke in the B1, B2 and B3 cores mainly consists of quartz and albite with minor plagioclase, K-feldspar, muscovite and calcite. The schists in the B1 and B2 cores contain chlorite, talc and dolomite or calcite with traces of muscovite. The amphibolite in the B2 cores is dominated by actinolite and tourmaline with traces of talc, chlorite and calcite. The total As content in cores were highly variable, ranging from below the detection limit ($<$ 2 mg/kg) up to 11 613 mg/kg according to XRF analysis (figure 2.2), and from 92 to 18 463 mg/kg in the subsamples selected for ICP-MS analysis following acid digestion (table 2.2). The core chemical compositions determined after acid digestion were consistent with XRF measurements, as shown in Appendix A. In the B1 cores, total As contents were generally below 100 mg/kg with the exception of a continuous interval between 32 m and 66 m, corresponding precisely to the talc-chlorite-carbonate schists. In this interval, total As contents mostly ranged from 700 to 1800 mg/kg and were strongly correlated with total Ni contents that mostly ranged between 500 and 1200 mg/kg (figure 2.2). By contrast, total Ni contents were generally below the detection limit of the XRF method outside this interval. In the B2 cores, total As contents exceeding several hundred to several thousand mg/kg were found at different depths, with the highest contents in the 37-41 m interval. Total Ni contents were only detected at significant concentrations (approximately 700-1300 mg/kg) between 38 and 58 m in the amphibolite and talc-chlorite-carbonate schists. In the talc-chlorite-carbonate schists, total As contents were comparatively low, mostly ranging from 100 to 500 mg/kg. In the B3 cores, high As contents were found at different depths between 32 and 58 m, with the highest contents occurring in the 43-48 m interval. Total Ni contents were generally below the detection limit of the XRF method.

Table 2.1. Distribution of As-bearing minerals in core samples according to the bedrock lithology.

	B1	B2	B3
Greywacke	Traces of gersdorffite and arsenian pyrite	Arsenopyrite	Arsenopyrite
Amphibolite	-	Arsenopyrite and minor gersdorffite	-
Talc-chlorite-carbonate schists	Gersdorffite and minor arsenian pyrite	Gersdorffite and minor arsenian pyrite	-

The mineral identification using SEM and electron microprobe techniques indicated that As is primarily present in disseminated submillimetersized sulfide minerals. Table 2.1 summarizes the distribution of As-bearing minerals in the core samples according to the bedrock lithology. In the B1 cores, arsenic was exclusively found to occur in fine-grained gersdorffite (less than 50 µm), particularly abundant in the talc-chlorite-carbonate schists (32-66 m interval) (figure 2.3 (A)). Sulfide minerals mainly consist of pyrite and gersdorffite with traces of chalcopyrite ($CuFeS_2$) and pyrrhotite ($Fe_{1-x}S$). Trace amounts of pentlandite ($(Fe,Ni)_9S_8$) were also identified in the lower part of the talc-chlorite-carbonate schists. Electron microprobe analysis indicated that pyrite may contain up to 0.1 % As while pyrrhotite and chalcopyrite do not contain detectable amount of As. Gersdorffite exhibits an average composition (n=15) of 23 % Ni, 45 % As, 19 % S, 10 % Fe, and 3 % Co, explaining the As and Ni contents in the core samples. In the B2 cores, the mineralogy of arsenic varies with the depth and the mineral assemblages. In the greywacke (10-38 m and 59-100 m intervals), arsenic is exclusively contained in arsenopyrite, consistent with the absence of Ni (figure 2.2). In the amphibolite zone (38-42 m interval), sulfide minerals mainly consist of arsenopyrite with minor fined-grained gersdorffite (figure 2.3 (B)). Arsenopyrite was found to contain between 0.3-1 % Ni. In the chloritic schists (42-59 m interval), gersdorffite is the main sulfide, accompanied by traces of pyrite and chalcopyrite. Pyrite was found to contain up to 0.4 % As while chalcopyrite does not contain any detectable amount of As. The average composition of gersdorffite (n=15) is 20 % Ni, 45 % As, 20 % S, 9 % Fe, and 6 % Co. In the B3 cores, sulfide minerals are dominated by pyrite and arsenopyrite, with traces of chalcopyrite. Electron probe microanalysis showed that arsenopyrite is the only As-bearing mineral.

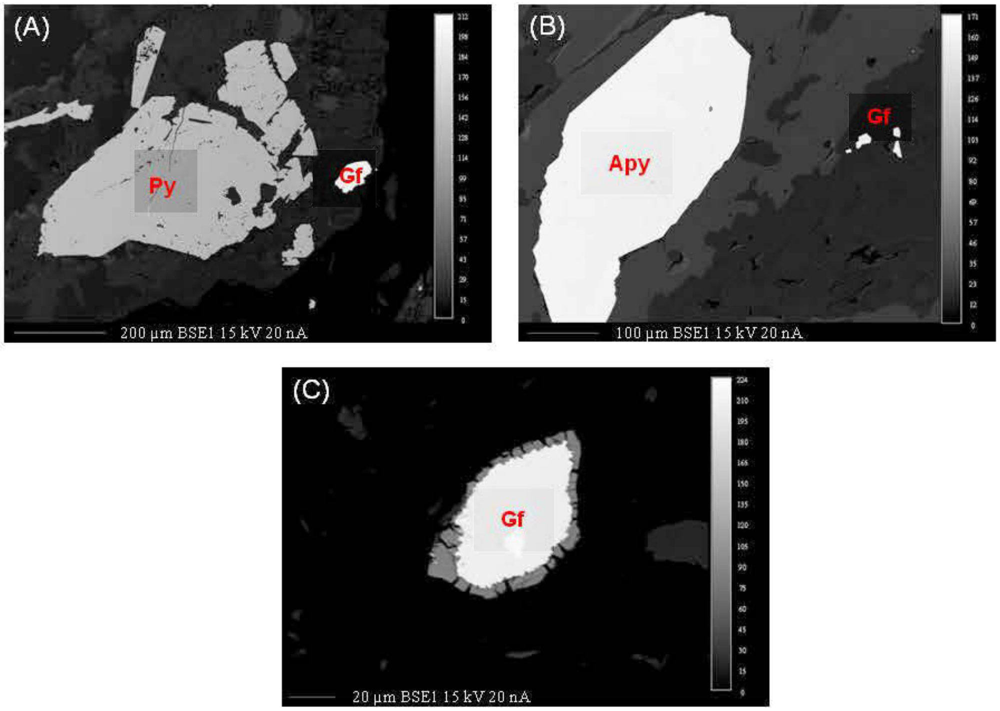

Figure 2.3. Backscattered electron (BSE) image of A) pyrite and fine-grained gersdorffite in the B1 cores (HC#3), B) arsenopyrite and fine-grained gersdorffite in the B2 cores (HC#5) and C) in situ altered gersdorffite grain after humidity cell tests (HC#5). Mineral abbreviations: Gf = gersdorffite, Apy = arsenopyrite, Py = pyrite.

2.4.2 Arsenic release from core samples

2.4.2.1 Batch leaching tests

Selected results of the batch leaching tests are presented in table 2.2. The pH conditions were alkaline, with values ranging from 8.71 to 9.35. The redox measurements indicated oxidizing conditions, with Eh values ranging from 309 to 453 mV. Bicarbonate (HCO_3), calcium (Ca) and magnesium (Mg) concentrations were positively correlated with the content of carbonate minerals. Sulfate (SO_4) concentrations were not correlated with As concentrations in core samples and were highest in the B1-34.0, B1-58.0 and B2-58.1 leachates. Leachate metal concentrations were generally low with the exception of As and to a lesser degree Cd. Dissolved Ba, Co, Cr, Cu, Fe, Li, Mn, Mo, Ni, Pb, Sb, Se, Sn and Zn were generally below 0.1 mg/l; Cd ranged from below the detection limit of 0.003 mg/l to 2.84 mg/l; while As ranged from 0.12 mg/l to 59.31 mg/l. The Ni concentrations in leachates were low, ranging from below the detection limit of 0.0007 mg/l to 0.031 mg/l. The As and Ni concentrations in each leachate are presented in table 2.2. As illustrated in figure 2.4, the leachate As concentrations were not well correlated with the total As contents in rock samples. The results of acid digestion indicates that B2-37.0, B2-39.6 and B3-45.6 rock samples contained the highest As contents (above 15 000 mg/kg); B1-34.0, B1-58.0 and B2-58.1 rock samples presented medium As contents (from 500 to 1500 mg/kg); and B1-22.0, B2- 23.0, B2-70.0 and B3-22.0 rock samples contained the lowest As contents (below 500 mg/kg). The leachate As concentrations were found to be relatively high in B1-22.0, B1-34.0, B1-58.0 and B2-58.1 in comparison to B2-37.0 and B3-45.6, with respect to the total As content in the rock samples (figure 2.4). In this way, gersdorffite-rich samples may be more likely to release large amounts of arsenic than arsenopyrite-rich samples. It is noteworthy that dissolved As is also thought to be derived from the dissolution of very fine sulfide fragments related

Table 2.2. Selected chemical analyses of batch leachates and associated rock samples.

# Sample	Leachate chemistry				Core chemistry	
	pH	Eh (mV)	As (mg/l)	Ni (mg/l)	As (mg/kg)	Ni (mg/kg)
B1-22.0	9.07	453	2.00	0.001	92	184
B1-34.0	9.04	345	4.91	0.006	1334	842
B1-58.0	8.71	348	8.64	0.031	558	829
B2-23.0	8.73	432	0.12	<0.0007	413	215
B2-37.0	8.86	335	12.63	0.003	17234	318
B2-39.6	9.35	309	59.31	0.007	18345	784
B2-58.1	8.71	331	24.78	0.031	952	901
B2-70.0	9.23	335	0.24	<0.0007	112	198
B3-22.0	9.23	333	0.27	0.001	163	154
B3-45.6	8.99	333	10.29	0.001	18463	127

to crushing, particularly in high As rock samples. The amount of As in leachates is expected to be closely related to the oxidation of As-bearing sulfides owing to the limited As sequestration. The PHREEQC calculations reveal that common secondary As minerals including arsenolite (As_2O_3), annabergite ($Ni_3(AsO_4)_2{\cdot}8H_2O$), claudetite ($As_2O_3$), mansfieldite ($AlAsO_4{\cdot}2H_2O$), scorodite ($FeAsO_4{\cdot}2H_2O$), sterlinghillite ($Mn_3(AsO_4)_2{\cdot}4H_2O$), and Ca-arsenates ($Ca_3(AsO_4)_2{\cdot}4H_2O$; $Ca_4(OH)_2$-$(AsO_4)_2{\cdot}4H_2O$; $Ca_5(AsO_4)_3(OH)$; $Ca_5(HAsO_4)_2(AsO_4)_2{\cdot}9H_2O$; $CaHAsO_4{\cdot}H_2O$) were not predicted to precipitate, with the exception of $Ca_3(AsO_4)_2{\cdot}4H_2O$ in B2-39.6 and B2-58.1. The leachates were generally oversaturated with respect to Al-oxyhydroxides such as bohemite and gibbsite, Mn-oxyhydroxides such as hausmannite and manganite, and Fe-oxyhydroxides such as goethite, hematite and $Fe(OH)_3$. Nevertheless, the sorption of As oxyanions onto metal oxyhydroxides is expected to be low at pH above 8.5, owing to the mineral surfaces that are negatively charged (Ravenscroft et al., 2009). The sorption onto clay minerals is also expected to be low under alkaline conditions, although the desorption of As from chlorite is known to be limited at high pH (Lin and Puls, 2000).

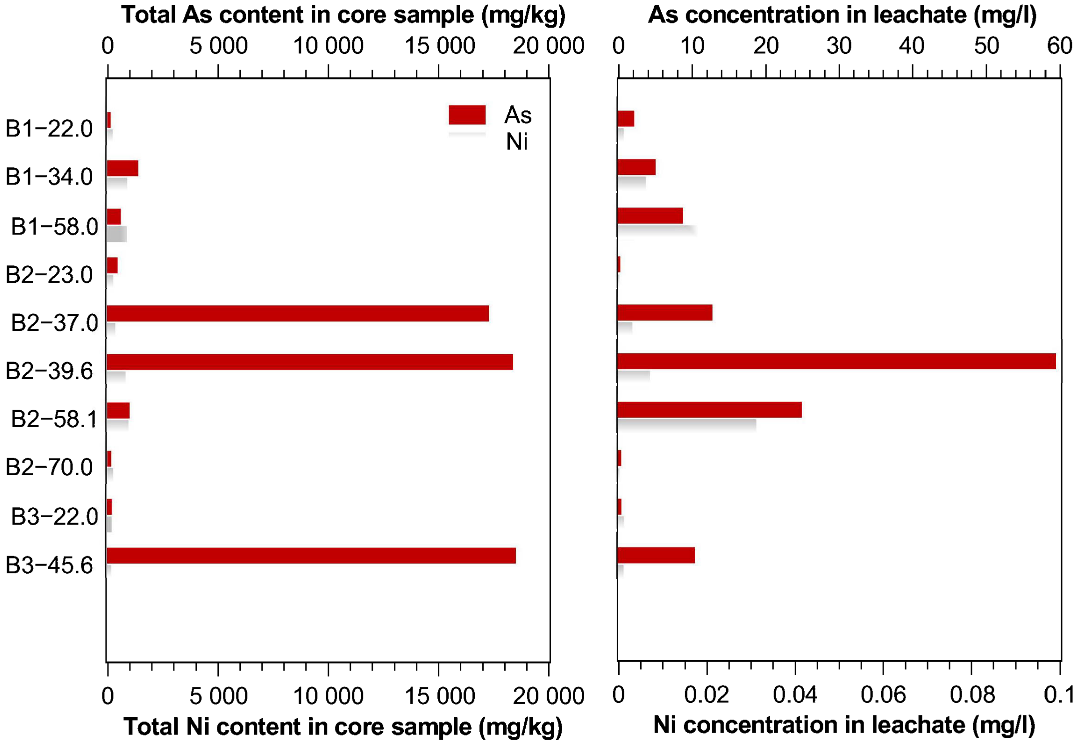

Figure 2.4. Arsenic and nickel contents in core samples and concentrations in the corresponding leachates.

The low Ni concentrations in leachates were likely related to sequestration mechanisms. The leachate Ni concentrations were correlated with total Ni contents in core samples, the latter being derived from the weathering of gersdorffite and, to a lesser degree, pentlandite. The geochemical calculations performed with PHREEQC suggest that Ni did not precipitate as nickel hydroxide ($NiOH_2$), except in the B2-39.6 leachate. Hence, the sequestration of Ni is believed to be principally related to the sorption onto Fe-Mn oxyhydroxides, clay minerals and carbonate minerals (Green-Pedersen et al., 1997; Plante et al., 2010; Belova et al., 2014). The PHREEQC calculations suggest the precipitation of carbonates such as calcite and dolomite in the leachates, in particular those associated with high carbonate rock samples.

2.4.2.2 Humidity cell tests

The variations in leachate chemistry during the humidity cell tests are illustrated in figure 2.5. The Eh measurements ranged from approximately 350 to 550 mV, with no noticeable differences between the humidity cells. The pH was weakly alkaline, with average values ranging from 7.66 to 8.21. The pH was positively correlated to HCO_3 concentration and, therefore, was generally higher for humidity cells containing carbonate minerals, in particular HC#6 (figure 2.5 (A) and (C)). The total mineralization was mainly influenced by the HCO_3, Ca and Mg concentrations (figure 2.5 (B), (C) and (D)) associated with the dissolution of carbonate minerals. Sulfate concentrations were low, generally below 4 mg/l, and show no correlation with dissolved metals. In accordance with the batch experiments, the dissolved metal concentrations were low, with the exception of dissolved As (figure 2.5 (E)). The As concentration was highly variable among the humidity cells, varying from 0.01 to 8 mg/l during the experiments. The amount of As released from HC#1, HC#4 and HC#7 shows similar trends exhibiting low and steady concentrations around 0.04, 0.12 and 0.03 mg/l, respectively, from the beginning to the end of the experiments. The As concentration in HC#5 leachates sharply decreased from approximately 8 mg/l to less than 2 mg/l during the first three weeks, and stabilized around 0.5 mg/l for the following weeks and until the end of the experiments. The leachates from HC#2, HC#3 and HC#6 contained the highest dissolved As concentrations, varying in the range 1.5-2.5 mg/l after stabilization. In the HC#2 leachates, the arsenic concentration decreased from 5.3 mg/l to 1.8 mg/l between weeks 1 and 3, and stabilized around 2 mg/l until

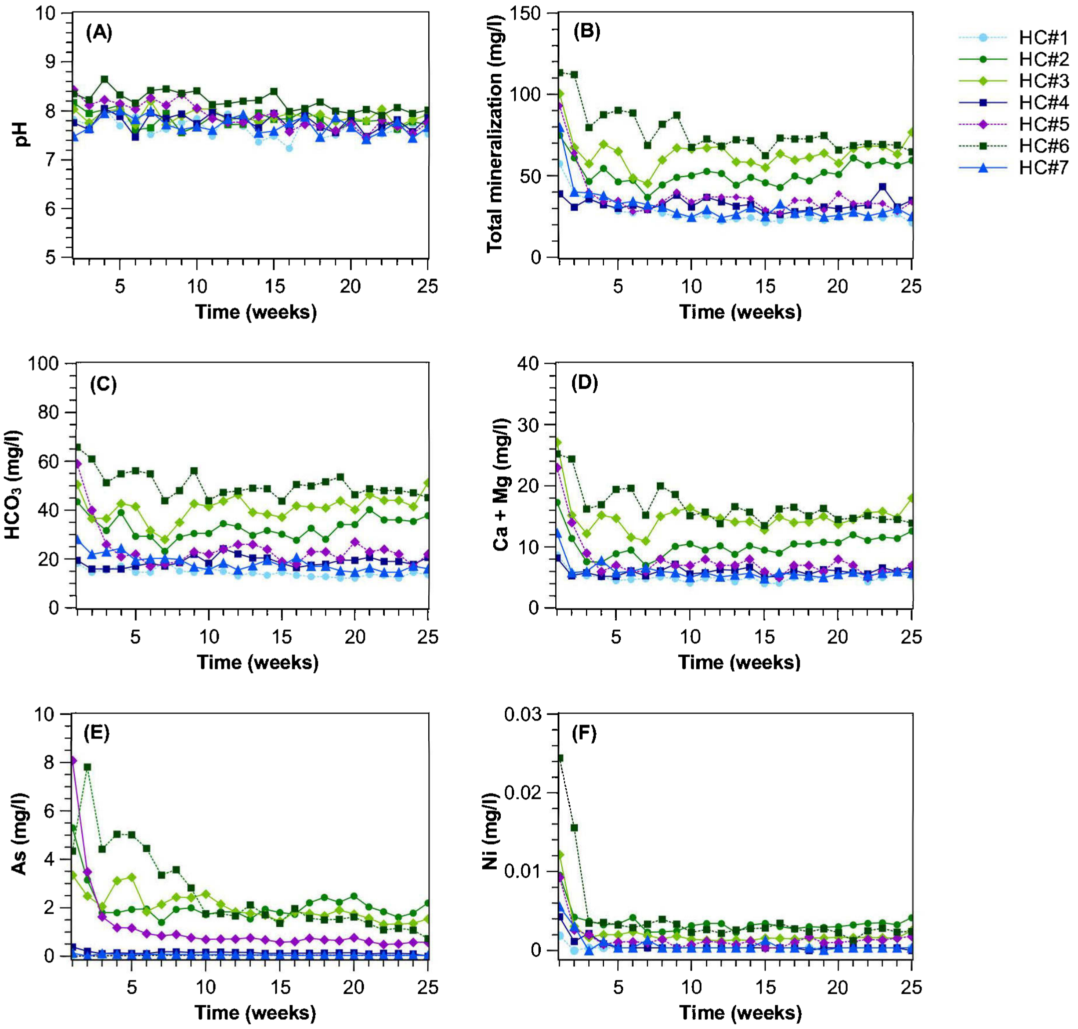

Figure 2.5. Variations in (A) pH, (B) total mineralization, (C) HCO_3 concentrations, (D) Ca + Mg concentrations, (E) dissolved As concentrations and (F) dissolved Ni concentrations during the humidity cells tests.

week 25. In the leachates from HC#3, the As concentration varied between 2.0 and 3.3 mg/l for the first 5 weeks, then around 2.5 mg/l until week 14 and stabilized around 1.8 mg/l until the end of the experiments. In the HC#6 leachates, dissolved arsenic was the highest during the first 10 weeks, decreasing from 5.0 to 2.8 mg/l, before stabilizing around 1.8 mg/l until week 20, and 1.0 mg/l at week 25. The highest As concentrations in leachates were clearly associated with the occurrence of gersdorffite, while leachate As concentrations associated with arsenopyrite were low, irrespective of the bulk As content in rock samples (figures 2.5 and 2.6). The amounts of As released from HC#2, HC#3 and HC#6 were the highest, while the measured bulk As contents were of 1293, 1264 and 530 mg/kg, respectively. In contrast, the amounts of As released from HC#4 and HC#7 were relatively low, although bulk As contents exceeded 25 000 mg/kg and 3 900 mg/kg, respectively. In HC#5, where As was mainly present in arsenopyrite and, to a lesser extent, in gersdorffite, the leachates contained medium As concentrations. Finally, the low As concentration in the HC#1 leachate appears to be related to the low As content in rock samples. Moreover, high As concentrations were also found to be associated with high pH and elevated HCO_3 concentrations that are known to increase the desorption of As from mineral surfaces (Sharma and Sohn, 2009). The PHREEQC calculations show that the leachates are undersaturated with respect to common secondary As minerals. By contrast, the PHREEQC calculations and the low leachate Fe concentrations suggest the precipitation of Fe-oxyhydroxides. Sorption onto Fe-oxyhydroxides and clay minerals was likely to be the main mechanism responsible for the sequestration of As in leachates. As a result, the competitive adsorption of bicarbonate ions could affect the As concentration in leachates (Stachowicz et al., 2007), in particular in humidity cells containing high contents of carbonate minerals. However, the absence of correlation of dissolved As with the variation in pH and HCO_3 concentration in each leachate and the limited range in pH and HCO_3 concentration suggest that these factors did not significantly influence the difference in the amounts of As leached. It is likely that the release of As closely reflected the oxidation rates of As-bearing sulfides given the physico-chemical conditions and the mineralogy of As in core samples. Similarly to the batch leaching tests, the Ni concentrations in leachates were low (figure 2.5 (F)), likely owing to its sorption onto metal oxyhydroxides, clays, and carbonate minerals.

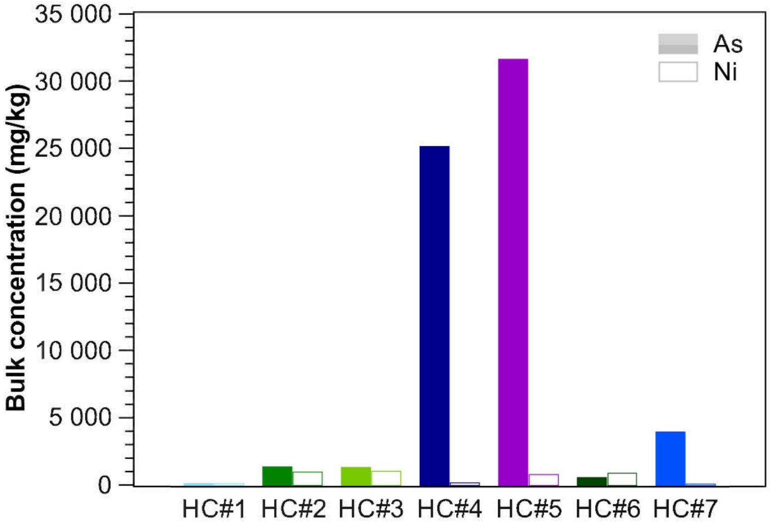

Figure 2.6. Bulk As and Ni contents in humidity cell composite samples.

2.4.3 Dissolved arsenic in groundwater

The water level measurements conducted during the sampling campaign indicated that the water table was shallow in the boreholes: 0.1 m, 0.4 m and 0.3 m below the ground surface for B1, B2 and B3, respectively, and was not significantly affected by pumping during sampling procedures (< 1 m drawdown). These data confirm that the bedrock aquifer is confined by the overlying Quaternary sediments. The physico-chemical parameters and concentrations of selected elements in the boreholes are presented in table 2.3. The groundwater was near neutral and mildly reducing, predominantly of Ca-HCO_3 water type. The B2 and B3 boreholes exhibited similar groundwater composition including major elements and metal concentrations, while groundwater in the B1 borehole appeared to be more diluted (table 2.3). Sulfate concentrations were below the detection limit of 0.5 mg/l in all the wells, suggesting that sulfate is affected by the co-precipitation

Table 2.3. Physico-chemical parameters and concentrations of selected elements in borehole waters.

Variables	B1	B2	B3
T (°C)	8.3	7.2	8.0
pH	7.83	7.25	7.09
SC (µS/cm)	305	586	613
Eh (mV)	82	116	114
HCO_3 (mg/l)	195	427	390
SO_4 (mg/l)	<0.5	<0.5	<0.5
Cl (mg/l)	1.9	2.3	2.7
NO_3 (mg/l)	<0.02	<0.02	<0.02
Ca (mg/l)	55	100	97
Mg (mg/l)	4.2	18.0	13.0
Na (mg/l)	4.9	12.0	11.0
K (mg/l)	2.4	3.4	3.1
Si (mg/l)	6.6	14.0	13.0
As (mg/l)	0.11	0.31	0.46
Ni (mg/l)	<0.01	<0.01	<0.01
Fe (mg/l)	1.0	5.4	10.0
Mn (mg/l)	0.35	1.30	1.40

in secondary minerals or more probably by reduction, as suggested by the characteristic smell of H_2S in the boreholes. Dissolved metal concentrations were low with the exception of Fe, Mn and As. Dissolved As concentration ranged from 0.11 mg/l in B1 to 0.46 mg/l in B3, with B2 containing 0.31 mg/l As. Although a negative correlation between dissolved As and pH was observed, the oxidation of sulfides is not expected to significantly affect the pH of groundwater. The pH is likely controlled by the dissolution of abundant minerals, in particular carbonates. On the other hand, the low redox potential and the correlation of dissolved As with elevated dissolved Fe and Mn concentrations in the boreholes suggests that the reductive dissolution of metal oxyhydroxides could be involved in the mobilization of arsenic in groundwater. Although the mildly reducing conditions measured in well waters are not expected to cause the dissolution of Fe and Mn oxyhydroxides, dissolved As is believed to originate from more reducing groundwater from deep and poorly connected fractures, as suggested by a previous study of bedrock wells in the region (Bondu et al., 2017). Indeed, geochemical calculations using PHREEQC indicate precipitation of Fe-oxyhydroxides including $Fe(OH)_3$, goethite and hematite in B1, B2 and B3 waters as well as sterlinghillite ($Mn_3(AsO_4)_2{\cdot}4H_2O$) in B2 and B3 waters. Open boreholes are likely to receive water from multiple discrete fractures with contrasting chemistry and redox status (Shapiro, 2002; Harte et al., 2012). The boreholes are located in a downgradient confined portion of the aquifer, and are likely to contain geochemically evolved groundwater, with a chemical composition reflecting an extended contact time between water and crystalline rock. Geochemically evolved groundwater can provide favorable redox conditions for the dissolution of Fe-Mn oxyhydroxides, while the sorption of As onto Fe and Mn oxyhydroxides is considered to be the major mechanism of As sequestration in bedrock groundwater (Lipfert et al., 2006; Yang et al., 2015). These results are in agreement with previous studies that found that reductive dissolution is an important mechanism for arsenic mobilization in bedrock aquifers (Foley and Ayuso, 2008; Yang et al., 2015). It is noteworthy that the presence of many boreholes in the area is not believed to significantly affect the oxidation of sulfides by promoting the entry of oxygen into groundwater because most of the boreholes are sealed and the redox conditions are typical of confined bedrock aquifers in the region.

2.5 Discussion

2.5.1 Arsenic release from sulfide minerals

The results of the leaching experiments suggest that the mineralogy influences the release of arsenic into solution. Under oxidizing and weak alkaline conditions, the amount of As leached from gersdorffite-rich samples was greater than the amount of As leached from arsenopyrite-rich samples. Although knowledge on the leaching behavior of As from sulfide minerals is limited (Lengke et al., 2009), there is some evidence that gersdorffite oxidation can release large amounts of As. A recent study by Chopard et al. (2015) based on kinetic tests conducted on pure sulfide minerals revealed that gersdorffite is rapidly oxidized in comparison to various sulfide minerals including arsenopyrite and pyrite. The authors noted that the oxidation of gersdorffite was associated with a high initial release of As. Moreover, in a previous study of the alteration of gersdorffite in aerated water, Jackson et al. (2003) found that As is oxidized more rapidly than S and Ni upon exposure to oxidizing conditions. Arsenites and arsenates were identified as the main oxidation products at the oxidized gersdorffite surface. The occurrence of soluble arsenic species at the mineral surface is consistent with the release of large amounts of As in solution. As member of the cobaltite group, gersdorffite is structurally similar to pyrite, being derived by an ordered substitution of As for S and some combination of Co^{2+} and/or Ni^{2+} substituting for some or all of the Fe^{2+} (Foley and Ayuso, 2008). Within the pyrite lattice, Co, As and to a lesser degree Ni impurities have been demonstrated to increase the pyrite oxidation rate owing to the introduction of vacant defect states, often within the band gap, that alter the electronic structure of the stoichiometric crystal (Lehner and Savage, 2008). Similarly to pyrite, it is possible that the chemical composition of gersdorffite influences its oxidation rate. In particular, the enrichment in Co at the expense of Ni may result in a higher dissolution rate, consistent with the high initial amount of As released from HC#6 relative to HC#2 and HC#3. The BSE images of humidity cell rock samples confirmed the advanced weathering of gersdorffite relative to arsenopyrite. Free gersdorffite grains were found to be surrounded by a thick alteration rim in comparison to other sulfide minerals, as illustrated in figure 2.3 (C). In relation to this, the susceptibility to weathering of major mineral constituents could also play a role in the release of As. In fact, the weathering of major minerals enclosing sulfides is likely to increase the surface area of sulfide minerals exposed to oxidation. This could have influenced the oxidation of sulfide minerals since the assemblage talc-chlorite-carbonate associated with gersdorffite appears to be less resistant to weathering than the assemblage quartz-albite generally associated with arsenopyrite (Essington, 2004).

