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Title: Regional assessment of concentrations and sources of pharmaceutically active compounds, pesticides, nitrate and E. coli in post-glacial aquifer environments (Canada)

Article Type: Research Paper

Keywords: Groundwater; Post-glacial geology; pharmaceutically active compounds (PhACs); pesticides; nitrate and E. coli; vulnerability

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Abstract: There is growing concern worldwide about the exposure of groundwater resources to pharmaceutically active compounds (PhACs) and agricultural contaminants, such as pesticides, nitrate, and Escherichia coli. For regions with a low population density and an abundance of water, regional contamination assessments are not carried out systematically due to the typically low concentrations and high costs of analyses. The objectives of this study were to evaluate regional-scale contaminant distributions in untreated groundwater in a rural region of Quebec (Canada). The geological and hydrogeological settings of this region are typical of post-glacial regions around the world, where groundwater flow can be complex due to heterogeneous geological conditions. A new spatially distributed Anthropogenic Footprint Index (AFI), based on land use data, was developed to assess surface pollution risks. The Hydrogeochemical Vulnerability Index (HVI) was computed to estimate aquifer vulnerability. Nine wells had detectable concentrations of one to four of the 13 tested PhACs, with a maximum concentration of 116 ng.L-1 for benzafibrate. A total of 34 of the 47 tested pesticides were detected in concentrations equal to or greater than the detection limit, with a maximum total pesticide concentration of 692 ng.L-1. Nitrate concentrations exceeded 1 mg.L-1 N-NO3 in 15.3% of the wells, and the Canadian drinking water standard was exceeded in one well. Overall, 13.5% of the samples had detectable E. coli. Including regional-scale sources of pollutants to the assessment of aquifer vulnerability with the AFI did not lead to the identification of contaminated wells, due to the short groundwater flow paths between recharge and the sampled wells. Given the occurrence of contaminants, the public health concerns stemming from these new data on regional-scale PhAC and pesticide concentrations, and the local flow conditions observed in post-glacial terrains, there is a clear need to investigate the sources and behaviours of local-scale pollutants.

Response to Reviewers: Response to reviewer

Reviewer #1

Comment No. 1: I have revised this manuscript and I believe it improved from its original version.

We thank the reviewer for this positive comment.

Comment No. 2: However, I cannot with confidence say that it is up to the STOTEN standards as some of the conclusions seem to bold for the data available.

We don't really see in what the conclusion of the paper are "bold" given that we recommend more studies, with more data, and performed at local scales. We are aware that in this research some analyses were performed on a limited number of samples due to analysis costs, and our conclusions reflect this situation. Nevertheless, we believe that the results presented in this paper deserve to be published in a high impact factor journal such as STOTEN.

Comment No. 3: The authors have stated that other data were not available to conduct further analyses but maybe this is not conclusive and innovative enough for this journal.

The type of analyses performed for this research are entirely new for PhACs in the province of Quebec. Given the importance of the environmental and scientific questions raised, we believe that it is crucial to publish these results and have them available to a maximum of scientists. This is especially true in Canada where water resources are generally widely available and of high quality.

Comment No. 4: Can one make a decision on the scientific impact based on how expensive data acquisition is if they do not come up with an alternative, cheaper approach?

We believe this research provides important results that deserve to be published. More data would obviously be welcome and these could be acquired in future complementary studies, in particular to better understand local sources of contaminants.

Comment No. 5: The other aspect is related to the changes made to the manuscript in terms of writing style. Those portions of text need extensive revisions in my opinion.

We thank the reviewer for this comment. The manuscript has been completely reviewed by an English speaking scientist.

Comment No. 6: I feel this study is inconclusive and that a journal such as Water, Air, & Soil Pollution may be more appropriate.

Again, we believe this research brings important results to the scientific community and that it sufficiently innovative and original to be published in a high impact factor journal such as STOTEN.

Montréal, 8th November 2016
Marion Saby
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Attention to:
Dr. D. Barcelò
IRCA Institut Català de Recerca de l'Aigua
Parc Científic i Tecnològic de la Universitat de Girona,
Edifici H2O.,
Emili Grahit ,101- 17003 Girona, España

V/Ref: submission of a **revised** manuscript to Science of the Total Environment

Dear Dr. D. Barcelò,

Please find enclosed the re-revised manuscript by Saby et al. entitled « Regional assessment of concentrations and sources of pharmaceutically active compounds, pesticides, nitrate and *E. coli* in post-glacial aquifer environments (Canada)» prepared for Science of the Total Environment.

All the comments have been noted and we answered them the best we could.

We hope that the revised manuscript will meet the requirements for publication on Science of the Total Environment.

Sincerely,

Marion Saby (corresponding author)

Response to reviewer

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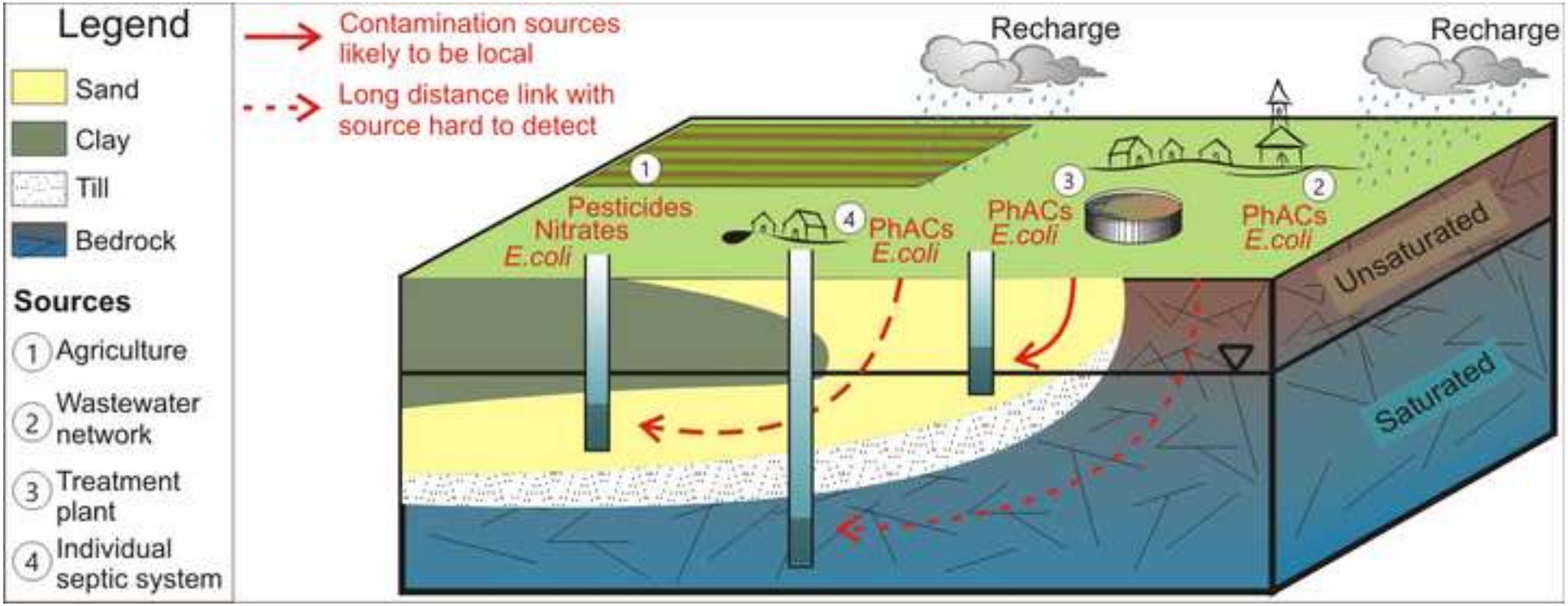
*Graphical Abstract



***Highlights (for review)**

Highlights

- PhACs, pesticides, nitrate, and *E.coli* were measured regionally in groundwater.
- Results show the presence of all of these contaminants at the regional scale.
- Landscape-scale contaminant source data did not predict groundwater pollution
- Results suggest local sources drive groundwater contamination
- PhACs and pesticides behaviors in the environment are difficult to predict at the regional scale.

Regional assessment of concentrations and sources of pharmaceutically active compounds, pesticides, nitrate, and *E. coli* in post-glacial aquifer environments (Canada)

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Abstract

There is growing concern worldwide about the exposure of groundwater resources ~~being exposed~~ to pharmaceutically active compounds (PhACs) and agricultural contaminants, such as pesticides, nitrate, and Escherichia coli. For regions with a low population density and an abundance of water, regional contamination assessments are not ~~systematic because of~~ carried out systematically due to the typically low concentrations and high ~~analysis~~ costs of analyses. The objectives of this study were to evaluate regional-scale contaminant ~~distribution~~distributions in untreated groundwater in a rural region of Quebec (Canada). The geological and hydrogeological settings of this region are typical of post-glacial regions around the world, where groundwater flow can be complex due to heterogeneous geological conditions. ~~Contaminant concentrations were assessed in private, municipal, and observation wells.~~ A new spatially distributed Anthropogenic Footprint Index (AFI~~)~~), based on land use data, was developed to assess surface pollution risks. The Hydrogeochemical Vulnerability Index (HVI) was computed to estimate aquifer vulnerability. Nine wells had ~~between one and four~~ detectable concentrations ~~for~~of one to four of the 13 tested PhACs, with a maximum concentration of 116 ng.L-1 for benzafibrate. A total of 34 of the 47 tested pesticides were detected in concentrations equal to or greater ~~to~~than the detection limit~~ in the wells~~, with a maximum total pesticide concentration of 692 ng.L-1. Nitrate concentrations exceeded 1 mg.L-1 N-NO3 in 15.3% of the wells, and the Canadian drinking water standard was exceeded in one well. Overall, 13.5% of the samples had detectable E. coli. Including regional-scale sources of pollutants to the assessment of aquifer vulnerability with the AFI ~~didn't~~did not lead to the identification of contaminated wells~~. The~~, due to the short groundwater flow paths between recharge and the sampled wells~~ explain these results.~~. Given the occurrence of contaminants~~ and~~, the public health concerns stemming from these new data ~~for~~on

regional-scale PhAC and pesticide concentrations, and the local flow conditions observed in post-~~glaciated terrain~~glacial terrains, there is a clear need to investigate ~~local-scale pollutant~~the sources and ~~their behaviour~~behaviours of local-scale pollutants.

Keywords: Groundwater, post-~~glaciated~~glacial geology, pharmaceutically active compounds~~,~~ (PhACs), pesticides, nitrate, *E. coli*, vulnerability

1. INTRODUCTION

As groundwater pollution increases worldwide (UNEP, 2003), assessing aquifer vulnerability to contamination is a priority for governmental agencies at all levels. Groundwater pollution from pharmaceutically active compounds (PhACs), pesticides, nitrate, and bacteria can originate from ~~different~~various sources (e.g., inorganic and organic fertilizers, individual septic systems, wastewater collection pipes, landfills). The presence of certain types of molecules in groundwater has already been linked ~~among other~~ to the leakage of ~~such~~ buried ~~infrastructures~~infrastructure, among other determinants (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Marsalek, 2008). Because PhACs and pesticides are typically detected in low concentrations in groundwater, and have high analytical costs, regional-scale assessments of their presence in aquifers are rarely available. As these compounds are not often analyzed in routine groundwater monitoring, and because it is often difficult to identify their ~~origin~~origins and ~~input to~~locations of influx into the aquifer, their potential ~~contribution~~contributions to aquifer ~~impairment~~contamination and vulnerability ~~is~~are often poorly understood.

PhACs have been increasingly ~~been~~ detected in groundwater around the world over the past decades (US EPA, 1993; Ma et al., 2015; Lopez et al., 2015). ~~These include, among~~Among others, these include molecules that compose sleeping pills, painkillers, contraceptives, ~~or~~and anti-depressants (Lapworth et al., 2012; Sorensen et al., 2015). PhACs are ~~related to~~associated with urban areas or wastewater treatment zones, and can also be linked to agricultural activity (e.g., pharmaceuticals from animal feedlots, ~~biosolids~~biosolid application, etc.; Prosser and Sibley, 2015). Pesticides are increasingly detected in groundwater from a variety of environments (Köck-Schulmeyer et al., 2014; Lopez et al., 2015; Zhao and Pei, 2012). ~~They~~These can be ~~linked with~~from agricultural sources, but can also originate from municipal or residential water uses

(e.g., golf courses, parks, and residential gardening). PhAC and pesticide molecules are typically difficult to trace in groundwater. Sorption to organic matter and clay minerals, ion exchange in the soil and aquifer, and microbial degradation can modify PhAC and pesticide concentrations in groundwater (Lapworth et al., 2012). Studies carried out in the USA (Barnes et al., 2008; Focazio et al., 2008; Kolpin et al., 2004) and in European countries (Jurado et al., 2012; Loos et al., 2010, 2009; Stuart et al., 2012) have shown the ubiquitous presence of PhACs and pesticides in groundwater in a wide variety of geological and climatic conditions. This situation~~ and~~, in combination with the limited understanding of their ~~cumulated~~cumulative, chronic, and long-term effects on humans and ecosystems (see references in Barnes et al., 2008~~) bring urgency to assess~~), make assessing their current concentrations urgent.

Several studies have shown the presence of high nitrate concentrations in groundwater in different regions around the world~~ and are~~, often linked to agricultural sources (e.g., Czekaj et al., 2015; Pérez-Martin et al., 2016; Pisciotta et al., 2015; Rojas Fabro et al., 2015). Nitrate concentrations are frequently used to assess groundwater vulnerability, because of their low reactivity and relatively limited transformation in groundwater (Rodriguez-Galiano et al., 2014), as well as the low costs associated with their analysis. Similarly, bacterial counts are used as indicators of the impact of human activity in contamination and vulnerability studies (Scott et al., 2002), allowing ~~to~~human and animal sources of contamination ~~from humans and animals~~ to be discriminated from others (e.g., *Escherichia coli* is only found in feces). Bacteria can be linked with agricultural sources (manure spreading and storage) and to private and municipal wastewater collection and treatment.

Groundwater vulnerability assessment methods include the DRASTIC index (Aller et al., 1987), the AQUIPRO method (Chowdhury et al., 2003), the LHT method (Mansoor et al., 2014),

and, more recently, methods based on groundwater ~~isotopique geochemistry (Murguket~~isotopic (Murgulet and Tick, 2013) and major ~~ions~~ion geochemistry (Meyzonnat et al., 2016). These semi-quantitative methods are often used as first assessment ~~techniques to manage~~in groundwater ~~resources~~resource management, and generally do not ~~include~~indicate specific potential contaminant sources. Different studies have attempted to improve these methods by identifying a link between land use, contaminant sources, and groundwater contamination (e.g., Bojórquez-Tapia et al., 2009; Zhou et al., 2012; Chen et al., 2013; Murgulet and Tick, 2015). Land use data has the potential to determine zones of contamination risk ~~regarding~~as a function of the type of human activity occurring on the ground, notably relating the extent of agricultural and urban areas ~~that are related~~ to specific ~~contaminants~~contaminant types. However, ~~this link is~~such links are often unclear because of the dynamic nature of groundwater flow, and the reactivity of contaminants in different geological environments (Fatta-Kassinos et al., 2011; Kormos et al., 2010; Salgado et al., 2013; Schulz et al., 2008). ~~It still needs to be demonstrated in which~~ The conditions in which it is useful to seek a source-contaminant link remain to be demonstrated.

Groundwater vulnerability assessment is a particular challenge in post-glacial geological environments, where bedrock aquifers are often overlain by a complex stratigraphy of more or less permeable sediments. These conditions produce highly heterogeneous recharge and percolation pathways ~~for~~ through which the contaminants ~~to~~ reach the groundwater, which create complex flow conditions and a combination of short and long flow paths that ~~is~~are not often well understood (Cassidy et al., 2014; Fleckenstein et al., 2006). This type of environment is encountered in many regions covered by the last glaciation in Northern America (Dyke, 2004). Similar geological environments and hydrostratigraphic contexts are also found in Fenno-

Scandinavia (Harff et al., 2011), as well as in ~~the North of~~northern Germany and Denmark (Scheck and Bayer, 1999; Thomsen et al., 2004).

