UNIVERSITÉ DU QUÉBEC EN ABITIBI-TÉMISCAMINGUE

TRAÇAGE HYDROGÉOCHIMIQUE DES SYSTÈMES AQUIFÈRES-AQUITARDS DE LA CEINTURE ARGILEUSE BARLOW-OJIBWAY

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« L’eau !

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Tu es la plus grande richesse qui soit au monde, et tu es aussi la plus délicate, toi si pure au ventre de la terre. » Antoine de Saint Exupéry (1939) Terre des Hommes, p. 180.

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A mon grand-père et à ma mère, les deux
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Cette thèse de doctorat, présentée dans le cadre du doctorat en sciences de l'environnement de l'Université du Québec à Montréal, réalisée à l'Université du Québec en Abitibi-Témiscamingue, s'articule autour de trois articles scientifiques qui constituent les trois chapitres principaux de cette thèse :

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

L'élaboration de la méthodologie et la collecte des données de la première portion du territoire de l'Abitibi-Témiscamingue (partie est de l'Abitibi) proviennent des travaux réalisés par le GRES (Groupe de Recherche sur l'Eau Souterraine) implanté sur le campus d'Amos et dirigé par le professeur Vincent Cloutier, dans le cadre du projet PACES-AT1 (Projet d'Acquisition de Connaissances sur les Eaux Souterraines de l'Abitibi-Témiscamingue, partie 1). Ce projet, financé par le Ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (MDDELCC), a permis à l'étudiante d'acquérir une base de données géochimiques exhaustive et de qualité. La collecte des données de la deuxième portion du territoire de l'étude (partie ouest de l'Abitibi et le Témiscamingue) s'est effectuée dans le cadre des travaux du PACES-AT2 (partie 2) et a été réalisée essentiellement par la candidate au Doctorat avec le support de stagiaires. L'analyse et l'interprétation des données géochimiques ainsi que la rédaction ont été réalisées principalement par le premier auteur des trois articles scientifiques proposés dans cette thèse. Vincent Cloutier, directeur de recherche, a contribué au financement du projet, au support dans l'élaboration de la méthodologie, à la collecte, à l'analyse et à l'interprétation des données géochimiques pour les articles 2 et 3 ainsi qu'à la rédaction des trois articles en général. L'apport d'Éric Rosa, co-directeur de recherche, a porté sur l'analyse et l'interprétation des données géochimiques isotopiques et à la rédaction de l'article 1. Eric Rosa a participé aussi à l'analyse et l'interprétation des données géochimiques ainsi qu'à la rédaction des articles 2 et 3. René Lefebvre, co-directeur de recherche, a contribué à bonifier de façon significative à l'analyse et à l'interprétation des données de l'article 1, ainsi qu'à sa rédaction. René Lefebvre, qui est coauteur des articles 2 et 3, a validé les manuscrits dans le cadre de la révision de la thèse. L'assistance de Daniel

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RÉSUMÉ

Les travaux des Projets d'acquisition de connaissances sur les eaux souterraines en Abitibi-Témiscamingue (PACES-AT) ont permis d'établir le modèle hydrogéologique régional sur la base de données physiques recensées à l'échelle du territoire et de dresser le portrait de la qualité des eaux souterraines. Cette thèse de doctorat entre dans le cadre des travaux des PACES-AT pour réaliser une étude hydrogéochimique intégrée des eaux souterraines d'un système aquifère complexe au sein de la ceinture argileuse Barlow-Ojibway. L'objectif général de cette thèse est d'améliorer, par l'intégration de l'hydrogéochimie, les connaissances des systèmes d'écoulement à l'échelle régionale dans un système aquifère dominé par la présence d'une couverture argileuse qui recouvre près de 80% du territoire en contexte de Bouclier canadien. Pour ce faire, le travail de recherche (1) s'intéresse au traçage isotopique du cycle de l'eau, incluant les précipitations, les eaux de surface, les sources et les eaux souterraines, (2) définit les principaux processus géochimiques qui contrôlent la géochimie des eaux souterraines et son évolution spatio-temporelle, (3) identifie l'influence du contexte géologique et hydrogéologique ainsi que les sources des éléments chimiques dissous dans les eaux, dictant la signature géochimique des eaux souterraines au sein du système d'écoulement et (4) évalue la qualité régionale des eaux souterraines, par le calcul d'un indice de contamination, dans une optique de santé humaine. Pour répondre à ces objectifs, le projet de recherche s'appuie sur des travaux d'échantillonnage sur le terrain de divers types d'eau, des analyses chimiques au laboratoire ainsi que des travaux de modélisation conceptuels. La base de données de ce travail de recherche contient 706 échantillons analysés pour les ions majeurs, les nutriments et les éléments traces incluant les précipitations (neige et pluie), la neige au sol, les eaux de surface,

les eaux souterraines et les sources. Parmi ces 706 échantillons, 645 échantillons ont été analysés pour les isotopes stables de la molécule d'eau (δ^2H-δ^{18}O) et 98 échantillons de source et d'eau souterraine ont été analysés pour l'activité tritium. L'introduction (chapitre 1) présente les enjeux de l'eau souterraine en région, le cadre dans lequel le travail de recherche s'inscrit, les objectifs spécifiques et la méthodologie suivie. Le chapitre 2, dédié au traçage isotopique des divers ensembles d'eaux régionales échantillonnées, explique le cycle de l'eau global régional. La composition isotopique des précipitations montre qu'elles suivent un cycle saisonnier qui dépend de la température, tel qu'indiqué par les eaux de pluie estivales enrichies en isotopes lourds qui s'opposent aux précipitations hivernales appauvries en isotopes lourds. Les échantillons des précipitations forment la droite locale des eaux météoriques reliée à la latitude. Les échantillons de neige sont localisés dans la portion inférieure de la droite des eaux météoriques, révélant que le couvert nival conserve sa composition isotopique à la fonte des neiges. Les échantillons d'eau de surface sont localisés sur une droite évaporatoire locale qui s'éloigne de la droite météorique des eaux, indiquant que les eaux de surface ne rechargent pas les eaux souterraines. En région, la variabilité isotopique issue de la recharge très présente dans les aquifères granulaires à nappe libre s'atténue le long des lignes d'écoulement et tend vers une moyenne régionale en δ^{18}O dans les aquifères rocheux fracturés à nappe captive (-13‰) qui contiennent les eaux souterraines les plus évoluées et les plus chargées en éléments chimiques dissous. Le chapitre 3, qui porte sur l'interprétation des analyses chimiques de l'ensemble des échantillons d'eau, complémente les résultats obtenus par les isotopes stables de l'eau. Les eaux souterraines interagissent avec la lithologie des aquifères, depuis l'infiltration des précipitations dans les zones de recharge. L'augmentation observée des concentrations en éléments majeurs (Ca, Mg, Na, K, HCO_3, Si, Matières dissoutes totales-MDT), manganèse et fer, ainsi que la diminution du Eh le long des chemins d'écoulement suggèrent que les eaux évoluent à partir des aquifères granulaires à nappe libre aux aquifères rocheux fracturés à nappe captive. Le contexte de nappe captive induit par la plaine argileuse combiné au temps de résidence de l'eau influence l’augmentation de la matière dissoute totale dans les eaux souterraines des aquifères les plus éloignés des zones de recharge que sont les aquifères rocheux fracturés à nappe captive. Localement, dans les aquifères rocheux à nappe libre, l’interaction entre la lithologie et les eaux souterraines est à l’origine de la présence d’éléments traces spécifiques tels l’uranium et le fluor, qui proviennent des roches intrusives plutoniques, et l’arsenic et le chrome, associés aux roches volcaniques. La combinaison des sources géogéniques ponctuelles et de l’évolution des eaux souterraines accentuée par l’effet du contexte de nappe captive prévalant sur une vaste partie de la région dicte la composition géochimique des eaux souterraines dans chaque partie du système d’écoulement. Les processus géochimiques majeurs qui influencent la composition géochimique des eaux souterraines sont la dissolution des carbonates et des silicates, l’oxydation des sulfures et la réduction des sulfates. Le chapitre 4 s’intéresse plus particulièrement à la santé des résidents qui utilisent les eaux souterraines à des fins d’approvisionnement en eau potable et se concentre sur les éléments chimiques qui dépassent les normes de recommandations gouvernementales de qualité d’eau afin de dresser un indice de contamination des eaux souterraines (ICES). Les eaux souterraines régionales sont affectées par le fer et le manganèse qui dépassent les valeurs seuils fixées pour les objectifs esthétiques et par des concentrations en arsenic et en uranium qui excèdent les normes de santé. Les échantillons dont les concentrations dépassent les concentrations maximales acceptables fixées pour les critères de santé ont été retirés pour l’élaboration de l’indice de contamination puisque jugés « impropre à la consommation humaine ». Les résultats ont révélé que 79% des puits régionaux contiennent une eau souterraine avec un niveau de contamination «faible» dont la qualité est considérée bonne et concerne particulièrement les eaux des aquifères granulaires à nappe libre qui constituent les aquifères régionaux les plus vulnérables. Les eaux souterraines présentes dans les aquifères constitués de roches plutoniques sont de meilleure qualité que ceux constitués de roches volcaniques. Le chapitre 5 conclue cette étude en rappelant que les résultats de ce travail de recherche viennent accroître les connaissances sur la compréhension globale des systèmes aquifères-aquitard de

l’Abitibi-Témiscamingue, apportant ainsi des précisions sur la dynamique du système d’écoulement complexe des eaux souterraines en contexte de Bouclier canadien. Les nouvelles connaissances permettent de combler les lacunes scientifiques concernant l’origine des eaux souterraines, son évolution géochimique et sa qualité. Les principales retombées de ce travail de recherche sur la société concernent la gestion du territoire pour un meilleur aménagement en adéquation avec la protection et la préservation des ressources en eau souterraine pour les générations futures, surtout lorsqu’elles constituent la source majeure d’eau potable et qu’elle est soumise à une forte pression due à diverses activités anthropiques sur le territoire.

Mots clés : Aquifères granulaires à nappe captive et à nappe libre, Aquifères rocheux fracturés à nappe captive et à nappe libre, Ceinture argileuse Barlow-Ojibway, Interaction eau-roche, Qualité de l’eau souterraine, Bouclier canadien.

ABSTRACT

The work of the Groundwater knowledge acquisition projects in Abitibi-Témiscamingue (PACES-AT) allowed to establish the regional hydrogeological model on the basis of physical data identified at the scale of the territory and to draw the quality portrait of the groundwater of the region. This thesis takes place within the PACES-AT work and was carried out as an integrated hydrogeochemical study of the groundwater of a complex aquifer system in the heart of the Barlow-Ojibway clay belt. The overall objective of this thesis is to improve knowledge of regional-scale flow systems in an aquifer system dominated by the presence of a clay cover that covers close to 80% of the territory in the Canadian Shield context. To do this, the research work (1) focuses on the isotopic tracing of the water cycle of precipitation, surface water, springs and groundwater, (2) defines the main geochemical processes that control groundwater geochemistry and its spatio-temporal evolution, (3) identifies the influence of the geological and hydrogeological context as well as the sources of the dissolved chemical elements in water dictating the geochemical signature of the groundwater within the flow system and (4) assesses the regional quality of groundwater, by the calculation of a contamination index, for a human health perspective. To meet these objectives, the research work relies on fieldwork sampling of various water types, chemical analyses in the laboratory and conceptual modelling work. The database of this research work contains 706 samples analyzed for major ions, nutrients and trace elements including precipitation (snow and rain), ground snow, surface water, groundwater and springs. Of these 706 samples, 645 samples were analyzed for stable isotopes of the water molecule ($\delta^{2}H$-$\delta^{18}O$) and 98 springs and groundwater samples were analyzed for tritium activity. The introduction (chapter 1)

indicates the challenges related to groundwater in the region, the framework in which the research work took place, the specific objectives and the followed methodology. Chapter 2, dedicated to isotope tracing of selected regional watersheds, explains the global regional water cycle. The isotopic composition of precipitations shows that they follow a seasonal temperature-dependent cycle which indicates that summer rainwater is enriched in heavy isotopes that oppose to heavy-isotope-depleted winter precipitation. Precipitation samples constitute the local meteoric waters line related to latitude. The snow samples are located in the lower portion of the meteoric waters line revealing that the snow cover maintains its isotopic composition at snowmelt. Surface water samples are located on a local evaporative line that pull away from the meteoric waters line, indicating that surface water does not recharge the groundwater. In the region, the isotopic variability resulting from the highly present recharge in unconfined granular aquifers decreases along the flow lines and tends towards a $\delta^{18}O$ regional average in confined fractured rock aquifers (-13‰) that contain the most evolved and the most charged in dissolved chemical elements groundwater. The chapter 3, which deals with the interpretation of the chemical analyses of all the water samples, confirms the results obtained by the water stable isotopes. Groundwater interacts with aquifer lithology since precipitation infiltration into recharge areas. The observed increase of major elements (Ca, Mg, Na, K, HCO_3, Si, Total dissolved solids-TDS), manganese and iron, as well as the decrease of Eh along the flow lines, indicates that waters evolve from unconfined granular aquifers to confined fractured rock aquifers. The confinement induced by the clay plain combined with the residence time of water influences the total dissolved solids increase in groundwater in the aquifers furthest away from the recharge zone, which are the confined fractured rock aquifers. At the local level, in unconfined rock aquifers, the interaction between lithology and groundwater is responsible for the presence of specific trace elements such as uranium and fluoride, which come from the plutonic intrusive rocks and the arsenic and chromium associated with volcanic rocks. The combination of specific geogenic sources and groundwater evolution accentuated by the effect of confinement dictates

the geochemical composition of the groundwater in each part of the flow system. The major geochemical processes that influence the geochemical signature of groundwater are the dissolution of carbonates and silicates, the oxidation of sulphides and the reduction of sulphates. The chapter 4 focuses on the health of residents for who groundwater provide drinking water for their domestic use and focuses on chemicals that exceed the water quality guideline to develop a groundwater contamination index (GWCI). Regional groundwater is affected by iron and manganese that exceed threshold values for aesthetic objectives and by arsenic and uranium concentrations that exceed health standards. Groundwater samples whose concentrations exceed the maximum acceptable concentrations set for the health criteria, considered "non-potable water", have been removed for contamination index calculation. The results revealed that about 79% of the regional wells have groundwater with a "low" degree of contamination considered as good and particularly the unconfined granular aquifers waters that are the most vulnerable regional aquifers. Groundwater in plutonic rock aquifers is of better quality than in volcanic rocks aquifers. The chapter 5 concludes this study by recalling that the results of this research work add to the knowledge on the global understanding of Abitibi-Témiscamingue aquifers-aquitard systems, providing information on the dynamics of this complex groundwater flow system in a Canadian Shield context. This new knowledge is filling scientific gaps on the origin of groundwater, its geochemical evolution and its quality. The main benefits of this research for society concern the management of the territory for a better development in adequacy with the protection and the preservation of the groundwater resources for the future generations, especially when they constitute the major source of drinking water and that it is under strong pressure from various anthropogenic activities.

Keywords : Confined and unconfined granular aquifers, Confined and unconfined fractured rock aquifers, Clay Belt Barlow Ojibway, Water-rock interaction, Groundwater quality, Canadian Shield.

CHAPITRE I

INTRODUCTION GÉNÉRALE

1.1 L’eau souterraine : une richesse inestimable

1.1.1 Les défis liés à la préservation de la qualité de l’eau souterraine

L’eau douce est inégalement répartie dans le monde en qualité et en quantité. Les ressources en eau potable se raréfient et d’ici 2025, elles auront diminué de moitié dans le monde (WHO, 2017). Les eaux souterraines constituent le plus grand réservoir d’eau douce accessible et représentent environ le tiers des prélèvements d’eau douce dans le monde (Famiglietti, 2014; Siebert et al., 2010). En plus de jouer un rôle clé pour plusieurs écosystèmes et d’être un élément majeur du cycle hydrologique, les eaux souterraines représentent une source d'eau potable essentielle pour environ la moitié de la population mondiale (Kløve et al., 2013; Taylor et al., 2013). La surexploitation et la contamination des eaux souterraines sont devenues des problèmes globaux et majeurs de la planète (Gregory et al., 2013; Zheng et Liu, 2013). Dans un contexte de changements climatiques, les effets cumulatifs d’une croissance démographique fulgurante, de l’urbanisation, de l’utilisation excessive et irrationnelle de l’eau, du changement d'affectation des sols, des techniques de forage et de pompage peu coûteuses, de l’industrialisation, de l’expansion de l'agriculture irriguée, des changements institutionnels et des normes de qualité de l'eau peu strictes ont mené à une utilisation généralisée et souvent non gérée des eaux souterraines à travers le monde (Gorelick et Zheng, 2015). Les défis à relever pour préserver les eaux souterraines à l’époque actuelle sont nombreux. L’importance d’accroître les connaissances sur la ressource en eau souterraine est essentielle à sa préservation ainsi qu’à sa gestion durable et réfléchie. Les suivis de la qualité et de la quantité des eaux souterraines dans le temps sont nécessaires pour mieux comprendre son évolution et pour prévenir sa détérioration. La protection des zones sensibles et vulnérables est indispensable à la préservation de la qualité de la ressource en eau potable. Il est primordial que l’exploitation de la ressource en eau souterraine s’effectue sans que son intégrité ne soit compromise pour les générations futures.

1.1.2 L’eau souterraine en Abitibi-Témiscamingue

L’eau souterraine est une ressource élémentaire et de plus en plus sollicitée au Québec. Cependant, sa gestion a été négligée et sous-évaluée dans cette province (CAC, 2009). En Abitibi-Témiscamingue, l’eau souterraine est un véritable enjeu puisqu’elle alimente environ 73% de la population en eau potable, ce qui correspond à environ 110 700 personnes, dont 41% possèdent des puits d’approvisionnement en eau potable. Certains secteurs sont plus vulnérables que d’autres, notamment les eskers. Ces derniers correspondent à des formations fluvio-glaciaires de sables et de graviers, sous la forme d'une crête allongée, rectiligne ou sinueuse, pouvant atteindre plusieurs kilomètres de longueur et quelques dizaines de mètres de hauteur. Les eskers sont réputés pour avoir une eau d’excellente qualité constituant une zone de recharge pour les aquifères. En région, cette ressource n’est pas à l’abri d’une surexploitation et de contaminations diverses et variées. L’Abitibi-Témiscamingue est une région marquée par l’exploitation et l’extraction de sable et de gravier. La pression exercée par l’exploitation de sablières et de gravières sur les ressources aquifères formées par les eskers et les moraines de la région peut être considérable, notamment dans les endroits où le nombre des puits d’approvisionnement en eau potable est conséquent et où la ressource en eau souterraine est fortement utilisée pour combler les besoins de consommation de la population humaine.

La région, en raison de son hétérogénéité géologique et de son réseau de failles minéralisées, est au cœur de gisements d'or et d'éléments polymétalliques qui font de l'Abitibi-Témiscamingue la plus importante région minière du Québec. Néanmoins, cette minéralogie diversifiée et les conditions physico-chimiques exposent l'eau souterraine à plusieurs contaminants géogéniques. Les aquifères liés au roc fracturé présentent une eau souterraine contaminée au fer, au manganèse et à l'arsenic dans plusieurs secteurs sur le territoire (Bondu et al., 2017; 2018). Cette situation démontre le nécessité de sensibiliser la population à l'importance d'assurer un suivi de la qualité de l'eau ciblant surtout les puits de particuliers les plus concernés par les problématiques de contamination naturelle des eaux de consommation par les métaux.

Le développement économique et social que connaît actuellement la région souligne l'importance d'étudier et de parfaire les connaissances sur le fonctionnement des systèmes aquifères régionaux en vue d'une gestion durable de la ressource, tant en terme de sa quantité que de sa qualité.

1.2 Le contexte de l'étude

1.2.1 Les travaux du PACES (Programme d'acquisition de connaissances sur les eaux souterraines) au Québec

Le projet de doctorat s'inscrit dans le cadre des travaux du PACES, dont l'acronyme signifie le Programme d'Acquisition de Connaissances sur les Eaux Souterraines du Québec. Avant 2008, l'état des connaissances sur la ressource en eau souterraine à l'échelle du Québec demeurait incomplet et limité. Les données étaient limitées ou encore difficilement accessibles. Peu d'études avaient abordé la caractérisation des eaux souterraines dans une perspective régionale. Afin de remédier à ce manque de connaissances, le ministère du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (MDDELCC) a instauré et financé en 2008 le Programme PACES afin de parfaire la connaissance de la ressource en eau souterraine des territoires municipalisés du Québec méridional. L'objectif principal est de connaître la ressource en eau souterraine (en quantité et en qualité) afin de mieux la protéger et la préserver pour les générations futures. L'initiative PACES repose sur la volonté de répondre à l'engagement numéro 5 de la Politique nationale de l'eau relative à l'inventaire des grands aquifères du Québec.

Entre 2009 et 2015 un nombre de 13 projets du PACES se sont développés à travers le Québec méridional en collaboration avec des universités du Québec (Figure 1.1). Les équipes de recherche des universités impliquées, incluant l'UQAT, se sont mobilisées et ont collaboré au développement de protocoles uniformisés pour une réalisation concertée des projets à l'échelle de la province.

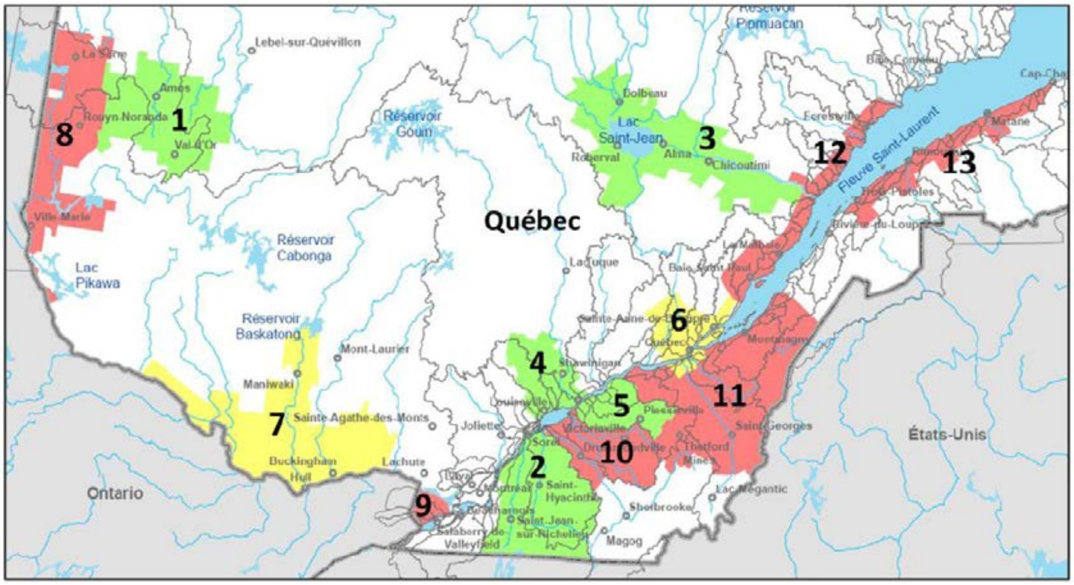


Figure 1.1. Localisation des projets du PACES au Québec (2009-2015).
1 : Abitibi-Témiscamingue-1 (UQAT), 2 : Montérégie-Est (INRS-ETE), 3 : Saguenay-Lac-Saint-Jean (UQAC), 4 : Mauricie (UQTR), 5 : Bécancour (UQAM), 6 : Communauté métropolitaine de Québec (Université Laval), 7 : Outaouais (Université Laval), 8 : Abitibi-Témiscamingue-2 (UQAT), 9 : Vaudreuil-Soulanges (UQAM), 10 : Centre-du-Québec (UQAM), 11 : Chaudières-Appalaches (INRS-ETE), 12 : Chalevoix/Haute-Côte-Nord (UQAC), 13 : Bas-Saint-Laurent (UQAR). Les polygones verts correspondent aux projets de l'appel d'offre de 2009, ceux de couleur jaune font référence à l'appel d'offre de 2010 et ceux en rouge à l'appel d'offre de 2012.

En Abitibi-Témiscamingue, les projets du PACES se sont déroulés en deux phases afin de couvrir la totalité du territoire municipalisé. La phase 1, connue sous le nom de PACES-AT1, concerne la portion Nord-Est du territoire couvrant principalement les municipalités régionales de comté d'Abitibi et de La Vallée-de-l'Or. La phase 2, appelée PACES-AT2, couvre la portion ouest du territoire d'étude et complète le reste de la superficie des municipalités régionales de comté de l'Abitibi-Ouest et de la Ville de Rouyn-Noranda et inclue celle de Témiscamingue.

Les objectifs des projets du PACES sont d’établir le portrait hydrogéologique d’un territoire afin de générer des connaissances indispensables à la protection des ressources aquifères et d’intégrer les acteurs de l’eau ainsi que les gestionnaires du territoire afin d’accroître leur participation dans la mise en œuvre d’une gestion saine et durable de la ressource. Les travaux des projets du PACES consistent en (1) le recensement et la compilation des données hydrogéologiques préexistantes, (2) la réalisation de travaux de terrain pour acquérir des données complémentaires et (3) l’analyse des données, leur représentation en cartes et le transfert aux acteurs de l’eau et du territoire. L’ensemble des projets du PACES au Québec a permis (1) le développement de bases de données hydrogéologiques et géochimiques régionales géoréférencées homogènes et compatibles à l’échelle provinciale et (2) l’acquisition de connaissances relatives aux caractéristiques physiques des aquifères afin de répondre au besoin gouvernemental d’assurer une gestion saine et durable de la ressource en eau souterraine.

La base de données géochimiques issue des travaux des projets PACES AT1-AT2 a été étudiée dans le cadre de cette thèse afin d’approfondir les analyses et les interprétations de la géochimie en relation avec de l’écoulement de l’eau souterraine dans les aquifères granulaires et les aquifères rocheux fracturés du Bouclier Canadien, dans un contexte d’une ceinture argileuse prédominante. Le travail de recherche repose sur l’étude de la dynamique régionale de l’écoulement de l’eau souterraine et de la caractérisation géologique et hydrogéologique des aquifères déterminés dans le cadre des PACES-AT (Cloutier et al., 2015).

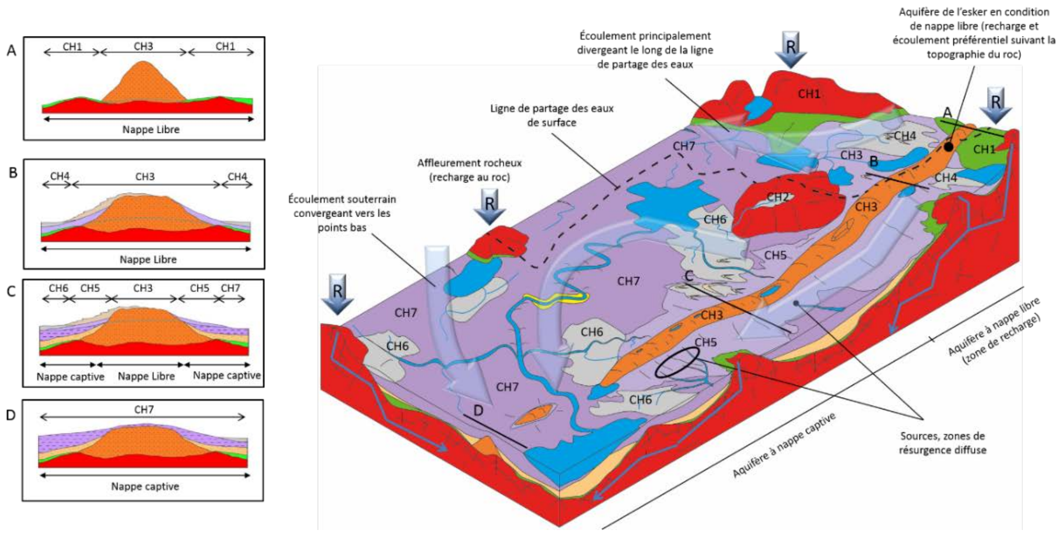
Le territoire d’étude de cette thèse surpasse les frontières imposées par les municipalités régionales de comté de l’Abitibi-Témiscamingue car il intègre l’ensemble des systèmes aquifères recouverts par la ceinture argileuse Barlow-Ojibway responsable par endroit du confinement des aquifères régionaux.

1.2.2 Le cadre hydrogéologique régional

La région de l'Abitibi-Témiscamingue, située au Nord-Ouest du Québec méridional, couvre un territoire d'une superficie totale de 57 320,55 km^2 (MAMH, 2019). Située au cœur du Bouclier canadien, avec le socle rocheux archéen le plus ancien (3,5 Ga) de l'histoire de la terre, la région recoupe deux provinces géologiques principales, soit la province du Supérieur et celle de Grenville (Veillette et al., 2005). La province du Supérieur, qui englobe la sous-province de l'Abitibi et la sous-province du Pontiac, est composée d'alternance de roches volcaniques (ex. : basalte, gabbro, rhyolite) et métasédimentaires (ex. : argilites, grauwacke) datant de 2,7 Ga recoupées par des intrusions de granitoïdes (ex. : syénite, monzonite). La sous-province de l'Abitibi constitue le plus grand ensemble volcano-sédimentaire archéen au monde (Hocq et al., 1993). La composition géologique du substratum de la sous-province du Pontiac est faite de roches granitiques et de paragneiss et présente une résistance plus forte à l'érosion par rapport à la ceinture volcano-sédimentaire de la sous-province de l'Abitibi (Landry et Mercier, 1992). La province de Grenville occupe la portion sud de la région, elle est constituée de roches plus jeunes issues de l'orogénèse (1,5 Ga) essentiellement felsiques (roches acides) et métamorphiques (amphibolites) (Hocq et al., 1993). La région est entrecoupée d'un système de failles archéennes abondantes d'orientation préférentielle NO-SE, dont le potentiel minier est important en raison de leur tendance à la minéralisation donnant lieu à de nombreux gisements de métaux précieux (Au-Ag) et polymétalliques (Cu-Zn) (Hocq et Verpaelst, 1994; Veillette et al., 2005). Les événements du Quaternaire (entre 8 000 et 10 000 ans) ont laissé une empreinte géomorphologique considérable sur la région. Le retrait et la fonte du glacier issu de la glaciation wisconsinienne a donné lieu à la création de nombreux lacs d'eau douce dans le Sud-Ouest du Québec, comme le lac proglaciaire Barlow-Ojibway, où se sont déposés les argiles et les limons glaciolacustres qui forment aujourd'hui les aquitards régionaux. Le retrait glaciaire est à l'origine aussi de plusieurs types de dépôts de surface : les eskers et les moraines, sédiments fluvioglaciaires formant les aquifères granulaires les plus productifs de la région (Nadeau et al., 2015) et les tills composés de sables, de silts et d'argiles glaciaires (Veillette, 1994). Les sédiments fins d'argiles glaciolacustres déposés en eau profonde dans le lac Barlow-Ojibway sont à l'origine de la ceinture argileuse Barlow-Ojibway à l'échelle régionale (Veillette, 1996; Roy et al., 2011).

Le socle rocheux fracturé et les formations granulaires affleurent par endroit sur le territoire et constituent les points hauts de la région. Des couches plus ou moins épaisses de formations granulaires et d'argile recouvrent le socle précambrien. Cet héritage géologique et géomorphologique de l'Achéen et du Quaternaire a permis la mise en place de quatre types d'aquifères majeurs en région : les aquifères au roc fracturé à nappe libre et à nappe captive présents sous la couverture argileuse, puis les aquifères granulaires à nappe libre et à nappe captive sous les dépôts glaciolacustres.

Les travaux réalisés dans le cadre des projets du PACES en Abitibi-Témiscamingue (Cloutier et al., 2013; 2015) ont permis le recensement, l'acquisition et la compilation d'un nombre conséquent de données relatives au territoire, qui sont incluses au sein de bases de données géoréférencées contenant l'ensemble des informations géologiques et hydrogéologiques disponibles sur la région d'étude. Cloutier et al. (2013) ont proposé un modèle hydrogéologique conceptuel régional permettant une représentation simplifiée des caractéristiques, de l'architecture et des conditions d'écoulement de l'eau au sein des six contextes hydrogéologiques (CH) observés au niveau du territoire (Figure 1.2). Cloutier et al. (2016) a répertorié également un nombre de 15 séquences stratigraphiques sur le territoire, qui schématisent les types de superposition des dépôts régionaux sur le roc et qui sont susceptibles d'être rencontrés sur le territoire.



⬜ **Tourbière**
🟫 **Sédiments éoliens (dunes)**
🟪 **Sables littoraux**
🟪 **Argile glaciolacustre**
🟨 **Sables d'épandage subaquatique**
🟧 **Sables et graviers fluvioglaciaires (eskers)**
🟩 **Till**
🟥 **Roc fracturé**

Figure 1.2. Bloc diagramme 3D conceptuel de la dynamique d'écoulement de l'eau souterraine et des contextes hydrogéologiques du territoire à l'étude. CH1 : Affleurements rocheux et till; CH2 : Tourbières sur Roc; CH3 : Eskers et Moraine; CH4 : Flancs d'eskers; CH5 : Tourbières sur granulaire; CH6 : Tourbières sur argile; CH7 : Plaine argileuse. Les coupes transversales à l'esker présentent les contextes hydrogéologiques pour A) l'esker non enfoui, B) l'esker en position sublittoral, C) l'esker semi-enfoui et D) l'esker enfoui (Cloutier et al., 2016).

1.3 La problématique du traçage hydrogéochimique des systèmes aquifères-aquitards de la ceinture argileuse Barlow-Ojibway

1.3.1 Géochimie des eaux souterraines régionales : de la recharge à l’émergence

L’écoulement de l’eau souterraine à l’échelle régionale débute par une zone de recharge qui accueille les précipitations (neige, pluie), une zone de transfert dans laquelle les eaux s’infiltrent, transitent et interagissent avec le milieu et une zone d’émergence où les eaux finissent par ressortir. A l’échelle régionale, l’écoulement de l’eau est contrôlé par la topographie, c’est-à-dire que les eaux s’écoulent d’un point haut qui correspond à des zones de recharge vers un point bas.

L’hétérogénéité des roches et la diversité des minéraux qui constituent les aquifères ont une influence significative sur la chimie de l’eau souterraine, car celle-ci interagit depuis son entrée jusqu’à sa sortie avec la matrice des aquifères dans le temps et suivant son trajet (Ingebritsen et Sanford, 1998).

La composition chimique de l’eau est dictée par plusieurs facteurs, notamment le temps de résidence de l’eau et les processus d’interaction entre l’eau, ainsi que la composition minéralogique des roches de l’aquifère rocheux fracturé et celle des grains de l’aquifère granulaire, comme expliqué par la Figure 1.3. L’étude menée par Tóth (1999) démontre que l’écoulement de l’eau souterraine entraîne des modifications dans la composition chimique de l’eau. Il mentionne que les interactions chimiques représentent, avec les processus physiques et de transport, l’un des principaux types d’interaction entre l’eau souterraine et son environnement hydrogéologique. L’évolution chimique est causée par les réactions et processus géochimiques qui se produisent depuis l’infiltration de l’eau dans les zones de recharge jusqu’aux zones de résurgence (hydrolyse, oxydo-réduction, dissolution et précipitation de minéraux, échange ionique) (Hounslow, 1995). Ces processus sont le résultat de l’interaction entre l’eau, les minéraux et, dans la zone non saturée, la phase gazeuse. La composition finale de l’eau dépend alors de la nature lithologique et structurale de l'aquifère, du temps de résidence de l'eau, mais aussi des possibles mélanges d'eaux d'origines différentes (Cloutier et al., 2008). L'interaction eau-minéraux liée aux événements quaternaires peut influencer à la fois les propriétés chimiques de l'eau souterraine des aquifères granulaires de surface et des aquifères profonds (mélange des eaux) (Valder et al., 2012).

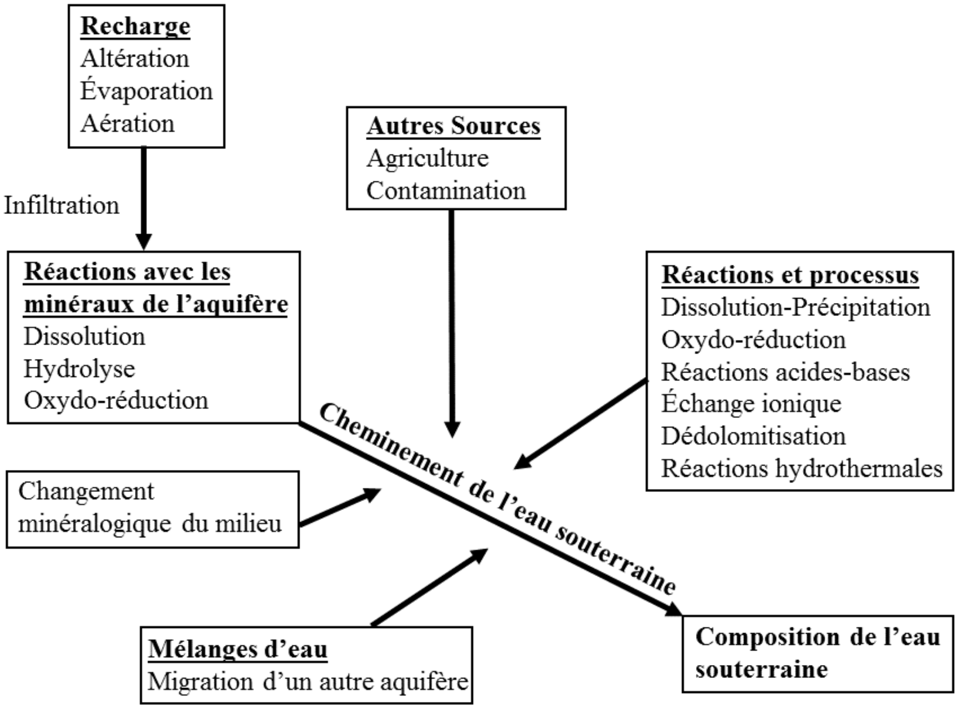


Figure 1.3. Synthèse des réactions géochimiques susceptibles de modifier la composition finale de l'eau souterraine (Adaptée de Hounslow, 1995).

La géochimie intègre aussi les traceurs isotopiques. Le marquage isotopique $\delta^{18}O$-$\delta^{2}H$ de diverses sources d'eau constitue l'une des techniques les plus appliquées en hydrogéologie et en hydrologie (Birks et Gibson, 2009; Gibson et al., 2005). La distribution des signatures isotopiques de l'eau ($\delta^{18}O$-$\delta^{2}H$) a été utilisée pour mieux comprendre l'origine et l'écoulement de l'eau dans des aquifères sédimentaires tel celui de Williston (Rostron et Holmden, 2003) et de Winnipeg (Ferguson et al., 2007). Les traceurs isotopiques des précipitations et des eaux souterraines ont servi à mieux comprendre la dynamique d'écoulement des systèmes aquifères et des eskers (Blanchette et al., 2011). Dans les conditions propres aux systèmes aquifères, la signature isotopique de l'eau souterraine (δ^{18}O-δ^{2}H) est fonction de processus physiques liés au cycle de l'eau (précipitations, évaporation, transpiration, recharge, mélange). La composition isotopique des précipitations reflète la saisonnalité très marquée dans une région où les températures sont contrastées et reflète les variations induites par cette saisonnalité, avec un appauvrissement en isotopes lourds dans les précipitations hivernales et un enrichissement en isotopes lourds durant la saison estivale (Clark et Fritz, 1997). La composition isotopique de l'eau des aquifères représente les plages de valeurs enregistrées dans les précipitations même si des processus ultérieurs aux précipitations sont susceptibles de modifier la signature isotopique de l'eau (évaporation, évolution du couvert nival, mélange avec les eaux de surface). Le traçage isotopique de la recharge des systèmes aquifères et de l'écoulement de l'eau souterraine dans les aquifères dans une région ayant une forte saisonnalité s'avère un outil indéniable dans la compréhension de l'écoulement régional.

1.3.2 Objectifs de recherche

L'objectif général de cette thèse de doctorat est d'approfondir les connaissances sur les processus géochimiques et hydrogéologiques qui dictent l'évolution chimique naturelle des eaux souterraines régionales. Cette thèse vise ainsi d'améliorer la compréhension de la dynamique de l'écoulement des eaux souterraines au sein des systèmes aquifères en conditions de nappe captive et de nappe libre en contexte de Bouclier canadien. Les quatre types d'aquifères sont formés à la fois par des dépôts granulaires du Quaternaire et par une géologie hétérogène sous forme d'un socle fracturé issu de roches archéennes anciennes (3.5 Ga) du Bouclier canadien. Ces aquifères rocheux fracturés sont recouverts par endroits par des dépôts argileux du Quaternaire. La richesse géologique des aquifères donnant lieu à une diversité de minéraux, l'interaction entre ceux-ci et l'eau qui s'infiltre et s'écoule au sein des aquifères confère aux eaux souterraines un faciès géochimique bien défini.

Pour répondre à l'objectif général, ce travail de recherche traite trois grands axes complémentaires qui définissent les trois chapitres de cette thèse rédigés sous forme d'articles scientifiques.

Le chapitre 2 évalue la saisonnalité de la recharge des aquifères régionaux. S'inscrivant dans le cadre hydrogéologique préétabli, ce chapitre vise à améliorer la compréhension des systèmes d'écoulement régionaux des eaux de surface et des eaux souterraines dans la partie sud de la ceinture argileuse Barlow-Ojibway sur la base de données géochimiques. La présente étude se concentre sur les isotopes stables (^{2}H-^{18}O) et radioactifs (^{3}H) de la molécule d'eau. L'approche proposée comprend une évaluation complète à l'échelle régionale des données isotopiques dans toutes les composantes hydrologiques: précipitations, manteau neigeux hivernal, eaux de surface, eaux souterraines et sources. Les objectifs spécifiques relatifs au traçage de la recharge des systèmes aquifères rocheux et granulaires en condition de nappe captive et de nappe libre, ainsi que le bilan géochimique isotopique et les liens entre les divers compartiments hydrologiques (précipitations, neige au sol, eaux de surface, eaux souterraines, sources), sont les suivants :

1) Documenter les processus atmosphériques entraînant des variations spatio-temporelles de la composition isotopique des précipitations et calculer la droite météorique des eaux régionales de l'Abitibi-Témiscamingue ;

2) Évaluer les interactions potentielles et les processus de mélange entre les eaux de surface et les quatre types d'aquifères régionaux;

3) Déchiffrer les mécanismes qui contrôlent la variabilité de la composition isotopique de l'eau dans les aquifères régionaux.

Dans ce chapitre, les données sont interprétées pour soutenir un modèle hydrogéologique conceptuel amélioré des systèmes d'écoulement régionaux des eaux souterraines représentatifs des conditions hydrogéologiques et géochimiques observées.

Le chapitre 3 s’appuie sur l’étude des éléments chimiques (majeurs, mineurs, éléments traces) pour définir les processus géochimiques dominants depuis les zones de recharge (affleurements rocheux, aquifères granulaires à nappe libre) aux zones d’émergence (les sources en flanc d’eskers) vers les aquifères à nappe captive qui sont à l’origine de la signature géochimique des eaux des différents compartiments hydrologiques sur le territoire. Dans le contexte préétabli, ce chapitre cible le développement d’une approche pour cartographier la géochimie des eaux souterraines. Les objectifs spécifiques associés à l’étude géochimique des eaux sont :

1) Identifier les sources géogéniques et anthropiques des matières dissoutes totales dans les eaux souterraines;

2) Évaluer les principaux processus géochimiques dictant l'évolution géochimique des eaux souterraines dans les systèmes d'écoulement des eaux souterraines ;

3) Dresser des cartes prédictives de la géochimie des eaux souterraines.

Ce chapitre complète les études antérieures qui ont permis de documenter la géochimie régionale des eaux souterraines dans la province de Québec au Canada (Simard et Des Rosiers, 1975; Cloutier et al., 2006; Blanchette et al., 2010; Montcoudiol et al., 2015; Meyzonnat et al., 2016; Beaudry et al., 2018).

Finalement, le chapitre 4 s’intéresse à la qualité des eaux souterraines des puits d’approvisionnement en eau potable à l’échelle du territoire et aux sources géogéniques de contamination naturelle de l’eau souterraine liées aux lithologies régionales. Ce chapitre vise à développer une approche pour communiquer des informations sur la qualité des eaux souterraines afin de soutenir les utilisations sécuritaires de ces eaux et de protéger les aquifères d'eau souterraine de haute qualité. Pour ce faire, ce volet de l’étude propose le calcul d’un indice de contamination des eaux souterraines afin :

1) D'évaluer la distribution spatiale de l'indice de contamination des eaux souterraines (ICES) dans les systèmes d'écoulement des eaux souterraines de l'Abitibi-Témiscamingue ;

2) De tester la sensibilité de l’indice de contamination des eaux souterraines soumis aux changements des recommandations et des normes, avec un accent particulier pour le manganèse. Considéré uniquement comme un objectif esthétique avant 2019, le manganèse a basculé au Canada comme paramètre nuisible à la santé humaine depuis mai 2019 ;

3) D’appliquer une approche combinée ICES - DRASTIC pour promouvoir l'utilisation de mesures de protection par les propriétaires, particulièrement en zone rurale, et pour soutenir la protection des eaux souterraines de faible contamination et de haute qualité.