2.5.2 Source and mobilization of arsenic in groundwater

The mineralogical data suggest that dissolved As in groundwater is primarily derived from the weathering of sulfide minerals. Arsenopyrite, gersdorffite and to a lesser degree arsenian pyrite can act as sources of arsenic in groundwater. Apart from the fault core structure, the mineralogical information provided by the Hecla Mining Company reveal that arsenopyrite is the predominant sulfide at the property scale. As suggested by the leaching experiments, the groundwater originating from the gersdorffite-rich zones can be expected to contain elevated As concentrations. However, the distribution of arsenic in boreholes show that high levels of As were not associated with the presence and extent of gersdorffite-rich zones. This discrepancy may be related to (1) the mechanism of arsenic mobilization and (2) the characteristics of groundwater flow in fractures. The local weathering of sulfide minerals is not expected to be the major source of As in the confined bedrock aquifer. As illustrated in figure 2.7, arsenic is thought to

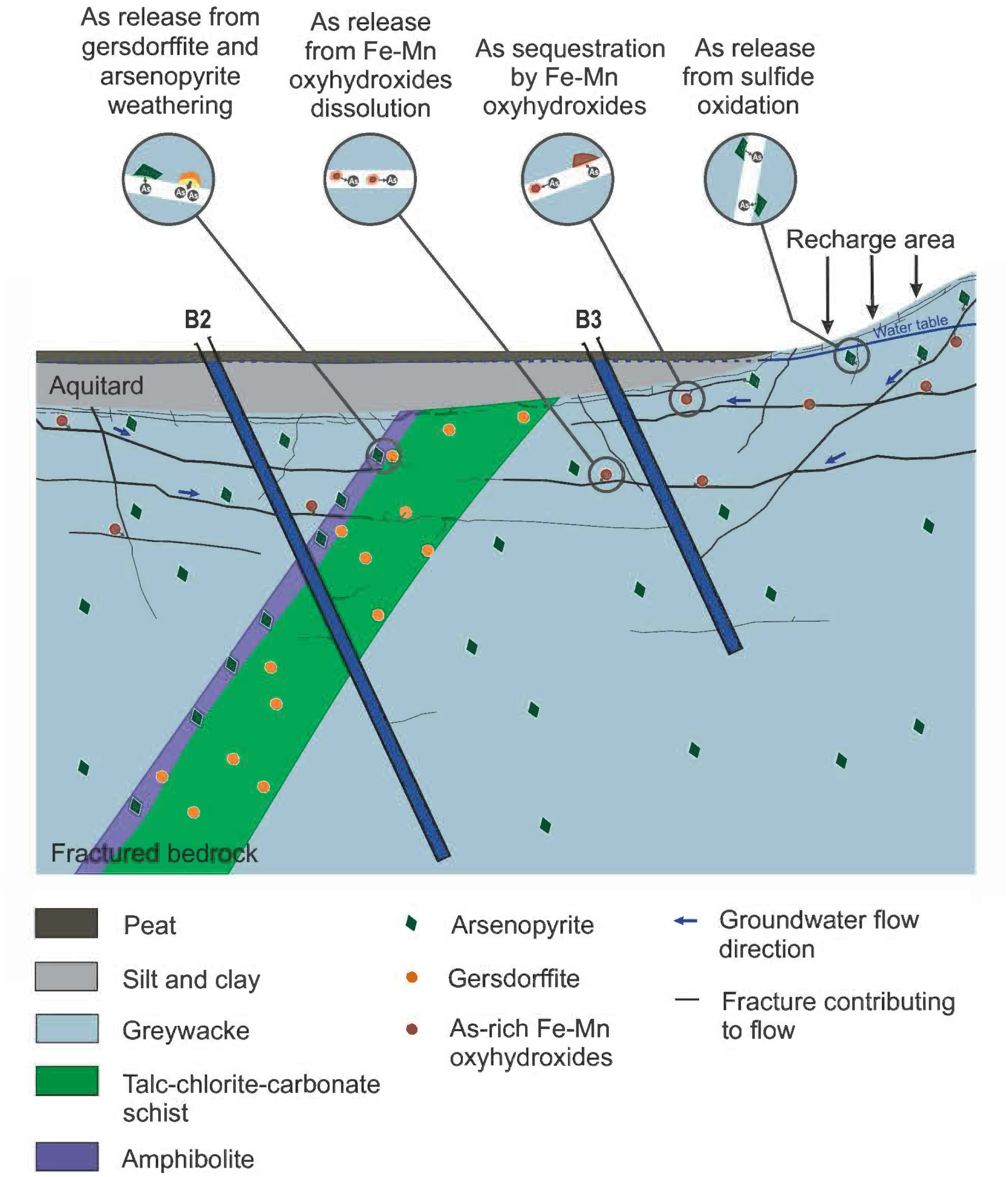

Figure 2.7. Conceptual model of arsenic mobilization in the bedrock aquifer.

be primarily derived from the weathering of sulfides under more oxidizing conditions, such as those prevailing in unconfined recharge areas. Under these conditions, As is known to adsorb strongly onto Fe-Mn oxyhydroxides and clay minerals and to precipitate as arsenate minerals. The sequestration of arsenic is expected to be limited to the oxidizing portion of the aquifer. Groundwater flow is likely to transport As in dissolved and particulate forms through the fracture network (Yang et al., 2015). Hence, high As concentrations may occur in the reducing portion of the aquifer, as the result of the reductive dissolution of Fe-Mn oxyhydroxides (figure 2.7). The redox potential is expected to decrease along the flow path with the geochemical evolution of groundwater. Moreover, open well water generally reflects a mixture of groundwater from multiple discrete fractures contributing to flow (Bondu et al., 2017). These fractures may contain groundwater with different chemistry and have different contribution to the well discharge according to their transmissivity (Shapiro, 2002). In this way, it is conceivable that the low permeability of the talc-chlorite-carbonate schists is responsible for the small contribution of As-rich groundwater associated with the weathering of gersdorffite. Although sulfide oxidation is not believed to be the major mechanism of arsenic mobilization, the oxidation of sulfide minerals may occur in fractures containing mildly reducing groundwater. In addition, the contribution of fractures containing As-free groundwater may affect the total As concentration in boreholes. In particular, the high proportion of diluted, less chemically evolved groundwater with low As concentrations may be responsible for the relatively low concentration of As, such as in the B1 borehole.

2.6 Conclusion

In the present study, the relation between the primary arsenic-bearing sulfides and the concentration of arsenic in groundwater was investigated in a fractured bedrock aquifer. Mineralogical analysis of core samples revealed that arsenic is mainly present in gersdorffite (NiAsS) and arsenopyrite (FeAsS). Leaching tests demonstrated that gersdorffite-rich samples release greater amounts of arsenic than arsenopyrite-rich samples under oxidizing and weak alkaline conditions. The difference in the amount of arsenic released is believed to be related to the higher oxidation rate of gersdorffite relative to common sulfide minerals such as arsenopyrite and pyrite. However, the local weathering of gersdorffite is not expected to be the major source of arsenic in groundwater. In fact, the groundwater composition suggests that arsenic is mobilized by reductive dissolution of Fe and Mn oxyhydroxides in the confined parts of the aquifer. In addition, gersdorffite-rich zones are not considered to significantly contribute to groundwater flow owing to their low permeability. It is proposed that arsenic is primarily released through the oxidation of sulfides under more oxidizing conditions, transported in the fractures in dissolved and particulate forms, and mobilized under the low redox conditions prevailing in downgradient groundwater.

The findings of this study improve the understanding of the implication of As-bearing sulfides in the naturally occurring arsenic contamination of bedrock groundwater. In particular, they highlight the potential influence of the sulfide mineralogy in the release of arsenic in mineralized environments. These results have implications not only for the groundwater contamination but also for the management of As-rich mining waste and tailings in hardrock mines (Craw and Bowell, 2014). In this respect, more information is needed on the dissolution of As-bearing sulfides, including the minerals of the cobaltite group (Foster, 2003; Lengke et al., 2009). In addition, more knowledge is required regarding the behavior of arsenic-bearing minerals under natural aquifer conditions. In this sense, geochemical and mineralogical investigations on fracture surfaces can be particularly useful (Lipfert et al., 2006; Yang et al., 2015). This work also contributes to a better understanding of the influence of the hydrogeological parameters on the mobilization of arsenic. Future research should consider both the influence of groundwater flow at the aquifer scale and at the local scale to significantly improve knowledge on the processes controlling the natural arsenic contamination in bedrock aquifers.

Acknowledgments

This project was funded by the Quebec Ministry of the Environment (Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques) through the Groundwater Knowledge Acquisition Program (PACES) with significant contributions from regional partners involved in the PACES, including the Regional County Municipalities (Abitibi, Vallée-de-l'Or, Abitibi-Ouest, Ville de Rouyn-Noranda, Témiscamingue) and the Regional Conference of Elected Officials of Abitibi-Temiscamingue. The authors acknowledge the Foundation of the University of Quebec in Abitibi-Temiscamingue (FUQAT) and the Canadian Institute of Mining (Amos section) for scholarships and support to the project of Raphaël Bondu, respectively. We wish to acknowledge Patrick Lavoie, Sébastien Vigneau and Daniel Bernard of the Hecla Mining Company for support in samples selection, providing data and core samples, and access to the exploratory boreholes. We also thank Benoît Plante for advice on laboratory experiments; Marc Choquette for help with the electron microprobe analysis; Alain Perreault and Mathieu Villeneuve for support in the laboratory work; Marc Paquin for the chemical analyses; and Daniel Blanchette, Simon Nadeau and Marika Labbé for assistance during field work.

Appendix A - Supplementary data

Total As and Ni contents measured by acid digestion and XRF analysis

# Sample	$As_{digestion}$ (mg/kg)	As_{XRF} (mg/kg)	$Ni_{digestion}$ (mg/kg)	Ni_{XRF} (mg/kg)
B1 - 22,0	92	112	84	56
B1 - 34,0	1334	1679	842	982
B1 - 58,0	558	516	829	664
B2 - 23,0	413	239	115	< LOD
B2 - 37,0	17234	6128	118	< LOD
B2 - 39,6	18345	9631	784	953
B2 - 58,1	952	590	901	1117
B2 - 70,0	112	24	98	< LOD
B3 - 22,0	163	65	54	< LOD
B3 - 45,6	18463	11523	27	88

LOD = limit of detection

References

ASTM, 2013. Standard test method for laboratory weathering of solid materials using a humidity cell. D5744-13. ASTM International.

Ayotte, J. D., Montgomery, D. L., Flanagan, S. M., Robinson, K. W., 2003. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environmental Science & Technology 37, 2075–2083.

Belova, D. A., Lakshtanov, L., Carneiro, J., Stipp, S. L. S., 2014. Nickel adsorption on chalk and calcite. Journal of Contaminant Hydrology 170, 1–9.

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2016. A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. Water, Air, & Soil Pollution 227 (9), 296.

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2017. Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada. Science of The Total Environment 574, 509–519.

Bottomley, D., 1984. Origins of some arseniferous groundwaters in Nova Scotia and New Brunswick, Canada. Journal of Hydrology 69, 223–257.

Bowell, R. J., Alpers, C. N., Jamieson, H. E., Nordstrom, D. K., Majzlan, J., 2014. The environmental geochemistry of arsenic - An overview. Reviews in Mineralogy and Geochemistry 79 (1), 1–16.

CEAEQ, 2012. Protocole de lixiviation pour les espèces inorganiques. MA. 100 - Lix.com.1.1. Centre d'expertise en analyse environnementale du Québec. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA100Lixcom11.pdf.

CEAEQ, 2014. Détermination des métaux : méthode par spectrométrie de masse à source ionisante au plasma d'argon. MA. 200 - Mét 1.2. Centre d'expertise en analyse environnementale du Québec. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA200Met12.pdf.

Chandra, A., Gerson, A. R., 2010. The mechanisms of pyrite oxidation and leaching: a fundamental perspective. Surface Science Reports 65 (9), 293–315.

Chopard, A., Benzaazoua, M., Plante, B., Bouzahzah, H., Marion, P., 2015. Kinetic tests to evaluate the relative oxidation rates of various sulfides and sulfosalts. In: ICARDS2015 Proceedings, Santiago du Chile (Chile).

Cloutier, V., Veillette, J., Roy, M., Gagnon, F., Bois, D., 2007. Regional hydrogeochemistry of groundwater in fractured Canadian Shield rock and glaciofluvial formations in Abitibi, Quebec. In: Proceedings, 60th Canadian Geotechnical Conference and 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa (Canada).

Craw, D., Bowell, R. J., 2014. The characterization of arsenic in mine waste. Reviews in Mineralogy and Geochemistry 79 (1), 473–505.

Essington, M. E., 2004. Soil and water chemistry: An integrative approach. CRC press, Boca Raton (USA).

Foley, N. K., Ayuso, R. A., 2008. Mineral sources and transport pathways for arsenic release in a coastal watershed, USA. Geochemistry: Exploration, Environment, Analysis 8, 59–75.

Foster, A. L., 2003. Spectroscopic investigations of arsenic species in solid phases. In: Welch, A. H., Stollenwerk, K. G. (Eds.), Arsenic in Ground Water: Geochemistry and Occurrence. Springer, Massachusetts: Kluwer Academic, pp. 27–65.

Gagnon, F., Lampron-Goulet, É., Normandin, L., Langlois, M.-F., 2016. Measurements of arsenic in the urine and nails of individuals exposed to low concentrations of arsenic in drinking water from private wells in a rural region of Quebec, Canada. Journal of Environmental Health 78 (6), 76–83.

Green-Pedersen, H., Jensen, B., Pind, N., 1997. Nickel adsorption on MnO_2, $Fe(OH)_3$, montmorillonite, humic acid and calcite: a comparative study. Environmental Technology 18 (8), 807–815.

Harte, P. T., Ayotte, J. D., Hoffman, A., Revesz, K. M., Belaval, M., Lamb, S., Boehlke, J. K., 2012. Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire, USA. Hydrogeology Journal 20, 1189–1201.

Henke, K., 2009. Arsenic: environmental chemistry, health threats and waste treatment. John Wiley & Sons, West Sussex (UK).

Hocq, M., Verpaelst, P., 1994. Les sous-provinces de l'Abitibi et du Pontiac. In: Dubé, C. (Ed.), Géologie du Québec. Ministère des Ressources naturelles, Gouvernement du Québec, pp. 21–37.

Jackson, D. A., Nesbitt, H. W., Scaini, M. J., Duggal, A., Bancroft, G. M., 2003. Gersdorffite (NiAsS) chemical state properties and reactivity toward air and aerated, distilled water. American Mineralogist 88 (5-6), 890–900.

Lampron-Goulet, É., 2012. Surveillance biologique de l'exposition à l'arsenic inorganique et des perturbations endocriniennes associées dans une population s'approvisionnant en eau potable par des puits privés dans la région de l'Abitibi-Témiscamingue, au Québec. Master's thesis, Université de Sherbrooke.

Lehner, S., Savage, K., 2008. The effect of As, Co, and Ni impurities on pyrite oxidation kinetics: Batch and flow-through reactor experiments with synthetic pyrite. Geochimica et Cosmochimica Acta 72 (7), 1788–1800.

Lengke, M. F., Sanpawanitchakit, C., Tempel, R. N., 2009. The oxidation and dissolution of arsenic-bearing sulfides. The Canadian Mineralogist 47 (3), 593–613.

Lin, Z., Puls, R., 2000. Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. Environmental Geology 39 (7), 753–759.

Lipfert, G., Reeve, A. S., Sidle, W. C., Marvinney, R., 2006. Geochemical patterns of arsenic-enriched ground water in fractured, crystalline bedrock, Northport, Maine, USA. Applied Geochemistry 21, 528–545.

Lottermoser, B., 2003. Mine wastes: characterization, treatment and environmental impacts. Springer Berlin Heidelberg, New York (USA).

Majzlan, J., Drahota, P., Filippi, M., 2014. Parageneses and crystal chemistry of arsenic minerals. Reviews in Mineralogy and Geochemistry 79 (1), 17–184.

MDDELCC, 2015. Portrait régional de l'eau - Abitibi-Témiscamingue. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.mddelcc.gouv.qc.ca/eau/regions/region08/08-abitibi

Parkhurst, D. L., Appelo, C., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Investigations Report 99-4259, Denver (USA).

Plante, B., Benzaazoua, M., Bussière, B., 2011. Predicting geochemical behaviour of waste rock with low acid generating potential using laboratory kinetic tests. Mine Water and the Environment 30 (1), 2–21.

Plante, B., Benzaazoua, M., Bussière, B., Biesinger, M., Pratt, A., 2010. Study of Ni sorption onto Tio mine waste rock surfaces. Applied Geochemistry 25 (12), 1830–1844.

Poissant, L.-M., 1997. La contamination par l'arsenic des puits domestiques en Abitibi-Témiscamingue. Régie régionale de la santé et des services sociaux de l'Abitibi-Témiscamingue, Direction de la santé publique, Rouyn-Noranda (Canada).

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic pollution: a global synthesis. Wiley-Blackwell, West Sussex (UK).

Rouleau, A., Clark, I. D., Bottomley, D. J., Roy, D. W., 2013. In: Rivera, A. (Ed.), Canada's Groundwater Resources. Fitzhenry & Whiteside, pp. 415–442.

Shapiro, A. M., 2002. Cautions and suggestions for geochemical sampling in fractured rock. Groundwater Monitoring & Remediation 22 (3), 151–164.

Sharma, V. K., Sohn, M., 2009. Aquatic arsenic: Toxicity, speciation, transformations, and remediation. Environment International 35, 743–759.

Smedley, P., Kinniburgh, D. G., 2013. Arsenic in groundwater and the environment. In: Selinus, O., Alloway, B., Centeno, J., Finkelman, R., Fuge, R., Lindh, U., Smedley, P. (Eds.), Essentials of Medical Geology. Springer, pp. 279–310.

Stachowicz, M., Hiemstra, T., Van Riemsdijk, W. H., 2007. Arsenic-bicarbonate interaction on goethite particles. Environmental Science & Technology 41 (16), 5620–5625.

Verplanck, P. L., Mueller, S. H., Goldfarb, R. J., Nordstrom, D. K., Youcha, E. K., 2008. Geochemical controls of elevated arsenic concentrations in groundwater, Ester Dome, Fairbanks district, Alaska. Chemical Geology 255, 160–172.

WHO, 2011. Guidelines for drinking-water quality. Geneva: World Health Organization.

Yang, Q., Culbertson, C. W., Nielsen, M. G., Schalk, C. W., Johnson, C. D., Marvinney, R. G., Stute, M., Zheng, Y., 2015. Flow and sorption controls of groundwater arsenic in individual boreholes from bedrock aquifers in central Maine, USA. Science of The Total Environment 505, 1291–1307.

CHAPITRE 3

MOBILITY AND SPECIATION OF GEOGENIC ARSENIC IN BEDROCK GROUNDWATER FROM THE CANADIAN SHIELD IN WESTERN QUEBEC, CANADA

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M. (2017). Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada. Science of the total environment, 574, 509-519.

Résumé

Des concentrations élevées d'arsenic ont été mesurées dans l'eau souterraine provenant d'un aquifère rocheux fracturé situé dans l'Ouest du Québec. Le prélèvement et l'analyse d'eau souterraine issue de 59 puits individuels montrent que plus de la moitié des puits creusés dans le socle rocheux dépassent la norme de potabilité canadienne pour l'arsenic fixée à 10 µg/l. En revanche, les puits de surface creusés dans les dépôts superficiels non consolidés ne sont pas concernés par la contamination. L'altération des minéraux sulfurés riches en arsenic présents le long de la zone de faille minéralisée est considérée comme la source primaire d'arsenic dans l'eau souterraine. Les puits contaminés à l'arsenic sont le plus souvent caractérisés par des conditions légèrement réductrices (Eh $<$ 250 mV), un pH légèrement alcalin (pH $>$ 7.4), de faibles ratios Ca/Na, des concentrations élevées en fer en manganese, et une proportion importante d'arsénite (As(III)). Les puits individuels dans le socle rocheux sont des forages ouverts susceptibles de recevoir de l'eau souterraine en provenance de différents systèmes de fractures. Par conséquent, l'arsenic apparaît comme étant principalement issu de la contribution d'eau évoluée géochimiquement riche en arsenic, ayant un faible Eh, un pH alcalin et une proportion importante d'arsénite. Une eau souterraine géochimiquement évoluée offre des conditions favorables pour la mobilisation de l'arsenic par dissolution réductrice des oxyhydroxydes de fer et de manganese ainsi que par désorption alcaline sur les surfaces minérales. Ainsi, les puits contaminés à l'arsenic sont susceptibles de contenir une grande proportion d'eau géochimiquement évoluée. À l'inverse, les eaux de recharge oxydantes et à faible pH ont tendance à entraîner la dilution et la séquestration de l'arsenic. En lien avec l'évolution chimique de l'eau souterraine le long des chemins d'écoulement, la majorité des puits contaminés est localisée dans les parties captives de l'aquifère, alors que les puits dans les parties libres ne sont généralement pas contaminés. L'existence de puits contaminés ayant une grande proportion d'As(V) est attribuée à l'oxydation de quantités importantes de minéraux sulfurés riches en arsenic et à la désorption alcaline. Ce travail montre que la détermination des espèces d'arsenic constitue un outil précieux pour étudier le comportement de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés.

Mots-clés

Arsenic, Spéciation, Aquifères rocheux fracturés, Puits individuels, Qualité de l'eau souterraine, 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 ($Eh < 250$ 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.

Keywords

Arsenic, Speciation, Fractured bedrock aquifer, Private wells, Groundwater quality, Abitibi-Temiscamingue.

3.1 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 (As(V)) under oxidizing conditions, in the form of monovalent $H_2AsO_4^-$ and divalent $HAsO_4^{2-}$, or as arsenite (As(III)) under more reducing conditions, in the form of uncharged H_3AsO_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 As(III) (Sharma and Sohn, 2009). Owing to its neutral charge below pH 9.2, As(III) is regarded as more mobile than 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 µg/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.

3.2 Study area

The study area covers about 30 km^2 located in the Rapide-Danseur and Duparquet municipalities, in the western part of the Province of Quebec, Canada (figure 3.1). 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 (figure 3.1 (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 (figure 3.1 (B)). In the study area, the bedrock is mainly composed of basalts from the Deguisier Formation north of the Pocupine-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 Pocupine-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) (figure 3.1 (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

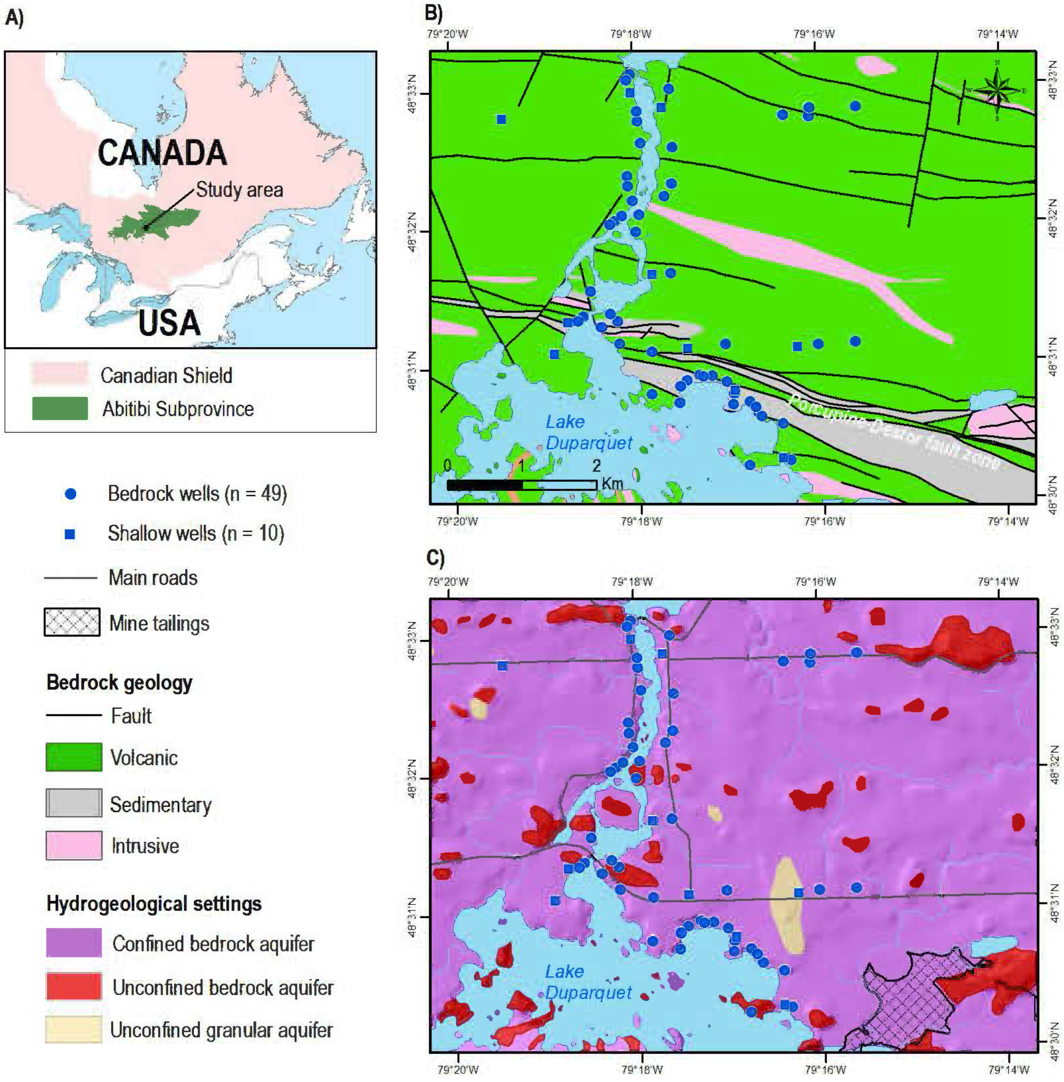

Figure 3.1. A) Location map of the study area in the Canadian Shield and the Abitibi Greenstone belt, B) bedrock geology and C) hydrogeological settings maps of the study area showing sampling wells.

bedrock is largely covered by Quaternary sediments deposited during the last ice retreat and consisting of (1) local glaciofluvial deposits of pebble, sand and gravel up to a few meters thick and (2) expanded glaciolacustrine clay and silt rhythmites up to several meters thick (Cloutier et al., 2015; Thibaudeau and Veillette, 2005) (figure 3.1 (C)).

Private wells are the predominant source of domestic water in the study area, few households using surface water from Lake Duparquet. Although some wells are completed in shallow, unconsolidated aquifers found in fluvioglacial deposits, the majority of private domestic wells produce from the fractured bedrock. In the region, shallow aquifers found in surficial deposits generally contain significant groundwater resources, but are discontinuous and of limited extent (Cloutier et al., 2015; Nadeau et al., 2015). By contrast, the fractured bedrock aquifer provides an almost ubiquitous water resource and represents the only reliable source of water in most of the study area. The wells completed in the bedrock generally consist of unscreened boreholes open to bedrock over their entire length. In areas where Quaternary sediments cover the bedrock, casings are installed at the top of the wells through the deposits. The fractured bedrock aquifer is characterized by a low primary porosity and a variable hydraulic conductivity mostly determined by the presence and characteristic of fractures (Cloutier et al., 2007). The hydraulic conductivity of the bedrock ranges approximately from 4.10^{-9} to 1.10^{-4} m/s at the regional scale (Cloutier et al., 2015). The groundwater flow mainly occurs within the fracture network resulting from the tectonic history and the fracturing of the Precambrian bedrock during the glacial-deglacial cycles. On the other hand, the major east-west trending Archean fractures observed throughout the study area are generally sealed structures that are not expected to significantly influence groundwater flow (J. Goutier, personal communication). In most of the study area, the bedrock aquifer is confined by overlying glaciolacustrine clays (figure 3.1 (C)). The recharge mostly occurs in the unconfined bedrock areas (figure 3.1 (C)), while confined areas are located further along the flow path.

3.3 Material and methods

3.3.1 Sampling and field measurements

Groundwater samples were collected from 59 private wells, including 10 shallow wells in unconsolidated surficial deposits and 49 bedrock wells, from June to August 2014 and in September 2015 (figure 3.1). Water treatment systems such as water softeners and reverse osmosis devices were avoided by collecting samples from untreated taps, pre-treatment access points or by turning off treatment systems. All available information related to wells (e.g. well type, depth, pump type, flow rate, well water use) was obtained from owners. Measurements of temperature (T), specific conductance (SC), pH, redox potential (Eh) and dissolved oxygen (DO) were recorded in the field using a multiparameter probe (YSI 556). Prior to sampling, each well was pumped approximately 15-20 min until stabilization of T, SC and pH values in order to ensure that water was drawn directly from the aquifer. The samples were collected in pre-cleaned HDPE bottles and include (1) one unfiltered and unacidified sample for alkalinity determination (2) one filtered and unacidified sample for anions analysis (3) one filtered, acidified sample for major cations and trace analysis (4) one filtered, acidified sample for As(III) determination. Bottles were pre-acidified with ultra-pure nitric acid (*environmental grade, Anachemia*) and filtration was carried out in the field with 0.45 µm membrane filters using disposable plastic syringes. The samples were stored in ice in sealed plastic bags until delivery to the laboratory on the same day and subsequently stored at 4°C until analysis.

3.3.2 Separation of arsenic species

Separation of dissolved arsenic species was carried out in the field using the solid-phase extraction (SPE) cartridge methodology developed by Watts et al. (2010). This method allows the separation of four major species of arsenic in natural water: inorganic arsenite (As(III)), inorganic arsenate (As(V)), monomethylarsonic acid (MMA(V)) and dimethylarsinic acid (DMA(V)). Preconditioning of both strong anion exchange (500 mg Bond Elut Jr-SAX, Agilent Technologies) and strong cation exchange (*500 mg Bond Elut Jr-SCX, Agilent Technologies*) cartridges was carried out in order to wash the resin and promote the adsorption of the arsenic species. The strong cation exchange (SCX) cartridge was preconditioned using 15 ml of 50 % methanol (*environmental grade, Alfa Aesar*) followed by 15 ml of 1 M phosphoric acid (*ACS reagent grade, Anachemia*) and 5 ml of deionized water (18 MΩ cm). The strong anion exchange (SAX) cartridge was preconditioned using 15 ml of 50 % methanol and 5 ml of deionized water. The separation was carried out in the field by passing a 30 ml water sample collected in a plastic syringe through a membrane filter of 0.45 µm into an SCX cartridge connected in series to an SAX cartridge. Positively charged DMA(V) was retained onto the SCX cartridge while both negatively charged MMA(V) and As(V) were retained onto the SAX cartridge. Uncharged As(III) was not retained and was collected in the effluent. After sampling, each SAX and SCX cartridges were stored in individual sealed plastic bags. An elution technique was required to remove the different species from each cartridge. The latter was achieved using 5 ml of 1 M nitric acid (*environmental grade, Anachemia*) for DMA(V) on the SCX cartridge and 5 ml of 80 mM acetic acid (*environmental grade, Anachemia*) for MMA(V) followed by 5 ml of 1 M nitric acid for As(V) on the SAX cartridge. As the original 30 ml sample was eluted with 5 ml acid solution on the SPE cartridges, a preconcentration factor of 6 was applied to the eluted fractions of As(V), MMA(V) and

DMA(V) (Farnfield et al., 2012). Preconditioning, separation and elution were achieved at an extraction flow rate of 1 drop per second. Each subsample was analyzed for total dissolved arsenic.

3.3.3 Analytical methods

All chemical analyses were conducted at the Research Institute of Mining and the Environment of the University of Quebec in Abitibi-Temiscamingue (UQAT). Alkalinity (as HCO_3^-) was determined by titration with sulfuric acid using an automatic titrator (*Metrohm Titrino Plus 870 KF*). Major anions (SO_4^{2-}, Cl^-, NO_3^-, F^- and Br^-) were measured by ion chromatography (*Metrohm 881 Compact IC Pro*). Major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and silica (Si) were determined by Inductively-Coupled Plasma Atomic-Emission Spectroscopy (*ICP-AES; Perkin Elmer 3000 DV*). Minor and traces elements (Al, As, B, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Se, Sr, Ti, U, V, Zn) were measured by Inductively-Coupled Plasma Mass Spectrometry (*ICP-MS; Agilent 7700x*) according to the standard procedure MA. 200 - Mét. 1.2 of the province of Quebec's Ministry of the Environment (CEAEQ, 2014). Calibration standard solutions ranging from of 5 to 500 µg/l As were prepared from a certified stock standard solution of 10,000 mg/l As (*SCP Science*). Quality control validation was performed using a CEAEQ standard reference sample. The detection limit was of 0.2 µg/l for total dissolved As and As(III) and 0.03 for As(V), MA(V) and DMA(V). Quality-control procedures included the analysis of standard reference material, blanks and duplicate samples, as well as calculation of charge balances. Charge balances were within ± 10 % for all samples except P45 and P56 (within 15 %). Duplicate concentrations for major, minor, and trace elements were almost always within ± 10 % relative standard deviation (RSD). Triplicate samples for arsenic speciation indicate a good accuracy of the method with a percentage of each arsenic species generally varying within 2 %. The WATEQ4F thermodynamic database of the PHREEQC program (Parkhurst and Appelo, 1999) was used for the calculation of saturation indices (SI) in the groundwater samples.

3.4 Results and discussion

3.4.1 Groundwater composition and origin of dissolved elements in bedrock groundwater

3.4.1.1 Physico-chemical parameters

A statistical summary of field parameters and selected elements of the 49 bed-rock well samples is presented in table 3.1. In all samples, specific conductance ranged from 171 to 928 µS/cm and temperature varied from 6.0 to 13.2 °C. However, a groundwater temperature exceeding 8 °C always corresponded to (1) incomplete purging of the well owing to very low water yield, (2) shallow wells in close contact with the atmosphere or (3) bedrock wells located in unconfined areas. Groundwater were slightly acidic to weakly alkaline with pH ranging from 6.42 to 8.15 (mean: 7.47 ± 0.3) in bedrock wells and from 7.03 to 7.66 (mean: 7.40 ± 0.18) in shallow wells. Field Eh measurements indicated mildly reducing conditions to oxidizing conditions in bedrock wells (range: 79-450 mV) and more oxidizing conditions in shallow wells (range: 139-398 mV). Most bedrock wells characterized by oxidizing conditions were located within, or close to, unconfined areas whereas all wells characterized by mildly reducing conditions were located in confined areas.

3.4.1.2 Major chemical species

Shallow and bedrock groundwater were predominantly of Ca-(Mg)-HCO_3 water type (figure 3.2). Calcium (Ca) was generally the dominant cation followed by magnesium (Mg). However, several bedrock wells had a Ca-(Na)-HCO_3 composi-

Table 3.1. Statistical summary of hydrochemical data of bedrock wells (n = 49).