In cold and humid climates, such as southern Quebec (Canada~~)~~), where water sources are abundant, groundwater contamination from anthropogenic sources in aquifers often remains relatively poorly understood. There are very few studies on emerging groundwater contaminants in Quebec, but research in other Canadian provinces has shown that PhACs can be found in wells and treated sewage effluents (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Kleywegt et al., 2007). Although few studies have focused on the presence of pesticides in groundwater in Canada, this is becoming a concern in some parts of the country (CLE, 2015; Environment Canada, ~~2010~~2012; Giroux and Sarrasin, 2011; Giroux, 2010; Woudneh et al., 2009). Pesticides and their metabolites ~~were~~have also been identified in fluvial wetlands near intensive agricultural ~~activities~~activity (Poissant et al., 2008). The presence of nitrate in Quebec groundwater has certainly been the most frequently investigated contaminant, ~~with~~ generally revealing low concentrations ~~revealed~~ (Carrier et al., 2013; Giroux and Sarrasin, 2011; Giroux 2003; Levallois et al., 1998; Meyzonnat et al., 2016; Quebec, 2004a), which nonetheless often exceed the natural (non-anthropogenic) background of 1 mg $N\text{-}NO_3.L^{-1}$ (Dubrovsky et al., 2010).

The ~~objectives~~objective of this study ~~were~~was to evaluate the distribution of PhACs, pesticides, nitrate, and bacteria in untreated groundwater in the low population density Centre-du-Quebec region of the St. Lawrence Lowlands (Quebec, Canada), as an example of ~~contaminants~~contaminant distribution in post-~~glaciated~~glacial regions around the world. This research was carried out as part of a regional-scale aquifer characterization study on the Nicolet River watershed and on the lower portion of the Saint-François River watershed, both located in the Centre-du-Quebec region (Larocque et al., 2015). ~~Geological~~Related geological contexts,

aquifer confinement, soil and crop types, spatially distributed recharge, major ion analyses (fully described in Saby et al., 2016), and a DRASTIC index map are also included in the Larocque et al. (2015) report. Presented here are results from groundwater sampling undertaken to assess the presence of nitrates, bacteria (*E. coli*), pesticides, and PhACs. A new Anthropogenic Footprint Index (AFI~~),~~) was developed, based on the estimated density of agricultural and urban areas, both considered to be potential sources of contamination~~ sources, was developed~~. The ~~new~~ Hydrogeochemistry Vulnerability Index (HVI~~)~~), developed recently by Meyzonnat et al. (2016~~)~~), was used to provide an ~~alternative~~alternate estimate of aquifer vulnerability, based on major ion analyses reported by Saby et al. (2016). Statistical analyses were performed to assess explanatory factors for the water quality results, using the spatially distributed data reported in Larocque et al. (2015) for ~~crop type,~~ presence of a crop, crop type, soil drainage, aquifer confinement, aquifer type, and recharge.

2. STUDY AREA

2.1 Geology and hydrogeology

The study area (4584 km^2) corresponds to the Nicolet River watershed and to the lower portion of the Saint-François River watershed, in the Centre-du-Quebec administrative region (Figure 1a). The regional fractured aquifer is composed of rocks belonging to two geological provinces: the Appalachian Mountains in the southeastern portion of the basin, and the St. Lawrence Platform in the northwestern portion. Geographically, the two geological provinces are part of the St. Lawrence Lowlands.

The St. Lawrence Platform is a Cambrian-Lower Ordovician siliciclastic and carbonate platform, formed in an extensional context related to the opening of the Iapetus Ocean~~,~~ and

overlain by Middle-Late Ordovician foreland carbonate-clastic deposits, deposited during the closure of Iapetus and the Appalachian Mountains buildup. In the Appalachian piedmont, outcropping terrains are the Cambrian green and red shale of the Sillery Group, and the slate, limestone, and sandstone conglomerate of the Bourret Formation. The schist of the Drummondville Olistostrome, the calcareous slate of the Bulstrode and Melbourne Formation, as well as the schist, shale, sandstone, and conglomerates of the Shefford, Oak Hill, and Sutton-Bennett Groups (Globensky, 1993) are also present.

Unconsolidated Quaternary fluvioglacial deposits cover the fractured Paleozoic aquifer (Lamothe, 1989). Basal deposits are tills from the last two Quaternary deglaciation episodes, followed by glaciolacustrine, sandy, and organic deposits. A thick clay layer, deposited during the Champlain Sea episode following the last deglaciation, covers sandy deposits over a strip of 30 km along the St. Lawrence River (Lamothe and St-Jacques, 2014). This clay creates confining conditions for the underlying fractured bedrock aquifer. Further upgradient, a flat area composed of sand, patches of clay, and shale induces a heterogeneous and semi-confined hydrogeological context, while still further upgradient, the outcropping of reworked till and bedrock leaves the fractured aquifer unconfined in its main recharge area (Figure 1b).

The study area is divided into two main aquifer systems, further described in Larocque et al. (2015): the shallower Quaternary aquifers of relatively limited thickness and extent, and the underlying Paleozoic fractured bedrock aquifer, composed of sedimentary rocks. Hydraulic conductivities in the fractured bedrock aquifer are heterogeneous and range from $5x10^{-9}$ $m.s^{-1}$ to $7x10^{-6}$ $m.s^{-1}$. Confining zones have ~~been~~ previously been estimated using a 3D model of the Quaternary sediment architecture, based on the thickness of the impermeable units. Results were interpolated over 250 m x 250 m cells (see Figure 1b). Confined conditions were defined as when

either more than 3 m of clay or more than 5 m of compact till were present. Semi-confined conditions corresponded to areas where 1 to 3 m of clay or 3 to 5 m of compact till were found. Unconfined conditions referred to areas where less than 1 m of clay and less than 3 m of compact till were found. Unconfined zones were found to represent 55% of the studied surface area, while semi-confined and confined zones represent 18% and 27% respectively (Larocque et al., 2015).

2.2 Previously available data

The spatially distributed water budget of the study area was described in detail by Larocque et al. (2015). The 1961-2010 average annual temperature for the study area was 5.6°C, and the average annual precipitation was 1018 mm (25% falls as snow; Nicolet and Drummondville stations; Environment Canada, 2012). Precipitation usually falls as snow between the months of November and March. The average annual recharge of the fractured bedrock is 152 $mm.yr^{-1}$ for the 1989-2009 period. Recharge occurs preferentially in the Appalachian piedmont, while it is almost nonexistent under the clay layer of the Champlain Sea. The piezometric map (Figure 1a) shows that groundwater flow directions are generally from the Appalachian Piedmont towards the St. Lawrence River. However, Larocque et al. (2015) have demonstrated that there is only limited regional-scale groundwater flow, and less than 1 $mm.yr^{-1}$ flowing into the St. Lawrence River, with the many rivers and streams locally draining ~~locally~~ the bedrock and granular aquifers. The mean water table depth is 4.4 m.

Groundwater geochemistry evolves from a Ca-HCO_3 water type at recharge, which corresponds mainly to the Appalachian piedmont, to a Na-HCO_3 water type downgradient, closer to the St. Lawrence River. Geology and rock-water interactions control the regional evolution of groundwater chemistry (Saby et al., 2016). $^3H/^3He$ groundwater ages range from 4.8±0.4 years in

the upgradient portion of the study area, to more than 60±3.2 yrs in its downgradient portion (Saby et al., 2016). SF_6 residence times reported in Larocque et al. (2015) show values of a similar magnitude, between 1±0.5 year upgradient of the study area, where the Quaternary deposit cover is thin and recharge is direct, and 34±5.6 years downgradient. Saby et al. (2016) also calculated older ^{14}C groundwater ages, from 280±56 to 17050±3410 years. These results clearly indicate mixing between modern groundwater and a paleo-groundwater component circulating slowly in the deepest, less permeable layers of bedrock, creating this apparent contradiction in age (Vautour et al., 2015; Saby et al., 2016). Older groundwater likely infiltrated the bedrock aquifer through subglacial recharge when the Laurentide Ice Sheet covered the study area (Saby et al., 2016).

Larocque et al. (2015) present a crop type map built from a database of insured crop acreage ~~crops~~ (Martineau, 2014). A total of 48% of the studied surface ~~of the study~~ area is dedicated to agriculture, mainly along the St. Lawrence River, while forest covers 45% of the area, principally in the Appalachian piedmont (Figure 1c). Wetlands, urban areas, and surface water occupy 3.7%, 2.0%, and 1.1% of the region respectively. A detailed description of the study area is found in Larocque et al. (2015). Agriculture is dominated by cereal (54%) and hay (22%) production, with a minor presence of mixed crops, vegetables, and small fruit production (3%) located mainly in the lower part of the study area where the bedrock aquifer is covered by ~~the~~ Champlain Sea clay. No information is available for the remaining 21% of the study area. ~~This~~The study area is considered to be among the most agriculturally productive in the province of Quebec (UPA, 2012).

Larocque et al. (2015) have built a soil drainage map using data from the database of the *Institut national de recheche et de développement en agroenvironnement* (IRDA, 2013). For the

lower and central parts of the study area, soil drainage varies from very well drained to poorly drained. Sandy soils dominate in this area, but clay soils are also present in a spatially heterogeneous matter. In addition to sand and clay, discontinuous till covers the lower portion of the study area, and is increasingly visible towards the Appalachian piedmont. The Appalachian area is dominated by till soils ranging from well ~~drained~~ to poorly drained. Organic deposits ~~corresponding to peatlands~~ are also present as peatlands in the central portion of the study area.

Larocque et al. (2015) computed the DRASTIC index (Aller et al., 1987) ~~on~~for 500 m x 500 m cells for the bedrock aquifer of the study area using the usual parameters and associated parametric weights (see annex A1 for details of the method). Vulnerability values of the DRASTIC index for the bedrock aquifer vary from 24 to 185 for the study area. ~~The~~ Quebec legislation (Quebec, 2015) labels ~~as~~ "low vulnerability" regions as those where the DRASTIC index is below 100, ~~as~~ "medium vulnerability" regions as those where the DRASTIC index is between 100 and 180, and ~~as~~ "high vulnerability" regions as those with a DRASTIC index above 180 (see Figure 1 in annex A1). Based on these categories, 28% of the study area ~~has a~~is low vulnerability and 72% ~~has a~~is medium vulnerability. Only 0.02% of the area ~~has a~~is high vulnerability. The medium and high vulnerability ~~values~~areas are located in the ~~Appalachian area~~Appalachians, where recharge is high and sediment cover is thin. A vast portion of the central part of the study area is also characterised by ~~a~~ medium vulnerability, mainly because of the high water table and the high permeability of the ~~sediments~~sediment. The lower part and some areas around the Saint-François and Nicolet Rivers in the central section ~~have~~are of low vulnerability ~~values~~. The thick clay layer combined with low recharge rates ~~explains~~explain these low DRASTIC values.

In the study area, 56% of the groundwater extracted for drinking water, for agriculture, or for industrial use is ~~extracted~~done so through individual wells (Larocque et al., 2015). It is estimated that a similar proportion of the houses are linked to private septic tanks. In the larger municipalities, such as Victoriaville and Drummondville, wastewater is collected through a municipal network connected to a wastewater treatment plant. In rural areas, individual properties collect wastewater in private septic tanks.

3. METHODS

3.1 Groundwater sampling and analysis

Between June and August 2013, 190 groundwater samples were collected from private wells (157 wells), municipal wells (11 wells), 1" PVC observation wells (12 wells), and 6" steel tubing observation wells (10 wells) (see locations in Figure 1c and well ~~description~~descriptions in Table A1). Well depths range between 5 and 250 m for the 145 open borehole bedrock wells, and from 1.2 to 50 m for the 45 wells taping a granular aquifer (granular wells ~~are~~ either ~~with~~have a steel casing or are drive points). All samples were analyzed for nitrate and *E. coli*. Major ~~ions~~ion data (Ca^{2+}, Na^{2+}, Mg^{2+}, K^{+}, and HCO_3^{-}, SO_4^{2-}, Cl^{-}) are available for all the wells and are reported in Saby et al. (2016). In September 2014, 33 wells were ~~re-sampled~~resampled (six private wells, nine municipal wells, 11 1" PVC observation wells, and seven 6" steel tubing observation wells). This water was analyzed for 13 different PhAC compounds (antibiotics, beta-blockers, mood stabilizer and anticonvulsant, antilipemic agents, chemotherapy medication, and prescription and non-prescription non-steroidal anti-inflammatory agents) and 46 different pesticides (herbicides, fungicides, and insecticides~~) (~~; see list of PhAC and pesticide molecules analyzed in Table A2).

All the wells were purged prior to sampling, and water was sampled prior to any treatment once the physiochemical parameters (pH, temperature, redox potential, and electric conductivity) measured in an air-tight cell had stabilized (MDDELCC, 2011). Groundwater was collected from the observation wells using a submersible pump with speed control (Redi-Flo2®), maintaining the whole sampling line under pressure to prevent water degassing. All samples were filtered in the field to 0.45 µm. Samples were kept at 4°C during storage and transport. Samples for PhACs and pesticides were collected in 1L Nalgene® bottles, and were sent to the Environmental Engineering Laboratory ~~at~~of the University of Sherbrooke ~~University~~ for analysis. The samples were first extracted using a solid phase extraction procedure, ~~then~~and the liquid phase was then analyzed by liquid chromatography coupled with a triple ~~quadrupoles~~quadrupole mass spectrometer (Ba et al., 2014; Haroune et al., 2014). The detection limit of the method for pesticides and PhACs was 5 ng.L^{-1}. The calibration was validated by verifying the calculation of the deviation for each point (criteria < 20%). Each series of samples was validated for a spiked sample (recovering criteria ~~on~~between 70% - 120%). No field blanks or duplicates were analyzed for ~~pestices and~~pesticides or PhACs because of the high analytical cost. Groundwater for nitrate analysis was sampled in 125 ml Nalgene® bottles and analyzed by colorimetry in a private laboratory (ISO/CEI 17025), with a detection limit of 0.1 mg N-NO_3.L^{-1}. Laboratory blanks for nitrate analyses were done systematically for each sample, but no field blank ~~has been~~was taken. A total of 10 duplicates ~~was~~were sampled for the 190 samples analyzed for nitrate.

Groundwater was also sampled for bacteria content, in 250 ml Nalgene® bottles, kept at 4°C during storage and transport, and sent daily to a private laboratory. *E. coli* was analyzed using the presence/absence method, meaning that each *E. coli* bacteria is counted~~,~~ if present (SOP-BA-076; ISO/CEI 17025). This method relies on the « 9223 B. ENZYME SUBSTRATE TEST » of the

~~referenced manual~~ *Standard Methods for the Examination of Water and Wasterwater* reference manual (APHA, AWWA ~~et~~and WEF, 2012). ~~Ten duplicates were sampled for~~Of the 190 samples analyzed for bacterial counts, duplicates of ten were analyzed.

3.2 Anthropogenic Footprint Index (AFI) and Hydrogeochemical Vulnerability Index (HVI)

The Anthropogenic Footprint Index (AFI) developed in this study is derived from the farm density (FD) and anthropic activity density (AAD) data presented in Larocque et al. (2015). FD is the number of farm buildings per square kilometer. AAD is a weighted sum of risks per square kilometer. AAD takes into account the ~~type~~types of anthropic ~~activities~~activity (punctual infrastructures) and their impact~~,~~ in terms of groundwater pollution risks. This method was adapted from similar projects in the United States and elsewhere in the world (Foster and Hirata, 1998; EPA Office of Water, 1991; SESAT, 2010). Each parameter is weighted following the methodology presented in Larocque et al. (2015), and the ~~global~~overall impact is calculated as follows:

$$AAD = (TC + CQ + IZA)\, x\, RCD \qquad \text{(eq. 1)}$$

~~Where~~where TC is the weighted sum of contaminant toxicity, CQ is the weighted sum of contaminant quantities, IZA is the weighted sum of impacted areas, and RCD is the recurrence of contaminant discharge. The contaminants used for each type of anthropic activities were derived from a study by the Oregon Government (1996). The weight of contaminant toxicity is associated ~~to~~with the type of activity and depends on the toxicity classification ~~from~~of the Workplace ~~hazardous materials information system~~Hazardous Materials Information System (WHMIS)

(CSST, 2007). The weight of the contaminant quantity is based on contaminant quantity and concentration for a given anthropogenic activity (modified from SESAT, 2010). The impacted area refers to the potential extent of the activity (punctual, local, or regional). Finally, contaminant discharge is either recurrent (systematic and linked to the activity itself), or accidental. Each parameter is evaluated qualitatively~~ with~~, assigned to one of four classes (low, moderate, high, very high~~)~~), and weighted following the tables available in Larocque et al. (2015). The parameters required to calculate the FD and AAD were extracted from a property assessment database describing the type of anthropic activity (MAMROT, 2010). The AAD values were computed for each point of anthropic activity on the land surface and ~~are~~were interpolated on a 250 m x 250 m grid.