1.3.3 Démarche scientifique et méthodologie

La démarche scientifique employée dans les chapitres 2, 3 et 4 de cette thèse se base essentiellement sur l’échantillonnage des divers ensembles d’eau, l’analyse des paramètres chimiques dans un laboratoire accrédité et l’analyse des isotopes stables et radioactifs de la molécule d’eau dans un laboratoire spécialisé en traceurs isotopiques, l’intégration données géochimiques qui en découlent et l’interprétation de celles-ci.

L’échantillonnage des puits municipaux, des puits d’observation et des puits de particuliers a été réalisé suivant trois périodes de temps qui correspondent à un projet pré-PACES (2006) et aux deux phases du PACES-AT (2009-2013 et 2012-2015). Un échantillonnage des puits domestiques, en collaboration avec les habitants, a été effectué sur l’ensemble du territoire en espaçant l’échantillonnage d’environ 7 km entre les puits de particuliers afin d’assurer une couverture régionale représentative de la qualité naturelle des eaux souterraines selon les conditions du milieu de prélèvement. Les puits individuels ciblés ont été identifiés dans la base de données regroupant les puits sous le nom de système d’information hydrogéologique (SIH) appartenant au ministère de l’environnement. Les informations concernant la géologie du socle rocheux, les dépôts de surface, les séquences stratigraphiques régionales et les contextes hydrogéologiques sont tirées des rapports des projets PACES (Cloutier et al., 2013; 2015) produits par le Groupe de recherche sur l’eau souterraine (GRES) de l’UQAT. Les eaux de surface ont été échantillonnées dans des lacs et des rivières à l’échelle du territoire. Les sites d’échantillonnage des carottes de neige ont été sélectionnés dans la partie ouest du territoire en concordance avec les sites d’observation du Centre d’Expertise Hydrique du Québec (CEHQ) qui servent aux calculs des apports verticaux régionaux. Le suivi mensuel de la pluie et de la neige fondue s’est effectué dans quatre stations espacées sur la région d’étude. Trois stations correspondent à celles du réseau de surveillance du climat du ministère de l’environnement du Québec et une station se situe sur le toit du campus d’Amos de l’UQAT. Les échantillons de sources proviennent d’un projet de maîtrise d’une étudiante effectué à l’UQAT (Castelli, 2012). Les protocoles d’échantillonnage ont été établis dans le cadre du PACES (Blanchette et Cloutier, 2010) à partir des guides d'échantillonnage des eaux souterraines du ministère de l’environnement du Québec (MDDELCC, 2008; 2011). Les informations relatives aux puits sont collectées auprès des propriétaires et sur la base du SIH. La mesure des paramètres physico-chimiques (température, pH, Eh, conductivité électrique spécifique) est réalisée sur le terrain en utilisant une sonde multiparamétrique YSI. Les analyses chimiques réalisées au laboratoire accrédité concernent la détermination des anions majeurs par chromatographie ionique (IC), l'identification des métaux dissous par spectroscopie de masse à plasma d'argon ionisant (ICP-MS), l'identification de l'alcalinité totale en $CaCO_3$ par titration, l'identification des sulfures par le bleu de méthylène et la détermination du phosphore inorganique et de l'azote ammoniacal par colorimétrie automatisée avec du molybdate d'ammonium et du salicylate de sodium, respectivement. Les données ont été analysées et interprétées par le biais de statistiques descriptives et de représentations graphiques spécifiques. La spéciation et les indices de saturation ont été calculées en utilisant le logiciel *PHREEQC* (Parkhust et Appelo, 1999).

Les chapitre 2 et 3 concernent l'ensemble des eaux échantillonnés et sont bâtis sur les interprétations des données physicochimiques et isotopiques définissant les processus géochimiques qui régissent la composition chimique de l'eau souterraine et son évolution dans le temps et dans l'espace. Le chapitre 4 utilise les résultats chimiques pour calculer un indice de contamination des eaux souterraines afin de se pencher sur la qualité régionale de l'eau souterraine dans une dimension plus sociale, en vue de sensibiliser les particuliers à la nécessité de faire analyser régulièrement l'eau de leurs puits pour une consommation saine et durable. Ce calcul d'indice de contamination des eaux souterraines est fondé sur un calcul mathématique qui inclue les valeurs maximales acceptables fixées par le gouvernement aux paramètres chimiques jugés susceptibles d'être dommageables à la santé humaine et à ceux qui sont nuisibles sur le plan esthétique. Le chapitre 4 procure une synthèse des liens entre la qualité d'eau avec la géologie du roc et les contextes hydrogéologiques régionaux.

CHAPITRE II

USING WATER STABLE ISOTOPES FOR TRACING SURFACE AND GROUNDWATER FLOW SYTEMS IN THE BARLOW-OJIBWAY CLAY BELT, QUEBEC, CANADA

Rey, N., Rosa, E., Cloutier, V., & Lefebvre, R. (2018). Using water stable isotopes for tracing surface and groundwater flow systems in the Barlow-Ojibway Clay Belt, Quebec, Canada: Canadian Water Resources Journal / Revue canadienne des ressources hydriques, v. 43, no. 2, p. 173-194.

Résumé

Cette étude vise à mieux comprendre les systèmes d'écoulement dans une région de 19,549 km^2 au sein de la ceinture argileuse Barlow-Ojibway (ouest du Québec, Canada). La base de données contient 645 échantillons analysés pour les isotopes stables de l'eau (δ^2H-δ^{18}O) et inclue les précipitations, la neige au sol, les eaux de surface, les eaux souterraines et les sources, alors que 98 échantillons d'eau souterraine et de sources ont été analysés pour l'activité tritium. La composition isotopique des précipitations présente un cycle saisonnier dépendant de la température et définissant une droite locale des eaux météoriques (DLEM) sans tendance δ^2H-δ^{18}O reliée à la latitude. Les données de neige au sol tombent sur la DLEM, ce qui suggère que le couvert nival préserve sa composition isotopique en hiver, avant la fonte des neiges printanières. Les échantillons d'eau de surface définissent une droite évaporatoire locale (DEL) et les rapports de l'évaporation sur les flux intrants varient entre 0% et 36% à l'échelle régionale. Les données d'eau souterraine et de sources suggèrent que les processus d'évaporation sont limités avant l'infiltration et que les eaux de surface contribuent peu à la recharge. Les aquifères à nappe libre peu profonds présentent une plus grande variabilité isotopique par rapport aux aquifères à nappe captive situés en aval le long des lignes d'écoulement, ce qui suggère une atténuation de la variabilité isotopique issue de la recharge le long des systèmes régionaux. Un bilan géochimique appuyé sur les données isotopiques et de conductivité électrique de l'eau permet de quantifier ces mélanges. L'interprétation des données isotopiques permet de contraindre des modèles conceptuels représentant les systèmes d'écoulement régionaux et de documenter les processus de recharge, d'évaporation, de mélange et de résurgence.

Mots-clés

Isotopes stables de l’eau, Eau souterraine, Eau de surface, Précipitations, Région boréale

Abstract

This study aims to improve the understanding of surface and groundwater flow systems based on water stable isotopes data in a 19,549 km^2 region of the Barlow-Ojibway Clay Belt, in western Quebec, Canada. The available geochemical database contains 645 samples including precipitation, snow cores, surface waters, groundwater and springs. All samples were analyzed for water stable isotopes (δ^2H-δ^{18}O) and complementary tritium analyses were conducted on 98 groundwater and spring samples. Precipitations depict a clear temperature-dependent seasonal pattern and define a local meteoric water line (LMWL) without a latitudinal trend in δ^2H-δ^{18}O. Samples collected from the snowpack plot on the LMWL, suggesting that the bulk snowpack preserves the isotopic composition of precipitation throughout the frozen period, prior to the spring snowmelt. Surface water samples define a local evaporation line (LEL) and evaporation over inflow (E/I) ratios range between 0% and 36%. Groundwater and springs samples are evenly distributed around the LMWL, suggesting that evaporation processes are limited prior to infiltration and that surface waters do not significantly contribute to groundwater recharge. Shallow unconfined aquifers present a greater variability in δ^2H-δ^{18}O compared to confined aquifers located further down gradient, suggesting the mixing of varied recharge waters along the regional groundwater flow system. A three-component mixing model based on isotopic and specific electrical conductivity data allows the quantification of such mixing processes. The interpretation of isotopic data constrains a regional-scale conceptual model of groundwater flow systems and describes processes related to the timing of recharge, evaporation, mixing and discharge.

Keywords

Water stable isotopes, Groundwater, Surface waters, Precipitation, Boreal region

2.1 Introduction

Groundwater plays key functions for several ecosystems and represents an essential source of potable water for approximately half of the world's population (Taylor et al., 2013). Nevertheless, groundwater resources have been heavily used for human water supply and agriculture for many years on a global scale (WWAP, 2009) and climate change will most likely affect the hydrological cycle and aquifers in the near future (Green et al., 2011). Groundwater resources are expected to be increasingly stressed in response to demographic growth and growing water demand (Vörösmarty et al., 2000). It is estimated that by 2025, nearly 50% of the world's population will be living in water-stressed regions (WHO, 2017). Such considerations stress the critical need to better understand hydrogeological processes at various scales to support concrete actions aimed at protecting groundwater resources, to maintain ecosystems and meet water supply needs of future generations. Regionally and locally, groundwater protection must rely on land management strategies that are based on an appropriate understanding of the hydrogeological system. This is especially important in areas where most of the population relies on groundwater for potable water supply, as is the case for the Abitibi-Temiscamingue region in western Quebec. This region is renowned for its large eskers and moraines and for the remarkable quality of groundwater found within the aquifers associated with these formations (Veillette et al., 2004; Collini et al., 2007). However, these shallow unconfined aquifers are highly vulnerable to contamination and face increasing human pressures such as forest operations, sand and gravel extraction, former in-trench disposal sites, private and municipal wells and commercial water bottling (MRNF, 2006; Nadeau et al., 2015; Cloutier et al., 2016). The impacts on the groundwater resources associated with eskers might also affect aquifers located down-gradient, further highlighting the need to better understand regional hydrogeological processes. In this context, providing regional stakeholders with a coupled understanding of physical and geochemical conditions is mandatory to ensure that land-use decisions related to groundwater protection are based on reliable information.

Geochemical tracers are included in a wide spectrum of hydrological studies. They are increasingly used to delineate flowpaths and quantify the processes affecting surface and groundwater resources at various scales and in various regions of the world (e.g. Jeelani et al., 2013; Kortelainen and Karhu, 2004; Wassenaar et al., 2011). Among the wide range of geochemical tracers that have been exploited, water stable isotopes (^{2}H-^{18}O) data have provided unique insights into hydrological processes (Araguás-Araguás et al., 2000; Gibson et al., 2005; Birks and Gibson, 2009). The stable isotopes of water are partitioned within a hydrological system, mainly in response to systematic fractionation mechanisms occurring within the water cycle, including phase-change (solid-liquid-vapour) processes, diffusion and rainout (Craig, 1961; Rozanski et al., 1993; Gat, 1996; Clark and Fritz, 1997). The isotopic composition of water is widely used in theoretical and applied hydrological studies to document sources of atmospheric moisture and precipitation patterns (Dansgaard, 1964; Fritz at al., 1987), snow and ice-melting (Siegel and Mandle, 1984), evaporation processes in cold regions (Gat et al., 1994) and drylands (Kebede et al., 2009), sources mixing (Ferguson et al., 2007; Wolfe et al., 2007) and groundwater recharge (Praamsma et al., 2009), among other applications.

Cloutier et al. (2013; 2015; 2016) provided a comprehensive assessment of groundwater resources in the Abitibi-Témiscamingue region, within the framework of the *Programme d'Acquisition de Connaissances sur les Eaux Souterraines* (PACES) supported by the Quebec Ministry of the Environment. A regional scale conceptual hydrogeological model representing regional flowpaths from unconfined aquifers, located in recharge areas, to confined aquifers, found beneath the clay belt, was proposed through the course of these studies. Nevertheless, the proposed conceptual model is mainly constructed on the basis of physical hydrogeological data, whereas geochemical data have not been yet fully exploited, which leads to important limitations in the understanding of regional hydrogeological dynamics. Fitting into the pre-established framework, this study aims to improve the understanding of regional surface and groundwater flow systems in the southern portion of the Barlow-Ojibway Clay Belt (Abitibi-Témiscamingue, Quebec, Canada) on the basis of geochemical data. The present study focuses on the stable (^{2}H-^{18}O) and radioactive (^{3}H) isotopes of the water molecule. The proposed approach involves a regional-scale comprehensive assessment of isotopic data within all hydrological components: precipitations, winter snowpack, surface waters, groundwater and springs. The specific objectives of the present study are (1) to document the atmospheric processes driving spatiotemporal variations in precipitation isotopic composition, (2) to assess the potential interactions and mixing processes between surface waters and aquifers, and (3) to decipher the mechanisms controlling the water isotopic variability in regional aquifers. Ultimately, the data are interpreted to support an improved conceptual model of regional groundwater flow systems representative of observed hydrogeological and geochemical conditions.

2.2 Study Area

The study area (Figure 2.1) covers 19,549 km^{2} and corresponds to the municipalized territory of the Abitibi-Temiscamingue region in western Quebec, Canada. It encompasses the City of Rouyn-Noranda and the Regional County Municipalities (RCM) of *La Vallée-de-l'Or, Abitibi, Abitibi-Ouest and Témiscamingue*, for a total population of approximately 148,000 inhabitants (MAMROT, 2016). It is estimated that more than 70% of this population relies on groundwater as a source of domestic drinking water. The characteristics of the study area are briefly summarized below. Further details about the hydrogeological framework can be found in Nadeau et al. (2015), Cloutier et al. (2016), Nadeau et al. (2017) and within the geological maps of the Geological Survey of Canada (Veillette, 1986; 1987a; 1987b; Thibaudeau and Veillette, 2005; Paradis, 2005; 2007).

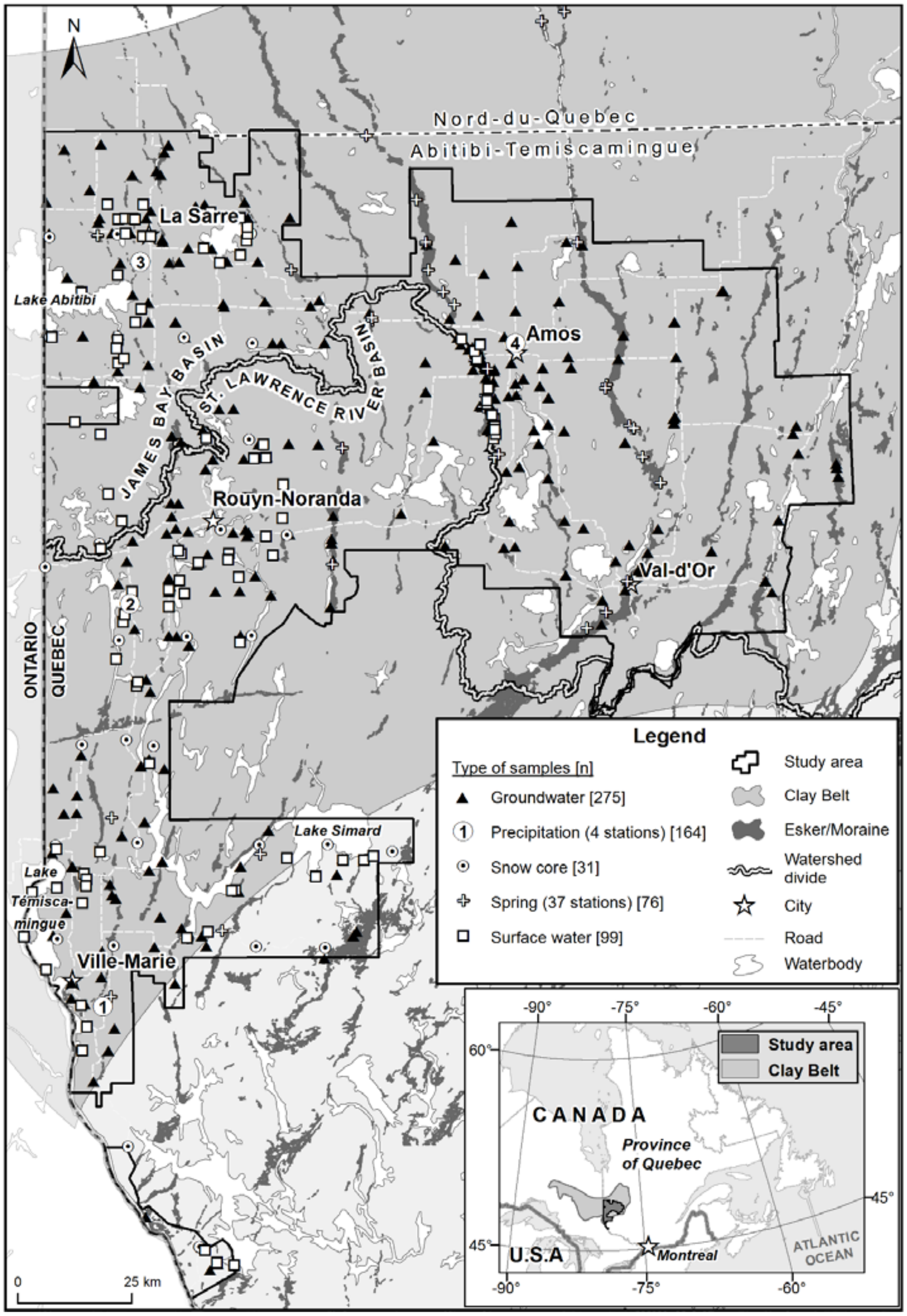


Figure 2.1. Study area with the location of sampling sites.The number (n) of available samples is shown brackets in the legend. The limits of the study area correspond to those of previous studies from Cloutier et al. (2013; 2015). The continental water divide between the St. Lawrence and the James Bay basins is also shown.

2.2.1 Physiography and hydrography

The landscape of the study area is relatively flat, with elevations generally ranging between 280 m and 320 m. The main positive reliefs correspond to heterogeneously distributed bedrock outcrops, while the main depressions are associated with large lakes (Abitibi, Témiscamingue and Simard; Figure 2.1). Despite its featureless landscape, the region is crossed by the continental water divide separating surface waters of the St. Lawrence River Basin (southern sector of the study area, Ottawa River watershed) and those of the James Bay Basin (northern sector of the study area, Moose, Harricana and Nottaway rivers watersheds).

2.2.2 Climate and air masses

The study region is characterized by a cold and humid continental climate with damp summers, rather cold and long winters and a marked seasonality. The average monthly air temperature remains below the freezing point from November to March (based on Quebec Ministry of the Environment climate data; 1981-2010). The region is characterized by a significant latitudinal thermal gradient and a difference of 2.1 °C between the average annual air temperature in Temiscamingue (south) and Abitibi (north) was reported by Asselin (1995). This difference is likely imparted by latitude and by the influence of the continental water divide that creates a discontinuity between the northern and southern sectors of the study area. The presence of numerous lakes on a territory characterized by a gentle relief likely favors the development of buffered microclimates. Such a phenomenon is documented in the vicinity of lakes Abitibi and Témiscamingue (Asselin 1995). Cloutier et al. (2015) provided daily air temperatures and vertical inflows based on interpolated data provided by *Centre d’Expertise Hydrique du Québec* (CEHQ) for a period ranging from 1900 to 2010 (Poirier et al., 2012). Vertical inflows correspond to the fluxes of water from liquid precipitations and from the melting of snow, and therefore to the fluxes of water that are available for infiltration or surface runoff. If the temperature is below the freezing point, vertical inflows can be null even if precipitation events are observed. In the absence of snow on the ground and when precipitations fall as liquid water, vertical inflows correspond to precipitation. Yearly average vertical inflows range between 790.5 and 856.5 mm at the regional scale. The vertical inflows associated with snow falling during the frozen period will mainly be observed during spring snowmelt. The greatest vertical inflows are recorded in April for most of the study area, except for the northernmost sector where maximum values are observed in May, probably due to later thaw (Cloutier et al., 2015). Minimum vertical inflows are recorded in January over the entire region due to temperatures that generally remain below the freezing point. Regional-scale monthly averages of daily maximum and minimum temperatures reveal that the warmest month is July (with daily average minimum and maximum temperatures of 11.2 °C and 23.7 °C, respectively) and the coldest month is January (with daily average minimum and maximum temperatures of -23.3 °C and -10.3 °C, respectively). The mean annual precipitation ranges from 875 mm for *La Vallée-de-l'Or* RCM and 989 mm in the city of Rouyn-Noranda (Quebec Ministry of the Environment climate data).

The main air masses affecting western Quebec are (1) the cold and dry Arctic, (2) the moist and warm Maritime-tropical air that originates from the Caribbean, subtropical Atlantic and Gulf of Mexico and migrates northwards following the Mississippi and Missouri valleys before being deflected eastwards across the Great Lakes basin and (3) the northern Pacific westerlies (Bryson, 1966; Bryson and Hare, 1974; Hare and Hay, 1974). The Pacific westerlies are dominant in the continental climate for much of the year (Hare and Hay, 1974). Summers in the study area are warm and humid, reflecting the dominance of Maritime-tropical air punctuated by intrusion of mild and dry westerlies. Winters are influenced by Artic air masses that lead to cold and dry conditions (Bryson and Hare, 1974). The Abitibi-Temiscamingue region is characterized by weather variability and instability reflecting the contribution of the different air masses. The dominant winds generally originate from the northwest during winter and southwest during summer. The polar jet stream, corresponding to the limit between the Arctic and Maritime-tropical air masses, crosses the study area along a sinuous west-east pattern at latitudes roughly corresponding to the position of the continental water divide.

2.2.3 Hydrogeological framework

The regional geological framework, as conceptually represented in Figure 2.2, is described in details in numerous previous studies (Nadeau et al., 2015; Cloutier et al., 2016; Nadeau et al., 2017; Veillette, 1986; 1987a; 1987b; Veillette et al., 2004; Thibaudeau and Veillette, 2005; Paradis, 2005; 2007) and it is thus only briefly presented here. Table 2.1 provides a summary of the hydrological domains (atmosphere, surface, subsurface), components (precipitation (snow, rain), surface water, groundwater, springs) and aquifers (granular (unconfined & confined), fractured rock (unconfined & confined)) that are discussed in this study, in relation with the main geological units of the region. The bedrock of the study area (geological unit A in Figure 2.2) is composed of a wide variety of igneous, metamorphic and metasedimentary rocks of the Abitibi and Pontiac sub-provinces, both components of the Superior Geological Province. Groundwater flow within the bedrock is controlled by the architecture of structural discontinuities. Cloutier et al. (2016) estimated hydraulic conductivities ranging between 10^{-9} and 10^{-4} m/s for this unit. However, there is currently no sufficient data to propose a regional-scale interpretation of bedrock hydrogeological characteristics based on structural interpretations. Nevertheless, Rouleau et al. (1999) proposed that groundwater flow within the bedrock of the study area is most likely restricted to depths shallower than 75 m where sub-horizontal fractures are sufficiently interconnected to allow significant groundwater flow. Most of the domestic wells of the region are withdrawing groundwater from this unit using wells that are cased through surficial sediments and open across the bedrock.

Table 2.1. Summarized characteristics of the regional hydrogeological framework. The numbers (1 to 8) of the sampled hydrological components and hydrogeological units correspond to those shown in figures 2.2 and 2.8. The till (B) is not an aquitard and neither an aquifer in itself, although it can contribute to the flow of overlying or underlying aquifers.

Domains	Hydrological components	Geological units	Hydrogeological units and aquifers
Atmosphere	(1) Precipitation (rain & snow)	-	-
Surface	(2) Snowpack (3) Surface water (4) Spring	-	-
Subsurface (groundwater)		C1 Eskers & moraines E Surface sediments near eskers	(5) Unconfined granular aquifer
		D Glaciolacustrine clay & silt	Regional aquitard
		C2 Sediments underlying clay	(6) Confined granular aquifer
		B Till	-
		A Fractured rock	(7) Unconfined or (8) confined fractured rock aquifer

The oldest unconsolidated unit of the region corresponds to the till associated with the last glaciation (geological unit B in Figure 2.2). It is recognized as a compact heterometric geological unit characterized by a matrix composed of sand, silt and clay (Cloutier et al., 2015). The hydrogeological characteristics of this unit are poorly documented because it is rarely exploited for groundwater supply, although it is not considered as a regional aquitard (Cloutier et al., 2013; 2015). This till unit is overlain in places by glaciofluvial sediments. The coarse grained glaciofluvial sediments (eskers and moraines; geological unit C1 in Figure 2.2) of the region were mainly deposited at the emergence of subglacial meltwater within proglacial Lake Barlow-Ojibway (Nadeau et al., 2015). These formations are characterized by relatively high hydraulic conductivities, 10^{-6} to 10^{-1} m/s according to Cloutier et al. (2016), and constitute the most productive unconfined aquifers of the region (Nadeau et al., 2015). Other glaciofluvial sediments, mainly consisting in finer sand and gravel, are also widespread between the main eskers and moraines of the region (geological unit C2 in Figure 2.2). This unit is generally characterized by hydraulic conductivities that are slightly lower than that of the eskers and moraines (Cloutier et al., 2013; 2015; 2016). The glaciofluvial sediments are covered in places by fine grained deep-water glaciolacustrine sediments deposited within proglacial Lake Barlow-Ojibway (identified as the Clay Belt in Figure 2.1; geological unit D in Figure 2.2). Owing to its structure consisting in centimeter-scale alternating layers of clay and silt (varves), this unit is considered as a regional aquitard (Cloutier et al., 2015), although silt horizons may allow preferential sub-horizontal groundwater flow. Sublittoral sands and beach or eolian sediments (geological unit E in Figure 2.2) overlying the fine grained deep-water glaciolacustrine sediments are spatially associated with the glaciofluvial deposits whereas organic deposits (geological unit F in Figure 2.2) are widespread across the region, with large peatlands often developing on the flanks of eskers and moraines.

Given this geological framework, and based on previous work from Cloutier et al. (2016) and Nadeau et al. (2017), four main types of aquifers are distinguished within the study region (Figure 2.2) and used to regroup the isotopic data:

(1) **Unconfined granular aquifers**, mainly associated with glaciofluvial formations (eskers and moraines; number 5 in Figure 2.2). These formations are characterized by relatively high hydraulic conductivities and represent the most productive aquifers of the region, providing a high quality resource to numerous municipal and private wells.

(2) **Confined granular aquifers**, in sectors where till and glaciofluvial sediments are covered by the fine grained deep-water glaciolacustrine sediments (number 6 in Figure 2.2);

(3) **Unconfined fractured rock aquifers**, essentially restricted to sectors characterized by bedrock and till outcrops (number 7 in Figure 2.2);

(4) **Confined fractured rock aquifers**, in sectors covered by fine grained deep-water glaciolacustrine sediments (number 8 in Figure 2.2). Most residences in rural sectors of the region withdraw water from private wells installed in this aquifer.

Cloutier et al. (2013; 2015; 2016) provided estimates of the average groundwater recharge rates (*GRR*) by calculating the water balance for each parcel of the study region on a monthly basis. The calculations were provided on a 100 m x 100 m grid over the study region, using the following equation:

$$GRR = VI - R - \Delta W_S - ET \qquad \text{Equation 1}$$

These water balance calculations are based on the vertical inflows (*VI*) provided by Poirier et al. (2012) and on hypotheses associated with the regional hydrogeological framework for estimating runoff (*R*), water storage within the unsaturated soil (ΔW_S) and evapotranspiration (*ET*). Runoff coefficients were estimated according to land use, soils characteristics and surface slopes, among others. Potential evapotranspiration rates were quantified using the Thornthwait (1944) equation with climate data from Poirier et al. (2012). The water storage within the unsaturated zone and the available water for transpiration were evaluated for the different soils based on estimates of water retention capacities, wilting points and thickness of the root zone. The calculated recharge rates range between less than 91 mm/yr in sectors where fine-grained deep-water glaciolacustrine sediments are found and more than 300 mm/yr, mainly in sectors corresponding to eskers / moraines and other unconfined granular aquifers. Overall, maximum recharge rates are observed during the snowmelt period whereas the lowest rates are recorded throughout the winter period, when temperatures are below the freezing point.

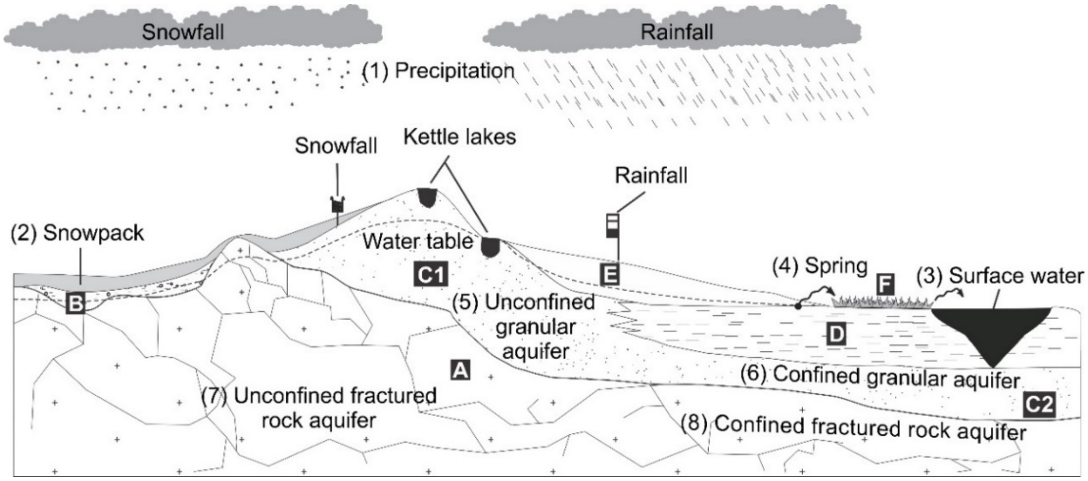


Figure 2.2. Regional hydrogeological conceptual model and water sampling scheme used to characterize the isotopic signature of all hydrological system components. (A) Fractured bedrock; (B) Till; (C1) Eskers and moraines; (C2) glaciofluvial sediments found between eskers and moraines, under the clay plain; (D) fine grained deep-water glaciolacustrine sediments; (E) Sublittoral sands and beach or eolian sediments; (F) Organic deposits. The numbers (1 to 8) correspond to the sampled hydrological components and hydrogeological units, as identified in table 2.1.

2.3 Methods

2.3.1 Sampling procedures and in situ measurements

Overall, 645 water samples were analyzed for their isotopic composition (δ^2H-δ^{18}O) as part of this study, over a period ranging from 2006 to 2015 (Figure 2.1; Table 2.2).

Table 2.2 provides a summary of the available data and associated sampling periods. From this dataset, 98 water samples (only springs and groundwater) were also analyzed for their tritium (^3H) content, over a period ranging from 2006 to 2011. The procedures associated with the sampling of precipitations, the snowpack, surface waters, springs and groundwater are presented separately below.

Table 2.2. Summary of available water stable isotope data. The number of available samples and associated timeline are shown. As reported, most samples were collected during the summer period. Further details about the surface water samples are provided in table 2.3.

Type of samples	Number of samples (n)	Sampling timeline
Precipitation	164	Monthly samples at four stations 2009-2015
Snowpack	31	March 2014 (n=31)
Springs	76	Summer 2009 (n=30) Summer-Autumn 2010 (n=41) Summer-Autumn 2013 (n=5)
Kettle lakes	14	Summer 2009 (n=14)
Surface waters	85	Summer-Autumn 2013 (n=85)
Confined fractured rock aquifer	105	Summer-Autumn 2006 (n=14) Summer-Autumn 2010 (n=26) Summer 2013 (n=65)
Unconfined fractured rock aquifers	38	Autumn 2006 (n=2) Summer 2010 (n=7) Summer-Autumn 2013 (n=29)
Confined granular aquifers	53	Summer-Autumn 2006 (n=2) Summer-Autumn 2010 (n=15) Summer 2013 (n=36)
Unconfined granular aquifers	79	Summer-Autumn 2006 (n=2) Summer 2009 (n=14) Summer-Autumn 2010 (n=25) Autumn 2011 (n=15) Summer-Autumn 2013 (n=23)
Total	645	2006-2015

2.3.1.1 Precipitation monitoring

Monthly composite precipitation samples were collected at four monitoring stations within the study area (Figure 1; Station 1 = Béarn; Station 2 = Montbeillard; Station 3 = Sainte-Hélène-de-Mancebourg; Station 4 = Amos). Samples were collected monthly from July 2013 to 2015 at stations 1-2-3 (Figure 2.1), three sites included in the Quebec

Ministry of the Environment Climate Monitoring Network. Rainfall samples were collected using a 10.1 cm inside diameter *All Weather P-2000* standard rain gauges from *Productive Alternatives*. A thin layer (approximately 1 cm) of paraffin oil (Mineral Oil, Light (NF/FCC), *Fisher Chemical*) was added to the rain gauges to prevent evaporation and plastic screens were installed at the base of the rain gauge funnels to block debris and insects. Snowfall samples were collected owing to the participation of local operators / observers associated with the monitoring network. These observers are mandated to make measurements of snow (calculated in terms of equivalent water) intercepted by shielded *Nipher* snow gauges. Snow samples are collected daily at stations 1 and 3 (but not at station 2 owing to logistical constraints), left to melt overnight and subsequently stored in 1 L high density polyethylene (HDPE) bottles. Daily samples are mixed in order to obtain composite monthly samples. Paraffin oil (Mineral Oil, Light (NF/FCC), Fisher Chemical) is added to the bottles in order to prevent evaporation. The Amos monitoring station (Station 4), in operation from September 2009 to 2015, is located on the roof of the university campus and is not associated with the MDDELCC climate network. At this station, rain and snow samples are collected daily using a 30 cm ID bucket. Snow samples were left to melt overnight at 4 °C and subsequently stored in HDPE bottles. Daily samples were combined to produce a monthly composite sample. In all cases, the volume of monthly composite samples was first evaluated in the laboratory and smaller aliquots were subsequently stored in 60 ml HDPE bottles and kept at 4 °C until stable isotopes (δ^2H-δ^{18}O) analyses.

2.3.1.2 Samples from the Snowpack

A sampling campaign was carried out in March 2014 in order to retrieve cores from the snowpack accumulated throughout the winter. Sampling sites were selected in the western part of the study region in an effort to collect data in the vicinity of the grid points used by the CEHQ for calculating vertical inflows (Poirier et al., 2012). At each site, a straight trench varying in length from 5 m to 6 m was first dug in a direction oriented perpendicular to the wind. Snow cores ($n \geqslant 5$) were subsequently sampled at $\leqslant 1$ m intervals, on the side of the trench facing the dominant wind. Snow cores were collected using 4.2 cm ID x 1.6 m length HDPE tubes allowing the collection of the snowpack over its entire height. Samples were weighed on site using a *Mettler Toledo* digital scale with a precision of 0.0001 kg in order to calculate equivalent water contents. For each site, the collected snow cores were transferred and combined within wide neck HDPE bottles in order to obtain > 800 g composite samples. Samples were kept frozen within the tightly sealed wide neck bottles during the field campaign and subsequently left to melt overnight at room temperature. The melted samples were filtered using 0.45 µm *Waterra FHT* cartridges to remove soil particles and/or windblown debris embedded in the snow. The filtered samples were transferred into 30-60 ml HDPE containers and stored at 4 °C until stable isotopes (δ^2H-δ^{18}O) analyses.

2.3.1.3 Surface waters

Surface water samples were collected in July 2009 and from July to October, 2013. Rivers and streams were sampled near the central part of the main channel, at depths of 0.5-1.5 m below surface. In situ parameters (pH, dissolved oxygen, conductivity, redox potential and temperature) were measured using a *YSI 556 MPS* probe, a few centimeters downstream of the sampling point. A 7.32 m *NASCO Swing* Sampler telescopic pole equipped with a 1 L HDPE bottle was used to collect samples from the banks of small rivers and streams. The perch and its container were rinsed on site at a point located a few meters downstream of the sampling site. Whenever sampling from a bridge was possible, the samples were collected using 1 L *Waterra ecobailers*. A nylon wire equipped with a float was attached to the bailer to indicate the sampling depth. The bailers were systematically rinsed on site, with water from rivers prior to sampling. Some of the streams and rivers were sampled immediately at the outlet of large lakes (Table 2.3). These samples are used to provide an instantaneous estimate of the isotopic composition of water in the epilimnon at the outlet of the lake. Grab samples were also collected from 16 additional lakes, including 14 kettle lakes (Table 2.3). The samples from Lake Témiscamingue were collected from a boat, at a depth of 1 m using a *NASCO Swing Sampler* telescopic pole equipped with a 1 L HDPE bottle. The samples from Lake Tee were collected from a boat, approximately 1 m below the surface, using a plastic tubing equipped with an inertial valve. The samples from kettle lakes were collected from the shoreline, approximately 1 m below surface, using a *NASCO Swing Sampler* telescopic pole equipped with a 1 L HDPE bottle. All surface water samples were filtered immediately after collection using 0.45 µm *Waterra FHT*. The samples collected for stable isotopes analyses (δ^{2}H-δ^{18}O) were stored in 30-60 ml HDPE bottles and kept at 4 °C until analysis.

Table 2.3. Summary of surface waters sampling conditions. Most of surface water samples were collected at a shallow depth below the surface, mainly during the summer period. Further details about the sampling procedures are provided in the text.

Surface waters	Names	Sampling techniques	Dates
Kettle lakes	-	1 m from the lake shore / Telescopic pole / 0.5-1.5 m below surface	Summer 2009
Fault Lakes	Opasatica		Summer 2013
	Rémigny		
	Témiscamingue	Boat / Telescopic pole / 0.5-1.5 m below surface	
	Tee	Boat / Plastic tubing equipped with an inertial valve / 0.5-1.5 m below surface	Autumn 2013
Lakes on clay	Macamic	Sampling at the outlet of the lake / Telescopic pole / 0.5-1.5 m below surface	Summer 2013
	Abitibi		
Rivers	Outaouais	Boat / Telescopic pole / central part of the main channel / 0.5-1.5 m below surface	
	Duparquet	Sampling near the central part of the main channel / Telescopic pole or Bailer / 0.5-1.5 m below surface	
	La Sarre		
	From lac Mance		
	Between Beauchastel and Montbeillard lakes		
	Between Routier and Vallet lakes		
	Between Rondelet and Des Quinze lakes		
	Between two lakes (Mont Brun sector)		
Small streams	-	Sampling near the central part of the main channel / Telescopic pole or Bailer / 0.5-1.5 m below surface	Summer/Autumn 2013

2.3.1.4 Springs

Groundwater springs were sampled between July 2009 and September 2011 through the course of a previous study (Castelli, 2012). These samples are associated with the Vaudray-Joannès, Launay and Saint-Mathieu-Berry eskers and with the Harricana Moraine. Other spring samples were collected during the summer of 2013. These correspond to springs that are equipped for drinking water supply. All spring samples were filtered immediately after collection using 0.45 µm *Waterra FHT carthridges*. The *in situ parameters* (pH, dissolved oxygen, specific electrical conductivity (SEC), redox potential and temperature) were measured on site using a multi-parameter probe. Further details about the sampling methodology can be found in Castelli (2012). The samples collected for stable isotopes analyses (δ^2H-δ^{18}O) were stored in 30-60 ml HDPE bottles. The samples collected for tritium (^{3}H) analyses were stored in 1 L HDPE bottles. Sampling bottles for stable isotopes analyses (δ^2H-δ^{18}O) and tritium (^{3}H) analyses were filled to the top with no head space and kept at 4 °C until analysis.

2.3.1.5 Groundwater

Municipal, private and observation wells were sampled during this study. The targeted wells were commonly identified using the Quebec Ministry of the Environment water well databases, including the Hydrogeological Information System (HIS). Complementary information about the characteristics of the sampled wells was obtained from the private owners or from municipal employees. Well logs were used to document the characteristics of the sampled observation wells. Two conditions had to be met prior to groundwater samples collection: the infrastructures had to be purged of a minimal volume of water and the monitored *in situ* parameters had to reach predefined stability criteria. Water was therefore systematically purged from domestic and observation wells before sample collection. This procedure allows draining the stagnant water from the infrastructure to obtain a water sample that represents groundwater from the aquifer. For private wells, it was assumed that water was withdrawn on a regular basis and that the minimal purge could be limited to the volume of the pressurized reservoirs. The purging was done from taps supplying untreated water. The minimum purging volume for observation wells corresponded to three times the total volume of water stored within the well and its gravel pack. In municipal wells, it was assumed that water is withdrawn at a sufficient rate to prevent stagnation within infrastructures and that no minimal purge was required. During the purge, *in situ* parameters (pH, dissolved oxygen, SEC, redox potential and temperature,) were measured using a multi-parameter probe. The samples were retrieved only after all of the in situ parameters had reached the stability criteria reported in Table 2.4 for three consecutive measurements separated by five minutes intervals. The samples collected for stable isotopes analyses ($\delta^{2}H$-$\delta^{18}O$) were stored in 30-60 ml HDPE bottles and kept at 4 °C until analysis. The samples collected for tritium (^{3}H) analyses were stored in 1 L HDPE bottles. Sampling bottles for tritium (^{3}H) analyses were filled under water in a bucket and capped under water with no head space following a filling procedure described by the USGS and kept at 4 °C until analysis.

Table 2.4. Stability criteria for groundwater sample collection.
Stability criteria for groundwater sample collection.
Groundwater samples were collected only when the stability criteria were reached for three consecutive measurements separated by five minutes intervals.

In situ parameters	Stability criteria
Temperature (°C)	± 0.1
pH (pH unit)	± 0.1
Specific electrical conductivity (µS/cm)	± 2%
Dissolved oxygen (mg/L)	± 0.2
Redox potential (mV)	± 10
Turbidity (visual observation)	Constant color/opacity

2.3.2 Analytical procedures

Water samples were analyzed for δ^2H and δ^{18}O at the stable isotopes laboratory of the Geotop-UQAM research center in Montreal, Canada. Measurements were made using a dual inlet *Micromass Isoprime*™ isotope ratio mass spectrometer coupled to an *Aquaprep*™ system. For oxygen and hydrogen isotopic analyses, 200 µl of water were transferred into septum vials and equilibrated in a heated rack with a known volume of CO_2 (H_2 in the case of hydrogen analyses, with a platinum catalyst). The isotopic compositions of samples were corrected using internal reference waters (δ^{18}O = -6.71‰, -13.98‰ and -20.31‰; δ^2H= -51.0‰, -99.0‰ and -155.4‰) calibrated on the VSMOW-SLAP scale (Coplen, 1996). Reference waters were systematically analyzed between series of samples in order to check for instrumental stability. The analytical uncertainty is $\leqslant$ 1‰ for δ^2H and $\leqslant$ 0.05‰ for δ^{18}O at the 1σ level. Values are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW). Water samples for tritium (^{3}H) analyses were measured by liquid scintillation counting (LSC) at the Environmental Isotope Laboratory of the University of Waterloo, Canada. The detection limit for enriched samples is 0.8 tritium units (TU).

2.3.3 Data organization and statistical analyzes

In order to support the interpretation of results, the isotopic data are organized according to the main hydrological components and aquifers that were presented previously (Table 2.1; Figure 2.2). Overall, eight distinct groups are identified for segregating the isotopic data. The latter include (with numbers corresponding to those reported in Figure 2) samples corresponding to (1) precipitation, (2) the snowpack, (3) surface waters, (4) springs, (5) unconfined granular aquifers, (6) confined granular aquifers, (7) unconfined fractured rock aquifers and (8) confined fractured rock aquifers. The basic statistical analyses conducted on the dataset and related plots were performed using the Statistica version 6 (*StatSoft Inc*., 2004) and *Microsoft Excel* software.

2.4 Results and discussion

The entire dataset associated with stable isotopes analyses is shown in Figure 2.3a, whereas Figure 2.3b allows a better representation of surface and groundwater data. Figure 2.3c presents the average values of groundwater and surface water groups in the same range as Figure 2.3b. As a complement, Figure 2.4 presents boxplots showing the non-outlier range, 25th and 75th percentiles and median SEC, $\delta^{18}O$ and ^{3}H values for selected groups of data. The non-outlier range is defined as maximum and minimum values within 1.5 times the interquartile range. It was chosen not to show the data outside of the non-outlier range in the boxplots (Figure 2.4) in order to allow a better representation of the data. Nevertheless, the entire dataset is shown in Figure 2.3. Results associated with three of the main components of the water cycle (namely precipitation, surface waters and groundwater) are first discussed separately to address specific topics and jointly interpreted afterward to propose a regional-scale conceptual model of groundwater flow.