Variables	Min.	Median	Max.	Mean	SD	CV (%)
T (°C)	6	7.2	13.2	7.6	1.4	18
pH	6.4	7.5	8.2	7.5	0.3	4
SC (µS/cm)	171	502	928	528	161	30.6
Eh (mV)	79	193	45	230	111	48.5
HCO_3 (mg/l)	146.3	385.3	670.6	393.8	118.4	30.1
SO_4 (mg/l)	3.9	11.9	84.4	15.7	12.5	79.9
Cl (mg/l)	<0.7	3.3	129.8	11.4	21.8	190.8
NO_3 (mg/l)	<0.7	<0.7	14	1.1	2.3	209.6
PO_4 (mg/l)	<0.9	<0.9	35.1	1.3	4.9	376.2
F (mg/l)	<0.2	<0.2	0.4	<0.2	<0.2	-
Br (mg/l)	<0.7	<0.7	1	<0.7	<0.7	-
Si (mg/l)	6.4	12	17.3	11.7	2.4	20.5
Ca (mg/l)	45.8	86.8	156	87.2	24.9	28.5
Mg (mg/l)	6	33.9	90.7	34.5	18	52.2
Na (mg/l)	2.7	17.1	45.1	17.9	8.7	48.5
K (mg/l)	0.4	1.6	3.8	1.6	0.8	46.7
As (µg/l)	**<0.2**	**10.2**	**326.4**	**43.4**	**70.5**	**162.6**
Al (µg/l)	<1	2	11	2.3	1.8	80.1
B (µg/l)	<1.4	16.3	464.3	46.9	82.2	175.4
Ba (µg/l)	<0.4	28.3	323.9	58.2	79.1	135.7
Cu (µg/l)	<1.1	<1.1	30.3	3.1	6.4	207.8
Fe (µg/l)	<1.5	151.8	2619.9	392	556.1	141.9
Mn (µg/l)	<0.4	93.1	3355.5	218.2	487.7	223.5
Sr (µg/l)	37.5	269.4	3174.9	434.6	520.8	119.9
Zn (µg/l)	<3.2	<3.2	12.6	<3.2	<3.2	-

SD = standard deviation; CV = coefficient of variation

tion. Bicarbonate (HCO_3) was by far the dominant anions in all wells, generally followed by sulfate (SO_4) and chloride (Cl) in some bedrock wells.

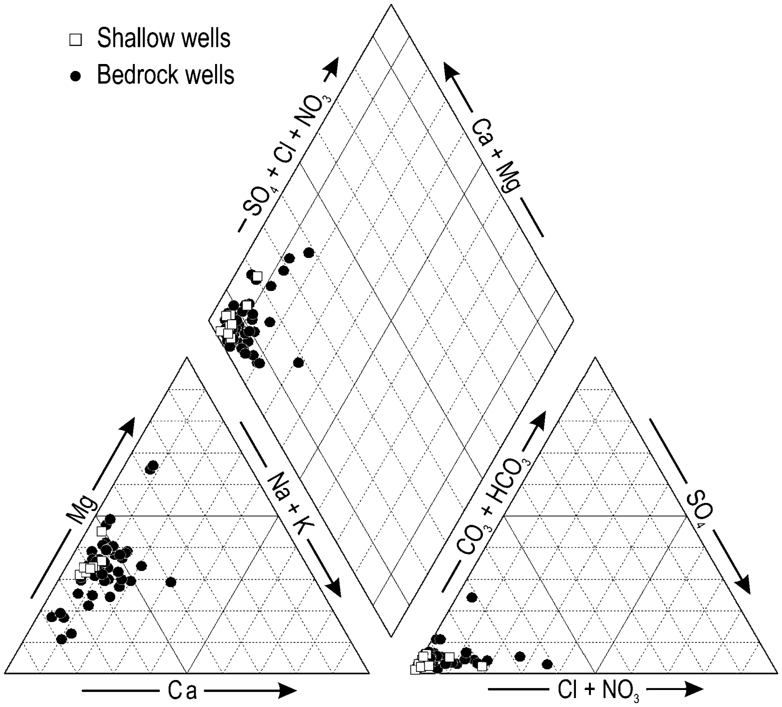

Figure 3.2. Piper diagram of shallow and bedrock groundwater samples.

Owing to the local geological framework, the enrichment of bedrock groundwater in Ca, Mg, Na and HCO_3 is believed to be mainly derived from the weathering of silicates. This is evidenced by the positive correlation of Ca, Mg, Na with Si (figure 3.3 (A)) and the PHREEQC calculations suggesting that most wells were oversaturated with respect to calcite (figure 3.3 (C)) but undersaturated with respect to silicate minerals such as anorthite (figure 3.3 (D)) (Montcoudiol et al., 2015). Nevertheless, carbonates dissolution can locally act as source of Ca, Mg and HCO_3, in particular in the mineralized fault zone that is known to contain carbonate minerals (Legault et al., 2005). The relatively high Na concentrations

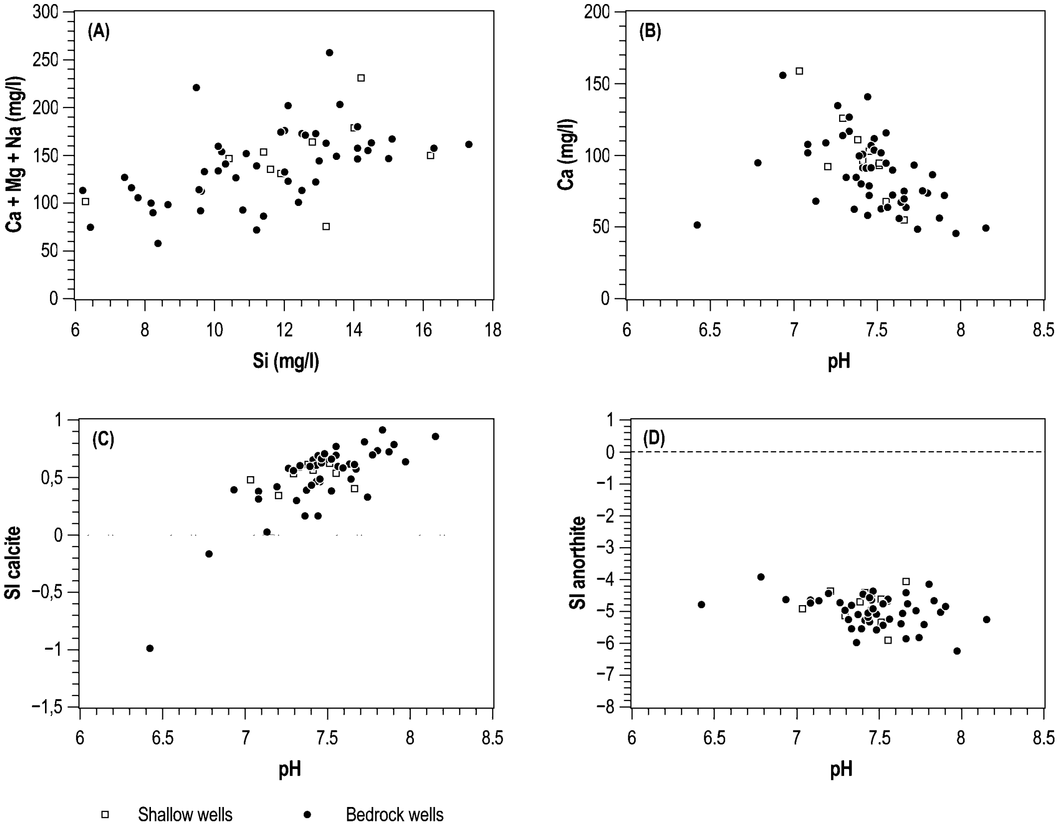

Figure 3.3. Scatter plots comparing (A) Ca + Mg + Na with Si, (B) Ca with pH and saturation index of (C) calcite and (D) anorthite with pH.

in some confined bedrock wells are likely related to the chemical evolution of groundwater that changes from Ca-(Mg)-HCO_3 to Ca-(Na)-HCO_3 composition along the flow path as the result of the interaction with Na-feldspar, calcite precipitation and ion exchange on clay minerals (Gascoyne and Kamineni, 1994). In fact, the release of Na through Na-feldspar hydrolysis and cation exchange generally requires longer reaction time than the release of Ca through carbonates dissolution and Ca-feldspar hydrolysis (Appelo and Postma, 2005). The presence of SO_4 is expected to be derived from the dissolution of sulfides and secondary sulfate minerals in the fractured bedrock. The relatively high Cl concentrations in some bedrock wells are believed to be related to the contribution to the well discharge of deep saline groundwater. In general, high Cl concentrations in bedrock well water are associated with high Ca concentrations and comparatively low Na concentrations. The occurrence of hypersaline calcium/chloride brines has been documented in other areas in the crystalline basement of the Archean Superior Province (Bottomley et al., 2003; Gascoyne and Kamineni, 1994). It is noteworthy that land-use activities can also be a source of Cl through road salt use ($CaCl_2$), leaching from septic tanks or farming activities, in particular in shallow wells. Nitrate (NO_3) concentrations were generally low (< 2.2 mg/l), suggesting that groundwater was not affected by pollution from septic tanks or agricultural activities. Of the four bedrock wells exceeding 5 mg/l NO_3 , three are located on livestock farming areas while the other one is located in the unconfined bedrock aquifer, suggesting rapid flow from the surface or eventually from a septic tank.

3.4.2 Dissolved arsenic and trace metal elements

Dissolved minor and trace metal concentrations in bedrock groundwater were relatively low, with the exception of As, Fe and Mn. Dissolved As concentrations ranged from below the detection limit of 0.2 µg/l to 326.4 µg/l (table 3.1). High As concentrations occurred exclusively in bedrock wells whereas As concentration did not exceed 4.1 µg/l in shallow wells. About 53 % of the bedrock wells exceeded the Canadian guideline value of 10 µg/l for As, 27 % exceeded 50 µg/l As. Most of the arsenic present in bedrock groundwater is believed to be primarily derived from the natural weathering of As-bearing sulfides in the oxic/suboxic zone of the aquifer. Although it is difficult to distinguish between natural and mining-induced As, the leachate from the As-rich mine tailings is not expected to significantly contribute to arsenic contamination of bedrock wells because (1) groundwater in the abandoned mining site flows towards the Lake Duparquet, (2) the wells located closest to the mine tailings are not contaminated, and (3) the main contaminated zone is located west of the river where groundwater inputs from the abandoned mine are unlikely. Dissolved Fe and Mn concentrations in bedrock groundwater were highly variable, ranging from below 1.5 to 2620 µg/l and from below 0.4 to 3356 µg/l, respectively (table 3.1). Fe concentrations exceeded the Canadian aesthetic objective of 0.3 mg/l in more than 33 % of the wells, including 2 shallow wells. Mn concentrations exceeded the Canadian aesthetic objective of 0.05 mg/l in 55 % of the wells including 3 shallow wells and exceeded the current WHO guideline value of 0.4 mg/l in 5 bedrock wells. Both Fe and Mn are expected to be derived from the weathering of multiple common bedrock minerals such as silicates, oxides, carbonates and sulfides.

3.4.3 Arsenic speciation

The distribution of dissolved arsenic species for each well water sample is presented in table 3.2. Overall, the range of recovery was consistent with those reported in groundwater studies using the SPE cartridges methodology (Christodoulidou et al., 2012; O'Reilly et al., 2010; Watts et al., 2010) . The recovery for low-As samples was generally less accurate because 1) recovery values are more sensitive to a slight discrepancy for low-As concentrations and 2) low-As samples may contain As species concentrations below or close to the quantification limit even though they account for a significant proportion of the total dissolved As concentration. The very low recovery for sample P13 is likely related to a problem in the SAX cartridge elution since one of the main As species, most probably As(V), is lacking. Note that incomplete elution of As(V) may be responsible for some incomplete recoveries such as for samples P20 and P35. The high concentration of MMA(V) responsible for the overestimation of the recovery in sample P56 is probably due to the contamination of the sample.

Table 3.2. Total dissolved arsenic and dissolved arsenic species concentrations in groundwater samples (n = 46). Only samples with total As concentration above the quantification limit are presented. Shallow well samples (n = 4) are shown in italics.

Samples	Total dissolved As	As(III)		As(V)		MMA(V)		DMA(V)		Sum As species	Recovery
	µg/l	µg/l	%	µg/l	%	µg/l	%	µg/l	%	µg/l	(%)
P1	1.1	0.6	48.4	0.3	23.1	0	3	0.3	25.5	1.3	114.7
P2	7.5	1.3	13.6	7.8	82.1	nd	0	0.4	4.1	9.5	127.9
P3	3.6	nd	0	3.4	86.8	0.1	1.4	0.3	8	3.8	105.5
P4	49.7	44.1	91.3	1	2.1	1.5	3.2	1.7	3.5	48.3	97.3
P5	5.3	0.7	10.9	4.7	78.6	0.1	1.4	0.5	9.1	6	113.2
P6	2	0.3	10.3	2	66.6	0	1.5	0.6	21.5	3	151.3
P8	119.8	104.9	90.1	5.8	5	2.4	2	3.3	2.9	116.4	97.2
P9	39.8	21.6	66.8	8.8	27.1	1.1	3.3	0.9	2.9	32.3	81.3
P10	17.1	17.9	88.5	1.3	6.3	0.5	2.2	0.6	2.9	20.2	117.7
P11	1.9	0.4	16.2	1.3	57.3	0.4	17.6	0.2	8.9	2.3	120.8
P13	18.8	0.5	97.2	0	0	nd	0	nd	0	0.5	2.9
P14	*1.2*	*0.8*	*56.1*	*0.5*	*39*	*0.1*	*4.9*	*nd*	*0*	*1.4*	*114.6*
P16	3.3	1.9	83.4	0.2	8	0.1	2.7	0.1	5.9	2.3	70.7
P17	263.4	233.4	84	27.5	9.9	10.8	3.9	6.1	2.2	277.7	105.5
P18	35.8	38.2	89.5	3.2	7.4	0.6	1.4	0.7	1.7	42.6	119
P20	12.8	nd	0	8	90.9	0.3	3.5	0.2	2.6	8.5	66.9
P22	8.8	4.8	70.5	1.5	21.9	nd	0	0.3	3.7	6.6	75
P23	86.4	79.3	84.9	11.3	12.1	1.4	1.5	1.4	1.5	93.4	108
P24	10.3	8.7	90.7	0.6	6	0.1	1.1	0.2	2.2	9.5	92.6
P25	43.6	34.1	85.6	3.9	9.9	0.8	1.9	1	2.5	39.8	91.2
P26	21.1	28.7	94.2	1.1	3.7	0.3	0.9	0.4	1.1	30.5	144.2

P27	0.7	nd	0	0.4	47.7	0.1	8.4	0.1	11.4	0.6	85.2
P28	1	0.7	70	0.1	11.2	0	4.6	0.1	14.2	1	102.1
P30	49.4	44.4	92.6	1.5	3.2	0.8	1.7	1.2	2.5	48	97
P31	23.5	24.3	89.7	1.4	5.1	0.7	2.6	0.7	2.6	27.1	115.7
P33	*3.2*	*3.2*	*86.5*	*0.2*	*6.7*	*nd*	*0*	*0.2*	*6.8*	*3.7*	*115.8*
P34	50.8	50.1	90.6	2.8	5.1	0.9	1.7	1.5	2.7	55.3	108.8
P35	326.4	2.4	1	246.8	97.5	0.6	0.2	3.4	1.3	253.1	77.5
P37	4.1	3.6	66	1.3	23.4	0.1	1.6	0.5	9	5.5	133.7
P38	*2.6*	*3.3*	*89.1*	*0.3*	*7.6*	*nd*	*0*	*0.1*	*3.3*	*3.7*	*141.3*
P40	72.9	54.8	76.1	14	19.4	1.5	2	1.8	2.5	72	98.9
P41	5.9	4.6	60.7	2.6	34.5	0.1	1.3	0.3	3.5	7.6	128.2
P42	113.1	92.1	88.7	5.8	5.6	2.8	2.7	3.2	3.1	103.9	91.9
P44	15.9	nd	0	19	92.2	1.1	5.3	0.3	1.3	20.4	128.2
P46	10.2	10.6	83.4	1.7	13.6	0.2	1.2	0.2	1.9	12.8	124.8
P49	*4.1*	*nd*	*0*	*2.3*	*89.6*	*0.1*	*5*	*nd*	*0*	*2.5*	*60.5*
P50	2.1	2.2	81.3	0.4	14	0	1.1	0.1	3.6	2.7	128.1
P51	8.7	9.6	90.1	0.4	4	0.5	4.6	0.1	1.4	10.6	121.9
P52	86.9	91.4	92.5	4.4	4.4	1.3	1.3	1.7	1.8	98.7	113.7
P53	140.9	111	89.4	5.3	4.3	4.8	3.8	3.1	2.5	124.2	88.2
P54	238.5	183.5	91.2	4.8	2.4	7.8	3.9	5.1	2.5	201.2	84.4
P55	10.2	0.3	3.4	8.5	92.5	0.1	1.4	0.3	2.7	9.2	90.5
P56	2.8	0.7	6.7	2.5	22.3	7.6	68.6	0.3	2.4	11	396.8
P57	83.1	86.6	92.1	3.2	3.5	2.4	2.5	1.8	1.9	94	113.2
P58	118	120.6	93.5	2.4	1.9	2.9	2.2	3.1	2.4	129	109.3
P59	6.8	5.9	88	0.3	4.7	0.1	1.6	0.4	5.7	6.7	98.3

The results of the arsenic speciation analysis reveal that dissolved arsenic occurred predominantly in inorganic form in both bedrock and shallow well waters, with As(III) being the dominant species in the majority of wells (table 3.2). About 84 % of the bedrock wells exceeding 10 µg/l As contained a high proportion of As(III), the other 16 % being dominated by As(V) (figure 3.4). In contrast, organoarsenicals were present at lower concentrations with MMA(V) and DMA(V) accounting for, on average, 2.8 % and 4.5 % of the speciated arsenic, respectively. These results are in agreement with previous studies that report low concentrations of organoarsenicals in natural groundwater (Christodoulidou et al., 2012; Maguffin et al., 2015; O'Reilly et al., 2010). Interestingly, a strong correlation exists between methylarsenicals and arsenite concentrations (figure 3.5). As suggested by Maguffin et al. (2015) who found similar results in a bedrock aquifer in Oregon, this provides evidence of microbial methylation of inorganic arsenic occurring in the bedrock aquifer.

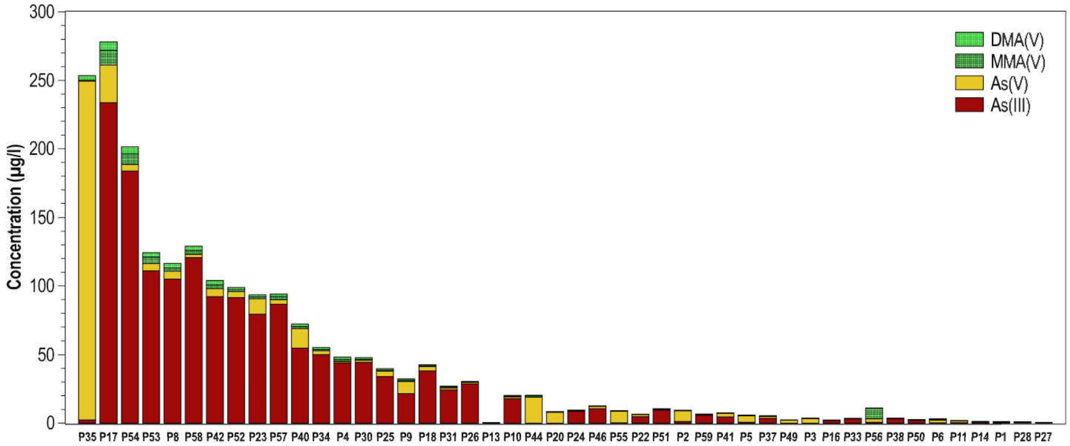

Figure 3.4. Distribution of dissolved As species in groundwater samples. Samples are presented by descending order of total dissolved As concentration.

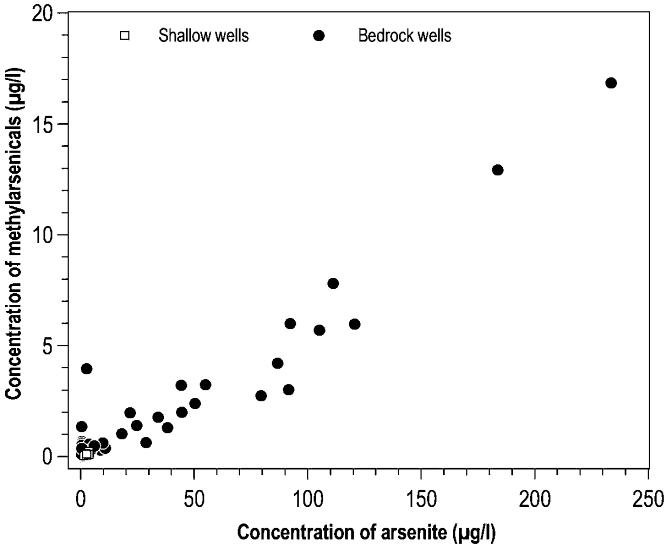

Figure 3.5. Relationship between methylarsenicals concentration and arsenite concentration.

Moreover, in accordance with previous studies in bedrock aquifers (Kim et al., 2012; Maguffin et al., 2015), our results show that the speciation of arsenic was largely determined by the redox conditions. As(III) prevailed under mildly reducing conditions, at Eh values below 250 mV, whereas As(V) prevailed under more oxidizing conditions (figure 3.6). However, the geochemical modeling indicates that As(V) was stable under the geochemical conditions measured in all samples as shown on the Eh-pH diagram (figure 3.7). Similar results have been reported for bedrock wells in Korea in a previous study by Kim et al. (2012). This discrepancy between modeled and measured As species distribution suggests that groundwater samples are out of equilibrium and may reflect a mixture of waters with different redox status. Thus, the predominance of As(III) in most wells may be the result of the contribution to the well discharge of fractures containing As(III)-rich reducing groundwater. The arsenic species did not have time to equilibrate with samples conditions before species separation. The occurrence of strong reducing conditions in the bedrock aquifer is supported by the characteristic smell of H_2S

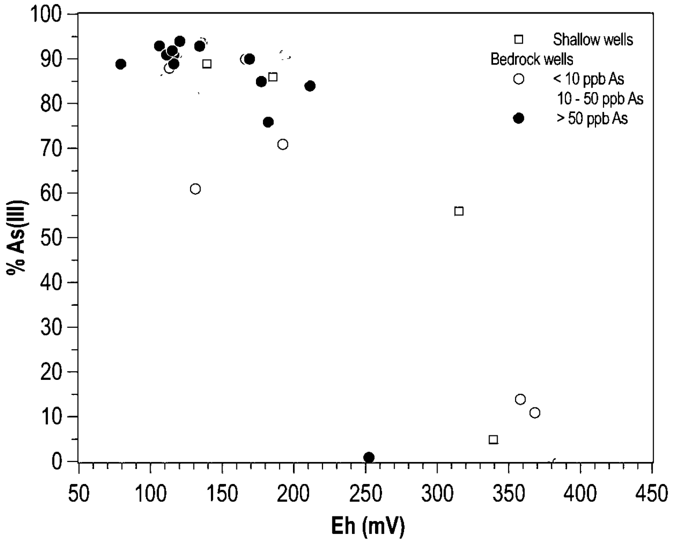

Figure 3.6. Relationship between As(III) fraction and Eh.

noted in several boreholes. In addition, the mixing between reducing and more oxidizing waters is supported by the fact that Fe oxyhydroxides were oversaturated in all samples, particularly at low Eh values, suggesting that there is a source of dissolved Fe into the boreholes. The primary release of arsenic as As(III) from sulfide minerals may also explain the dominance of As(III) in groundwater (Kim et al., 2012). However, the arsenic release by sulfide oxidation is expected to occur predominantly under oxic/suboxic conditions in which As(III) oxidation occurs rapidly, in particular in the presence of Fe and Mn oxyhydroxides (Campbell and Nordstrom, 2014). Moreover, the difference in adsorption between As(III) and As(V) is not expected to affect As species distribution since As(III) and As(V) are sorbed to similar extents under weakly alkaline conditions (Dixit and Hering, 2003; Ravenscroft et al., 2009). On the other hand, the predominance of As(V) in well waters with oxidizing conditions may result from the oxidation of sulfides at rates exceeding the sequestration by sorption. These results highlight that inferring arsenic speciation from Eh-pH diagrams must be considered with caution, in particular when groundwater mixing is suspected.

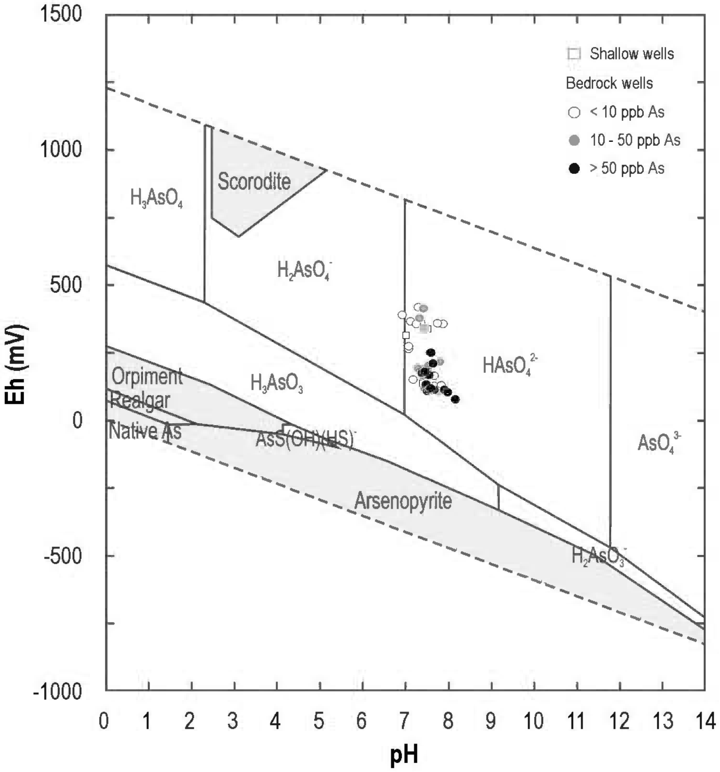

Figure 3.7. Plot of groundwater samples on the Eh-pH diagram for the system As-O-H-S-Fe at 25 °C, 1 bar, $\Sigma S = 10^3$ M, $\Sigma Fe = 10^6$ M and $\Sigma As = 10^6$ M (Lu and Zhu, 2011).

3.4.4 Geochemical controls on arsenic mobility

Even though sulfide oxidation represents the primary source of arsenic into groundwater, the relationship between dissolved As and geochemical conditions suggests that the mobility of arsenic is largely controlled by secondary sources. High As concentrations were generally found in well waters with low Eh values (figure 3.8 (A)). More than 83 % of the wells exceeding 50 µg/l As were associated with Eh values below 193 mV, which is the median Eh value in bedrock wells (table 3.1). In a similar way to As, high Fe and Mn concentrations occurred at low Eh values (figure 3.8 (C)). Although the relationship of As with Fe and Mn is not clear, it is important to emphasize that all wells exceeding 10 µg/l As contain more than 100 µg/l Fe, with the exception of five wells associated with oxidizing conditions (figure 3.8 (C)). The redox potential appears to be the major control on the formation of Fe and Mn oxyhydroxides in bedrock groundwater owing to the limited range of pH (table 3.1). In agreement with previous studies (Kim et al., 2012; Lipfert et al., 2006; Yang et al., 2015), this suggests that reducing conditions affecting the formation and dissolution of Fe-Mn oxyhydroxides are likely to be involved in the mobilization of arsenic in bedrock groundwater. Moreover, elevated As concentrations were generally observed under weakly alkaline conditions at pH values above 7.4 (figure 3.8 (B)). About 85 % of the wells exceeding 50 µg/l As were found above the median pH value of 7.46 (table 3.1). It is well known that the adsorption of arsenic oxyanions decreases as pH increases, particularly at pH above 7 to 8.5, depending on the specific mineralogy (Ravenscroft et al., 2009). Thus, alkaline desorption of As from Fe-Mn oxyhydroxides and clays minerals may occur in bedrock groundwater, as suggested by previous studies (Ayotte et al., 2003; Boyle et al., 1998; Peters and Blum, 2003).

However, the geochemical conditions measured in boreholes are not expected to cause the mobilization of arsenic. In fact, the mildly reducing conditions measured in high-As wells appear insufficient to cause reductive dissolution of metal oxyhydroxides. Geochemical calculations using PHREEQC indicate precipitation of Fe-oxyhydroxides under the range of Eh-pH values measured in all wells. In addition, the threshold pH value of 7.4 is too low to cause arsenic desorption in comparison to the point of zero charge (pH_{pzc}) of common Fe-oxyhydroxides such as goethite ($pH_{pzc} = 9.3$), hematite ($pH_{pzc} = 8.5$) and $Fe(OH)_3$ ($pH_{pzc} = 8.5$) (Appelo and Postma, 2005). These discrepancies, along with those in the distribution of As species, suggest that bedrock well waters are out of equilibrium,

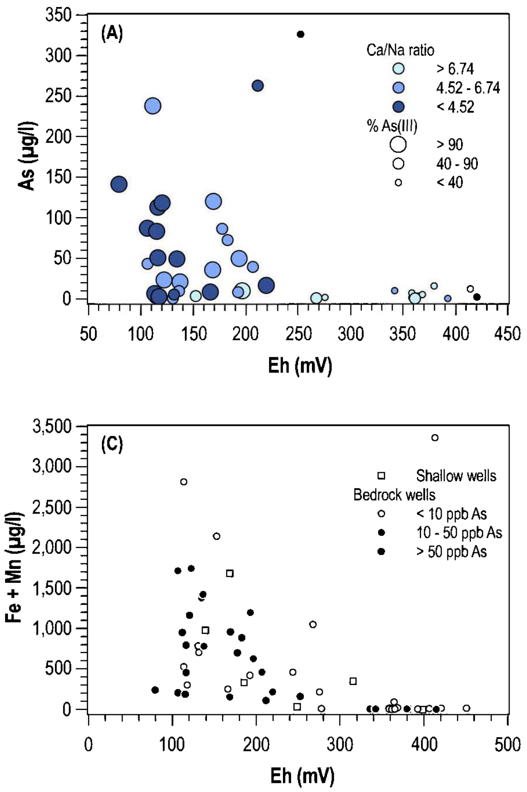

Figure 3.8. Relationship between As concentrations and (A) Eh, (B) pH and (D) Ca/Na ratios, and (C) Fe + Mn concentrations with Eh. For graphs (A) and (B), the three classes of Ca/Na ratios are based on the quantile method.

probably owing to the mixing of waters originating from discrete fractures with different redox and pH conditions. In this sense, the occurrence of dissolved arsenic in the most reducing and alkaline waters appears to be related to the contribution to the well discharge of more geochemically evolved groundwater, which has a chemical composition reflecting an increased contact time between water and crystalline rock. This is supported by the fact that high As concentrations are associated with low Ca/Na ratios (figure 3.8 (D)). As discussed in 4.1.2, Ca/Na ratios tend to decrease as groundwater evolves along the flow path. Geochemically evolved groundwater is expected to provide favorable conditions for arsenic release owing to a low Eh resulting from O_2 consumption through oxidation reactions, a high pH resulting from silicate and carbonate weathering as well as cation exchange processes, and an extended reaction time between arsenic minerals and water related to a high residence time. However, the reductive dissolution of Fe-Mn oxyhydroxides appears to be the dominant process responsible for arsenic mobilization in geochemically evolved groundwater. Indeed, the predominance of arsenic as As(III) (figure 3.8 (A) and (B)) suggests that the redox conditions are low enough to completely dissolve metal oxyhydroxides, thus restricting alkaline desorption to other minerals such as clay minerals. On the other hand, alkaline desorption could play an important role in the release of arsenic in more oxidizing groundwater where arsenic occurs as As(V). The occurrence of dissolved arsenic in chemically evolved water is in agreement with previous studies in bedrock aquifers (Lipfert et al., 2006; Ryan et al., 2013). As suggested in figure 3.8 (A) and (B), it is noteworthy that low to moderate As concentrations are likely the result of a limited groundwater evolution and a lack of mineralogical source.