The AFI cumulates the spatially distributed density values and therefore reflects the cumulated potential sources of contamination (Eq. 1). The AFI is mapped on 250 m x 250 m cells over the study area, similar to the FD and AAD. The AFI can vary between 0 (low risk) and 100% (maximum risk).

$$AFI = 100\left(\frac{FD}{FD_{max}} + \frac{AAD}{AAD_{max}}\right) \qquad \text{(eq. 2)}$$

The Hydrogeochemistry Vulnerability Index (HVI; Meyzonnat et al., 2016) uses major ion geochemistry to identify the presence of recently infiltrated water and water from further locations ~~at~~in a given well. This index is based on the evolution of groundwater geochemistry from recharge areas to more confined regions of a study area. It ~~links~~relates this evolution to the vulnerability of a bedrock aquifer by comparing the geochemistry with nitrate concentrations for each well (Meyzonnat et al., 2016). The HVI is then extrapolated to draw a portrait of the aquifer

vulnerability at a regional scale. It is calculated by plotting ($Na^+ - Cl^-$) against ($Ca^{2+} + Mg^{2+}$) – ($HCO_3^- + SO_4^-$). The HVI graphically illustrates how the groundwater chemical composition evolves from a (Ca, Mg)-HCO_3 type in the recharge area to a Na-HCO_3 type downgradient along a flow path. The HVI can vary between 0 (low vulnerability) and 10 (maximum vulnerability) along the linear regression from its orthogonal projection. In this study, the HVI was calculated using the major ion concentrations measured at the sampling points as reported in Saby et al. (2016).

3.3 Statistical analysis

~~Comparison of the~~The mean PhAC, pesticide, and nitrate concentrations for different ~~physical~~site parameters (crop type, presence of a crop, soil drainage, aquifer confinement, aquifer type, and recharge) ~~was done~~were compared using the Student-T test. *E. coli* data (presence or absence) were analyzed using a contingency table and the Chi-2 test. All the statistical analyses were done using JMP software (SAS Institute, 2012~~).~~), and a confidence level of 0.05. Sampling points with missing data were excluded. ~~The confidence level was set to 0.05.~~ For PhAC, pesticide, and nitrate data, concentrations were used in the analysis. Bacterial counts were transformed into a binary presence~~/~~ or absence. Crop type was assigned to the sampling points using the proximity tool of ArcGIS (ESRI, 2016), with a radius of 500 m set as the search criteria. Three crop types were considered; "absence of a crop", "cereals", and "hay". "Market ~~gardening~~garden" and "mixed crop" types were excluded from the analysis because of the limited number of samples in each category (one and four respectively). The ~~six~~seven soil drainage categories were reclassified into two categories, "well drained" (from previous "relatively well drained~~,~~", "well drained~~,~~", "very well drained~~,~~", and "extremely well drained" categories), and

"poorly drained" (from previous "very poorly drained~~,~~", "poorly drained~~,~~", and "imperfectly drained" categories). The aquifers tapped by the sampled wells were categorized as "unconfined~~,~~", "semi-confined~~,~~", and "confined~~-~~". Aquifer type was categorized as "granular" or "bedrock~~-~~". Recharge was divided into three categories: "low" for recharge values ~~below~~of less than 100 mm.yr^{-1}, "average" for recharge values between 100 and 200 mm.yr^{-1}, and "high" for recharge values ~~larger~~of higher than 200 mm.yr^{-1}. The influence of water table depth and well depth was analyzed for all parameters and all contaminants, but results are not reported here since they were insignificant for all analyses.

4. RESULTS

4.1. Contaminant occurrence

PhAC compounds were detected for ~~4~~four of the 13 tested molecules~~,~~ in ~~9~~nine of the 33 tested wells (27%), and the average total PhAC concentration was 9 ng.L^{-1} (Figure 2a and Table A3). The highest concentration of PhAC was found in a well in the granular deposits of the Appalachian piedmont (NSF504~~)~~), where 133 ng.L^{-1} of benzafibrate was measured. There are no drinking water quality standards for PhAC molecules in Canada or ~~in other countries.~~elsewhere. Major areas of low or undetectable concentrations of pesticides and PhACs were located in the less populated areas and in forested zones. ~~As for pesticide concentrations, none~~None of the tested parameters explained the differences observed in pesticide concentrations between the sampled wells (Table A4), and there was no clear link between well depth and PhAC concentrations.

Pesticides were detected for 34 of the 47 tested molecules (Figure 2b and Table A5), and 23 of the 33 sampled wells (70%) had at least one detected compound. None of the pesticide

concentrations exceeded the Canadian drinking water quality standards (MDDELCC, ~~2015~~2011). The highest total pesticide concentration was 692 ng.L^{-1}, in a municipal well ~~taping~~tapping a semi-confined granular aquifer in the Appalachian piedmont (NSF177). None of the tested parameters (crop type, soil drainage, aquifer confinement, aquifer type, or recharge) explained the observed differences~~ observed~~ in pesticide concentrations between the sampled wells (Table A6). No clear link was observed between well depth and pesticide concentrations.

A total of 29 wells (15.3% of all sampled wells) ~~wells~~ had nitrate concentrations ~~above~~higher than the natural background of 1 mg.L^{-1} N-NO_3 (Dubrovsky et al., 2010) (Figure 2c and Table A2). The majority of the wells (62.6%) had ~~no~~ nitrate ~~above~~in concentrations of less than the 0.1 mg.L^{-1} N-NO_3 detection limit. The maximum nitrate concentration, 12 mg.L^{-1} N-NO_3, was measured in well NSF250, a granular well located upgradient in the Appalachian piedmont. This is the only well exceeding the drinking water quality standard of 10 mg.L^{-1} N-NO_3 (Health Canada, 2014). The average nitrate concentration of all wells was 0.63 mg.L^{-1} N-NO_3. On average, wells near fields with hay crops had a significantly higher nitrate concentration (1.04 mg.L^{-1} N-NO_3) than those near fields which were not cultivated (0.16 mg.L^{-1} N-NO_3; $p=0.0297$) (Table A7). However, the simple presence of a crop near a well alone does not~~ itself~~ explain nitrate concentrations ($p>0.05$). Well drained soils had significantly higher concentrations (1.01 mg.L^{-1} N-NO_3) than poorly drained soils ($p=0.0241$). The average nitrate concentration in wells tapping an unconfined bedrock aquifer (1.05 mg.L^{-1} N-NO_3) was significantly higher than that in wells in semi-confined conditions (0.21 mg.L^{-1} N-NO_3; $p=0.0022$), and that in wells in confined conditions (0.16 mg.L^{-1} N-NO_3; $p=0.0017$). The average nitrate concentration for wells in a granular aquifer (1.16 mg.L^{-1} N-NO_3) was significantly higher ~~($p=0.0060$)~~ than for wells in

the Ordovician bedrock aquifer (0.47 mg.L^{-1} N-NO_3; p=0.0060). The three wells with nitrate concentrations higher than 7 mg.L^{-1} N-NO_3 were located in granular aquifers.

Overall, 13.5% of the samples had detectable *E. coli*. The spatial distribution of bacterial contamination ~~by bacteria~~ was highly heterogeneous throughout the area, and contamination was found ~~equally~~ in agricultural and in urbanized areas alike. None of the other tested parameters (crop type, presence of a crop, soil drainage, aquifer confinement, aquifer type, or recharge) explained the presence or absence of bacteria in the sampled wells (Table A8).

4.2. AFI and HVI identified areas of contamination risk

The AFI was used to identify zones of potential contamination risk ~~linked with~~related to land use (Figure 3). In the 190 wells sampled for nitrate and bacteria, the AFI varied between 1 and 38%, with an average of 15%. The highest AFI values (i.e., the maximum value in the whole study area; 42%) was observed in the intensive agricultural zones of the lower part of the study area. The two largest municipalities in the study area, Victoriaville and Drummondville, also had AFI values of 42%. The lowest AFI values were ~~found~~ mainly found in the forested zones located in the central and upper ~~part~~parts of the study area.

The mean HVI value was 8.5 (median of 9.1), ranging from a minimum value of 1 (NSF 147) to the highest value of 10 (NSF 150; Table A1). Overall, the highest values were found in the Appalachian piedmont, where recharge is greatest, and the lowest values were located in the lower portion of the study area, where the Champlain Sea clay largely limits groundwater recharge.

5. DISCUSSION

5.1. Groundwater contamination

~~Although the~~The drinking water quality standards were exceeded in only a limited number of wells (i.e., 13.5% of the wells for *E. coli*, one well for nitrate, and in none of the ~~wells~~ sampled wells for pesticides; there are no drinking water quality standards for PhACs~~),~~). However, the results ~~showed~~presented here have shown that groundwater in the study area is affected by all four contaminant types. This ubiquitous presence of PhAC and pesticides is similar to that reported in other studies (see summary in Lapworth~~,~~ et al., 2012), but was unexpected given the low population density in the study area.

The absence of a significant correlation between the tested parameters and PhAC or pesticide concentrations could be due to the limited number of wells sampled (n = 33), and does not conclusively exclude a relationship or a causal effect. The highest PhAC concentrations ~~could~~were not able be linked to agricultural or urban areas through the AFI. The low occurrence of PhAC (27% of the tested wells had at least one PhAC) could be related to the low population density and to the limited number of wells that were sampled near the denser population areas ~~where~~, whereas PhAC sources are expected to be higher due to the presence of public water distribution networks. ~~It~~This could also be related to the fact that some of the tested molecules have only recently been in use~~ only since recently.~~. Concentrations could ~~thus~~therefore increase with time if these compounds remain in use. Nonetheless, these results indicate a clear anthropogenic impact on groundwater resources. They figure among the few reported studies of this type for Canadian aquifers, and are the first at the regional~~-~~ scale for the ~~Quebec~~ province of Quebec.

The measured concentrations of pesticides were below the Canadian drinking water quality standards (MDDELCC, ~~2015~~2011). The average total pesticide concentration was 67 ng.L^{-1},

which is lower than the European limit for cumulated pesticides, of 500 ng.L^{-1} (CUE, 1998; there is no total pesticide water quality standard in Canada). The European limit was exceeded in one well (692 ng.L^{-1}; NSF177, a municipal well ~~taping~~tapping a confined granular aquifer), and was near the European limit in another well (479 ng.L^{-1}; NSF-R6, an observation well in the bedrock aquifer). These two wells are located upgradient, in the Appalachian piedmont, in areas where agricultural land surrounds the wells. The higher occurrence of pesticides in the tested wells (70%) compared to PhACs could be explained by more regionally distributed sources of the contaminant.

The measured nitrate concentrations are similar to those reported in other studies from southern Quebec (Carrier et al., 2013; Giroux and Sarrasin, 2011; Levallois et al., 1998; Meyzonnat et al., 2016; Quebec, 2004a). It is interesting to highlight that higher concentrations of nitrate, exceeding the drinking water quality standard (between 11 and 72 mg.L^{-1} N-NO_3), have been reported for shallow unconfined wells in a granular aquifer of the study area (e.g., BPR and Arrakis consultants, 2004). When comparing results from the current study with the previously available DRASTIC index values, the bedrock wells located in areas where the DRASTIC index was categorized as "medium" have significantly higher nitrate concentrations (0.52 mg.L^{-1} N-NO_3) than those located in areas where the DRASTIC index was categorized as "low~~-(~~" (<0.~~00~~1 mg.L^{-1} N-NO_3; p=0.0278). Similar to these results, a study in the Lanaudiere region of southern Quebec showed a correlation between nitrate concentrations and the DRASTIC index (Quebec, 2004a), with stronger correlations for wells tapping granular aquifers than for deep bedrock wells. In the current study, the limited proportion of concentrations higher than the anthropogenic background could be related to the presence of agricultural drainage, which transports nitrate to surface water before it can infiltrate to groundwater (Thériault, 2013). Poorly

drained soils ~~could also be more anoxic~~ with high organic contents could also be more anoxic, and thus produce nitrate-reducing conditions (Vogel et al., 1981; Liao et al., 2012). Denitrification tends to happen more often in soils and aquifers with high organic carbon content, and ~~thus~~therefore can sometimes be an important factor ~~of~~for nitrate removal. However, the sampling density combined with the relatively low nitrate concentrations in groundwater makes it difficult to assess this effect in the study area.

The observed bacteria (*E. coli*) occurrence in 13.5% of the sampled wells was similar to that reported by Leblanc et al. (2013) for the lower part of the Saint-Maurice River watershed in southern Quebec (*E. coli* present in 12 % of all sampled wells). Considering the relatively short residence time of *E. coli* in saturated conditions, Leblanc et al. (2013) concluded that bacterial contamination was caused mainly by local processes, such as the proximity of a private sewage system, or poor well construction or maintenance. Although the effect of aquifer type was not clear in the current study, the Lanaudiere study (Quebec, 2004b) showed a higher occurrence of *E. coli* in granular aquifers, with 49% of the granular wells having a positive detection. The highly heterogeneous coverage of Quaternary post-glacial deposits in the study area could explain the absence of significant correlations between the presence of bacteria and the tested parameters. Interestingly, the average nitrate concentration in the wells where *E. coli* was detected was significantly higher compared ~~to~~with the wells where no *E. coli* was detected (1.61 mg.L^{-1} N-~~NO_3versus~~NO3 versus 0.44 mg.L^{-1} N-NO_3 respectively; p=0.001). This could be due to the combination of manure spreading with ~~fertilizers~~other fertilizer application in agricultural areas.

Contaminants can be more or less reactive with their environment, depending on several parameters, such as their half-life in water, their adsorption coefficients, and their reactivity to

sunlight (Kleywegt et al., 2007; USDA, 2009). PhACs and pesticides, for example, can have relatively short half-lives, some ~~of them transform~~transforming into by-products, and are easily adsorbed on soil and organic matter particles. The spatial variability in measured concentrations ~~can reflect~~reflects different land uses, and chemical processes (e.g., adsorption, desorption, degradation, complexation) occurring at the land surface, in the unsaturated zone, and in the aquifer. It can also be due to surface and water infiltration conditions, such as the quantity of applied nitrate or pesticides, the concentrations of PhACs in the wastewater source, the soil pH, or the oxygen content of the groundwater.

Interestingly, the PhACs with the lowest log K_{ow} (octanol/water partition coefficient~~ see Table A2 for the list of calculated log K_{ow} values~~; the lower the log K_{ow}, the more highly soluble in water and potentially the more mobile in groundwater; see Table A2 for the list of calculated log K_{ow} values), were not the most frequently detected. Among the compounds with log K_{ow} of lower than one, only the PhAC trimethoprim was detected (in three wells). Counterintuitively, the PhAC mefenamic acid, which has the highest log K_{ow}, was detected in the highest number of wells (seven). Similarly to PhAC compounds, the low log K_{ow} pesticides were not the most frequently detected. Aldicarb-sulfone (log K_{ow} = -0.57) and imidacloprid (log K_{ow} = 0.57) were detected in only one well. Another soluble ~~pesticides~~pesticide was not detected (dimethoate, log K_{ow} = 0.78) while chlotianidin (log K_{ow} = 0.70) was detected in two wells. Permethrin, a pyrethroid compound frequently used in agriculture and for municipal uses, was detected in two wells (PZ2, a 9.1 m observation well in the unconfined surface sediments, and NSF177, a 39.0 m municipal well taping a semi-confined granular aquifer). This was unexpected since this insecticide has the highest log K_{ow} of the tested pesticides (log K_{ow} = 6.50) and is generally considered to be highly adsorbed. All the pesticides with a log K_{ow} of higher than 4 were detected

in one or more wells. The most frequently detected pesticides (kresoxim-methyl, in 9 wells; trifloxystrobin, in 7 wells; piperonyl butoxide, in 7 wells) had log K_{ow} of equal to or higher than 3.40.

