

Manuscript Number: STOTEN-D-16-04573R2

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

Corresponding Author: Ms. Marion Saby, M.Sc.

Corresponding Author's Institution: Université du Québec à Montréal

First Author: Marion Saby, M.Sc.

Order of Authors: Marion Saby, M.Sc.; Marie Larocque, Ph.D.; Daniele L Pinti, Ph.D.; Florent Barbecot, Ph.D.; Sylvain Gagné, M.Sc.; Diogo Barnetche, M.Sc.; Hubert Cabana, Ph.D.

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<sup>-1</sup> 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<sup>-1</sup>. Nitrate concentrations exceeded 1 mg.L<sup>-1</sup> N-NO<sub>3</sub> 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  
GEOTOP research center  
Université du Québec à Montréal  
H2X 3Y7 Montréal, QC, Canada

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**

### **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?*

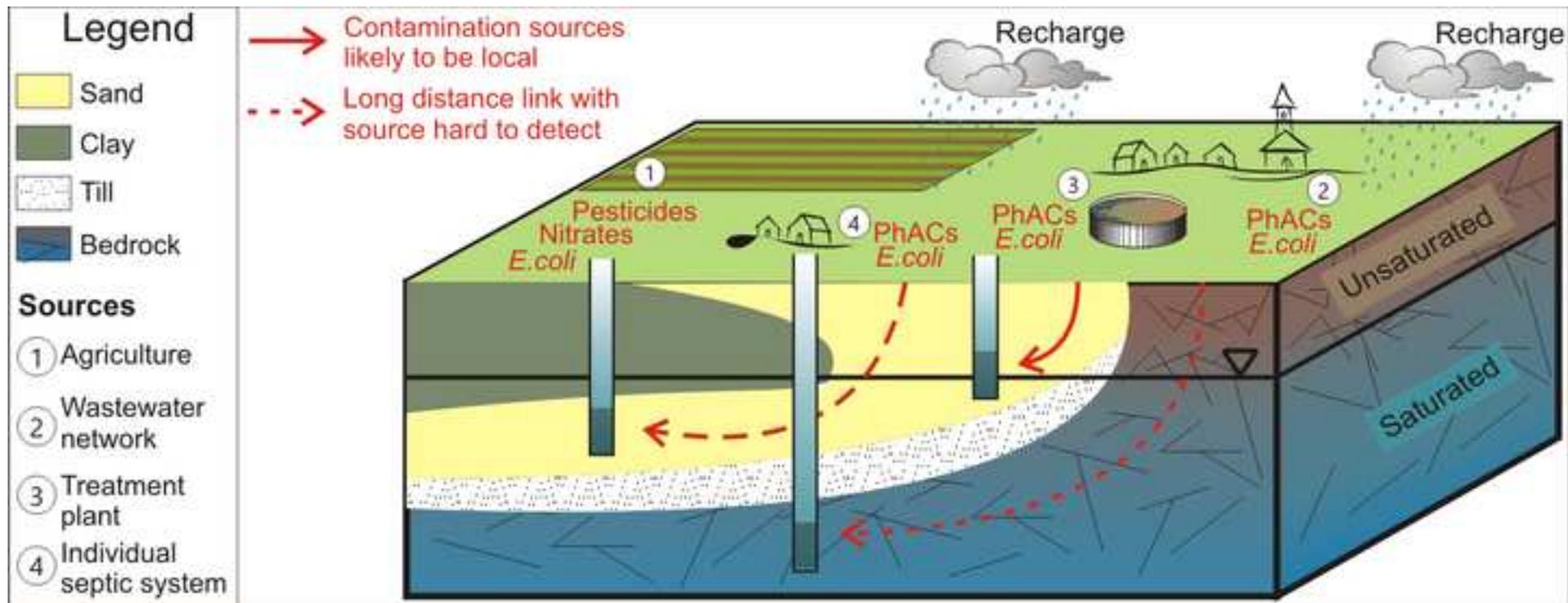
We believe this research provides important results that deserve to be published. More data would obviously be welcome and these could be acquired in future complementary studies, in particular to better understand local sources of contaminants.

*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.