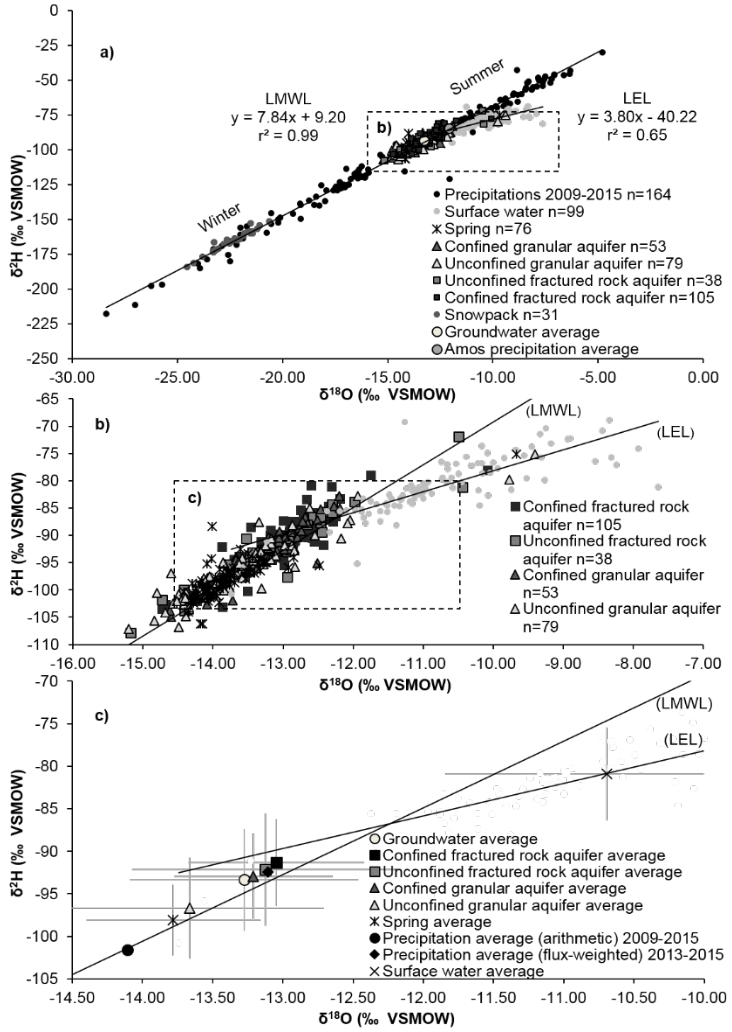


Figure 2.3. Isotopic composition of precipitation, surface waters, springs and groundwater. All data are shown in (a) whereas figure (b) provides a zoom on the surface and groundwater data. Average values are provided in figure (c). The flux-weighted average for precipitation is based on the three stations (Sainte-Hélène-de-Mancebourg, Amos, Bearn) where precipitation samples were collected between 2013 and 2015. The value correspond to the mean of the flux-weighted averages calculated for each station. The arithmetic average calculated for all precipitation samples is also shown. The error bars in (c) correspond to the standard deviation calculated for each sample series. The local meteoric water line (LMWL) and local evaporation line (LEL) derived from the data are also shown. Isotopic values are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW).

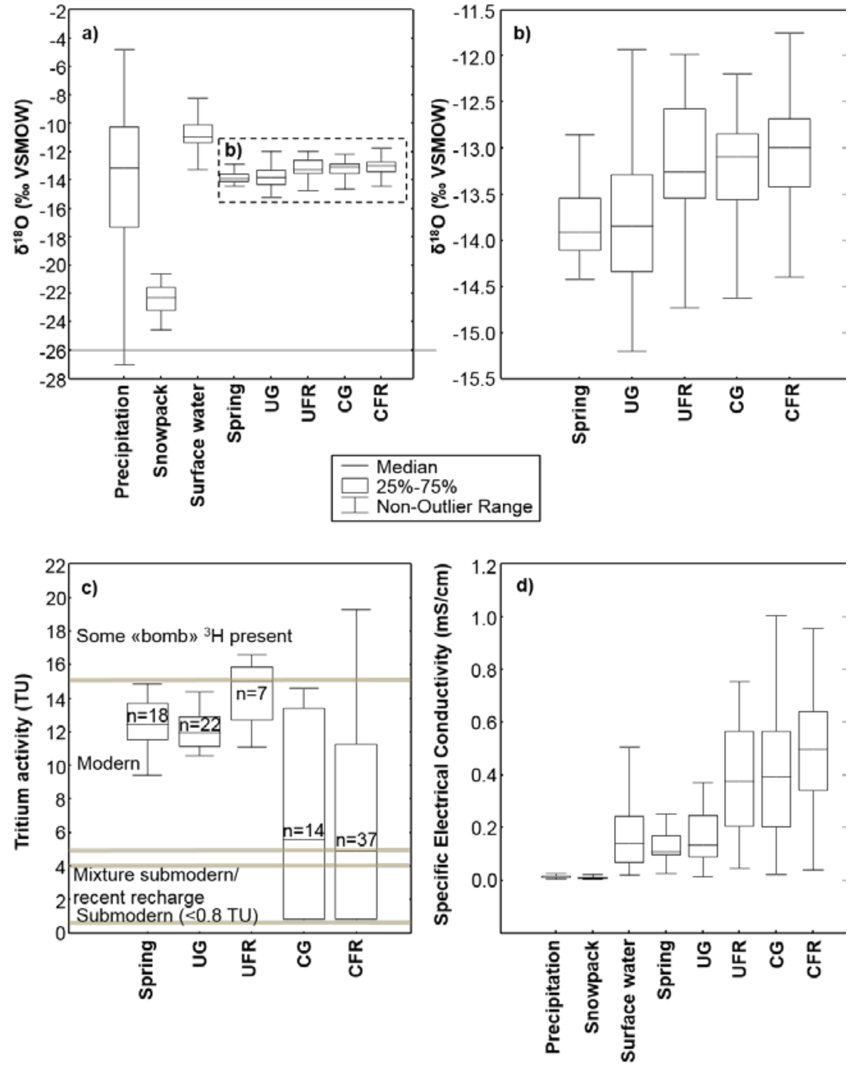


Figure 2.4. δ^{18}O (a; b), ^{3}H (c) and SEC (d) boxplots for precipitation, surface waters, springs and groundwater. Outlier data are excluded; the non-outlier range is defined as maximum and minimum values within 1.5 times the interquartile range. The available δ^{18}O data are shown in (a) whereas a clearer view of surface and groundwater data is provided in (b). The classification reported in (c) is adapted from Clark and Fritz (1997). UG: unconfined granular aquifers; UFR: unconfined fractured rock aquifers; CG: confined granular aquifers; CFR: confined fractured rock aquifers; SEC: specific electrical conductivity. In (a) and (d), the samples collected from the snowpack and at the precipitation monitoring stations are shown separately. δ^{18}O values (a,b) are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW).

2.4.1 The isotopic composition of precipitation: air masses and seasonal patterns

The δ^2H and δ^{18}O values of precipitation ranged from -217.9‰ to -29.9‰ and -28.4‰ to -4.8‰ respectively (Figure 2.3a). These data are used to define the Local Meteoric Water Line, calculated using precipitation (n=164) and snowpack data (n=31) (LMWL; $\delta^2H = 7.84\ \delta^{18}O + 9.20‰$ (n = 195, $r^2 = 0.99$); Figure 2.3). The LMWL is relatively close to Craig's global meteoric water line (GMWL; $\delta^2H = 8\ \delta^{18}O + 10‰$ SMOW; Craig, 1961). In terms of temporal variations, the monthly precipitation data revealed the expected temperature-dependant isotopic cycle, with heavy isotopes depletion during the colder period and enrichment during the warmer period (Figure 2.5). Such a pattern is typical of boreal regions with summer rains enriched in heavy isotopes and winter precipitation depleted in heavy isotopes in response to strong seasonal variations in temperature (Clark and Fritz, 1997). Overall, the temporal variations in the isotopic composition of precipitation reflect the marked seasonality of the study area.

The weighted mean annual isotopic compositions of precipitation at stations 1, 3 and 4 are shown in Table 2.5. The data do not show a clear relationship between precipitation δ^2H-δ^{18}O and latitude. The absence of a latitudinal gradient in precipitation isotopic composition could reflect the superimposed influence of the three major air masses that supply moisture over the study area, namely (1) the Arctic air mass (from the north), (2) the tropical vapor (from the south) and (3) the westerlies (Bryson, 1966; Fritz et al., 1987). Given the relatively flat landscape of the study area, the effect of altitude on precipitation δ^2H-δ^{18}O values is probably limited. Finally, evaporation processes might also influence the isotopic composition of precipitation at the local scale, near large water bodies such as the Témiscamingue, Simard and Abitibi lakes (Figure 2.1). Further data would be required to better explain spatial variations in the isotopic composition of precipitations at the scale of the study area.

Samples collected from the snowpack in March 2014 (prior to the onset of spring snowmelt) revealed δ^2H and δ^{18}O values ranging from -184.4‰ to -151.6‰ and –

24.5‰ to –20.6‰ respectively (Figure 2.3). Ice layers have been found in some places in the snowpack during sample collection. It is recognized that isotopic fractionation occurs during snowmelt (Taylor et al., 2001; Laudon et al., 2002). This suggests that the different layers identified within the sampled snowpack (which reflect melting / refreezing events) are most likely characterized by variable isotopic compositions. Nevertheless, here, the bulk samples (i.e. composite samples of the entire thickness of snow) collected from the snowpack prior to the onset of the snowmelt event plot uniformly on the left side of the LMWL (Figure 2.3), with values similar to that measured at the precipitation monitoring stations. This suggests that the bulk of the snowpack preserved an isotopic composition that is similar to that of precipitation prior to the onset of the spring snowmelt event. Overall, the isotopic compositions of samples retrieved from the snowpack do not define a clear latitudinal gradient at the regional scale.

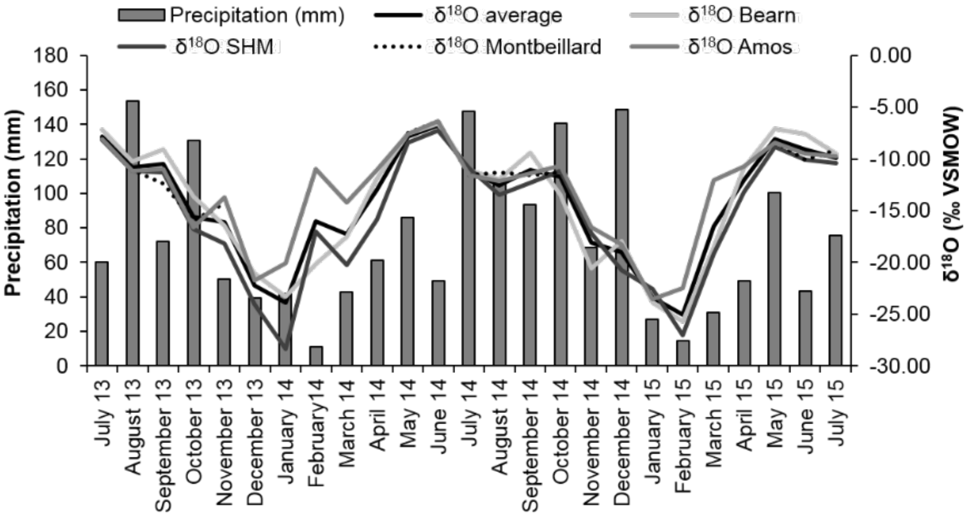


Figure 2.5. Seasonal variations in precipitation amounts and δ^{18}O composition. See Figure 2.1 for the location of monitoring stations. The histogram showing precipitation amounts is based on data from July 2013 to July 2015 as recorded at the monitoring stations. SHM: Sainte-Hélène-de-Mancebourg. δ^{18}O values are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW).

Table 2.5 Amount weighted average isotopic composition of precipitation at the four sampling stations (2013-2015).

Stations	n	δ^2H (‰ VSMOW)	δ^{18}O (‰ VSMOW)
Station 1 (Béarn)	24	-91.9	-13.0
Station 2 (Montbeillard)	13	NA	NA
Station 3 (Sainte-Hélène-de-Mancebourg)	24	-100.9	-14.2
Station 4 (Amos)	24	-84.5	-12.0

Refer to Figure 2.1 for stations locations; n: number of samples.
NA: averages values are not provided owing to a lack of data from November to April.
VSMOW: Vienna Standard Mean Ocean Water standard.

2.4.2 The isotopic composition of surface waters: inflows, evaporative enrichment and mixing

The regional dataset reveals a significant variability in surface waters δ^2H and δ^{18}O, with values ranging from -100.8‰ to -68.9‰ and -13.7‰ to -7.6‰, respectively (for regional average values of -80.9‰ (δ^2H) and -10.7‰ (δ^{18}O)). The isotopic composition of surface waters can present both spatial and temporal variations owing to the superimposed influence of precipitation, groundwater inflow, evaporation and tributary mixing processes (Yi et al., 2010). Temporal variations are commonly observed in regions characterized by a marked seasonality where heavy isotope depletion following snowmelt and enrichment caused by evaporation during the ice off period have been reported (e.g. see Telmer and Veizer, 2000; Yi et al., 2010). Here, most of the samples were collected in summer (Table 2.2), and the data plot below the LMWL, consistent with the hypothesis that surface waters have undergone heavy isotope enrichment owing to evaporation. A surface Local Evaporation Line (LEL): $\delta^2\text{H} = 3.80\ \delta^{18}\text{O} - 40.22$ ‰ ($n = 99$, $r^2 = 0.65$) (Figure 2.3a) is evaluated from the data. The evaporation over inflow ratio (E/I), as described by Gibson and Edwards (2002), corresponds to the water balance of a surface water body and relates to the combined effects of evaporative heavy isotope enrichment and dilution by inflowing waters. The E/I ratio is used here for evaluating the hydrological processes responsible for the distribution of surface water data plotting below the LMWL in δ^2H vs δ^{18}O graphs (Figure 2.3). The Hydrocalculator application from Skrzypek et al. (2015) was used to calculate evaporation over inflow (E/I) ratios under steady state conditions (shown over the LEL in Figure 2.6a). This application solves a modified form of the Craig and Gordon (1965) model:

$$\frac{E}{I} = \left[\frac{(\delta_L - \delta_P)}{(\delta^* - \delta_L) \times m}\right] \qquad \text{Equation 2}$$

Where δ_L corresponds to the isotopic composition of the sampled surface water, δ_P is the initial isotopic composition of water and δ^* is the limiting isotopic enrichment factor (a function of the isotopic fractionation factor and atmospheric isotopic composition and relative humidity). Similar approaches are used to evaluate the E/I ratios of rivers (e.g.: Telmer and Veizer, 2000) and lakes (e.g. Gibson and Edwards, 2002). Here, theoretical calculations are proposed for points falling directly on the LEL evaluated from the dataset, the latter corresponding to the δ_L term of equation 2. The initial isotopic composition of water (δ_P) is assumed to correspond to the intersection between the LMWL and the LEL. The isotopic composition of atmospheric moisture (δ_A), which is needed to evaluate δ^* in equation 2, is evaluated according to three scenarios:

1- δ_A is in equilibrium with the flux weighted average isotopic composition of precipitation between the months of May and August (δ_A = -141.21‰ ; -19.45‰);

2- δ_A is in equilibrium with the arithmetic average isotopic composition of precipitation between the months of May and August (δ_A = -137.42‰ ; -18.91‰);

3- δ_A is in equilibrium with δ_P (δ_A = -156.03‰ ; -21.63‰).

A temperature of 22 °C and a relative humidity of 70% are assumed, consistent with the conditions encountered during the warm ice off period within the study region. The isotope fractionation factors are calculated from the Horita and Wesolowski (1994) equations.

Depending on the model parameters used, E/I ratios ranging between 0% and 36% are evaluated from the regional dataset (Figure 6a). Based on this theoretical framework, surface water samples plotting closer to the LMWL most likely present the lowest E/I ratios. These surface waters might be affected by significant evaporation losses, but inflows (mostly precipitation and groundwater, both plotting along the LMWL) are sufficient to buffer the heavy isotope enrichment resulting from evaporation. On the contrary, the samples that are most enriched in heavy isotopes (i.e. plotting further along the right side of the LEL) most likely present the highest E/I ratios. Within the regional hydrogeological framework, it is most likely that evaporation mainly occurs within lakes and stagnant water bodies whereas dynamic in stream processes mainly reflect surface water / groundwater interactions and tributary mixing.

One distinctive feature of the regional dataset is that most of the kettle lakes plot on the right side of the LEL, suggesting overall high E/I ratios in comparison to other surface waters (Figure 2.6b). Recent studies by Isokangas et al. (2015) and Arnoux et al. (2017) provided novel methods to estimate the groundwater dependency of such lakes based on E/I ratios calculated from stable isotope data, among other. Here, quantifying the groundwater dependency of lakes is precluded by uncertainties related to volumes, surface water inflows and potential heterogeneities caused by thermal stratification and temporal variations. Nevertheless, the distinctive isotopic composition of kettle lakes stresses the need for conducting further studies aimed at quantifying their water balance to better anticipate their sensitivity to climate change and human pressure.

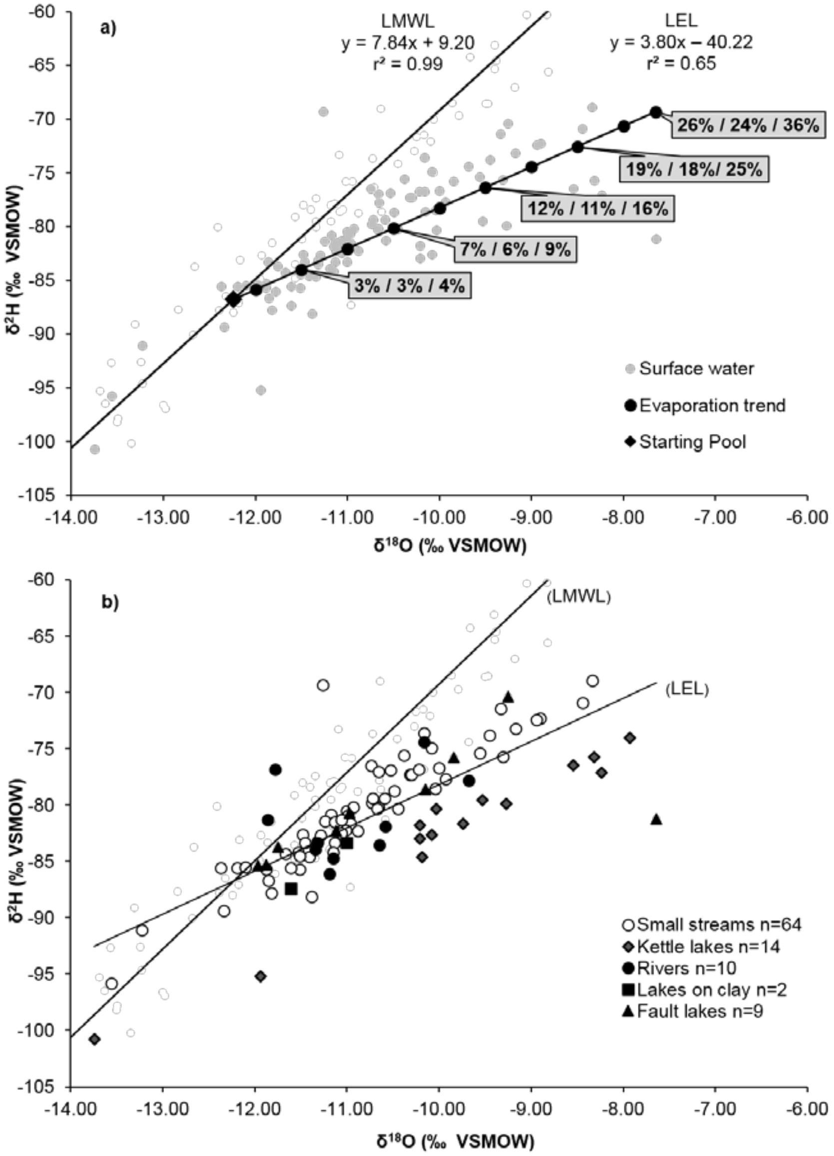


Figure 2.6. Interpretation of the isotopic compositions of surface waters. Data in (a) represent the local evaporation line evaluated using the 99 available surface water samples. The Evaporation over Inflow (E/I) ratios are shown for points plotting on the Local Evaporation Line (LEL) at 0.5‰ intervals along the x-axis. These E/I ratios are shown for three scenarios (see text for details). Further details with respect to the types of surface water samples are provided in (b) and in table 2.3. Isotopic values are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW).

2.4.3 The isotopic composition of groundwater and springs: recharge, discharge, mixing and regional flowpaths

The stable isotopes analyses (δ^2H-δ^{18}O) conducted on 351 groundwater and springs samples are shown on the graphs of Figures 2.3, 2.4a and 2.4b. The data associated with groundwater samples are represented according to the four main types of regional aquifers, as shown in Figure 2.2 (unconfined granular aquifers; unconfined fractured rock aquifers; confined granular aquifers; confined fractured rock aquifers). The δ^2H and δ^{18}O values of groundwater samples ranged from -107.8‰ to -71.9‰ and -15.2‰ to -9.4‰, respectively, for a regional average of -13.3‰ (δ^{18}O); -93.4‰ (δ^2H). The δ^2H and δ^{18}O values of spring samples ranged from -106.3‰ to -75.1 ‰ and -14.4‰ to -9.7‰, respectively for a regional average of -13.8‰ (δ^{18}O); -98.1‰ (δ^2H). Previous work by Castelli (2012) revealed that the isotopic composition of springs is fairly stable (1) throughout the ice-off season and (2) from year to year. Similarly, it is assumed here that the isotopic composition of groundwater is relatively constant in time. The focus is therefore set on spatial rather than temporal variations in isotopic compositions. The data associated with groundwater and springs are evenly distributed around the LMWL. This suggests that (1) infiltration and recharge processes are not significantly affected by evaporation losses and (2) aquifers are not significantly affected by inflows from evaporated surface waters. This is consistent with the regional hydrogeological framework because: (1) the main recharge areas consist of coarse grained glaciofluvial formations where high infiltration rates prevent surface pounding (and associated evaporation) and (2) physical measurements suggest that groundwater generally discharges into surface waters at the regional scale (Cloutier et al., 2013; 2015). Although water losses by plant transpiration prior to groundwater recharge might be significant, the available dataset does not allow the quantification of this process. Results also support the hypothesis that regional surface waters – groundwater interactions are essentially restricted to groundwater discharging into surface waters, and not the inverse (otherwise, some groundwater samples would most likely be plotting significantly below the LMWL owing to mixing with evaporated surface waters). The data do not show systematic latitudinal trends in the stable isotope composition of groundwater at the regional scale. This is most likely caused by the complex mixing of recharge originating from the main atmospheric air masses supplying precipitation over the study region.

The data associated with the four main types of aquifers present a significant dispersion and overlap within Figures 2.3 and 2.4b. Nevertheless, two main observations arise from the distribution of data within the δ^2H-δ^{18}O plots:

(1) The data associated with unconfined granular aquifers present a greater dispersion in comparison to the other types of aquifers (Figure 2.4b);

(2) Confined granular aquifers and fractured rock aquifers (both confined and unconfined) tend to plot further on the right side of LMWL in comparison to springs and unconfined granular aquifers (Figure 2.3c).

These observations are interpreted in an effort to further constrain the understanding of regional flowpaths within the hydrogeological environment conceptually represented in Figure 2.2. The unconfined granular aquifers represent the main regional recharge zones where rain and melted snow preferentially infiltrate at different periods of the year, depending on local climatic and hydrological conditions (Cloutier et al., 2016). The proposed interpretation of groundwater stable isotope data is that unconfined granular aquifers present a greater δ^2H-δ^{18}O variability owing to a shorter residence time of water within shallow and dynamic systems such as eskers and moraines. The results associated with ^{3}H analyzes (Figure 2.4c) further support this interpretation. Overall, the tritium data suggest that water samples from springs, unconfined granular aquifers and unconfined fractured rock aquifers correspond to modern waters (with values ranging between approximately 9 and 17 TU, consistent with the subdivisions proposed by Clark and Fritz, 1997). Such results suggest a relatively short residence time of water in these shallow components. In contrast, samples collected within confined aquifers (both granular and fractured) present tritium contents below 0.8 TU (consistent with submodern values according to the subdivisions proposed by Clark and Fritz, 1997). Such results suggest that within the region, confined aquifers generally contain older groundwater in comparison to unconfined aquifers.

The sampled springs are all located on the flanks of unconfined granular aquifers associated with glaciofluvial formations (eskers / moraines). Their heavy isotope depletion (Figure 2.3c) with respect to most groundwater samples suggests that superficial flow systems associated with springs are submitted to a greater influence of lighter precipitation. As previously discussed, within the study area, precipitations depict a clear seasonal pattern, with lighter values recorded during the cold period (Figure 2.5). Under such conditions, one likely explanation is that a significant proportion of the groundwater recharge associated with snowmelt contributes to springs discharge. This stands as a plausible explanation because the springs located on the flanks of eskers and moraines essentially consist in «overflows» allowing groundwater to discharge from unconfined granular aquifers towards the surface water network. From a physical perspective, it seems likely that «overflow» conditions would be favored following the thawing period, as groundwater levels are generally raising within the eskers and moraines of the region during this period (Cloutier et al., 2013; 2015). During the dryer summer period, recharge rates are likely reduced, therefore limiting the supply of heavier water associated with summer precipitation to shallow flow systems. In fall, at the end of the warmer period, when the uptake of water by vegetation is reduced and precipitation are increased, recharge rates most likely increase, further supplying water that is depleted in heavy isotopes to the shallow flow systems associated with springs. The loss of lighter isotopes resulting from groundwater discharge within springs could also partly explain why the confined aquifers, located further downstream within the flow systems, are slightly enriched in heavy isotopes with respect to springs and shallow unconfined aquifers (Figures 2.3c;

2.4b). One key regional observation discussed by Cloutier et al. (2016) is that extensive peatlands are developed on the flanks of several eskers and moraines of the region. The contacts between esker/moraines and these extensive peatlands are interpreted as diffuse groundwater seepage zones (Nadeau et al., 2015). The process related to the loss of lighter isotopes within punctual springs might therefore be generalized to most of the unconfined aquifers associated with extensive peatlands and diffuse groundwater seepage zones. In addition, it seems most likely that the areas associated with unconfined fractured rock aquifers are less prone to groundwater recharge during snowmelt in comparison to the areas associated with glaciofluvial formations (i.e. unconfined granular aquifers). This hypothesis is based on the contrast in hydraulic conductivity (K) between the fractured bedrock (lower K) and the eskers and moraines (higher K) (e.g. see Cloutier et al., 2015). The differences in the isotopic composition of unconfined granular aquifers and springs compared to that of confined granular aquifers and fractured rock aquifers (both confined and unconfined) could therefore reflect the relative contribution of snowmelt induced recharge for the different types of aquifers.

The interpretations discussed above are further illustrated in Figure 2.7a, where the SEC of springs and groundwater is plotted against the corresponding $\delta^{18}O$ values. The data presented therein reveals that confined fractured rock aquifers generally present the highest SEC values whereas the unconfined granular aquifers present the lowest SEC values. This is also depicted in Figure 2.4d where a gradual increase in SEC is observed from unconfined towards confined aquifers. SEC can thus be used as a proxy for groundwater residence time and geochemical evolution, higher SEC generally implying more evolved groundwater. This pattern most likely reflects the combined effects of (1) increased geochemical interactions between groundwater and the geological environment along regional flowpaths and (2) recharge of precipitation having very low dissolved solid concentration (thus quite low SEC) in unconfined granular aquifers areas. The mixing model shown in Figure 2.7a further supports the interpretations proposed above. Three end-members are proposed to explain the variability in both $\delta^{18}O$ and SEC values:

1- End-member «A» presents low SEC and $\delta^{18}O$, it is identified as representative of recent snowmelt induced recharge. The lowest non-outlier $\delta^{18}O$ value recorded in unconfined granular aquifers (lower end of the boxplot shown in Figure 2.4b) is used to characterize this end-member, whereas the SEC value is set to 0.05 mS/cm, corresponding to the lowest non-outlier SEC value recorded in unconfined granular aquifers (lower end of the boxplot shown in Figure 2.4d);

2- End-member «B» presents low SEC and high $\delta^{18}O$ close to -12‰, it is identified as representative of fall recharge affected by relatively high temperature rain. The highest non-outlier $\delta^{18}O$ value recorded in unconfined granular aquifers (higher end of the boxplot shown in Figure 2.4b) is used to characterize this end-member, whereas the SEC value is set to 0.05 mS/cm, as previously defined for end-member «A»;

3- End-member «C» presents high SEC and $\delta^{18}O$, it is identified as representative of well mixed water (from various recharge zones or various recharge periods) that is geochemically evolved owing to prolonged water-rock interactions along flowpaths, thus leading to a higher SEC. The median $\delta^{18}O$ isotopic composition of confined fractured rock aquifers is used to constrain this end-member, and the SEC is set to 1.8 mS/cm (the highest recorded value in the dataset, Figure 2.4d).

The dashed lines in Figure 2.7 a and b represent mixing lines between the three end-members, at 25% intervals. In this mixing model, the SEC is considered linearly related to the geochemical level of evolution of groundwater, which is most probably not linearly related to the groundwater residence time.

Six main outliers are identified among the groundwater/springs dataset in Figures 2.3b. These six points plot below the LMWL in Figure 2.3, suggesting an evaporative enrichment that is not observed in the other groundwater samples. Five of these points are associated with samples collected in the immediate vicinity of lakes whereas the fifth one was collected within a mining site. It is proposed that the five samples collected near lakes and presenting heavy isotope enrichment and low SEC values are directly affected by the supply of evaporated and low SEC lake waters. The wells characterized by low SEC and low $\delta^{18}O$ values are likely affected by nearby snowmelt induced groundwater recharge, whereas those with low SEC and significantly higher $\delta^{18}O$ values are likely affected by mixing with surface waters. In that sense, within the study region, stable isotope data could be used as a screening tool to detect groundwater wells that are affected by surface waters. Such wells would deserve a specific attention in groundwater monitoring programs because they might be more vulnerable to microbial contamination originating from surface waters. Finally, the sixth outlier point was collected in a groundwater well located within a mining site; its isotopic composition and SEC value most likely reflect anthropogenic effects.

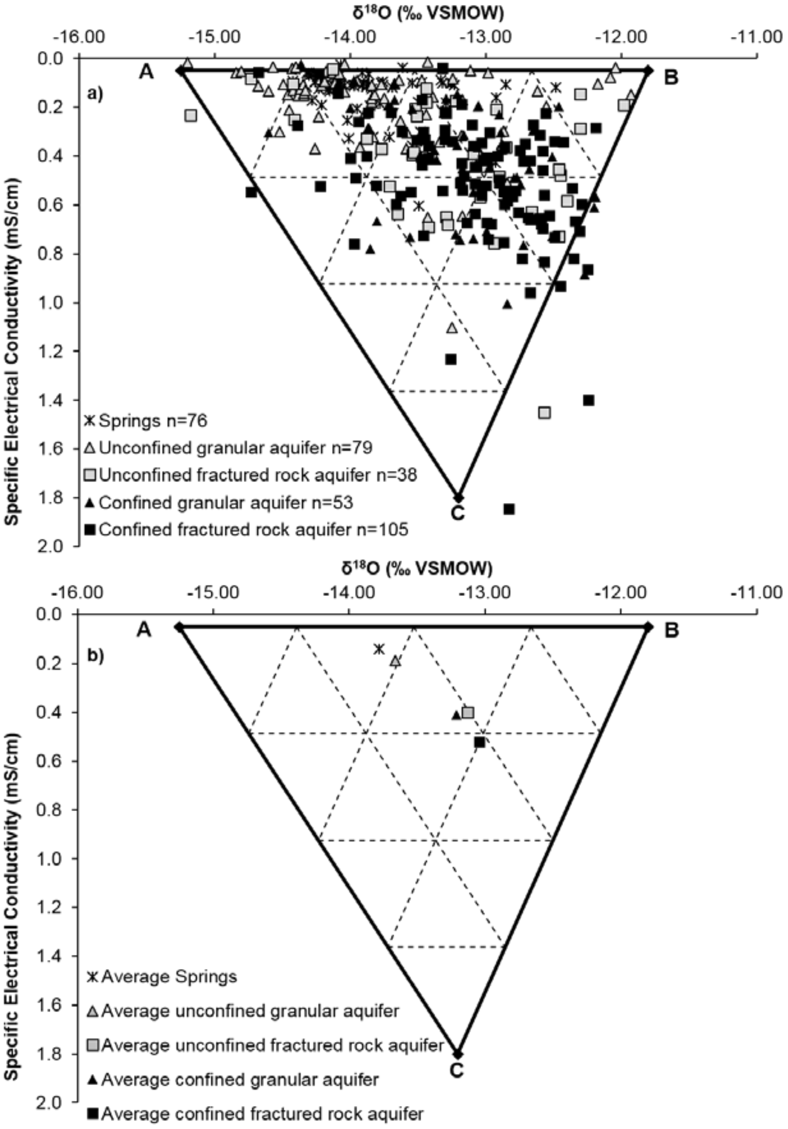


Figure 2.7. Specific electrical conductivity (SEC) vs δ^{18}O of springs, surface waters and groundwater. Three end-members are shown: «A» corresponds to groundwater recharged during snowmelt, «B» corresponds to groundwater that is less impacted by snowmelt induced recharge and «C» corresponds to geochemically evolved groundwater found further along regional flowpaths. See text for further details. The six main outliers (as described in the text) are not shown in this figure. Figure (a) shows the distribution of data whereas the corresponding averages are shown in (b). δ^{18}O values are reported in permil units (‰) against the Vienna Standard Mean Ocean Water standard (VSMOW).

2.4.4 Local and regional systems of groundwater flow: insights from water stable isotopes

Tóth (1963) proposed a conceptual model of groundwater flow in 2D cross sections involving local, intermediate and regional groundwater flow sub-systems. Such conceptual models constitute a central unifying concept to describe groundwater recharge, flow and discharge processes at various scales and provide a framework that is of upmost importance to interpret regional hydrogeochemical datasets. Tóth (1999) further developed his conceptual model by presenting groundwater as a geologic agent interacting with the environment and inheriting a geochemical composition that preserves an archive of hydrogeochemical processes and systematically evolves along flow paths. Following Toth's pioneer work, the different flow systems of the study area are interpreted with a focus on the isotopes of the water molecule itself, rather than other dissolved species. The working hypothesis is that within the considered spatiotemporal domain, the isotopic composition (δ^2H-δ^{18}O) of water is not significantly affected by water-rock interactions but rather mainly reflects the superimposed effects of precipitation isotopic composition, evaporation, recharge, mixing and discharge processes that vary in time and space. The average δ^2H-δ^{18}O compositions of precipitation (including snow samples), surface waters, springs and groundwater are shown in Figure 2.8, which consists in a more detailed representation of the regional hydrogeological conditions that was initially conceptualized in Figure 2.2.

The conceptual model illustrates precipitation showing the greatest isotopic variability and recharge occurring mainly within shallow unconfined aquifers, where the variability in the isotopic composition of water is attenuated with respect to precipitation due to mixing. Part of the water flowing within these unconfined aquifers discharges towards surface waters through springs and diffuse seepage zones that are generally depleted in heavy isotopes with respect to the average composition of groundwater. Surface waters are subsequently submitted to evaporation (causing heavy isotope enrichments) and to further dilution by precipitation and groundwater discharge. The remaining groundwater flows from unconfined recharge areas towards confined aquifers, allowing two key geochemical processes to occur along flow paths:

(1) Water rock interaction: groundwater becomes increasingly concentrated in dissolved ions owing to prolonged water-rock interactions, as shown by the gradual increase in SEC among the various hydrological components, from precipitations towards confined fractured rock aquifers (Figure 2.4d). This interpretation is further supported by the tritium analyses (Figure 2.4c), which suggest that confined aquifers are characterized by longer water residence times compared to springs and unconfined aquifers;

(2) Mixing: The isotopic composition of groundwater evolves towards a regional average owing to the mixing of water originating from various recharge zones or various recharge periods. This is illustrated in Figure 2.4b and Figure 2.7a, which suggest that mixing processes tend to damp the variability recorded in $\delta^{18}O$ values within confined aquifers. In other terms, the greater the proportion of unconfined aquifers in the vicinity on a given site, the greater the potential variability in the stable isotope composition of groundwater.

Clark and Fritz (1997) proposed a schematic representation of the attenuation of seasonal isotope variations in recharge waters within the unsaturated zone. These authors reported that temporal isotopic variations around an average value are gradually damped with increasing depth as a function of flowpaths lengths and residence times. A comparable interpretation is proposed here to explain the evolution of groundwater SEC and $\delta^{2}H$-$\delta^{18}O$ along local, intermediate and regional flow systems (Figures 2.7 and 2.8). On one hand, since recharge processes are primarily associated with sectors of unconfined aquifers and partly controlled by hydrogeological conditions that are highly heterogeneous at the regional scale, a significant variability is recorded in unconfined aquifers isotopic compositions. Overall, the unconfined granular aquifers associated with coarse grained glaciofluvial formations (eskers and moraines) are more prone to recharge during snowmelt and therefore present low δ^2H-δ^{18}O values in comparison to the other types of aquifers. Similarly, the springs found on the flanks of eskers and moraines are depleted in heavy isotopes. On the other hand, recharge areas associated with unconfined bedrock aquifers are more prone to runoff generation during the intense snowmelt event, and are therefore generally enriched in heavy isotopes in comparison to unconfined granular aquifers. Finally, the confined aquifers located further along groundwater flowpaths are fed by numerous interconnected unconfined aquifer areas that are heterogeneously distributed over the region. The result of the mixing processes occurring along flowpaths is a gradual evolution towards a regional average value within confined aquifers. Based on this interpretation, groundwater samples from confined aquifers that present an isotopic composition that significantly differs from the regional average most likely represents sites where the preferential influence of a nearby recharge area are recorded.

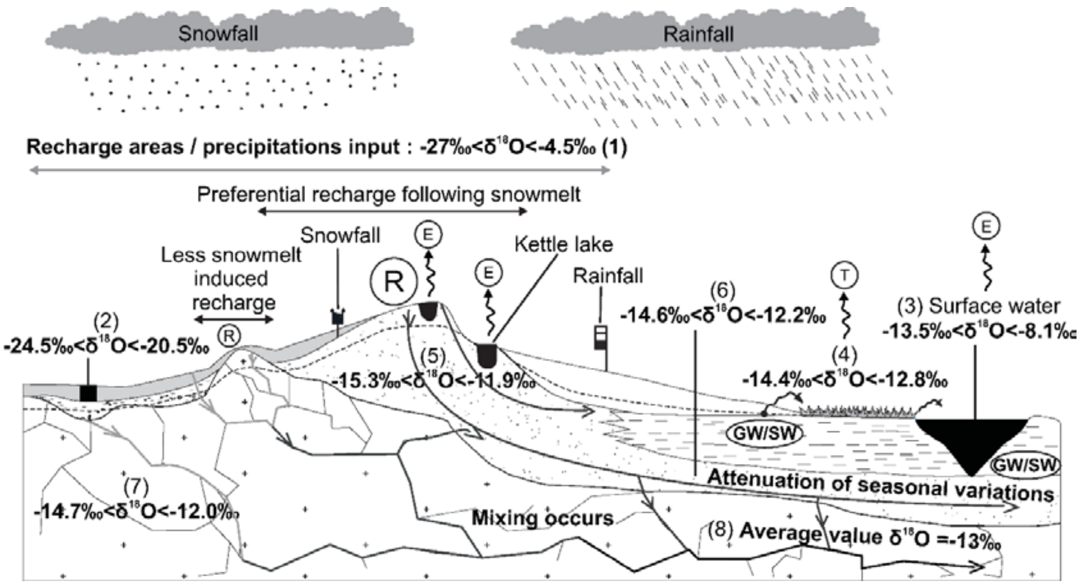


Figure 2.8. Isotopic variations within local, intermediate and regional flow systems. The range of measured isotopic compositions is shown for the sampled hydrological components and hydrogeological units, as identified in Tables 2.1 and 2.2. Areas of preferential snowmelt induced recharge are identified. Flowpaths at various scales are shown. (R) Recharge area; (E) Evaporation; (T) Transpiration; (GW/SW) Groundwater / surface water interactions (herein mainly groundwater exfiltration). The numbers (1 to 8) correspond to the sampled hydrological components and hydrogeological units, as identified in Table 2.1.

2.5 Conclusions

The isotopic composition of water (δ^2H-$\delta^{18}O$ and ^3H) in precipitation, surface waters, groundwater and springs was used to improve the understanding of regional flow systems in the southern portion of the Barlow-Ojibway Clay Belt. The data allowed the identification of the key hydrological processes driving spatiotemporal isotopic variations and deciphering the interaction pathways between the various components of the water cycle, from atmospheric moisture to groundwater discharge:

(1) Regional precipitations depict a clear seasonal pattern with heavy isotope depletion recorded in winter and heavy isotope enrichment in summer. The data did not reveal clear spatial trends in precipitation $\delta^{2}H$-$\delta^{18}O$, most likely in response to the complex mixing of inputs from the main air masses supplying moisture to the study region. Overall, precipitation data allowed the definition of the local meteoric water line (LMWL: $\delta^{2}H = 7.84\ \delta^{18}O + 9.20‰$; $n = 164$; $r^2 = 0.99$);

(2) Surface waters plot below the LMWL in a $\delta^{2}H$-$\delta^{18}O$ graph owing to evaporation losses. Calculations conducted using a modified form of the Craig and Gordon (1965) model with the Hydrocalculator application (Skrzypek et al., 2015) provided an estimation of evaporation over inflow (E/I) ratios ranging between 0% and 36% at the regional scale;

(3) Groundwater samples plot on the LMWL and are evenly distributed around the average isotopic composition of precipitation in a $\delta^{2}H$-$\delta^{18}O$ graph, suggesting that evaporation processes do not significantly affect regional recharge waters. The $\delta^{2}H$-$\delta^{18}O$ of groundwater in shallow unconfined aquifers presents a greater variability in comparison to confined aquifers owing to mixing processes that tend to buffer the isotopic variability along the regional groundwater flow paths. This buffering on the isotopic composition variability is accompanied by increasing values of the SEC of groundwater from unconfined to confined aquifers, most likely in response to increasing water-rock interaction timescales, consistent with generally lower tritium contents in confined aquifers;

(4) Unconfined granular aquifers and associated springs are generally slightly depleted in heavy isotopes in comparison to other groundwater samples, suggesting that these shallow flow systems are preferentially recharged during spring snowmelt within the region.

Overall, the observations and interpretations of this study support an improvement of a conceptual hydrogeological model of local and regional hydrological systems and flow paths that is consistent with the geological framework. This conceptual model illustrates how water isotopes can be used to constrain physically-based interpretations of local, intermediate and regional flow systems such as those inspired by the pioneering work of Tóth (1963), even in a highly heterogeneous region. The buffering of isotopic variability in groundwater from groundwater recharge areas located in unconfined aquifers towards groundwater discharge areas and confined aquifers located further along regional flow paths provides a framework for deciphering the processes associated with the geochemical evolution of groundwater, as a complement to understandings based on dissolved major ions and trace elements.

Acknowledgements

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CHAPITRE III

MAPPING GROUNDWATER GEOCHEMISTRY IN FLOW SYSTEMS OF THE BARLOW-OJIBWAY CLAY BELT IN ABITIBI-TEMISCAMINGUE, QUEBEC, CANADA

Rey, N., Cloutier, V., Rosa, E., Blanchette, D., & Lefebvre, R. Mapping groundwater geochemistry in flow systems of the Barlow-Ojibway Clay Belt in Abitibi-Temiscamingue, Quebec, Canada. En préparation.

Résumé

L’étude porte sur l’évaluation des sources et de l’issue des éléments chimiques dissous dans les systèmes d'écoulement des eaux souterraines de la ceinture argileuse Barlow-Ojibway en Abitibi-Témiscamingue (Québec, Canada). Elle permet aussi de cartographier la chimie des eaux souterraines dans une région où la majeure partie de la population dépend des eaux souterraines pour son approvisionnement en eau potable. La base de données géochimiques disponible contient 706 échantillons et comprend les précipitations (neige et pluie), les carottes de neige, les eaux de surface, les eaux souterraines et les sources analysées pour les ions majeurs, les nutriments et les éléments traces. Les données montrent les tendances prévisibles de l'évolution géochimique des eaux souterraines allant des aquifères granulaires à nappe libre aux aquifères rocheux fracturés à nappe captive, avec une augmentation de la concentration des constituants majeurs dissous, du manganèse et du fer et une diminution du Eh le long des chemins d’écoulement des eaux souterraines. Une approche de modélisation inverse réalisée à l'aide de *PHREEQC* a été utilisée pour évaluer les sources des éléments chimiques dissous dans les eaux souterraines. Les données recueillies dans les aquifères rocheux fracturés à nappe libre ont permis d'établir des liens entre les sources géogéniques et la lithologie du substrat rocheux. Bien que la géologie complexe du substrat rocheux du Bouclier canadien empêche les généralisations, certains éléments traces se sont avérés principalement associés aux roches intrusives (exemple : U, F), tandis que d'autres éléments traces sont associés à des roches volcaniques (exemple : As, Cr). Les résultats ont permis de créer une carte régionale de la qualité des eaux souterraines, en tenant compte à la fois des sources géogéniques et de l'évolution des eaux souterraines le long des chemins d'écoulement. Elle fournit des informations pour mieux gérer et protéger les ressources en eaux souterraines à l'échelle régionale. L'approche de cartographie des aquifères développée dans le présent document pourrait s’avérer pertinente pour l'étude des territoires où la disponibilité des données est limitée, à l'instar d'autres zones du Bouclier canadien.