These results indicate that the PhAC compounds and pesticides considered ~~having~~to have low leaching potential can reach an aquifer, possibly from nearby contaminated recharge and from local vertical flows. A low log K_{ow} PhAC or pesticide should thus not be considered ~~as having a~~to have low potential for groundwater contamination~~ potential~~. Sampling cores of sediments to analyze adsorbed phases of pesticides and PhAC compounds would help to further constrain these observations. A detailed examination of pesticide applications (e.g., application method, amounts used, frequency of ~~applications~~application, timing with respect to rain events) in the study area would help to better constrain pesticide sources.

5.2. Identifying contaminant sources with the Anthropogenic Footprint Index (AFI)

The comparison between the determined AFI values and contaminant concentrations in groundwater was intended to ~~evidence~~demonstrate a link between the risk of pollution and the presence of ~~specific~~certain pollutants. However, the results show that neither PhAC nor pesticide concentrations in groundwater seem to be correlated with the AFI (Figure 4a). The same was observed for nitrate and the presence of *E. coli* (Figure 4b). When the FD and AAD components of the AFI were compared separately with contaminant concentrations, the relationship did not improve (results not shown). It therefore does not appear that one of the two AFI components hides the effect of the other.

The fact that the AFI is not a useful indicator of contamination could be due to the design of ~~this~~the index, which might not take ~~into account~~ sufficient information into account to estimate

the risk of contamination from the surface. Additional information that might help to improve the indicator includes local information, such as the type of agricultural activity (crops or livestock), the type of animal waste storage, or the types and amounts of fertilizers (organic or inorganic) and pesticides used in the fields. The absence of a correlation between the AFI and the contaminants might also be explained by the fact that the presence of a potential contamination source at the surface does not necessarily result in contaminant percolation to the aquifer. In confined or semi-confined conditions, the contaminant might migrate preferentially toward surface water bodies. In fact, the results have shown that the strongest explanatory factors for nitrate concentrations and for the presence of *E. coli* were aquifer confinement (for nitrate concentrations) and aquifer type (for nitrate concentrations and for the occurrence of *E. coli*) (Table A7 and A8) . Aquifer confinement (see Figure 1b) and aquifer type (granular or bedrock) directly influence the infiltration of water and contaminants from the surface to the saturated zone. These results show that local infiltration conditions might have a greater impact on the water quality of a local well than does the presence of a contaminant or contaminants in a source located further upgradient. The Quebec (2004a) study reported similar results, with elevated nitrate concentrations being detected more frequently ~~detected~~ when there was both a high DRASTIC index and intensive agricultural activity. The ~~weakness~~inability of the AFI index to explain contaminant occurence could also be due to the small number of sampled wells in dense urban areas, where public water distribution networks are available, in contrast with more sampled wells in rural areas, where each house has its own well.

5.3. Estimating aquifer vulnerability

5.3.1. Aquifer recharge and groundwater dynamics

Recharge is often considered ~~as~~to be a reliable parameter with which to estimate vertical groundwater vulnerability (Aller et al., 1987). Water percolating through the unsaturated zone reflects the nature of the soils it passes through. Therefore, the aquifer areas covered with clay will receive limited recharge, even if a potential source of contamination is present (i.e., high AFI). ~~Inversely~~Conversely, an area with a high recharge rate will have very low contaminant concentrations if it is located far from agricultural areas or cities (i.e., low AFI). This is the case, for example, for some wells located in the upper portion of the study area, where recharge is high, but which are not close to potential sources of contamination (see Figure 5a). The relatively higher nitrate concentrations in areas of average recharge (between 200 and 250 $mm.yr^{-1}$) could be linked to the agricultural activities located in the middle portion of the study area, where unconfined and semi-confined conditions are found. However, this trend is not clear for either pesticide or PhAC concentrations (Figure 5b).

When comparing groundwater residence times (Larocque et al., 2015; Saby et al., 2016) with the spatial distribution of recharge, it becomes clear that groundwater travels more rapidly to the sampled wells in areas where recharge is the highest (Figure 5c). These results are consistent with both the regional flow path of the study area, and the gradual confinement of the bedrock aquifer. Thus, the younger the groundwater, the higher the risk ~~to find~~of finding a high contaminant concentration, if a source of contamination is present at the surface. These short residence times also point to the presence of relatively direct water flow and to possible contaminant migration between the surface and the saturated zone. Although it is also important to take attenuation factors into account, such as pesticide and PhAC degradation and adsorption on soil and the aquifer matrix, short residence ~~time~~times certainly ~~increases~~increase the vulnerability of groundwater.

Post-glacial terrains, such as those found in the study area, are ~~tridimensionnaly~~tridimensionally complex environments in which it is often difficult to assess recharge and groundwater residence times. This is due to the spatial heterogeneity of the permeability and the thickness of the Quaternary deposits, which determine aquifer confinement, an important parameter for nitrate migration. Intermediate confinement conditions in the Appalachian Piedmont, located in the central portion of the study area, can lead to a spatially complex juxtaposition of contrasting confinement conditions, making aquifer recharge assessment particularly imprecise.

5.3.1 ***Hydrogeochemical Vulnerability Index (HVI)***

The two wells with the highest total pesticide concentrations (NSFR6 and NSF177) also had among the highest HVI values (9.8 and 9.3 respectively) (Figure 6a). There was no apparent trend between PhAC concentrations and HVI. The comparison between nitrate concentrations and HVI (Figure 6b) showed that concentrations tended to be higher when the HVI was greater than 9 (maximum is 10), a result similar to that reported by Meyzonnat et al. (2016) in the neighboring Becancour watershed. Because it reflects the groundwater dynamics and the water-rock contact time, the HVI highlights flow conditions across different media and receiving infiltration from different land uses. The high HVI scores thus reflect the presence of groundwater near recharge areas with Ca,Mg-HCO_3, Ca-HCO_3, and Ca-SO_4 water types, while the low scores represent increasing confinement conditions and water type evolving to Na-HCO_3 and Na-Cl types (Meyzonnat et al., 2016). The high HVI wells in recharge areas are also those where residence times are the shortest (Figure 5c), which explains their association with the highest nitrate concentrations. The weaker link observed between PhAC and the HVI, and, to a

certain extent, pesticide concentrations and the HVI could be due to the small number of wells sampled for these contaminants (n = 33). It could also be explained by PhAC and pesticide degradation in the unsaturated zone. Overall, the HVI appears to be a good indicator of aquifer contamination risk from agricultural sources, but the results are less conclusive for PhAC and pesticide sources.

Results for the HVI ~~index~~ and ~~of~~ the DRASTIC ~~does~~index do not provide the same type of spatial vulnerability information because of the differences inherent to the methods. The HVI method provides information on groundwater flow paths, while DRASTIC focuses on vertical flows from the surface to the water table. Thus, in the ~~studied~~study area, the DRASTIC and the HVI indices ~~doesn't give~~do not provide the same results in comparison with ~~contaminants distribution.~~contaminant distributions. The HVI index ~~better~~ correlates more strongly with NO_3, *E. coli*, and ~~pesticides~~pesticide occurrences than does DRASTIC. For PhACs, the correlation is less clear for both DRASTIC and HVI. The ~~nitrate's~~ results for nitrate are similar to those of Meyzonnat et al. (2016~~)~~), who performed a complete comparison of the two methods on a neighboring watershed ~~set in~~with similar geological conditions. These authors found that the DRASTIC index was relatively ineffective ~~to evaluate~~in evaluating groundwater vulnerability, while the HVI method showed a clear correlation with nitrate concentrations.

5.4. Synthesis and recommendations

This study shows that all analyzed contaminants (PhACs, pesticides, nitrate, and *E. coli*) were detected, which is a clear indication that groundwater resources in the study area are not pristine and ~~have an imprint of~~are impacted by human ~~impact~~activity. PhAC molecules were less prevalent than pesticides, but were nevertheless detected throughout the study area. Pesticides

were widely observed, although all concentrations were below the Canadian drinking water quality standards. Pesticides and PhACs could not be linked to site parameters. The presence of a hay crop, the soil drainage, aquifer confinement, type of aquifer, and recharge are all parameters found to be significantly related to nitrate concentrations. The occurrence of *E. coli* was related to the specific set of local conditions, and could not be linked to any one site parameter in particular.

These results are expected to be of particular interest ~~-~~for areas in similar post-~~glaciated~~glacial environments and undergoing similar human ~~impact problems~~impacts elsewhere in the world, such as Scandinavia, Denmark, Germany, and the USA (Harff et al., 2011; Scheck and Bayer, 1999; Thomsen et al., 2004; Dyke, 2004). The results will also be useful for provincial and local water management agencies, since it is the first time that regional-scale PhAC and pesticide concentrations are measured in the province of Quebec. Although no measured concentration ~~exceeding~~was found to exceed drinking water standards ~~were detected~~ for pesticides (and no standards exist for PhACs), the mere presence of PhACs and pesticides in groundwater used for drinking is a public health concern and justifies long-term monitoring. This recommandation stands for the study area, but also for ~~other~~surrounding regions ~~around~~ set in similar high recharge post-glacial geological environments, and ~~facing~~under the same type of land uses. Nitrate concentrations and the presence of *E. coli* have been a concern for some time, and should be monitored so as to strengthen the implementation of better agricultural practices in general. Measuring pollutant concentrations through time would also be useful ~~to link~~in linking their presence to time-varying sources, such as the seasonality of recharge and of agricultural contaminant input, an important factor of groundwater contaminantion which was not assessed here. Long-term monitoring is especially important since PhAC and pesticide concentrations in groundwater could increase in the next decades due to industrial and agricultural developments

and to an increase ~~of~~in PhAC release from wastewater. This study shows that including PhAC and pesticides ~~reputed for they~~known or assumed to have limited leaching potential is important since they can ~~find pathways to~~reach the aquifer even in confined conditions. Regional scale assessment of concentrations in other regions of southern Quebec and elsewhere in Canada and in the world should also be a priority, even where population density is low.

It is currently extremely difficult to detect PhACs and pesticides in groundwater samples. ~~Acquiring a better~~Improving understanding of the behaviours of these compounds in the unsaturated zone and in the aquifer for different recharge and geological conditions is a key element in the assessment of groundwater vulnerability. Studies carried out at more local scales would contribute to better constraining how and under which conditions PhACs and pesticides migrate with groundwater and are adsorbed, or degraded into sub-compounds. More research and development is necessary to improve analytical methods and related detection limits.

The contaminants identified here indicate the influence of local conditions on the potential for well contamination. The high HVI scores found in this study, in addition to the short groundwater residence times reported by both Saby et al. (2016) and Larocque et al. (2015) confirm this observation. Larocque et al. (2015) and Larocque et al. (2013) reported that most of the recharge in the Centre-du-Quebec region is intercepted by streams and rivers, and that only limited groundwater outflow reaches the St. Lawrence River outlet. It is therefore expected that local conditions influence aquifer vulnerability, and that groundwater quality measured in wells is not substantially impacted by long-distance (i.e., regional-scale) contaminant sources. In this case, vulnerability assessment methods that have the potential to reflect local flow conditions, such as the DRASTIC index or the HVI appear to be the best options. Although successful attemps to combine contaminant sources with the DRASTIC index have been reported in the literature (e.g.,

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Shrestha et al., 2016), this study shows that including potential sources of contamination at the regional scale can be misleading because of local flow conditions~~ and~~, when the exact location of these sources is unknown. These conclusions are specific to the high recharge and post-glacial geological setting of ~~the~~this study area, but could be applied to similar environments elsewhere in the world. However, site-specific studies should be performed in zones suspected to be of high vulnerability ~~zones~~so as to assess local sources of pollutants and to plan land use accordingly, regardless the type of environment.

6. CONCLUSIONS

The ~~objectives~~objective of this study ~~were~~was to evaluate the distribution of~~ the previous~~ contaminants in untreated groundwater in a low population density region. This work was based on an extensive ~~data set for~~dataset of PhACs, pesticides, and nitrate concentrations, and *E. coli* presence. A new index, the Anthropogenic Footprint Index (AFI), was calculated with the intention of simultaneously considering agricultural and urban areas as potential contamination sources. Links were investigated between contaminant occurrence and crop type, presence of a crop, soil drainage, aquifer confinement, aquifer type, and recharge. Groundwater flow paths were estimated using the Hydrogeochemical Vulnerability Index (HVI).

The results of this study showed that groundwater quality is affected by all four contaminant types. The AFI index, which represents the source of contamination, was not found to correlate with any of the investigated contaminants, indicating that regional-scale sources of contamination are not visible ~~at~~in the sampled wells. ~~This~~The challenge ~~to identify~~of identifying contaminant sources at the regional scale was linked ~~in this post-glaciated environment~~ to the high spatial heterogeneity of the Quaternary deposits in this post-glaciated environment, which ~~create~~creates

complex local flow directions. Notwithstanding the importance of using regional-scale vulnerability indices such as the HVI or the DRASTIC index to refine knowledge of flow conditions in post-~~glaciated~~glacial terrains, more research needs to be done to downscale vulnerability assessments to local-scale conditions in order to pinpoint sources of contaminants and their reactivity under specific conditions. Given the occurrence of contaminants found in this study, as well as in other studies and environments throughout the world, and the public health concerns that they present, this topic deserves to be further investigated in ~~a diversity of~~diverse hydrogeological and land use conditions.

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Figure captions

Figure 1. Study area in the Nicolet and Lower Saint-François watersheds of southern Quebec (Canada); a) piezometric map, b) ~~Map~~map of the bedrock confinement zones, and c) sampling locations (wells), sample type, and land use. Data for the piezometric map, geology, and land use are from Larocque et al. (2015).

Figure 2. Pollutant concentrations in the study area; a) pharmaceutically active compound (PhAC) concentrations (33 sampled wells), b) pesticide concentrations (33 sampled wells), and c) nitrate concentrations and presence of *E. coli* (190 sampled wells).

Figure 3. Spatial distribution of the Anthropic Footprint Index (AFI) in the study area.

Figure 4. The Anthropogenic Footprint Index (AFI) in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and total pharmaceutically active compounds (PhAC) concentrations.

Figure 5. Recharge in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, b) total pesticide concentrations and total concentrations of pharmaceutically active compounds (PhACs), and c) groundwater residence time.

Figure 6. The Hydrogeochemical Vulnerability Index (HVI) in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and total concentrations of pharmaceutically active compounds (PhACs).

Regional assessment of concentrations and sources of pharmaceutically active compounds, pesticides, nitrate, and *E. coli* in post-glacial aquifer environments (Canada)

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Abstract

There is growing concern worldwide about the exposure of groundwater resources to pharmaceutically active compounds (PhACs) and agricultural contaminants, such as pesticides, nitrate, and Escherichia coli. For regions with a low population density and an abundance of water, regional contamination assessments are not carried out systematically due to the typically low concentrations and high costs of analyses. The objectives of this study were to evaluate regional-scale contaminant distributions in untreated groundwater in a rural region of Quebec (Canada). The geological and hydrogeological settings of this region are typical of post-glacial regions around the world, where groundwater flow can be complex due to heterogeneous geological conditions. A new spatially distributed Anthropogenic Footprint Index (AFI), based on land use data, was developed to assess surface pollution risks. The Hydrogeochemical Vulnerability Index (HVI) was computed to estimate aquifer vulnerability. Nine wells had detectable concentrations of one to four of the 13 tested PhACs, with a maximum concentration of 116 ng.L-1 for benzafibrate. A total of 34 of the 47 tested pesticides were detected in concentrations equal to or greater than the detection limit, with a maximum total pesticide concentration of 692 ng.L-1. Nitrate concentrations exceeded 1 mg.L-1 N-NO3 in 15.3% of the wells, and the Canadian drinking water standard was exceeded in one well. Overall, 13.5% of the samples had detectable E. coli. Including regional-scale sources of pollutants to the assessment of aquifer vulnerability with the AFI did not lead to the identification of contaminated wells, due to the short groundwater flow paths between recharge and the sampled wells. Given the occurrence of contaminants, the public health concerns stemming from these new data on regional-scale PhAC and pesticide concentrations, and the local flow conditions observed in post-glacial terrains, there is a clear need to investigate the sources and behaviours of local-scale pollutants.