3.4.5 Conceptual model of arsenic mobilization in bedrock wells

A conceptual model explaining arsenic concentrations in bedrock well water is summarized in figure 3.9. In this model, arsenic is initially released into groundwater by oxidation of As-bearing sulfides in the oxic/suboxic zone of the fractured bedrock aquifer. Arsenic is subsequently transported in dissolved and particulate forms within the fracture network along the groundwater flow paths (Yang et al., 2015). In the fracture network, the mobility and form of arsenic are controlled by the local geochemical conditions, especially the redox and pH conditions. Under oxidizing and slightly acidic to near-neutral pH conditions, such as those that allow sulfide oxidation, arsenic sorbs strongly onto mineral surfaces, especially Fe-Mn oxyhydroxides and clay minerals. By contrast, under reducing and alkaline conditions prevailing in more chemically evolved groundwater, arsenic is readily released into groundwater by reductive dissolution of metal oxyhydroxides and to a lesser degree desorption from mineral surfaces. Under strong reducing conditions, it is probable that sulfate reduction leads to the precipitation of secondary sulfide minerals, removing arsenic from groundwater. As Shapiro (2002) emphasized in a previous study, pumping from an open borehole intersected by multiple fractures results in flux-averaged water samples, where the contribution to the pump discharge from the concentration in each fracture is weighted by the transmissivity of that fracture. As open boreholes in fractured bedrock commonly intercept groundwater from multiple discrete fractures, bedrock well water generally reflect a mixture of groundwater with different redox and chemical characteristics (Harte et al., 2012). In this sense, groundwater from bedrock wells is expected to be a mixture occurring in the borehole and along the flow path between:

(1) Low-As fracture water characterized by short residence time, oxidizing conditions (Eh $>$ 350 mV), weakly acidic conditions (pH $<$ 7), high Ca/Na ratio, low dissolved Fe and Mn concentrations, and dissolved arsenic as As(V). This is the less geochemically evolved groundwater type generally occurring in recharge areas.

(2) High-As fracture water characterized by elevated residence time, reducing conditions (Eh $<$ 0 mV), alkaline conditions (pH $>$ 8), low Ca/Na ratio, elevated dissolved Fe and Mn concentrations, and dissolved arsenic as As(III). This is the more geochemically evolved groundwater type likely occurring in small, poorly connected and deep fractures as well as in fractures at the end of the groundwater flow path (Ryan et al., 2013; Yang et al., 2015).

The mixing of reducing, high pH water and oxidizing, low pH water may result in the measurement of mildly reducing and weak alkaline conditions in pumped groundwater. However, dissolved As(III) originating from reducing groundwater may not have time to be converted (i.e. sorbed and oxidized) under these conditions before sampling. In this way, the mixing of water with distinct chemistry is likely to result in the sampling of mildly reducing and weakly alkaline groundwater with high arsenic concentration as As(III). Nonetheless, mildly reducing and weakly alkaline well water may also contain low dissolved As owing to the lack of primary mineral source of arsenic and the contribution of reducing low As groundwater to the well discharge.

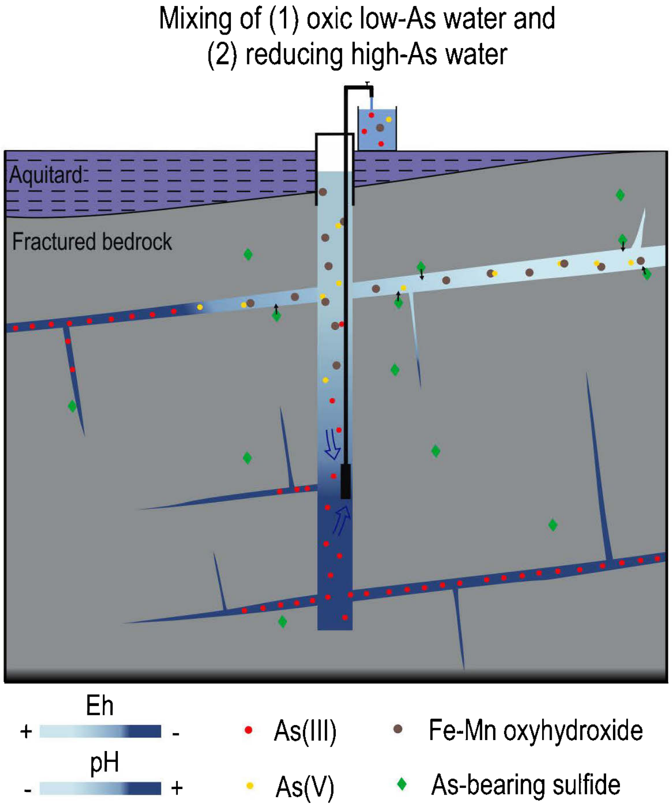

Figure 3.9. Conceptual model of arsenic mobilization in bedrock wells.

Therefore, the bedrock wells located within or close to unconfined areas generally contain low-As concentrations owing to the large proportion of oxidizing, low pH recharge water. Nevertheless, high-As(V) wells may occur in cases where sulfide oxidation exceeds the sorption capacities of minerals, and the high pH causes the desorption of arsenic. Note that the contribution of shallow groundwater to the well discharge may also increase the dilution of arsenic concentrations in the case of a borehole drilled into the bedrock underlying fluvioglacial deposits. In fact, natural or artificial hydraulic connections can occur between the bedrock aquifer and the overlying granular aquifer (Richard et al., 2014). On the other hand, the bedrock wells located in confined areas, i.e. further along the flow paths, are more likely to contain high-As concentrations owing to the large proportion of more reducing, alkaline geochemically evolved water. In addition to the heterogeneity in the distribution of arsenic minerals, the mixing of different fracture waters appears suitable to explain the large spatial variability in arsenic concentrations measured in wells being located within a few hundred meters apart.

3.4.6 Arsenic exposure and protection of public health

In the Province of Quebec, the safety of private well water is the responsibility of the well owners. Hence, in arsenic contaminated areas of the Abitibi-Temiscamingue region, the protection of public health mainly depends on the homeowner behaviors of mitigating As exposure. In our study, the information collected from homeowners during the sampling campaign indicate that 38 % of owners of wells exceeding 10 µg/l As were unaware of the contamination of their wells, while 50 % had knowledge of the contamination and take protective actions to mitigate As exposure, including drinking bottled water or treating their well water. The remaining 12 % were aware of the contamination but did not act to reduce their exposure, probably owing to a low risk perception and the cost associated with water treatment (Flanagan et al., 2015). These results strongly suggest that awareness and information campaigns are needed to encourage water testing and mitigating As exposure if necessary. In this respect, well test results and comments relative to drinking water standards were provided to households participating in the study. However, it is known that water treatment only partly reduce exposure to As owing to the consumption of water from untreated taps, treatment system failure or breakthrough (Smith et al., 2016; Spayd et al., 2015). The most reliable solution to ensure the protection of public health remains the supply of safe drinking water. In this sense, our findings suggest that alternative sources of drinking water should be considered in areas affected by geogenic arsenic contamination, including shallow groundwater from surficial aquifers and surface water in particular for households located near lakes. In the case where bedrock aquifer is the only available source of water, the boreholes depth should be limited to avoid the contribution of reducing fractures to the well discharge, particularly in confined areas which are likely to contain elevated As concentrations in the form of toxic As(III). Moreover, particular attention should be given to low yield wells that are likely to contain geochemically evolved water from low transmissive fractures.

3.5 Conclusions

Arsenic concentrations exceeding the WHO and Canadian drinking water standard of 10 µg/l were measured in groundwater collected from private bedrock wells in the Canadian Shield in western Quebec (Canada). The contamination is of natural origin, primarily derived from the weathering of As-bearing sulfides in the oxic/suboxic zone of the bedrock aquifer. High-As wells generally contain mildly reducing ($Eh < 250$ mV) and weak alkaline ($pH > 7.4$) conditions, low Ca/Na ratios, elevated dissolved Fe and Mn concentrations and high proportions of As(III). The relation between dissolved As and geochemical conditions suggests that secondary sources are involved in the mobilization of arsenic. However, the Eh-pH conditions measured in wells are not expected to cause the release of arsenic from Fe-Mn oxyhydroxides, which are considered to be the most important secondary arsenic minerals in the bedrock aquifer. In this sense, the presence of arsenic in open boreholes is believed to be derived from the contribution to the well discharge of more reducing and alkaline arsenic rich chemically evolved groundwater, likely originating from small, poorly connected and deep fractures as well as fractures at the end of the flow path. Reductive dissolution of Fe-Mn oxyhydroxides and to a lesser extent alkaline desorption onto mineral surfaces are likely responsible for the high dissolved arsenic concentration in chemically evolved groundwater. The predominance of As(III) in most bedrock wells strongly support the idea that arsenic originates from reducing groundwater. On the other hand, the low As concentrations are likely the result of either a lack of primary sources of As in the bedrock or an important proportion of oxidizing, low-pH recharge water that causes dilution and sequestration of dissolved arsenic. Interestingly, the elevated As(V) concentrations occurring in few wells characterized by oxidizing conditions are probably related to extensive sulfide oxidation as well as alkaline desorption from metal oxyhydroxides and clay minerals. This research suggests that the reductive dissolution of Fe-Mn oxyhydroxides could be the major mechanism of arsenic mobilization in bedrock aquifers. Nevertheless, it is believed that the release of arsenic in fractured bedrock aquifers is caused by multiple mechanisms including sulfide oxidation and alkaline desorption, in relation with the large heterogeneity in geochemical conditions and primary mineral sources. By contrast, the mobilization of arsenic in most porous aquifers in alluvial plains is generally thought to be entirely related to reductive dissolution of iron oxyhydroxides driven by microbial metabolism of sedimentary organic matter (Nickson et al., 2000; Postma et al., 2012).

This study contributes to improve knowledge about the speciation of arsenic in groundwater which is an important issue of public health in arsenic contaminated areas. The results regarding the predominance of toxic As(III) in most private wells emphasize the importance to consider the speciation of arsenic as an important parameter with respect to health exposure. The new data on methylated arsenic species increase knowledge about the occurrence of organic forms of arsenic in groundwater. Moreover, the determination of arsenic species is proved to be a valuable tool to assess the behavior of arsenic in bedrock groundwater. This research is also a step forward in understanding the mechanisms of arsenic mobilization in bedrock aquifers although our findings regarding the contribution of As-rich reducing fractures to high arsenic concentrations in open bedrock wells needs to be further evaluated. For this purpose, identifying and sampling water contributing fractures appears to be the most suitable method, although requiring complex investigations including specific equipment and good availability of wells (Yang et al., 2015). Evaluating the stable isotope composition of water could be useful for further understanding mixing processes within boreholes, in particular by identifying end-members for each groundwater type and calculating mixing proportions whenever possible (Douglas et al., 2000). Tracers of residence time could also provide valuable information to assess the link between dissolved arsenic and groundwater flow, particularly in relation with the chemical evolution of groundwater (Ayotte et al., 2003; Sidle and Fischer, 2003). Additional analyses could be helpful to better evaluate the geochemical conditions in groundwater such as the determination of H_2S concentration, Fe and Mn speciation, and suspended particulate arsenic. This work highlights the fact that it is critical that the interpretation of arsenic measurements in groundwater is associated with a good knowledge of the sampling well characteristics. A better understanding of the contribution and chemical signature of individual fractures appears to be the key to improve knowledge on the geochemical processes controlling arsenic mobilization in bedrock aquifers.

Acknowledgments

This project was funded by the Quebec Ministry of the Environment (Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques) through the Groundwater Knowledge Acquisition Program (PACES) with significant contributions from regional partners involved in the PACES, including the Regional County Municipalities (Abitibi, Vallée-de-l'Or, Abitibi-Ouest, Ville de Rouyn-Noranda, Témiscamingue) and the Regional Conference of Elected Officials of Abitibi-Temiscamingue. The authors acknowledge the Fondation of the University of Quebec in Abitibi-Temiscamingue (FUQAT) and the Canadian Institute of Mining (Amos section) for scholarships and support to the project of Raphaël Bondu, respectively. We thank Jean Goutier for the valuable discussions on the regional geology. We also thank Marc Paquin for the chemical analyses and Yacouba Fomba for assistance during field work. We would like to thank the homeowners of the Duparquet and Rapide-Danseur municipalities who permitted access to their wells. Finally, the authors would like to acknowledge three anonymous reviewers for their constructive comments which contributed to improve this article.

Appendix A. Supplementary data

Well ID	Well characteristics				Field parameters				Arsenic species concentrations (µg/l)				
	Type	Depth (m)	⊘ (cm)	Pump type	T (°C)	pH	SC (µS/cm)	Eh (mV)	Total As	As(III)	As(V)	MMA(V)	DMA(V)
P1	Bedrock well	27.4	15.2	Submersible	6.7	7.08	707	267	1.1	0.6	0.3	0.0	0.3
P2	Bedrock well	121.9	6.4	Surface	6.0	7.87	412	358	7.5	1.3	7.8	0.0	0.4
P3	Bedrock well	56.4	15.2	Submersible	8.4	7.37	409	364	3.6	0.2	3.4	0.1	0.3
P4	Bedrock well	30.5	15.2	Submersible	6.6	7.41	663	193	49.7	44.1	1.0	1.6	1.7
P5	Bedrock well	97.5	15.2	Submersible	7.5	7.13	364	368	5.3	0.7	4.7	0.1	0.5
P6	Bedrock well	76.2	5.1	Surface	8.1	7.08	620	275	2.0	0.3	2.0	0.1	0.6
P7	Bedrock well	45.7	5.1	Surface	7.0	7.52	384	243	0.4	0.0	0.4	0.0	0.2
P8	Bedrock well	45.7	3.8	Surface	6.6	7.55	690	169	119.8	104.9	5.8	2.4	3.3
P9	Bedrock well	18.3			8.0	7.55	563	206	39.8	21.6	8.8	1.1	0.9
P10	Bedrock well	85.3	10.2		12.4	7.80	428	219	17.2	17.9	1.3	0.5	0.6
P11	Bedrock well	39.6	5.1	Surface	9.1	7.26	827	358	1.9	0.4	1.3	0.4	0.2
P12	Shallow well	4.6	91.4	Surface	9.4	7.66	308	339	0.6	0.1	0.6	0.1	0.3
P13	Bedrock well	21.6	25.4	Submersible	6.7	7.44	921	335	18.8	0.6	0.0	0.0	0.0
P14	Shallow well	5.2	91.4	Submersible	6.8	7.03	834	315	1.2	0.8	0.5	0.1	0.0
P15	Bedrock well	48.8	15.2	Submersible	7.0	7.41	579	406	0.4	0.1	0.4	0.1	0.1
P16	Bedrock well	91.4	15.2	Submersible	8.3	7.45	501	117	3.3	1.9	0.2	0.1	0.1
P17	Bedrock well	58.5	15.2	Submersible	6.9	7.63	679	211	263.4	233.4	27.5	10.8	6.1
P18	Bedrock well	103.6	15.2	Submersible	6.4	7.43	577	168	35.8	38.2	3.2	0.6	0.7
P19	Shallow well	7.3	5.1	Surface	6.9	7.45	558	248	0.5	0.3	0.2	0.0	0.2
P20	Bedrock well	86.9	20.3	Submersible	7.2	7.43	402	414	12.8	0.3	8.0	0.3	0.2

Well ID	Major elements concentrations (mg/l)											Minor and trace elements concentrations (µg/l)													
	HCO_3	SO_4	Cl	NO_3	PO_4	F	Si	Ca	Mg	Na	K	Al	B	Ba	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Sr	Zn
P1	668	26.8	<0.7	<0.7	<0.9	<0.2	12.0	108.0	52.5	15.9	1.8	2.8	11	28	0.5	<0.5	<1.1	328	727	1.7	1.2	0.5	<0.4	355	<3.2
P2	406	19.0	1.9	7.8	<0.9	<0.2	8.7	56.6	36.1	6.2	0.4	3.1	19	7	<0.1	1.1	<1.1	7	9	0.5	1.7	0.5	0.5	589	<3.2
P3	376	9.6	11.2	14.0	<0.9	<0.2	7.8	84.8	12.2	8.9	1.5	2.5	35	19	0.6	<0.5	24.2	3	91	0.5	1.1	1.0	0.4	231	<3.2
P4	613	14.5	10.3	<0.7	<0.9	<0.2	14.5	101.0	45.6	16.9	2.9	1.1	15	249	1.0	<0.5	<1.1	1087	114	1.0	0.9	4.6	<0.4	414	<3.2
P5	339	7.5	0.7	<0.7	<0.9	<0.2	9.6	68.2	15.6	8.4	0.7	3.8	58	6	0.1	<0.5	3.8	4	17	0.3	<0.7	0.4	<0.4	155	<3.2
P6	567	6.5	2.4	<0.7	<0.9	<0.2	15.0	102.0	35.1	9.9	2.2	2.0	8	35	0.2	<0.5	6.1	126	93	0.4	1.0	0.5	<0.4	236	4.4
P7	347	12.7	0.8	<0.7	<0.9	<0.2	11.4	62.8	18.2	5.8	1.1	1.3	22	11	0.1	<0.5	<1.1	16	448	0.3	<0.7	4.8	<0.4	117	5.8
P8	500	42.2	3.5	<0.7	<0.9	<0.2	15.1	116.0	27.4	23.9	1.3	1.9	464	45	0.1	<0.5	<1.1	799	164	1.0	<0.7	12.7	<0.4	731	<3.2
P9	495	14.1	1.2	<0.7	<0.9	<0.2	13.0	94.8	33.5	16.4	1.9	2.6	78	163	0.2	<0.5	<1.1	278	185	1.3	<0.7	<0.3	<0.4	401	<3.2
P10	369	10.6	4.9	<0.7	<0.9	<0.2	12.1	73.9	22.7	26.8	1.2	5.2	239	13	0.2	<0.5	<1.1	152	67	0.7	<0.7	<0.3	<0.4	306	<3.2
P11	571	22.1	52.9	1.6	<0.9	<0.2	12.1	135.0	55.7	11.8	1.1	2.2	7	32	0.1	<0.5	8.4	6	3	<0.1	4.4	<0.3	<0.4	234	<3.2
P12	290	11.7	0.5	1.1	<0.9	<0.2	13.2	55.2	16.5	4.2	1.2	5.9	7	8	<0.1	0.6	<1.1	<1.5	<0.4	0.5	<0.7	<0.3	<0.4	56	<3.2
P13	454	14.6	129.8	1.9	<0.9	<0.2	9.5	141.0	35.2	45.1	1.9	1.4	48	17	<0.1	<0.5	2.6	<1.5	5	0.2	1.1	<0.3	0.5	267	<3.2
P14	665	12.6	11.8	<0.7	<0.9	<0.2	14.2	159.0	53.4	19.0	3.1	1.5	6	36	0.2	<0.5	<1.1	252	99	0.5	<0.7	1.6	<0.4	317	3.3
P15	590	18.6	1.0	<0.7	<0.9	<0.2	10.2	91.6	53.7	8.9	1.2	4.0	5	68	0.1	<0.5	4.6	6	4	1.4	<0.7	1.5	<0.4	146	<3.2
P16	471	19.1	14.5	<0.7	<0.9	<0.2	12.0	72.3	36.2	24.3	1.4	2.3	33	146	0.1	<0.5	<1.1	140	164	0.3	<0.7	<0.3	<0.4	528	<3.2
P17	634	23.6	0.7	<0.7	<0.9	<0.2	10.1	56.1	85.1	18.8	0.7	1.9	11	101	0.4	<0.5	<1.1	102	11	0.2	1.0	<0.3	<0.4	465	<3.2
P18	558	7.3	<0.7	<0.7	<0.9	<0.2	13.5	91.6	41.5	16.2	1.6	1.4	31	3	1.4	<0.5	<1.1	54	101	0.4	<0.7	<0.3	<0.4	328	<3.2
P19	519	11.0	<0.7	<0.7	<0.9	<0.2	10.4	103.0	32.7	11.1	2.9	3.3	4	23	0.1	<0.5	<1.1	21	17	0.9	1.5	<0.3	<0.4	105	<3.2
P20	366	9.9	3.5	2.2	<0.9	<0.2	9.6	91.4	14.1	7.5	1.0	2.1	13	3	0.1	<0.5	6.5	<1.5	5	0.1	<0.7	<0.3	<0.4	110	<3.2

Well ID	Well characteristics				Field parameters				Arsenic species concentrations (µg/l)				
	Type	Depth (m)	⊘ (cm)	Pump type	T (°C)	pH	SC (µS/cm)	Eh (mV)	Total As	As(III)	As(V)	MMA(V)	DMA(V)
P21	Bedrock well			Surface	9.0	7.36	423	277	0.2	0.4	0.2	0.1	0.2
P22	Bedrock well	30.8	15.2	Submersible	7.7	7.33	701	192	8.8	4.8	1.5	0.3	0.3
P23	Bedrock well	54.9	10.2	Surface	7.4	7.39	495	177	86.4	79.3	11.3	1.4	1.4
P24	Bedrock well	99.1	7.6	Surface	6.7	7.29	531	196	10.3	8.7	0.6	0.1	0.2
P25	Bedrock well	68.8	15.2	Submersible	10.5	7.77	391	106	43.6	34.1	3.9	0.8	1.0
P26	Bedrock well	82.3	5.7	Surface	6.8	7.48	525	137	21.1	28.7	1.1	0.3	0.4
P27	Bedrock well	91.4	4.4	Surface	9.3	7.74	171	361	0.7	0.3	0.4	0.1	0.1
P28	Bedrock well				6.9	7.66	412	130	1.0	0.7	0.1	0.1	0.1
P29	Shallow well	3.7	1.2	Surface	10.2	7.20	472	362	0.2	0.0	0.1	0.0	0.1
P30	Bedrock well	50.3	15.2	Submersible	7.4	7.40	502	134	49.4	44.4	1.5	0.8	1.2
P31	Bedrock well	22.9	5.1	Surface	7.9	7.46	569	122	23.5	24.3	1.4	0.7	0.7
P32	Bedrock well	83.8	15.2	Submersible	7.4	6.42	287	450	0.1	0.0	0.2	0.1	0.1
P33	Shallow well	13.7	5.1	Surface	8.6	7.51	501	185	3.2	3.2	0.2	0.0	0.3
P34	Bedrock well	64	15.2	Submersible	7.0	7.67	368	116	50.8	50.1	2.8	0.9	1.5
P35	Bedrock well	99.1	15.2	Submersible	7.4	7.45	473	252	326.4	2.4	246.8	0.6	3.4
P36	Bedrock well	90	5.1	Surface	7.2	6.93	928	392	0.6	0.0	0.7	0.1	0.2
P37	Bedrock well	18.3	15.2	Surface	7.2	7.19	601	152	4.1	3.6	1.3	0.1	0.5
P38	Shallow well	12.2	10.2	Surface	7.0	7.41	543	139	2.6	3.3	0.3	0.0	0.1
P39	Shallow well	8.8	15.2	Submersible	7.0	7.38	602	398	0.2	0.1	0.4	0.0	0.2
P40	Bedrock well	22.9	5.1	Surface	8.4	7.46	578	182	72.9	54.8	14.0	1.5	1.8

Well ID	Major elements concentrations (mg/l)											Minor and trace elements concentrations (µg/l)														
	HCO_3	SO_4	Cl	NO_3	PO_4	F	Si	Ca	Mg	Na	K	Al	B	Ba	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Sr	Zn
P21	305	10.0	33.7	<0.7	<0.9	<0.2	8.2	62.6	23.1	14.8	0.5	1.0	<1.4	3	<0.1	<0.5	<1.1	11	<0.4	<0.1	1.4	<0.3	<0.4	90	<3.2
P22	549	13.6	23.8	<0.7	<0.9	<0.2	14.1	117.0	46.1	17.4	2.8	<1	4	50	0.1	<0.5	<1.1	359	66	0.4	<0.7	<0.3	<0.4	211	<3.2
P23	549	6.2	<0.7	<0.7	<0.9	<0.2	14.1	100.0	38.9	19.0	2.6	<1	23	33	1.0	<0.5	<1.1	388	316	0.6	<0.7	<0.3	<0.4	238	12.6
P24	571	9.7	<0.7	<0.7	<0.9	<0.2	12.5	114.0	43.1	15.8	2.8	1.7	13	10	0.9	<0.5	<1.1	255	377	0.3	<0.7	<0.3	<0.4	216	<3.2
P25	349	4.8	<0.7	<0.7	<0.9	<0.2	6.2	75.6	24.2	13.8	2.4	1.3	10	22	0.7	<0.5	<1.1	1464	256	3.5	<0.7	<0.3	<0.4	269	<3.2
P26	539	15.5	10.6	0.9	<0.9	<0.2	12.6	112.0	41.0	18.3	3.2	1.5	17	24	0.4	<0.5	<1.1	723	59	1.0	<0.7	<0.3	<0.4	161	<3.2
P27	217	7.9	<0.7	<0.7	<0.9	<0.2	8.4	48.6	6.8	2.7	0.4	1.3	8	2	<0.1	<0.5	3.3	3	<0.4	<0.1	<0.7	<0.3	<0.4	38	<3.2
P28	377	6.7	<0.7	<0.7	<0.9	<0.2	12.5	75.2	25.7	12.6	1.3	3.7	24	41	0.5	<0.5	<1.1	134	652	0.9	<0.7	<0.3	<0.4	213	<3.2
P29	490	4.5	<0.7	<0.7	<0.9	<0.2	11.9	92.5	30.9	7.8	1.3	3.9	5	13	<0.1	1.1	31.4	11	4	<0.1	0.8	<0.3	<0.4	126	<3.2
P30	446	18.7	9.5	<0.7	<0.9	<0.2	10.3	80.2	37.7	23.5	1.7	3.7	32	324	2.3	<0.5	<1.1	1080	304	2.0	<0.7	<0.3	<0.4	1055	9.3
P31	551	11.2	<0.7	<0.7	<0.9	<0.2	14.4	91.7	44.7	19.2	2.3	3.3	19	261	0.5	<0.5	<1.1	1547	200	0.9	<0.7	<0.3	<0.4	1430	<3.2
P32	207	9.2	33.0	<0.7	<0.9	<0.2	11.2	51.6	10.2	10.5	0.9	5.2	2	29	0.4	<0.5	30.3	11	8	<0.1	3.9	0.4	<0.4	270	5.0
P33	461	14.8	1.0	<0.7	<0.9	<0.2	11.6	93.2	32.1	10.5	2.7	2.9	4	36	<0.1	<0.5	<1.1	261	74	1.6	<0.7	<0.3	<0.4	179	6.0
P34	388	11.3	0.8	<0.7	<0.9	<0.2	12.4	64.0	20.5	16.8	1.3	2.7	194	5	0.1	<0.5	<1.1	569	230	0.7	<0.7	<0.3	<0.4	227	<3.2
P35	445	9.8	3.3	1.5	<0.9	<0.2	9.7	79.0	29.3	25.0	2.0	2.8	132	7	1.1	<0.5	<1.1	29	137	1.8	<0.7	<0.3	<0.4	509	<3.2
P36	732	19.1	44.0	6.9	<0.9	<0.2	13.3	156.0	74.7	27.3	3.8	2.3	5	32	<0.1	<0.5	3.8	<1.5	7	0.1	1.5	0.4	<0.4	311	3.2
P37	532	10.6	1.2	<0.7	<0.9	<0.2	17.3	109.0	41.3	11.6	2.4	2.3	3	52	0.2	<0.5	<1.1	1976	172	0.1	0.8	<0.3	<0.4	181	<3.2
P38	497	11.0	<0.7	<0.7	<0.9	<0.2	16.2	96.6	37.8	15.7	3.0	2.6	5	42	0.1	<0.5	<1.1	855	124	<0.1	<0.7	<0.3	<0.4	268	<3.2
P39	530	8.1	3.3	<0.7	<0.9	<0.2	12.8	111.0	38.9	14.4	2.7	2.3	3	22	<0.1	1.6	2.6	<1.5	<0.4	0.9	1.5	<0.3	<0.4	150	<3.2
P40	512	8.7	4.0	<0.7	<0.9	<0.2	13.2	107.0	37.1	18.9	2.4	1.7	22	21	2.2	<0.5	<1.1	508	381	0.3	<0.7	<0.3	<0.4	269	10.4

Well ID	Well characteristics				Field parameters				Arsenic species concentrations (µg/l)				
	Type	Depth (m)	⊘ (cm)	Pump type	T (°C)	pH	SC (µS/cm)	Eh (mV)	Total As	As(III)	As(V)	MMA(V)	DMA(V)
P41	Bedrock well	61	15.2	Submersible	7.3	7.83	512	131	5.9	4.6	2.6	0.1	0.3
P42	Bedrock well	50.3	15.2	Submersible	7.5	7.90	420	116	113.1	92.1	5.8	2.8	3.2
P43	Bedrock well		5.1	Submersible	6.8	7.64	334	365	0.1	0.1	0.0	0.0	0.1
P44	Bedrock well	77.7	15.2	Submersible	6.8	7.33	747	379	15.9	0.3	19.0	1.1	0.3
P45	Shallow well	30.5	15.2	Submersible	6.8	7.55	555	380	0.3	0.0	0.2	0.2	0.2
P46	Bedrock well		15.2	Submersible	7.1	7.48	643	136	10.2	10.6	1.7	0.2	0.2
P47	Shallow well	9.1	91.4	Surface	11.8	7.29	704	168	0.2	0.1	0.0	0.0	0.0
P48	Bedrock well	97.5	15.2	Submersible	6.8	6.78	426	413	0.1	0.1	0.4	0.0	0.3
P49	Shallow well	15.2		Surface	6.6	7.51	592	339	4.1	0.1	2.3	0.1	0.0
P50	Bedrock well	28.2	15.2	Submersible	6.5	7.72	495	113	2.1	2.2	0.4	0.0	0.1
P51	Bedrock well	73.2	15.2	Submersible	6.4	7.66	458	166	8.7	9.6	0.4	0.5	0.2
P52	Bedrock well	91.4	15.2	Submersible	7.2	7.97	320	106	86.9	91.4	4.4	1.3	1.7
P53	Bedrock well	79.3	15.2	Submersible	8.0	8.15	420	79	140.9	111.1	5.3	4.8	3.1
P54	Bedrock well		15.2	Submersible	6.9	7.52	655	111	238.5	183.5	4.8	7.8	5.1
P55	Bedrock well	101.5	15.2	Submersible	6.8	7.44	302	342	10.2	0.3	8.5	0.1	0.3
P56	Bedrock well	91.4	15.2	Submersible	7.8	7.31	668	420	2.8	0.7	2.5	7.6	0.3
P57	Bedrock well	64	15.2	Submersible	7.2	7.56	822	115	83.1	86.6	3.3	2.4	1.8
P58	Bedrock well		25.2	Submersible	6.8	7.59	526	120	118.0	120.6	2.4	2.9	3.1
P59	Bedrock well	67.1	5.1	Submersible	13.2	7.59	454	113	6.8	5.9	0.3	0.1	0.4

Well ID	Major elements concentrations (mg/l)											Minor and trace elements concentrations (µg/l)													
	HCO_3	SO_4	Cl	NO_3	PO_4	F	Si	Ca	Mg	Na	K	Al	B	Ba	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Se	Sr	Zn
P41	473	11.8	2.5	0.9	<0.9	<0.2	14.1	86.8	38.9	21.0	2.1	2.4	16	304	1.0	<0.5	<1.1	560	149	1.1	<0.7	<0.3	<0.4	773	<3.2
P42	341	11.9	23.6	<0.7	<0.9	<0.2	12.9	72.2	24.7	25.5	1.9	2.2	142	48	0.2	<0.5	<1.1	282	178	0.6	<0.7	<0.3	<0.4	218	<3.2
P43	312	8.1	5.8	0.9	2.9	<0.2	10.8	67.4	18.8	6.8	1.2	2.1	6	2	<0.1	<0.5	2.1	3	5	0.4	<0.7	<0.3	<0.4	106	<3.2
P44	541	15.4	55.9	1.4	1.4	<0.2	13.6	127.0	59.7	17.1	2.0	1.8	4	22	0.9	<0.5	11.6	5	1	<0.1	15.2	0.3	<0.4	321	4.2
P45	455	18.4	12.8	12.7	<0.9	<0.2	6.3	67.9	24.2	10.0	1.5	1.4	1	15	<0.1	0.8	4.7	<1.5	7	0.5	<0.7	<0.3	<0.4	133	<3.2
P46	572	11.0	<0.7	<0.7	<0.9	<0.2	12.9	104.0	48.0	21.2	1.7	<1	9	149	2.2	<0.5	<1.1	695	733	0.1	1.5	<0.3	<0.4	500	<3.2
P47	486	10.1	55.4	<0.7	<0.9	<0.2	14.0	126.0	39.5	13.8	1.9	1.2	<1.4	32	0.8	<0.5	<1.1	1639	45	0.3	1.7	<0.3	<0.4	197	10.1
P48	361	3.9	10.7	1.7	<0.9	<0.2	7.6	95.1	7.9	13.4	1.6	11.0	<1.4	16	11.9	0.6	19.1	9	3356	<0.1	15.7	<0.3	<0.4	112	<3.2
P49	517	20.6	<0.7	<0.7	<0.9	<0.2	11.4	94.8	51.0	8.1	1.1	1.3	<1.4	25	<0.1	<0.5	1.4	2	<0.4	<0.1	5.9	<0.3	<0.4	146	<3.2
P50	438	13.3	2.1	<0.7	<0.9	<0.2	10.1	93.5	30.5	10.2	2.6	2.2	1	31	<0.1	<0.5	<1.1	489	40	1.0	<0.7	<0.3	<0.4	140	<3.2
P51	418	14.3	<0.7	<0.7	35.1	<0.2	10.6	69.8	33.9	23.3	0.7	<1	47	58	0.1	<0.5	<1.1	195	58	<0.1	<0.7	<0.3	<0.4	1950	<3.2
P52	304	10.0	3.4	<0.7	<0.9	<0.2	8.2	45.8	20.9	23.5	1.0	<1	200	9	<0.1	<0.5	<1.1	176	30	0.2	<0.7	<0.3	<0.4	254	<3.2
P53	327	17.0	20.9	<0.7	4.4	<0.2	9.5	49.4	21.8	43.4	1.6	2.3	122	123	<0.1	<0.5	<1.1	204	37	1.1	<0.7	<0.3	<0.4	536	<3.2
P54	466	39.6	6.3	<0.7	<0.9	0.4	16.3	102.0	33.9	21.8	1.6	1.7	153	26	0.1	<0.5	<1.1	743	213	1.1	<0.7	<0.3	<0.4	398	<3.2
P55	254	11.4	1.2	<0.7	<0.9	0.4	6.4	58.5	6.0	10.4	0.7	6.5	40	7	0.1	<0.5	6.5	6	0	0.1	1.4	<0.3	<0.4	96	<3.2
P56	367	16.3	<0.7	<0.7	<0.9	0.4	10.9	84.8	29.7	37.6	0.7	1.6	11	11	<0.1	<0.5	15.2	3	13	<0.1	<0.7	<0.3	<0.4	364	<3.2
P57	632	27.3	7.0	<0.7	<0.9	0.4	11.9	64.0	90.7	20.0	1.0	1.8	43	123	1.0	<0.5	<1.1	117	72	<0.1	1.2	<0.3	<0.4	3175	<3.2
P58	378	84.4	10.9	<0.7	<0.9	0.4	11.2	90.0	27.6	21.7	1.3	3.8	72	<0.4	<0.1	<0.5	<1.1	935	232	1.9	<0.7	<0.3	<0.4	652	<3.2
P59	446	22.0	1.8	<0.7	<0.9	0.4	7.4	72.6	32.4	22.5	1.9	<1	<1.4	65	<0.1	<0.5	<1.1	2620	202	1.1	<0.7	<0.3	<0.4	403	<3.2

References

Appelo, C. A. J., Postma, D., 2005. Geochemistry, groundwater and pollution, 2nd edition. A.A. Balkema Publishers, Amsterdam (Netherlands).