Mots-clés

Géochimie des eaux souterraines, Cartographie, Modélisation inverse, Évolution géochimique, Bouclier canadien

Abstract

This study focuses on evaluating the sources and fate of dissolved solids in groundwater flow systems of the Barlow-Ojibway Clay Belt in Abitibi-Témiscamingue (Quebec, Canada). It allows for mapping groundwater chemistry in an area where most of the population relies on groundwater for drinking water supply. The available geochemical database contains 706 samples including precipitation, snow cores, surface waters, groundwater and springs analyzed for major ions, nutrients and trace elements. The data show predictable trends of groundwater geochemical evolution from unconfined granular aquifers to confined bedrock aquifers, with an increase in dissolved major constituents, Mn and Fe and a decrease in Eh along groundwater flowpaths. An inverse modeling approach performed using *PHREEQC* is used for evaluating the sources of dissolved solids in groundwater. The data collected from unconfined bedrock aquifers allowed establishing links between geogenic sources and bedrock lithology. Although the complex geology of the Canadian Shield bedrock prevents generalizations, some trace elements were found to be mainly associated with intrusive rocks (e.g. U, F), while other are associated with volcanic rocks (e.g. As, Cr). The results allowed for creating a regional map of groundwater quality, accounting for both geogenic sources and groundwater evolution along flowpaths. It provides insights for better managing and protecting groundwater resources at the regional scale. The aquifer mapping approach developed herein could most likely be relevant for studying territories where data availability is limited as other areas of the Canadian Shield.

Keywords

Groundwater geochemistry, Mapping, Inverse modeling, Geochemical evolution, Canadian Shield

3.1 Introduction

A safe access to water is essential to ecosystems and humans. The ability of water to respond to its ecosystem functions depends on its quantity and quality. When considering water as a resource, inventories at different spatial scales are crucial. Such inventories make it possible to know the availability of the resource and its spatial distribution, with a view to protecting it. In recent decades, considerable scientific efforts have been invested to evaluate the volume and spatial distribution of water on the planet and it is now possible to document the volume and fluxes of water at the global scale (e.g. see Oki and Kanae, 2006). Of all the components of the water cycle, groundwater is particularly complex because its distribution and circulation depend on the characteristics of the geological substratum, hydro-climatic conditions and human impacts. Some of these characteristics are not visible from the surface, while the others vary greatly in time and space. As a result, global estimates of groundwater storage still show a marked uncertainty (Richey et al., 2015). Nevertheless, the available estimates of groundwater storage and fluxes allowed for robust scientific assessments on the state of the resource in the context of increasing human pressures over the last two decades (Shah et al., 2001; Foster and Chilton, 2003; Morris et al., 2003; Scanlon et al., 2005; Wada et al., 2010; Foster et al., 2013). It appears, however, that the state of knowledge remains more fragmented with respect to the question of the geochemical composition (or quality) of groundwater. To date, relatively few studies are available to estimate or predict spatial variations in groundwater geochemistry over vast regions. Recent studies focusing on statistical modeling and GIS-based approaches now allow bridging this gap. As leading examples, Amini et al. (2008a; 2008b) provided global predictive maps of fluorine and arsenic in groundwater. Other major initiatives from governmental agencies and academic institutions now allow for assessing the quality of groundwater over large areas. For example, this is the case for the United States (USGS - National Water Quality Assessment Program – DeSimone et al., 2014; Arnold et al., 2017) and Europe (European Environment Agency – Scheidleder, 1999; Edmund and Shand, 2008). Nevertheless, the mapping of groundwater geochemistry remains complex. If the general processes dictating the geochemical evolution of groundwater are known (Tóth, 1999; Edmunds and Shand, 2008), their representation is more often the object of conceptual models than of quantitative maps. This most likely stems from the challenge of transcribing a conceptual model to the complexity of a real geological environment. This is especially challenging in areas where the bedrock lithology is highly heterogeneous and where several local groundwater flow systems are superimposed to regional flow systems. However, establishing approaches to map the quality of groundwater is a priority issue. Such maps are imperative for considering the quality of the groundwater resource as a criterion in land use planning since geographic limits are generally used for delineating land use classes. The protection of groundwater resources for future generations comes with such an issue and the problem is of particular importance in areas where people depend on groundwater for domestic water supply. In addition, predictive maps of groundwater quality could provide useful insights for estimating the exposure of private groundwater well owners to undesirable dissolved constituents. In a broader scientific perspective, this study relies on the concept that increasingly precise regional scale assessments will contribute to reducing the uncertainty related to global scale inventories of the state of the groundwater resource. Progressively more precise global scale assessments of the groundwater resource will most likely rely on the aggregation of regional scale data.

Fitting into the pre-established context, the general objective of this study is to develop an approach for mapping groundwater geochemistry. It focuses on a 19,549 km^2 region of the Barlow-Ojibway Clay Belt in Abitibi-Temiscamingue, Quebec, Canada, where more than 70% of the population relies on groundwater as the main source of drinking water. The specific objectives are to (1) to identify geogenic and anthropogenic sources of dissolved solids in groundwater, (2) to evaluate the processes dictating groundwater geochemical evolution within the groundwater flow systems and (3) to draw predictive maps of groundwater geochemistry. This research stems from previous work conducted in the framework of the Quebec Groundwater Knowledge Acquisition Program (Cloutier et al., 2013; 2015; 2016; Nadeau et al., 2018; Rey et al., 2018). It complements previous studies documenting regional groundwater geochemistry in the province of Quebec, Canada (Simard and Des Rosiers 1975; Cloutier et al., 2006; Blanchette et al., 2010; Montcoudiol et al., 2015; Meyzonnat et al., 2016; Beaudry et al., 2018).

3.2 Study area

The study region covers a total area of 19,549 km^2 and is located in Abitibi-Témiscamingue, western Quebec, Canada (Figure 3.1). The hydrogeological framework of this region was described extensively in recent studies (e.g.: Nadeau et al., 2018; Rey et al., 2018; Rosa et al., 2018) and is briefly presented below.

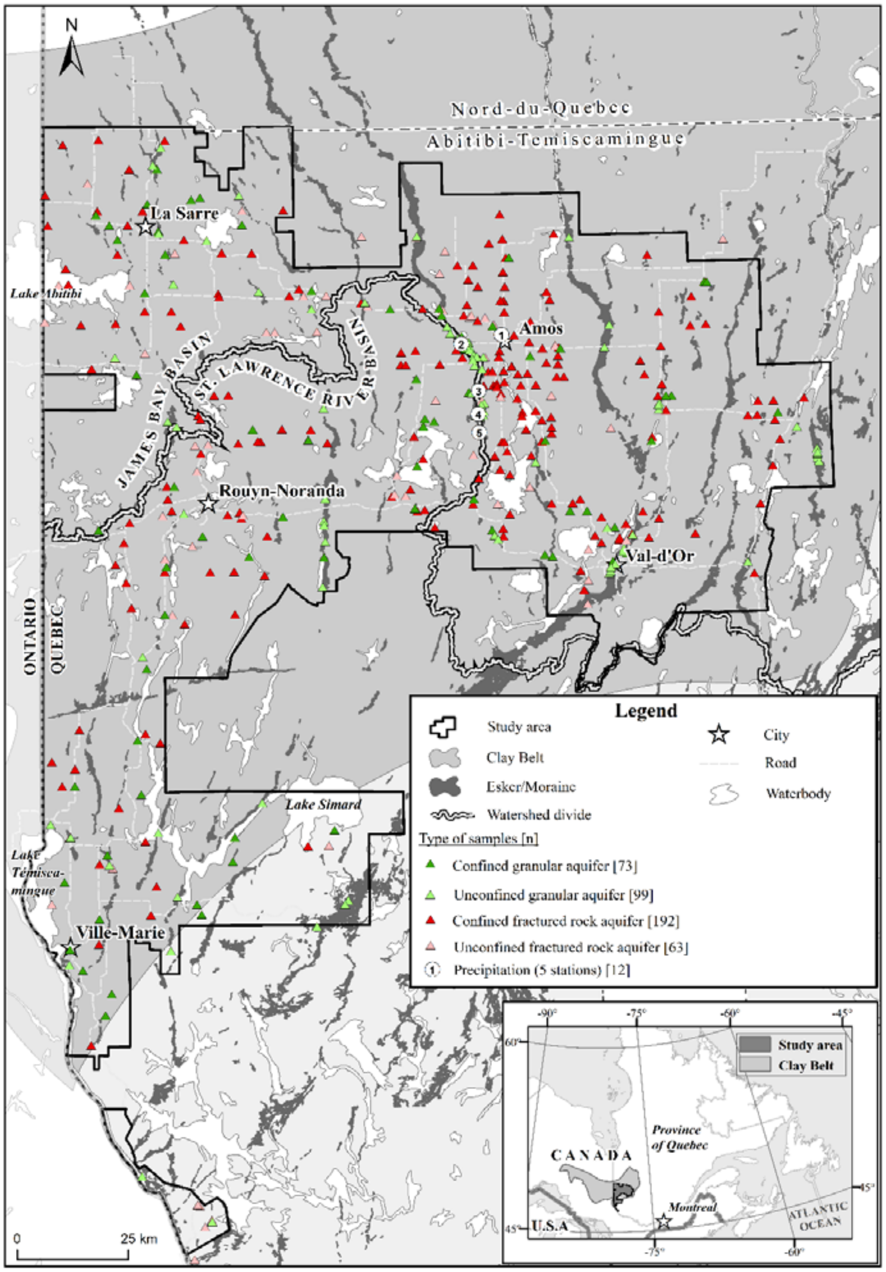

Figure 3.1. Study area and location of the sampling sites.The number [n] of available samples is shown in the legend. The limits of the study area correspond to that of the previous regional groundwater studies conducted in this area (Cloutier et al., 2016; Nadeau et al., 2018; Rey et al., 2018). The continental water divide between the James Bay and St. Lawrence basins is shown.

3.2.1 Climate and physiography

The study region is characterized by a cold and humid continental climate. Mean annual precipitation varies between 875 mm and 989 mm (Cloutier et al., 2013; 2015). Mean monthly air temperatures range between -23.3°C and 23.7°C in January and July, respectively. The area generally presents a low relief topography, mainly owing to the unconsolidated deposits that mask the rugged Precambrian shield over most of the region. Surface elevations range between 280 m and 572 m and the highest sectors mainly correspond to localized bedrock outcrops. The continental water divide separating the St. Lawrence River (south) and James Bay (north) watersheds sinuously crosses the study area from east to west (Figure 3.1), and the Témiscamingue and Abitibi lakes correspond to the lower reaches of the regional hydrographic network.

3.2.2 Surface deposits

The surface deposits of the study area are inherited from the last glaciation-deglaciation cycle, which occurred during Pliocene and Pleistocene (Dyke, 2004), with the advance and retreat of the Lautrentide Ice Sheet. The oldest unconsolidated unit of the region consists in a till presenting a matrix of sand, silt and clay. While this unit is widespread over the region, it is often covered by younger sediments, and its identification from the available borehole data remains challenging (Nadeau et al., 2018). Owing to its compact matrix, this till is not considered as a major aquifer within the region. During the retreat of the ice sheet, glaciofluvial ridges (eskers and moraines) that can reach kilometers in length and tens of meters in thickness formed at the glacial margin, within the Barlow-Ojibway proglacial Lake. Previous studies suggest that the eskers and moraines of the study region share hydrogeological similarities (Cloutier et al., 2013; 2015; 2016; Nadeau et al., 2015; 2018). The main eskers and moraines of the region are generally roughly oriented in a south-north axis, and consist in sinuous ridges characterized by a sand and gravel matrix. Several of these glaciofluvial formations make the most productive unconfined granular aquifers of the region (Nadeau et al., 2015). Following the ice retreat and the onset of glaciofluvial formations, most of the study area remained invaded by the waters of the Barlow-Ojibway proglacial Lake, for a period spanning from approximately 10.1 to 8 ka BP (Veillette, 1994). During this period, the fine-grained deep-water sediments were deposited, up to elevations reaching approximately 320 m (Nadeau et al., 2015). These sediments consist in varves (alternating cm-scale layers of silt and clay), and although the presence of silt horizons might favor horizontal groundwater flow, the unit is generally considered as a regional aquitard (Cloutier et al., 2016; Nadeau et al., 2018). The uppermost units of the regional stratigraphic column mainly consist in sublittoral sands, alluvium and organic deposits. These formations are generally not exploited for water supply.

3.2.3 Bedrock geology

The bedrock of the study area is composed of a wide variety of volcanic, sedimentary, plutonic and metamorphic rocks of the Canadian Shield, within the Superior Geological Province. The Cadillac-Larder Lake fault zone (CLLFZ) crosses the region along an East-West axis, separating the Abitibi (north) and Pontiac (south) geological sub-provinces. The Abitibi greenstone belt is of upper Archean age (2.85-2.65 Ga) (Mueller and Mortesen, 2002) and is one of the largest Archean volcano-sedimentary belts of the world (Hocq and Verpaelst, 1994). The volcanic and sedimentary rocks of the Abitibi sub-province mainly occur as elongated strips that are roughly oriented along a northwest-southeast axis. These rocks are intruded by Archean felsic, intermediate and mafic plutonic rocks. South of the CLLFZ, the bedrock of the Pontiac sub-province is mainly composed of Archean sedimentary rocks that are intruded by felsic and intermediate Archean plutonic rocks. The metasedimentary rocks of the Cobalt Group are spatially restricted to an area located near Lake Témiscamingue. The study area covers a large area characterized by complex geological assemblages. In this sense, a comprehensive description of the mineralogical characteristics of the rocks of the region would be beyond the scope of this study. Nevertheless, a comprehensive description of the geology of the Abitibi and Pontiac subprovinces is proposed by Card and Poulsen (1998). The work of Shaw et al. (1967) further provides an assessment of the chemical composition of the main rock types of the Canadian Shield.

3.2.4 Hydrogeological framework

The regional hydrogeological framework of the study region is described extensively by Nadeau et al. (2018) and Rey et al. (2018), two studies conducted as part of the *Quebec Groundwater Knowledge acquisition program* (see Cloutier et al., 2016). For the purpose of this study, four main types of aquifers are considered, consistent with the subdivisions initially proposed by the two aforementioned studies:

1- **Unconfined granular aquifers (UG)** mainly consist of glaciofluvial sediments (eskers and moraines). These aquifers are spatially associated with the main recharge zones of the region, and generally correspond to the up gradient portions of the regional groundwater flow system (Rey et al., 2018). Several municipal wells are installed in these highly productive shallow unconfined aquifers;

2- **Unconfined fractured rock aquifers (UFR)** mainly correspond to bedrock outcrops located in the zones of highest elevation (above the maximum elevation reached by the fine-grained deep-water glaciolacustrine sediments of the clay plain). The hydraulic conductivity of the fractured bedrock is not well constrained at the regional scale, but it is assumed that the groundwater flow mainly occurs within the sub-horizontal interconnected structural discontinuities found within the first ~75 m below bedrock surface (Rouleau et al., 1999);

3- **Confined granular aquifers (CG)** correspond to the areas where glaciofluvial sediments (and till, to a lesser extent) are covered by the fine-grained deep-water glaciolacustrine sediments of the Clay Belt, the latter being considered as a regional aquitard (Nadeau et al., 2015; 2018; Cloutier et al., 2016);

4- **Confined fractured rock aquifers (CFR)** correspond to the areas where the bedrock is covered by the fine-grained deep-water glaciolacustrine sediments of the Clay Belt. Most of the private wells of the region withdraw groundwater from this aquifer.

The four subdivisions proposed above allow for classifying groundwater samples and interpreting geochemical data. It also provides a framework that is consistent with previous studies documenting the groundwater flow systems of the study region.

3.3 Materials and methods

3.3.1 Sampling procedures and in situ measurements

Most of the samples discussed here were collected during the course of the sampling campaign described by Rey et al. (2018), who discussed the isotopic composition of water ($\delta^{2}H$-$\delta^{18}O$) at the regional scale. Overall, 706 water samples (Table 3.1) were analyzed for their chemical composition (major, minor, and trace elements) as part of this study, over a period spanning from 2006 to 2015 (Figure 3.1, Table 3.1). The procedures associated with the sampling of precipitation (rain and snow), groundwater, surface waters and springs are presented separately below.

Table 3.1. Summary of available data.The number of samples (n) and sampling years are shown. Groundwater samples are classified according to the types of aquifers (CFR, UFR, CG, UG).

Types of samples	n	Sampling years
Precipitation	12	2009-2015
Snow pack	31	2014
Spring	123	2009-2011
Surface water	113	2009, 2013 & 2014
Confined fractured rock aquifer (CFR)	192	2006-2013
Unconfined fractured rock aquifer (UFR)	63	2006-2013
Confined granular aquifer (CG)	73	2006-2013
Unconfined granular aquifer (UG)	99	2006-2013
Total	706	2006-2015

3.3.1.1 Precipitation

Precipitation samples (rain and snow, n=12) were collected occasionally between September 2009 and December 2010 at five different stations located in the northern sector of the study area (Figure 3.1). Rainfall samples were collected using standard rain gauges. A thin layer of paraffin oil was added to the rain gauges to prevent evaporation. Snowfall samples were collected at each snow event using clean buckets, left to melt overnight and subsequently stored in 1 L high density polyethylene (HDPE) bottles. For each station, aliquots were combined to produce monthly composite samples. The volume of monthly composite samples was first evaluated in the laboratory and smaller aliquots were stored in 60 ml HDPE bottles and kept at 4 °C until chemical analyses.

An additional sampling campaign was carried out in March 2014 to recover samples from the snowpack at the end of the frozen period, prior to snowmelt. Sampling sites were chosen in the western part of the study area in an effort to collect data near the grid points used by the Centre d’Expertise Hydrique du Québec for calculating vertical inflows and snow water equivalent data (Poirier et al., 2012). At each site (n = 31), a straight trench varying in length from 5 m to 6 m was dug perpendicular to the wind direction. Snow cores ($n \geq 5$ in each trench) were sampled at ≤ 1 m intervals. Snow cores were collected using 4.2 cm ID × 1.6 m length HDPE tubes. Snow samples were weighted on site using a Mettler Toledo digital scale for calculating equivalent water contents. For each site, snow cores samples were transferred into a 2 L wide neck HDPE bottle to form a composite sample ≥ 800 g. Samples were kept frozen during the field campaign and subsequently left to melt overnight at room temperature in the laboratory. Meltwater samples were then filtered using 0.45 μm Waterra FHT membranes connected to 60 ml syringes to remove soil particles embedded in the snow during the sampling. The filtered water samples were stored at 4°C before analysis.

3.3.1.2 Groundwater

Groundwater samples (n = 427) were collected during the summers of 2006, 2009, 2010, 2011 and 2013 from private, municipal and observation wells, as outlined in Table 3.1. The Quebec Ministry of the Environment Hydrogeological Information System (HIS) database was used to describe the characteristics of the sampled private wells, while complementary information (such as construction details, casing depth, total depth and stratigraphy) was obtained from landowners. Well logs were used for documenting the characteristics of the sampled observation and municipal wells.

Three conditions had to be met for groundwater samples collection (1) an untreated water tap had to be accessible, (2) unemployed wells had to be purged of a minimal amount of water and (3) the monitored in situ parameters had to reach predefined stability criteria, as described in Rey et al. (2018). During the purge, in situ parameters (pH, dissolved oxygen, electrical conductivity, oxidation-reduction potential, and temperature) were measured using a YSI 556 MPS multi-parameter probe.

3.3.1.3 Surface waters

Surface water samples (rivers, streams, lakes) were collected in July 2009 and from July to October 2013. Rivers and streams were sampled near the central part of the main channel, at depths of 0.5-1.5 m below the surface. Some of the streams and rivers were sampled immediately at the outlet of large lakes (see Rey et al., 2018 for details). A 7.32 m *NASCO Swing Sampler* telescopic pole equipped with a 1 L HDPE bottle was used for collecting samples from the banks of small rivers and streams. The pole and its container were rinsed on site at a point located a few meters downstream of the sampling site. Whenever sampling from a bridge was possible, the samples were collected using 1 L *Waterra ecobailers*. A nylon wire equipped with a float was attached to the bailer to indicate the sampling depth. The bailers were systematically rinsed on site, with water from rivers, prior to sampling. Grab samples were also collected from 16 additional lakes, including 14 kettle lakes on esker. The samples from kettle lakes were collected from the shoreline, approximately 1 m below surface, using a *NASCO Swing Sampler* telescopic pole equipped with a 1 L HDPE bottle. The samples from Lake Témiscamingue were collected from a boat, at a depth of 1 m using a *NASCO Swing Sampler* telescopic pole equipped with a 1 L HDPE bottle. The samples from Lake Tee were collected from a boat, approximately 1 m below the surface, using a plastic tubing equipped with an inertial valve. *In situ* parameters (temperature, pH, conductivity, dissolved oxygen and redox potential) were measured using a *YSI 556 MPS* multi-parameter probe, a few centimeters downstream of the sampling point. All surface water samples were filtered immediately after collection using 0.45 µm *Waterra FHT* cartridges.

3.3.1.4 Springs

Spring samples were collected between July 2009 and September 2011 through the course of a previous study (Castelli, 2012). These samples were taken at the margin of glaciofluvial formations. Other spring samples were collected during the summer of 2013. These correspond to springs that are equipped for drinking water supply. All spring samples were filtered immediately after collection using 0.45 µm *Waterra FHT* cartridges. The in situ parameters were measured on site using a *YSI 556 MPS* multi-parameter probe.

3.3.2 Sample storage and analytical procedures

Selected preservatives are included in the bottles for stabilizing the samples: nitric acid for metals, sulfuric acid for nutrients and zinc acetate plus sodium hydroxide for sulfides. The storage and preservation of samples was carried in compliance with the guidelines of the Quebec Ministry of the environment (MDDELCC, 2011). Depending on the provenance of the samples (precipitation, snowpack, surface waters, groundwater and springs), the selected analytical parameters included the total dissolved concentrations of major and minor constituents (total alkalinity, Ca, Mg, K, Na, Br, Cl, F, NO_3-NO_2 and SO_4, organic carbon (DOC), nutrients (Ammonia nitrogen (N-NH_3)) and total inorganic *P*), trace elements (Al, Sb, Ag, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Sn, Fe, Li, Mn, Hg, Mo, Ni, Pb, Se, Si, Sr, Ti, U, V, Zn) and sulfurs (Total S).

Samples from years 2006, 2010 to 2015 were analyzed at the Maxxam Analytics laboratory whereas, 2009 samples were analyzed at the Exova laboratory, both located in Montreal, Canada and both accredited by the Quebec Ministry of the environment (CEAEQ, 2014). Measurements of dissolved metals were performed by ICP-MS, with detection limits (DL) ranging from 0.0003 mg/l for Ag to 0.5 mg/l for Ca. Anions concentrations were determined using ion chromatography, with DL ranging from 0.02 mg/l for NO_3-NO_2 to 0.1 mg/l for Br. Fluoride concentrations were determined using the ion-selective electrode method, with a DL of 0.1 mg/l. Total alkalinity ($CaCO_3$) was measured by titration to a pH of 4.5, with a DL of 1 mg/l. Inorganic P concentrations were measured using the automated colorimetric method with ammonium molybdate, with a DL of 0.03 mg/l. Measurements of Ammonia nitrogen

(N-NH_3) were performed using the automated colorimetric method with sodium salicylate, with a DL of 0.03 mg/l. Sulfide concentrations were determined using the methylene blue method, with a DL of 0.02 mg/l. The electrical conductivity and pH of snowpack samples were measured at the Maxxam Analytics laboratory.

3.3.3 Data organization and statistical analyses

3.3.3.1 Data management and parameter calculations

Overall, 106 samples (out of the initial database containing 812 samples) were excluded during the preliminary data quality analysis. Results suggested that 48 of these samples are duplicates, four of these samples corresponded to treated waters, three were collected at sites strongly affected by former mining activities and three displayed a charge balance error exceeding 10%. In addition, 11 groundwater samples were excluded from the database because the data did not allow identifying the aquifer from where the water was collected. The remaining samples include samples analyzed in 2006 and again in 2010/2011, the most recent sample is preserved in the database. The remaining samples (n = 706) were organized as outlined in Table 3.1.

For statistical calculations, the concentrations < DL were replaced by half the value of the DL, as proposed by Farnham et al., (2002). Total dissolved solids (TDS) were calculated (in mg/L) using all the constituents concentrations excepted total Alkalinity in $CaCO_3$, dissolved inorganic and organic carbon. Ammonium, nitrate and phosphate have been converted to NH_3, NO_3 and PO_4 in mg/L to calculate TDS.

The *Diagrammes* software (Simler, 2014) was used for defining water types and generating Piper diagrams (Piper, 1944). The charge balance, speciation and saturation indices (SI) were calculated using *PHREEQC* (Parkhurst and Appelo, 1999). Inverse modeling was also performed using *PHREEQC*. Carbonate and bicarbonate concentrations were determined using total alkalinity (in mg/L) as input using *PHREEQC*. Statistics were calculated using *R*, *Statistica* and *Microsoft Excel*.

3.4 Results and discussion

The complete results dataset is provided as supplementary electronic material, while boxplots (Figures 3.2; 3.3; 3.4; 3.5; 3.7; 3.8; 3.9; 3.10) are used for a more convenient representation of the data. In figures 3.2-3.6, the data are organized according to the eight hydrological components of the Abitibi-Témiscamingue region, as identified by Rey et al. (2018) and Nadeau et al. (2018), namely:

1- Precipitation (rain, snow)

2- Samples from the snowpack

3- Surface waters

4- Groundwater springs

5- Unconfined granular aquifers (UG)

6- Unconfined fractured bedrock aquifers (UFR)

7- Confined granular aquifers (CG)

8- Confined fractured rock aquifers (CFR)

This organization allows for an interpretation of water geochemical evolution along the hydrological flow paths, from the precipitation to confined bedrock aquifers. Previous data from Rey et al. (2018) and Nadeau et al. (2018) support the general understanding that the unconfined aquifers of the study area (hydrological components 5 and 6 above) correspond to the main recharge areas, while local groundwater flow systems feed springs and regional groundwater flow systems feed confined aquifers (hydrological components 7 and 8 above).

In figures 3.8-3.10, the data are organized according to the main rock types found in the study region, namely plutonic, volcanic and sedimentary rocks. These figures allow for an interpretation of the links between groundwater geochemistry and bedrock lithology.

Kruskal-Wallis tests were conducted on the groundwater data in order to guide the interpretation of the data shown in the boxplots. This allows for a statistical evaluation of the differences between the median concentrations values of dissolved constituents in groundwater. This nonparametric statistical approach is valid for data that do not follow a normal distribution, which is the case here. Since it is a median-based approach, the leverage effect of extreme values is limited. For the present case, the differences between the 4 classes of aquifers (UG, UFR, CG, CFR) are tested for each of the six possible pairs, as reported in table 3.2. The null hypothesis (H_0, that the medians of the two classes of aquifers compared are identical) is tested with an $\propto$ threshold set at 0,05. For each of the pairs shown in table 3.2, $\propto$ values <0,05 indicate that the medians are statistically different. The same approach is later used for comparing the median concentrations measured in unconfined fractured rock aquifers set in plutonic, volcanic and sedimentary rocks.

Hereinafter, the expression "major constituents" is used to describe all of the dissolved constituents that have the highest concentrations in the groundwater studied, namely Ca, Mg, Na, K, Si, HCO_3, Cl and SO_4. The expression «trace constituents » is used for all other dissolved constituents. Dissolved substances that are considered to remain in solution once dissolved into groundwater are described here as conservative constituents, while constituents likely to be immobilized-remobilized owing to changes in Eh-pH and secondary minerals precipitation/weathering are described as non-conservative constituents.

3.4.1 Geochemical evolution along the groundwater flow system

3.4.1.1 Conservative constituents and the gradual spatiotemporal trend

The available results suggest that most of the major constituents (Ca, Mg, Na, K, Si) follow a geochemical evolution trend suggesting a conservative geochemical behavior. The term "conservative" is used here to define an element characterized by a high mobility during weathering and transport processes. The conservative (and mobile) elements thus identified are consistent with the relative mobility of the elements during alteration and transport processes, as proposed by Gaillardet et al. (2003). Most of the major constituents (Ca, Mg, Na, K, Si) and TDS present increasing concentrations according to the following trend: precipitation and snowpack < springs < surface waters < unconfined granular aquifers < unconfined fractured rock aquifers < confined granular aquifers < confined fractured rock aquifers (Figure 3.2).

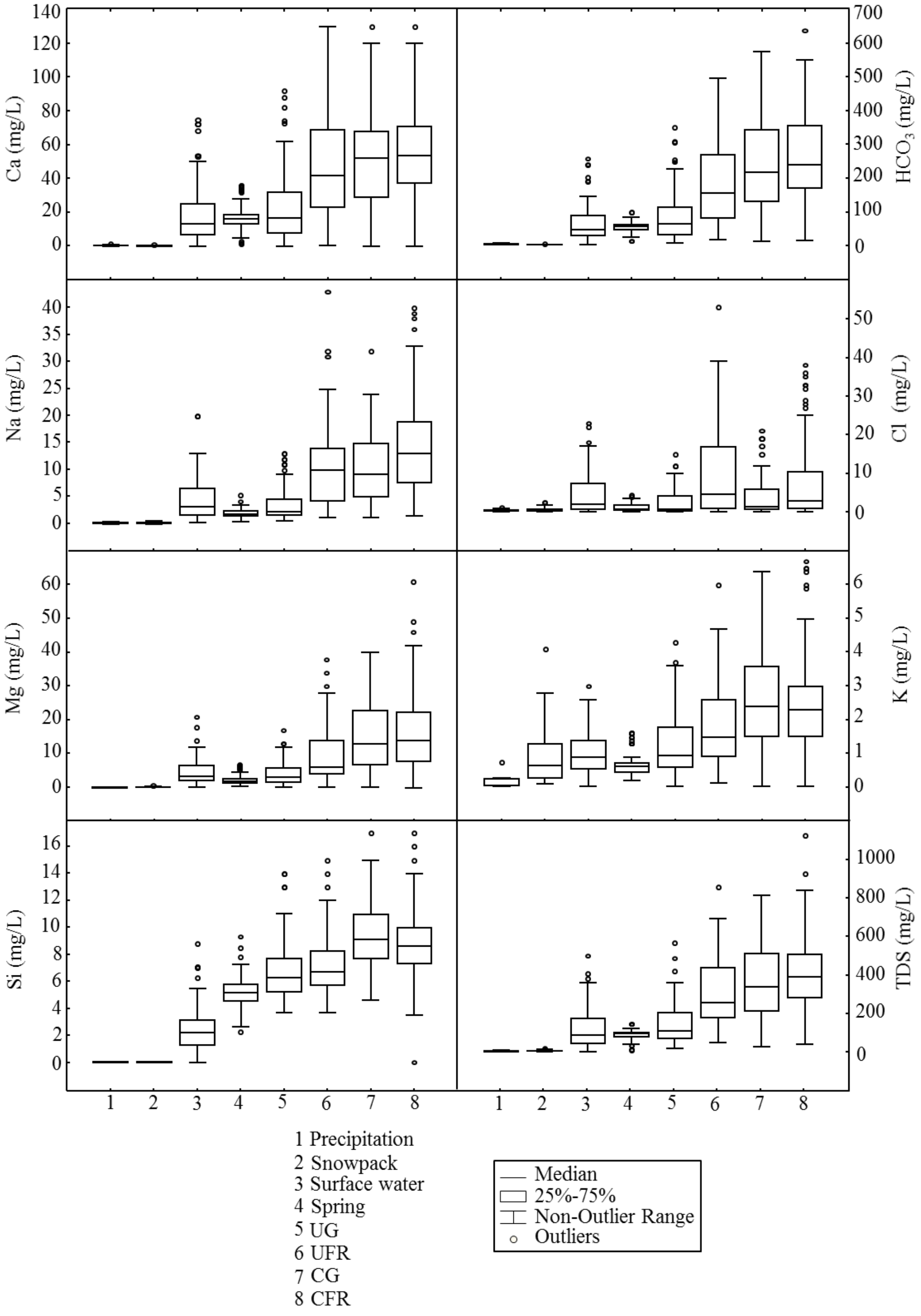

Figure 3.2. Concentrations of major dissolved species measured in the eight hydrological components of the regional hydrogeological system.

This trend is consistent with the previous interpretations of the regional hydrogeological system as presented by Rey et al. (2018) and Nadeau et al. (2018), who proposed a groundwater flow system with a sequence from unconfined granular aquifers to confined fractured rock aquifers. Furthermore, the results of the Kruskal-Wallis reveal that these constituents generally present statistically different median concentrations when pairs of aquifers are compared (Table 3.2). These observations support the hypothesis that the geochemical evolution of water causes significant changes in the concentrations of major dissolved constituents, as explained below.

Table 3.2. Summary of results from the Kruskal-Wallis test conducted to compare the median concentrations of dissolved species in the four classes of aquifers (UG, UFR, CG, CFR). The null hypothesis (H_0, that the medians of the two classes of aquifers compared are identical) is tested with $\propto=0,05$. Values of **$\propto < 0,05$** suggest a statistical difference between the median concentration calculated in each of the two types of aquifers being compared, for a specific dissolved species.

Parameters	UG-UFR	UG-CG	UG-CFR	UFR-CG	UFR-CFR	CG-CFR
Ca	**<0.01**	**<0.01**	**<0.01**	0.2695	0.0068	0.1857
Eh	0.964	0.0524	**0.0077**	**0.041**	**0.0085**	0.8075
HCO_3	**<0.01**	**<0.01**	**<0.01**	**0.0165**	**<0.01**	0.0636
pH	0.8354	0.6835	0.2498	0.4862	0.0764	0.3686
Na	**<0.01**	**<0.01**	**<0.01**	0.4117	**0.0001**	**0.002**
Mn	**<0.01**	**<0.01**	**<0.01**	0.9774	0.4139	0.2926
Fe	**0.0057**	**0.00002**	**0.00008**	0.2287	0.6644	0.305
Cl	**0.0001**	0.0752	**0.00002**	**0.0139**	0.2605	**0.0245**
Mg	**<0.01**	**<0.01**	**<0.01**	**0.0006**	**<0.01**	0.5258
SO4	**0.00003**	0.2186	0.5257	**0.0317**	**0.0022**	0.5786
K	**0.0021**	**<0.01**	**<0.01**	**0.0012**	**0.0006**	0.3685
TDS	**<0.01**	**<0.01**	**<0.01**	**0.0445**	**0.00002**	0.0988
Si	0.0574	**<0.01**	**<0.01**	**<0.01**	**<0.01**	0.5544
Sr	**<0.01**	**<0.01**	**<0.01**	0.6561	0.0799	**0.0034**
As	0.2208	0.8674	**0.0013**	0.2048	0.2	**0.0037**
Zn	**0.0008**	**0.0434**	**0.0004**	0.243	0.3786	0.6107
F	**0.00003**	**0.00006**	**<0.01**	0.3269	0.5644	**0.0384**
Cr	**0.0068**	**0.0058**	**0.00007**	0.9814	0.7069	0.6142
Mo	**0.0399**	**0.0001**	**<0.01**	0.4256	**0.028**	**0.0444**
Pb	0.817	**0.0016**	0.0654	**0.004**	0.1684	0.0501
Ba	**0.0003**	**<0.01**	**<0.01**	**0.048**	0.2151	0.1405
B	**<0.01**	**0.00002**	**<0.01**	0.2463	0.2674	0.0021

Except for precipitation (rain and the snowpack), the lowest median concentrations of dissolved major constituents are measured in groundwater springs located at the margin of unconfined granular aquifers associated. These springs represent the outlet of local shallow groundwater flow systems located at the head of the regional groundwater flow system, within glaciofluvial formations. Precipitation waters preferentially infiltrates within the coarse grained soils of these formations to recharge the shallow unconfined aquifers. When the hydraulic head in the unconfined granular aquifer exceeds the elevation of the surrounding impervious fine-grained glaciolacustrine deposits, groundwater exfiltrates at the contact between both formations (Champagne, 1988; Nadeau et al., 2018; Rosa et al., 2018). The residence time of water and the length of flowpaths in such shallow systems are likely very limited, and dissolved solids concentrations inherited from water-rock interactions remain low.

The unconfined aquifers generally present intermediate Ca, Mg, Na, K and Si, concentrations between springs and confined aquifers. This is interpreted as resulting from the configuration of the regional flow system, with groundwater recharging within unconfined aquifers and flowing towards confined aquifers. The increasing concentrations in this trend reflect the greater influence of water-rock interactions with increased groundwater flow distances and mean residence times. The water saturation indices calculated for carbonates and plagioclases tend to further support this interpretation. These saturation indices gradually increase along the pre-established trend, suggesting the cumulative effect of weathering processes occurring along groundwater flowpaths (Figure 3.3). The removal of major ions through mineral precipitation processes does not seem to significantly affect the observed geochemical trend, although some groundwater may be oversaturated with respect to carbonates and plagioclases, especially in the down gradient confined aquifers. The greater concentrations measured in groundwater from fractured rocks aquifers in comparison to granular aquifers (both for unconfined and confined conditions) most likely reflects the effects of groundwater residence time, given the lower hydraulic conductivity of the bedrock in comparison to that of glaciofluvial sediments (Cloutier et al., 2016).

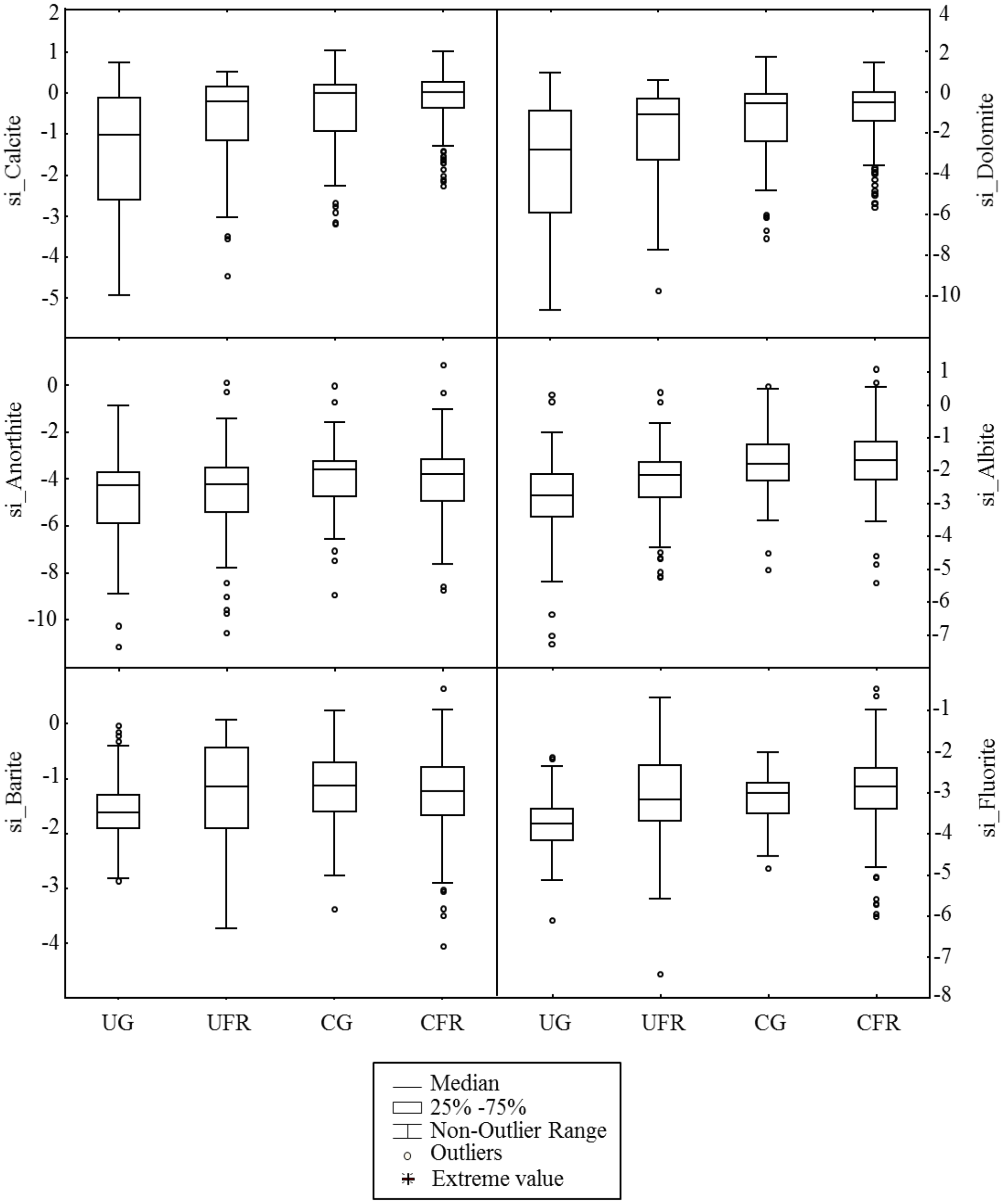

Figure 3.3. Box plot of saturation indices (SI) calculated for carbonates (calcite, dolomite), barite, fluorite and plagioclases (anorthite, albite) in the four classes of aquifers. UG: unconfined granular aquifer; CG: confined granular aquifer; UFR: unconfined fractured rock aquifer; CFR: confined fractured rock aquifer.

3.4.1.2 Eh-pH and the stepwise variations along flowpaths

Eh and pH variations between regional hydrogeological components are shown in figure 3.4. The data show lowest pH values in precipitation, and a sharp increase until a plateau defined by groundwater data, with median pH values ranging between 7,4 and 7,6. The Kruskal-Wallis test conducted on the data further reveals the absence of a statistical difference between the median pH values calculated for the four types of aquifers (Table 3.2). These observations suggest that pH buffering quickly occurs within recharge areas in unconfined aquifers and that subsequent rock weathering processes are not sufficient to cause further significant pH increase. Key process that could explain the stabilization of pH along groundwater flowpaths are the potential competing effects between low pH water supply from precipitation infiltrating in recharge zones, sulfide weathering and carbonate precipitation (all supplying H^+) and silicate weathering, carbonate weathering and SO_4 conversion to sulfide (all consuming H^+). Some of the waters collected from the confined aquifers are nearly saturated with respect to calcite and dolomite (Figure 3.3), suggesting that carbonate precipitation could affect pH values in some down gradients zones of the groundwater flow system.

Eh presents a median value of 375 mV in spring waters located at the outlet of local hydrogeological systems associated with unconfined aquifers. A stepwise decrease in Eh is then observed between springs, unconfined aquifers (median values of 299 mV to 275 mV) and confined aquifers (median values of 214 mV to 212 mV). This is attributed to the supply of oxygenated waters in the recharge areas associated with the unconfined aquifers (Figure 3.4) and to the gradual consumption of e- owing to redox processes along flowpaths, leading to lower Eh values in confined aquifers. The Kruskal-Wallis test conducted on the data further reveals a statistical difference between the median Eh values calculated for the transition between unconfined and confined aquifers (Table 3.2), consistent with the interpretation proposed above.

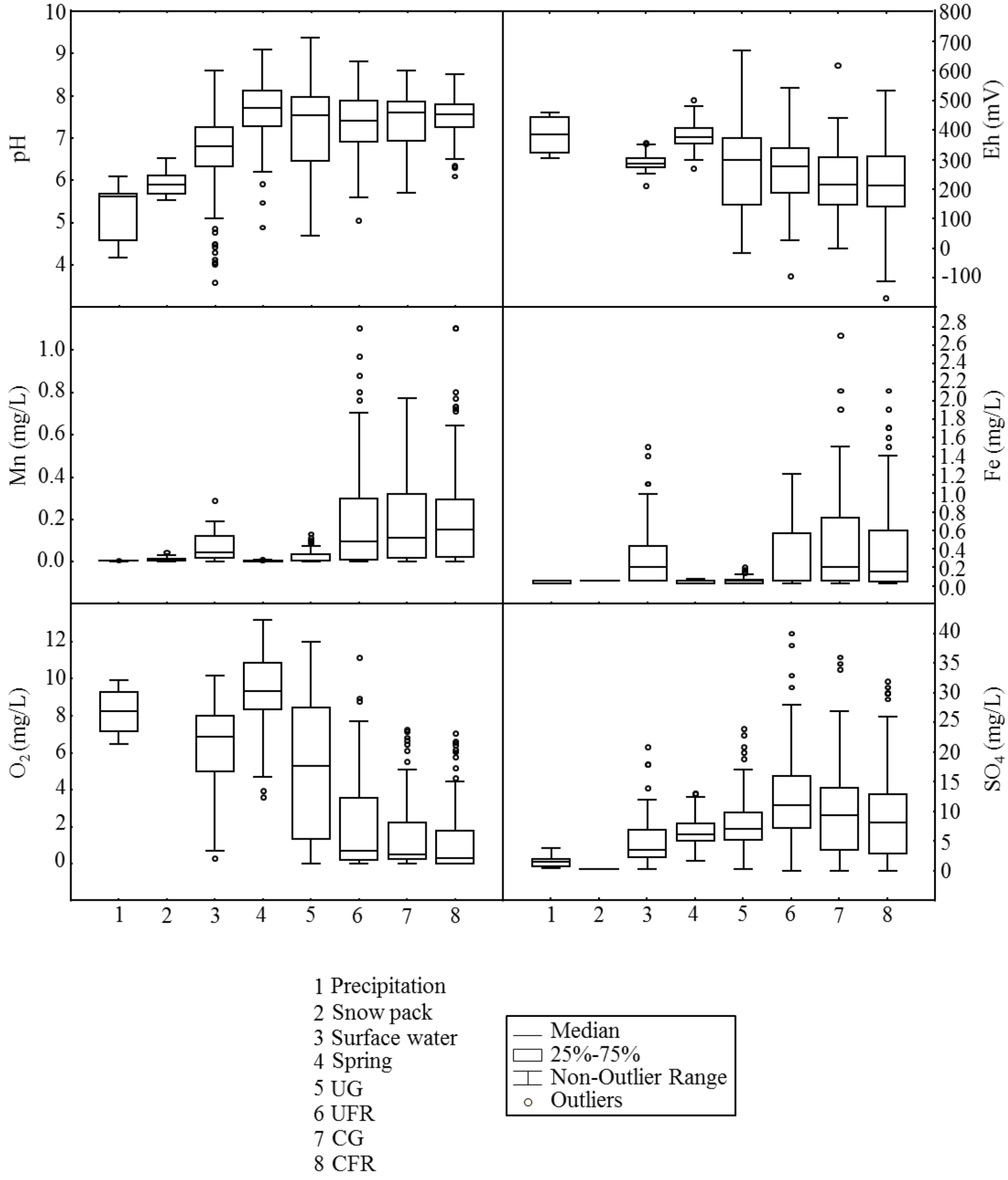

Figure 3.4. pH, Eh and concentrations of selected redox-sensitive species measured in the eight hydrological components of the regional hydrogeological system. UG: unconfined granular aquifer; CG: confined granular aquifer; UFR: unconfined fractured rock aquifer; CFR: confined fractured rock aquifer. Dissolved oxygen and Eh has not been measured for Snowpack.