Keywords: Groundwater, post-glacial geology, pharmaceutically active compounds (PhACs), pesticides, nitrate, *E. coli*, vulnerability

1. INTRODUCTION

As groundwater pollution increases worldwide (UNEP, 2003), assessing aquifer vulnerability to contamination is a priority for governmental agencies at all levels. Groundwater pollution from pharmaceutically active compounds (PhACs), pesticides, nitrate, and bacteria can originate from various sources (e.g., inorganic and organic fertilizers, individual septic systems, wastewater collection pipes, landfills). The presence of certain types of molecules in groundwater has already been linked to the leakage of buried infrastructure, among other determinants (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Marsalek, 2008). Because PhACs and pesticides are typically detected in low concentrations in groundwater, and have high analytical costs, regional-scale assessments of their presence in aquifers are rarely available. As these compounds are not often analyzed in routine groundwater monitoring, and because it is often difficult to identify their origins and locations of influx into the aquifer, their potential contributions to aquifer contamination and vulnerability are often poorly understood.

PhACs have been increasingly detected in groundwater around the world over the past decades (US EPA, 1993; Ma et al., 2015; Lopez et al., 2015). Among others, these include molecules that compose sleeping pills, painkillers, contraceptives, and anti-depressants (Lapworth et al., 2012; Sorensen et al., 2015). PhACs are associated with urban areas or wastewater treatment zones, and can also be linked to agricultural activity (e.g., pharmaceuticals from animal feedlots, biosolid application, etc.; Prosser and Sibley, 2015). Pesticides are increasingly detected in groundwater from a variety of environments (Köck-Schulmeyer et al., 2014; Lopez et al., 2015; Zhao and Pei, 2012). These can be from agricultural sources, but can also originate from municipal or residential water uses (e.g., golf courses, parks, and residential gardening). PhAC and pesticide molecules are typically difficult to trace in groundwater. Sorption to organic matter and clay minerals, ion exchange in the soil and aquifer, and microbial

degradation can modify PhAC and pesticide concentrations in groundwater (Lapworth et al., 2012). Studies carried out in the USA (Barnes et al., 2008; Focazio et al., 2008; Kolpin et al., 2004) and in European countries (Jurado et al., 2012; Loos et al., 2010, 2009; Stuart et al., 2012) have shown the ubiquitous presence of PhACs and pesticides in groundwater in a wide variety of geological and climatic conditions. This situation, in combination with the limited understanding of their cumulative, chronic, and long-term effects on humans and ecosystems (see references in Barnes et al., 2008), make assessing their current concentrations urgent.

Several studies have shown the presence of high nitrate concentrations in groundwater in different regions around the world, often linked to agricultural sources (e.g., Czekaj et al., 2015; Pérez-Martin et al., 2016; Pisciotta et al., 2015; Rojas Fabro et al., 2015). Nitrate concentrations are frequently used to assess groundwater vulnerability, because of their low reactivity and relatively limited transformation in groundwater (Rodriguez-Galiano et al., 2014), as well as the low costs associated with their analysis. Similarly, bacterial counts are used as indicators of the impact of human activity in contamination and vulnerability studies (Scott et al., 2002), allowing human and animal sources of contamination to be discriminated from others (e.g., *Escherichia coli* is only found in feces). Bacteria can be linked with agricultural sources (manure spreading and storage) and to private and municipal wastewater collection and treatment.

Groundwater vulnerability assessment methods include the DRASTIC index (Aller et al., 1987), the AQUIPRO method (Chowdhury et al., 2003), the LHT method (Mansoor et al., 2014), and, more recently, methods based on groundwater isotopic (Murgulet and Tick, 2013) and major ion geochemistry (Meyzonnat et al., 2016). These semi-quantitative methods are often used as first assessment in groundwater resource management, and generally do not indicate specific potential contaminant sources. Different studies have attempted to improve these methods by identifying a link between land use, contaminant sources, and groundwater contamination (e.g.,

Bojórquez-Tapia et al., 2009; Zhou et al., 2012; Chen et al., 2013; Murgulet and Tick, 2015). Land use data has the potential to determine zones of contamination risk as a function of the type of human activity occurring on the ground, notably relating the extent of agricultural and urban areas to specific contaminant types. However, such links are often unclear because of the dynamic nature of groundwater flow, and the reactivity of contaminants in different geological environments (Fatta-Kassinos et al., 2011; Kormos et al., 2010; Salgado et al., 2013; Schulz et al., 2008). The conditions in which it is useful to seek a source-contaminant link remain to be demonstrated.

Groundwater vulnerability assessment is a particular challenge in post-glacial geological environments, where bedrock aquifers are often overlain by a complex stratigraphy of more or less permeable sediments. These conditions produce highly heterogeneous recharge and percolation pathways through which the contaminants reach the groundwater, which create complex flow conditions and a combination of short and long flow paths that are not often well understood (Cassidy et al., 2014; Fleckenstein et al., 2006). This type of environment is encountered in many regions covered by the last glaciation in Northern America (Dyke, 2004). Similar geological environments and hydrostratigraphic contexts are also found in Fenno-Scandinavia (Harff et al., 2011), as well as in northern Germany and Denmark (Scheck and Bayer, 1999; Thomsen et al., 2004).

In cold and humid climates, such as southern Quebec (Canada), where water sources are abundant, groundwater contamination from anthropogenic sources in aquifers often remains relatively poorly understood. There are very few studies on emerging groundwater contaminants in Quebec, but research in other Canadian provinces has shown that PhACs can be found in wells and treated sewage effluents (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Kleywegt et al., 2007). Although few studies have focused on the presence of pesticides in groundwater in

Canada, this is becoming a concern in some parts of the country (CLE, 2015; Environment Canada, 2012; Giroux and Sarrasin, 2011; Giroux, 2010; Woudneh et al., 2009). Pesticides and their metabolites have also been identified in fluvial wetlands near intensive agricultural activity (Poissant et al., 2008). The presence of nitrate in Quebec groundwater has certainly been the most frequently investigated contaminant, generally revealing low concentrations (Carrier et al., 2013; Giroux and Sarrasin, 2011; Giroux 2003; Levallois et al., 1998; Meyzonnat et al., 2016; Quebec, 2004a), which nonetheless often exceed the natural (non-anthropogenic) background of 1 mg N-$NO_3.L^{-1}$ (Dubrovsky et al., 2010).

The objective of this study was to evaluate the distribution of PhACs, pesticides, nitrate, and bacteria in untreated groundwater in the low population density Centre-du-Quebec region of the St. Lawrence Lowlands (Quebec, Canada), as an example of contaminant distribution in post-glacial regions around the world. This research was carried out as part of a regional-scale aquifer characterization study on the Nicolet River watershed and on the lower portion of the Saint-François River watershed, both located in the Centre-du-Quebec region (Larocque et al., 2015). Related geological contexts, aquifer confinement, soil and crop types, spatially distributed recharge, major ion analyses (fully described in Saby et al., 2016), and a DRASTIC index map are also included in the Larocque et al. (2015) report. Presented here are results from groundwater sampling undertaken to assess the presence of nitrates, bacteria (*E. coli*), pesticides, and PhACs. A new Anthropogenic Footprint Index (AFI) was developed, based on the estimated density of agricultural and urban areas, both considered to be potential sources of contamination. The Hydrogeochemistry Vulnerability Index (HVI), developed recently by Meyzonnat et al. (2016), was used to provide an alternate estimate of aquifer vulnerability, based on major ion analyses reported by Saby et al. (2016). Statistical analyses were performed to assess explanatory factors for the water quality results, using the spatially distributed data reported in Larocque et al.

(2015) for presence of a crop, crop type, soil drainage, aquifer confinement, aquifer type, and recharge.

2. STUDY AREA

2.1 Geology and hydrogeology

The study area (4584 km^2) corresponds to the Nicolet River watershed and to the lower portion of the Saint-François River watershed, in the Centre-du-Quebec administrative region (Figure 1a). The regional fractured aquifer is composed of rocks belonging to two geological provinces: the Appalachian Mountains in the southeastern portion of the basin, and the St. Lawrence Platform in the northwestern portion. Geographically, the two geological provinces are part of the St. Lawrence Lowlands.

The St. Lawrence Platform is a Cambrian-Lower Ordovician siliciclastic and carbonate platform, formed in an extensional context related to the opening of the Iapetus Ocean and overlain by Middle-Late Ordovician foreland carbonate-clastic deposits, deposited during the closure of Iapetus and the Appalachian Mountains buildup. In the Appalachian piedmont, outcropping terrains are the Cambrian green and red shale of the Sillery Group, and the slate, limestone, and sandstone conglomerate of the Bourret Formation. The schist of the Drummondville Olistostrome, the calcareous slate of the Bulstrode and Melbourne Formation, as well as the schist, shale, sandstone, and conglomerates of the Shefford, Oak Hill, and Sutton-Bennett Groups (Globensky, 1993) are also present.

Unconsolidated Quaternary fluvioglacial deposits cover the fractured Paleozoic aquifer (Lamothe, 1989). Basal deposits are tills from the last two Quaternary deglaciation episodes, followed by glaciolacustrine, sandy, and organic deposits. A thick clay layer, deposited during the Champlain Sea episode following the last deglaciation, covers sandy deposits over a strip of

30 km along the St. Lawrence River (Lamothe and St-Jacques, 2014). This clay creates confining conditions for the underlying fractured bedrock aquifer. Further upgradient, a flat area composed of sand, patches of clay, and shale induces a heterogeneous and semi-confined hydrogeological context, while still further upgradient, the outcropping of reworked till and bedrock leaves the fractured aquifer unconfined in its main recharge area (Figure 1b).

The study area is divided into two main aquifer systems, further described in Larocque et al. (2015): the shallower Quaternary aquifers of relatively limited thickness and extent, and the underlying Paleozoic fractured bedrock aquifer, composed of sedimentary rocks. Hydraulic conductivities in the fractured bedrock aquifer are heterogeneous and range from $5x10^{-9}$ $m.s^{-1}$ to $7x10^{-6}$ $m.s^{-1}$. Confining zones have previously been estimated using a 3D model of the Quaternary sediment architecture, based on the thickness of the impermeable units. Results were interpolated over 250 m x 250 m cells (see Figure 1b). Confined conditions were defined as when either more than 3 m of clay or more than 5 m of compact till were present. Semi-confined conditions corresponded to areas where 1 to 3 m of clay or 3 to 5 m of compact till were found. Unconfined conditions referred to areas where less than 1 m of clay and less than 3 m of compact till were found. Unconfined zones were found to represent 55% of the studied surface area, while semi-confined and confined zones represent 18% and 27% respectively (Larocque et al., 2015).

2.2 Previously available data

The spatially distributed water budget of the study area was described in detail by Larocque et al. (2015). The 1961-2010 average annual temperature for the study area was 5.6°C, and the average annual precipitation was 1018 mm (25% falls as snow; Nicolet and Drummondville stations; Environment Canada, 2012). Precipitation usually falls as snow between the months of November and March. The average annual recharge of the fractured bedrock is 152 $mm.yr^{-1}$ for

the 1989-2009 period. Recharge occurs preferentially in the Appalachian piedmont, while it is almost nonexistent under the clay layer of the Champlain Sea. The piezometric map (Figure 1a) shows that groundwater flow directions are generally from the Appalachian Piedmont towards the St. Lawrence River. However, Larocque et al. (2015) have demonstrated that there is only limited regional-scale groundwater flow, and less than 1 $mm.yr^{-1}$ flowing into the St. Lawrence River, with the many rivers and streams locally draining the bedrock and granular aquifers. The mean water table depth is 4.4 m.

Groundwater geochemistry evolves from a Ca-HCO_3 water type at recharge, which corresponds mainly to the Appalachian piedmont, to a Na-HCO_3 water type downgradient, closer to the St. Lawrence River. Geology and rock-water interactions control the regional evolution of groundwater chemistry (Saby et al., 2016). $^3H/^3He$ groundwater ages range from 4.8±0.4 years in the upgradient portion of the study area, to more than 60±3.2 yrs in its downgradient portion (Saby et al., 2016). SF_6 residence times reported in Larocque et al. (2015) show values of a similar magnitude, between 1±0.5 year upgradient of the study area, where the Quaternary deposit cover is thin and recharge is direct, and 34±5.6 years downgradient. Saby et al. (2016) also calculated older ^{14}C groundwater ages, from 280±56 to 17050±3410 years. These results clearly indicate mixing between modern groundwater and a paleo-groundwater component circulating slowly in the deepest, less permeable layers of bedrock, creating this apparent contradiction in age (Vautour et al., 2015; Saby et al., 2016). Older groundwater likely infiltrated the bedrock aquifer through subglacial recharge when the Laurentide Ice Sheet covered the study area (Saby et al., 2016).

Larocque et al. (2015) present a crop type map built from a database of insured crop acreage (Martineau, 2014). A total of 48% of the studied surface area is dedicated to agriculture, mainly along the St. Lawrence River, while forest covers 45% of the area, principally in the Appalachian

piedmont (Figure 1c). Wetlands, urban areas, and surface water occupy 3.7%, 2.0%, and 1.1% of the region respectively. A detailed description of the study area is found in Larocque et al. (2015). Agriculture is dominated by cereal (54%) and hay (22%) production, with a minor presence of mixed crops, vegetables, and small fruit production (3%) located mainly in the lower part of the study area where the bedrock aquifer is covered by Champlain Sea clay. No information is available for the remaining 21% of the study area. The study area is considered to be among the most agriculturally productive in the province of Quebec (UPA, 2012).

Larocque et al. (2015) have built a soil drainage map using data from the database of the *Institut national de recheche et de développement en agroenvironnement* (IRDA, 2013). For the lower and central parts of the study area, soil drainage varies from very well drained to poorly drained. Sandy soils dominate in this area, but clay soils are also present in a spatially heterogeneous matter. In addition to sand and clay, discontinuous till covers the lower portion of the study area, and is increasingly visible towards the Appalachian piedmont. The Appalachian area is dominated by till soils ranging from well to poorly drained. Organic deposits are also present as peatlands in the central portion of the study area.

Larocque et al. (2015) computed the DRASTIC index (Aller et al., 1987) for 500 m x 500 m cells for the bedrock aquifer of the study area using the usual parameters and associated parametric weights (see annex A1 for details of the method). Vulnerability values of the DRASTIC index for the bedrock aquifer vary from 24 to 185 for the study area. Quebec legislation (Quebec, 2015) labels “low vulnerability” regions as those where the DRASTIC index is below 100, “medium vulnerability” regions as those where the DRASTIC index is between 100 and 180, and “high vulnerability” regions as those with a DRASTIC index above 180 (see Figure 1 in annex A1). Based on these categories, 28% of the study area is low vulnerability and 72% is medium vulnerability. Only 0.02% of the area is high vulnerability. The medium and high

vulnerability areas are located in the Appalachians, where recharge is high and sediment cover is thin. A vast portion of the central part of the study area is also characterised by medium vulnerability, mainly because of the high water table and the high permeability of the sediment. The lower part and some areas around the Saint-François and Nicolet Rivers in the central section are of low vulnerability. The thick clay layer combined with low recharge rates explain these low DRASTIC values.

In the study area, 56% of the groundwater extracted for drinking water, for agriculture, or for industrial use is done so through individual wells (Larocque et al., 2015). It is estimated that a similar proportion of the houses are linked to private septic tanks. In the larger municipalities, such as Victoriaville and Drummondville, wastewater is collected through a municipal network connected to a wastewater treatment plant. In rural areas, individual properties collect wastewater in private septic tanks.