Ayotte, J. D., Montgomery, D. L., Flanagan, S. M., Robinson, K. W., 2003. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environmental Science & Technology 37, 2075–2083.

Bednar, A., Garbarino, J., Burkhardt, M., Ranville, J., Wildeman, T., 2004. Field and laboratory arsenic speciation methods and their application to natural-water analysis. Water Research 38 (2), 355–364.

Bottomley, D., 1984. Origins of some arseniferous groundwaters in Nova Scotia and New Brunswick, Canada. Journal of Hydrology 69, 223–257.

Bottomley, D., Chan, L., Katz, A., Starinsky, A., Clark, I., 2003. Lithium isotope geochemistry and origin of Canadian Shield brines. Ground Water 41 (6), 847–856.

Boyle, D. R., Turner, R. J. W., Hall, G. E. M., 1998. Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. Environmental Geochemistry and Health 20, 199–212.

Campbell, K. M., Nordstrom, D. K., 2014. Arsenic speciation and sorption in natural environments. Reviews in Mineralogy and Geochemistry 79 (1), 185–216.

CEAEQ, 2014. Détermination des métaux : méthode par spectrométrie de masse à source ionisante au plasma d'argon. MA. 200 - Mét 1.2. Centre d'expertise en analyse environnementale du Québec. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.ceaeq.gouv.qc.ca/methodes/pdf/MA200Met12.pdf.

Christodoulidou, M., Charalambous, C., Aletrari, M., Kanari, P. N., Petronda, A., Ward, N., 2012. Arsenic concentrations in groundwaters of Cyprus. Journal of hydrology 468, 94–100.

Cloutier, V., Rosa, E., Nadeau, S., Dallaire, P.-L., Blanchette, D., Roy, M., 2015. Projet d'acquisition de connaissances sur les eaux souterraines de l'Abitibi-Témiscamingue (partie 2). Rapport final déposé au Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques dans le cadre du Programme d'acquisition de connaissances sur les eaux souterraines du Québec. Rapport de recherche P002. R3.

Cloutier, V., Veillette, J., Roy, M., Gagnon, F., Bois, D., 2007. Regional hydrogeochemistry of groundwater in fractured Canadian Shield rock and glaciofluvial formations in Abitibi, Quebec. In: Proceedings, 60th Canadian Geotechnical Conference and 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa (Canada).

Dixit, S., Hering, J. G., 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals: implications for arsenic mobility. Environmental Science & Technology 37 (18), 4182–4189.

Douglas, M., Clark, I., Raven, K., Bottomley, D., 2000. Groundwater mixing dynamics at a Canadian Shield mine. Journal of Hydrology 235 (1), 88–103.

Farnfield, H. R., Marcilla, A. L., Ward, N. I., 2012. Arsenic speciation and trace element analysis of the volcanic río Agrio and the geothermal waters of Copahue, Argentina. Science of the Total Environment 433, 371–378.

Flanagan, S. V., Marvinney, R. G., Zheng, Y., 2015. Influences on domestic well water testing behavior in a Central Maine area with frequent groundwater arsenic occurrence. Science of the Total Environment 505, 1274–1281.

Gagnon, F., Lampron-Goulet, É., Normandin, L., Langlois, M.-F., 2016. Measurements of arsenic in the urine and nails of individuals exposed to low concentrations of arsenic in drinking water from private wells in a rural region of Quebec, Canada. Journal of Environmental Health 78 (6), 76–83.

Gascoyne, M., Kamineni, D., 1994. The hydrogeochemistry of fractured plutonic rocks in the Canadian Shield. Applied Hydrogeology 2 (2), 43–49.

Goutier, J., Lacroix, S., 1992. Géologie du secteur de la Faille de Porcupine-Destor dans les cantons de Destor et Duparquet. Ministère de l'Énergie et des Ressources: Québec, MB, 92–06.

Grantham, D. A., Jones, J. F., 1977. Arsenic contamination of water wells in Nova Scotia. Journal (American Water Works Association) 69 (12), 653–657.

Harte, P. T., Ayotte, J. D., Hoffman, A., Revesz, K. M., Belaval, M., Lamb, S., Boehlke, J. K., 2012. Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire, USA. Hydrogeology Journal 20, 1189–1201.

Kim, K., Kim, S.-H., Jeong, G. Y., Kim, R.-H., 2012. Relations of As concentrations among groundwater, soil, and bedrock in Chungnam, Korea: Implications for As mobilization in groundwater according to the As-hosting mineral change. Journal of Hazardous Materials 199, 25–35.

Lalonde, J.-P., Chouinard, N., Bergeron, R., 1981. Atlas géochimique des eaux souterraines, région de l'Abitibi. Ministère de l'Énergie et des Ressources, Direction générale de la recherche géologique et minérale, Service de géophysique-géochimie.

Lampron-Goulet, É., 2012. Surveillance biologique de l'exposition à l'arsenic inorganique et des perturbations endocriniennes associées dans une population s'approvisionnant en eau potable par des puits privés dans la région de l'Abitibi-Témiscamingue, au Québec. Master's thesis, Université de Sherbrooke.

Legault, M., Goutier, J., Beaudoin, G., M, A., 2005. Synthèse métallogénique de la Faille de Porcupine-Destor, Sous-province de l'Abitibi. Ministère des Ressources Naturelles et de la Faune, Québec.

Lipfert, G., Reeve, A. S., Sidle, W. C., Marvinney, R., 2006. Geochemical patterns of arsenic-enriched ground water in fractured, crystalline bedrock, Northport, Maine, USA. Applied Geochemistry 21, 528–545.

Lu, P., Zhu, C., 2011. Arsenic Eh–pH diagrams at 25 °C and 1 bar. Environmental Earth Sciences 62 (8), 1673–1683.

Maguffin, S. C., Kirk, M. F., Daigle, A. R., Hinkle, S. R., Jin, Q., 2015. Substantial contribution of biomethylation to aquifer arsenic cycling. Nature Geoscience 8 (4), 290–293.

MDDELCC, 2015. Portrait régional de l'eau - Abitibi-Témiscamingue. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.mddelcc.gouv.qc.ca/eau/regions/region08/08-abitibi

MDDELCC, 2016. Répertoire des dépôts de sols et de résidus industriels. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http://www.mddelcc.gouv.qc.ca/sol/residusind/resultats.asp.

MERN, 2016. Système d'information géominière (SIGEOM). Ministère de l'Énergie et des Ressources naturelles du Québec. sigeom.mines.gouv.qc.ca.

Montcoudiol, N., Molson, J., Lemieux, J.-M., 2015. Groundwater geochemistry of the Outaouais Region (Québec, Canada): a regional-scale study. Hydrogeology Journal 23 (2), 377–396.

Nadeau, S., Rosa, E., Cloutier, V., Daigneault, R.-A., Veillette, J., 2015. A GIS-based approach for supporting groundwater protection in eskers: Application to sand and gravel extraction activities in Abitibi-Témiscamingue, Quebec, Canada. Journal of Hydrology: Regional Studies 4, 535–549.

Nickson, R., McArthur, J., Ravenscroft, P., Burgess, W., Ahmed, K., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry 15 (4), 403–413.

O'Reilly, J., Watts, M., Shaw, R., Marcilla, A., Ward, N., 2010. Arsenic contamination of natural waters in San Juan and La Pampa, Argentina. Environmental Geochemistry and Health 32 (6), 491–515.

Parkhurst, D. L., Appelo, C., 1999. User's guide to PHREEQC (Version 2): A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Investigations Report 99-4259, Denver (USA).

Peters, S. C., Blum, J. D., 2003. The source and transport of arsenic in a bedrock aquifer, New Hampshire, USA. Applied Geochemistry 18, 1773–1787.

Poissant, L.-M., 1997. La contamination par l'arsenic des puits domestiques en Abitibi-Témiscamingue. Régie régionale de la santé et des services sociaux de l'Abitibi-Témiscamingue, Direction de la santé publique, Rouyn-Noranda (Canada).

Postma, D., Larsen, F., Thai, N. T., Trang, P. T. K., Jakobsen, R., Nhan, P. Q., Long, T. V., Viet, P. H., Murray, A. S., 2012. Groundwater arsenic concentrations in Vietnam controlled by sediment age. Nature Geoscience 5 (9), 656–661.

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic pollution: a global synthesis. Wiley-Blackwell, West Sussex (UK).

Richard, S. K., Chesnaux, R., Rouleau, A., Morin, R., Walter, J., Rafini, S., 2014. Field evidence of hydraulic connections between bedrock aquifers and overlying granular aquifers: examples from the Grenville Province of the Canadian Shield. Hydrogeology journal 22 (8), 1889–1904.

Ryan, P. C., Kim, J. J., Mango, H., Hattori, K., Thompson, A., 2013. Arsenic in a fractured slate aquifer system, New England, USA: Influence of bedrock geochemistry, groundwater flow paths, redox and ion exchange. Applied Geochemistry 39, 181–192.

Serpa, C., Batterson, M., Guzzwell, K., 2009. The influence of bedrock and mineral occurrences on arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. Current Research. Newfoundland and Labrador Department of Natural Resources Geological Survey, Report 09–1, 315–337.

Shapiro, A. M., 2002. Cautions and suggestions for geochemical sampling in fractured rock. Groundwater Monitoring & Remediation 22 (3), 151–164.

Sharma, V. K., Sohn, M., 2009. Aquatic arsenic: Toxicity, speciation, transformations, and remediation. Environment International 35, 743–759.

Sidle, W. C., Fischer, R. A., 2003. Detection of ^{3}H and ^{85}Kr in groundwater from arsenic-bearing crystalline bedrock of the Goose River basin, Maine. Environmental Geology 44, 781–789.

Smith, A. E., Lincoln, R. A., Paulu, C., Simones, T. L., Caldwell, K. L., Jones, R. L., Backer, L. C., 2016. Assessing arsenic exposure in households using bottled water or point-of-use treatment systems to mitigate well water contamination. Science of The Total Environment 544, 701–710.

Sorg, T. J., Chen, A. S., Wang, L., 2014. Arsenic species in drinking water wells in the USA with high arsenic concentrations. Water Research 48, 156 – 169.

Spayd, S. E., Robson, M. G., Buckley, B. T., 2015. Whole-house arsenic water treatment provided more effective arsenic exposure reduction than point-of-use water treatment at New Jersey homes with arsenic in well water. Science of the Total Environment 505, 1361–1369.

Thibaudeau, P., Veillette, J., 2005. Géologie des formations en surface et histoire glaciaire: Lac Chicobi, Québec. Commission géologique du Canada.

Watts, M., O'Reilly, J., Marcilla, A., Shaw, R., Ward, N., 2010. Field based speciation of arsenic in UK and Argentinean water samples. Environmental geochemistry and health 32 (6), 479–490.

WHO, 2011. Guidelines for drinking-water quality. Geneva: World Health Organization.

Yang, Q., Culbertson, C. W., Nielsen, M. G., Schalk, C. W., Johnson, C. D., Marvinney, R. G., Stute, M., Zheng, Y., 2015. Flow and sorption controls of groundwater arsenic in individual boreholes from bedrock aquifers in central Maine, USA. Science of The Total Environment 505, 1291–1307.

Zheng, Y., Ayotte, J. D., 2015. At the crossroads: Hazard assessment and reduction of health risks from arsenic in private well waters of the northeastern United States and Atlantic Canada. Science of The Total Environment 505, 1237–1247.

CHAPITRE 4

A REVIEW AND EVALUATION OF THE IMPACTS OF CLIMATE CHANGE ON GEOGENIC ARSENIC IN GROUNDWATER FROM FRACTURED BEDROCK AQUIFERS

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M. (2016). A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. Water, Air, & Soil Pollution, 227(9), 296.

Résumé

Les changements climatiques vont vraisemblablement affecter la qualité de l'eau souterraine en modifiant la recharge, les niveaux piézométriques, l'écoulement de l'eau souterraine ainsi que l'utilisation des sols. Dans les aquifères rocheux fracturés, la qualité de l'eau souterraine est une question sensible, en particulier dans les zones touchées par la contamination naturelle à l'arsenic. Comprendre comment les changements climatiques vont influencer la géochimie de l'arsenic présent naturellement dans l'eau souterraine est essentiel pour assurer une utilisation durable de la ressource, en particulier comme source d'eau potable. Cet article présente une revue des impacts potentiels des changements climatiques sur les concentrations en arsenic dans les aquifères rocheux et identifie les questions qui restent en suspens. Lors des étiages sévères et prolongés, la baisse des niveaux piézométriques devrait accroître l'oxydation des minéraux sulfurés riches en arsenic dans la zone non-saturée. En outre, les faibles écoulements d'eau souterraine pourraient augmenter la proportion d'eau chimiquement évoluée riche en arsenic et ainsi favoriser la mobilisation de l'arsenic par dissolution réductrice et désorption alcaline. En revanche, les épisodes de recharge extrêmes devraient diminuer les concentrations en arsenic en raison d'une plus grande dilution par une eau oxygénée au pH faible. Dans certains cas, la mobilisation de l'arsenic pourrait être indirectement provoquée par les changements climatiques via des changements dans l'utilisation des sols, en particulier ceux entraînant une augmentation des prélèvements d'eau et de la pollution. L'impact global des changements climatiques sur les concentrations en arsenic va vraissemblablement varier en fonction des propriétés des aquifères rocheux qui déterminent la sensibilité du système aquifère aux changements du climat. Jusqu'à présent, la manque de données sur la variabilité temporelle de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés constitue le principal obstacle à l'évaluation de l'évolution de la qualité de la ressource.

Mots-clés

Mobilisation de l'arsenic, Changements climatiques, Aquifères rocheux fracturés, Qualité de l'eau souterraine, Oxydation des sulfures, Variabilité temporelle.

Abstract

Climate change is expected to affect the groundwater quality by altering recharge, water table elevation, groundwater flow, and land use. In fractured bedrock aquifers, the quality of groundwater is a sensitive issue, particularly in areas affected by geogenic arsenic contamination. Understanding how climate change will affect the geochemistry of naturally occurring arsenic in groundwater is crucial to ensure sustainable use of this resource, particularly as a source of drinking water. This paper presents a review of the potential impacts of climate change on arsenic concentration in bedrock aquifers and identifies issues that remain unresolved. During intense and prolonged low flow, the decline in the water table is expected to increase the oxidation of arsenic-bearing sulfides in the unsaturated zone. In addition, reduced groundwater flow may increase the occurrence of geochemically evolved arsenic-rich groundwater and enhance arsenic mobilization by reductive dissolution and alkali desorption. In contrast, the occurrence of extreme recharge events is expected to further decrease arsenic concentrations because of the greater dilution by oxygenated, low-pH water. In some cases, arsenic mobilization could be indirectly induced by climate change through changes in land use, particularly those causing increased groundwater withdrawals and pollution. The overall impact of climate change on dissolved arsenic will vary greatly according to the bedrock aquifer properties that influence the sensitivity of the groundwater system to climate change. To date, the scarcity of data related to the temporal variability of arsenic in fractured bedrock groundwater is a major obstacle in evaluating the future evolution of the resource quality.

Keywords

Arsenic mobilization, Climate change, Fractured bedrock aquifers, Groundwater quality, Sulfide oxidation, Temporal variability.

4.1 Introduction

Groundwater is generally considered to be a high quality ubiquitous resource that supports the supply of drinking water for nearly half of the world's population (World Water Assessment Programme, 2009; Taylor et al., 2013). However, although groundwater is generally free from significant microbial contamination, its quality may be compromised by naturally occurring contaminants such as arsenic (Bretzler and Johnson, 2015). The occurrence of geogenic arsenic has emerged as a major concern for groundwater quality in many countries during the last two decades (Smedley and Kinniburgh, 2002; Ravenscroft et al., 2009). Arsenic exposure through drinking water is known to cause multiple adverse effects on human health including skin, lung, liver, bladder, and kidney cancers; diabetes; and cardiovascular, neurological, and reproductive alterations (Ravenscroft et al., 2009; Naujokas et al., 2013). It is estimated that more than 200 million people drink water exceeding the World Health Organization safety standard of 10 µg/l for arsenic worldwide (Naujokas et al., 2013). In terms of exposure, arsenic contamination is particularly problematic in densely populated alluvial basins in Asia. Elsewhere, arsenic contamination is mostly associated with a diversity of bedrock aquifers (Ravenscroft et al., 2009). Natural arsenic contamination is of great concern in fractured bedrock aquifers, which provide an important source of drinking water in many regions of the world (e.g. Smedley et al., 2007; Zheng and Ayotte, 2015). The use of groundwater is expected to increase in the coming decades owing to the increased water demand and the predicted decline in surface water availability under future climate conditions (Kundzewicz and Doell, 2009; Green et al., 2011). According to the Intergovernmental Panel on Climate Change (Intergovernmental Panel on Climate Change, 2014), the warming of the global system caused by an increase in the atmospheric concentration of greenhouse gases is unequivocal and is likely to continue, at least in the near future. Changes in major climatic variables such as temperature and precipitation will affect the hydrological cycle with changes in recharge, groundwater levels, flow processes, and storage (Jyrkama and Sykes, 2007; Green et al., 2011; Stuart et al., 2011). The increase in surface temperature may reach 0.3 to 4.8°C by the end of the twenty-first century, and the contrast in precipitation between wet and dry regions, as well as that between wet and dry seasons, will likely increase over the same period (Intergovernmental Panel on Climate Change, 2014). In addition, extreme drought periods may be interspersed with more frequent heavy precipitation events, increasing the risk of flooding (Green et al., 2011; Taylor et al., 2013). As a result, the mean annual groundwater recharge may decrease in arid, semi-arid, and Mediterranean regions (Serrat-Capdevila et al., 2007; Carneiro et al., 2010) and increase in wet and cold regions (Jyrkama and Sykes, 2007; Okkonen et al., 2010). However, there is no consensus regarding quantitative changes in the mean annual recharge in mid-latitude regions (Jackson et al., 2011; Dams et al., 2012). In most regions, recharge and groundwater levels may increase during winter months and decrease during the rest of the year, particularly during summer months. Groundwater temperature may rise by several degrees, and seasonal thermal variations may increase within aquifers (Taylor and Stefan, 2009; Kurylyk et al., 2013). Although an increasing number of publications investigating the effects of climate change on groundwater appeared in recent years, most of these studies focus on processes that affect groundwater quantity such as recharge and discharge. In contrast, the impacts of climate change on groundwater quality remain poorly documented even though the water quality may be a limiting factor for some intended uses such as drinking or irrigation water supply (Green et al., 2011; Gurdak et al., 2012). This issue is of significant importance in the case of geogenic contaminants such as arsenic that are likely to threaten drinking water resources. Although many groundwater studies have focused on arsenic contamination and others have reported the impacts of climate change on groundwater resources (Niu et al., 2014), the link between climate change and arsenic concentration in groundwater remains sparsely documented and not fully understood. This paper provides an overview of the potential impacts of climate change on the geochemistry of naturally occurring arsenic in groundwater from fractured bedrock aquifers. The specific objectives of this study include (1) a review of current knowledge on geogenic arsenic contamination in fractured bedrock aquifers, (2) a comprehensive assessment of the potential changes in the mechanisms controlling the mobilization of naturally occurring arsenic in bedrock groundwater under climate change, and (3) the proposal of data acquisition strategies to improve this knowledge.

4.2 Review of arsenic occurrences in fractured bedrock aquifers

The natural occurrence of arsenic in groundwater has been intensively studied during the last two decades (Ravenscroft et al., 2009; Niu et al., 2014). However, most studies have focused on unconsolidated sedimentary aquifers set in alluvial plains and deltas, particularly in Asia. Comparatively few studies exist regarding arsenic occurrence in fractured bedrock aquifers (Smedley et al., 2007; O'Shea et al., 2015). However, such research has increased substantially during the last few years, as shown in table 4.1. In the present study, we consider fractured bedrock as a geological formation consisting of fractured metamorphic and igneous rocks (table 4.1). As reported in previous research (Yang et al., 2012), although each region is characterized by distinct bedrock formations, similarities exist in their tectonic settings and geologic history. Fractured bedrocks frequently consist of metavolcanic and metasedimentary rocks intruded by granitoids that are occasionally overlain by younger deposits such as glacial sediments. Natural arsenic concentration in groundwater is driven by three major variables: geogenic sources, arsenic mobility, and groundwater flow (Smedley and Kinniburgh, 2002).

Table 4.1. Selected studies documenting arsenic concentrations in fractured bedrock aquifers.

Region Country/ Province/ State	**References**
Northeastern United States and Eastern Canada	
Maine	Sidle et al. (2001); Sidle (2002); Sidle and Fischer (2003); Ayotte et al. (2003); Lipfert et al. (2006); Lipfert et al. (2007); Foley and Ayuso (2008); Yang et al. (2009); Yang et al. (2012); Yang et al. (2015); O'Shea et al. (2015)
New Hampshire	Peters and Blum (2003); Ayotte et al. (2003); Harte et al. (2012)
Vermont	Ryan et al. (2011); Ryan et al. (2013); Ryan et al. (2015); Mango and Ryan (2015)
New Brunswick	Bottomley (1984); Klassen et al. (2009)
Newfoundland	Serpa et al. (2009)
Nova Scotia	Grantham and Jones (1977); Bottomley (1984); Meranger et al. (1984)
Northwestern United States and Western Canada	
Alaska	Verplanck et al. (2008)
Washington	Frost et al. (1993)
British Columbia	Boyle et al. (1998)
South America	
Brazil (Southeastern)	Borba et al. (2003)
Eastern Asia	
South-Korea	Ahn (2012); Kim et al. (2012); Ahn and Cho (2013)
Southern Asia	
India (Central)	Sahoo and Pandalai (2000); Acharyya et al. (2005); Pandey et al. (2006); Shukla et al. (2010)
West Africa	
Burkina Faso	Smedley et al. (2007)
Ghana	Smedley (1996); Bhattacharya et al. (2012)
Scandinavian countries	
Finland	Loukola-Ruskeeniemi et al. (1999); Ruskeeniemi et al. (2011); Parviainen et al. (2015)
Sweden	Bhattacharya et al. (2010)
Norway	Frengstad et al. (2000)
Europe	
France	Pili et al. (2013); Tisserand et al. (2014)
Italy	Reyes et al. (2015)
Greece	Zkeri et al. (2015)

These aspects are discussed separately below.

4.2.1 Sources, sinks, and fate of arsenic in groundwater

4.2.1.1 Primary mineral sources

Arsenic concentrations in groundwater are primarily controlled by release from primary mineral sources. The amount of arsenic released depends mainly on the occurrence and abundance of arsenic-bearing minerals exposed to weathering and on their properties such as arsenic content and stability. In fractured bedrock aquifers, arsenic is initially released into groundwater owing to the oxidation of arsenic-bearing sulfides and sulfosalts. Sulfide minerals can be oxidized in the presence of water by O_2, Fe^{3+}, NO_3^- or by mineral catalysts such as MnO_2 (Ravenscroft et al., 2009; Nordstrom et al., 2015). For example, the reaction of arsenopyrite oxidation by O_2 can be expressed as follows:

$$4FeAsS + 11O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4H_3AsO_3 + 4SO_4^{2-} \quad (1)$$

The oxidation rates of sulfides depend strongly on the crystal chemistry of minerals (Foley and Ayuso, 2008; Chopard et al., 2015), the oxidant concentration, the presence of microbial catalysis, and, to a lesser degree, pH and temperature (Appelo and Postma, 2005; Asta et al., 2010; Nordstrom et al., 2015). Of the more than 300 arsenic minerals occurring in nature, approximately 20 % are sulfides and sulfosalts (Drahota and Filippi, 2009). All of these arsenic sulfide minerals can potentially act as sources of arsenic in groundwater. The most commonly cited minerals are arsenopyrite (FeAsS) (e.g. Peters and Blum, 2003; Kim et al., 2012) and arsenian pyrite ($Fe(S,As)_2$) (e.g. Ryan et al., 2013; O'Shea et al., 2015), which are the most abundant arsenic-bearing sulfides in the natural environment. Nevertheless, as reported in a previous study of a fractured metasedimentary aquifer in coastal Maine (Foley and Ayuso, 2008), the oxidation of these abundant sulfides cannot be separated geochemically from the oxidation of other strongly intermixed Fe-sulfide, Co-arsenide, or Ni-arsenide minerals. The contribution of less common arsenic-rich sulfides such as orpiment (As_2S_3), realgar (AsS), löllingite ($FeAs_2$), niccolite (NiAs), cobaltite (CoAsS), gersdorffite (NiAsS) or enargite (Cu_3AsS_4), may be significant, owing, in particular, to the overlapping instabilities of certain minerals (Foley and Ayuso, 2008). It is worth noting that arsenic can also occur in varying concentrations within other common sulfides such as chalcopyrite, galena, and marcasite (Smedley and Kinniburgh, 2002). Mineral properties including arsenic content and stability also affect the release of arsenic into groundwater. Minerals with high arsenic contents are generally identified as the main sources of arsenic in groundwater (e.g. Foley and Ayuso, 2008; Kim et al., 2012). However, the stability of arsenic-bearing minerals is rarely discussed even though it may play a major role in arsenic release (Foley and Ayuso, 2008).

The arsenic content in bedrock varies widely, which means that arsenic minerals are distributed heterogeneously (Kim et al., 2012; O'Shea et al., 2015). Localized enrichments have been reported in hydrothermally altered zones surrounding granitoid intrusions (Peters and Blum, 2003; Lipfert et al., 2006; Shukla et al., 2010) and within mineralized shear zones (Boyle et al., 1998; Verplanck et al., 2008). Moreover, arsenic minerals may be disseminated in low-grade metasedimentary rocks formed under reducing conditions (O'Shea et al., 2015; Ryan et al., 2013).

4.2.1.2 Arsenic mobility and secondary sources

Arsenic concentrations depend largely on the formation and behavior of secondary As-bearing minerals, which determine the mobility of arsenic in groundwater (figure 4.1). Secondary arsenic minerals typically consist of simple or more complex phases with arsenic, oxygen, and various metals (Drahota and Filippi, 2009). Arsenic can be sequestered in secondary minerals by sorption or by incorporation in crystal structures (Foley and Ayuso, 2008). In bedrock groundwater, dissolved metals occur as products of the alteration of sulfide minerals (Equation 1) and common minerals such as silicates and carbonates. Hence, in the presence of oxygen, secondary As minerals such as Fe-arsenates and Fe-hydroxides (Equation 2) can precipitate and remove arsenic from water.

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ \text{ (2)}$$

For this reason, the mobility of arsenic is likely to be limited under the oxidizing conditions that allow sulfide oxidation. Sorption by Fe-oxyhydroxides and, to a lesser extent, by Mn-oxyhydroxides is generally considered as the most important mechanism responsible for arsenic immobilization in fractured bedrock aquifers (e.g. Lipfert et al., 2006; Foley and Ayuso, 2008; Yang et al., 2015). Particulate Fe is believed to occur both on fracture surfaces and in colloidal form in groundwater (Yang et al., 2015). Clay minerals can also be involved in arsenic sorption, particularly in altered zones owing to their abundance (Smedley et al., 2007). Moreover, several secondary arsenic minerals that incorporate arsenic by covalent bonding have been identified in natural conditions in bedrock aquifers. This is the case of scorodite ($FeAsO_4{\cdot}2H_2O$) (Peters and Blum, 2003; Verplanck et al., 2008) claudetite (As_2O_3), orpiment (As_2S_3), secondary arsenopyrite and jarosite-natrojarosite ($K,NaFe_3(SO_4,AsO_4)_2(OH)_6$) (Foley and Ayuso, 2008).

However, the formation and behavior of secondary minerals are greatly affected by geochemical conditions, which may be implicated in arsenic (re)mobilization (figure 4.1). Oxides are formed in environments with steady sources of oxygen and conversely dissolve in anaerobic environments (Ravenscroft et al., 2009). Hence, the occurrence of reducing conditions in aquifers tends to inhibit the formation of secondary oxyhydroxides and promote their dissolution, leading to high arsenic

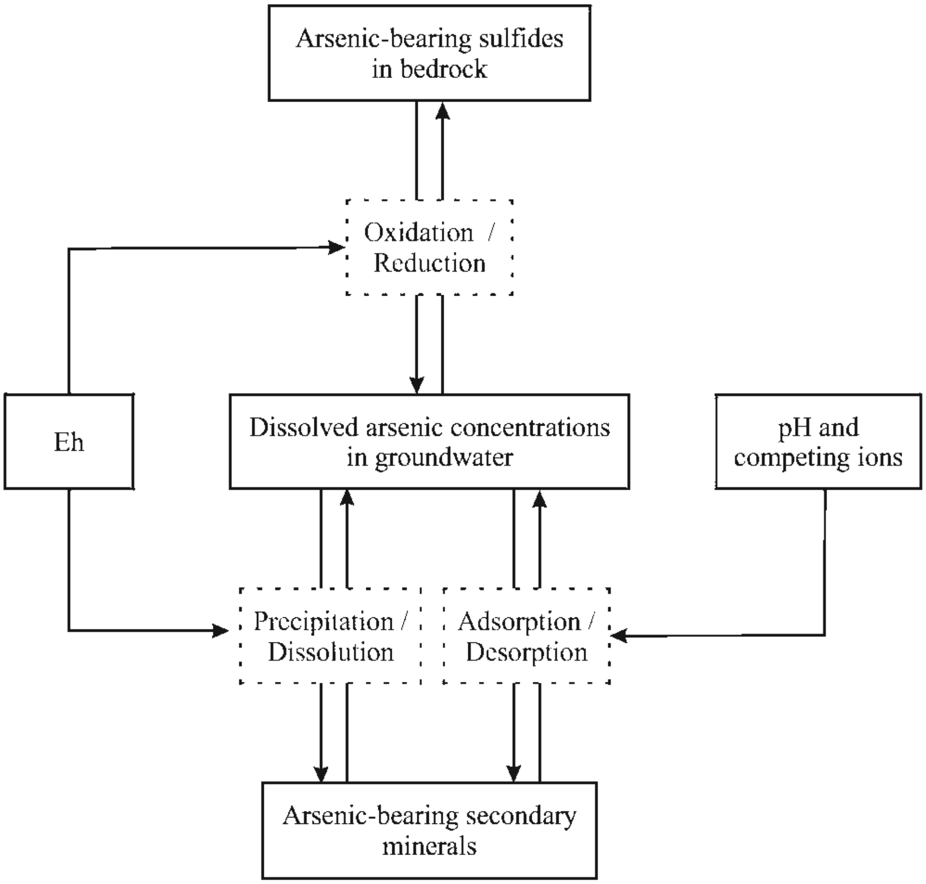

Figure 4.1. Sources and mobility of geogenic arsenic in bedrock groundwater.

concentrations in groundwater (figure 4.1). Previous studies of bedrock aquifers suggest that fractures can contain sufficient reducing conditions to trigger arsenic release by reductive dissolution of metal oxyhydroxides (e.g. Lipfert et al., 2006; Yang et al., 2015). As suggested in previous research (Weldon and MacRae, 2006), the reductive dissolution of Fe-oxyhydroxides is likely to be microbially mediated in bedrock aquifers. It is noteworthy that strong reducing conditions caused by anthropogenic sources of carbon from landfills or waste leachate may enhance the mobility of in situ arsenic (Peters, 2008; Harte et al., 2012). Moreover, the sorption processes affecting arsenic solubility strongly depend on pH and, to a lesser degree, on arsenic speciation and the presence of competing ions (figure 4.1).