3.4.1.3 Fe, Mn and SO_4 : redox processes and fracture connectivity

The trends observed for Fe, Mn and SO_4 (Figure 3.4) suggest the combined effects of local bedrock sources and redox processes. While Fe and Mn are omnipresent in soils and rocks of the Canadian Shield, the median dissolved concentrations measured in unconfined granular aquifers are 0.05 mg/l and 0.005 mg/l, respectively. The Kruskal-Wallis tests conducted on the data reveal that these values are significantly lower than those observed for the other types of aquifers (Table 3.2). A plausible explanation is that the Eh-pH conditions prevailing in unconfined granular aquifers are prone to the precipitation of Fe/ Mn oxyhydroxides, thus explaining low dissolved Fe and Mn concentrations measured therein. However, one key observation is that Fe and Mn are significantly higher in unconfined fractured rock aquifers in comparison to unconfined granular aquifers, although these two types of aquifers present similar Eh-pH conditions (Figure 3.4), as confirmed by the Kruskal-Wallis test (Table 3.2). This could reflect the impact of groundwater mixing within unconfined bedrock aquifer wells, with deeper fractures presenting groundwater with lower Eh and higher Fe-Mn concentrations and shallower fractures presenting groundwater with higher Eh and lower Fe-Mn concentrations. The water collected from a bedrock well fed by these two types of fractures could present high Fe-Mn concentrations despite high Eh values owing to the short time given to Fe and Mn to form oxyhydroxides before the samples are filtered and acidified, once pumped from the bedrock well. Such a process could obscure the Eh control on Fe-Mn concentrations in unconfined bedrock aquifers. Bondu et al. (2017) suggested a similar mechanism for explaining As^{3+}, As^{5+}, Fe and Mn concentrations measured in other bedrock wells of the study region. Another key observation is that confined aquifers generally present higher Fe-Mn concentrations than unconfined aquifers. This most likely reflects the greater mobility of Fe-Mn under the more reducing conditions prevailing in confined aquifers.

Redox processes could also influence the SO_4 concentration trend along the groundwater flow system, with a gradual increase in SO_4 from precipitation to unconfined granular and fractured rocks aquifers; and a subsequent decrease in confined aquifers. Such a trend could reflects SO_4 conversion to sulfide under reducing conditions in deep fractures. The precipitation of sulfides within confined aquifers could further explain this observation. Nevertheless, sulfide was only detected (>LD) in 11 of the 427 available groundwater samples, thus preventing generalizations. The pyrite saturation indice calculation can't be used to interpret the results of sulphides detected in insufficient quantity in water.

3.4.1.4 Trace elements: non-conservative behaviors and local processes

The trace elements which have significant box plot differences between the different water compartments of the samples are shown in figure 3.5. The Kruskal-Wallis test conducted on these data are reported in table 3.2. These data suggest that trace elements such as Sr and F present higher concentrations in fractured rocks aquifers with respect to granular aquifers. Edmunds and Shand (2008) suggested that the concentrations of these two dissolved constituents in groundwater essentially reflect water-rock interactions. Therefore, one plausible explanation for the observation reported above is that the minerals bearing Sr and F elements are mainly derived from bedrock sources that are depleted in unconfined granular aquifers. This could result from the deposition mode of the glaciofluvial formations associated with unconfined aquifers. These formations were deposited in high-energy environments, in subglacial waters at the ice margin (Nadeau et al., 2015). Therefore, it is likely that glaciofluvial deposits present a distinct mineralogy due to sorting processes that occurred during deposition. Another hypothesis is that the water residence time in unconfined aquifers could be insufficient for allowing the weathering processes responsible for the mobilization of these elements. Glaciofluvial formations are characterized by the highest hydraulic conductivities among the regional geological units and they correspond to recharge areas that partly discharge into springs and diffuse seepage zones (Cloutier et al., 2016). Therefore, the time allowed for water-rock interactions in the local flow systems associated with unconfined aquifers might be too short to allow for the weathering of Sr and F bearing minerals. A similar explanation could likely account for the observed Ba and B concentrations, which are also greater in fractured rocks aquifers in comparison to granular aquifers (Figure 3.5, Table 3.2). Calculations performed using *PHREEQC* reveal that fluorite ($SI \leq -2$) and barite ($SI \leq 0$) are both undersaturated in granular aquifers (Figure 3.3). Therefore, the removal of F and Ba from solution owing to fluorite and barite precipitation in granular aquifers is not a plausible explanation for the observed trends.

Dissolved Cr shows a distinctive behavior. It is enriched in unconfined granular aquifers and springs with respect to the other types of aquifers (Figure 3.5, Table 3.2). The Cr concentrations measured in precipitation are low, suggesting that an airborne anthropogenic source of Cr to unconfined aquifers is not likely. These observations rather suggest a geogenic source of Cr that remains mobile in glaciofluvial sediments, and a subsequent immobilization process in confined aquifers. This is most likely related to the Eh-pH control on Cr mobility. Chromium has nine possible oxidation numbers, from -2 to +6. The trivalent (Cr^{3+}) and hexavalent forms (Cr^{6+}) are most common in groundwater. The solubility of the less oxidized form (Cr^{3+}) depends on pH conditions. Below a pH of 6, hydrolysis will contribute to the formation of soluble ($CrOH^{2+}$, $Cr(OH)_2^{+}$, $Cr(OH)_3$) and polynuclear ($Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$) molecules. Above this pH threshold, Cr^{3+} precipitates as $Cr(OH)_3$ and $Cr_xFe_{1-x}(OH)_3$. Nonetheless, Cr^{3+} can be soluble at pH 6-8 owing to its association with dissolved ligands like phosphate (PO_4^{3-}), fluoride (F^-), citrate ($C_6H_5O_7^{3-}$)), humic and fulvic acid as well as organic ligands (Armienta and Quéré, 1995). Given the prevailing Eh-pH conditions, it is most likely that Cr originates from the oxidation of Cr bearing minerals in glaciofluvial sediments and remains mobile under its hexavalent form in unconfined granular aquifers. As groundwater subsequently flows towards confined aquifers, more reducing conditions will contribute to the reduction of Cr^{6+} to Cr^{3+}, which precipitates under the prevailing alkaline pH conditions.

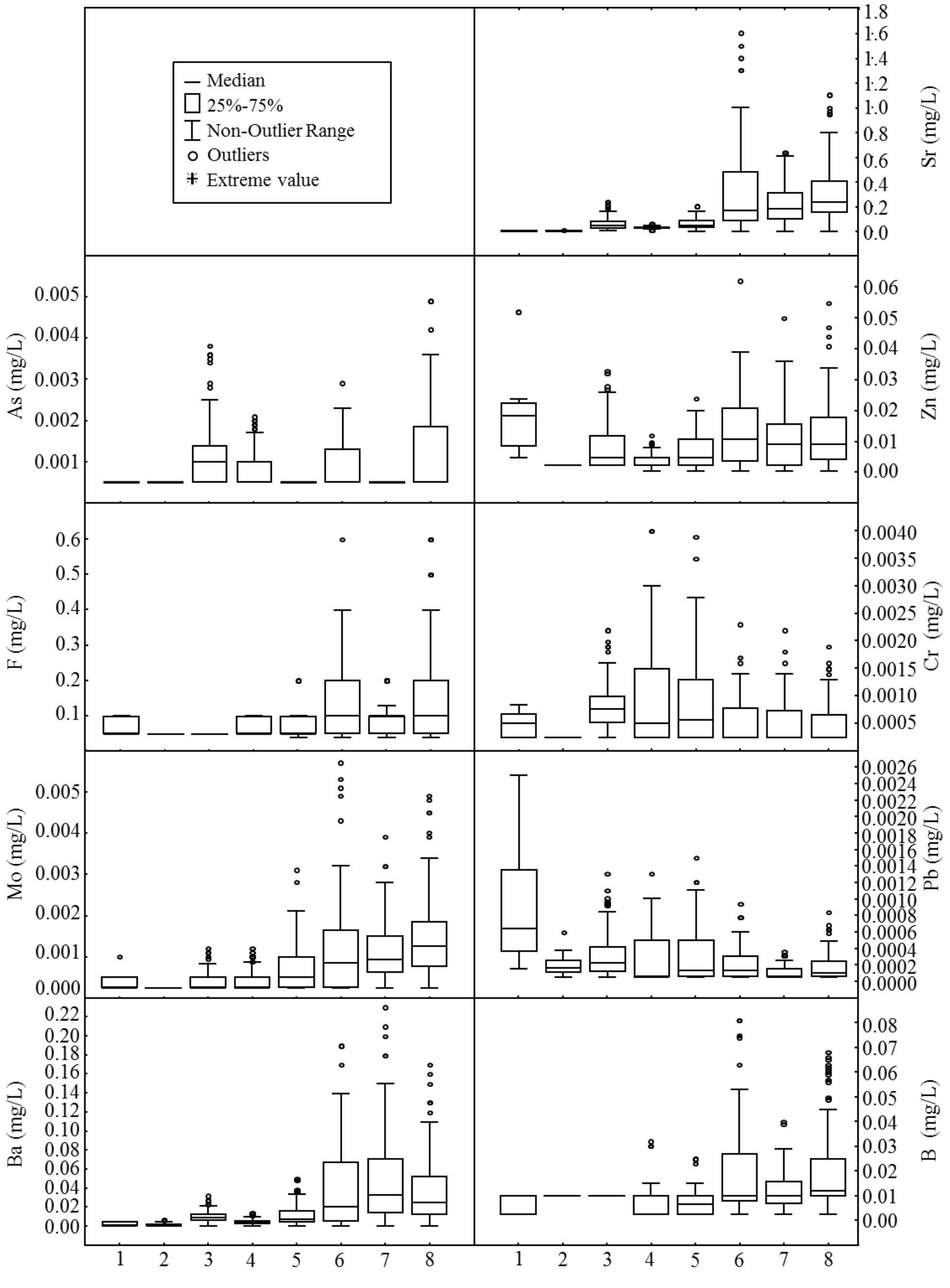

Figure 3.5. Concentrations of dissolved trace elements measured in the eight hydrological components of the regional hydrogeological system. 1: precipitation; 2: snow pack; 3: surface water; 4: spring; 5: unconfined granular aquifer; 6: unconfined fractured rock aquifer; 7: confined granular aquifer; 8: confined fractured rock aquifer.

3.4.1.5 Piper diagrams and water types

The Piper diagrams show that groundwater and spring samples are mainly found in the Ca-Mg-HCO_3 zone of the diamond shaped filed whereas the precipitation and samples from the snowpack present a greater dispersion towards the Cl and Na+K poles (Figure 3.6). Precipitation samples containing higher SO_4 concentrations may reflect anthropogenic pollution (Chin and Jacob, 1996). Surface waters tend to present intermediate values between precipitation and groundwater, consistent with a mixture of direct runoff and groundwater discharge feeding the streams and lakes of the region (Rey et al., 2018). For the unconfined granular aquifer, the occurrence of Ca-Cl and Na-Cl water may be the result of a contamination from de-icing road salts. Some groundwater samples from confined and unconfined rock aquifers plot in the Na-HCO_3, Na-Cl and Ca-SO_4 zones of the Piper diagram (Figure 3.6) suggesting a greater geochemical evolution in comparison to granular aquifers or the effect of sources of salts.

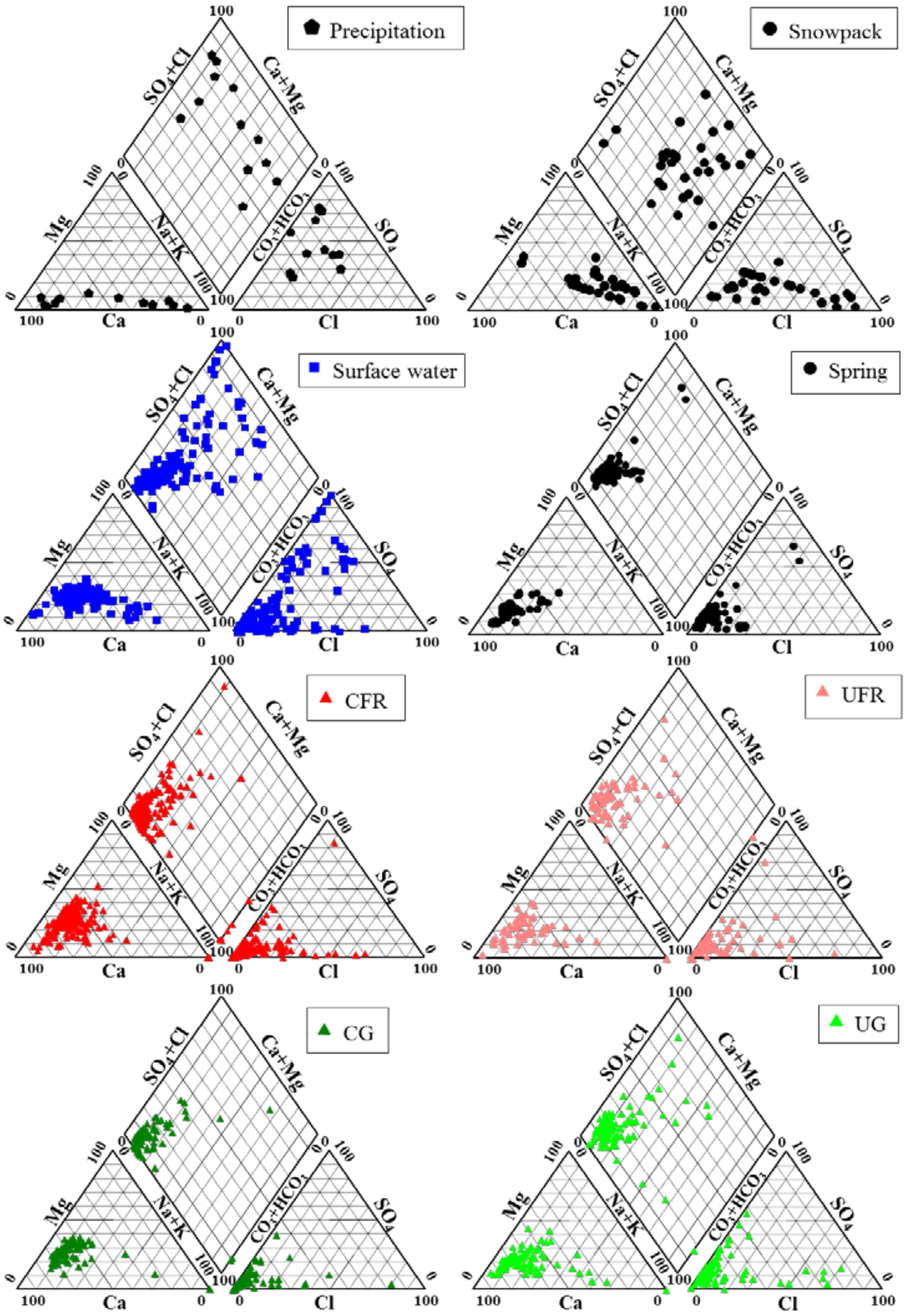

Figure 3.6. Piper diagrams for the eight hydrological components of the regional hydrogeological system. UG: unconfined granular aquifer; CG: confined granular aquifer; UFR: unconfined fractured rock aquifer; CFR: confined fractured rock aquifer.

3.4.2 Deciphering the sources of dissolved solids

3.4.2.1 Atmospheric sources: trace elements in rain and snow

Precipitation data (rain and the snowpack) represent the atmospheric input to the groundwater flow system. These samples present median pH values ranging between 5,6 and 5,9 (Figure 3.4) and generally low dissolved solids concentrations in comparison to groundwater (Figure 3.2). Of all of the trace elements measured in precipitation, Pb and Zn show marked enrichments in rain with respect to snow. The values measured for Pb in snow range between 0,00005 mg/l and 0,011 mg/l, for a median value of 0,00016 mg/l. In comparison, the Pb concentrations measured in rain had a median value of 0,0006 mg/l. Similarly, with respect to Zn, 30 out of 31 of the snow samples yielded Zn concentrations below the detection limit of 0,0025 mg/l, while the median value measured in rain is 0,0185 mg/l. This suggests that a significant atmospheric source of Pb-Zn affects precipitation (especially rain) in the study area. The most comprehensive evaluation of atmospheric deposition within the study region is proposed by Telmer et al. (2004). These authors proposed background Pb and Zn concentrations in snow of 0,0017 mg/l and 0,0016 mg/l, respectively. In comparison, Simonetti et al. (2000) measured average Pb and Zn concentrations of 0,00008 mg/l and 0,0169 mg/l in snow samples of the north shore of the St. Lawrence River, in southern Quebec. Despite the high variability of Pb-Zn atmospheric concentrations, as outlined above, the generally lower Pb-Zn concentrations measured in groundwater with respect to precipitation, even in unconfined aquifers areas (Figure 3.5), suggest that these two trace metals largely originate from airborne sources within the study area. For Pb, the lower concentrations measured in confined aquifers (Figure 3.5) suggest that the trace element is fixed within unconfined aquifers. The decrease in Pb concentrations from unconfined to confined areas suggest that it is immobilized in unconfined aquifers. This is consistent with the generally recognized low mobility of

Pb under oxidizing and near-neutral pH conditions and the potential effects of lead adsorption onto soil organic matter and its affinity for Mn oxides (Hem, 1985).

3.4.2.2 Geogenic and anthropogenic sources of major dissolved constituents: a mass balance approach

The contributions from different geogenic and anthropogenic sources to dissolved major constituents in groundwater are evaluated using an inverse modeling approach with *PHREEQC*. Mass balance calculations are preformed based on the differences measured between dissolved constituents concentrations in snow and groundwater. The stoichiometry of mineral phases and weathering reactions is considered for solving the problem and the following assumptions are made:

Carbonates (calcite, dolomite), feldspars (albite, anorthite, microcline), and phyllosilicate (phlogopite) are the dominant sources of dissolved major ions in groundwater. Such minerals are commonly found in rocks of the Canadian Shield (Hans Wedepohl 1995; Rogers et al., 2010);

The H^+ required for weathering reactions are mainly derived from carbonic acid ($H_2CO_3^*$ generated by CO_2 dissolution) and sulfuric acid (H_2SO_4 generated by sulfide oxidation);

Silicates undergo an incongruent weathering process leading to the precipitation of kaolinite;

Given the absence of geogenic salts deposits within the study area, dissolved Cl mainly originates from anthropogenic sources or shield brines. For either cases, Cl is assumed to originate from halite (NaCl) or calcium chloride ($CaCl_2$);

Other anthropogenic sources of dissolved solids may intervene, but these sources cannot be included in the inverse modeling approach given their unknown stoichiometry;

A composite sample presenting the median concentrations of dissolved elements measured in snow samples adequately represents the inputs to the groundwater flow systems. The HCO_3^- concentration of this composite sample is adjusted to satisfy for electroneutrality, a prerequisite for the inverse modeling approach;

The Nahcolite, a carbonate, is required as source of $NaHCO_3$ for the model.

Table 3.3 presents the stoichiometry of the general dissolution and weathering reactions used for the mass balance approach described by equation 3.1 (Appelo and Postma, 2005):

$$\Delta m_{T,k} = m_{T,k\,(final)} - m_{T,k\,(initial)} = \sum_{P=1}^{P} \alpha_p b_{P,k} \qquad \text{Equation 1}$$

Where $\Delta m_{T,k}$ is the total change in the molar concentration of element k in phase m, α_p terms are solved as unknowns in a system of equations with P reactants and product phases and represents the mass transfer associated with a given reaction of known stoichiometry $b_{P,k}$. Here, as expressed in table 3.3, the studied system contains 12 elements used for constraining 17 equations of known stoichiometry. The 17 mass transfer coefficients are the unknown to be solved mathematically.

The mass balance (Equation 1) is solved mathematically, without thermodynamic and kinetic constraints. Saturation indices are therefore calculated using the wateq4f database from *PHREEQC* to verify if the weathering and precipitation processes inferred from the mass balance calculations are realistic. This verification is not straightforward since the geochemical compositions of the water samples are used for checking saturation indices, while the weathering reactions likely occurred previously, when geochemical conditions were different. Nevertheless, the calculations performed using *PHREEQC* provide a first order estimate to check the inverse modeling solutions. These calculations revealed that all of the considered mineral phases are undersaturated except kaolinite, consistent with the general reactions used for the mass balance approach, where all phases dissolve except kaolinite.

Table 3.3. Geochemical reactions used for the inverse modeling calculations performed using *PHREEQC*.

These inverse modeling calculations are used to evaluate the contributions of different sources and processes to the dissolved species measured in groundwater from unconfined fractured rock aquifers. Two sources of acid are considered as responsible for the weathering reactions (either H_2CO_3 or H_2SO_4, both shown in red). The numbers shown in the right side columns show the proportions of dissolved species that are released during weathering processes, based on the stoichiometry of the proposed reactions.

Geochemical reactions		**Dissolved species released from weathering**							
		Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}	H_4SIO_4	Cl^-
H_2SO_4 dissolution	$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$						1		
CO_2 dissolution	$H_2O + CO_2 \rightarrow H_2CO_3^*$								
Pyrite oxydation	$2FeS_2 + \frac{15}{2}O_2 + 5H_2O \rightarrow 2FeOOH + 4H_2SO_4$								
Halite dissolution	$NaCl \rightarrow Na^+ + Cl^-$	1							1
$CaCl_2$ dissolution	$CaCl_2 \rightarrow Ca^{2+} + 2Cl^-$				1				2
Calcite dissolution	$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-$				1	2			
	$H_2SO_4 + 2CaCO_3 \rightarrow SO_4^{2-} + 2Ca^{2+} + 2HCO_3^-$				2	2	1		
Dolomite dissolution	$2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^-$			1	1	4			
	$2H_2SO_4 + 2CaMg(CO_3)_2 \rightarrow 2Ca^{2+} + 2Mg^{2+} + SO_4^{2-} + 2HCO_3^-$			2	2	2	1		
Albite to kaolinite	$2NaAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + 2HCO_3^- + 4H_4SiO_4$	2				2		4	

Table 3.4. Geochemical reactions used for the inverse modeling calculations performed using *PHREEQC*. These inverse modeling calculations are used to evaluate the contributions of different sources and processes to the dissolved species measured in groundwater from unconfined fractured rock aquifers. Two sources of acid are considered as responsible for the weathering reactions (either H_2CO_3 or H_2SO_4, both shown in red). The numbers shown in the right side columns show the proportions of dissolved species that are released during weathering processes, based on the stoichiometry of the proposed reactions.

Geochemical reactions		**Dissolved species released from weathering**							
		Na^+	K^+	Mg^{2+}	Ca^{2+}	HCO_3^-	SO_4^{2-}	H_4SIO_4	Cl^-
Albite to kaolinite	$2NaAlSi_3O_8 + H_2SO_4 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2Na^+ + SO_4^{2-} + 4H_4SiO_4$	2					1	4	
Anorthite to kaolinite	$Ca(Al_2Si_2)O_8 + H_2CO_3 + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + 2HCO_3^-$				1	2			
	$Ca(Al_2Si_2)O_8 + H_2SO_4 + H_2O \rightarrow Al_2Si_2O_5(OH)_4 + Ca^{2+} + SO_4^{2-}$				1		1		
Adularia to kaolinite	$2KAlSi_3O_8 + 2H_2CO_3 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + 2HCO_3^- + 4H_4SiO_4$		2			2		4	
	$2KAlSi_3O_8 + H_2SO_4 + 9H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2K^+ + SO_4^{2-} + 4H_4SiO_4$		2				1	4	
Phlogopite to kaolinite	$KMg_3AlSi_3O_{10}(OH)_2 + 10H^+ \rightarrow K^+ + 3Mg^{2+} + Al^{3+} + 3H_4SiO_4$		1	3				3	
Nahcolite	$NaHCO_3 \rightarrow Na^+ + HCO_3^-$	1				1			

The results from mass balance calculations are shown in figure 3.7. Since the inverse modeling approach does not yield unique results, boxplots are used for illustrating the model outputs. These results suggest that H_2CO_3* is the main source of H^+ responsible for weathering reactions yielding dissolved solids to groundwater, while H_2SO_4 plays a marginal role. According to the models results, carbonate weathering represents a major source of dissolved solids both in confined and unconfined aquifers, despite the relatively rare occurrence of carbonates in comparison to silicates in the study region. Nevertheless, carbonates were found in highly mineralized fault zones in Abitibi-Témiscamingue (Legault et al., 2005; Pearson and Daigneault, 2009). Disseminated carbonates are also found in fractures, veins and fine particles in the matrix of unconsolidated deposits. These sources appear to influence water chemistry, despite their low abundance in shield rocks. Contrastingly, silicate weathering generally creates a more limited impact on groundwater chemistry in the region. These findings most likely reflect the influence of three key factors:

1- Fresh minerals availability: the study area recently underwent a glaciation-deglaciation cycle. This allowed exposing fresh carbonate minerals in soils, unconsolidated sediments and at the bedrock surface and promote the predominance of carbonate weathering. The weathering system is geologically «young», and carbonates are still available for weathering;

2- Kinetics: carbonates weathering is a faster process than silicate weathering, and carbonates are sufficient for driving Ca-Mg-HCO_3 contents in groundwaters despite their low abundance in comparison to silicates;

3- Saturation indices: given the relatively low dissolved ion concentrations in the studied groundwater, carbonates remain unsaturated along the regional groundwater flow system. This allows carbonate weathering in all types of aquifers of the region.

Halite and $CaCl_2$ dissolution appears to contribute to the dissolved constituents for some models, especially for fractured rock aquifers (Figure 3.7). Given the absence of geogenic salts deposits in the region, dissolved Cl is most likely derived from anthropogenic sources (e.g.: road salts) or shield brines. The influence of shield brines in some bedrock wells cannot be ruled out, but previous data from Rey et al. (2018) did not allow identifying $\delta^{2}H$-$\delta^{18}O$ isotopic shifts suggesting a marked influence of brines (such as ^{2}H enrichment, see Douglas et al., 2000). In addition, the high Cl concentrations measured in unconfined aquifers suggest that the hypothesis of a dominant anthropogenic source of salt is most realistic. Since most of the samples were collected in private wells located near roads, deicing salts (NaCl and $CaCl_2$) represent the most plausible source of Cl. In addition, the tests conducted for optimizing the inverse models revealed that an additional source of Na, other than albite and halite, was required for balancing the equations. Based on trial and error attempts, adding $NaHCO_3$ (nahcolite) as an initial phase in the model allowed balancing the equations. This addition of nahcolite is fictitious, but it reveals that the mineral phases initially included in the model did not allow for balancing Na and HCO_3. Given the heterogeneity of the bedrock and the scale of the study region, it is assumed here that such a source of uncertainty is acceptable.

Despite the results from the inverse modeling approach, the heterogeneity of the regional hydrogeological framework complicates the identification of the main geogenic sources of dissolved solids. The granular aquifers of the region mainly consist in glaciofluvial sediments inherited from the erosion of the underlying bedrock. These formations are heterogeneous in terms of mineralogy owing to the sedimentary transport and mixing processes that occurred during the last glaciation-deglaciation cycle. In addition, the groundwater flowing in the confined aquifers is located in the down-gradient zone of the regional groundwater flow system. The geochemical composition of this groundwater reflects weathering, transport and immobilization processes that occurred over great distances. In this context, unconfined fractured rock aquifers are likely the only areas that possess key characteristics for documenting groundwater geochemistry in specific lithology. These aquifers generally correspond to recharge areas located in uppermost portions of the groundwater flow system (Nadeau et al., 2018).

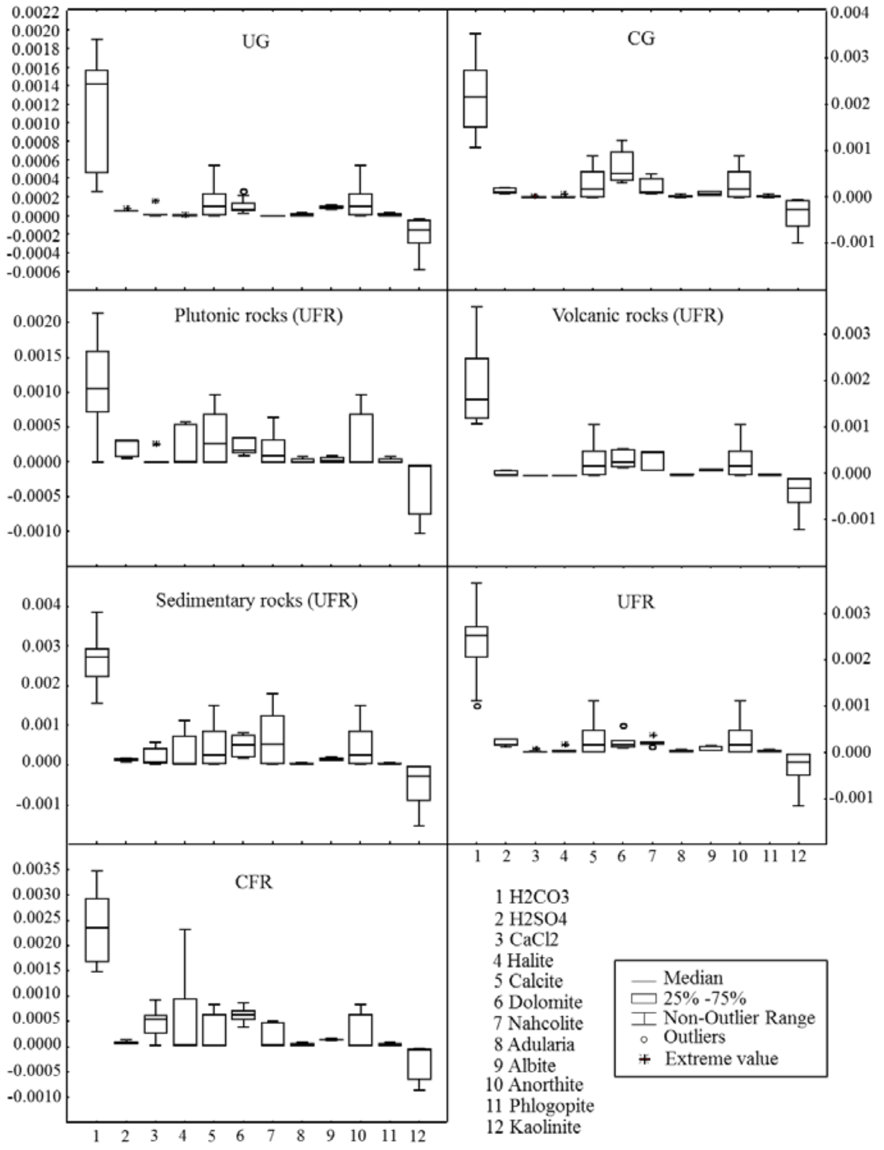

Figure 3.7. Results of the inverse modeling calculations performed using *PHREEQC*. Since the inverse modeling approach does not yield unique results, boxplots are used for illustrating the model outputs. The number of included models and uncertainty criteria are also shown for each subplot. The graph illustrates the contribution (in mg/L) of the different mineral phases (1-12) for the different hydrogeological context (UG-CG-UFR-CFR).

In such areas, groundwater geochemistry most likely reflects local water-rock interactions. Additional tests were therefore performed in order to compare groundwater samples collected in unconfined fractured rock aquifers set in (1) plutonic, (2) volcanic and (3) sedimentary rocks (Figures 3.8; 3.9; 3.10). The boxplots illustrating major ions concentrations in these three classes of unconfined fractured rocks aquifers suggest that groundwater flowing in sedimentary and volcanic rocks generally present higher dissolved Ca, Mg, Na and HCO_3 concentrations in comparison to groundwater from plutonic rocks; whereas highest K and Si concentrations are generally found in plutonic rocks aquifers (Figure 3.8).

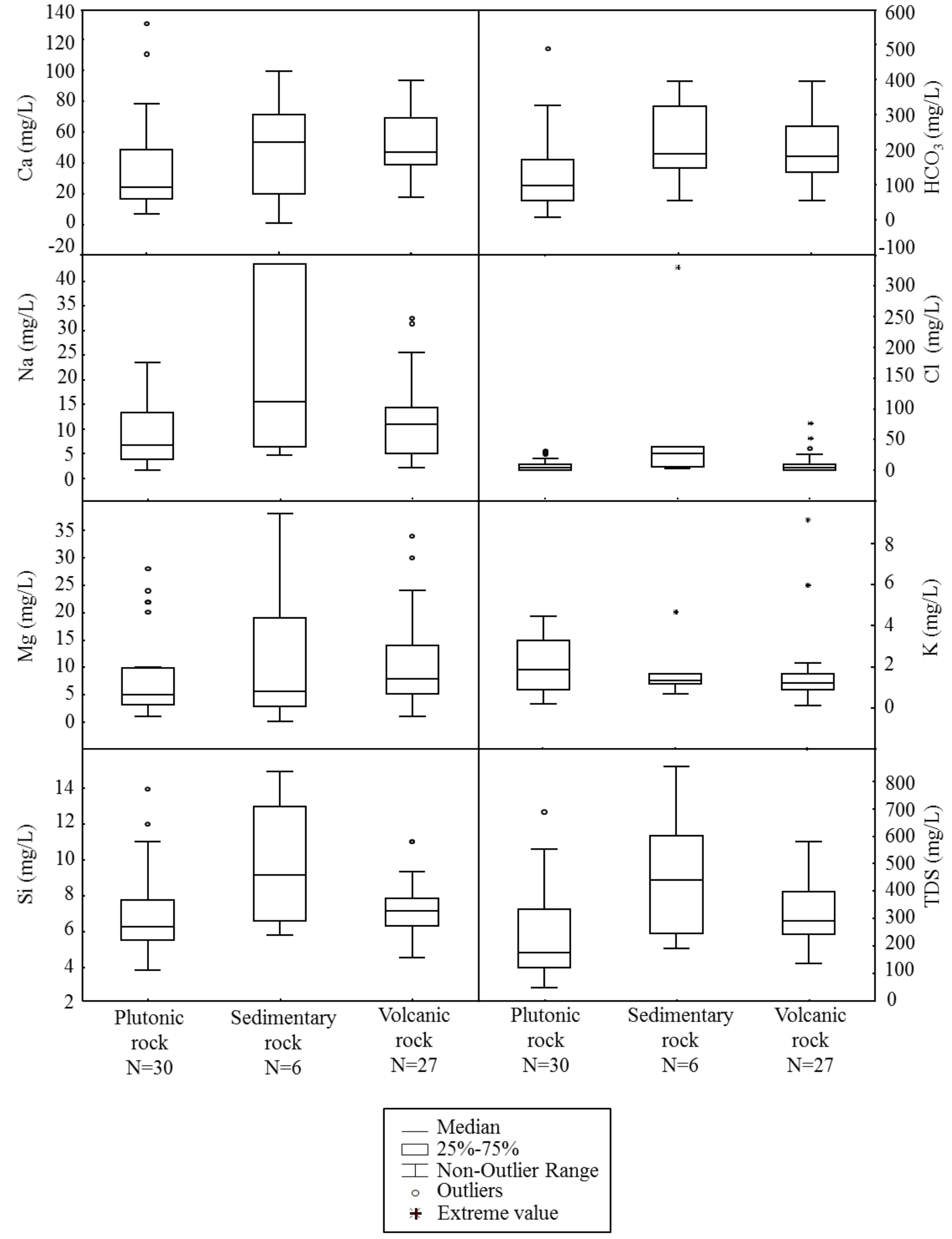

Figure 3.8. Concentrations of major dissolved species measured in unconfined fractured rock (UFR) aquifers set in plutonic, volcanic and sedimentary rocks.

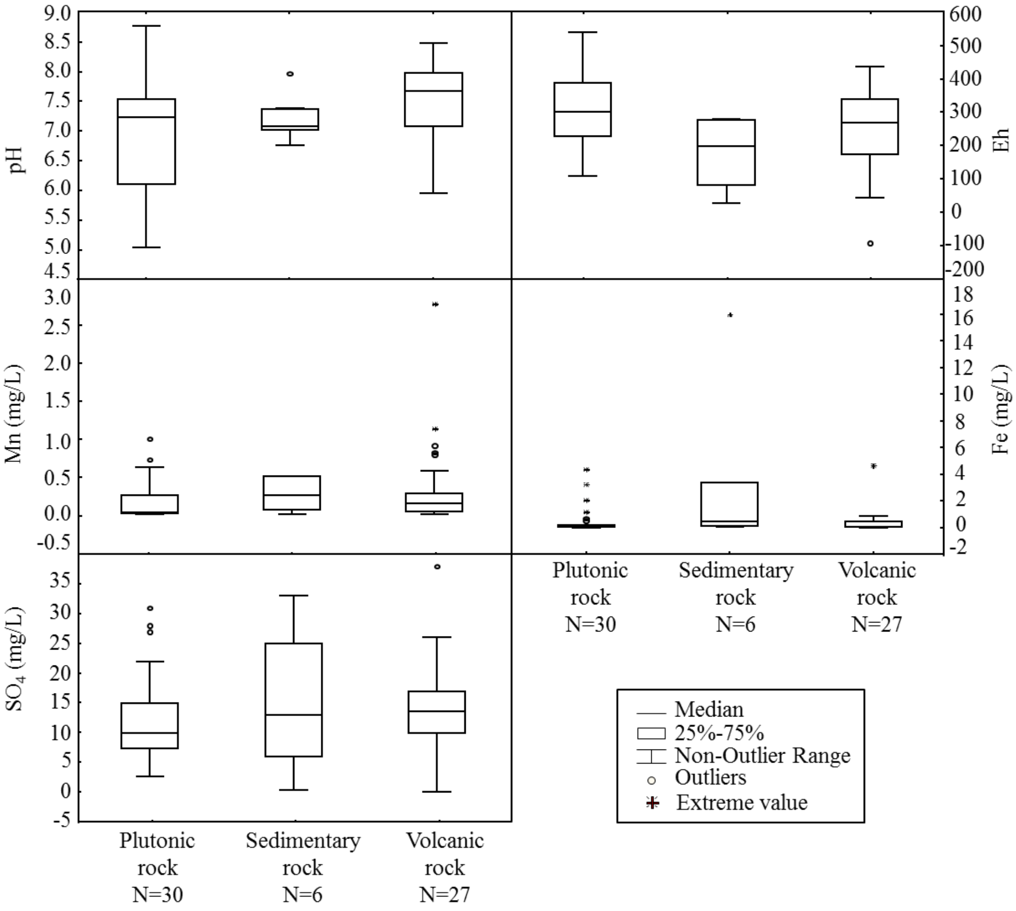

Figure 3.9. pH, Eh and concentrations of selected redox-sensitive species measured in unconfined fractured rock (UFR) aquifers set in plutonic, volcanic and sedimentary rocks.

These findings are consistent with the elemental molar ratios calculated for composite cafemic and calcareous rocks of the Canadian Shield (Table 3.5, based on data from Shaw et al., 1967). Here, it is assumed that plutonic and volcanic rocks are similar to the quartzofeldspathic and cafemic composite rocks from Shaw et al. (1967), respectively, while sedimentary rocks are similar to a mixture between cafemic and calcareous rocks. While the concentrations of major cations found in the groundwater from unconfined fractured rocks aquifers can overlap, notwithstanding bedrock lithology, the differences shown in the interquartile and median concentrations for the three classes of aquifers suggest that groundwater inherits a geochemical composition that reflects bedrock lithology. This is illustrated by the data from table 3.4, as the Kruskal-Wallis tests revealed statistically different median values between at least two rock types for pH, $CaHCO_3$, TDS, and Si. This suggests that the bedrock lithology could be used for predicting groundwater geochemistry in areas of unconfined fractured rocks where wells are not available. This could allow a preliminary first order evaluation of groundwater quality in the vast and remote areas of the Canadian Shield where groundwater geochemistry remains poorly documented.

Table 3.5 Summary of results from the Kruskal-Wallis test conducted to compare the median concentrations of dissolved species in unconfined fractured rock aquifers set in plutonic, volcanic and sedimentary rocks. The null hypothesis (H_0, that the medians of the two classes of aquifers compared are identical) is tested with $\alpha = 0{,}05$. Values of $\boldsymbol{\alpha < 0{,}05}$ suggest a statistical difference between the median concentration calculated in each of the two types of aquifers being compared, for a specific dissolved species. PR : plutonic rocks; SR : sedimentary rocks; VR : volcanic rocks.

Parameters	PR_SR	PR_VR	SR_VR
Ca	0.5663	**0.0062**	0.8279
Eh	**0.0273**	0.2719	0.1615
HCO3	0.0818	**0.0021**	0.7721
pH	0.9831	**0.0369**	0.1919
U	0.1217	**0.0002**	**0.0455**
Mn	0.1952	0.1285	0.7536
Fe	**0.0239**	0.4193	0.1086
Cu	0.0964	0.2797	0.2024
Mg	0.8818	**0.034**	0.5301
K	0.5954	0.0773	0.5298
TDS	**0.0155**	**0.005**	0.1924
Si	**0.0337**	0.1108	0.134
Sr	0.7663	0.9541	0.8658
As	0.0619	**0.0001**	0.47
F	0.2018	0.0535	0.9795
Cr	0.5767	0.1877	0.7447
Pb	0.2816	0.626	0.8785
Ba	0.7501	0.5266	0.9036
B	0.7786	0.5097	**—**

Table 3.6. Element ratios calculated for different rocks of the Canadian Shield according to data from Shaw et al. (1967). Composite samples are from Northern Quebec and rocks samples are from Quartzofeldspathic rocks (QF: granite, granitic gneiss, pegmatite, rhyolite, arkose, sandstone), Cafemic rocks (CAF: basalt, gabbro, greenstone, amphibolite, peridotite, serpentinite, anorthosite) and Calcareous rocks (MA: limestone, dolomite, marble). The element ratios measured in unconfined fractured rock aquifers set in plutonic, volcanic and sedimentary rocks is also shown. The use of element ratios instead of absolute concentrations allows for a comparison between groundwater and bedrock data.

Molar ratios	QF	CAF	MA	UFR - plutonic	UFR - volcanic	UFR - sedimentary
Ca/Na	1.48	4.25	12.67	2.54	2.84	0.44
Mg/Na	1.3	4.22	14.49	0.87	0.99	0.18
Si/Na	34.44	26.79	8.33	0.66	0.56	0.12
Sr/Na	0.01	0.01	0.0006	0.02	0.007	0.004
K/Na	0.52	0.13	0.02	0.14	0.09	0.02
Fe/Na	0.96	3.21	0.79	0.02	0.02	0.02
Cr/Na	0.004	0.006	0.01	0.00003	0.00003	0.000009
F/Na	0.08	0.06	0.05	0.03	0.01	0.002

3.4.2.3 Trace elements in unconfined fractured rocks aquifers: the role of local geogenic sources

Most geogenic trace elements, once released into solution by weathering processes, do not behave conservatively owing to their participation in geochemical processes such as sorption and redox reactions. Therefore, the link between trace elements concentrations in groundwater and bedrock lithology is only indirect. Nevertheless, based on the available data, the presence of some trace elements in groundwater seems to be mainly associated with a specific lithology. For instance, U and F concentrations are generally higher in plutonic unconfined fractured rocks aquifers in comparison to volcanic and sedimentary unconfined rocks aquifers (Figure 3.10; see table 3.4 for

Kruskal-Wallis tests results). In opposition, As and Cr were found to present higher concentrations volcanic and sedimentary unconfined rocks aquifers in comparison to plutonic unconfined fractured rocks aquifers (Figure 3.10; see table 3.4 for Kruskal-Wallis tests results). These findings are consistent with the composite values proposed by Shaw et al. (1967), as reported in table 3.5.