3. METHODS

3.1 Groundwater sampling and analysis

Between June and August 2013, 190 groundwater samples were collected from private wells (157 wells), municipal wells (11 wells), 1" PVC observation wells (12 wells), and 6" steel tubing observation wells (10 wells) (see locations in Figure 1c and well descriptions in Table A1). Well depths range between 5 and 250 m for the 145 open borehole bedrock wells, and from 1.2 to 50 m for the 45 wells taping a granular aquifer (granular wells either have a steel casing or are drive points). All samples were analyzed for nitrate and *E. coli*. Major ion data (Ca^{2+}, Na^{2+}, Mg^{2+}, K^{+}, and HCO_3^-, SO_4^{2-}, Cl^-) are available for all the wells and are reported in Saby et al. (2016). In September 2014, 33 wells were resampled (six private wells, nine municipal wells, 11 1" PVC observation wells, and seven 6" steel tubing observation wells). This water was analyzed for 13

different PhAC compounds (antibiotics, beta-blockers, mood stabilizer and anticonvulsant, antilipemic agents, chemotherapy medication, and prescription and non-prescription non-steroidal anti-inflammatory agents) and 46 different pesticides (herbicides, fungicides, and insecticides; see list of PhAC and pesticide molecules analyzed in Table A2).

All the wells were purged prior to sampling, and water was sampled prior to any treatment once the physiochemical parameters (pH, temperature, redox potential, and electric conductivity) measured in an air-tight cell had stabilized (MDDELCC, 2011). Groundwater was collected from the observation wells using a submersible pump with speed control (Redi-Flo2®), maintaining the whole sampling line under pressure to prevent water degassing. All samples were filtered in the field to 0.45 µm. Samples were kept at 4°C during storage and transport. Samples for PhACs and pesticides were collected in 1L Nalgene® bottles, and were sent to the Environmental Engineering Laboratory of the University of Sherbrooke for analysis. The samples were first extracted using a solid phase extraction procedure, and the liquid phase was then analyzed by liquid chromatography coupled with a triple quadrupole mass spectrometer (Ba et al., 2014; Haroune et al., 2014). The detection limit of the method for pesticides and PhACs was 5 $ng.L^{-1}$. The calibration was validated by verifying the calculation of the deviation for each point (criteria < 20%). Each series of samples was validated for a spiked sample (recovering criteria between 70% - 120%). No field blanks or duplicates were analyzed for pesticides or PhACs because of the high analytical cost. Groundwater for nitrate analysis was sampled in 125 ml Nalgene® bottles and analyzed by colorimetry in a private laboratory (ISO/CEI 17025), with a detection limit of 0.1 mg $N\text{-}NO_3.L^{-1}$. Laboratory blanks for nitrate analyses were done systematically for each sample, but no field blank was taken. A total of 10 duplicates were sampled for the 190 samples analyzed for nitrate.

Groundwater was also sampled for bacteria content, in 250 ml Nalgene® bottles, kept at 4°C during storage and transport, and sent daily to a private laboratory. *E. coli* was analyzed using the presence/absence method, meaning that each *E. coli* bacteria is counted if present (SOP-BA-076; ISO/CEI 17025). This method relies on the « 9223 B. ENZYME SUBSTRATE TEST » of the *Standard Methods for the Examination of Water and Wasterwater* reference manual (APHA, AWWA and WEF, 2012). Of the 190 samples analyzed for bacterial counts, duplicates of ten were analyzed.

3.2 Anthropogenic Footprint Index (AFI) and Hydrogeochemical Vulnerability Index (HVI)

The Anthropogenic Footprint Index (AFI) developed in this study is derived from the farm density (FD) and anthropic activity density (AAD) data presented in Larocque et al. (2015). FD is the number of farm buildings per square kilometer. AAD is a weighted sum of risks per square kilometer. AAD takes into account the types of anthropic activity (punctual infrastructures) and their impact in terms of groundwater pollution risks. This method was adapted from similar projects in the United States and elsewhere in the world (Foster and Hirata, 1998; EPA Office of Water, 1991; SESAT, 2010). Each parameter is weighted following the methodology presented in Larocque et al. (2015), and the overall impact is calculated as follows:

$$AAD = (TC + CQ + IZA)\ x\ RCD \qquad \text{(eq. 1)}$$

where TC is the weighted sum of contaminant toxicity, CQ is the weighted sum of contaminant quantities, IZA is the weighted sum of impacted areas, and RCD is the recurrence of contaminant discharge. The contaminants used for each type of anthropic activities were derived from a study by the Oregon Government (1996). The weight of contaminant toxicity is associated with the

type of activity and depends on the toxicity classification of the Workplace Hazardous Materials Information System (WHMIS) (CSST, 2007). The weight of the contaminant quantity is based on contaminant quantity and concentration for a given anthropogenic activity (modified from SESAT, 2010). The impacted area refers to the potential extent of the activity (punctual, local, or regional). Finally, contaminant discharge is either recurrent (systematic and linked to the activity itself), or accidental. Each parameter is evaluated qualitatively, assigned to one of four classes (low, moderate, high, very high), and weighted following the tables available in Larocque et al. (2015). The parameters required to calculate the FD and AAD were extracted from a property assessment database describing the type of anthropic activity (MAMROT, 2010). The AAD values were computed for each point of anthropic activity on the land surface and were interpolated on a 250 m x 250 m grid.

The AFI cumulates the spatially distributed density values and therefore reflects the cumulated potential sources of contamination (Eq. 1). The AFI is mapped on 250 m x 250 m cells over the study area, similar to the FD and AAD. The AFI can vary between 0 (low risk) and 100% (maximum risk).

$$AFI = 100\left(\frac{FD}{FD_{max}} + \frac{AAD}{AAD_{max}}\right) \qquad \text{(eq. 2)}$$

The Hydrogeochemistry Vulnerability Index (HVI; Meyzonnat et al., 2016) uses major ion geochemistry to identify the presence of recently infiltrated water and water from further locations in a given well. This index is based on the evolution of groundwater geochemistry from recharge areas to more confined regions of a study area. It relates this evolution to the vulnerability of a bedrock aquifer by comparing the geochemistry with nitrate concentrations for each well (Meyzonnat et al., 2016). The HVI is then extrapolated to draw a portrait of the aquifer

vulnerability at a regional scale. It is calculated by plotting ($Na^+ - Cl^-$) against ($Ca^{2+} + Mg^{2+}$) – ($HCO_3^- + SO_4^-$). The HVI graphically illustrates how the groundwater chemical composition evolves from a (Ca, Mg)-HCO_3 type in the recharge area to a Na-HCO_3 type downgradient along a flow path. The HVI can vary between 0 (low vulnerability) and 10 (maximum vulnerability) along the linear regression from its orthogonal projection. In this study, the HVI was calculated using the major ion concentrations measured at the sampling points as reported in Saby et al. (2016).

3.3 Statistical analysis

The mean PhAC, pesticide, and nitrate concentrations for different site parameters (crop type, presence of a crop, soil drainage, aquifer confinement, aquifer type, and recharge) were compared using the Student-T test. *E. coli* data (presence or absence) were analyzed using a contingency table and the Chi-2 test. All the statistical analyses were done using JMP software (SAS Institute, 2012), and a confidence level of 0.05. Sampling points with missing data were excluded. For PhAC, pesticide, and nitrate data, concentrations were used in the analysis. Bacterial counts were transformed into a binary presence or absence. Crop type was assigned to the sampling points using the proximity tool of ArcGIS (ESRI, 2016), with a radius of 500 m set as the search criteria. Three crop types were considered; “absence of a crop”, “cereals”, and “hay”. “Market garden” and “mixed crop” types were excluded from the analysis because of the limited number of samples in each category (one and four respectively). The seven soil drainage categories were reclassified into two categories, “well drained” (from previous “relatively well drained”, “well drained”, “very well drained”, and “extremely well drained” categories), and “poorly drained” (from previous “very poorly drained”, “poorly drained”, and “imperfectly drained” categories). The aquifers tapped by the sampled wells were categorized as

"unconfined", "semi-confined", and "confined". Aquifer type was categorized as "granular" or "bedrock". Recharge was divided into three categories: "low" for recharge values of less than 100 $mm.yr^{-1}$, "average" for recharge values between 100 and 200 $mm.yr^{-1}$, and "high" for recharge values of higher than 200 $mm.yr^{-1}$. The influence of water table depth and well depth was analyzed for all parameters and all contaminants, but results are not reported here since they were insignificant for all analyses.

4. RESULTS

4.1. Contaminant occurrence

PhAC compounds were detected for four of the 13 tested molecules in nine of the 33 tested wells (27%), and the average total PhAC concentration was 9 $ng.L^{-1}$ (Figure 2a and Table A3). The highest concentration of PhAC was found in a well in the granular deposits of the Appalachian piedmont (NSF504), where 133 $ng.L^{-1}$ of benzafibrate was measured. There are no drinking water quality standards for PhAC molecules in Canada or elsewhere. Major areas of low or undetectable concentrations of pesticides and PhACs were located in the less populated areas and in forested zones. None of the tested parameters explained the differences observed in pesticide concentrations between the sampled wells (Table A4), and there was no clear link between well depth and PhAC concentrations.

Pesticides were detected for 34 of the 47 tested molecules (Figure 2b and Table A5), and 23 of the 33 sampled wells (70%) had at least one detected compound. None of the pesticide concentrations exceeded the Canadian drinking water quality standards (MDDELCC, 2011). The highest total pesticide concentration was 692 $ng.L^{-1}$, in a municipal well tapping a semi-confined granular aquifer in the Appalachian piedmont (NSF177). None of the tested parameters (crop type, soil drainage, aquifer confinement, aquifer type, or recharge) explained the observed

differences in pesticide concentrations between the sampled wells (Table A6). No clear link was observed between well depth and pesticide concentrations.

A total of 29 wells (15.3% of all sampled wells) had nitrate concentrations higher than the natural background of 1 $mg.L^{-1}$ $N\text{-}NO_3$ (Dubrovsky et al., 2010) (Figure 2c and Table A2). The majority of the wells (62.6%) had nitrate in concentrations of less than the 0.1 $mg.L^{-1}$ $N\text{-}NO_3$ detection limit. The maximum nitrate concentration, 12 $mg.L^{-1}$ $N\text{-}NO_3$, was measured in well NSF250, a granular well located upgradient in the Appalachian piedmont. This is the only well exceeding the drinking water quality standard of 10 $mg.L^{-1}$ $N\text{-}NO_3$ (Health Canada, 2014). The average nitrate concentration of all wells was 0.63 $mg.L^{-1}$ $N\text{-}NO_3$. On average, wells near fields with hay crops had a significantly higher nitrate concentration (1.04 $mg.L^{-1}$ $N\text{-}NO_3$) than those near fields which were not cultivated (0.16 $mg.L^{-1}$ $N\text{-}NO_3$; $p=0.0297$) (Table A7). However, the simple presence of a crop near a well alone does not explain nitrate concentrations ($p>0.05$). Well drained soils had significantly higher concentrations (1.01 $mg.L^{-1}$ $N\text{-}NO_3$) than poorly drained soils ($p=0.0241$). The average nitrate concentration in wells tapping an unconfined bedrock aquifer (1.05 $mg.L^{-1}$ $N\text{-}NO_3$) was significantly higher than that in wells in semi-confined conditions (0.21 $mg.L^{-1}$ $N\text{-}NO_3$; $p=0.0022$), and that in wells in confined conditions (0.16 $mg.L^{-1}$ $N\text{-}NO_3$; $p=0.0017$). The average nitrate concentration for wells in a granular aquifer (1.16 $mg.L^{-1}$ $N\text{-}NO_3$) was significantly higher than for wells in the Ordovician bedrock aquifer (0.47 $mg.L^{-1}$ $N\text{-}NO_3$; $p=0.0060$). The three wells with nitrate concentrations higher than 7 $mg.L^{-1}$ $N\text{-}NO_3$ were located in granular aquifers.

Overall, 13.5% of the samples had detectable *E. coli*. The spatial distribution of bacterial contamination was highly heterogeneous throughout the area, and contamination was found in agricultural and in urbanized areas alike. None of the other tested parameters (crop type, presence

of a crop, soil drainage, aquifer confinement, aquifer type, or recharge) explained the presence or absence of bacteria in the sampled wells (Table A8).

4.2. AFI and HVI identified areas of contamination risk

The AFI was used to identify zones of potential contamination risk related to land use (Figure 3). In the 190 wells sampled for nitrate and bacteria, the AFI varied between 1 and 38%, with an average of 15%. The highest AFI values (i.e., the maximum value in the whole study area; 42%) was observed in the intensive agricultural zones of the lower part of the study area. The two largest municipalities in the study area, Victoriaville and Drummondville, also had AFI values of 42%. The lowest AFI values were mainly found in the forested zones located in the central and upper parts of the study area.

The mean HVI value was 8.5 (median of 9.1), ranging from a minimum value of 1 (NSF 147) to the highest value of 10 (NSF 150; Table A1). Overall, the highest values were found in the Appalachian piedmont, where recharge is greatest, and the lowest values were located in the lower portion of the study area, where the Champlain Sea clay largely limits groundwater recharge.

5. DISCUSSION

5.1. Groundwater contamination

The drinking water quality standards were exceeded in only a limited number of wells (i.e., 13.5% of the wells for *E. coli*, one well for nitrate, and in none of the sampled wells for pesticides; there are no drinking water quality standards for PhACs). However, the results presented here have shown that groundwater in the study area is affected by all four contaminant types. This ubiquitous presence of PhAC and pesticides is similar to that reported in other studies

(see summary in Lapworth et al., 2012), but was unexpected given the low population density in the study area.

The absence of a significant correlation between the tested parameters and PhAC or pesticide concentrations could be due to the limited number of wells sampled (n = 33), and does not conclusively exclude a relationship or a causal effect. The highest PhAC concentrations were not able be linked to agricultural or urban areas through the AFI. The low occurrence of PhAC (27% of the tested wells had at least one PhAC) could be related to the low population density and to the limited number of wells that were sampled near the denser population areas, whereas PhAC sources are expected to be higher due to the presence of public water distribution networks. This could also be related to the fact that some of the tested molecules have only recently been in use. Concentrations could therefore increase with time if these compounds remain in use. Nonetheless, these results indicate a clear anthropogenic impact on groundwater resources. They figure among the few reported studies of this type for Canadian aquifers, and are the first at the regional scale for the province of Quebec.

The measured concentrations of pesticides were below the Canadian drinking water quality standards (MDDELCC, 2011). The average total pesticide concentration was 67 $ng.L^{-1}$, which is lower than the European limit for cumulated pesticides, of 500 $ng.L^{-1}$ (CUE, 1998; there is no total pesticide water quality standard in Canada). The European limit was exceeded in one well (692 $ng.L^{-1}$; NSF177, a municipal well tapping a confined granular aquifer), and was near the European limit in another well (479 $ng.L^{-1}$; NSF-R6, an observation well in the bedrock aquifer). These two wells are located upgradient, in the Appalachian piedmont, in areas where agricultural land surrounds the wells. The higher occurrence of pesticides in the tested wells (70%) compared to PhACs could be explained by more regionally distributed sources of the contaminant.

The measured nitrate concentrations are similar to those reported in other studies from southern Quebec (Carrier et al., 2013; Giroux and Sarrasin, 2011; Levallois et al., 1998; Meyzonnat et al., 2016; Quebec, 2004a). It is interesting to highlight that higher concentrations of nitrate, exceeding the drinking water quality standard (between 11 and 72 $mg.L^{-1}$ $N\text{-}NO_3$), have been reported for shallow unconfined wells in a granular aquifer of the study area (e.g., BPR and Arrakis consultants, 2004). When comparing results from the current study with the previously available DRASTIC index values, the bedrock wells located in areas where the DRASTIC index was categorized as "medium" have significantly higher nitrate concentrations (0.52 $mg.L^{-1}$ $N\text{-}NO_3$) than those located in areas where the DRASTIC index was categorized as "low" (<0.1 $mg.L^{-1}$ $N\text{-}NO_3$; $p=0.0278$). Similar to these results, a study in the Lanaudiere region of southern Quebec showed a correlation between nitrate concentrations and the DRASTIC index (Quebec, 2004a), with stronger correlations for wells tapping granular aquifers than for deep bedrock wells. In the current study, the limited proportion of concentrations higher than the anthropogenic background could be related to the presence of agricultural drainage, which transports nitrate to surface water before it can infiltrate to groundwater (Thériault, 2013). Poorly drained soils with high organic contents could also be more anoxic, and thus produce nitrate-reducing conditions (Vogel et al., 1981; Liao et al., 2012). Denitrification tends to happen more often in soils and aquifers with high organic carbon content, and therefore can sometimes be an important factor for nitrate removal. However, the sampling density combined with the relatively low nitrate concentrations in groundwater makes it difficult to assess this effect in the study area.