Because mineral surfaces are negatively charged under alkaline conditions, the adsorption of arsenic oxyanions decreases significantly as the pH increases above 7 to 8.5, depending on the specific mineralogy (Ravenscroft et al., 2009). For this reason, elevated arsenic concentrations are most often found above a threshold pH value of 7 to 8.5 in bedrock aquifers (e.g. Boyle et al., 1998; Ayotte et al., 2003; Ryan et al., 2013). With regard to speciation, arsenic predominantly occurs in bedrock groundwater either as arsenate (As(V)), which is an oxidizing negatively charged form, or as arsenite (As(III)), a more toxic reduced uncharged form at pH less than 9.2; a negative charge occurs above pH 9.2 (Smedley and Kinniburgh, 2002; Sharma and Sohn, 2009). In general, arsenite occurs in reducing/suboxic waters, whereas arsenate occurs in oxic waters (Kim et al., 2012; Yang et al., 2015). Owing to its neutral charge below pH 9.2, arsenite is generally regarded as a more mobile species than arsenate (Ryan et al., 2013; Yang et al., 2015) except under weak alkaline conditions in which arsenate adsorption onto the Fe-oxyhydroxides is believed to decrease more significantly compared with arsenite (Kim et al., 2012). In addition, some negatively charged ions can reduce arsenic adsorption by competing for sorption sites. Phosphate (${PO_4}^{3-}$) and, to a lesser degree, the anionic species of silicic acid (H_4SiO_4) are recognized to significantly reduce the adsorption of arsenic (Ravenscroft et al., 2009; Sharma and Sohn, 2009). Nevertheless, competitive adsorption has rarely been mentioned in discussions of arsenic concentration in bedrock aquifers. For example, it has been considered that phosphate and sulfate concentrations are too low to affect the arsenic concentrations in fractured bedrock aquifers in New England (Ayotte et al., 2003). Moreover, there is still uncertainty concerning the role of other anions such as bicarbonate (HCO_3^-) (Ravenscroft et al., 2009), which is generally the major anionic species in bedrock groundwater.

4.2.2 Influence of groundwater flow

Groundwater flow affects the spatial and temporal variability in arsenic concentrations by influencing the dilution processes and water chemistry. In fractured bedrock aquifers, large spatial variability often occurs in arsenic concentrations, as evidenced by the contrast in dissolved arsenic measured in wells located within a few hundred meters apart (Smedley et al., 2007; Peters, 2008; Ahn, 2012). Indeed, fractures likely contain groundwater with distinct geochemistry owing to the heterogeneity in arsenic mineral distribution and flow paths in the fractured bedrock (Harte et al., 2012; O'Shea et al., 2015) (figure 4.2). Several studies have suggested that arsenic concentrations vary along the flow paths relative to the geochemical evolution of groundwater (Lipfert et al., 2006; Ryan et al., 2013). More geochemically evolved groundwater (older groundwater) is likely to contain elevated dissolved arsenic as a result of increased reaction time between arsenic minerals and water, increased pH related to silicate and carbonate weathering, and decreased redox potential owing to O_2 consumption through oxidation reactions such as sulfide oxidation (Ryan et al., 2013). By contrast, less geochemically evolved groundwater (younger groundwater) generally contains low arsenic concentrations owing to the prevailing low-pH, oxidizing conditions associated with a significant proportion of recharge water (Harte et al., 2012; Ayotte et al., 2015). Therefore, as the geochemical composition of groundwater evolves along the flow path, arsenic concentrations are likely to increase with depth (Smedley et al. 2007) and from recharge to discharge areas (Lipfert et al., 2006; Ryan et al., 2013) (figure 4.2). Moreover, although the temporal variability of arsenic concentration remains poorly understood in bedrock aquifers, recent studies suggested that arsenic concentrations may exhibit temporal variation according to groundwater flow conditions (Ayotte et al., 2015; Zkeri et al., 2015). In bedrock wells from New England, Ayotte et al. (2015) have reported that arsenic concentrations

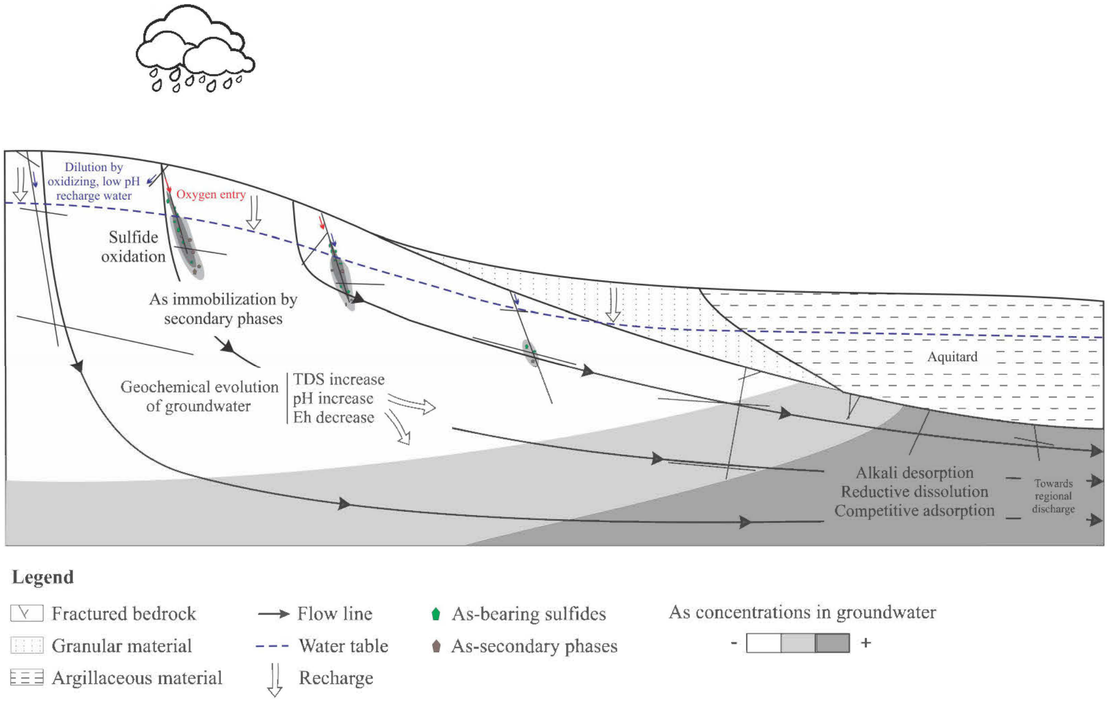

Figure 4.2. Spatio-temporal variability in arsenic concentrations in a fractured bedrock aquifer.

were generally lowest during January through March and were highest during October through December in relation with groundwater levels. Similarly, in groundwater from volcanic and metamorphic aquifers on Levlos Island in Greece, Zkeri et al. (2015) have observed that arsenic concentrations showed a general increase during summer followed by a decrease during the wet months. These results are in agreement with a former study in Snohomish County (Washington, USA) (Frost et al., 1993) that found high temporal variability of dissolved arsenic in private wells, with the highest concentrations recorded during the summer months. Therefore, increasing groundwater levels could be associated with hydrodynamic and geochemical conditions that decrease arsenic concentrations as a result of significant dilution by oxidizing, low-pH recharge water. In contrast, decreasing groundwater levels could be associated with increased arsenic concentrations owing to limited dilution by recharge water and the occurrence of more geochemically evolved groundwater (Ayotte et al., 2015). Moreover, the amount of arsenic released by sulfide oxidation is likely enhanced during drought periods owing to the oxygen entry in the unsaturated zone (Verplanck et al., 2008; Pili et al., 2013) (figure 4.2). It is noteworthy that pumping rates can also account for the temporal variability of arsenic concentration in boreholes by promoting atmospheric oxygen entry into aquifers (Pili et al., 2013) or by mixing fracture waters characterized by contrasted geochemistry (Ayotte et al., 2015; Yang et al., 2015).

4.3 Impacts of climate change on the processes controlling arsenic concentrations in groundwater

4.3.1 Increase in sulfide oxidation

Climate change is expected to increase water table fluctuations and groundwater temperature. Sulfide weathering may be enhanced as a result of falling water tables and, to a lesser extent, rising groundwater temperature (figures 4.3 and 4.4 (1)). Recent studies have reported large increases in solute concentrations, particularly dissolved metals and sulfates in lakes (Mast et al., 2011), streams (Todd et al., 2012), and groundwater (Manning et al., 2013) from mineralized mountain areas in the southern Rocky Mountains in Colorado, USA. These studies suggest that the increase in dissolved metals is caused mainly by the increased oxidation of sulfide minerals owing to a decline in the water table. Indeed, sulfide oxidation rates are largely dependent on oxygen availability in the subsurface (Appelo and Postma, 2005; Manning et al., 2013). Falling water tables enhance the exposure of mineralized rock to oxygen, which diffuses through the unsaturated zone; the relatively low diffusivity of oxygen in water limits sulfide oxidation in the saturated zone (Mast et al., 2011; Todd et al., 2012; Pili et al., 2013). Therefore, the newly exposed rocks might contain sulfides with fresher and thus more reactive mineral surfaces such as those without coatings of secondary minerals (Todd et al., 2012; Manning et al., 2013). In particular, sulfide oxidation may increase in recharge areas (figure 4.4 (1)). Indeed, recharge areas are expected to exhibit greater water table fluctuations than discharge areas under climate change because variations in recharge are diffused and attenuated along the groundwater flowpaths (Waibel et al., 2013). With respect to the water table decline, it has been reported that the increase in dissolved metals occurred in all seasons over 30 years in a stream from a mineralized alpine watershed but that the highest concentrations were associated with low-flow conditions (Todd et al., 2012). Similarly, an increase in sulfate concentrations during droughts has been reported for springs of a mineralized mountain area in the French Alps, suggesting an increase in pyrite dissolution (Pili et al., 2013). That study revealed that, although it was not measured, the arsenic concentration might also have increased. Moreover, sulfide oxidation rates are temperature dependent. However, an increase of 1-3°C in groundwater temperature is not expected to significantly enhance the sulfide oxidation reaction rates, according to the Arrhenius equation, particularly in comparison with the effect of falling water tables (Todd et al., 2012; Manning et al., 2013). In cold regions, however, the melting of the permafrost and seasonally frozen ground resulting from increased temperatures may enhance the sulfide oxidation by allowing the migration of water and oxygen into the subsurface, where such penetration could not have occurred previously over such a long period in the year (Mast et al., 2011; Todd et al., 2012).

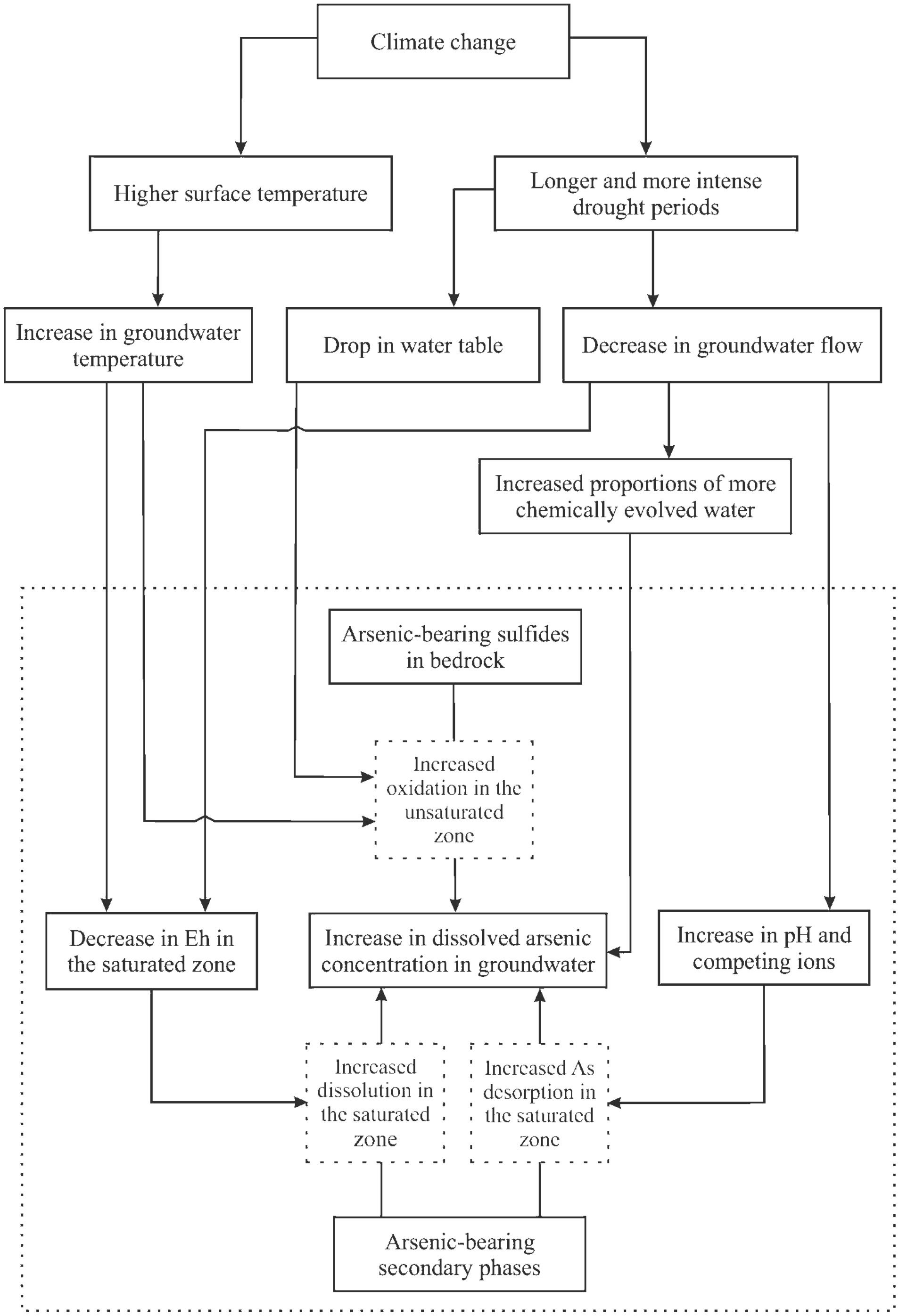

Figure 4.3. Direct impacts of extreme drought on dissolved arsenic concentrations in fractured bedrock aquifers.

4.3.2 Changes in groundwater flow and geochemical evolution

Changes in groundwater flow will likely affect arsenic concentrations in bedrock aquifers. Reduced groundwater flow could increase the occurrence of more geochemically evolved groundwater, which generally contains higher arsenic concentrations than less geochemically evolved groundwater. In fact, the proportion of geochemically evolved groundwater contributing to flow is expected to increase during prolonged low-flow periods as a result of decreased dilution by recharge water (figures 4.3 and 4.4 (3)). Furthermore, reduced groundwater flow may correspond to further geochemical evolution of groundwater owing to increased residence time and thus more extensive water-rock interaction, particularly in the unsaturated zone. This may result in more favorable conditions for arsenic mobilization by reductive dissolution, alkali desorption, and eventually competitive adsorption (figures 4.3 and 4.4 (4)). It is noteworthy that the increase in groundwater temperature can also contribute to a decrease in dissolved oxygen concentration and redox potential (Figura et al., 2011), thus increasing the arsenic release by reductive dissolution. In particular, very high arsenic concentrations may occur in downgradient areas that already contain geochemically evolved groundwater. It is important to note that the higher concentrations of arsenic in the form of toxic arsenite caused by more reducing conditions are likely to pose a greater threat to public health. In contrast, extreme recharge events could significantly decrease the arsenic concentrations owing to more substantial dilution by oxygenated, low-pH water. Nevertheless, the early stages of recharge events may show increased peaks in arsenic concentrations, particularly during events preceded by extended dry periods. Indeed, sudden increases in sulfate and metal concentrations have been observed during the rising limb of discharge for rainstorms in mine wastes and unmined mineralized areas (Nordstrom, 2009; Pili et al., 2013). This phenomenon is caused by the dissolution of soluble salts and the flushing of mineralized water that accumulated during drought periods (Nordstrom, 2009). To the best of our knowledge, no study has specifically reported this process for arsenic even though it likely occurs within arsenic-contaminated aquifers (Pili et al., 2013; Tisserand et al., 2014). In fractured bedrock aquifers, significant recharge events may rapidly remobilize arsenic contained in secondary phases formed in the unsaturated zone during drought and flush water with elevated arsenic concentrations in fractures (figure 4.4 (5)). As highlighted by Nordstrom (2009), this flushing effect may be magnified under climate change as a result of longer dry periods associated with more intense rainstorms.

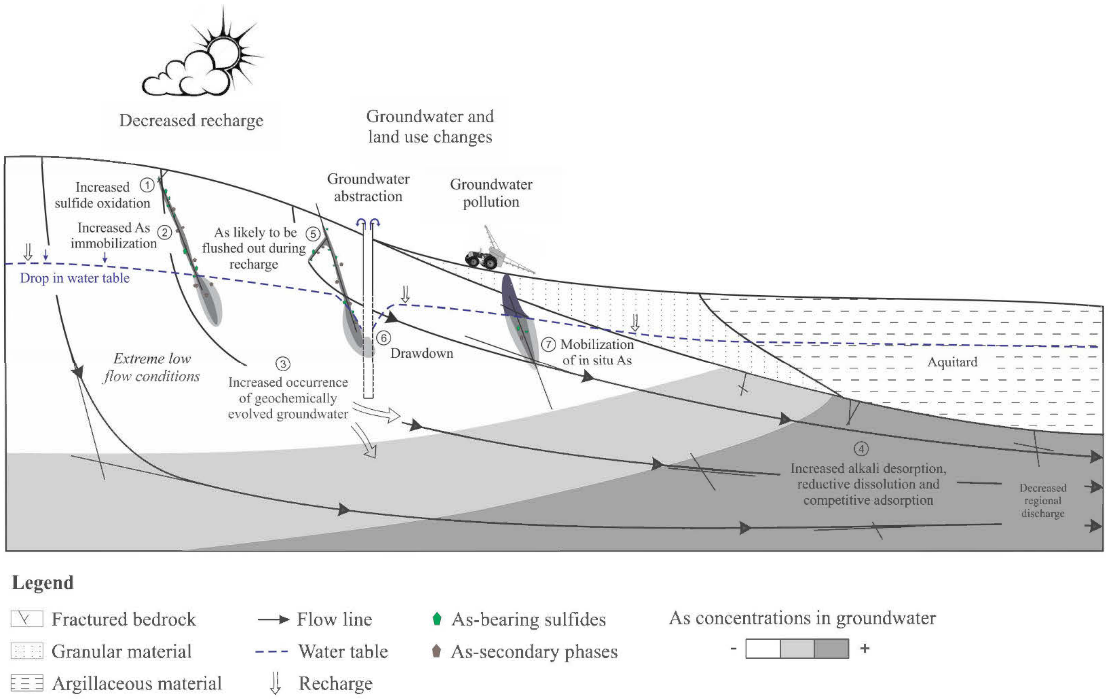

Figure 4.4. Effects of an extreme drought period on the geochemistry of naturally occurring arsenic in a fractured bedrock aquifer.

4.3.3 Indirect impacts of changing human activities

Land use affects groundwater resources by changing the abstractions for water supply and recharge rates and by causing groundwater quality problems through both point and diffuse sources of pollution (Lerner and Harris, 2009). Therefore, climate-driven land use changes will likely affect the water quality and dissolved arsenic concentrations in bedrock aquifers. In particular, increased groundwater withdrawals and decreased recharge may result in more favorable hydrological conditions for arsenic mobilization in groundwater. Climate change will influence groundwater use for agricultural, industrial, and domestic water supplies (World Water Assessment Programme, 2009). Groundwater withdrawals may increase during drought periods as surface water becomes less available (figure 4.4 (6)) (Kundzewicz and Doell, 2009; Kløve et al., 2014). In particular, groundwater abstraction could significantly increase for agricultural irrigation, which accounts for the most important water use sector with about 70 % of the water withdrawals in 2000 (Zhou et al., 2010). In mineralized areas, groundwater abstraction could also increase for the mining industry, which has high water consumption (Lerner and Harris, 2009). In addition, changing land use can, in some cases, reduce recharge by modifying surface-water hydrology, soils, and vegetation (van Roosmalen et al., 2009; Kløve et al., 2014). Moreover, climate change may increase the risk of groundwater pollution. Future land use and increased recharge intensity may lead to increased concentrations of fertilizers and pesticides in groundwater (Bloomfield et al., 2006; Stuart et al., 2011). Flooding in urban areas could increase the loading of common urban contaminants such as oil, solvents, and sewage to groundwater (Green et al., 2011). In a similar manner, rainstorm events could increase the release of contaminants from active and post-operational mining sites in mineralized areas (Pearce et al., 2011). While some compounds such as oil and sewage may promote reducing conditions, others such as nitrate and phosphate may increase the sulfide oxidation and competition for sorption sites, respectively (figure 4.4 (7)).

4.3.4 Influence of aquifer properties

Aquifer properties can influence the changes in water table elevation and geochemical conditions that are initially triggered by climate change. As discussed previously in Section 4.3.1, sulfide oxidation is expected to increase as the water table declines. However, such changes in sulfide oxidation will primarily depend on the distribution of sulfide minerals in the bedrock and on the range of water table fluctuation. Small, shallow, unconfined aquifers are likely to be more sensitive and to respond more rapidly to climate change than large, deep, confined aquifers (Kløve et al., 2014). As a result, shallow unconfined aquifers may exhibit more pronounced water table declines than larger, deeper, and, in particular, confined aquifers. The effective porosity and water table gradient also affect the range of water table fluctuation. For example, in low-porosity rocks such as fractured crystalline rocks, small decreases in recharge may result in large water table declines (Manning et al., 2013). Similarly, in mountain watersheds with steep water table gradients typical of recharge areas, small declines in recharge could produce relatively large water table declines (Todd et al., 2012). It is noteworthy that a water table dropping below the depth of oxygen penetration will produce limited increase in sulfide weathering (Manning et al., 2013). Finally, small aquifers with short water residence time may be more rapidly and intensively affected by changes in geochemical conditions than large confined aquifers. For such aquifers, this may result in more arsenic release by reductive dissolution and alkaline desorption during low-flow periods.

4.4 Concluding remarks and perspectives

Climate change is expected to affect groundwater resources by altering recharge, flow dynamics, and water quality. The deterioration of groundwater quality may threaten the sustainability of drinking water supplies, particularly in groundwater systems prone to geogenic contamination. In fractured bedrock aquifers, natural arsenic contamination of groundwater is a major public health concern, particularly for rural populations that rely on bedrock groundwater for their drinking water. The direct effects of changes in recharge and indirect effects of changes in land use may affect arsenic mobilization in bedrock groundwater. In particular, intense and prolonged drought periods may be associated with increased arsenic concentrations owing to the following factors:

- An increase in arsenic sulfide oxidation in the unsaturated zone in response to falling water table elevation
- The occurrence of more geochemically evolved and potentially arsenic-rich groundwater and more favorable conditions for arsenic mobilization by reductive dissolution and alkali desorption related to the decreased groundwater flow
- The occurrence of larger sudden releases of dissolved arsenic during the early stages of recharge events owing to the flushing of arsenic that accumulated in the unsaturated zone during droughts

On the contrary, the occurrence of extreme recharge events is expected to further decrease arsenic concentrations because of the greater dilution by oxygenated, low-pH water. Importantly, the impact of climate change on dissolved arsenic in fractured bedrock aquifers will vary widely according to the aquifer properties that influence changes in water table elevations and groundwater flow.

Thus far, little is known about the link between climate change and arsenic concentrations in fractured bedrock environments. The evaluation of the temporal variability of arsenic in groundwater related to the variations in hydrological conditions is likely the most significant knowledge gap. Studies documenting the temporal variability in concentrations remain limited, particularly in fractured bedrock aquifers. The few studies that have investigated temporal arsenic variability in groundwater have often reported little variations in most wells but significant variations for some. However, the reasons explaining the large variability measured in some wells remain unclear (Sorg et al., 2014; Ayotte et al., 2015). Addressing this scientific gap requires long-term monitoring data of the water level and groundwater quality combined with a thorough knowledge of local hydrogeological settings and the mechanisms governing arsenic mobilization. A good understanding of the mechanisms underlying arsenic variations is necessary to properly interpret the data and allow comparisons between different monitoring programs and studies. In this sense, table 4.2 provides a summary of certain key considerations that appear to be relevant for orienting the design of such data collection and monitoring programs. Moreover, there is a lack of knowledge regarding the influence of microorganisms on the speciation and mobility of arsenic in bedrock aquifers. Climate change could significantly affect the activity of microorganisms by changing the conditions in the aquifers, and these changes need to be evaluated. Future research focusing on the effects of climate change on groundwater quality is critically needed. A better understanding of the future evolution of groundwater quality is essential for ensuring the availability and sustainability of water supplies in future decades.

Table 4.2. Summary of key considerations for orienting the design of monitoring programs.

	Considerations	**Justifications**	**Suggested references**
Temporal variations	Evaluate the effect of droughts and recharge events on arsenic concentrations	Changes in sulfide oxidation (4.3.1) and geochemical conditions (4.3.2) between low-flow and high-flow conditions	Manning et al. (2013); Pili et al. (2013) and Ayotte et al. (2015)
		Changes in the amplitude of flushing effects during the early stage of recharge events (4.3.2)	Nordstrom (2009); Pili et al. (2013)
	Establish monitoring programs for water quality to assess seasonal and inter-annual variations in arsenic concentrations	Changes in arsenic concentrations according to the seasonality (4.3.1 and 4.3.2)	Ayotte et al. (2015)
		Long-term trends of changes in arsenic concentrations ?	
	Discriminate direct and indirect impacts of climate change on water table elevation and groundwater quality	Impacts of human activities on groundwater exploitation, recharge and groundwater quality (4.3.3)	Bloomfield et al. (2006); van Roosmalen et al. (2009); Zhou et al. (2010); Stuart et al. (2011); Taylor et al. (2013)
Spatial variations	Consider the position of sampling sites along the flow paths (recharge and down gradient zones)	Various response to climate change as well as the mechanisms of arsenic mobilization between recharge and down-gradient zones (4.3.1 and 4.3.2)	Dams et al. (2012); Waibel et al. (2013) and Lipfert et al. (2006); Ryan et al. (2013)
	Consider local hydrogeological settings such as aquifer size, type, and porosity	Influence of hydrogeological settings on changes in groundwater level fluctuations and geochemical conditions (4.3.4)	Kløve et al. (2014)
	Take into account the properties and usage of sampling infrastructures (wells) on the representativeness of samples	Effect of pumping depth, time, and rate on arsenic concentrations	Yang et al. (2015)

Acknowledgments

This project was funded by the Quebec Ministry of the Environment (Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques) through the Groundwater Knowledge Acquisition Program (PACES) with significant contributions from regional partners involved in the PACES, including the Regional County Municipalities (Abitibi, Vallée-de-lâOr, Abitibi-Ouest, Ville de Rouyn-Noranda, Témiscamingue) and the Regional Conference of Elected Officials of Abitibi-Temiscamingue. The authors acknowledge the Foundation of the University of Quebec in Abitibi-Temiscamingue (FUQAT) and the Canadian Institute of Mining (Amos section) for scholarships and support to the project of Raphaël Bondu, respectively. Finally, the authors would like to acknowledge two anonymous reviewers for their constructive comments which contributed to improve this article.

References

Acharyya, S. K., Shah, B. A., Ashyiya, I. D., Pandey, Y., 2005. Arsenic contamination in groundwater from parts of Ambagarh-Chowki block, Chhattisgarh, India: source and release mechanism. Environmental Geology 49, 148–158.

Ahn, J. S., 2012. Geochemical occurrences of arsenic and fluoride in bedrock groundwater: a case study in Geumsan County, Korea. Environmental Geochemistry and Health 34, 43–54.

Ahn, J. S., Cho, Y.-C., 2013. Predicting natural arsenic contamination of bedrock groundwater for a local region in Korea and its application. Environmental Earth Sciences 68, 2123–2132.

Appelo, C. A. J., Postma, D., 2005. Geochemistry, groundwater and pollution, 2nd edition. A.A. Balkema Publishers, Amsterdam (Netherlands).

Asta, M. P., Cama, J., Ayora, C., Acero, P., de Giudici, G., 2010. Arsenopyrite dissolution rates in O_2-bearing solutions. Chemical Geology 273, 272 – 285.

Ayotte, J. D., Belaval, M., Olson, S. A., Burow, K. R., Flanagan, S. M., Hinkle, S. R., Lindsey, B. D., 2015. Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States. Science of the Total Environment 505, 1370–1379.

Ayotte, J. D., Montgomery, D. L., Flanagan, S. M., Robinson, K. W., 2003. Arsenic in groundwater in eastern New England: occurrence, controls, and human health implications. Environmental Science & Technology 37, 2075–2083.

Bhattacharya, P., Jacks, G., Brömssen, M. v., 2010. Arsenic in Swedish groundwater - Mobility and risk for naturally elevated concentrations: Final Report. Universitetsservice AB.

Bhattacharya, P., Sracek, O., Eldvall, B., Asklund, R., Barmen, G., Jacks, G., Koku, J., Gustafsson, J.-E., Singh, N., Balfors, B. B., 2012. Hydrogeochemical study on the contamination of water resources in a part of Tarkwa mining area, Western Ghana. Journal of African Earth Sciences 66-67, 72–84.

Bloomfield, J. P., Williams, R. J., Gooddy, D. C., Cape, J. N., Guha, P., 2006. Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater - a UK perspective. Science of the Total Environment 369, 163–177.

Borba, R. P., Figueiredo, B. R., Matschullat, J., 2003. Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil. Environmental Geology 44, 39–52.

Bottomley, D., 1984. Origins of some arseniferous groundwaters in Nova Scotia and New Brunswick, Canada. Journal of Hydrology 69, 223–257.

Boyle, D. R., Turner, R. J. W., Hall, G. E. M., 1998. Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. Environmental Geochemistry and Health 20, 199–212.

Bretzler, A., Johnson, C. A., 2015. The geogenic contamination handbook: Addressing arsenic and fluoride in drinking water. Applied Geochemistry 63, 642–646.

Carneiro, J. F., Boughriba, M., Correia, A., Zarhloule, Y., Rimi, A., El Houadi, B., 2010. Evaluation of climate change effects in a coastal aquifer in Morocco using a density-dependent numerical model. Environmental Earth Sciences 61, 241–252.

Chopard, A., Benzaazoua, M., Plante, B., Bouzahzah, H., Marion, P., 2015. Kinetic tests to evaluate the relative oxidation rates of various sulfides and sulfosalts. In: ICARDS2015 Proceedings, Santiago du Chile (Chile).

Dams, J., Salvadore, E., Van Daele, T., Ntegeka, V., Willems, P., Batelaan, O., 2012. Spatio-temporal impact of climate change on the groundwater system. Hydrology and Earth System Sciences 16, 1517–1531.

Drahota, P., Filippi, M., 2009. Secondary arsenic minerals in the environment: A review. Environment International 35, 1243–1255.

Figura, S., Livingstone, D. M., Hoehn, E., Kipfer, R., 2011. Regime shift in groundwater temperature triggered by the Arctic Oscillation. Geophysical Research Letters 38, L23401.

Foley, N. K., Ayuso, R. A., 2008. Mineral sources and transport pathways for arsenic release in a coastal watershed, USA. Geochemistry: Exploration, Environment, Analysis 8, 59–75.

Frengstad, B., Skrede, A. K. M., Banks, D., Krog, J. R., Siewers, U., 2000. The chemistry of Norwegian groundwaters: III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques. Science of The Total Environment 246 (1), 21–40.

Frost, F., Franke, D., Pierson, K., Woodruff, L., Raasina, B., Davis, R., Davies, J., 1993. A seasonal study of arsenic in groundwater, Snohomish County, Washington, USA. Environmental Geochemistry and Health 15, 209–214.