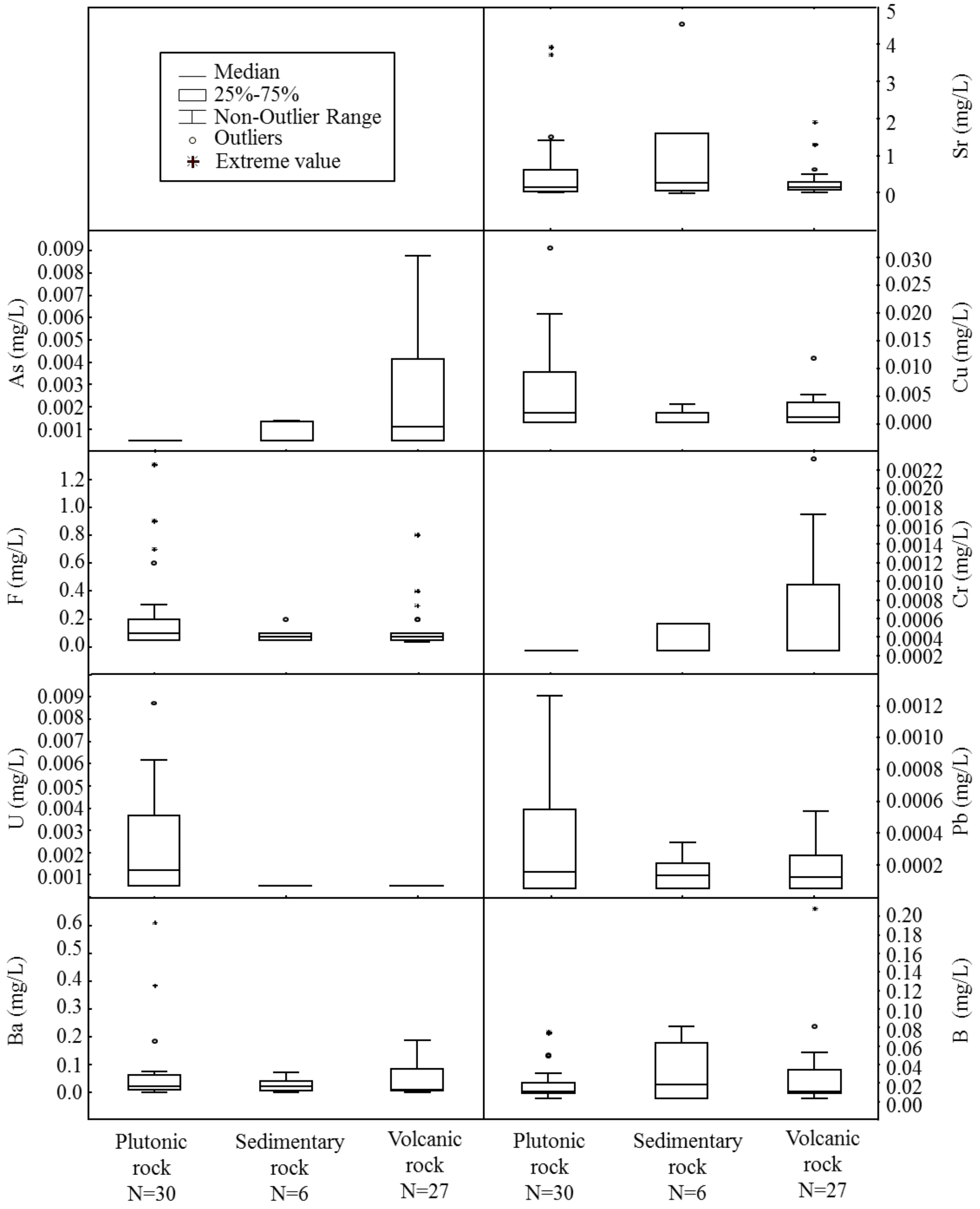

Figure 3.10. Concentrations of dissolved trace elements measured in unconfined fractured rock (UFR) aquifers set in plutonic, volcanic and sedimentary rocks.

3.4.3 A predictive map of groundwater geochemistry

Developing predictive maps of groundwater geochemistry must rely on an assessment of the sources and fate of dissolved solids in the groundwater flow systems. Here, the available data suggest that groundwater chemistry can be linked with statistical significance (tables 3.2 and 3.4) to the position of aquifers in the groundwater flow system (section 3.4.1) and to bedrock lithology (section 3.4.2). Both of these characteristics are illustrated in figures 3.11-3.12 and the map captions provide a statistical estimate of the concentrations of dissolved solids in groundwater for six types of aquifers. The maps allow for a statistical prediction of groundwater geochemistry in areas where groundwater samples are not available. The six classes allow subdividing unconfined fractured rocks aquifers according to bedrock lithology (plutonic, volcanic and sedimentary rocks) and separating unconfined granular aquifers, confined granular aquifers and confined fractured rock aquifers. The thicknesses of granular aquifers, as estimated by Cloutier et al. (2016) and Nadeau et al. (2018) are also shown in figure 3.11. This allows for a joint assessment of groundwater quality and quantity in granular aquifers, assuming that the porosity is similar at the regional scale within these sand and gravel aquifers. The volume of fractured rock aquifers is not shown because it would require a precise knowledge of the geometry of bedrock structural discontinuities contributing to groundwater flow, and this information is still lacking.

Figure 3.11 is a simplified version of map number 16 in the hydrogeological Atlas of Abitibi-Témicamingue (Cloutier et al., 2016). The map of figure 3.11 shows the granular aquifers thickness across the region. The elaboration of figure 3.12 is based on the groundwater table flow conditions from the data of map number 15 in the hydrogeological Atlas of Abitibi-Témicamingue (Cloutier et al., 2016). The bedrock geology was extracted from map number 9 in the hydrogeological Atlas to indicate the confined and unconfined aquifers conditions on the fractured bedrock. The bedrock geology is present under unconfined and confined aquifers conditions on the scale of the region. The methodology for creating maps 9, 15 and 16 is included in the PACES reports (Cloutier et al., 2013; 2015).

3.4.3.1 Observations and recommendations for the Abitibi-Témiscamingue region

Based on the available data, relatively low TDS are expected in the unconfined granular aquifers shown in figure 3.11 (see map caption). Given the oxidizing conditions prevailing in these aquifers, low Fe-Mn concentrations are expected therein. Among the six types of aquifers of the region, the unconfined granular aquifers tend to present the lowest concentrations of undesirable dissolved elements such as As, F, Zn, and Ba. This makes unconfined granular aquifers regional hot spots for water quality. In addition, these shallow unconfined aquifers are recognized for their high productivity and high vulnerability (Cloutier et al., 2016). These three arguments underlie the critical need for an increased protection as a mean of preserving the groundwater resource for future generations. Increased groundwater quality monitoring should also be conducted in these aquifers. First, the data revealed the highest dissolved Cr concentrations among all of the regional aquifer types. Given the recognized toxicity of Cr, especially in its hexavalent form (CEP, 2015), a better understanding of the sources and fate of this element in unconfined granular aquifers seems much needed. Second, since shallow unconfined aquifers could undergo changes in water quality under climate change (Bondu et al., 2016), a temporal monitoring of these aquifers seems much needed for better anticipating undesirable changes in groundwater quality.

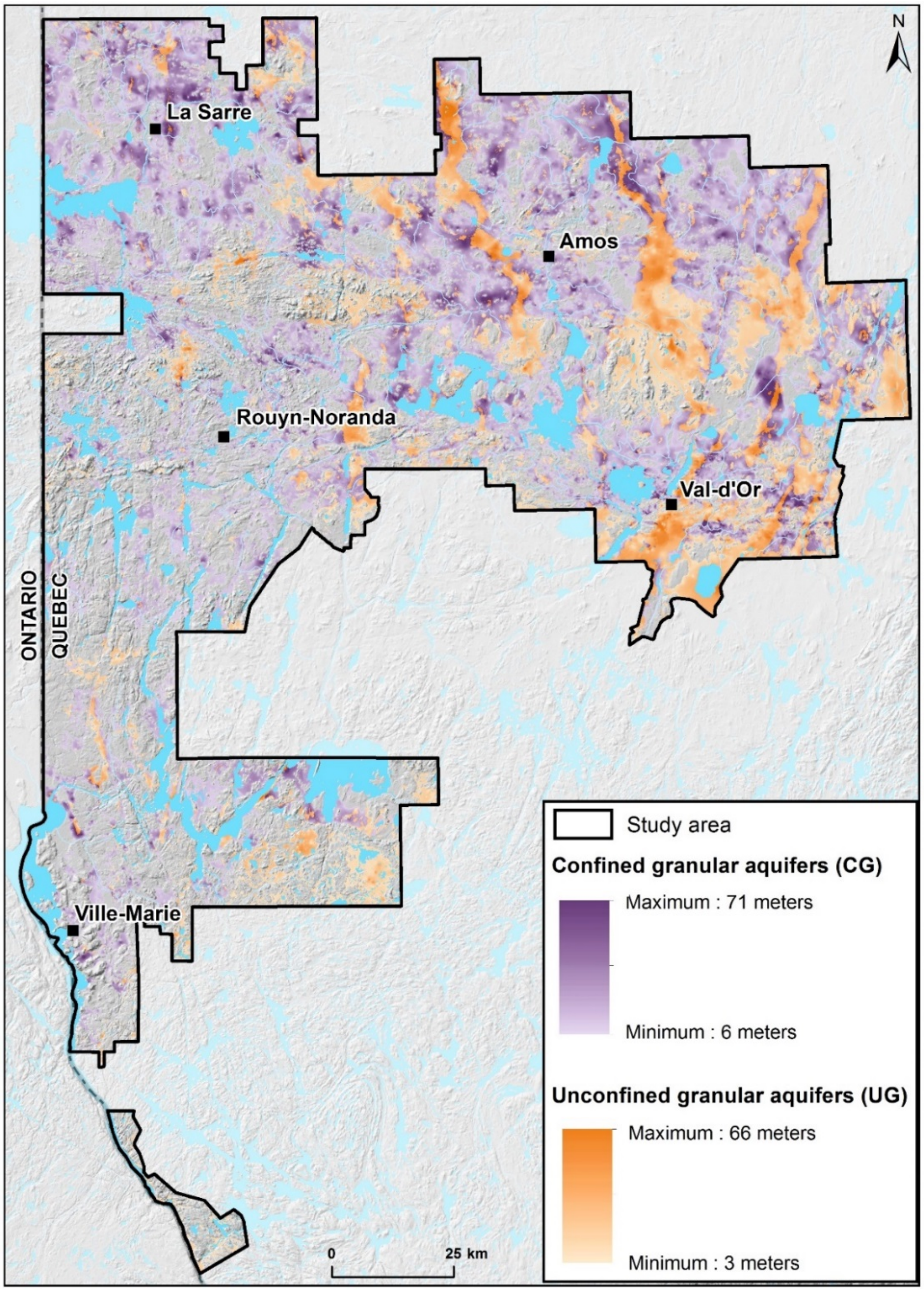

Figure 3.11. Predictive regional map of groundwater geochemistry in granular aquifers.

Table 3.7. Caption for map of figure 3.11.

	UG	CG
	Range of values	Range of values
Eh	-17.26 – 668.74	-0.88 - 618.39
pH	4.7 – 9.38	5.7 - 8.6
Ca^{2+}	0.15 - 92	0.15 – 130
Mg^{2+}	0.05 - 48	0.05 - 40
Na^{+}	0.6 - 150	1.2 - 180
K^{+}	0.05 – 5.9	0.05 - 15
H_4SiO_4	3.68 – 14	4.6 - 17
SO_4^{2-}	0.25 - 42	0.05 - 78
Fe^{2+}	0.015 – 13	0.015 - 6
Mn^{2+}	0.0002 - 2	0.0002 - 1.3
F^{-}	0.04 – 0.3	0.04 – 0.3
Ba	0.001 – 0.2	0.001 – 0.23
B	0.0025 – 0.049	0.0025 - 0.2
Pb	0.00005 - 0.0023	0.00005 - 0.0023
Zn	0.0005 – 0.67	0.0005 - 0.76
Sr^{2+}	0.001 – 0.46	0.001 – 1.3
TDS	19.5 – 764.9	28.8 – 813.1

Figures 3.11 and 3.12 show the extent of confined granular aquifers and confined fractured rock aquifers, respectively. In figure 3.12, areas of confined rocks aquifers found below a confined granular aquifers are not shown, to avoid confusion (only the uppermost aquifer is shown). The greatest groundwater reserves associated with confined granular aquifers are found in the northern portion of the study area, north of the line linking Val-d’Or to La Sarre. Several of the thickest confined granular aquifers are found at the margin of unconfined granular aquifers, especially in the northeastern portion of the study region. These aquifers are most likely fed by groundwater recharging within the nearby unconfined granular aquifer area (Nadeau et al., 2018). The available data suggest that most of the confined aquifers of the region tend to

present high levels of dissolved solids in comparison to unconfined aquifers. High concentrations of As, Fe, Mn, F and B are likely to occur in these aquifers. Based on the Quebec's Government *Hydrogeological Information Database* (HIS), it is estimated that 5226 private wells tap groundwater from these aquifers within the region. An increased monitoring of these wells would help evaluating the population's exposure to such elements. Among others, dissolved Mn deserves a special attention because there is currently no health criteria in Quebec for this parameter, while its toxicity and wide occurrence in groundwater is increasingly documented (Bouchard et al., 2011; Oulhote et al., 2014; Bondu et al., 2018).

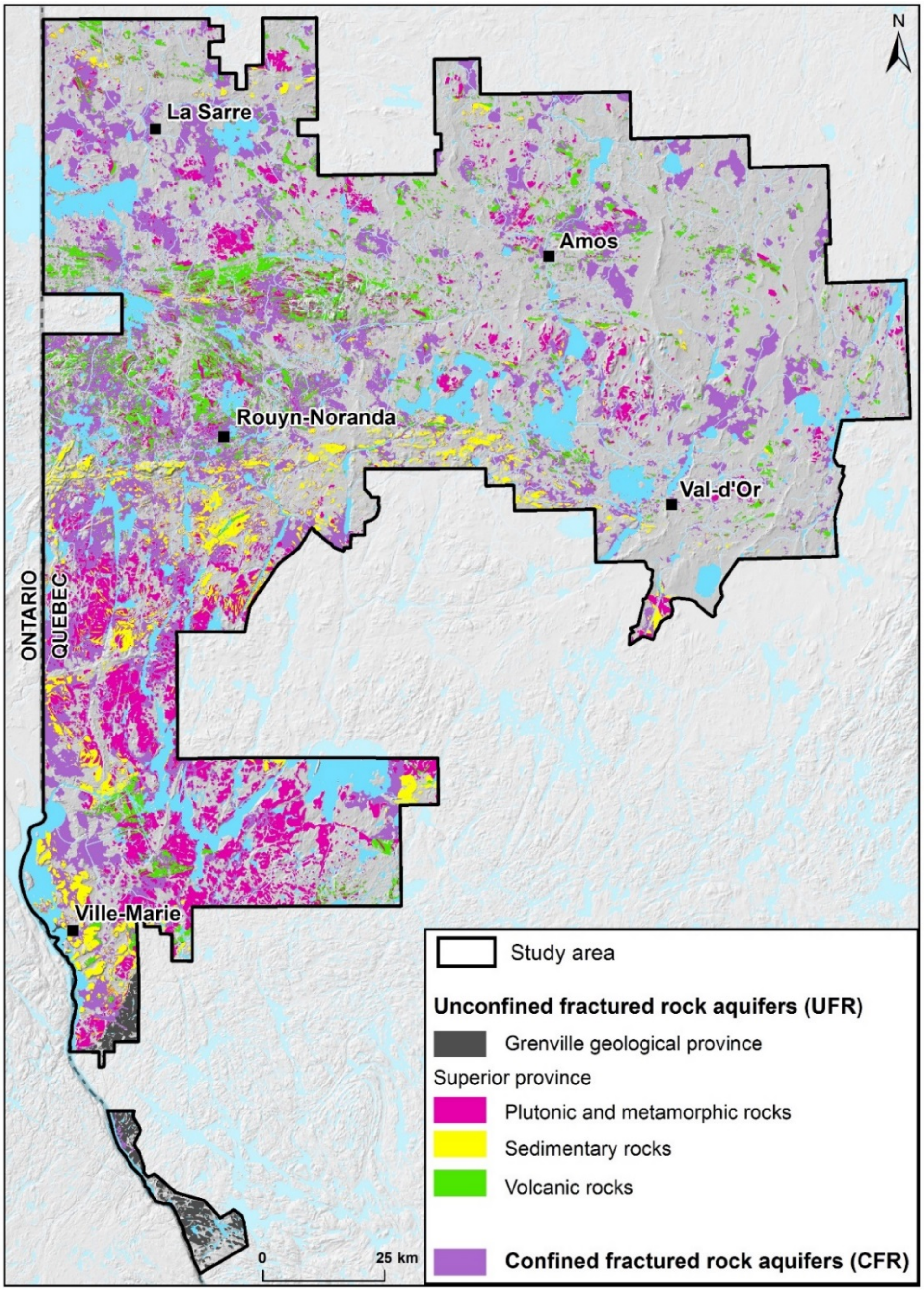

Figure 3.12. Predictive regional map of groundwater geochemistry in fractured rock aquifers.

Table 3.8. Caption for map of figure 3.12

	UFR – P	UFR – S	UFR – V	CFR
	Range of values	Range of values	Range of values	Range of values
$\boldsymbol{Eh}$	108.11 - 539.83	26.57 - 280.56	-92.92 – 437.4	-166.55 – 531.07
$\boldsymbol{pH}$	5.06 - 8.8	6.79 - 7.99	5.97 - 8.5	5.39 – 8.5
$\boldsymbol{Ca^{2+}}$	6.4 – 130	0.32 - 99	17 - 93	0.084 - 320
$\boldsymbol{Mg^{2+}}$	0.9 – 28	0.05 - 38	1 - 34	0.005 - 61
$\boldsymbol{Na^{+}}$	1.2 – 23	4.3 - 300	1.7 - 32	1.6 - 220
$\boldsymbol{K^{+}}$	0.23 – 4.5	0.69 - 4.7	0.13 - 9.2	0.05 - 18
$\boldsymbol{H_4SiO_4}$	3.7 - 14	5.7 - 15	4.4 - 11	0.05 - 17
$\boldsymbol{SO_4^{2-}}$	2.6 – 250	0.25 - 33	0.05 - 38	0.05 - 870
$\boldsymbol{Fe^{2+}}$	0.015 - 4.4	0.05 - 16	0.015 - 4.7	0.015 – 6.1
$\boldsymbol{Mn^{2+}}$	0.0002 - 0.97	0.001 - 0.49	0.0002 - 2.7	0.0002 – 1.7
$\boldsymbol{Sr^{2+}}$	0.01 – 3.9	0.002 - 4.5	0.029 - 1.9	0.001 - 24
$\boldsymbol{F^{-}}$	0.05 - 1.3	0.05 - 0.2	0.04 - 0.8	0.04 – 1.8
$\boldsymbol{Ba}$	0.001 - 0.62	0.001 - 0.07	0.001 - 0.19	0.001 – 6.1
$\boldsymbol{B}$	0.0025 - 0.075	0.0025 - 0.08	0.0025 - 0.21	0.0025 – 0.26
$\boldsymbol{Pb}$	0.00005 - 0.002	0.00005 - 0.0003	0.00005 - 0.05	0.00005 – 0.002
$\boldsymbol{Zn}$	0.002 – 0.29	0.0025 - 0.02	0.0005 - 1.4	0.0005 – 0.39
$\boldsymbol{TDS}$	50.5 – 691.2	193.6 – 857.6	139.2 – 581.8	42.8 – 1438.2

Figure 3.12 provides a closer look at unconfined fractured rock aquifers set in plutonic, volcanic and sedimentary rocks. The map shows the greater abundance of unconfined aquifers set in volcanic rocks in the western portion of the study region, between Rouyn-Noranda and La Sarre. Most unconfined fractured rock aquifers associated with sedimentary rocks are located along the Cadillac Larder-Lake fault and south of this structure (Figure 3.12). Trace elements such as Cr and As are likely to occur in greater concentrations in these rocks in comparison to plutonic rock. Unconfined fractured rocks aquifers associated with plutonic rocks are sparsely distributed north of the

Cadillac-Larder-Lake fault, and highly abundant south of this structure. Among unconfined fractured rocks aquifers, the groundwater found in these plutonic rocks is likely to present the highest U and F concentrations.

3.4.3.2 Perspectives and limitations

Predictive groundwater geochemical maps allow estimating the likelihood of a given dissolved element to occur within a given range of concentrations over a continuous coverage of the territory. This is an advantage for vast regions where groundwater data are sparse and where the hydrogeological environment is heterogeneous. An important perspective related to the use of predictive maps of groundwater geochemistry is the assessment of the state of the resource for northern Quebec. In this vast and remote region, the realization of groundwater sampling campaigns allowing a refined spatial coverage seems impossible. In this context, the establishment of approaches to estimate the probability of observing concentrations of different dissolved constituents in a range of known values in different aquifers whose geometric boundaries are known seems essential. It is in this context that the mapping approach developed for Abitibi-Témiscamingue is of interest to other sectors of the Canadian Shield.

Despite its advantages, the map proposed here must be interpreted with caution. Its purpose is to provide an estimate of the statistical probability to find selected dissolved constituents within given ranges of concentrations. Numerous studies have shown the great spatial variability in groundwater geochemistry at different scales. Among others, the work of Bondu et al. (2017), which was conducted within the study region, highlighted significant differences in dissolved As concentrations at the local scale. Such differences were interpreted as resulting from water-rock interaction processes occurring at the fracture scale. The map proposed here does not reflect such local-scale variations in groundwater chemistry, but rather illustrates the statistical probability of observing constituents within given ranges of concentrations over the study area.

3.5 Concluding remarks

Understanding the processes controlling water geochemical evolution in groundwater flow systems is required for assessing the state of the resource at different scales. When working at the regional scale (10^4 km^2), one of the key challenges relates to the evaluation of the main factors controlling the spatial variations in groundwater chemistry. This evaluation inevitably implies an understanding of the sources and fate of dissolved constituents in groundwater flow systems. The question is complex in areas such as the Canadian Shield, where bedrock lithology is highly heterogeneous and where the surficial cover consists of a sequence of discontinuous units generating a relatively flat relief. Under these conditions, mixed geogenic sources contribute to superimposed local and regional flow systems.

The current study was realized in this context, with the aim of deciphering the sources and fate of dissolved solids in groundwater flow systems over a 19,549 km^2 region found in the southern portion of the Barlow-Ojibway Clay Belt, in Abitibi-Témiscamingue, Quebec, Canada. The calculated saturations indices revealed that most of the main mineral phases remain undersaturated within the entire groundwater flow system and conservative major ions show a gradual increase in concentrations from recharge to down-gradient areas. This reflects the impact of prolonged water-rock interactions. Once incorporated into groundwater, the fate of the non-conservative dissolved solids appears to mainly reflect the impact of redox processes. These redox processes reflect the extent of the Clay Belt, with more oxidizing conditions within unconfined aquifers and more reducing conditions within confined aquifers. These conditions control the fate of redox-sensitive dissolved solids such as Mn, Fe, with concentrations increasing at the unconfined → confined transition.

The main geogenic and anthropogenic sources of dissolved solids were evaluated using an inverse modeling approach. The results revealed that carbonates (disseminated calcite and dolomite) represent the main source of dissolved solids in groundwater, despite the predominance of silicate rocks within the Canadian Shield. The more detailed evaluation of the chemical compositions measured within unconfined fractured rocks aquifers located in the uppermost portions of the groundwater flow system allowed highlighting the link between bedrock lithology and groundwater geochemistry.

The links highlighted between the source and fate of dissolved solids and the characteristics of the geological environment (lithology, confinement) allowed for proposing a predictive map of groundwater chemistry over the study region. While this map is not meant to replace local groundwater sampling, it provides a tool for estimating the state of the groundwater resource at the regional scale. Such information is important for land management purposes because water quality (and not solely water quantity) can be a limitation in the use of the resource. Therefore, there is an interest in protecting aquifers with the best water quality for future generations in the context of land use planning. It also provides a tool that could be used for evaluating the exposure of private well owners to undesirable dissolved constituents. The coupled mass-balance and mapping approach used in this study could further provide valuable insights for the study of groundwater quality in remote areas of the Canadian Shield, where data acquisition is complex due to logistical constraints. The use of groundwater geochemistry maps stands as a valuable tool for estimating the state of the groundwater resource in vast territories where data availability is limited

Acknowledgements

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CHAPITRE IV

A COMBINED GROUNDWATER CONTAMINATION INDEX – DRASTIC APPROACH FOR SUPPORTING SAFE GROUNDWATER USES AND PROTECTION IN ABITIBI-TÉMISCAMINGUE, QUÉBEC, CANADA

Rey, N., Cloutier, V., Rosa, E., Lefebvre, R. A combined Groundwater Contamination Index – DRASTIC approach for supporting safe groundwater uses and protection in Abitibi-Témiscamingue, Québec, Canada. En préparation.

Résumé

La qualité des eaux souterraines est d’une importance primordiale pour garantir la protection de la santé publique. Dans les zones rurales où les eaux souterraines constituent la principale source d'eau potable, comme en Abitibi-Témiscamingue (Québec, Canada), la sensibilisation des résidents sur la qualité des eaux souterraines demeure un défi à relever pour identifier les risques potentiels pour la santé et promouvoir l'utilisation de mesures de protection. Dans le cadre d'un projet intégré de cartographie hydrogéologique, la qualité des eaux souterraines des aquifères rocheux fracturés et granulaires a été étudiée par l'échantillonnage de 427 puits dans une zone d'étude de 19,549 km^2 au sein de la ceinture argileuse Barlow-Ojibway, dans l'ouest du Québec. L'analyse des eaux souterraines a révélé que l'eau des puits est affectée à la fois par des problèmes d’ordre esthétique et de santé. Les problèmes d’ordre esthétique sont reliés à des concentrations élevées en fer, manganèse et matières dissoutes totales (MDT) qui dépassent les Recommandations pour la qualité de l'eau potable au Canada. Les problèmes de santé concernent principalement la présence d'arsenic et d'uranium dépassant les normes du Règlement sur la qualité de l'eau potable pour les substances inorganiques du Québec. Des études antérieures sur les eaux souterraines des aquifères rocheux fracturés du Bouclier canadien ont indiqué que la présence de ces contaminants inorganiques est d'origine géogénique et qu'elle est liée à l'altération des minéraux favorisée par des conditions géochimiques spécifiques. Un Indice de Contamination des Eaux Souterraines (ICES), basé sur ces recommendations d’ordre esthétique et normes de santé, a été calculé afin de produire un portrait régional intégré de la qualité des eaux souterraines. Les échantillons présentant des concentrations qui dépassent les concentrations maximales acceptables pour les paramètres de santé, pour un total de 23 échantillons, ont été retirés de la base de données pour le calcul de l’ICES. Ainsi, 94.6% des sites échantillonnés ne présentent aucun dépasement des normes de santé. Les

résultats de l’ICES montrent que 79.4% des puits échantillonnés ont une eau souterraine avec un niveau de contamination «faible». La qualité des eaux souterraines des aquifères granulaires est généralement supérieure à celle des aquifères rocheux fracturés. Les aquifères rocheux fracturés à nappe captive ont des eaux souterraines de qualité inférieure, en particulier ceux constitués par les roches volcaniques. L'un des inconvénients de l'utilisation de l’ICES concerne l'évolution des recommendations et normes de qualité de l'eau potable. Par exemple, une nouvelle recommandation pour la santé pour le manganèse a été ajoutée en 2019 aux Recommandations pour la qualité de l'eau potable au Canada, ainsi qu’une révision de l’objectif d’ordre esthétique pour ce même élément. Pour aborder cette question, l'ICES a été recalculé en tenant compte des nouvelles recommandations pour le manganèse, pour produire l’ICES_Mn2019. Pour cette évaluation de l’ICES_Mn2019, 161 échantillons supplémentaires ont été retirés puisqu’ils présentent des dépassements de la norme de santé pour Mn. Avec cette nouvelle norme, 56.9% des sites échantillonnés ne présente aucun dépasement des normes de santé, et 55.9% des puits échantillonnés ont une eau souterraine avec un niveau de contamination «faible». Comparé à l’ICES initial (ICES_Pré-Mn2019), l’ICES_Mn2019 présente un portrait régional de l'eau souterraine d’une qualité inférieure, confirmant l'importance de mettre à jour l’ICES avec l'évolution des normes et les contaminants émergents. Étant donné que l’exposition des résidents aux contaminants inorganiques pourrait avoir des effets indésirables sur leur santé s’ils ne prennent pas de mesures de protection, la sensibilisation de la population sur l’importance de tester leurs eaux souterraines s’avère essentielle. L'utilisation combinée de l’ICES avec l’indice DRASTIC indique que les eaux souterraines avec un niveau de contamination «faible» sont présentes dans les zones ayant des indices DRASTIC élevés, principalement dans les aquifères granulaires à nappe libre. Les résultats de cette approche combinée ICES – DRASTIC suggèrent l’importance

d’assurer la protection des aquifères granulaires à nappe libre à haute vulnérabilité afin de maintenir la qualité des eaux souterraines qui leur sont associées.

Mots-clés

Indice de contamination eaux souterraines (ICES), Manganèse, DRASTIC, Santé publique, Abitibi-Témiscamingue.

Abstract

Groundwater quality is of paramount importance to ensure the protection of public health. In rural areas where groundwater is the principal source of freshwater, as in Abitibi-Témiscamingue (Québec, Canada), communicating groundwater quality information to homeowners remains a challenge that has to be overcome to identify potential health risks and promote the use of protective measures. As part of a comprehensive hydrogeological mapping project, the inorganic groundwater quality from fractured bedrock and granular aquifers was investigated through the sampling of 427 wells over a 19,549 km^2 study area within the Barlow-Ojibway Clay Belt in western Quebec. Groundwater analyses reveal that the sampled groundwater wells are affected by both aesthetic and health issues. Aesthetic problems are mainly related to concentrations exceeding the guidelines for iron, manganese, and total dissolved solids (TDS) relative to the Guidelines for Canadian Drinking Water Quality. Health issues are mainly related to the presence of arsenic and uranium exceeding the Regulation respecting the quality of drinking water for inorganic substances of Quebec. Previous studies in this fractured bedrock aquifer of the Canadian Shield indicated that the occurrence of these inorganic contaminants is of geogenic origin, being related to weathering of minerals favored by specific geochemical conditions. A Groundwater contamination index (GWCI), based on these aesthetic and heath guidelines, was calculated to produce a regional integrated portrait of the groundwater quality. The groundwater samples with concentrations that exceed the maximum acceptable concentrations fixed for the health parameters, for a total of 23 samples, have been removed from the database for the GWCI calculation. Thus, 94.6% of the sites sampled show no exceedance of health standards. The results of the GWCI reveal that 79.4% of the sampled wells have groundwater with a "low" degree of contamination. The quality of the groundwater in granular aquifers is generally higher than that of fractured rock aquifers. Fractured confined rock aquifers have inferior groundwater quality, especially those formed by volcanic rocks. One of the drawbacks of the use of GWCI relates to the evolution of water quality guidelines. For example, a new health guideline for manganese was added in 2019 to the Guidelines for Canadian Drinking Water Quality, and the aesthetic objective for manganese was also revised. To address this issue, the GWCI was recalculated considering the new 2019 manganese guidelines, to produce the GWCI_Mn2019. For this evaluation of the GWCI_Mn2019, 161 additional samples were removed since they show exceedances of the health standard for Mn. With this new standard, 56.9% of the sites sampled show no exceedance of health standards, and 55.9% of the wells sampled have groundwater with a "low" degree of contamination. Compared to the initial GWCI (GWCI_Pre-Mn2019), the GWCI_Mn2019 presents a regional portrait of groundwater of lower quality, confirming the importance of updating the GWCI with the evolution of standards and emerging contaminants. As the exposure of residents to inorganic contaminants could lead to adverse health effects if protective measures are not adopted, public awareness campaigns on the importance of testing their groundwater is essential to protect the public health. The combined use of GWCI with DRASTIC shows that high-quality grounwater with a "low" degree of contamination is present in areas with elevated DRASTIC indices, mainly in areas of unconfined granular aquifers. The results of this combined GWCI – DRASTIC approach highlights the importance to support the protection of high-vulnerability unconfined granular aquifers to maintain its associated high-quality groundwater.

Keywords

Groundwater Contamination Index (GWCI), Manganese, DRASTIC, Public health, Abitibi-Témiscamingue.

4.1 Introduction

Groundwater is among the most vital, rare and precious resource among all the natural resources in the world (Taylor et al., 2013). Groundwater is a primary source of drinking water and water supply for industrial purposes (Wada et al., 2014). It is also a strategic global resource, particularly because of its nearly ubiquitous distribution and because of the increasing human pressures on surface waters (Green et al., 2011). As of today, it is estimated that approximately half of the world population depends on groundwater as a primary source of drinking water (WWAP, 2009). Water demand in the world will increase, especially for groundwater supply due to population growth (Gorelick and Zheng, 2015). Nevertheless, while aquifers can often supply sufficient water for domestic uses, water quality can be an important issue, particularly in areas where geogenic and anthropogenic sources of inorganic dissolved constituents may affect the aesthetic character of the water and sometimes even render it unfit for consumption. This is the case in the Abitibi-Témiscamingue region (Québec, Canada) where groundwater is affected by dissolved metals such as iron (Fe) and manganese (Mn) at concentrations often exceeding the Guidelines for Canadian Drinking Water Quality (Health Canada, 2019a), and locally by exceedance of dissolved trace elements concentrations relative to the Regulation respecting the quality of drinking water for inorganic substances (Québec, 2019), such as is the case for arsenic (As) (Bondu et al., 2017a, 2017b, 2018). When such conditions are encountered, treatment systems are generally employed to make water suitable for consumption. Water treatment is a useful approach, especially in the case of public drinking water distribution systems run by competent authorities that must comply with regulations ensuring the safety of users. Nevertheless, the situation is more complex in the case of private wells exploited by inhabitants of rural areas that are not served by a public water distribution system. According to the Regulation respecting the quality of drinking water (Québec, 2019), the water from a private well used for human consumption must meet standards of drinking water quality. The Québec Ministry of the Environment thus recommends private well owners to perform water analyses, including microbiological and physico-chemical parameters. On the other hand, as private wells are not subject to quality control by the Regulation, water quality is sometimes unknown by owners.

To increase knowledge on the groundwater resource, including its quality, the Government of Québec implemented the Groundwater Knowledge Acquisition Program (PACES program). From 2009 to 2015, 13 hydrogeological mapping projects were completed by seven universities in Québec's municipal territory (Larocque et al., 2018), including the Abitibi-Témiscamingue region (Cloutier et al., 2013; 2015; 2016). Despite these important contributions, knowledge transfer on groundwater quality and wells owners awareness on health issues related to water consumption remain a major challenge. There is thus a need to provide public health authorities with approaches to communicate groundwater quality information and to advise private well owners to perform water quality monitoring in order to promote the use of protective measures to reduce exposure to undesirable elements in groundwater.

Water quality indices could be an effective tool to contribute meeting this need. The first water quality indices were developed and used to describe surface water quality in many regions of the world (Sládecek, 1973; Ott, 1978; Dojlido and Best, 1993) using different techniques (Kung et al., 1992; Clarke et al., 2003; Peng, 2004; Beamonte et al., 2005; Ocampo-Duke et al., 2006). Various types of water quality indices were then developed for groundwater resources to address groundwater quality issues in different countries (Backman et al., 1998; Soltan, 1999; Ramesh et al., 2010; Ketata-Rokbani et al., 2011). Characterizing the quality of a groundwater sample through the aggregation of its chemical parameters by using an index such as the Groundwater Contamination

Index (GWCI) can facilitate knowledge transfer on groundwater quality. The DRASTIC method (Aller et al., 1987) is an index-based method commonly used in hydrogeology to quantify the vulnerability of an aquifer to surface contamination. With the use of geographic information systems (GIS), there are opportunities to link information from different indices such as the GWCI and DRASTIC, as tools to improve groundwater resources management by taking into account both groundwater quality and aquifer vulnerability.

To address these challenges, the main objective of this study is to develop an approach to communicate groundwater quality information to support safe groundwater uses and to protect aquifers of high-quality groundwater. The specific objectives are (1) to evaluate the spatial distribution of the Groundwater Contamination Index (GWCI) within groundwater flow systems of Abitibi-Témiscamingue, (2) to test the sensitivity of the GWCI to changes in guideline values, with a focus on the Mn guideline, and (3) to apply a combined GWCI – DRASTIC approach to promote the use of protective measures by homeowners and to support the protection of high-quality groundwater.

4.2 Study area

The study area corresponds to the inhabited area of the Abitibi-Témiscamingue region. It covers a territory of 19,549 km^2 located in western Quebec, Canada (Figure 4.1). This region counts approximately 146 000 inhabitants living in the Regional County Municipalities (RCM) of *La Vallée-de-l'Or*, *Abitibi*, *Abitibi-Ouest*, *Témiscamingue,* and *Ville de Rouyn-Noranda* (MAMH, 2019). It is estimated that more than 73% of the population of Abitibi-Témiscamingue relies on groundwater for domestic water supply (MELCC, 2019). Of this 73%, approximately 59% of the population is supplied by municipal water distribution systems, as for the cities of Amos and Val-d'Or. On the other hand, about 41% of the population depending on groundwater relies on private wells. The groundwater from such private wells could be affected by geogenic contaminants with potential health risks. Most of these private wells are present in rural areas and are withdrawing groundwater from fractured bedrock aquifers, and in some areas from granular aquifers.

The topography of the study area is relatively flat, with elevations mainly ranging between 280 m and 320 m in Abitibi and between 260 m and 340 m in Témiscamingue. With the highest summit reaching 572 m, the main culminating points correspond to bedrock outcrops and the lower points are associated with large lakes (Figure 4.1). A cold and humid continental climate defines this region. Mean annual precipitation ranges between 875 mm and 989 mm and mean monthly air temperatures range between 23.3°C and 23.7°C in January and July, respectively (Cloutier et al., 2013; 2015). The continental water divide separating the James Bay Basin (North) and St. Lawrence River Basin (South) crosses the study area from east to west (Figure 4.1).

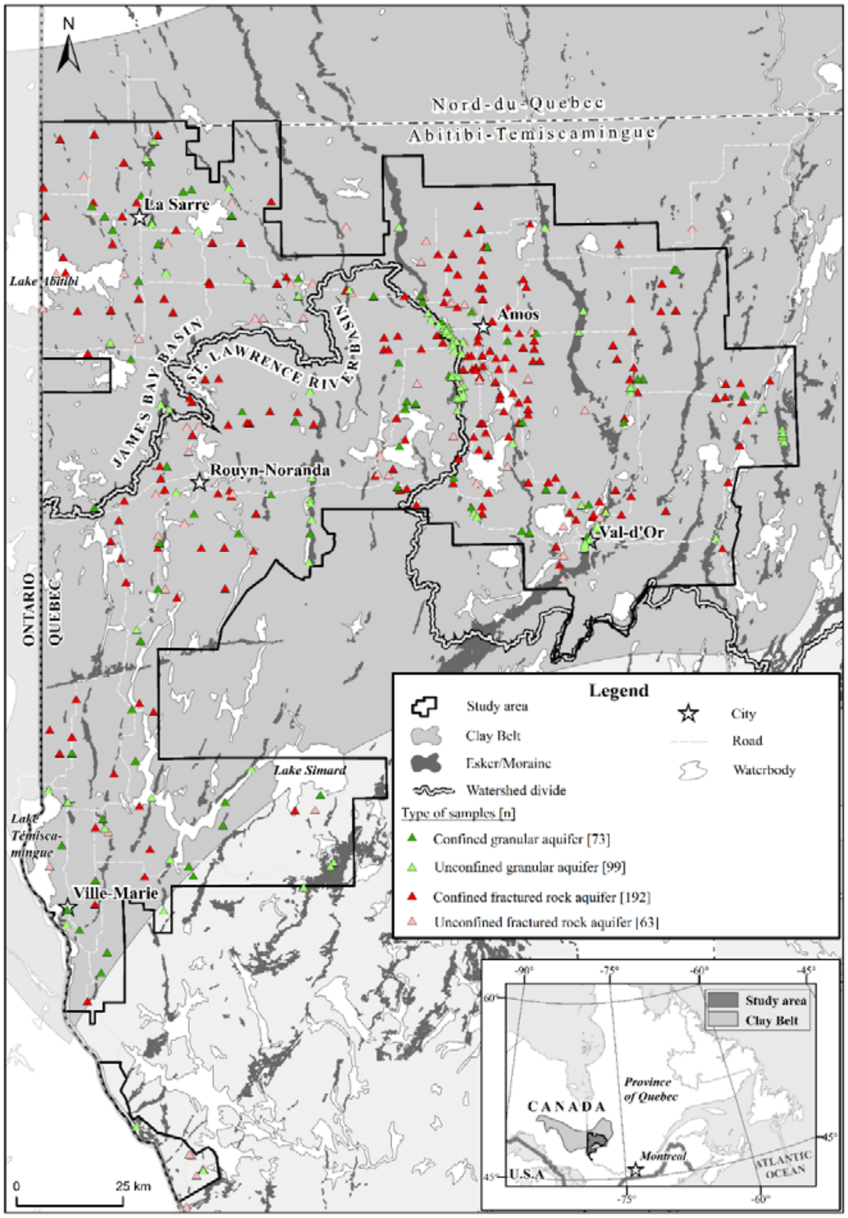

Figure 4.1. Study area with the location of the groundwater sampling sites. The number (n) of available groundwater samples is shown in the legend. The limits of the study area are those of the PACES projects in Abitibi-Témiscamingue (Cloutier et al., 2016). The continental water divide between James Bay and St. Lawrence basins is also indicated.

4.2.1 Geological and hydrogeological setting

The geology of the region is described with details in numerous previous studies (Thibaudeau and Veillette, 2005; Nadeau et al., 2015, 2018; Cloutier et al., 2016; Rey et al., 2018). The bedrock is composed of crystalline Precambrian igneous, metamorphic and sedimentary rocks of the Canadian Shield. The Precambrian bedrock is covered by Quaternary sediments deposited during the last glaciation-deglaciation cycle. These sediments include glaciofluvial formations (eskers and moraines) consisting of sand and gravel, as well as glaciolacustrine fine-grained deep-water deposits of Lake Barlow-Ojibway that form the Clay Belt (Figure 4.1) (Veillette, 1996; Roy et al., 2011). These fined grained glaciolacustrine sediments form the clay plain and constitute a regional aquitard (Cloutier et al., 2016; Nadeau et al., 2018). This geological setting led to the formation of four main types of aquifers within the region, with (1) the unconfined granular aquifers associated to the glaciofluvial sediments (eskers and moraines, these represent the most productive aquifers of the region (Nadeau et al., 2015)), (2) the unconfined fractured rock aquifers characterized by a lower hydraulic conductivity, (3) the confined granular aquifers and (4) the confined fractured rock aquifers that are both covered by the glaciolacustrine sediments (Rey et al., 2018).

4.2.2 Regional hydrogeochemical context

The hydrogeochemistry of the Abitibi-Témiscamingue aquifer-aquitard system, characterized by a heterogeneous bedrock lithology and a relatively flat topography, was studied in details by Rey et al., (in preparation). Overall, groundwater and springs correspond to the Ca-Mg – HCO_3 water type, typical of recharge areas, whereas precipitation and samples from the snowpack plot in the Na+K – Cl pole of the Piper diagram (Rey et al., in preparation). Surface waters mainly correspond to a water type that seems to result from the mixing between precipitation and the groundwater feeding the regional lakes and streams. Some groundwater samples from unconfined and confined rock aquifers have Na – Cl, Na – HCO_3 and Ca – SO_4 water types, suggesting a geochemical evolution in comparison to groundwater of typical Ca-Mg – HCO_3 water type from granular aquifers that are not affected by anthropogenic contamination. Most of the dissolved majors constituents and total dissolved solids (TDS) concentrations increase along the groundwater flow system from shallow unconfined aquifers down-gradient, following this trend: TDS of precipitation and snowpack having lowest concentrations < springs < surface waters < unconfined granular aquifers < unconfined fractured rock aquifers < confined granular aquifers < confined fractured rock aquifers. This increase in TDS reflects water-rock interactions with increasing groundwater flow distance and residence time.

Rey et al. (in preparation) identified silicates, carbonates (calcite and dolomite) and sulfides weathering among the dominant geochemical processes controlling groundwater geochemistry in the study area. Redox processes, coupled to local bedrock sources and to the influence of the clay aquitard affect the Fe and Mn concentrations which are significantly higher in confined fractured rock aquifers under more reducing conditions, in comparison to unconfined granular aquifers under more oxidizing conditions. Redox processes also influence the SO_4 concentration with a gradual increase from precipitation to unconfined granular and fractured rocks aquifers, and a subsequent decrease in confined aquifers, likely due to SO_4 conversion to sulfide under reducing conditions in deep fractures. The hydrogeochemistry of the unconfined fractured rock aquifers was used to established links between geogenic sources and bedrock lithology. Groundwater flowing in sedimentary and volcanic unconfined fractured rock aquifers presents higher dissolved As, Cr, Ca, Mg, Na and HCO_3 concentrations in comparison to groundwater from plutonic unconfined fractured rock aquifers. On the other hand, the highest K and Si concentrations are generally found in plutonic fractured rock aquifers. Some trace elements are also associated with intrusive rocks, such as U and F, with concentrations generally higher in plutonic unconfined fractured rock aquifers.