## 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.

1 Regional assessment of concentrations and sources of pharmaceutically active compounds,  
2 pesticides, nitrate, and *E. coli* in post-glacial aquifer environments (Canada)  
3

4 Marion SABY<sup>1\*</sup>, Marie LAROCQUE<sup>1</sup>, Daniele L. PINTI<sup>1</sup>, Florent BARBECOT<sup>1</sup>, Sylvain  
5 GAGNÉ<sup>1</sup>, Diogo BARNETCHE<sup>1</sup>, Hubert CABANA<sup>2</sup>  
6  
7

8 <sup>1</sup> GEOTOP and Département des sciences de la Terre et de l'atmosphère, Université du Québec à  
9 Montréal, CP8888 succ. Centre-Ville, Montréal, QC, Canada

10 <sup>2</sup> Département de génie civil, Université de Sherbrooke, 2500 boul. de l'Université, Sherbrooke,  
11 QC, Canada

12 \* Corresponding author: marion.saby23@gmail.com  
13  
14  
15  
16

17 **Abstract**

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

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

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

## 45 1. INTRODUCTION

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

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

68 (e.g., golf courses, parks, and residential gardening). PhAC and pesticide molecules are typically  
69 difficult to trace in groundwater. Sorption to organic matter and clay minerals, ion exchange in  
70 the soil and aquifer, and microbial degradation can modify PhAC and pesticide concentrations in  
71 groundwater (Lapworth et al., 2012). Studies carried out in the USA (Barnes et al., 2008; Focazio  
72 et al., 2008; Kolpin et al., 2004) and in European countries (Jurado et al., 2012; Loos et al., 2010,  
73 2009; Stuart et al., 2012) have shown the ubiquitous presence of PhACs and pesticides in  
74 groundwater in a wide variety of geological and climatic conditions. This situation ~~and, in~~  
75 ~~combination with~~ the limited understanding of their ~~accumulated~~cumulative, chronic, and long-term  
76 effects on humans and ecosystems (see references in Barnes et al., 2008) ~~bring urgency to~~  
77 ~~assess~~, make assessing their current concentrations urgent.

78 Several studies have shown the presence of high nitrate concentrations in groundwater in  
79 different regions around the world ~~and are~~, often linked to agricultural sources (e.g., Czekaj et al.,  
80 2015; Pérez-Martin et al., 2016; Pisciotta et al., 2015; Rojas Fabro et al., 2015). Nitrate  
81 concentrations are frequently used to assess groundwater vulnerability, because of their low  
82 reactivity and relatively limited transformation in groundwater (Rodríguez-Galiano et al., 2014),  
83 as well as the low costs associated with their analysis. Similarly, bacterial counts are used as  
84 indicators of the impact of human activity in contamination and vulnerability studies (Scott et al.,  
85 2002), allowing ~~to~~human and animal sources of contamination ~~from humans and animals~~ to be  
86 discriminated from others (e.g., *Escherichia coli* is only found in feces). Bacteria can be linked  
87 with agricultural sources (manure spreading and storage) and to private and municipal  
88 wastewater collection and treatment.

89 Groundwater vulnerability assessment methods include the DRASTIC index (Aller et al.,  
90 1987), the AQUIPRO method (Chowdhury et al., 2003), the LHT method (Mansoor et al., 2014),

91 and, more recently, methods based on groundwater ~~isotopique geochemistry (Murgulet isotopic~~  
92 ~~(Murgulet~~ and Tick, 2013) and major ~~ion~~ geochemistry (Mezzonati et al., 2016). These  
93 semi-quantitative methods are often used as first assessment ~~techniques to manage~~ groundwater  
94 ~~resources~~ resource management, and generally do not ~~include~~ indicate specific potential  
95 contaminant sources. Different studies have attempted to improve these methods by identifying a  
96 link between land use, contaminant sources, and groundwater contamination (e.g., Bojórquez-  
97 Tapia et al., 2009; Zhou et al., 2012; Chen et al., 2013; Murgulet and Tick, 2015). Land use data  
98 has the potential to determine zones of contamination risk ~~regarding as a function of~~ the type of  
99 human activity occurring on the ground, notably relating the extent of agricultural and urban  
100 areas ~~that are related~~ to specific ~~contaminants~~ contaminant types. However, ~~this link is~~ such links  
101 are often unclear because of the dynamic nature of groundwater flow, and the reactivity of  
102 contaminants in different geological environments (Fatta-Kassinos et al., 2011; Kormos et al.,  
103 2010; Salgado et al., 2013; Schulz et al., 2008). ~~It still needs to be demonstrated in which~~ The  
104 conditions in which it is useful to seek a source-contaminant link remain to be demonstrated.