Grantham, D. A., Jones, J. F., 1977. Arsenic contamination of water wells in Nova Scotia. Journal (American Water Works Association) 69 (12), 653–657.

Green, T. R., Taniguchi, M., Kooi, H., Gurdak, J. J., Allen, D. M., Hiscock, K. M., Treidel, H., Aureli, A., 2011. Beneath the surface of global change: Impacts of climate change on groundwater. Journal of Hydrology 405, 532–560.

Gurdak, J. J., McMahon, P. B., Bruce, B. W., 2012. Vulnerability of groundwater quality to human activity and climate change and variability, High Plains aquifer, USA. In: Treidel, H., Martin-Bordes, J. L., Gurdak, J. J. (Eds.), Climate Change Effects on Groundwater Resources - A Global Synthesis of Findings and Recommendations. Taylor & Francis Group, pp. 145–168.

Harte, P. T., Ayotte, J. D., Hoffman, A., Revesz, K. M., Belaval, M., Lamb, S., Boehlke, J. K., 2012. Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire, USA. Hydrogeology Journal 20, 1189–1201.

Intergovernmental Panel on Climate Change, 2014. Climate change 2013: The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change (eds Stocker, T. F. et al.). Cambridge University Press (UK).

Jackson, C. R., Meister, R., Prudhomme, C., 2011. Modelling the effects of climate change and its uncertainty on UK Chalk groundwater resources from an ensemble of global climate model projections. Journal of Hydrology 399, 12–28.

Jyrkama, M. I., Sykes, J. F., 2007. The impact of climate change on spatially varying groundwater recharge in the grand river watershed (Ontario). Journal of Hydrology 338 (3), 237–250.

Kim, K., Kim, S.-H., Jeong, G. Y., Kim, R.-H., 2012. Relations of As concentrations among groundwater, soil, and bedrock in Chungnam, Korea: Implications for As mobilization in groundwater according to the As-hosting mineral change. Journal of Hazardous Materials 199, 25–35.

Klassen, R., Douma, S., Ford, A., Rencz, A., Grunsky, E., 2009. Geoscience modelling of relative variation in natural arsenic hazard potential in New Brunswick. Geological Survey of Canada, Current Research 2009-7, 9 p.

Kløve, B., Ala-Aho, P., Bertrand, G., Gurdak, J. J., Kupfersberger, H., Kværner, J., Muotka, T., Mykrä, H., Preda, E., Rossi, P., et al., 2014. Climate change impacts on groundwater and dependent ecosystems. Journal of Hydrology 518, 250–266.

Kundzewicz, Z. W., Doell, P., 2009. Will groundwater ease freshwater stress under climate change? Hydrological Sciences Journal 54 (4), 665–675.

Kurylyk, B., Bourque, C.-A., MacQuarrie, K., 2013. Potential surface temperature and shallow groundwater temperature response to climate change: an example from a small forested catchment in east-central New Brunswick (Canada). Hydrology and Earth System Sciences 17, 2701–2716.

Lerner, D. N., Harris, B., 2009. The relationship between land use and groundwater resources and quality. Land Use Policy 26, Supplement 1, S265–S273.

Lipfert, G., Reeve, A. S., Sidle, W. C., Marvinney, R., 2006. Geochemical patterns of arsenic-enriched ground water in fractured, crystalline bedrock, Northport, Maine, USA. Applied Geochemistry 21, 528–545.

Lipfert, G., Sidle, W. C., Reeve, A. S., Ayuso, R. A., Boyce, A. J., 2007. High arsenic concentrations and enriched sulfur and oxygen isotopes in a fractured-bedrock ground-water system. Chemical Geology 242, 385–399.

Loukola-Ruskeeniemi, K., Tanskanen, H., Lahermo, P., 1999. Anomalously high arsenic concentrations in spring waters in Kittilä, Finnish Lapland. Geological Survey of Finland Special Paper 27, 97–102.

Mango, H., Ryan, P., 2015. Source of arsenic-bearing pyrite in southwestern Vermont, USA: Sulfur isotope evidence. Science of The Total Environment 505, 1331–1339.

Manning, A. H., Verplanck, P. L., Caine, J. S., Todd, A. S., 2013. Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed. Applied Geochemistry 37, 64–78.

Mast, M. A., Turk, J. T., Clow, D. W., Campbell, D. H., 2011. Response of lake chemistry to changes in atmospheric deposition and climate in three high-elevation wilderness areas of Colorado. Biogeochemistry 103, 27–43.

Meranger, J., Subramanian, K., McCurdy, R., 1984. Arsenic in Nova Scotian groundwater. Science of The Total Environment 39, 49–55.

Naujokas, M. F., Anderson, B., Ahsan, H., Aposhian, H. V., Graziano, J. H., Thompson, C., Suk, W. A., 2013. The broad scope of health effects from chronic arsenic exposure: update on a worldwide public health problem. Environmental Health Perspectives (Online) 121 (3), 295.

Niu, B., Loáiciga, H. A., Wang, Z., Zhan, F. B., Hong, S., 2014. Twenty years of global groundwater research: A Science Citation Index Expanded-based bibliometric survey (1993-2012). Journal of Hydrology 519, Part A, 966 – 975.

Nordstrom, D. K., 2009. Acid rock drainage and climate change. Journal of Geochemical Exploration 100, 97–104.

Nordstrom, D. K., Blowes, D. W., Ptacek, C. J., 2015. Hydrogeochemistry and microbiology of mine drainage: An update. Applied Geochemistry 57, 3–16.

Okkonen, J., Jyrkama, M., Kløve, B., 2010. A conceptual approach for assessing the impact of climate change on groundwater and related surface waters in cold regions (Finland). Hydrogeology Journal 18 (2), 429–439.

O'Shea, B., Stransky, M., Leitheiser, S., Brock, P., Marvinney, R. G., Zheng, Y., 2015. Heterogeneous arsenic enrichment in meta-sedimentary rocks in central Maine, United States. Science of The Total Environment 505, 1308–1319.

Pandey, P. K., Sharma, R., Roy, M., Roy, S., Pandey, M., 2006. Arsenic contamination in the Kanker district of central-east India: geology and health effects. Environmental Geochemistry and Health 28, 409–420.

Parviainen, A., Loukola-Ruskeeniemi, K., Tarvainen, T., Hatakka, T., Härmä, P., Backman, B., Ketola, T., Kuula, P., Lehtinen, H., Sorvari, J., Pyy, O., Ruskeeniemi, T., Luoma, S., 2015. Arsenic in bedrock, soil and groundwater - The first arsenic guidelines for aggregate production established in Finland. Earth-Science Reviews 150, 709–723.

Pearce, T. D., Ford, J. D., Prno, J., Duerden, F., Pittman, J., Beaumier, M., Berrang-Ford, L., Smit, B., 2011. Climate change and mining in Canada. Mitigation and Adaptation Strategies For Global Change 16, 347–368.

Peters, S. C., 2008. Arsenic in groundwaters in the Northern Appalachian Mountain belt: A review of patterns and processes. Journal of Contaminant Hydrology 99, 8–21.

Peters, S. C., Blum, J. D., 2003. The source and transport of arsenic in a bedrock aquifer, New Hampshire, USA. Applied Geochemistry 18, 1773–1787.

Pili, E., Tisserand, D., Bureau, S., 2013. Origin, mobility, and temporal evolution of arsenic from a low-contamination catchment in Alpine crystalline rocks. Journal of Hazardous Materials 262, 887–895.

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic pollution: a global synthesis. Wiley-Blackwell, West Sussex (UK).

Reyes, F. A. P., Crosta, G. B., Frattini, P., Basiricò, S., Della Pergola, R., 2015. Hydrogeochemical overview and natural arsenic occurrence in groundwater from alpine springs (upper Valtellina, Northern Italy). Journal of Hydrology 529, 1530–1549.

Ruskeeniemi, T., Backman, B., Loukola-Ruskeeniemi, K., Sorvari, J., Lehtinen, H., Schultz, E., Mäkelä-Kurtto, R., Rossi, E., Vaajasaari, K., Ämer Bilaletdin, 2011. Arsenic in the Pirkanmaa region, Southern Finland: from identification through to risk assessment to risk managment. Geological Survey of Finland, Special Paper 49, 21–227.

Ryan, P. C., Kim, J., Wall, A. J., Moen, J. C., Corenthal, L. G., Chow, D. R., Sullivan, C. M., Bright, K. S., 2011. Ultramafic-derived arsenic in a fractured bedrock aquifer. Applied Geochemistry 26, 444–457.

Ryan, P. C., Kim, J. J., Mango, H., Hattori, K., Thompson, A., 2013. Arsenic in a fractured slate aquifer system, New England, USA: Influence of bedrock geochemistry, groundwater flow paths, redox and ion exchange. Applied Geochemistry 39, 181–192.

Ryan, P. C., West, D. P., Hattori, K., Studwell, S., Allen, D. N., Kim, J., 2015. The influence of metamorphic grade on arsenic in metasedimentary bedrock aquifers: A case study from Western New England, USA. Science of the Total Environment 505, 1320–1330.

Sahoo, N. R., Pandalai, H. S., 2000. Secondary geochemical dispersion in the Precambrian auriferous Hutti-Maski schist belt, Raichur district, Karnataka, India. Part I: anomalies of As, Sb, Hg and Bi in soil and groundwater. Journal of Geochemical Exploration 71, 269–289.

Serpa, C., Batterson, M., Guzzwell, K., 2009. The influence of bedrock and mineral occurrences on arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. Current Research. Newfoundland and Labrador Department of Natural Resources Geological Survey, Report 09–1, 315–337.

Serrat-Capdevila, A., Valdés, J. B., Pérez, J. G., Baird, K., Mata, L. J., Maddock, T., 2007. Modeling climate change impacts–and uncertainty–on the hydrology of a riparian system: The San Pedro Basin (Arizona/Sonora). Journal of Hydrology 347, 48–66.

Sharma, V. K., Sohn, M., 2009. Aquatic arsenic: Toxicity, speciation, transformations, and remediation. Environment International 35, 743–759.

Shukla, D. P., Dubey, C. S., Singh, N. P., Tajbakhsh, M., Chaudhry, M., 2010. Sources and controls of arsenic contamination in groundwater of Rajnandgaon and Kanker District, Chattisgarh Central India. Journal of Hydrology 395, 49–66.

Sidle, W. C., 2002. $^{18}O_{SO_4}$ and $^{18}O_{H_2O}$ as prospective indicators of elevated arsenic in the Goose River ground-watershed, Maine. Environmental Geology 42, 350–359.

Sidle, W. C., Fischer, R. A., 2003. Detection of ^{3}H and ^{85}Kr in groundwater from arsenic-bearing crystalline bedrock of the Goose River basin, Maine. Environmental Geology 44, 781–789.

Sidle, W. C., Wotten, B., Murphy, E., 2001. Provenance of geogenic arsenic in the Goose River basin, Maine, USA. Environmental Geology 41, 62–73.

Smedley, P. L., 1996. Arsenic in rural groundwater in Ghana. Journal of African Earth Sciences 22, 459–470.

Smedley, P. L., Kinniburgh, D. G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry 17, 517–568.

Smedley, P. L., Knudsen, J., Maiga, D., 2007. Arsenic in groundwater from mineralised Proterozoic basement rocks of Burkina Faso. Applied Geochemistry 22, 1074–1092.

Sorg, T. J., Chen, A. S., Wang, L., 2014. Arsenic species in drinking water wells in the USA with high arsenic concentrations. Water Research 48, 156 – 169.

Stuart, M. E., Gooddy, D. C., Bloomfield, J. P., Williams, A. T., 2011. A review of the impact of climate change on future nitrate concentrations in groundwater of the UK. Science of the Total Environment 409, 2859–2873.

Taylor, C. A., Stefan, H. G., 2009. Shallow groundwater temperature response to climate change and urbanization. Journal of Hydrology 375, 601–612.

Taylor, R. G., Scanlon, B., Döll, P., Rodell, M., Van Beek, R., Wada, Y., Longuevergne, L., Leblanc, M., Famiglietti, J. S., Edmunds, M., et al., 2013. Ground water and climate change. Nature Climate Change 3, 322–329.

Tisserand, D., Pili, E., Hellmann, R., Boullier, A.-M., Charlet, L., 2014. Geogenic arsenic in groundwaters in the western Alps. Journal of Hydrology 518, Part C, 317–325.

Todd, A. S., Manning, A. H., Verplanck, P. L., Crouch, C., McKnight, D. M., Dunham, R., 2012. Climate-change-driven deterioration of water quality in a mineralized watershed. Environmental Science & Technology 46, 9324–9332.

van Roosmalen, L., Sonnenborg, T. O., Jensen, K. H., 2009. Impact of climate and land use change on the hydrology of a large-scale agricultural catchment. Water Resources Research 45, W00A15.

Verplanck, P. L., Mueller, S. H., Goldfarb, R. J., Nordstrom, D. K., Youcha, E. K., 2008. Geochemical controls of elevated arsenic concentrations in groundwater, Ester Dome, Fairbanks district, Alaska. Chemical Geology 255, 160–172.

Waibel, M., Gannett, M., Chang, H., Hulbe, C., 2013. Spatial variability of the response to climate change in regional groundwater systems - Examples from simulations in the Deschutes Basin, Oregon. Journal of Hydrology 486, 187 – 201.

Weldon, J. M., MacRae, J. D., 2006. Correlations between arsenic in Maine groundwater and microbial populations as determined by fluorescence in situ hybridization. Chemosphere 63, 440–448.

World Water Assessment Programme, 2009. The United Nations World Water Development Report 3: Water in a Changing World. Paris: UNESCO, and London: Earthscan.

Yang, Q., Culbertson, C. W., Nielsen, M. G., Schalk, C. W., Johnson, C. D., Marvinney, R. G., Stute, M., Zheng, Y., 2015. Flow and sorption controls of groundwater arsenic in individual boreholes from bedrock aquifers in central Maine, USA. Science of The Total Environment 505, 1291–1307.

Yang, Q., Jung, H. B., Culbertson, C. W., Marvinney, R. G., Loiselle, M. C., Locke, D. B., Cheek, H., Thibodeau, H., Zheng, Y., 2009. Spatial pattern of groundwater arsenic occurrence and association with bedrock geology in greater Augusta, Maine. Environmental Science & Technology 43, 2714–2719.

Yang, Q., Jung, H. B., Marvinney, R. G., Culbertson, C. W., Zheng, Y., 2012. Can arsenic occurrence rates in bedrock aquifers be predicted? Environmental Science & Technology 46, 2080–2087.

Zheng, Y., Ayotte, J. D., 2015. At the crossroads: Hazard assessment and reduction of health risks from arsenic in private well waters of the northeastern United States and Atlantic Canada. Science of The Total Environment 505, 1237–1247.

Zhou, Y., Zwahlen, F., Wang, Y., Li, Y., 2010. Impact of climate change on irrigation requirements in terms of groundwater resources. Hydrogeology journal 18, 1571–1582.

Zkeri, E., Aloupi, M., Gaganis, P., 2015. Natural occurrence of arsenic in groundwater from Lesvos Island, Greece. Water, Air, & Soil Pollution 226 (9), 1–16.

CHAPITRE 5

CONCLUSION GÉNÉRALE

5.1 Portée de la thèse pour la science et la société

5.1.1 Principales avancées scientifiques

Ce travail de doctorat a permis des avancées significatives à plusieurs niveaux dans la compréhension de la contamination naturelle à l'arsenic dans les aquifères rocheux fracturés. Il a tout d'abord contribué à accroître les connaissances portant sur les sources primaires d'arsenic que constituent les minéraux sulfurés. Les résultats des investigations minéralogiques indiquent que les minéraux sulfurés représentent les sources primaires d'arsenic dans les eaux souterraines de l'aquifère rocheux fracturé en Abitibi-Témiscamingue. Dans la région, les sulfures riches en arsenic sont généralement abondants à proximité des zones de failles minéralisées. Ainsi, dans la majorité des cas, les concentrations élevées d'arsenic sont mesurées dans les eaux souterraines à proximité des grandes structures minéralisées, principalement les failles de Cadillac-Larder Lake et de Porcupine-Destor. Plusieurs minéraux sulfurés ont été identifiés comme étant potentiellement source d'arsenic dans l'eau souterraine dont l'arsénopyrite, la gersdorffite et la pyrite arsénifère. Une des contributions majeures de ce travail réside dans la mise en évidence de l'importance de la minéralogie et des conditions géochimiques dans l'aquifère vis-à-vis de la libération d'arsenic à partir des minéraux primaires. En effet, la stabilité des minéraux sulfurés par rapport à l'oxydation peut constituer un facteur important dans la libération d'arsenic. Les minéraux sulfurés du groupe de la cobaltite, telle que la gersdorffite, apparaissent particulièrement solubles en conditions oxydantes et pourraient constituer une source significative d'arsenic dans l'eau souterraine. Les concentrations en arsenic dérivées de l'altération de ces minéraux pourraient être particulièrement élevées dans le cas où les conditions sont favorables à l'oxydation de quantités importantes de sulfures. L'oxydation des sulfures pourrait ainsi constituer un important mécanisme de mobilisation de l'arsenic dans des zones de recharge non captives (à nappe libre) exposées à des fluctuations du niveau piézométrique et à des entrées d'oxygène. Par contre, la stabilité des sulfures par rapport à l'altération aurait peu d'impact dans des zones captives où la mobilisation de l'arsenic est davantage liée à des sources secondaires. En ce sens, cette thèse a montré que la mobilisation de l'arsenic par l'oxydation des sulfures dépend grandement des paramètres hydrogéologiques et des conditions hydrodynamiques dans l'aquifère. Une approche conceptuelle a permis de mettre en évidence qu'une baisse des niveaux piézométriques causée par les changements climatiques pourrait augmenter la libération d'arsenic par oxydation des sulfures et ainsi affecter significativement la qualité de l'eau souterraine. L'oxydation des sulfures, qui se produit pour l'essentiel dans la zone non saturée, pourrait croître avec la baisse des niveaux piézométriques et l'augmentantion de la quantité de sulfures exposés à l'oxydation.

Par ailleurs, les résultats de cette thèse ont montré que la mobilisation de l'arsenic n'est pas uniquement due à l'oxydation des sulfures. En effet, il est vraisemblable que divers mécanismes de mobilisation de l'arsenic soient à l'oeuvre dans les aquifères rocheux fracturés. Dans le cas des aquifères rocheux confinés par des dépôts argileux, les fortes concentrations en arsenic apparaissent généralement liées à la dissolution ou à la non-formation d'oxyhydroxides métalliques en conditions réductrices. Les oxyhydroxides de Fe et de Mn sont considérés comme les principaux minéraux secondaires responsables de la séquestration de l'arsenic dans l'eau souterraine, avec les minéraux argileux qui peuvent être abondants dans les zones d'altération. Les résultats de spéciation de l'arsenic, basés sur une méthode novatrice de séparation sur le terrain, ont révélé la prédominance de l'arsénite (As(III)) dans les puits individuels creusés dans l'aquifère rocheux captif, en lien avec les conditions réductrices. Cela se révèle être un problème majeur en termes de santé publique car l'arsénite est connue comme étant l'espèce inorganique la plus toxique de l'arsenic. D'un autre côté, l'arséniate (As(V)) constitue généralement la principale espèce d'arsenic dans les puits localisés au sein, ou à proximité, des zones de recharge à nappe libre où les conditions sont davantage oxydantes. Ceci suggère que la mobilisation de l'arsenic dans ces zones est probablement liée à l'oxydation des sulfures ou à la désorption alcaline. À noter que des espèces organiques méthylées d'arsenic ont également été mesurées à des concentrations significatives, ce qui pourrait indiquer l'influence de l'activité de microorganismes sur les formes d'arsenic dans l'eau souterraine. L'écoulement de l'eau souterraine, fonction des paramètres hydrogéologiques et des conditions hydrologiques, se présente comme un facteur déterminant dans la mobilisation de l'arsenic. Les changements climatiques pourraient affecter les écoulements d'eau souterraine notamment en diminuant les débits lors des épisodes de sécheresse prolongée. Dans ces conditions, l'augmentation des temps de résidence et de l'évolution géochimique des eaux souterraines pourraient mener à l'accroissement des concentrations en arsenic. Au contraire, les forts épisodes de recharge, prévus lors des phénomènes de précipitation extrême, pourraient contribuer à diminuer les concentrations en arsenic en raison de la dilution et de l'apport d'eau oxygénée au pH faible. Ce travail a aussi mis en évidence que l'impact des changements climatiques sur la géochimie de l'arsenic pouvait agir de manière indirecte, en entraînant des modifications de l'activité humaine et de l'occupation des sols. En effet, les changements du climat pourraient notamment entraîner des modifications du pompage et de la qualité (pollution) des eaux souterraines qui sont susceptibles de se répercuter sur les mécanismes de mobilisation de l'arsenic. En abordant le lien entre la contamination à l'arsenic et le climat, ce travail constitue une des premières tentatives d'évaluer les modifications de la qualité de l'eau souterraine sous l'influence des changements climatiques.

Pour finir, outre les résultats mentionnés ci-dessus, ce travail de doctorat a démontré l'intérêt d'adopter une approche pluridisciplinaire pour aborder un problème environnemental complexe tel que la mobilisation de l'arsenic dans les eaux naturelles. La combinaison d'approches conceptuelle, de terrain, de laboratoire et de modélisation paraît désormais incontournable pour accroître significativement nos connaissances dans ce domaine.

5.1.2 Retombées pour la société

Les résultats de cette thèse ont des implications pour les sociétés dépendantes de la ressource en eau souterraine des aquifères rocheux fracturés, en particulier en termes de santé publique. En raison de la présence d'arsenic, la qualité de l'eau souterraine peut s'avérer problématique pour les résidents des secteurs ruraux dont la principale source d'eau potable provient de puits individuels creusés dans le socle rocheux. Dans la province de Québec, comme dans de nombreuses régions dans le monde, le contrôle de la qualité de l'eau des puits individuels est du ressort des propriétaires lorsqu'ils sont utilisés à des fins domestiques. Ces nouvelles connaissances sur la mobilisation et la distribution de l'arsenic dans l'eau souterraine vont dans le sens d'une meilleure protection des populations contre l'intoxication à l'arsenic. Dans la région de l'Abitibi-Témiscamingue, les fortes concentrations d'arsenic s'observent pour l'essentiel dans des puits creusés dans le socle rocheux, à proximité de zones de failles minéralisées. Les teneurs les plus problématiques apparaissent dans les aquifères sous couverture argileuse où l'arsenic existe sous sa forme la plus toxique (arsénite). Dans ces secteurs, il convient donc de se tourner dans la mesure du possible vers d'autres sources d'eau potable telles que les eaux souterraines des aquifères granulaires superficiels (eskers, moraines) et les eaux de surface, notamment pour les habitations situées à proximité de lacs et de rivières. Si le socle rocheux constitue l'unique source d'eau, les puits doivent autant que possible être limités en profondeur pour éviter la contribution d'eaux réductrices riches en arsenic. Les puits à faible rendement doivent faire l'objet d'une attention particulière en lien avec l'existence d'eau géochimiquement évoluée potentiellement riche en arsenic. Des campagnes d'information et de promotion pour tester l'eau des puits s'avèrent probablement être la meilleure solution à l'heure actuelle. Des solutions pour éviter la consommation d'eau contaminée existent, notamment l'utilisation d'eau en bouteille ou d'un système de traitement de l'eau. C'est dans cette optique que les résultats des analyses d'eau réalisées dans le cadre de cette thèse ont été directement communiqués aux propriétaires des puits participants à l'étude. C'est également dans ce but que ce travail de doctorat a été réalisé en collaboration avec l'Agence de la Santé et des Services Sociaux de l'Abitibi-Témiscamingue.

Les résultats de ce travail, en particulier ceux ayant trait à la géochimie et à la minéralogie de l'arsenic, ont également des implications pour la gestion des matériaux riches en arsenic, comme les stériles et les résidus miniers. Les sites miniers d'extraction de l'or et de métaux de base sont souvent associés à des problèmes de pollution liés à l'abondance de déchets riches en arsenic, et leur gestion constitue un enjeu pour l'environnement. Les nouvelles connaissances sur les sources minérales d'arsenic pourraient être utiles à l'industrie afin d'adapter ses actions en vue de réduire la contamination des eaux minières. En particulier, la minéralogie et le comportement géochimique de l'arsenic doivent être pris en compte pour prévenir les problèmes de drainage minier contaminé et leurs effets néfastes sur l'environnement. C'est dans cet objectif que l'Institut canadien des mines, de la métallurgie et du pétrole section Amos a contribué au financement de ce projet, et assure la communication des résultats scientifiques avec l'industrie minière dans la région.

5.2 Considérations pour les futures recherches

Ce travail de doctorat a apporté de nouveaux éléments de réponse sur l'origine et la distribution de l'arsenic dans l'eau souterraine des aquifères rocheux fracturés. Se faisant, il a également contribué à mettre en lumière des lacunes de connaissances que la recherche scientifique devra tenter de combler à l'avenir. Ces lacunes scientifiques concernent essentiellement la spéciation de l'arsenic, le rôle des sources primaires et secondaires dans la mobilisation de l'arsenic et la variabilité spatio-temporelle des concentrations en arsenic. À cela on peut ajouter des éléments qui ont simplement été évoqués dans le cadre de cette thèse, à savoir le rôle des microorganismes et l'influence des activités humaines sur la géochimie de l'arsenic géogène.

La spéciation de l'arsenic a besoin d'être davantage étudiée dans les aquifères rocheux. La plupart des études se sont jusqu'à présent concentrées sur la phase dissoute de l'arsenic, or il est vraissemblable que les phases colloïdale et particulaire jouent un rôle déterminant dans la mobilité et le transport de l'arsenic. En particulier, la méthodologie consistant à filtrer à 0,45 µm et à acidifier les échantillons empêche l'identification de ces phases en incluant les colloïdes et particules fines en suspension dans la phase dissoute, et en écartant les plus grossières. Les futurs travaux devront trouver de nouvelles méthodes afin de mieux comprendre la répartition de l'arsenic entre les différentes phases et leurs implications dans la mobilisation de l'arsenic. En outre, des informations sur les variations dans la distribution spatio-temporelle des espèces d'arsenic seraient particulièrement utiles, notamment en relation avec les paramètres hydrogéologiques et les conditions d'écoulement. Par ailleurs, l'acquisition de données sur les espèces organiques, qui pourraient représenter une proportion plus importante des espèces d'arsenic qu'escomptée, constitue un enjeu important afin de mieux comprendre le rôle des eaux souterraines dans le cycle géochimique global de l'arsenic. Les concentrations des principales espèces dissoutes d'arsenic devraient être plus souvent déterminées dans les études portant sur l'arsenic dans l'eau souterraine, alors que des méthodes d'analyse fiables, faciles à mettre en œuvre et peu couteûses sont désormais disponibles.

Les mécanismes contrôlant la libération de l'arsenic dans l'eau souterraine ont encore besoin d'être précisés. Si la plupart des minéraux primaires d'arsenic sont connus, leur contribution potentielle à la contamination à l'arsenic reste à évaluer. Ainsi, la recherche devra s'attacher à mieux comprendre les facteurs responsables de l'altération des minéraux sulfurés dans les aquifères, notamment les liens avec les conditions géochimiques, les taux de dissolution des minéraux ou encore les interactions eau-roche à la surface des fractures. Le comportement des sources secondaires nécessite également d'être approfondi. L'identification des minéraux impliqués dans la séquestration de l'arsenic dans les fractures, couplée à des progrès dans la modélisation hydrogéochimique, est indispensable pour mieux appréhender le rôle des sources secondaires d'arsenic. Bien que représentant un défi technique, des investigations minéralogiques à la surface des fractures pourraient considérablement améliorer les connaissances sur les sources d'arsenic dans l'eau souterraine. Ces investigations pourraient être menées dans différents contextes (aquifère captif/libre, zone saturée/non saturée) susceptibles d'être le siège de mécanismes de mobilisation différents.

La variabilité spatiale des concentrations en arsenic dans les eaux souterraines a également besoin d'être documentée. Des progrés sont particulièrement attendus pour expliciter davantage le lien entre les mécanismes de mobilisation et les paramètres hydrogéologiques. En outre, les variations locales au sein des systèmes de fractures doivent également être considérées. Celles-ci ont vraisemblablement un impact majeur sur les concentrations mesurées dans les infrastructures de captage. La méconnaissance des caractéristiques chimiques de l'eau souterraine issues des factures contribuant à l'écoulement est problématique pour l'interpretation des données. Les techniques permettant d'échantillonner l'eau des fractures telles que l'usage d'obturateurs (« packers ») peuvent être utiles, mais elles doivent être associées à une connaissance approfondie de l'écoulement dans les infrastructures de captage. Sur un autre plan, la variabilité temporelle des concentrations en arsenic constitue une question essentielle qui nécessite d'être abordée rapidement. La progression des connaissances passera par la mise en œuvre de suivis temporels dans les aquifères. L'interprétation des données devra se baser sur de solides connaissances des paramètres hydrogéologiques et des mécanismes de mobilisation pour expliciter les processus à l'origine de ces variations. Les variations saisonnières devront probablement être considérées en priorité, avant d'envisager les changements pluriannuels relatifs à l'impact des changements climatiques.

Enfin, des éléments importants qui n'ont pas fait l'objet d'investigations spécifiques dans le cadre de cette thèse peuvent encore être cités. Le rôle des microorganismes sur la géochimie de l'arsenic dans les aquifères rocheux reste en grande partie à élucider. Bien que les microorganismes soient considérés comme peu abondants dans les aquifères rocheux, certaines études dans différents contextes hydrogéologiques suggèrent que l'activité microbienne est un facteur déterminant pour la spéciation de l'arsenic, l'oxydation des minéraux sulfurés, la précipitation et dissolution des minéraux secondaires et divers autres mécanismes affectant la qualité de l'eau. Par ailleurs, les impacts indirects des activités humaines sur l'arsenic géogène ont également besoin d'être documentés. Les activités qui exploitent l'eau souterraine et celles susceptibles de dégrader la qualité de la ressource (agriculture, industrie, activités minières) auront probablement les impacts indirects les plus significatifs. À noter que ces activités auront également besoin d'être prises en compte pour évaluer les impacts des changements climatiques sur la qualité de l'eau souterraine.

BIBLIOGRAPHIE GÉNÉRALE

Acharyya, S. K., Shah, B. A., Ashyiya, I. D., Pandey, Y., 2005. Arsenic contamination in groundwater from parts of Ambagarh-Chowki block, Chhattisgarh, India : source and release mechanism. Environmental Geology 49, 148–158.

Ahn, J. S., 2012. Geochemical occurrences of arsenic and fluoride in bedrock groundwater : a case study in Geumsan County, Korea. Environmental Geochemistry and Health 34, 43–54.

Ahn, J. S., Cho, Y.-C., 2013. Predicting natural arsenic contamination of bedrock groundwater for a local region in Korea and its application. Environmental Earth Sciences 68, 2123–2132.

Appelo, C. A. J., Postma, D., 2005. Geochemistry, groundwater and pollution, 2nd edition. A.A. Balkema Publishers, Amsterdam (Netherlands).

Asta, M. P., Cama, J., Ayora, C., Acero, P., de Giudici, G., 2010. Arsenopyrite dissolution rates in O_2-bearing solutions. Chemical Geology 273, 272 – 285.

ASTM, 2013. Standard test method for laboratory weathering of solid materials using a humidity cell. D5744-13. ASTM International.

Ayotte, J. D., Belaval, M., Olson, S. A., Burow, K. R., Flanagan, S. M., Hinkle, S. R., Lindsey, B. D., 2015. Factors affecting temporal variability of arsenic in groundwater used for drinking water supply in the United States. Science of the Total Environment 505, 1370–1379.

Ayotte, J. D., Montgomery, D. L., Flanagan, S. M., Robinson, K. W., 2003. Arsenic in groundwater in eastern New England : occurrence, controls, and human health implications. Environmental Science & Technology 37, 2075–2083.

Bednar, A., Garbarino, J., Burkhardt, M., Ranville, J., Wildeman, T., 2004. Field and laboratory arsenic speciation methods and their application to natural-water analysis. Water Research 38 (2), 355–364.

Belova, D. A., Lakshtanov, L., Carneiro, J., Stipp, S. L. S., 2014. Nickel adsorption on chalk and calcite. Journal of Contaminant Hydrology 170, 1–9.

Berg, M., Tran, H. C., Nguyen, T. C., Pham, H. V., Schertenleib, R., Giger, W., 2001. Arsenic contamination of groundwater and drinking water in Vietnam : a human health threat. Environmental Science & Technology 35 (13), 2621–2626.

Bhattacharya, P., Jacks, G., Brömssen, M. v., 2010. Arsenic in Swedish groundwater - Mobility and risk for naturally elevated concentrations : Final Report. Universitetsservice AB.