4.3 Materials and methods

4.3.1 Groundwater sampling, *in situ* measurements and analytical procedures

This study is based on the geochemical database from Rey et al. (in preparation). Overall, 427 groundwater samples were collected from private, municipal and observation wells during summer over a period ranging from 2006 to 2013. Most of the groundwater samples were obtained from wells installed in the fractured bedrock aquifers (n = 255) (Table 4.1; Figure 4.1). The Hydrogeological Information System (HIS) of the Québec Ministry of the Environment was used to identify and select private wells to sample according to wells characteristics and lithology. Complementary information about the well construction details, as the casing depth and the total depth, as well as the stratigraphy, was obtained from the well owners or from the municipal employees. The samples were collected from untreated water taps. Private and observation wells were systematically purged before sampling, after *in situ* parameters (pH, dissolved oxygen, electrical conductivity, redox potential, and temperature) measured using a YSI 556 MPS multi-parameter probe reached predefined stability criteria. A standard sampling protocol was adopted for all samples, respecting the order of bottles filling in order to avoid contaminating the water sampled with the selected preservatives included in the bottles for stabilizing the samples: nitric acid for metals, sulfuric acid for nutrients and zinc acetate plus sodium hydroxide for sulfides. The protocol was established within the framework of the PACES program (Blanchette and Cloutier, 2010) based on the Québec Ministry of the Environment groundwater sampling guide (MDDEP, 2011). Samples were kept at 4°C before being sent to the laboratory. The samples were analyzed for their chemical composition, including the total dissolved concentrations of major and minor constituents (total alkalinity $CaCO_3$, Ca, Mg, K, Na, Br, Cl, F, NO_3-NO_2 and SO_4, organic carbon (DOC), nutrients (Ammonia nitrogen (N-NH_3) and total inorganic P), trace elements (Al, Sb, Ag, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Sn, Fe, Li, Mn, Hg, Mo, Ni, Pb, Se, Si, Sr, Ti, U, V, Zn) and sulfides (Total S) at the Maxxam Analytics and the Exova laboratories, both located in Montréal, Canada and accredited by the Québec Ministry of the Environment. Assurance quality was ensured by taking about 10% duplicates and 1% blanks.

At the Maxxam Analytics laboratory, measurements of dissolved metals were performed using the argon plasma ionizing source spectrometry method (ICP-MS). The detection limits range between 0.0003 mg/l for Ag to 0.5 mg/l for Ca. Determination of anions concentrations were made using the ion chromatography method with detection limits ranging between 0.02 mg/l (nitrate-nitrite) and 0.1 mg/l for bromides. Measurements of fluoride concentrations were performed using the ion-selective electrode method with a detection limit of 0.1 mg/l. Total alkalinity in $CaCO_3$ (final pH 4.5) was determined using the titration method, with a detection limit of 1 mg/l. Inorganic phosphorus concentrations were measured using the automated colorimetric method with ammonium molybdate, with a detection limit of 0.03 mg/l. Measurements of ammoniacal nitrogen concentrations were made using the automated colorimetric method with sodium salicylate with a detection limit of 0.03 mg/l. Determination of sulfide concentrations were made using the methylene blue method with a detection limit of 0.02 mg/l.

Table 4.1. Summary of available groundwater samples, with number of samples and associated sampling years.Further details about the sampling periods appear in Table 2 of Rey et al. (2018). Groundwater samples are grouped according to main aquifers types (CFR, UFR, CG, UG).

Groundwater samples	Number of samples (n)	Sampling years
Confined fractured rock aquifer (CFR)	192	2006-2013
Unconfined fractured rock aquifer (UFR)	63	2006-2013
Confined granular aquifer (CG)	73	2006-2013
Unconfined granular aquifer (UG)	99	2006-2013
Total	427	2006-2013

4.3.2 Aesthetic objectives and health based guideline for drinking water

Overall, in the study area, drinking water quality in each aquifer type is affected by aesthetic problems related to exceedances in Cl, Fe, Mn, Na, SO_4 and TDS, for which concentrations exceed the aesthetic objectives of the Guidelines for Canadian Drinking Water Quality (Health Canada, 2019a) (Table 4.2). Drinking water quality, especially in fractured rock aquifers, is also affected by some exceedances of the maximum acceptable concentrations recommended by the Regulation respecting the quality of drinking water for inorganic substances (Québec, 2019) for As, Ba, Cd, F, and U (Table 4.2). The documented Mn exceedances are related to the new guideline published by Health Canada (2019b), which also includes a revised aesthetic objective for Mn (see the notes of Table 4.2).

Table 4.2 reveals that the main aesthetic problems for groundwater quality are related to Mn, Fe and TDS, with 229 (Pre-Mn2019 guideline of 0.05 mg/L), 132 and 85 samples above the guideline values, respectively, out of the 427 wells sampled. When using the Mn2019 aesthetic guideline of 0.02 mg/L, the number of Mn exceedances increases to 268 samples. Exceedances are also observed for As and U, with 16 and 4 samples above the guideline, respectively. With the Mn2019 health guideline of 0.12 mg/L, the major concern on groundwater quality becomes the presence of Mn, with 176 samples showing Mn concentrations above the guideline.

Groundwater from bedrock aquifers, more particularly from confined fractured rock aquifers, is more affected by water quality problems than granular aquifers, both for aesthetic and health issues (Table 4.2). Confined fractured rock aquifers are affected by exceedances in Mn (n = 106 for Mn2019 health criteria, n = 142 for Mn2019 aesthetic objective), As (n = 13), Fe (n = 72) and TDS (n = 50). In general, the groundwater from granular aquifers, especially from unconfined granular aquifers, is of better quality than groundwater from bedrock aquifers (Table 4.2).

Table 4.2. Summary of descriptive statistics for the 427 groundwater samples (GW) for parameters having exceeding of aesthetic objectives and health based guideline, with the number of exceeding according to main aquifer types (UG, CG, UFR and CFR).

	Parameters	N	Median	Min	Max	SD	N under DL	GV (mg/L)	GW (N=427)	UG (N=99)	CG (N=73)	UFR (N=63)	CFR (N=192)
Aesthetic Objectives (Health Canada, 2019a)	Cl	427	2.1	0.05	400	37.8	31	250	3		1	1	1
	Fe	427	0.06	0.02	16	1.4	196	0.3	132	13	26	21	72
	Mn	427	0.07	0.0002	2.7	0.3	34	0.05* 0.02**	229 268	20 31	44 51	37 44	128 142
	Na	427	9.3	0.6	300	28.6	0	200	3			1	2
	SO_4	427	8.7	0.1	870	44.1	25	500	1				1
	TDS	427	305.9	19.5	1438.3	202.2	ND	500	85	3	21	11	50
Health criteria (Québec, 2019)	As	427	0.001	0.001	0.05	0.006	313	0.01	16			3	13
	Ba	427	0.02	0.001	6.1	0.3	39	1	1				1
	Cd	427	0.0001	0.0001	0.03	0.002	419	0.005	1		1		
	F	422	0.1	0.04	1.8	0.2	317	1.5	1				1
	Mn	427	0.07	0.0002	2.7	0.3	34	0.12***	176	8	33	29	106
	U	353	0.001	0.001	0.2	0.01	266	0.02	4			3	1

Notes: SD : Standard deviation
N : number of samples
DL : Detection limit
GV : Guideline values
0.05*: Aesthetic objective of Mn guideline (before 2019)
0.02**: Aesthetic objective of Mn guideline value adopted in 2019 (Health Canada, 2019b)
0.12***: Health criteria of Mn guideline value adopted in 2019 (Health Canada, 2019b)

4.3.3 Groundwater contamination index (GWCI)

The water quality index (WQI) is a mathematical tool that allows transforming a large quantity of chemical data into a single score that represents the water quality of a given sample (Saeedi et al., 2010). The calculated scores express the water quality into a scale of values representing a gradation in water quality levels. Horton (1965) developed the first modern water quality index (the Horton Index) in a new mathematical form of WQI by selecting physical, chemical and biological parameters to obtain a numerical value. The selection of parameters is based on the Delphi method (Linstone and Turoff, 1975), a sensitive method using weights. Each parameter is weighted according to its relative impact on water quality. Brown et al., (1970) have improved the Horton Index with the support from the US National Sanitation Foundation (NSF) to produce an index known as the NFSWQI. This index was used to determine the water quality for different purposes, including drinking and irrigation. It is one of the two water quality index models that have inspired a multitude of models in several countries, the other being the CCMEWQI (Canadian Water Quality Index, also known as Canadian Council of Ministers of the Environment Water Quality Index) (Abbasi and Abbasi, 2011). The CCMEWQI was endorsed by the United Nations Environment Program (UNEP) in 2007 as a model for the Global Drinking Water Quality Index (GDWQI) (Lumb et al., 2011). Backman et al., (1998) proposed a contamination index for evaluating and mapping the degree of groundwater contamination in Southwestern Finland and Central Slovakia. Different water quality indices were successful to study groundwater quality in several countries, as for evaluating the groundwater quality in Egypt (Soltan, 1999), for drinking purposes in Iran (Saeedi et al., 2010), for drinking purposes and groundwater quality assessment in India (Ramesh et al., 2010; Vasanthavigar et al., 2010), and for evaluating deep aquifer groundwater quality in Tunisia (Ketata-Rokbani et al., 2011).

The groundwater quality index used in this study, to assess the regional quality of groundwater in the aquifers of Abitibi-Témiscamingue, is the contamination index derived from Backman et al., (1998). The advantage of this index compared to other groundwater quality index is that it is based on a mathematical calculation that doesn't use the subjective method of weights. In addition to the objectivity of the method, the aquifers' conditions and geomorphology studied in Finland and Slovakia are similar to the regional aquifers of the Abitibi-Témiscamingue region. The developed groundwater contamination index (GWCI) uses both the Guidelines for Canadian Drinking Water Quality (Health Canada, 2019a) and the Regulation respecting the quality of drinking water for inorganic substances (Québec, 2019). The GWCI is an approach to assess and to view the affected areas by ionics species potentially harmful that exceed the water quality guidelines. The objective is to represent the GWCI on a regional map to visualise the degree of groundwater contamination which takes into consideration the number of parameters and the concentrations exceeding the water quality guidelines. The calculation of the GWCI is based on the inorganic parameters that exceed the water quality guidelines for aesthetic objectives. However, the GWCI also accounts for health issue parameters, even if the latter do not exceed the highest permissible concentration values. The health parameters (As, Ba, Cd, F and U) presented in Table 4.2 constitutes a regional health problem. Before calculating the index, all the samples with parameters that exceed the regulation for health criteria were removed as they are considered as "non-potable water" since they exceed the maximum acceptable concentrations fixed for health parameters for at least one paremeter. As groundwater sampling was performed between 2006 and 2013, the GWCI was first calculated with the Pre-2019 Mn guideline (GWCI_Pre-Mn2019). To test the sensitivity of GWCI to changes in guideline values (specific objective #2 of this study), the GWCI was recalculated with the Mn2019 guideline to produce the GWCI_Mn2019 (see Section 4.4.2).

The main steps for computing GWCI are presented in Figure 4.2, using the guideline values for the Pre-Mn2019 and the Mn2019 guidelines. In the first step, parameters with samples having exceedances of aesthetic objectives (Cl, Fe, Mn, Na, SO_4, TDS) and health based guideline (As, Ba, Cd, F, U) are selected. In step 2, samples with concentrations that exceed the water quality guidelines for health issues for at least one parameters are removed prior to the GWCI calculation. According to Table 4.2, 23 samples were removed from the database for the GWCI calculation taking into account the Pre-Mn2019 regulation. A number of 161 additional samples were removed from the database for the GWCI calculation taking into account the Mn2019 regulation. In Step 3, a contamination factor (C_{fi}) is calculated for each parameter using the following equation:

$$C_{fi} = (C_{Ai}/C_{Ni}) -1$$

Where C_{Ai} is the concentration measured of each chemical parameter in each water sample, in mg/L and C_{NI} is the guideline value for each chemical parameter, in mg/L. The contamination factor C_{fi} is calculated for each parameter by dividing its measured concentration (C_{AI}) in each water sample by its respective guideline value (C_{NI}) according to the guidelines of Health Canada (2019a) and Québec (2019).

Finally, a GWCI score is computed for each sample as the sum of C_{fi} for all parameters (Step 4; Figure 4.2):

$$GWCI = \Sigma\ C_{fi}$$

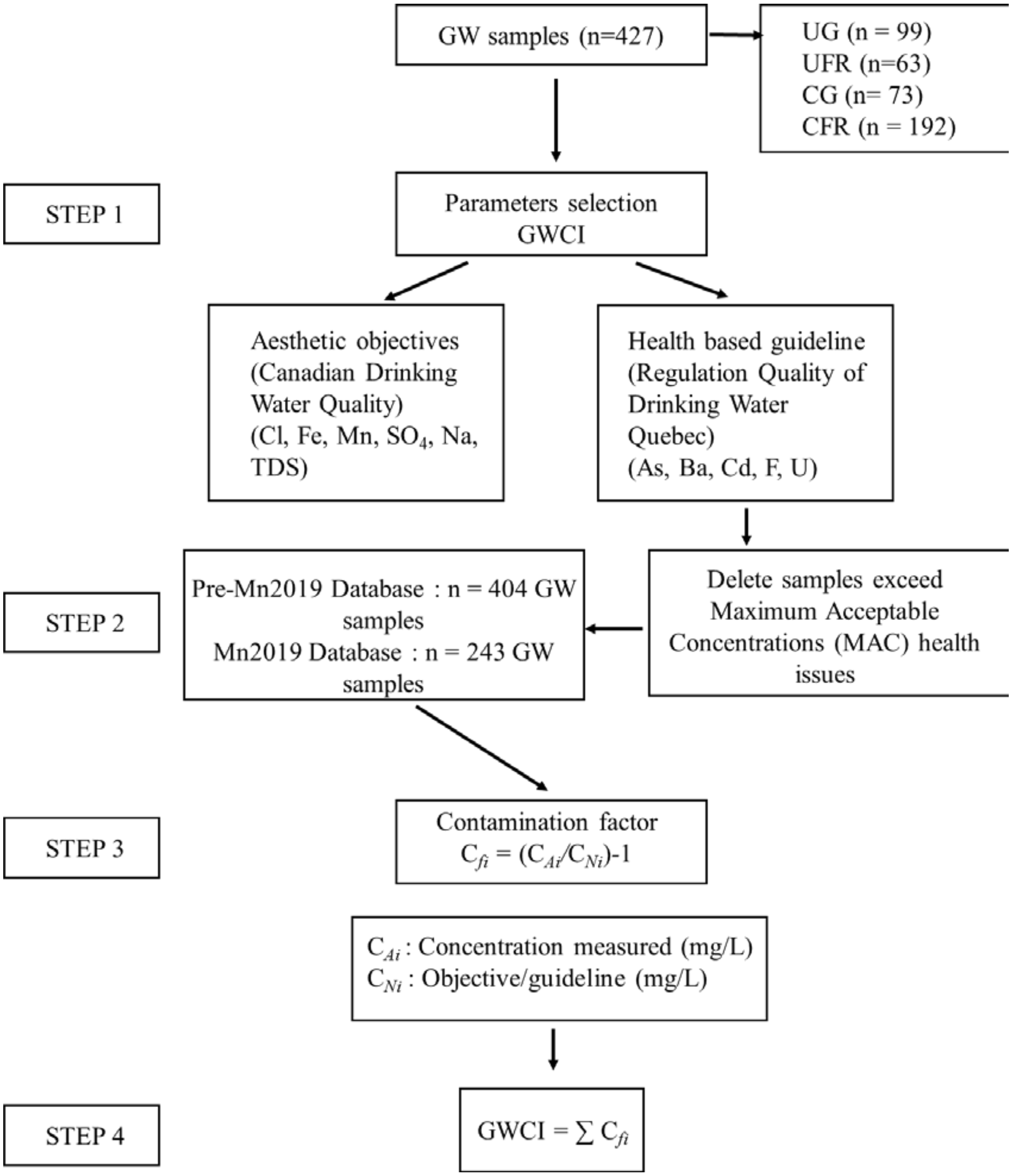

Figure 4.2. Methodological flow chart to compute GWCI.

4.4 Results and discussion

4.4.1 GWCI and the main aquifer types

The Abitibi-Temiscamingue is renowned for the excellent quality of the groundwater found in eskers (Nadeau et al., 2015; Cloutier et al., 2016). Nevertheless, some areas of the region face problems with respect to water quality, especially for groundwater from bedrock wells (Bondu et al., 2018). Significant exceedances of parameters of geogenic origin are observed over the region, as for Fe, Mn, TDS, As and U (Table 4.2). Even if Fe and Mn concentrations are below the detection limit for most of the samples, high concentrations of Fe and Mn are observed in the region, with median values of 0.06 mg/L for Fe and 0.07 mg/L for Mn (Table 4.2). Dissolved Mn concentrations range from the detection limit of 0.0002 mg/L to 2.7 mg/L, with a standard deviation of 0.3 mg/L. Dissolved Fe concentrations range from the detection limit of 0.02 mg/L to 16 mg/L, with a standard deviation 1.4 mg/L. With TDS values ranging from 19.5 to 1 438.8 mg/L, exceedances in TDS are also observed (n=85, Table 4.2). Most of the exceedances in TDS are found in the confined aquifers, particularly in the confined fractured rock aquifers presenting the most evolved groundwater geochemistry (n=50, Table 4.2). With respect to health risks, the presence of As and U above guideline values was only recorded in fractured rock aquifers (n = 16 for As, n = 4 for U; Table 4.2). Dissolved As concentrations ranged between the detection limit of 0.001 mg/L and 0.05 mg/L. Dissolved U concentrations ranged between the detection limit of 0.001 mg/L and 0.2 mg/L.

The GWCI calculated with the Pre-2019Mn guideline are interpreted using a classification of a three grade scale degree of groundwater contamination as proposed by Backman et al. (1998). The three degree of groundwater contamination are the following : "low" (GWCI <1), "medium" (1< GWCI <3) and "hight" (GWCI >3).

For the groundwater quality evaluation with the Pre-Mn2019 guideline, 94.6% of the samples have no health issues, while the other 5.4% are considered as "non-potable water" (Table 4.3). The GWQI calculated for the samples having no health issues were classified using the categories defined by Backman et al., (1998). The degree of groundwater contamination is "low" for 339 samples (79.4%) having a GWCI below 1, and "medium" for 14 samples (3.3%) (GWCI from 1 to 3). These results thus reveal that about 83% of the wells sampled in Abitibi-Témiscamingue present a good groundwater quality relative to water quality guidelines. Table 4.3 shows that approximately 12% of the groundwater samples present a "high" degree of groundwater contamination (n = 51). These 51 samples are all characterized by iron and manganese concentrations exceeding the aesthetic guideline values.

Table 4.3. Classification of groundwater quality in Abitibi-Témiscamingue according to the GWCI computed with Pre-Mn2019 guideline (GWCI Grade Scale from Backman et al. (1998)).

GWCI Grade Scale	Degree of groundwater contamination	N	%
<1	Low	339	79.4
1-3	Medium	14	3.3
>3	High	51	11.9
Not evaluated	Groundwater samples with health issues "non-potable water"	23	5.4

N: Number of groundwater samples

Box plot diagrams were produced to illustrate the relation between the GWCI calculated with the Pre-Mn2019 guideline for groundwater samples and the four main aquifer types of Abitibi-Témiscamingue (Figure 4.3). Overall, the median GWCI values for groundwater in unconfined granular and fractured bedrock aquifers is inferior to the median GWCI values from confined granulars and fractured bedrock aquifers. The box plots, with the removal of extreme values, allow for a better comparison of GWCI between aquifer types.

Groundwater in unconfined granular aquifers, which are known to be associated with recharge areas, is generally of excellent quality, with most samples having a GWCI below 0, except few samples with extreme values. These samples correspond to groundwater affected by exceedances in Fe and Mn. Groundwater index values from unconfined granular aquifers show low variability. Groundwater from confined granular aquifers is of lower quality compared to groundwater from unconfined granular aquifer, with GWCI values ranging between -10.6 and 20.4 (Figure 4.3). This could be explained by the longer residence time and travel distance of the groundwater in confined aquifers. Groundwater from unconfined fractured rock aquifers shows significant GWCI variability, with GWCI values ranging between -10.4 and 60.2 (Figure 4.3). The diversified bedrock lithology, and the absence of a confining unit, could explain the variability of the GWCI in relation to water-rock interaction processes. Groundwater in confined fractured rock aquifers shows GWCI values ranging between -10.6 and 26.1 (Figure 4.3). Overall, the extreme values present in unconfined and confined fractured rock aquifer are associated with elevated Mn and Fe concentrations, as well as elevated concentrations in trace elements such as As.

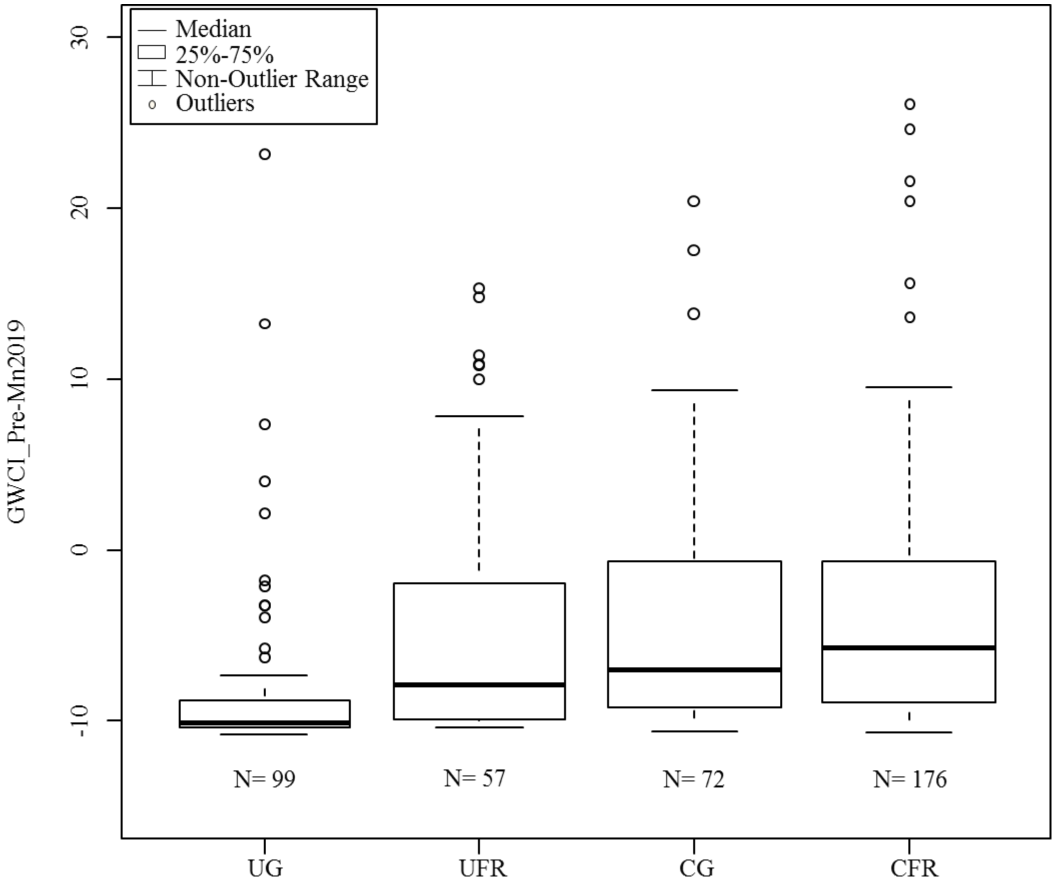

Figure 4.3. Box plot of GWCI for the groundwater samples from the four main aquifer types (GWCI computed with Pre-Mn2019 guideline). UG: unconfined granular aquifer (n=99); CG: confined granular aquifer (n=72); UFR: unconfined fractured rock aquifer (n=57); CFR: confined fractured rock aquifer (n=176).

As highlighted in the regional hydrogeochemical study of Abitibi-Témiscamingue by Rey et al. (in preparation), the evolution of groundwater geochemistry reflects local water-rock interactions, especially in unconfined fractured rocks aquifers. Additional box plots were thus produced to compare the GWCI calculated with Pre-Mn2019 guideline for groundwater samples collected in confined and unconfined fractured rock aquifers set in plutonic, volcanic and sedimentary rocks (Figure 4.4). In the case of unconfined fractured rock aquifers, because sedimentary rocks (n = 5) are less represented compared to plutonic rocks (n = 27) and volcanic rocks (n = 24) (upper box plots; Figure 4.4), these will not be considered in the interpretation of the data. Groundwater in unconfined plutonic rock aquifers is of better quality than in unconfined volcanic rocks aquifers. This is consistent with the study of Rey et al. (in preparation) that revealed that groundwater geochemistry associated with unconfined fractured volcanic rocks generally presents higher dissolved Ca, Mg, Na and HCO_3 concentrations in comparison to groundwater from unconfined fractured plutonic rocks which is characterized by higher K and Si concentrations. The presence of geogenic arsenic is mainly related to metasedimentary and volcanic rocks, as it is the case along the Cadillac Fault, a mineralized fault zone known to have groundwater containing elevated arsenic concentrations (Bondu et al., 2017b).

For the confined fractured rock aquifers, even if the box plots seem to present little difference between the types of rocks, the median GWCI values suggest that groundwater in volcanic and sedimentary rocks is of better quality than in plutonic rocks (Figure 4.4 : lower box plots). The confining clay unit plays a major role in the groundwater quality of confined bedrock aquifers. Groundwater in confined fractured rock aquifers contains elevated concentration of TDS (Table 4.2), and has the highest median GWCI compared to other aquifer types (Figure 4.3).

A correlation matrix, established between the GWCI and the chemical parameters, revealed a significant correlation between the GWCI and Fe concentrations (correlation coefficient = 0.81) and between the GWCI and manganese concentrations (correlation coefficient = 0.88). This indicates that the quality of the water is greatly influenced by iron and manganese in the study area. These aesthetic parameters are thus determinant in the regional groundwater quality.

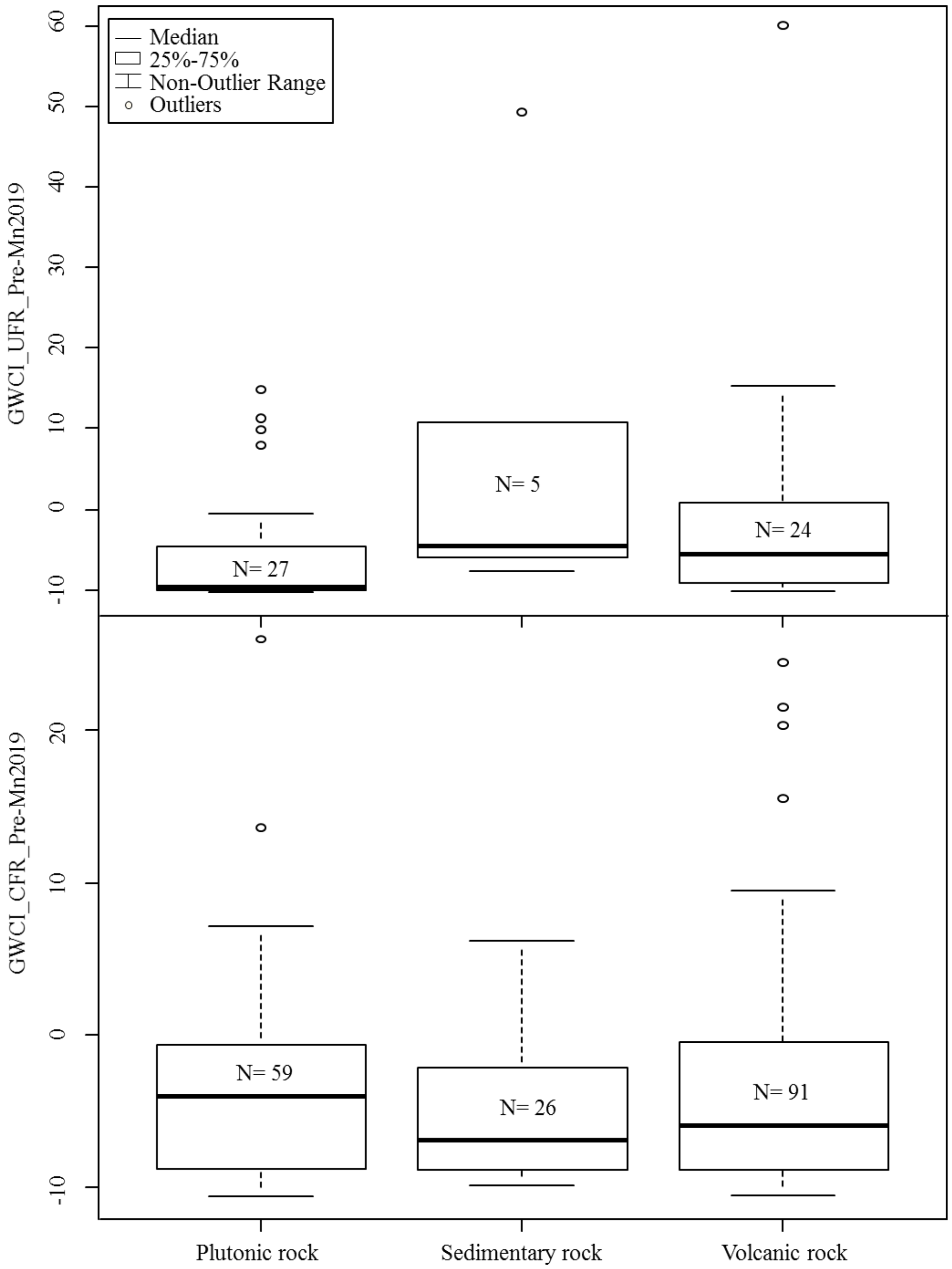

Figure 4.4. Box plot of GWCI for groundwater samples from fractured rock aquifers set in plutonic, volcanic and sedimentary rocks for unconfined (upper box plots) and confined (lower box plots) fractured rock aquifers (GWCI computed with Pre-Mn2019 guideline).

4.4.2 GWCI considering Mn guideline review

The GWCI calculated in Section 4.4.1 provides a specific portrait of the groundwater quality taking into consideration the Pre-Mn2019 water quality standards. However, the evolution of water quality guidelines make the GWCI likely to evolve in time. If the guideline value changes for a parameter, or if an aesthetic objective switches to an health guideline, the calculation of the GWCI will change. This is the case for Mn, which used to be considered solely as an aesthetic problem in Canada. However, recent studies have highlighted its neurotoxicity for humans, with more important consequences to children (Wasserman et al., 2006; Bouchard et al., 2007). A revised aesthetic objective (0.02 mg/L) and a new health based guideline (0.12 mg/L) for manganese were thus published in 2019 (Health Canada, 2019b).

To test the sensitivity of GWCI to changes in guideline values, this section presents the results of GWCI calculations based on the Mn2019 guideline to produce the GWCI_Mn2019, which will be compared to the GWCI_Pre-2019 results. The methodology to calculate the GWCI_Mn2019 is the same as for calculating GWCI_Pre-Mn2019 and was adapted to take into account the change in the guideline value for the Mn2019 guideline with an aesthetic objective of 0.02 mg/L (Health Canada, 2019a). For the samples with Mn concentrations below the health criteria of 0.12 mg/L, the C_{fi} presented in Figure 4.2 were used to compute their GWCI_Mn2019, with 0.02 mg/L as aesthetic guideline (C_{Ni}) value for Mn. The samples with parameters above health criteria, including Mn concentrations above the health criteria of 0.12 mg/L, were removed prior to GWCI calculation, for a total of 184 samples. This methodology allowed for calculating GWCI_Mn2019 scores for the remaining 243 samples.

Table 4.4. Classification of groundwater quality in Abitibi-Témiscamingue according to the GWCI computed with Mn2019 guideline (GWCI Grade Scale from Backman et al. (1998)).

GWCI Grade Scale	Degree of groundwater contamination	GWCI_Pre-Mn2019		GWCI_Mn2019	
		N	%	N	%
<1	Low	339	79.4	239	55.9
1-3	Medium	14	3.3	2	0.5
>3	High	51	11.9	2	0.5
Not evaluated	Groundwater samples with health issues "non-potable water"	23	5.4	184	43.1

N: Number of groundwater samples

Table 4.4 presents the classification of groundwater quality for GWCI_Mn2019, with the initial GWCI_Pre-Mn2019 from Table 4.3 as a comparison. The results show that changes in guideline values can have a significant influence on the computed GWCI, and thus, on the groundwater quality portrait of a region. While the initial GWCI indicates that about 79% of the wells sampled in Abitibi-Témiscamingue have a "low" degree of groundwater contamination, this percentage decreases to about 56% (n = 239 of 427 samples) for GWCI_Mn2019 (Table 4.4), with 0.5% of the groundwater samples of "medium" degree (n = 2) and 0.5% of "high" degree of groundwater contamination. When considering the Mn2019 health guideline of 0.12 mg/L, the number of samples having no health issues decreases from 94.6% for the Pre-Mn2019 guideline to 56.9% for Mn2019 guideline, with the other 43.1% of the samples considered as "non-potable water" (Table 4.4). The GWCI_Mn2019 that considers the revised guidelines for manganese has a significant impact on the results, with an overall decrease in regional groundwater quality compared to the initial GWCI calculated using the Pre-Mn2019 guideline. In view of these results, even if the GWCI represents a valuable tool to define the regional groundwater quality portrait, one of its drawbacks relates to its sensitivity to changes in watervquality guidelines. This stresses the importance of updating the GWCI with changes in regulations.

The scatter plot of Figure 4.5 illustrates the relation between the initial GWCI (GWCI_Pre-Mn2019) and the GWCI_Mn2019 for the 243 common samples identified by main aquifer types. By comparing the initial GWCI with GWCI_Mn2019, Figure 4.5 shows an increase in GWCI for all aquifer types. This is coherent with the fact that the esthetic objective of Mn was changed from 0.05 mg/L to 0.02 mg/L in 2019 (Health Canada, 2019b).

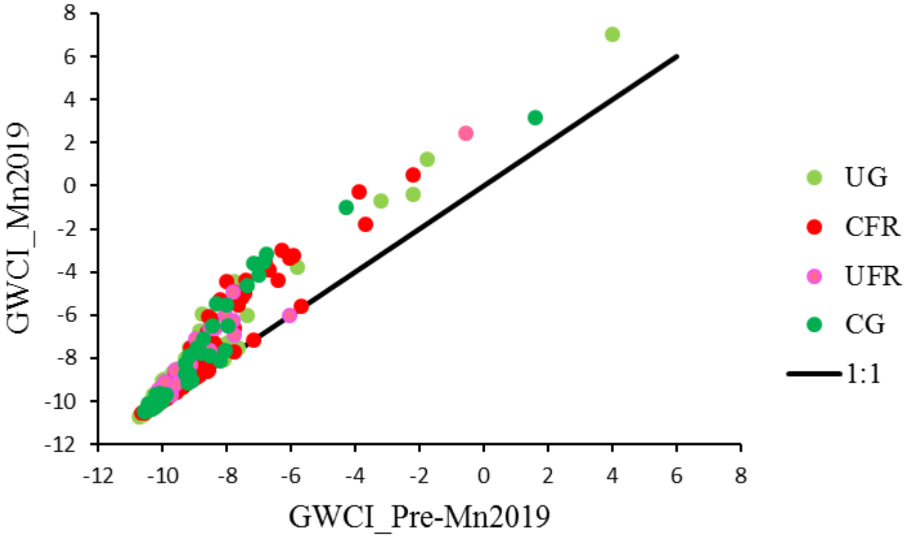

Figure 4.5. Scatter plot of the initial GWCI (Pre-2019 guideline) versus the GWCI_Mn2019 for the four main aquifer types. UG: unconfined granular aquifer; CG: confined granular aquifer; UFR: unconfined fractured rock aquifer; CFR: confined fractured rock aquifer.

4.4.3 Combined GWCI – DRASTIC approach: recommendation for public health and aquifers protection

Following the calculation of the GWCI for the study area, there is an opportunity to evaluate the potential of combining this water quality index with an aquifer vulnerability index, with the objective to develop tools to facilitate communication of groundwater related information. Cloutier et al., (2016) evaluated groundwater vulnerability in Abitibi-Témiscamingue based on the DRASTIC method. The vulnerability of an aquifer evaluated with DRASTIC represents its susceptibility of being affected by a contaminant from the surface (Aller et al., 1987). Cloutier et al., (2016) highlighted that the aquifers with the highest vulnerability are associated to unconfined aquifers (UG, UFR), particularly the unconfined granular aquifers of eskers, and that the ones with low vulnerability are associated with confined aquifers (CG, CFR) in the clay plain. In this study, the initial GWCI results allowed to identify that the granular aquifers (UG, CG) generally present higher groundwater qualities than the fractured rock aquifers (UFR, CFR).

Figure 4.6 shows the relation between the GWCI_Pre-Mn2019 and DRASTIC indices for the study area. The data associated with the four main types of aquifers present a significant dispersion. This observation allows dividing the scatter plot of groundwater samples into four quadrants. The quadrants are delimited by two dark lines. The horizontal line is related to the groundwater quality and was fixed at a GWCI value of 1, the limit between "low" (below 1) and "medium" (above 1) degree of groundwater contamination. medium contamination (Table 4.4). The vertical line is related the aquifer vulnerability and was fixed at a DRASTIC value of 130, the limit between lower vulnerability (below 130) and higher vulnerability (above 130) (Cloutier et al., 2016). Figure 4.6 can be interpreted in relation to the four quadrants:

- Quadrant 1: This area of the scatter plot regroups data associated with lower quality water coupled to lower vulnerability. Groundwater samples that dominate in quadrant 1 belong to CFR, follow by UFR, with some CG.

- Quadrant 2: This area of the scatter plot regroups data associated with lower quality water coupled to higher vulnerability. Few samples from UG and UFR are present in quadrant 2.

- Quadrant 3: This area of the scatter plot regroups data associated with higher quality water coupled to lower vulnerability. This quadrant contains most of the groundwater samples, and is characterized by samples from CFR, CG, and some UFR.

- Quadrant 4: This area of the scatter plot regroups data associated with higher quality water coupled to higher vulnerability. This quadrant is characterized by samples from UG, with some UFR.

The observations associated to the dispersion of the groundwater samples within the four quadrants bring key information regarding public health and aquifers protection:

- First, sampling sites located in unconfined granular aquifers (UG) clearly dominate in quadrant 4. Thus, unconfined granular aquifers are characterized by a "low" degree of groundwater contamination (GWCI < 1) and higher vulnerability (DRASTIC > 130). It is thus critical to protect these unconfined granular aquifers to maintain their associated high groundwater quality. In Abitibi-Témiscamingue, these UG generally corresponds to eskers and moraines.

- Second, sampling sites from fractured rock aquifers, both confined (CFR) and unconfined aquifers (UFR), dominate in quadrant 1, with some confined granular (CG). Thus, CFR-UFR-CG are characterized by "medium" to "high" degree of groundwater contamination (GWCI > 1 and >3) and lower vulnerability (DRASTIC < 130). It is thus critical to promote protective measure to owners of wells in fractured rock aquifers and confined aquifers.

- Third, most of the samples from CFR, UFR, and CG are in quadrant 3, characterized by a "low" degree of groundwater contamination (GWCI < 1) and lower vulnerability (DRASTIC < 130). This is coherent with the initial GWCI_Pre-Mn2019 results that about 79% of the wells sampled have groundwater with a "low" degree of groundwater contamination, as well as the extension of the clay plain that act as a regional confining layer.

A similar scatter plot was produced with the GWCI_Mn2019 (Figure 4.7). The observation made from Figure 4.6 can be found in Figure 4.7, with a general increase in the GWCI as it was discussed in previous section. Due to the removal of 161 additional samples for GWCI calculation taking into account the Mn2019 regulation, most of the sample for GWCI_Mn2019 are distributed in quadrant 3 and 4.

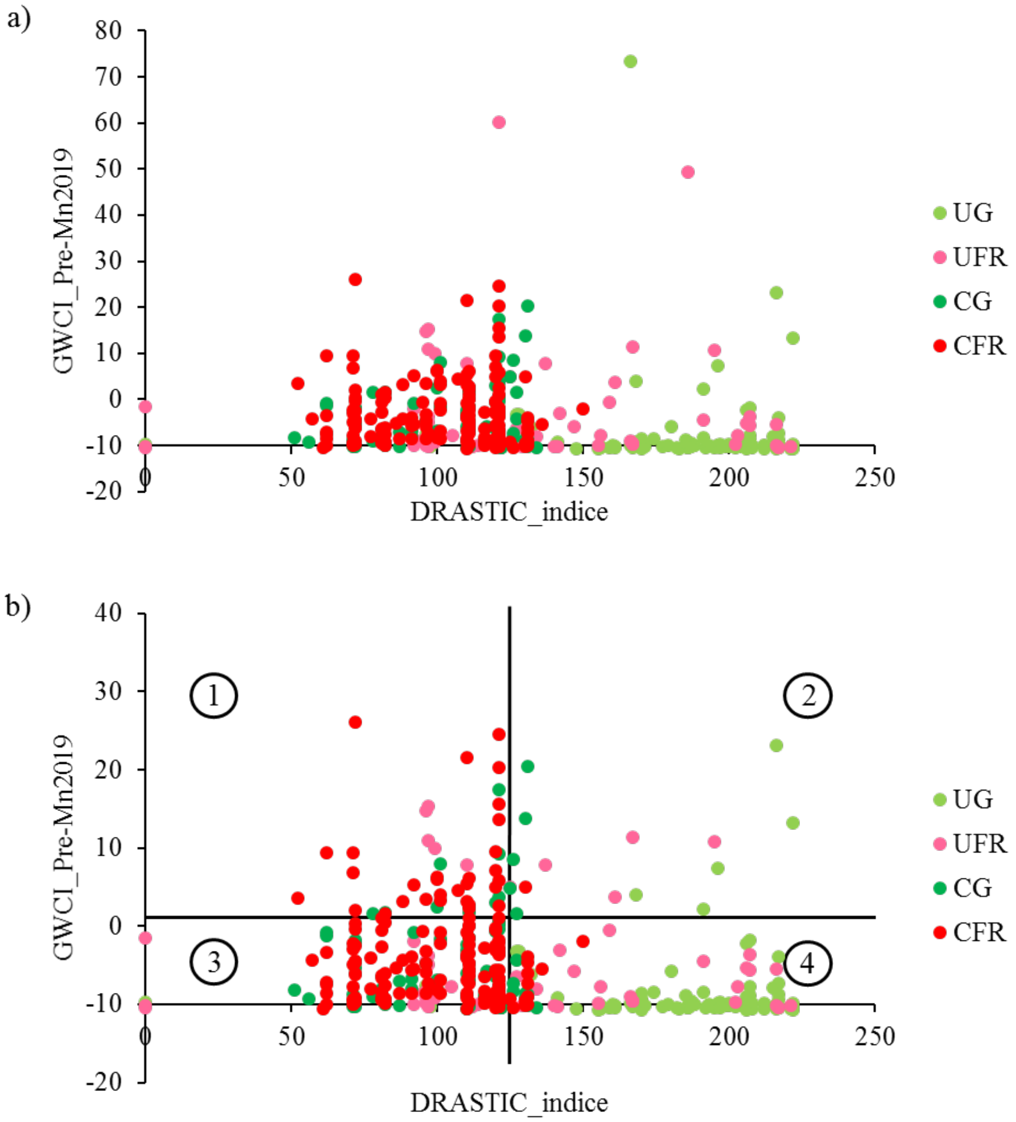

Figure 4.6. Relation of GWCI_Pre-Mn2019 with DRASTIC Index. All data are shown in (a) whereas (b) provides a zoom to better observe the dispersion of points that are classified by aquifer type. Dark lines define the limits fixed for groundwater quality (horizontal line at GWCI = 1) and aquifer vulnerability (vertical line at DRASTIC = 130). These lines divide the space into for quadrants (1-2-3-4) to support the discussion of the relations between the two indices. UG (n = 99); UFR (n = 57); CG (n = 72); CFR (n = 176).

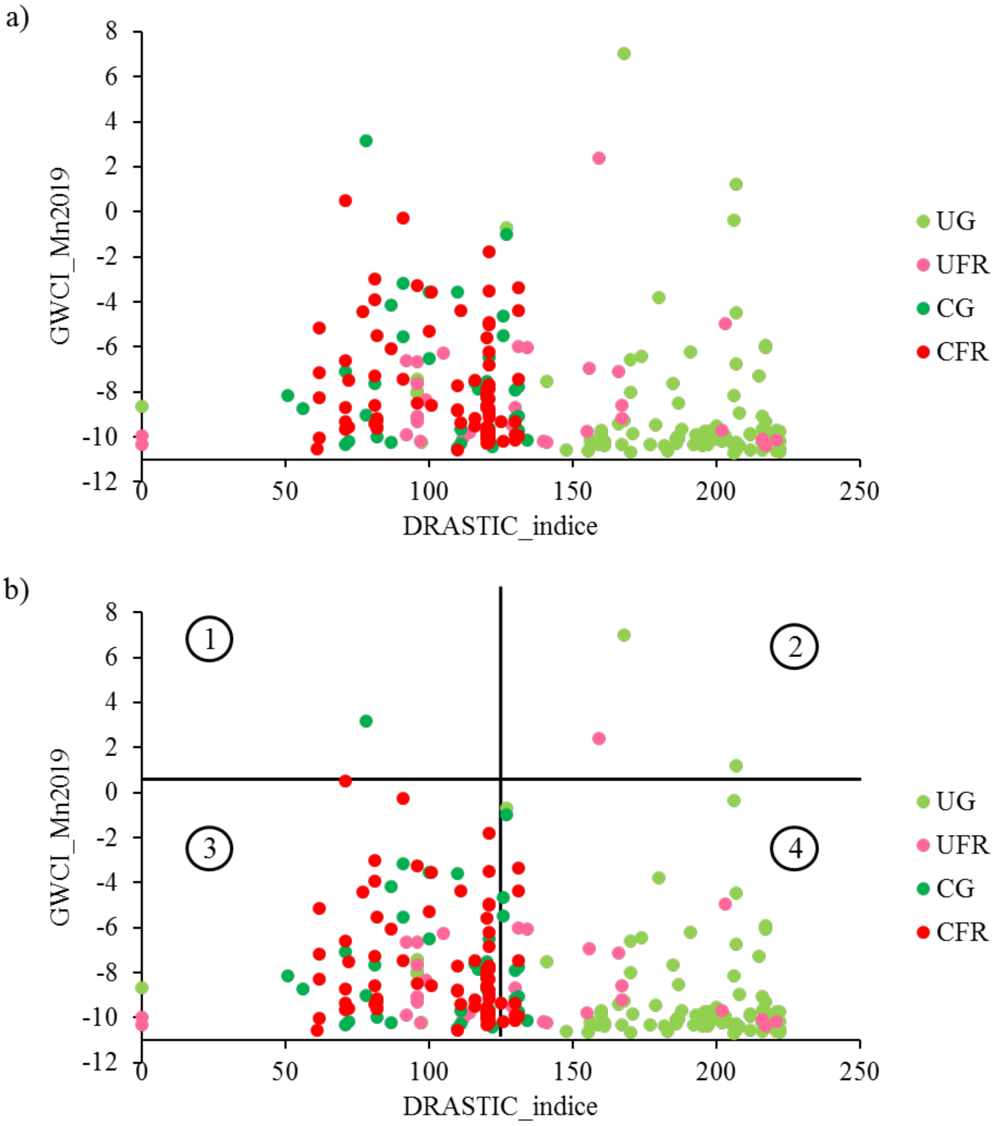

Figure 4.7. Relation of GWCI-Mn2019 with DRASTIC Index. All data are shown in a) with samples identified by aquifer types, whereas b) shows the four quadrants as identified in Figure 4.6b. Dark lines define the limits fixed for groundwater quality (horizontal line at GWCI = 1) and aquifer vulnerability (vertical line at DRASTIC = 130). These lines divide the space into for quadrants (1-2-3-4) to support the discussion of the relations between the two indices. UG (n = 91); UFR (n = 32); CG (n = 40); CFR (n = 80).