The observed bacteria (*E. coli*) occurrence in 13.5% of the sampled wells was similar to that reported by Leblanc et al. (2013) for the lower part of the Saint-Maurice River watershed in southern Quebec (*E. coli* present in 12 % of all sampled wells). Considering the relatively short residence time of *E. coli* in saturated conditions, Leblanc et al. (2013) concluded that bacterial

contamination was caused mainly by local processes, such as the proximity of a private sewage system, or poor well construction or maintenance. Although the effect of aquifer type was not clear in the current study, the Lanaudiere study (Quebec, 2004b) showed a higher occurrence of *E. coli* in granular aquifers, with 49% of the granular wells having a positive detection. The highly heterogeneous coverage of Quaternary post-glacial deposits in the study area could explain the absence of significant correlations between the presence of bacteria and the tested parameters. Interestingly, the average nitrate concentration in the wells where *E. coli* was detected was significantly higher compared with the wells where no *E. coli* was detected (1.61 $mg.L^{-1}$ N-NO3 versus 0.44 $mg.L^{-1}$ N-NO_3 respectively; p=0.001). This could be due to the combination of manure spreading with other fertilizer application in agricultural areas.

Contaminants can be more or less reactive with their environment, depending on several parameters, such as their half-life in water, their adsorption coefficients, and their reactivity to sunlight (Kleywegt et al., 2007; USDA, 2009). PhACs and pesticides, for example, can have relatively short half-lives, some transforming into by-products, and are easily adsorbed on soil and organic matter particles. The spatial variability in measured concentrations reflects different land uses, and chemical processes (e.g., adsorption, desorption, degradation, complexation) occurring at the land surface, in the unsaturated zone, and in the aquifer. It can also be due to surface and water infiltration conditions, such as the quantity of applied nitrate or pesticides, the concentrations of PhACs in the wastewater source, the soil pH, or the oxygen content of the groundwater.

Interestingly, the PhACs with the lowest log K_{ow} (octanol/water partition coefficient; the lower the log K_{ow}, the more highly soluble in water and potentially the more mobile in groundwater; see Table A2 for the list of calculated log K_{ow} values), were not the most frequently detected. Among the compounds with log K_{ow} of lower than one, only the PhAC trimethoprim

was detected (in three wells). Counterintuitively, the PhAC mefenamic acid, which has the highest log K_{ow}, was detected in the highest number of wells (seven). Similarly to PhAC compounds, the low log K_{ow} pesticides were not the most frequently detected. Aldicarb-sulfone (log K_{ow} = -0.57) and imidacloprid (log K_{ow} = 0.57) were detected in only one well. Another soluble pesticide was not detected (dimethoate, log K_{ow} = 0.78) while chlotianidin (log K_{ow} = 0.70) was detected in two wells. Permethrin, a pyrethroid compound frequently used in agriculture and for municipal uses, was detected in two wells (PZ2, a 9.1 m observation well in the unconfined surface sediments, and NSF177, a 39.0 m municipal well taping a semi-confined granular aquifer). This was unexpected since this insecticide has the highest log K_{ow} of the tested pesticides (log K_{ow} = 6.50) and is generally considered to be highly adsorbed. All the pesticides with a log K_{ow} of higher than 4 were detected in one or more wells. The most frequently detected pesticides (kresoxim-methyl, in 9 wells; trifloxystrobin, in 7 wells; piperonyl butoxide, in 7 wells) had log K_{ow} of equal to or higher than 3.40.

These results indicate that the PhAC compounds and pesticides considered to have low leaching potential can reach an aquifer, possibly from nearby contaminated recharge and from local vertical flows. A low log K_{ow} PhAC or pesticide should thus not be considered to have low potential for groundwater contamination. Sampling cores of sediments to analyze adsorbed phases of pesticides and PhAC compounds would help to further constrain these observations. A detailed examination of pesticide applications (e.g., application method, amounts used, frequency of application, timing with respect to rain events) in the study area would help to better constrain pesticide sources.

5.2. Identifying contaminant sources with the Anthropogenic Footprint Index (AFI)

The comparison between the determined AFI values and contaminant concentrations in groundwater was intended to demonstrate a link between the risk of pollution and the presence of certain pollutants. However, the results show that neither PhAC nor pesticide concentrations in groundwater seem to be correlated with the AFI (Figure 4a). The same was observed for nitrate and the presence of *E. coli* (Figure 4b). When the FD and AAD components of the AFI were compared separately with contaminant concentrations, the relationship did not improve (results not shown). It therefore does not appear that one of the two AFI components hides the effect of the other.

The fact that the AFI is not a useful indicator of contamination could be due to the design of the index, which might not take sufficient information into account to estimate the risk of contamination from the surface. Additional information that might help to improve the indicator includes local information, such as the type of agricultural activity (crops or livestock), the type of animal waste storage, or the types and amounts of fertilizers (organic or inorganic) and pesticides used in the fields. The absence of a correlation between the AFI and the contaminants might also be explained by the fact that the presence of a potential contamination source at the surface does not necessarily result in contaminant percolation to the aquifer. In confined or semi-confined conditions, the contaminant might migrate preferentially toward surface water bodies. In fact, the results have shown that the strongest explanatory factors for nitrate concentrations and for the presence of *E. coli* were aquifer confinement (for nitrate concentrations) and aquifer type (for nitrate concentrations and for the occurrence of *E. coli*) (Table A7 and A8) . Aquifer confinement (see Figure 1b) and aquifer type (granular or bedrock) directly influence the infiltration of water and contaminants from the surface to the saturated zone. These results show that local infiltration conditions might have a greater impact on the water quality of a local well than does the presence of a contaminant or contaminants in a source located further upgradient.

The Quebec (2004a) study reported similar results, with elevated nitrate concentrations being detected more frequently when there was both a high DRASTIC index and intensive agricultural activity. The inability of the AFI index to explain contaminant occurence could also be due to the small number of sampled wells in dense urban areas, where public water distribution networks are available, in contrast with more sampled wells in rural areas, where each house has its own well.

5.3. Estimating aquifer vulnerability

5.3.1. Aquifer recharge and groundwater dynamics

Recharge is often considered to be a reliable parameter with which to estimate vertical groundwater vulnerability (Aller et al., 1987). Water percolating through the unsaturated zone reflects the nature of the soils it passes through. Therefore, the aquifer areas covered with clay will receive limited recharge, even if a potential source of contamination is present (i.e., high AFI). Conversely, an area with a high recharge rate will have very low contaminant concentrations if it is located far from agricultural areas or cities (i.e., low AFI). This is the case, for example, for some wells located in the upper portion of the study area, where recharge is high, but which are not close to potential sources of contamination (see Figure 5a). The relatively higher nitrate concentrations in areas of average recharge (between 200 and 250 $mm.yr^{-1}$) could be linked to the agricultural activities located in the middle portion of the study area, where unconfined and semi-confined conditions are found. However, this trend is not clear for either pesticide or PhAC concentrations (Figure 5b).

When comparing groundwater residence times (Larocque et al., 2015; Saby et al., 2016) with the spatial distribution of recharge, it becomes clear that groundwater travels more rapidly to the sampled wells in areas where recharge is the highest (Figure 5c). These results are consistent with

both the regional flow path of the study area, and the gradual confinement of the bedrock aquifer. Thus, the younger the groundwater, the higher the risk of finding a high contaminant concentration, if a source of contamination is present at the surface. These short residence times also point to the presence of relatively direct water flow and to possible contaminant migration between the surface and the saturated zone. Although it is also important to take attenuation factors into account, such as pesticide and PhAC degradation and adsorption on soil and the aquifer matrix, short residence times certainly increase the vulnerability of groundwater.

Post-glacial terrains, such as those found in the study area, are tridimensionally complex environments in which it is often difficult to assess recharge and groundwater residence times. This is due to the spatial heterogeneity of the permeability and the thickness of the Quaternary deposits, which determine aquifer confinement, an important parameter for nitrate migration. Intermediate confinement conditions in the Appalachian Piedmont, located in the central portion of the study area, can lead to a spatially complex juxtaposition of contrasting confinement conditions, making aquifer recharge assessment particularly imprecise.

5.3.1 ***Hydrogeochemical Vulnerability Index (HVI)***

The two wells with the highest total pesticide concentrations (NSFR6 and NSF177) also had among the highest HVI values (9.8 and 9.3 respectively) (Figure 6a). There was no apparent trend between PhAC concentrations and HVI. The comparison between nitrate concentrations and HVI (Figure 6b) showed that concentrations tended to be higher when the HVI was greater than 9 (maximum is 10), a result similar to that reported by Meyzonnat et al. (2016) in the neighboring Becancour watershed. Because it reflects the groundwater dynamics and the water-rock contact time, the HVI highlights flow conditions across different media and receiving infiltration from different land uses. The high HVI scores thus reflect the presence of

groundwater near recharge areas with Ca,Mg-HCO_3, Ca-HCO_3, and Ca-SO_4 water types, while the low scores represent increasing confinement conditions and water type evolving to Na-HCO_3 and Na-Cl types (Meyzonnat et al., 2016). The high HVI wells in recharge areas are also those where residence times are the shortest (Figure 5c), which explains their association with the highest nitrate concentrations. The weaker link observed between PhAC and the HVI, and, to a certain extent, pesticide concentrations and the HVI could be due to the small number of wells sampled for these contaminants (n = 33). It could also be explained by PhAC and pesticide degradation in the unsaturated zone. Overall, the HVI appears to be a good indicator of aquifer contamination risk from agricultural sources, but the results are less conclusive for PhAC and pesticide sources.

Results for the HVI and the DRASTIC index do not provide the same type of spatial vulnerability information because of the differences inherent to the methods. The HVI method provides information on groundwater flow paths, while DRASTIC focuses on vertical flows from the surface to the water table. Thus, in the study area, the DRASTIC and the HVI indices do not provide the same results in comparison with contaminant distributions. The HVI index correlates more strongly with NO_3, *E. coli*, and pesticide occurrences than does DRASTIC. For PhACs, the correlation is less clear for both DRASTIC and HVI. The results for nitrate are similar to those of Meyzonnat et al. (2016), who performed a complete comparison of the two methods on a neighboring watershed with similar geological conditions. These authors found that the DRASTIC index was relatively ineffective in evaluating groundwater vulnerability, while the HVI method showed a clear correlation with nitrate concentrations.

5.4. Synthesis and recommendations

This study shows that all analyzed contaminants (PhACs, pesticides, nitrate, and *E. coli*) were detected, which is a clear indication that groundwater resources in the study area are not pristine and are impacted by human activity. PhAC molecules were less prevalent than pesticides, but were nevertheless detected throughout the study area. Pesticides were widely observed, although all concentrations were below the Canadian drinking water quality standards. Pesticides and PhACs could not be linked to site parameters. The presence of a hay crop, the soil drainage, aquifer confinement, type of aquifer, and recharge are all parameters found to be significantly related to nitrate concentrations. The occurrence of *E. coli* was related to the specific set of local conditions, and could not be linked to any one site parameter in particular.

These results are expected to be of particular interest for areas in similar post-glacial environments and undergoing similar human impacts elsewhere in the world, such as Scandinavia, Denmark, Germany, and the USA (Harff et al., 2011; Scheck and Bayer, 1999; Thomsen et al., 2004; Dyke, 2004). The results will also be useful for provincial and local water management agencies, since it is the first time that regional-scale PhAC and pesticide concentrations are measured in the province of Quebec. Although no measured concentration was found to exceed drinking water standards for pesticides (and no standards exist for PhACs), the mere presence of PhACs and pesticides in groundwater used for drinking is a public health concern and justifies long-term monitoring. This recommandation stands for the study area, but also for surrounding regions set in similar high recharge post-glacial geological environments, and under the same type of land uses. Nitrate concentrations and the presence of *E. coli* have been a concern for some time, and should be monitored so as to strengthen the implementation of better agricultural practices in general. Measuring pollutant concentrations through time would also be useful in linking their presence to time-varying sources, such as the seasonality of recharge and of agricultural contaminant input, an important factor of groundwater

contaminantion which was not assessed here. Long-term monitoring is especially important since PhAC and pesticide concentrations in groundwater could increase in the next decades due to industrial and agricultural developments and to an increase in PhAC release from wastewater. This study shows that including PhAC and pesticides known or assumed to have limited leaching potential is important since they can reach the aquifer even in confined conditions. Regional scale assessment of concentrations in other regions of southern Quebec and elsewhere in Canada and in the world should also be a priority, even where population density is low.

It is currently extremely difficult to detect PhACs and pesticides in groundwater samples. Improving understanding of the behaviours of these compounds in the unsaturated zone and in the aquifer for different recharge and geological conditions is a key element in the assessment of groundwater vulnerability. Studies carried out at more local scales would contribute to better constraining how and under which conditions PhACs and pesticides migrate with groundwater and are adsorbed, or degraded into sub-compounds. More research and development is necessary to improve analytical methods and related detection limits.

The contaminants identified here indicate the influence of local conditions on the potential for well contamination. The high HVI scores found in this study, in addition to the short groundwater residence times reported by both Saby et al. (2016) and Larocque et al. (2015) confirm this observation. Larocque et al. (2015) and Larocque et al. (2013) reported that most of the recharge in the Centre-du-Quebec region is intercepted by streams and rivers, and that only limited groundwater outflow reaches the St. Lawrence River outlet. It is therefore expected that local conditions influence aquifer vulnerability, and that groundwater quality measured in wells is not substantially impacted by long-distance (i.e., regional-scale) contaminant sources. In this case, vulnerability assessment methods that have the potential to reflect local flow conditions, such as the DRASTIC index or the HVI appear to be the best options. Although successful attemps to

combine contaminant sources with the DRASTIC index have been reported in the literature (e.g., Shrestha et al., 2016), this study shows that including potential sources of contamination at the regional scale can be misleading because of local flow conditions, when the exact location of these sources is unknown. These conclusions are specific to the high recharge and post-glacial geological setting of this study area, but could be applied to similar environments elsewhere in the world. However, site-specific studies should be performed in zones suspected to be of high vulnerability so as to assess local sources of pollutants and to plan land use accordingly, regardless the type of environment.

6. CONCLUSIONS

The objective of this study was to evaluate the distribution of contaminants in untreated groundwater in a low population density region. This work was based on an extensive dataset of PhACs, pesticides, and nitrate concentrations, and *E. coli* presence. A new index, the Anthropogenic Footprint Index (AFI), was calculated with the intention of simultaneously considering agricultural and urban areas as potential contamination sources. Links were investigated between contaminant occurrence and crop type, presence of a crop, soil drainage, aquifer confinement, aquifer type, and recharge. Groundwater flow paths were estimated using the Hydrogeochemical Vulnerability Index (HVI).

The results of this study showed that groundwater quality is affected by all four contaminant types. The AFI index, which represents the source of contamination, was not found to correlate with any of the investigated contaminants, indicating that regional-scale sources of contamination are not visible in the sampled wells. The challenge of identifying contaminant sources at the regional scale was linked to the high spatial heterogeneity of the Quaternary deposits in this post-glaciated environment, which creates complex local flow directions. Notwithstanding the

importance of using regional-scale vulnerability indices such as the HVI or the DRASTIC index to refine knowledge of flow conditions in post-glacial terrains, more research needs to be done to downscale vulnerability assessments to local-scale conditions in order to pinpoint sources of contaminants and their reactivity under specific conditions. Given the occurrence of contaminants found in this study, as well as in other studies and environments throughout the world, and the public health concerns that they present, this topic deserves to be further investigated in diverse hydrogeological and land use conditions.

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Figure captions

Figure 1. Study area in the Nicolet and Lower Saint-François watersheds of southern Quebec (Canada); a) piezometric map, b) map of the bedrock confinement zones, and c) sampling locations (wells), sample type, and land use. Data for the piezometric map, geology, and land use are from Larocque et al. (2015).