Bhattacharya, P., Sracek, O., Eldvall, B., Asklund, R., Barmen, G., Jacks, G., Koku, J., Gustafsson, J.-E., Singh, N., Balfors, B. B., 2012. Hydrogeochemical study on the contamination of water resources in a part of Tarkwa mining area, Western Ghana. Journal of African Earth Sciences 66-67, 72–84.

Bloomfield, J. P., Williams, R. J., Gooddy, D. C., Cape, J. N., Guha, P., 2006. Impacts of climate change on the fate and behaviour of pesticides in surface and groundwater - a UK perspective. Science of the Total Environment 369, 163–177.

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2016. A review and evaluation of the impacts of climate change on geogenic arsenic in groundwater from fractured bedrock aquifers. Water, Air, & Soil Pollution 227 (9), 296.

Bondu, R., Cloutier, V., Rosa, E., Benzaazoua, M., 2017. Mobility and speciation of geogenic arsenic in bedrock groundwater from the Canadian Shield in western Quebec, Canada. Science of The Total Environment 574, 509–519.

Borba, R. P., Figueiredo, B. R., Matschullat, J., 2003. Geochemical distribution of arsenic in waters, sediments and weathered gold mineralized rocks from Iron Quadrangle, Brazil. Environmental Geology 44, 39–52.

Bottomley, D., 1984. Origins of some arseniferous groundwaters in Nova Scotia and New Brunswick, Canada. Journal of Hydrology 69, 223–257.

Bottomley, D., Chan, L., Katz, A., Starinsky, A., Clark, I., 2003. Lithium isotope geochemistry and origin of Canadian Shield brines. Ground Water 41 (6), 847–856.

Bowell, R. J., Alpers, C. N., Jamieson, H. E., Nordstrom, D. K., Majzlan, J., 2014. The environmental geochemistry of arsenic - An overview. Reviews in Mineralogy and Geochemistry 79 (1), 1–16.

Boyle, D. R., Turner, R. J. W., Hall, G. E. M., 1998. Anomalous arsenic concentrations in groundwaters of an island community, Bowen Island, British Columbia. Environmental Geochemistry and Health 20, 199–212.

Bretzler, A., Johnson, C. A., 2015. The geogenic contamination handbook : Addressing arsenic and fluoride in drinking water. Applied Geochemistry 63, 642–646.

Campbell, K. M., Nordstrom, D. K., 2014. Arsenic speciation and sorption in natural environments. Reviews in Mineralogy and Geochemistry 79 (1), 185–216.

Carneiro, J. F., Boughriba, M., Correia, A., Zarhloule, Y., Rimi, A., El Houadi, B., 2010. Evaluation of climate change effects in a coastal aquifer in Morocco using a density-dependent numerical model. Environmental Earth Sciences 61, 241–252.

CEAEQ, 2012. Protocole de lixiviation pour les espèces inorganiques. MA. 100 - Lix.com.1.1. Centre d'expertise en analyse environnementale du Québec. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http ://www.ceaeq.gouv.qc.ca/methodes/pdf/MA100Lixcom11.pdf.

CEAEQ, 2014. Détermination des métaux : méthode par spectrométrie de masse à source ionisante au plasma d'argon. MA. 200 - Mét 1.2. Centre d'expertise en analyse environnementale du Québec. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http ://www.ceaeq.gouv.qc.ca/methodes/pdf/MA200Met12.pdf.

Chandra, A., Gerson, A. R., 2010. The mechanisms of pyrite oxidation and leaching : a fundamental perspective. Surface Science Reports 65 (9), 293–315.

Chatterjee, A., Das, D., Chakraborti, D., 1993. A study of ground water contamination by arsenic in the residential area of Behala, Calcutta due to industrial pollution. Environmental Pollution 80 (1), 57–65.

Chopard, A., Benzaazoua, M., Plante, B., Bouzahzah, H., Marion, P., 2015. Kinetic tests to evaluate the relative oxidation rates of various sulfides and sulfosalts. In : ICARDS2015 Proceedings, Santiago du Chile (Chile).

Christodoulidou, M., Charalambous, C., Aletrari, M., Kanari, P. N., Petronda, A., Ward, N., 2012. Arsenic concentrations in groundwaters of Cyprus. Journal of hydrology 468, 94–100.

Cloutier, V., Rosa, E., Nadeau, S., Dallaire, P.-L., Blanchette, D., Roy, M., 2015. Projet d'acquisition de connaissances sur les eaux souterraines de l'Abitibi-Témiscamingue (partie 2). Rapport final déposé au Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques dans le cadre du Programme d'acquisition de connaissances sur les eaux souterraines du Québec. Rapport de recherche P002. R3.

Cloutier, V., Veillette, J., Roy, M., Gagnon, F., Bois, D., 2007. Regional hydrogeochemistry of groundwater in fractured Canadian Shield rock and glaciofluvial formations in Abitibi, Quebec. In : Proceedings, 60th Canadian Geotechnical Conference and 8th Joint CGS/IAH-CNC Groundwater Conference, Ottawa (Canada).

Craw, D., Bowell, R. J., 2014. The characterization of arsenic in mine waste. Reviews in Mineralogy and Geochemistry 79 (1), 473–505.

Dams, J., Salvadore, E., Van Daele, T., Ntegeka, V., Willems, P., Batelaan, O., 2012. Spatio-temporal impact of climate change on the groundwater system. Hydrology and Earth System Sciences 16, 1517–1531.

D'Angelo, E., Zeigler, G., Beck, E. G., Grove, J., Sikora, F., 2012. Arsenic species in broiler (gallus gallus domesticus) litter, soils, maize (zea mays l.), and groundwater from litter-amended fields. Science of The Total Environment 438, 286–292.

Dixit, S., Hering, J. G., 2003. Comparison of arsenic (V) and arsenic (III) sorption onto iron oxide minerals : implications for arsenic mobility. Environmental Science & Technology 37 (18), 4182–4189.

Douglas, M., Clark, I., Raven, K., Bottomley, D., 2000. Groundwater mixing dynamics at a Canadian Shield mine. Journal of Hydrology 235 (1), 88–103.

Drahota, P., Filippi, M., 2009. Secondary arsenic minerals in the environment : A review. Environment International 35, 1243–1255.

Essington, M. E., 2004. Soil and water chemistry : An integrative approach. CRC press, Boca Raton (USA).

Farnfield, H. R., Marcilla, A. L., Ward, N. I., 2012. Arsenic speciation and trace element analysis of the volcanic río Agrio and the geothermal waters of Copahue, Argentina. Science of the Total Environment 433, 371–378.

Figura, S., Livingstone, D. M., Hoehn, E., Kipfer, R., 2011. Regime shift in groundwater temperature triggered by the Arctic Oscillation. Geophysical Research Letters 38, L23401.

Flanagan, S. V., Marvinney, R. G., Zheng, Y., 2015. Influences on domestic well water testing behavior in a Central Maine area with frequent groundwater arsenic occurrence. Science of the Total Environment 505, 1274–1281.

Foley, N. K., Ayuso, R. A., 2008. Mineral sources and transport pathways for arsenic release in a coastal watershed, USA. Geochemistry : Exploration, Environment, Analysis 8, 59–75.

Foster, A. L., 2003. Spectroscopic investigations of arsenic species in solid phases. In : Welch, A. H., Stollenwerk, K. G. (Eds.), Arsenic in Ground Water : Geochemistry and Occurrence. Springer, Massachusetts : Kluwer Academic, pp. 27–65.

Frengstad, B., Skrede, A. K. M., Banks, D., Krog, J. R., Siewers, U., 2000. The chemistry of Norwegian groundwaters : III. The distribution of trace elements in 476 crystalline bedrock groundwaters, as analysed by ICP-MS techniques. Science of The Total Environment 246 (1), 21–40.

Frost, F., Franke, D., Pierson, K., Woodruff, L., Raasina, B., Davis, R., Davies, J., 1993. A seasonal study of arsenic in groundwater, Snohomish County, Washington, USA. Environmental Geochemistry and Health 15, 209–214.

Gagnon, F., Lampron-Goulet, É., Normandin, L., Langlois, M.-F., 2016. Measurements of arsenic in the urine and nails of individuals exposed to low concentrations of arsenic in drinking water from private wells in a rural region of Quebec, Canada. Journal of Environmental Health 78 (6), 76–83.

Gascoyne, M., Kamineni, D., 1994. The hydrogeochemistry of fractured plutonic rocks in the Canadian Shield. Applied Hydrogeology 2 (2), 43–49.

Goutier, J., Lacroix, S., 1992. Géologie du secteur de la Faille de Porcupine-Destor dans les cantons de Destor et Duparquet. Ministère de l'Énergie et des Ressources : Québec, MB, 92–06.

Grantham, D. A., Jones, J. F., 1977. Arsenic contamination of water wells in Nova Scotia. Journal (American Water Works Association) 69 (12), 653–657.

Green, T. R., Taniguchi, M., Kooi, H., Gurdak, J. J., Allen, D. M., Hiscock, K. M., Treidel, H., Aureli, A., 2011. Beneath the surface of global change : Impacts of climate change on groundwater. Journal of Hydrology 405, 532–560.

Green-Pedersen, H., Jensen, B., Pind, N., 1997. Nickel adsorption on MnO_2, $Fe(OH)_3$, montmorillonite, humic acid and calcite : a comparative study. Environmental Technology 18 (8), 807–815.

Gurdak, J. J., McMahon, P. B., Bruce, B. W., 2012. Vulnerability of groundwater quality to human activity and climate change and variability, High Plains aquifer, USA. In : Treidel, H., Martin-Bordes, J. L., Gurdak, J. J. (Eds.), Climate Change Effects on Groundwater Resources - A Global Synthesis of Findings and Recommendations. Taylor & Francis Group, pp. 145–168.

Harte, P. T., Ayotte, J. D., Hoffman, A., Revesz, K. M., Belaval, M., Lamb, S., Boehlke, J. K., 2012. Heterogeneous redox conditions, arsenic mobility, and groundwater flow in a fractured-rock aquifer near a waste repository site in New Hampshire, USA. Hydrogeology Journal 20, 1189–1201.

Henke, K., 2009. Arsenic : environmental chemistry, health threats and waste treatment. John Wiley & Sons, West Sussex (UK).

Hocq, M., Verpaelst, P., 1994. Les sous-provinces de l'Abitibi et du Pontiac. In : Dubé, C. (Ed.), Géologie du Québec. Ministère des Ressources naturelles, Gouvernement du Québec, pp. 21–37.

Intergovernmental Panel on Climate Change, 2014. Climate change 2013 : The physical science basis. Contribution of working group I to the fifth assessment report of the intergovernmental panel on climate change (eds Stocker, T. F. et al.). Cambridge University Press (UK).

Jackson, C. R., Meister, R., Prudhomme, C., 2011. Modelling the effects of climate change and its uncertainty on UK Chalk groundwater resources from an ensemble of global climate model projections. Journal of Hydrology 399, 12–28.

Jackson, D. A., Nesbitt, H. W., Scaini, M. J., Duggal, A., Bancroft, G. M., 2003. Gersdorffite (NiAsS) chemical state properties and reactivity toward air and aerated, distilled water. American Mineralogist 88 (5-6), 890–900.

Jyrkama, M. I., Sykes, J. F., 2007. The impact of climate change on spatially varying groundwater recharge in the grand river watershed (Ontario). Journal of Hydrology 338 (3), 237–250.

Kim, K., Kim, S.-H., Jeong, G. Y., Kim, R.-H., 2012. Relations of As concentrations among groundwater, soil, and bedrock in Chungnam, Korea : Implications for As mobilization in groundwater according to the As-hosting mineral change. Journal of Hazardous Materials 199, 25–35.

Klassen, R., Douma, S., Ford, A., Rencz, A., Grunsky, E., 2009. Geoscience modelling of relative variation in natural arsenic hazard potential in New Brunswick. Geological Survey of Canada, Current Research 2009-7, 9 p.

Kløve, B., Ala-Aho, P., Bertrand, G., Gurdak, J. J., Kupfersberger, H., Kværner, J., Muotka, T., Mykrä, H., Preda, E., Rossi, P., et al., 2014. Climate change impacts on groundwater and dependent ecosystems. Journal of Hydrology 518, 250–266.

Kundzewicz, Z. W., Doell, P., 2009. Will groundwater ease freshwater stress under climate change? Hydrological Sciences Journal 54 (4), 665–675.

Kurylyk, B., Bourque, C.-A., MacQuarrie, K., 2013. Potential surface temperature and shallow groundwater temperature response to climate change : an example from a small forested catchment in east-central New Brunswick (Canada). Hydrology and Earth System Sciences 17, 2701–2716.

Lalonde, J.-P., Chouinard, N., Bergeron, R., 1981. Atlas géochimique des eaux souterraines, région de l'Abitibi. Ministère de l'Énergie et des Ressources, Direction générale de la recherche géologique et minérale, Service de géophysique-géochimie.

Lampron-Goulet, É., 2012. Surveillance biologique de l'exposition à l'arsenic inorganique et des perturbations endocriniennes associées dans une population s'approvisionnant en eau potable par des puits privés dans la région de l'Abitibi-Témiscamingue, au Québec. Master's thesis, Université de Sherbrooke.

Legault, M., Goutier, J., Beaudoin, G., M, A., 2005. Synthèse métallogénique de la Faille de Porcupine-Destor, Sous-province de l'Abitibi. Ministère des Ressources Naturelles et de la Faune, Québec.

Lehner, S., Savage, K., 2008. The effect of As, Co, and Ni impurities on pyrite oxidation kinetics : Batch and flow-through reactor experiments with synthetic pyrite. Geochimica et Cosmochimica Acta 72 (7), 1788–1800.

Lengke, M. F., Sanpawanitchakit, C., Tempel, R. N., 2009. The oxidation and dissolution of arsenic-bearing sulfides. The Canadian Mineralogist 47 (3), 593–613.

Lerner, D. N., Harris, B., 2009. The relationship between land use and groundwater resources and quality. Land Use Policy 26, Supplement 1, S265–S273.

Lin, Z., Puls, R., 2000. Adsorption, desorption and oxidation of arsenic affected by clay minerals and aging process. Environmental Geology 39 (7), 753–759.

Lipfert, G., Reeve, A. S., Sidle, W. C., Marvinney, R., 2006. Geochemical patterns of arsenic-enriched ground water in fractured, crystalline bedrock, Northport, Maine, USA. Applied Geochemistry 21, 528–545.

Lipfert, G., Sidle, W. C., Reeve, A. S., Ayuso, R. A., Boyce, A. J., 2007. High arsenic concentrations and enriched sulfur and oxygen isotopes in a fractured-bedrock groundwater system. Chemical Geology 242, 385–399.

Lottermoser, B., 2003. Mine wastes : characterization, treatment and environmental impacts. Springer Berlin Heidelberg, New York (USA).

Loukola-Ruskeeniemi, K., Tanskanen, H., Lahermo, P., 1999. Anomalously high arsenic concentrations in spring waters in Kittilä, Finnish Lapland. Geological Survey of Finland Special Paper 27, 97–102.

Lu, P., Zhu, C., 2011. Arsenic Eh–pH diagrams at 25 °C and 1 bar. Environmental Earth Sciences 62 (8), 1673–1683.

Maguffin, S. C., Kirk, M. F., Daigle, A. R., Hinkle, S. R., Jin, Q., 2015. Substantial contribution of biomethylation to aquifer arsenic cycling. Nature Geoscience 8 (4), 290–293.

Majzlan, J., Drahota, P., Filippi, M., 2014. Parageneses and crystal chemistry of arsenic minerals. Reviews in Mineralogy and Geochemistry 79 (1), 17–184.

Mango, H., Ryan, P., 2015. Source of arsenic-bearing pyrite in southwestern Vermont, USA : Sulfur isotope evidence. Science of The Total Environment 505, 1331–1339.

Manning, A. H., Verplanck, P. L., Caine, J. S., Todd, A. S., 2013. Links between climate change, water-table depth, and water chemistry in a mineralized mountain watershed. Applied Geochemistry 37, 64–78.

Mast, M. A., Turk, J. T., Clow, D. W., Campbell, D. H., 2011. Response of lake chemistry to changes in atmospheric deposition and climate in three high-elevation wilderness areas of Colorado. Biogeochemistry 103, 27–43.

MDDELCC, 2015. Portrait régional de l'eau - Abitibi-Témiscamingue. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http ://www.mddelcc.gouv.qc.ca/eau/regions/region08/08-abitibi

MDDELCC, 2016. Répertoire des dépôts de sols et de résidus industriels. Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques du Québec. http ://www.mddelcc.gouv.qc.ca/sol/residusind/resultats.asp.

Meranger, J., Subramanian, K., McCurdy, R., 1984. Arsenic in Nova Scotian groundwater. Science of The Total Environment 39, 49–55.

MERN, 2016. Système d'information géominière (SIGEOM). Ministère de l'Énergie et des Ressources naturelles du Québec. sigeom.mines.gouv.qc.ca.

Montcoudiol, N., Molson, J., Lemieux, J.-M., 2015. Groundwater geochemistry of the Outaouais Region (Québec, Canada) : a regional-scale study. Hydrogeology Journal 23 (2), 377–396.

Nadeau, S., Rosa, E., Cloutier, V., Daigneault, R.-A., Veillette, J., 2015. A GIS-based approach for supporting groundwater protection in eskers : Application to sand and gravel extraction activities in Abitibi-Témiscamingue, Quebec, Canada. Journal of Hydrology : Regional Studies 4, 535–549.

Naujokas, M. F., Anderson, B., Ahsan, H., Aposhian, H. V., Graziano, J. H., Thompson, C., Suk, W. A., 2013. The broad scope of health effects from chronic arsenic exposure : update on a worldwide public health problem. Environmental Health Perspectives (Online) 121 (3), 295.

Nickson, R., McArthur, J., Ravenscroft, P., Burgess, W., Ahmed, K., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Applied Geochemistry 15 (4), 403–413.

Niu, B., Loáiciga, H. A., Wang, Z., Zhan, F. B., Hong, S., 2014. Twenty years of global groundwater research : A Science Citation Index Expanded-based bibliometric survey (1993-2012). Journal of Hydrology 519, Part A, 966 – 975.

Nordstrom, D. K., 2009. Acid rock drainage and climate change. Journal of Geochemical Exploration 100, 97–104.

Nordstrom, D. K., Blowes, D. W., Ptacek, C. J., 2015. Hydrogeochemistry and microbiology of mine drainage : An update. Applied Geochemistry 57, 3–16.

O'Day, P. A., 2006. Chemistry and mineralogy of arsenic. Elements 2 (2), 77–83.

Okkonen, J., Jyrkama, M., Kløve, B., 2010. A conceptual approach for assessing the impact of climate change on groundwater and related surface waters in cold regions (Finland). Hydrogeology Journal 18 (2), 429–439.

O'Reilly, J., Watts, M., Shaw, R., Marcilla, A., Ward, N., 2010. Arsenic contamination of natural waters in San Juan and La Pampa, Argentina. Environmental Geochemistry and Health 32 (6), 491–515.

O'Shea, B., Stransky, M., Leitheiser, S., Brock, P., Marvinney, R. G., Zheng, Y., 2015. Heterogeneous arsenic enrichment in meta-sedimentary rocks in central Maine, United States. Science of The Total Environment 505, 1308–1319.

Pandey, P. K., Sharma, R., Roy, M., Roy, S., Pandey, M., 2006. Arsenic contamination in the Kanker district of central-east India : geology and health effects. Environmental Geochemistry and Health 28, 409–420.

Parkhurst, D. L., Appelo, C., 1999. User's guide to PHREEQC (Version 2) : A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations. U.S. Geological Survey Water-Investigations Report 99-4259, Denver (USA).

Parviainen, A., Loukola-Ruskeeniemi, K., Tarvainen, T., Hatakka, T., Härmä, P., Backman, B., Ketola, T., Kuula, P., Lehtinen, H., Sorvari, J., Pyy, O., Ruskeeniemi, T., Luoma, S., 2015. Arsenic in bedrock, soil and groundwater - The first arsenic guidelines for aggregate production established in Finland. Earth-Science Reviews 150, 709–723.

Pearce, T. D., Ford, J. D., Prno, J., Duerden, F., Pittman, J., Beaumier, M., Berrang-Ford, L., Smit, B., 2011. Climate change and mining in Canada. Mitigation and Adaptation Strategies For Global Change 16, 347–368.

Peryea, F., Creger, T., 1994. Vertical distribution of lead and arsenic in soils contaminated with lead arsenate pesticide residues. Water, Air, & Soil Pollution 78 (3-4), 297–306.

Peters, S. C., 2008. Arsenic in groundwaters in the Northern Appalachian Mountain belt : A review of patterns and processes. Journal of Contaminant Hydrology 99, 8–21.

Peters, S. C., Blum, J. D., 2003. The source and transport of arsenic in a bedrock aquifer, New Hampshire, USA. Applied Geochemistry 18, 1773–1787.

Pili, E., Tisserand, D., Bureau, S., 2013. Origin, mobility, and temporal evolution of arsenic from a low-contamination catchment in Alpine crystalline rocks. Journal of Hazardous Materials 262, 887–895.

Plante, B., Benzaazoua, M., Bussière, B., 2011. Predicting geochemical behaviour of waste rock with low acid generating potential using laboratory kinetic tests. Mine Water and the Environment 30 (1), 2–21.

Plante, B., Benzaazoua, M., Bussière, B., Biesinger, M., Pratt, A., 2010. Study of Ni sorption onto Tio mine waste rock surfaces. Applied Geochemistry 25 (12), 1830–1844.

Poissant, L.-M., 1997. La contamination par l'arsenic des puits domestiques en Abitibi-Témiscamingue. Régie régionale de la santé et des services sociaux de l'Abitibi-Témiscamingue, Direction de la santé publique, Rouyn-Noranda (Canada).

Postma, D., Larsen, F., Thai, N. T., Trang, P. T. K., Jakobsen, R., Nhan, P. Q., Long, T. V., Viet, P. H., Murray, A. S., 2012. Groundwater arsenic concentrations in Vietnam controlled by sediment age. Nature Geoscience 5 (9), 656–661.

Ravenscroft, P., Brammer, H., Richards, K., 2009. Arsenic pollution : a global synthesis. Wiley-Blackwell, West Sussex (UK).

Reyes, F. A. P., Crosta, G. B., Frattini, P., Basiricò, S., Della Pergola, R., 2015. Hydrogeochemical overview and natural arsenic occurrence in groundwater from alpine springs (upper Valtellina, Northern Italy). Journal of Hydrology 529, 1530–1549.

Richard, S. K., Chesnaux, R., Rouleau, A., Morin, R., Walter, J., Rafini, S., 2014. Field evidence of hydraulic connections between bedrock aquifers and overlying granular aquifers : examples from the Grenville Province of the Canadian Shield. Hydrogeology journal 22 (8), 1889–1904.

Rodríguez-Lado, L., Sun, G., Berg, M., Zhang, Q., Xue, H., Zheng, Q., Johnson, C. A., 2013. Groundwater arsenic contamination throughout China. Science 341 (6148), 866–868.

Rouleau, A., Clark, I. D., Bottomley, D. J., Roy, D. W., 2013. In : Rivera, A. (Ed.), Canada's Groundwater Resources. Fitzhenry & Whiteside, pp. 415–442.

Ruskeeniemi, T., Backman, B., Loukola-Ruskeeniemi, K., Sorvari, J., Lehtinen, H., Schultz, E., Mäkelä-Kurtto, R., Rossi, E., Vaajasaari, K., Ämer Bilaletdin, 2011. Arsenic in the Pirkanmaa region, Southern Finland : from identification through to risk assessment to risk managment. Geological Survey of Finland, Special Paper 49, 21–227.

Ryan, P. C., Kim, J., Wall, A. J., Moen, J. C., Corenthal, L. G., Chow, D. R., Sullivan, C. M., Bright, K. S., 2011. Ultramafic-derived arsenic in a fractured bedrock aquifer. Applied Geochemistry 26, 444–457.

Ryan, P. C., Kim, J. J., Mango, H., Hattori, K., Thompson, A., 2013. Arsenic in a fractured slate aquifer system, New England, USA : Influence of bedrock geochemistry, groundwater flow paths, redox and ion exchange. Applied Geochemistry 39, 181–192.

Ryan, P. C., West, D. P., Hattori, K., Studwell, S., Allen, D. N., Kim, J., 2015. The influence of metamorphic grade on arsenic in metasedimentary bedrock aquifers : A case study from Western New England, USA. Science of the Total Environment 505, 1320–1330.

Sahoo, N. R., Pandalai, H. S., 2000. Secondary geochemical dispersion in the Precambrian auriferous Hutti-Maski schist belt, Raichur district, Karnataka, India. Part I : anomalies of As, Sb, Hg and Bi in soil and groundwater. Journal of Geochemical Exploration 71, 269–289.

Serpa, C., Batterson, M., Guzzwell, K., 2009. The influence of bedrock and mineral occurrences on arsenic concentrations in groundwater wells in the Gander Bay Area, Newfoundland. Current Research. Newfoundland and Labrador Department of Natural Resources Geological Survey, Report 09–1, 315–337.

Serrat-Capdevila, A., Valdés, J. B., Pérez, J. G., Baird, K., Mata, L. J., Maddock, T., 2007. Modeling climate change impacts–and uncertainty–on the hydrology of a riparian system : The San Pedro Basin (Arizona/Sonora). Journal of Hydrology 347, 48–66.

Shapiro, A. M., 2002. Cautions and suggestions for geochemical sampling in fractured rock. Groundwater Monitoring & Remediation 22 (3), 151–164.

Sharma, V. K., Sohn, M., 2009. Aquatic arsenic : Toxicity, speciation, transformations, and remediation. Environment International 35, 743–759.

Shukla, D. P., Dubey, C. S., Singh, N. P., Tajbakhsh, M., Chaudhry, M., 2010. Sources and controls of arsenic contamination in groundwater of Rajnandgaon and Kanker District, Chattisgarh Central India. Journal of Hydrology 395, 49–66.

Sidle, W. C., 2002. $^{18}O_{SO_4}$ and $^{18}O_{H_2O}$ as prospective indicators of elevated arsenic in the Goose River ground-watershed, Maine. Environmental Geology 42, 350–359.

Sidle, W. C., Fischer, R. A., 2003. Detection of ^{3}H and ^{85}Kr in groundwater from arsenic-bearing crystalline bedrock of the Goose River basin, Maine. Environmental Geology 44, 781–789.

Sidle, W. C., Wotten, B., Murphy, E., 2001. Provenance of geogenic arsenic in the Goose River basin, Maine, USA. Environmental Geology 41, 62–73.

Smedley, P., Kinniburgh, D. G., 2013. Arsenic in groundwater and the environment. In : Selinus, O., Alloway, B., Centeno, J., Finkelman, R., Fuge, R., Lindh, U., Smedley, P. (Eds.), Essentials of Medical Geology. Springer, pp. 279–310.

Smedley, P. L., 1996. Arsenic in rural groundwater in Ghana. Journal of African Earth Sciences 22, 459–470.

Smedley, P. L., Kinniburgh, D. G., 2002. A review of the source, behaviour and distribution of arsenic in natural waters. Applied Geochemistry 17, 517–568.

Smedley, P. L., Knudsen, J., Maiga, D., 2007. Arsenic in groundwater from mineralised Proterozoic basement rocks of Burkina Faso. Applied Geochemistry 22, 1074–1092.

Smith, A. E., Lincoln, R. A., Paulu, C., Simones, T. L., Caldwell, K. L., Jones, R. L., Backer, L. C., 2016. Assessing arsenic exposure in households using bottled water or point-of-use treatment systems to mitigate well water contamination. Science of The Total Environment 544, 701–710.

Sorg, T. J., Chen, A. S., Wang, L., 2014. Arsenic species in drinking water wells in the USA with high arsenic concentrations. Water Research 48, 156 – 169.

Spayd, S. E., Robson, M. G., Buckley, B. T., 2015. Whole-house arsenic water treatment provided more effective arsenic exposure reduction than point-of-use water treatment at New Jersey homes with arsenic in well water. Science of the Total Environment 505, 1361–1369.

Stachowicz, M., Hiemstra, T., Van Riemsdijk, W. H., 2007. Arsenic-bicarbonate interaction on goethite particles. Environmental Science & Technology 41 (16), 5620–5625.

Stuart, M. E., Gooddy, D. C., Bloomfield, J. P., Williams, A. T., 2011. A review of the impact of climate change on future nitrate concentrations in groundwater of the UK. Science of the Total Environment 409, 2859–2873.

Taylor, C. A., Stefan, H. G., 2009. Shallow groundwater temperature response to climate change and urbanization. Journal of Hydrology 375, 601–612.

Taylor, R. G., Scanlon, B., Döll, P., Rodell, M., Van Beek, R., Wada, Y., Longuevergne, L., Leblanc, M., Famiglietti, J. S., Edmunds, M., et al., 2013. Ground water and climate change. Nature Climate Change 3, 322–329.

Thibaudeau, P., Veillette, J., 2005. Géologie des formations en surface et histoire glaciaire : Lac Chicobi, Québec. Commission géologique du Canada.

Tisserand, D., Pili, E., Hellmann, R., Boullier, A.-M., Charlet, L., 2014. Geogenic arsenic in groundwaters in the western Alps. Journal of Hydrology 518, Part C, 317–325.

Todd, A. S., Manning, A. H., Verplanck, P. L., Crouch, C., McKnight, D. M., Dunham, R., 2012. Climate-change-driven deterioration of water quality in a mineralized watershed. Environmental Science & Technology 46, 9324–9332.

Treidel, H., Martin-Bordes, J., Gurdak, J. (Eds.), 2012. Climate change effects on groundwater resources : a global synthesis of findings and recommendations. CRC Press/Balkema, Leiden (Netherlands).

UNESCO, 2008. Groundwater Resources Assessment under the Pressures of Humanity and Climate Change (GRAPHIC) : A Framework Document. GRAPHIC Series Number 2. United Nations Educational, Scientific, and Cultural Organization (UNESCO), Paris (France).

van Roosmalen, L., Sonnenborg, T. O., Jensen, K. H., 2009. Impact of climate and land use change on the hydrology of a large-scale agricultural catchment. Water Resources Research 45, W00A15.

Verplanck, P. L., Mueller, S. H., Goldfarb, R. J., Nordstrom, D. K., Youcha, E. K., 2008. Geochemical controls of elevated arsenic concentrations in groundwater, Ester Dome, Fairbanks district, Alaska. Chemical Geology 255, 160–172.

Waibel, M., Gannett, M., Chang, H., Hulbe, C., 2013. Spatial variability of the response to climate change in regional groundwater systems - Examples from simulations in the Deschutes Basin, Oregon. Journal of Hydrology 486, 187 – 201.

Watts, M., O'Reilly, J., Marcilla, A., Shaw, R., Ward, N., 2010. Field based speciation of arsenic in UK and Argentinean water samples. Environmental geochemistry and health 32 (6), 479–490.

Weldon, J. M., MacRae, J. D., 2006. Correlations between arsenic in Maine groundwater and microbial populations as determined by fluorescence in situ hybridization. Chemosphere 63, 440–448.

WHO, 2011. Guidelines for drinking-water quality. Geneva : World Health Organization.

Williams, M., 2001. Arsenic in mine waters : an international study. Environmental Geology 40 (3), 267–278.

World Water Assessment Programme, 2009. The United Nations World Water Development Report 3 : Water in a Changing World. Paris : UNESCO, and London : Earthscan.

Yang, Q., Culbertson, C. W., Nielsen, M. G., Schalk, C. W., Johnson, C. D., Marvinney, R. G., Stute, M., Zheng, Y., 2015. Flow and sorption controls of groundwater arsenic in individual boreholes from bedrock aquifers in central Maine, USA. Science of The Total Environment 505, 1291–1307.

Yang, Q., Jung, H. B., Culbertson, C. W., Marvinney, R. G., Loiselle, M. C., Locke, D. B., Cheek, H., Thibodeau, H., Zheng, Y., 2009. Spatial pattern of groundwater arsenic occurrence and association with bedrock geology in greater Augusta, Maine. Environmental Science & Technology 43, 2714–2719.

Yang, Q., Jung, H. B., Marvinney, R. G., Culbertson, C. W., Zheng, Y., 2012. Can arsenic occurrence rates in bedrock aquifers be predicted ? Environmental Science & Technology 46, 2080–2087.

Zheng, Y., Ayotte, J. D., 2015. At the crossroads : Hazard assessment and reduction of health risks from arsenic in private well waters of the northeastern United States and Atlantic Canada. Science of The Total Environment 505, 1237–1247.

Zhou, Y., Zwahlen, F., Wang, Y., Li, Y., 2010. Impact of climate change on irrigation requirements in terms of groundwater resources. Hydrogeology journal 18, 1571–1582.

Zkeri, E., Aloupi, M., Gaganis, P., 2015. Natural occurrence of arsenic in groundwater from Lesvos Island, Greece. Water, Air, & Soil Pollution 226 (9), 1–16.