For a better spatial visualization of the GWCI – DRASTIC index combination, maps representing both the degree of groundwater contamination and the vulnerability of the aquifers were constructed for the regional main aquifers type (Figures 4.8; 4.9; 4.10 and 4.11). The maps presenting both the unconfined/confined granular and fractured rock aquifers conditions come from the Hydrogeological Atlas of Abitibi-Témiscamingue (Cloutier et al., 2016). The degree of contamination is determined by the size of the circles and the vulnerability is indicated by a color code ranging from yellow for lower vulnerability to red for higher vulnerability. The quadrants detailed in section 4.4.3 are represented in the maps. The areas of higher vulnerability with lower groundwater contamination are located at the esker and moraine for both GWCI_Pre-Mn2019 and GWCI_Mn2019 (Figures 4.9; 4.11). As described in quadrant 1, both confined (CFR) and unconfined fractured rock aquifers (UFR) are characterized by a "medium" to "high" degree of groundwater contamination and lower vulnerability (Figure 4.8). Most of the groundwater samples from CFR, UFR and CG described in quadrant 3, are characterized by lower groundwater contamination and lower vulnerability (Figures 4.8; 4.9). This is coherent with the fact that about 79% of the wells sampled have groundwater with a "low" degree of groundwater contamination. Concerning the GWCI_Mn2019, most of the groundwater samples are characterized by a "low" degree of groundwater contamination and low to medium vulnerability (Figure 4.10).

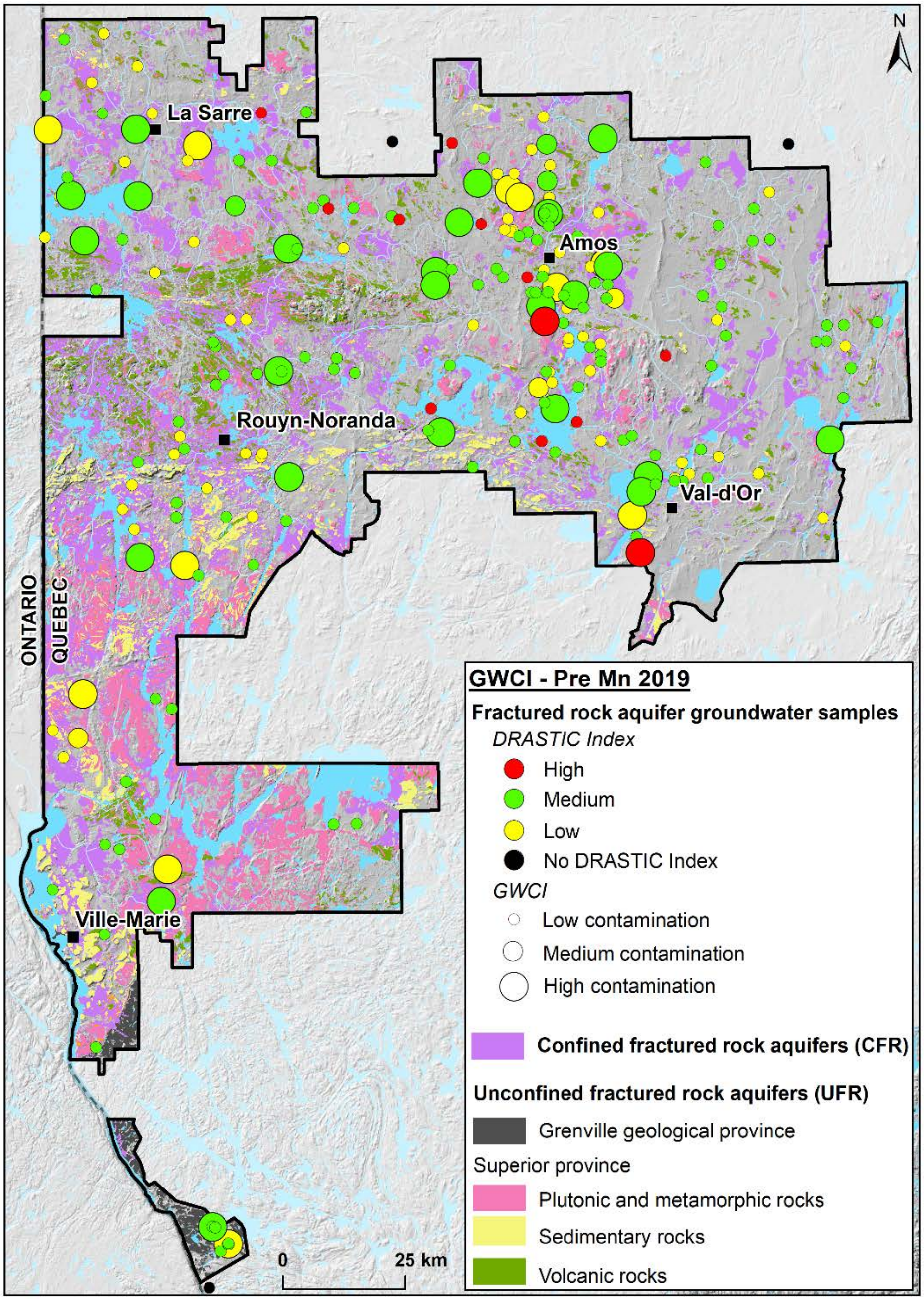

Figure 4.8. Map depicting GWQI for groundwater samples calculated with the Pre-Mn2019 guideline and the Drastic Index for the unconfined and confined fractured rock aquifer.

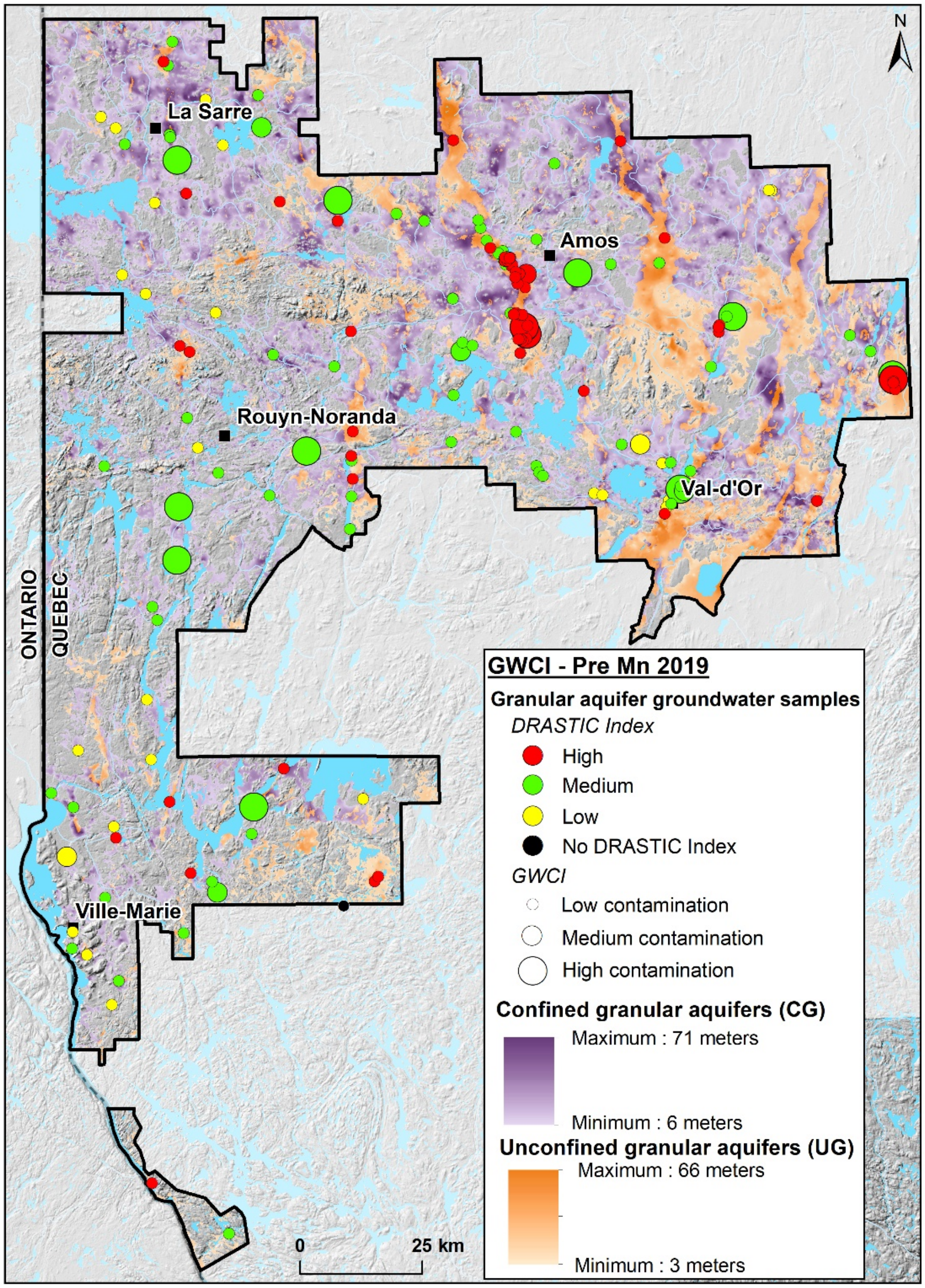

Figure 4.9. Map depicting GWQI for groundwater samples calculated with the Pre-Mn2019 guideline and the Drastic Index for the unconfined and confined granular aquifer.

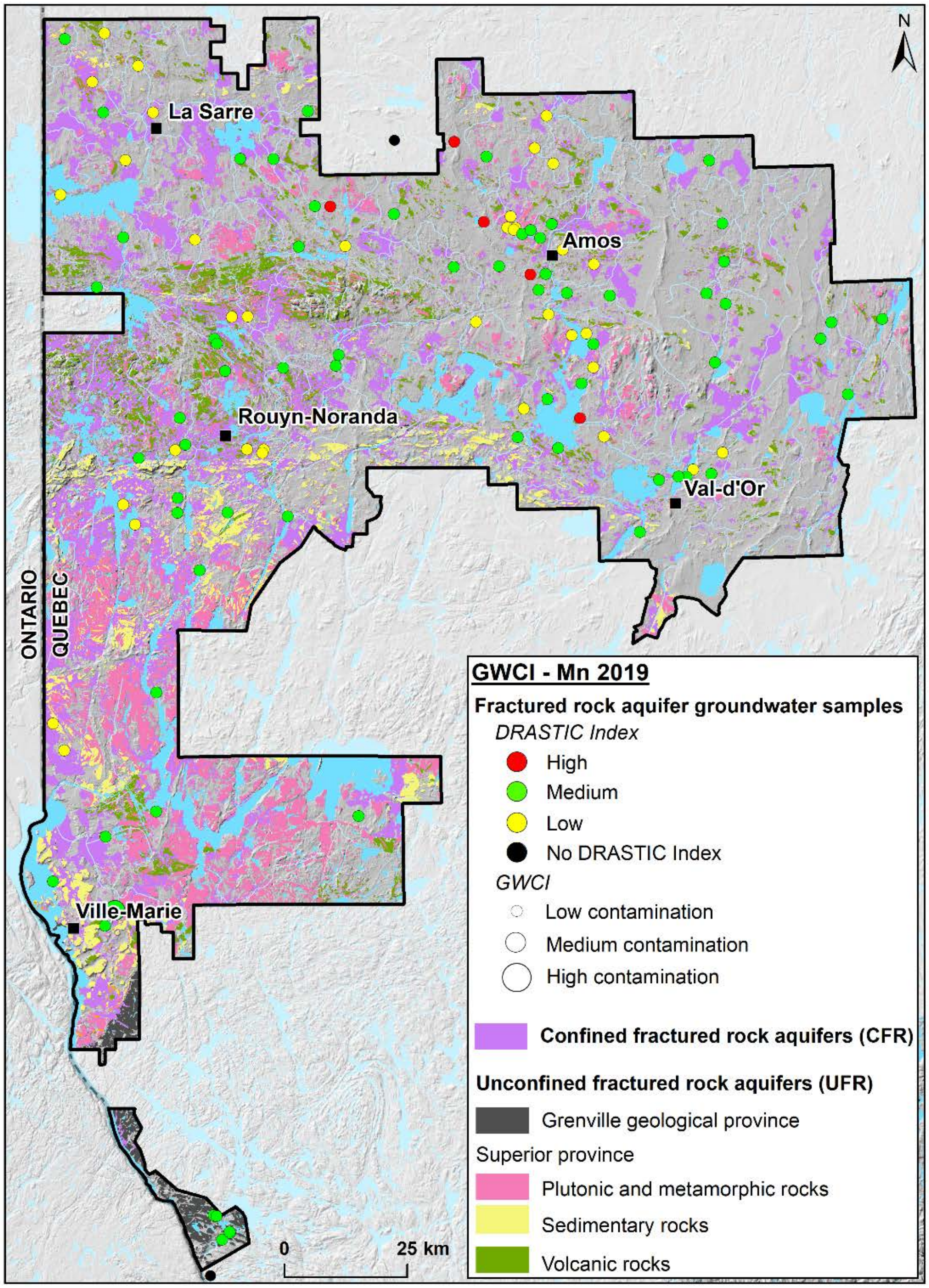

Figure 4.10. Map depicting GWQI for groundwater samples calculated with the Mn2019 guideline and the Drastic Index for the unconfined and confined fractured rock aquifer.

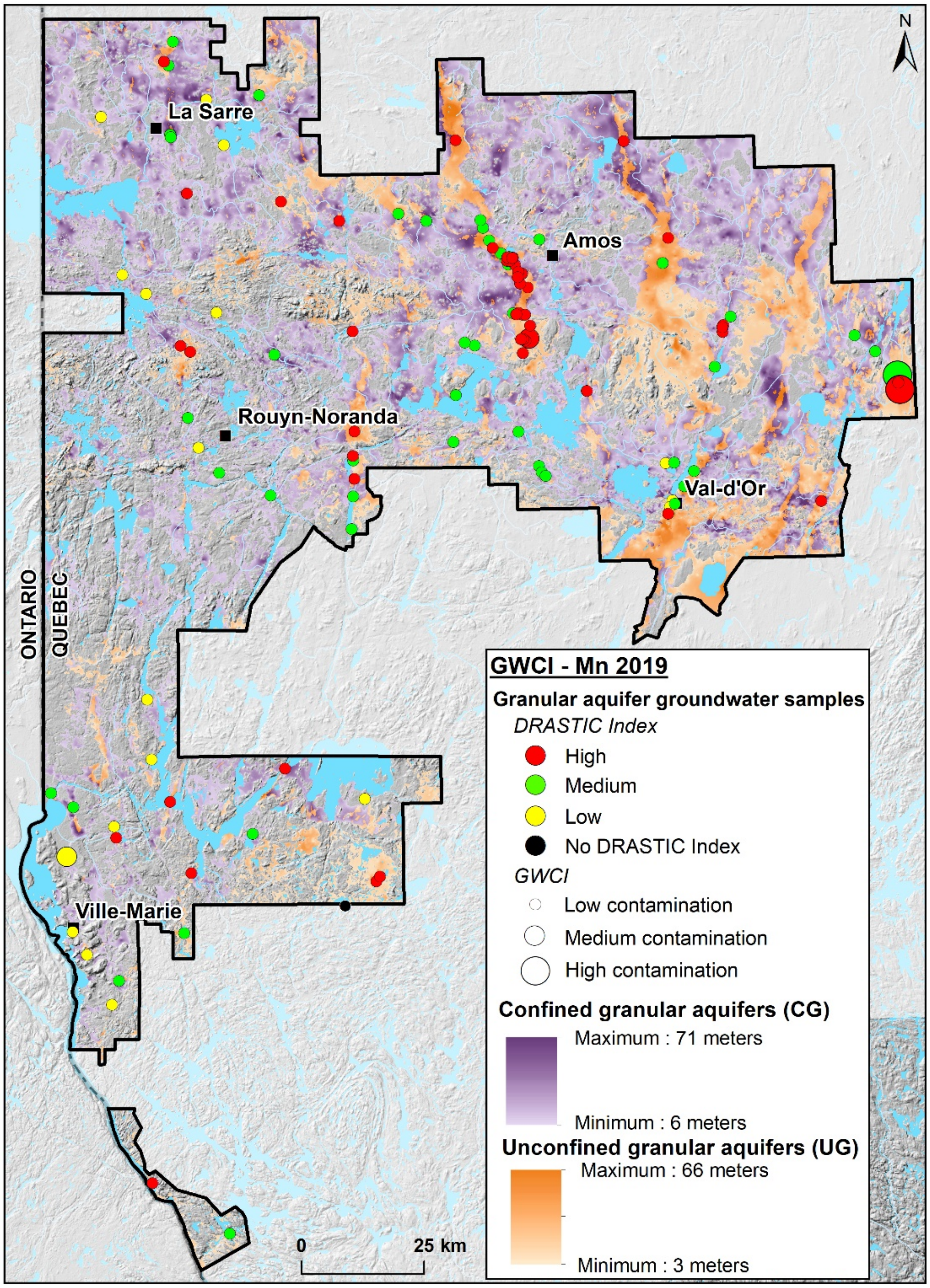

Figure 4.11. Map depicting GWQI for groundwater samples calculated with the Mn2019 guideline and the Drastic Index for the unconfined and confined granular aquifer.

4.5 Conclusion

Groundwater sampling and chemical analysis were conducted on 427 private, municipal and observation wells in Abitibi-Témiscamingue region. The wells are completed in confined and unconfined fractured volcanic, metasedimentary and plutonic aquifers of the Canadian Shield, as well as in confined and unconfined granular aquifers. The results indicate that aesthetic problems tend to be the regional issue, with exceedances of aesthetic objectives for manganese (Mn > 0.05 mg/L; n = 229), for iron (Fe > 0.3 mg/L; n = 132), and for TDS (TDS > 500 mg/L; n = 85). The results also indicate that groundwater exceeds the guideline values for health parameters, especially for arsenic (As > 0.01 mg/L; n = 16) and uranium (U > 0.02 mg/L; n = 4). When using the Mn2019 guideline values (Health Canada, 2019a, 2019b), the number of Mn exceeding the Mn2019 health guideline of 0.12 mg/L proved to be 176 groundwater samples.

To calculate the Groundwater Contamination Index (GWCI), the samples with parameters with concentrations exceeding the Maximum Acceptable Concentrations (MAC) fixed for the health criteria were removed. Using the Pre-Mn2019 guideline, the results of the GWCI calculated for the study area indicate that about 79% of the groundwater samples are categorized as having a "low" degree of groundwater contamination. Overall, groundwater in confined and unconfined fractured rock aquifers is of generally lower quality than the one in unconfined and confined granular aquifers. Groundwater from bedrock aquifers, and more particularly from confined fractured rock aquifer, is more affected by water quality problems (aesthetic and health issues) than granular aquifers. Groundwater in unconfined fractured rock aquifer is of better quality in plutonic rock than in volcanic rocks. These results confirm that eskers, that constitute important unconfined granular aquifers for the region, have higher groundwater quality. The sensibility of GWCI calculation was tested with the Mn2019 guideline. Compare to the initial GWCI_Pre-Mn2019, the GWCI_Mn2019 evaluation shows a decrease in the regional groundwater quality, indicating the importance to update GWCI with guidelines evolution and emerging contaminants. The combined GWCI – DRASTIC approach highlights the need to promote protective measures to wells owners in fractured rock aquifers and confined aquifers. This approach also highlights the link between higher vulnerability – higher quality groundwater for samples in unconfined granular aquifer and the importance to support the protection of high-vulnerability unconfined granular aquifers to maintain its associated high-quality groundwater.

The domestic wells completed in crystalline bedrock aquifers are a vital source of water for people living in rural areas and are more likely to be affected by geogenic contaminants. The results of this study highlight the importance to regularly test water drawn from wells for drinking water supply and ensure that water is safe for human consumption. The household with water quality issues must be aware that it is important to take appropriate mitigation measures to preserve public health from groundwater contamination. Awareness campaigns for better understanding the contaminants toxicity and the health risk related to drinking "non-potable water" is recommended for protecting the public health, especially for well users in rural areas. This research contributes to increase the knowledge on the regional groundwater quality related to the main regional aquifers types in different geological, hydrogeological and geochemical contexts. This study is the first in Abitibi-Témiscamingue to give a GWCI based on parameters that exceed guideline values and to produce a regional portrait of the groundwater quality of the region. The combined GWCI – DRASTIC represented by regional maps, that facilitate the communication of water quality and vulnerability concepts in an integrated and intelligible way, could contribute to communicate groundwater quality information to the public to support safe groundwater uses and help the decision makers to protect aquifers of high-quality groundwater.

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CHAPITRE V

CONCLUSION GÉNÉRALE ET PERSPECTIVES

5.1 Apport de la thèse sur le plan scientifique et societal

5.1.1 Contributions scientifiques et avancée des connaissances sur la compréhension globale des systèmes aquifères-aquitard de l'Abitibi-Témiscamingue

Ce travail de doctorat a contribué à accroître les connaissances à plusieurs échelles sur la compréhension de la géochimie régionale des eaux souterraines liant les unités géologiques et hydrogéologiques régionales à la dynamique naturelle de l'écoulement des eaux souterraines pour un système aquifère complexe sur le vaste territoire de l'Abitibi-Témiscamingue. Il a permis d'améliorer les connaissances sur l'origine et l'évolution géochimique des eaux souterraines dans l'espace et dans le temps le long des chemins d'écoulements empruntés par les eaux souterraines par le biais du traçage isotopique, de l'analyse physicochimique et de l'évaluation de la qualité des eaux souterraines régionales. Ce projet a ainsi permis d'affiner la compréhension des interactions qui existent entre les eaux souterraines et les différentes unités hydrogéologiques leur servant d'aquifère et leur influence sur la composition chimique de l'eau, afin de mettre en évidence le temps de résidence des eaux dans l'optique de caractériser l'ensemble du cycle de l'eau régional, depuis l'infiltration des eaux météoriques dans les zones de recharge jusqu'aux zones de résurgence que constituent les sources naturelles. Cette étude a aussi contribué à préciser le rôle et l'influence significative du confinement induit par les argiles déposées dans le lac Barlow-Ojibway sur la signature géochimique des eaux souterraines, considérant que ces dépôts glaciolacustres de diverses épaisseurs couvrent près de 80% de la superficie du territoire.

La région a hérité d’un socle rocheux fracturé complexe par sa diversité géologique issue des roches anciennes du Bouclier canadien, incluant les roches volcaniques, métasédimentaires et plutoniques, partiellement recouvert de dépôts plus récents datant du dernier retrait glaciaire. Dans ce contexte régional, le travail de recherche s’est donc intéressé à l’étude de ces unités géologiques superficielles que sont les dépôts fluvio-glaiciares (eskers et moraines), les sédiments de surface en flanc d’eskers (sables et limons), les dépôts glaciolacustres (argile et silts) et les dépôts glaciaires (till) qui ont façonné ce territoire. Aussi, le travail de ce doctorat s’est penché sur l’étude des unités hydrogéologiques qui constituent les quatre types d’aquifères régionaux que sont les aquifères rocheux fracturés à nappe captive et libre et les aquifères granulaires à nappe captive et libre. Ce travail de recherche a également permis l’étude de chaque compartiment hydrologique séparément que sont les eaux météoriques (précipitations de neige et de pluie), la neige au sol, les eaux de surfaces, les sources et les eaux souterraines.

Une des spécificités de cette thèse est de parvenir à relier ensemble les grands éléments du cadre hydrogéologique régional suite à l’interprétation des analyses géochimiques des divers ensembles d’eaux échantillonnés afin de décrire le cycle global de l’eau et le système d’écoulement. Les résultats de la composition isotopique des précipitations ont permis de dresser la droite météorique locale des eaux de précipitation de l’Abitibi-Témiscamingue comme référence régionale. Les précipitations régionales suivent un cycle saisonnier qui dépend de la température, étant soumises à une saisonnalité marquée par des températures très basses et négatives en hiver et très élevées et positives en été. L’analyse de la composition isotopique des précipitations de neige fondue et des précipitations ont montré que les pluies estivales sont plus enrichies en isotopes lourds que les précipitations hivernales, qui sont plus appauvries en isotopes lourds. La moyenne isotopique annuelle des eaux souterraines a indiqué que la recharge des eaux souterraines est le résultat d’un mélange des eaux de neige fondue et de pluie. Une des contributions majeures de l’étude des isotopes stables de l’eau dans le cadre de cette thèse est le traçage de l’écoulement des eaux souterraines au sein des quatre principaux types d’aquifères de la région. Les aquifères superficiels à nappe libre constituent les zones de recharges en région, qu’ils soient liés au roc ou granulaires, présentent des eaux souterraines dont la signature isotopique est variable, avec une palette de valeurs allant des eaux les plus enrichies aux plus appauvries en isotopes lourds. Le confinement joue un rôle majeur dans l’atténuation de la variabilité saisonnière de la composition isotopique vers une valeur moyenne isotopique qui reflète le mélange des eaux en provenance de diverses zones de recharge qui évoluent en transitant vers les aquifères les plus profonds et à nappe captive. Les eaux de surface présentent un signal isotopique évaporatoire typique qui permet d’établir leur propre droite évaporatoire locale et qui s’éloigne de la droite locale météorique des eaux, indiquant que les eaux de surface ne rechargent pas les eaux souterraines. Il existe plusieurs types de lacs dans la zone d’étude : les lacs de kettle perchés et en contact avec les eaux souterraines, les lacs profonds de faille et les lacs sur argile. Les eaux des lacs les plus superficiels, déconnectés des eaux souterraines et soumis à l’évaporation, sont enrichies en isotopes lourds, tandis que lacs de failles et de kettle, connectés aux eaux souterraines, épousent la signature isotopique des eaux souterraines avec des eaux plus appauvries en isotopes lourds. Ces travaux ont montré que, pour la région, ce sont généralement les eaux souterraines qui alimentent les lacs.

Par ailleurs, les résultats physicochimiques de cette thèse ont révélé que la composition chimique de la ressource en eau souterraine varie à différentes échelles et que des processus géochimiques majeurs contrôlent l’évolution géochimique des eaux souterraines localement et à l’échelle régionale. Bien que la région soir caractérisée par un relief relativement plat, l’hétérogénéité du matériel granulaire formant les aquifères granulaires combinée à celle de la lithologie formant le socle rocheux régional influence significativement la composition chimique de l’eau souterraine. Celle-ci, considérée comme un agent géologique, interagit avec les minéraux depuis son infiltration dans les zones de recharges et tout le long de son parcours au travers des chemins d’écoulement. Le temps de résidence des eaux souterraines dans les unités géologiques est un élément fondamental dans la composition chimique de la ressource en eau. En effet, plus le temps de résidence de l’eau souterraine sera long dans les aquifères, plus son interaction avec les minéraux de l’aquifère sera long et plus les eaux souterraines seront chargées en éléments dissous. En région, les eaux les moins chargées en éléments dissous sont celles des formations granulaires et des aquifères rocheux fracturés à nappe libre et superficiels et celles des sources en flanc d’esker ayant un temps de résidence court. Elles expriment un type d’eau Ca-Mg-HCO_3 typique des zones de recharges. En revanche, les eaux des aquifères granulaires et rocheux fracturés en condition de nappes captives présentent des eaux plus chargées en éléments dissous, ayant eu un temps de résidence plus long, elles sont de types d’eau Na-Cl, Na-HCO_3 et Ca-SO_4, qui reflètent des eaux plus évoluées. Un des facteurs qui influence l’évolution géochimique des eaux souterraines est la géologie de l’aquifère. Cette influence se manifeste particulièrement dans les aquifères rocheux fracturés à nappe libre, affranchis du confinement, où les eaux souterraines présentent une variabilité de signature géochimique ayant interagi avec une minéralogie hétérogène et variée. Les eaux qui s’écoulent dans des aquifères de roches plutoniques sont plus enrichies en uranium, en fluor, en potassium et en silicium. Celles qui s’écoulent dans des roches volcaniques et métasédimentaires sont plus susceptibles de contenir de l’arsenic, du chrome, du calcium, du magnésium et du sodium. Les processus géochimiques qui dictent la signature géochimique des eaux souterraines sont principalement la dissolution des carbonates (calcite, dolomite), qui dominent dans les zones de recharge, et la dissolution des silicates (albite, anorthite), qui expliquent la présence du Na, Ca et HCO_3 dans les eaux souterraines des aquifères plus profonds. L'oxydo-réduction des sulfures/sulfates et des oxydes de Fe-Mn, fortement influencée par la présence/absence des argiles à l'origine des conditions oxydantes et réductrices, explique la présence du fer, du manganèse et des sulfates/sulfures dans les eaux souterraines. Enfin, le réseau des fractures souterraines contribue au mélange des eaux plus ou moins chargées en éléments dissouts. L'analyse du tritium a indiqué que les eaux les plus évoluées, qui ont parcouru un plus long chemin d'écoulement, sont les eaux les plus anciennes (tritium sous la limite de détection), alors que le tritium est détecté dans les eaux superficielles, plus jeunes, typiques des zones de recharges. L'analyse chimique a également montré que les eaux les plus évoluées contiennent des chlorures et sont concentrées dans les aquifères rocheux fracturés à nappe captive.

Enfin, dans une optique de sensibiliser la population qui s'approvisionne en eau potable directement via leurs puits privés, surtout en milieu rural, et qui concerne plus de 70 % de la population régionale, une des préoccupations de ce travail de recherche a été de dresser un indice de contamination des eaux souterraines à l'échelle du territoire afin de cibler les zones à potentiel plus élevé de contamination géogénique et les zones où l'eau est de meilleure qualité. En dépit du fait que 79 % des puits échantillonnés ont une eau souterraine avec un niveau de contamination «faible» et donc de bonne qualité, certains secteurs sont caractérisés par des concentrations élevées de certains paramètres chimiques qui dépassent les normes de recommandation gouvernementales de qualité de l'eau potable pour des objectifs esthétiques et des critères de santé. La région est concernée principalement par des dépassements en fer et en manganèse, et plus localement par des dépassements en arsenic et en uranium, des paramètres problématiques pour la santé humaine. Aussi, les zones où la ressource en eau est la plus vulnérable coïncident avec celles où les eaux ont un niveau de contamination «faible», localisées essentiellement au niveau des eskers et de la moraine. Les secteurs où l'eau souterraine a un niveau de contamination plus élevée, et donc de moins bonne qualité, coïncident généralement avec les zones les moins vulnérables que sont les aquifères rocheux et granulaires à nappe captive. Il s'avère que les zones les plus problématiques sont celles des formations volcaniques et métasédimentaires plus minéralisées. De ce fait, les travaux de ce doctorat mettent l'accent sur la nécessité de mettre en place des mesures de protection plus efficaces et effectives, et de poursuivre les efforts afin de protéger de toute forme de contamination les zones les plus vulnérables fragilisées par leur géomorphologie naturelle et assurer, sur le long terme, une eau d'excellente qualité.

Les trois chapitres qui constituent le cœur de la thèse (Chapitres 2,3 et 4), écrits sous forme d'articles scientifiques, sont liés et se suivent naturellement de façon à couvrir tous les aspects de l'étude des flux hydrogéochimiques au sein des systèmes d'écoulement de l'eau souterraine de l'Abitibi-Témiscamingue. L'objectif principal de ce travail de recherche est d'améliorer la compréhension des systèmes aquifères-aquitards régionaux par la réalisation d'une étude hydrogéochimique intégrée. Le premier chapitre est le socle de la thèse. Il détermine le traçage du cycle hydrologique et permet d'expliquer les mécanismes d'écoulement au sein des aquifères régionaux depuis les précipitations qui rechargent les eaux souterraines à leur résurgence en passant par les processus d'évaporation et de mélange. Le second chapitre s'appuie sur les résultats du premier article. Il trace les processus d'interaction eau-roche en mettant en évidence les processus géochimiques dominants qui dictent la signature chimique des eaux souterraines en relation avec les conditions d'écoulement. Le troisième chapitre clôture la thèse en utilisant les résultats chimiques pour dresser un indice de contamination des eaux souterraines. L'évaluation de la qualité de l'eau souterraine à titre de ressource en eau potable consommée par la population régionale constitue la suite logique du chapitre deux.

5.1.2 Retombées des connaissances sur la société

Les résultats de cette thèse, d’un point de vue régional, s’adressent directement à la population de l’Abitibi-Témiscamingue qui s’approvisionne en eau souterraine pour ses besoins domestiques et pour sa consommation en eau potable. D’un point de vue plus large, l’approche méthodologique de ce travail de recherche s’applique à toutes les sociétés qui puisent de l’eau souterraine pour leurs besoins au quotidien dans des formations aquifères similaires à celles présentes en Abitibi-Témiscamingue, mais peuvent convenir aussi à toute autre formation aquifère. Connaître et comprendre la qualité de l’eau souterraine qui sert à la consommation humaine dans un contexte de santé publique est impératif à l’échelle mondiale, peu importe le contexte géologique et hydrogéologique en question.

Ce travail de recherche a été fondamental pour mettre en lumière le manque de connaissances, et parfois la négligence ou l’imprudence de la population face aux risques auxquels elle est confrontée lorsque les particuliers consomment l’eau de leurs puits sans la tester au préalable. La population est protégée lorsque celle-ci dépend de l’eau potable acheminée par les aqueducs sous la responsabilité des autorités locales qui assurent un suivi rigoureux de la qualité de l’eau. Les résidents des secteurs ruraux, éloignés des villes, sont en revanche les plus concernés par les problématiques d’une eau impropre à la consommation humaine, par exemple lorsqu’elle est affectée par des contaminants inorganiques géogéniques en fortes concentrations et nocifs à la santé humaine. En région, les individus les plus touchés sont ceux avec un puits installé dans le socle rocheux recouvert par les argiles, dont l’eau est susceptible de contenir des métaux tels l’arsenic, l’uranium et le chrome, et ce, particulièrement dans des secteurs de roches volcaniques et métasédimentaires. Le gouvernement n’impose pas de contrôle à la responsabilité d’un particulier de faire analyser l’eau de son puits, mais émet des recommandations concernant la procédure à suivre et la période où des analyses de qualité d’eau sont nécessaires. En effet, il est de la responsabilité de chaque individu ayant son propre puits d’approvisionnement en eau potable de contrôler son eau à des fins domestiques. Un besoin crucial de sensibilisation se fait ressentir concernant la présence, la nature, les sources et la propagation des contaminants inorganiques dans l’eau de consommation humaine. Des campagnes de sensibilisation devraient s’effectuer à la grandeur du territoire sur la qualité de l’eau que consomment les particuliers et les risques auxquels ils sont exposés par le bais de transfert de connaissances et de campagnes de recensement des individus ayant testé leur eau, principalement auprès de la population rurale. La population est potentiellement soumise à l’ingestion d’eau contenant de fortes teneurs en manganese, qui constitue la principale problématique régionale, étant donné que près de la moitié des puits échantillonnés en région sont affectés par la présence de cet élément chimique. Le manganèse fait l’objet d’une attention particulière quant à sa toxicité et les dommages neurologiques qu’il peut causer, en particulier chez les enfants, au point que le gouvernement du Canada a décidé de lui appliquer une norme santé depuis mai 2019.

Connaître la qualité de la ressource en eau souterraine permet de protéger la population contre diverses formes d’intoxication. Il existe des moyens efficaces et simples pour pallier à ces formes de contamination tels que les procédés d’osmose inverse pour contrer l’arsenic, et les traitements à l’adoucisseur pour contrer le fer et le manganèse. La méconnaissance que montrent les particuliers face à la qualité de l’eau consommée s’avère un problème majeur en region, puisqu’elle limite la protection de la santé de la population. Le travail de cette thèse a participé grandement à véhiculer les informations concernant la qualité de l’eau des propriétaires des puits qui ont collaboré à la campagne d’échantillonnage du projet de recherche. Les résultats des analyses chimiques réalisées au laboratoire suite à l’échantillonnage de l’eau chez les résidents leur ont été acheminés, ce qui a été utile pour déceler, chez certains d’entre eux, des contaminations en arsenic et autres éléments chimiques dans leur eau de consommation et dont ils ignoraient l’existence.

Grâce aux nouvelles connaissances apportées par cette recherche, la population, les acteurs locaux de l’eau et les municipalités sont en mesure d’avoir l’information nécessaire afin de cerner plus facilement les secteurs concernés par des eaux fortement minéralisées et les zones les plus problématiques pour la qualité de l’eau. Celles-ci se trouvent dans les secteurs rocheux fracturés enfouis sous la couverture argileuse régionale. Les puits les plus profonds sous conditions réductrices, particulièrement dans des environnements géologiques volcaniques et métasédimentaires, sont susceptibles de contenir les eaux souterraines les plus évoluées et les plus riches en fer et en manganese ainsi qu’en métaux nuisibles pour la santé humaine.

Ce travail de recherche, ayant permis de définir que ce sont les secteurs les plus vulnérables qui regorgent d’une eau souterraine d’excellente qualité, favorisera la mise en place de mesures de protection et de préservation plus efficaces pour pérenniser la qualité de la ressource en eau, et d’un aménagement du territoire qui tient compte de la vulnérabilité des aquifères. C’est en transférant les connaissances issues de cette recherche aux acteurs de l’eau et aux municipalités, et en vulgarisant la recherche scientifique auprès de la population, que des mesures préventives pourront être mises en œuvre pour le bien être des residents, la préservation de la ressource en eau pour les générations futures et plus particulièrement dans un contexte de changements climatiques.

5.2 Ouvertures et perspectives pour des travaux futurs

Ce doctorat a amélioré les connaissances du cycle global de l’eau en Abitibi-Témiscamingue en traçant les divers types d’eau qui circulent sur le territoire, depuis l’infiltration des eaux de précipitation dans le sol à leur exutoire au niveau des sources. Se faisant, il a permis de contraindre le modèle hydrogéologique régional construit sur la base des données géologiques et hydrogéologiques recensées sur le territoire étudié. Les recherches sont venues combler des lacunes relatives à la compréhension de l’écoulement régional dans un contexte de systèmes aquifères-aquitards complexes. Cependant, certaines lacunes scientifiques ont été mises en évidences, concernant entre autre l’écoulement de l’eau souterraine dans le réseau complexe de fractures des aquifères rocheux. Une étude géochimique plus approfondie, sur plusieurs lignes d’écoulement bien déterminées, pourrait contribuer à répondre à certaines questions soulevées et viendrait combler les lacunes concernant l’évolution géochimique de l’eau souterraine à différentes profondeurs. Cela donnerait plus de précision sur la composition chimique de l’eau, qui se voit biaisée par le mélange des eaux de diverses provenances dans le cas de l’échantillonnage de puits privés ouverts sur des épaisseurs importantes de roc fracturé. Ce travail de recherche, étant réalisé à une échelle régionale, comporte plusieurs défis. Étant donné que la superficie de la zone étudiée est très grande, il est difficile de définir avec précision et de suivre la composition chimique de l’eau souterraine à une échelle plus locale. Afin de compléter ce travail de recherche, des études géochimiques plus localisées pourraient être faites également au travers d’un échantillonnage multi-niveaux, afin de mieux cerner et quantifier les processus géochimiques, et évaluer les variations de la qualité de l’eau avec la profondeur des aquifères. Aussi, une étude minéralogique plus approfondie des minéraux des eskers et des moraines pourrait être réalisée afin de mieux expliquer la signature géochimique de l’eau qui s’écoule dans ces milieux aquifères et de déterminer les fractions dominantes qui contribuent à la composition chimique des eaux des zones de recharge.

Ce travail de recherche a permis de mettre en lumière des secteurs affectés par de l’uranium qu’il serait intéressant d’investiguer et d’étudier de manière plus approfondie, au même titre que cela a été réalisé pour l'arsenic en région. L'uranium étant un élément nocif pour la santé humaine, l'étude de sa mobilisation et de sa propagation apporterait des connaissances supplémentaires utiles dans une optique de prévention de la santé des résidents.

Il serait pertinent d'entreprendre des études plus poussées sur le contexte argileux en région afin de valider le caractère imperméable de cette unité considérée comme l'aquitard régional. La structure des argiles glaciolacustres sous forme de varves, composée d'une alternance de silt et d'argile, préconiserait un écoulement horizontal. Il serait intéressant d'analyser les eaux interstitielles des argiles pour valider si des vestiges des eaux issues de la dernière glaciation sont présents dans des séquences d'épaisseurs importantes. Dans le cadre de cette thèse, des piézomètres avaient été installés dans les argiles pour étudier le comportement de l'aquitard et tester si l'écoulement vertical des eaux serait favorisé dans les argiles. Bien que ces travaux n'aient pas été complétés, il serait intéressant de poursuivre les recherches dans ce domaine pour compléter l'étude régionale des système aquifère-aquitard.

Ce travail de doctorat a soulevé de nouvelles réflexions sur le manganèse. En effet, ce dernier est présent dans les eaux souterraines des quatre types aquifères et ne semble pas être associé à un processus géochimique spécifique ou à des conditions d'oxydo-réduction particulières. Des études plus approfondies pourraient être réalisées concernant ce paramètre chimique dans les eaux souterraines afin d'augmenter la compréhension de la mobilisation et de la présence de cet élément dans les eaux souterraines

Ce travail de recherché, bien qu'élaboré sur une durée de 5 ans, a permis de dresser le portrait géochimique de la région à un instant "t". Il serait intéressant de procéder à un suivi temporel de sites types afin d'observer si des changements se sont opérés dans la qualité de l’eau souterraine en terme de concentration d’éléments et de détection de nouveaux contaminants dans l’eau.

Une des contributions majeures de ce travail de recherche est de définir le portrait de la qualité régionale des eaux souterraines, utilisées à des fins d’eau potable, de cibler les grandes problématiques de contamination locale et régionale et de définir les zones les plus vulnérables à protéger afin de maintenir la qualité des eaux souterraines. L’indice de contamination des eaux souterraines créé pour la région de l’Abitibi-Témiscamingue est transposable à l’échelle du Québec méridional pour ce qui est des études sur les eaux souterraines. Cet indice pourrait être calculé pour toutes les études régionales portant sur les eaux souterraines réalisées dans le cadre des PACES, afin d’établir un comparatif entre les régions et de cibler les problématiques principales de contamination à des fins de sensibilisation de la population. Suite à ce travail, la diffusion des connaissances acquises sur la qualité de l’eau à la population contribuera à éclairer les propriétaires des puits résidentiels qui ignorent l’importance que représente le fait de faire tester régulièrement leur eau de consommation. Un manque majeur de sensibilisation face aux risques que les propriétaires peuvent encourir dû à l’absence de données sur la qualité de leur eau et de la toxicité des contaminants inorganiques présents en excès est un point crucial que ces travaux ont permis de révéler. Le transfert des connaissances en vue de délimiter les zones à haut potentiel de qualité d’eau et les plus vulnérables aussi soumis aux pressions anthropiques et sensibles à toute modification de l’environnement permettrait de mettre en place des mesures de protection appliquées pour la préservation des milieux sensibles, sinon, en mesurer l’efficacité.

L’eau souterraine est inéluctablement le joyau de cette région. L’Abitibi-Témiscamingue est riche de l’excellente qualité de son eau, l’indice de contamination des eaux souterraines ayant révélé que 79% des puits recèlent d’une eau souterraine avec un niveau de contamination «faible» et donc de bonne qualité. Étant la source principale d’eau potable puisée par la population, l’eau souterraine figure parmi les enjeux majeurs du développement durable de l’Abitibi-Témiscamingue. Ce travail de recherche soulève l’importance d’une bonne gestion et d’un bon aménagement territorial, dans le respect et la protection de cette ressource souterraine, pour contrer l’impact des activités anthropiques susceptibles d’en altérer sa qualité et, qui plus est, dans un contexte de changements climatiques.

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