Figure 2. Pollutant concentrations in the study area; a) pharmaceutically active compound (PhAC) concentrations (33 sampled wells), b) pesticide concentrations (33 sampled wells), and c) nitrate concentrations and presence of *E. coli* (190 sampled wells).

Figure 3. Spatial distribution of the Anthropic Footprint Index (AFI) in the study area.

Figure 4. The Anthropogenic Footprint Index (AFI) in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and total pharmaceutically active compounds (PhAC) concentrations.

Figure 5. Recharge in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, b) total pesticide concentrations and total concentrations of pharmaceutically active compounds (PhACs), and c) groundwater residence time.

Figure 6. The Hydrogeochemical Vulnerability Index (HVI) in the study area as an explanatory variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and total concentrations of pharmaceutically active compounds (PhACs).

Figure
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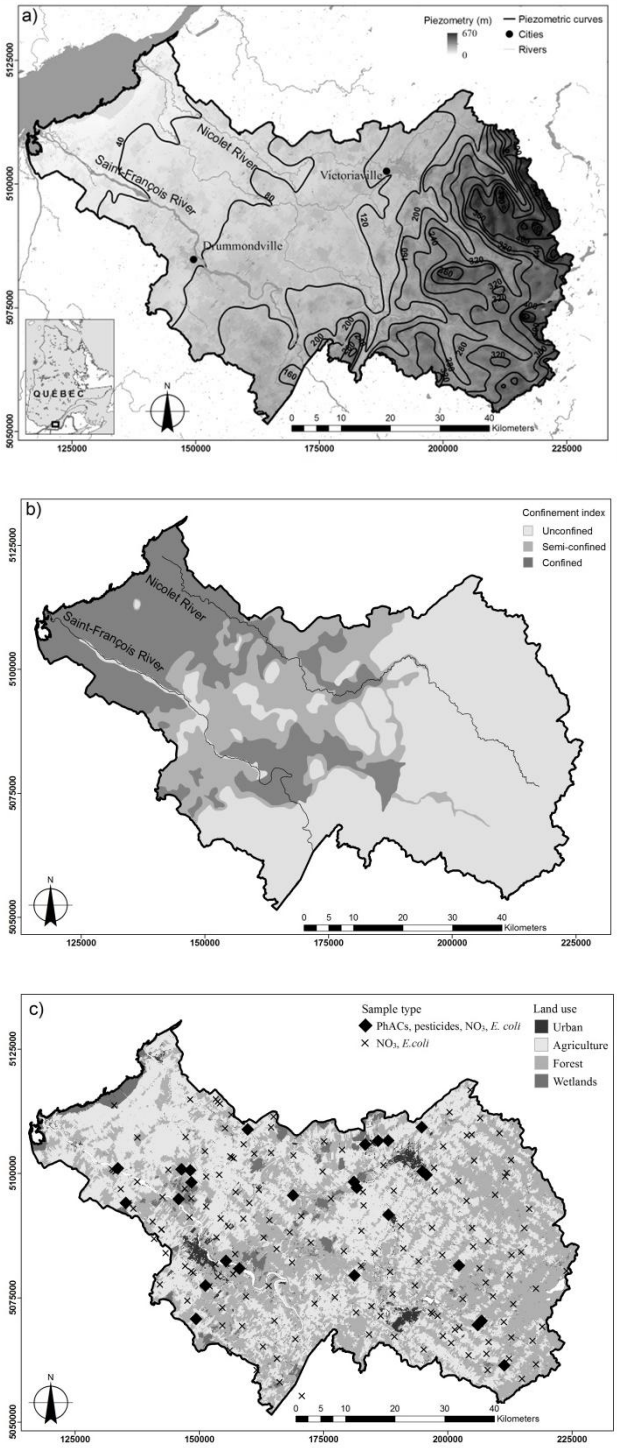

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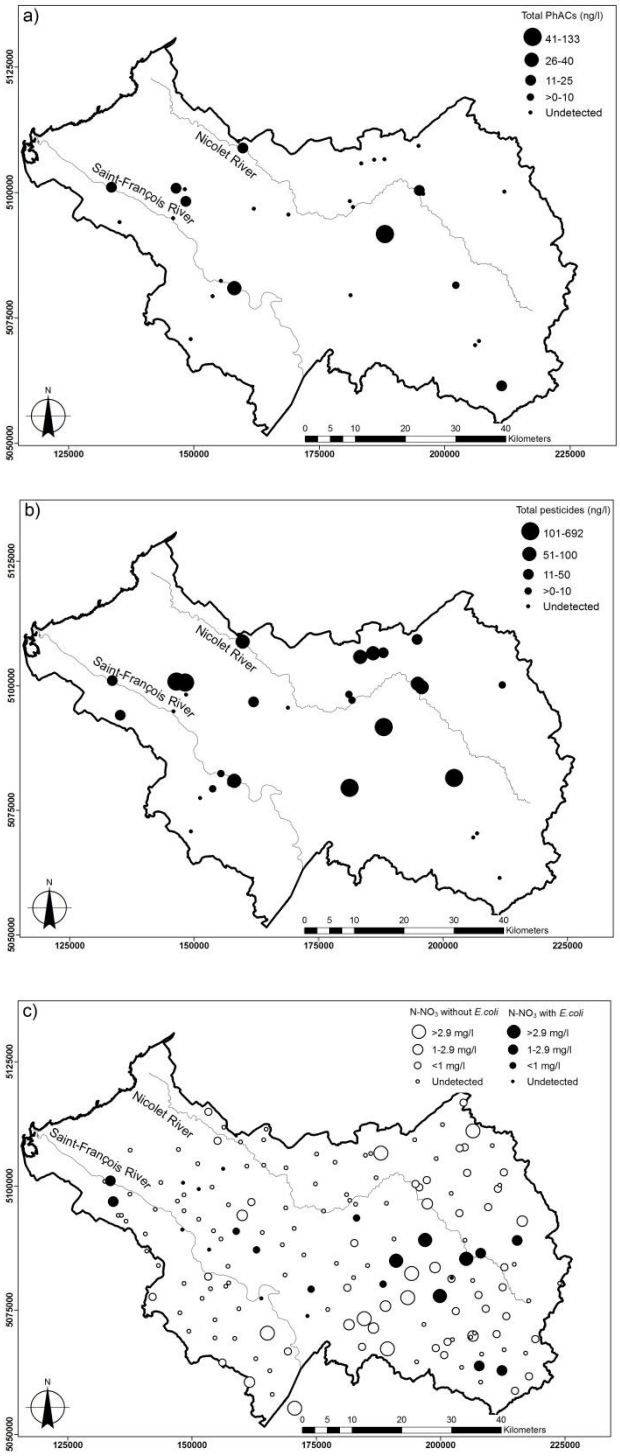

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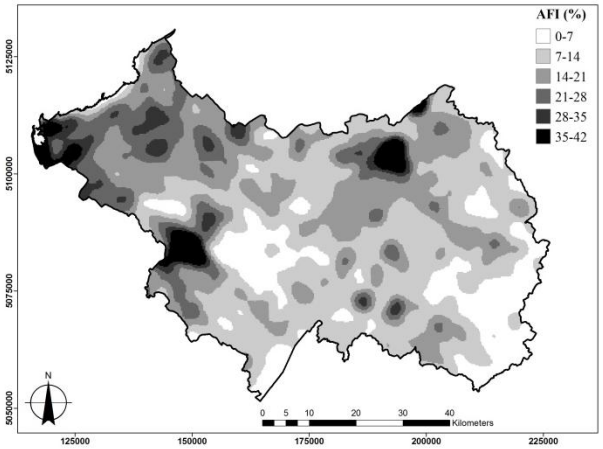

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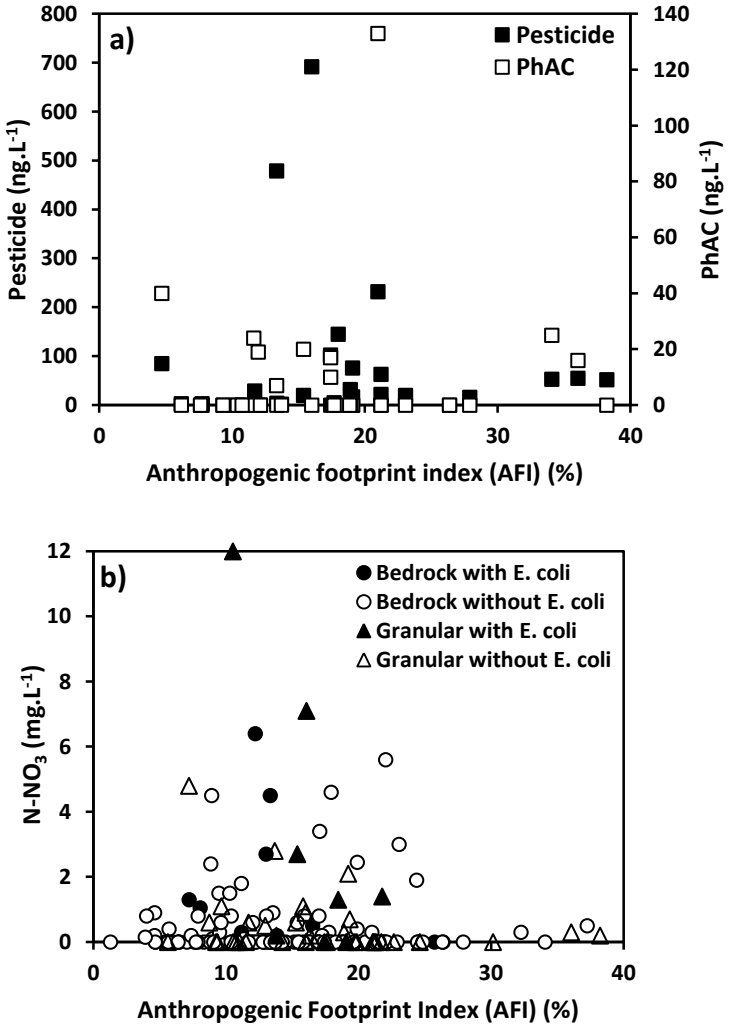

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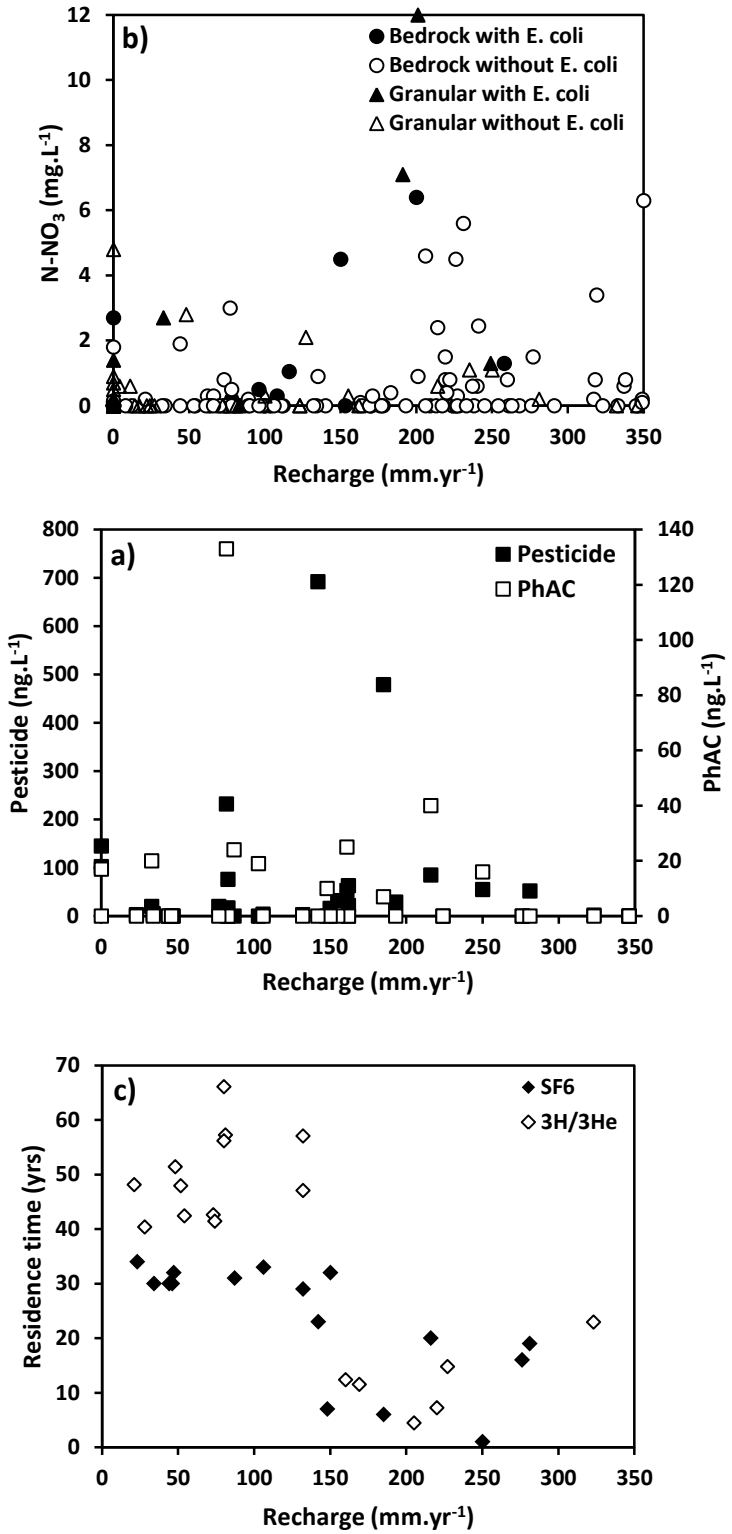

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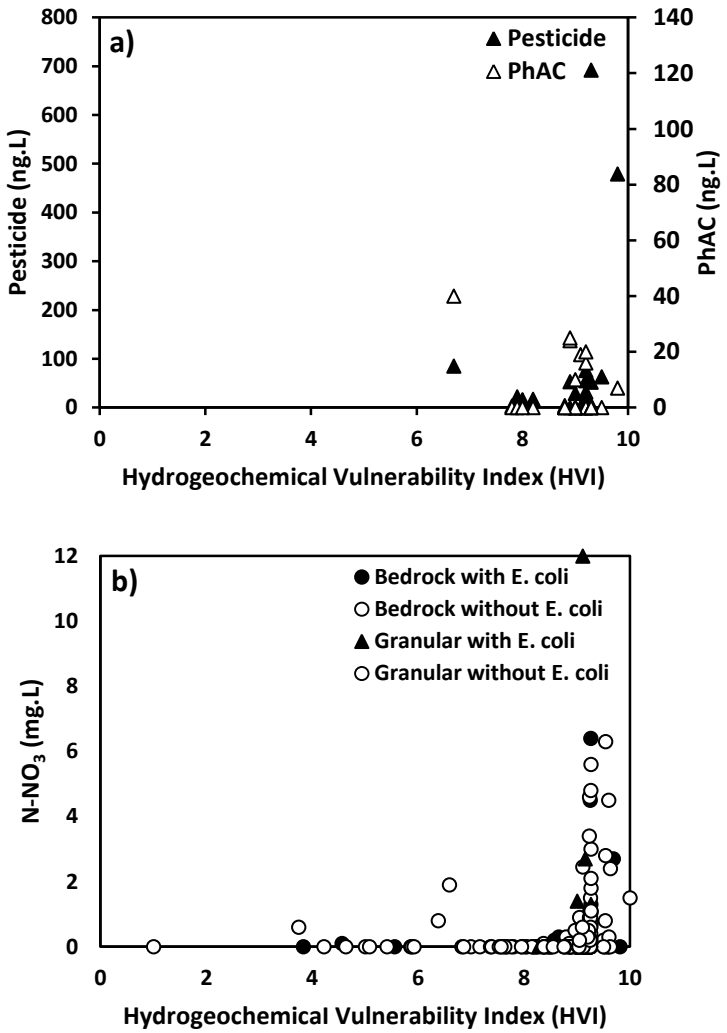

Figure 6
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