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

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

115 | In cold and humid climates, such as southern Quebec (Canada), where water sources are  
116 | abundant, groundwater contamination from anthropogenic sources in aquifers often remains  
117 | relatively poorly understood. There are very few studies on emerging groundwater contaminants  
118 | in Quebec, but research in other Canadian provinces has shown that PhACs can be found in wells  
119 | and treated sewage effluents (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Kleywegt et al.,  
120 | 2007). Although few studies have focused on the presence of pesticides in groundwater in  
121 | Canada, this is becoming a concern in some parts of the country (CLE, 2015; Environment  
122 | Canada, ~~2010~~2012; Giroux and Sarrasin, 2011; Giroux, 2010; Woudneh et al., 2009). Pesticides  
123 | and their metabolites ~~were~~have also been identified in fluvial wetlands near intensive agricultural  
124 | ~~activities~~activity (Poissant et al., 2008). The presence of nitrate in Quebec groundwater has  
125 | certainly been the most frequently investigated contaminant, ~~with~~ generally revealing low  
126 | concentrations ~~revealed~~ (Carrier et al., 2013; Giroux and Sarrasin, 2011; Giroux 2003; Levallois  
127 | et al., 1998; Meyzonnat et al., 2016; Quebec, 2004a), which nonetheless often exceed the natural  
128 | (non-anthropogenic) background of 1 mg N-NO<sub>3</sub>.L<sup>-1</sup> (Dubrovsky et al., 2010).

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

136 aquifer confinement, soil and crop types, spatially distributed recharge, major ion analyses (fully  
137 described in Saby et al., 2016), and a DRASTIC index map are also included in the Larocque et  
138 al. (2015) report. Presented here are results from groundwater sampling undertaken to assess the  
139 presence of nitrates, bacteria (*E. coli*), pesticides, and PhACs. A new Anthropogenic Footprint  
140 Index (AFI) ~~was developed~~, based on the estimated density of agricultural and urban areas, both  
141 considered to be potential ~~sources of contamination~~ ~~sources, was developed~~. The ~~new~~  
142 Hydrogeochemistry Vulnerability Index (HVI) ~~developed recently~~ by Meyzonnat et al. (2016) ~~was~~  
143 was used to provide an ~~alternative~~ ~~alternate~~ estimate of aquifer vulnerability, based on major ion  
144 analyses reported by Saby et al. (2016). Statistical analyses were performed to assess explanatory  
145 factors for the water quality results, using the spatially distributed data reported in Larocque et al.  
146 (2015) for ~~crop type~~, presence of a crop, ~~crop type~~, soil drainage, aquifer confinement, aquifer  
147 type, and recharge.

148

## 149 2. STUDY AREA

### 150 2.1 Geology and hydrogeology

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

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

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

166 | Unconsolidated Quaternary fluvioglacial deposits cover the fractured Paleozoic aquifer  
167 | (Lamothe, 1989). Basal deposits are tills from the last two Quaternary deglaciation episodes,  
168 | followed by glaciolacustrine, sandy, and organic deposits. A thick clay layer, deposited during  
169 | the Champlain Sea episode following the last deglaciation, covers sandy deposits over a strip of  
170 | 30 km along the St. Lawrence River (Lamothe and St-Jacques, 2014). This clay creates confining  
171 | conditions for the underlying fractured bedrock aquifer. Further upgradient, a flat area composed  
172 | of sand, patches of clay, and shale induces a heterogeneous and semi-confined hydrogeological  
173 | context, while still further upgradient, the outcropping of reworked till and bedrock leaves the  
174 | fractured aquifer unconfined in its main recharge area (Figure 1b).

175 | The study area is divided into two main aquifer systems, further described in Larocque et al.  
176 | (2015): the shallower Quaternary aquifers of relatively limited thickness and extent, and the  
177 | underlying Paleozoic fractured bedrock aquifer, composed of sedimentary rocks. Hydraulic  
178 | conductivities in the fractured bedrock aquifer are heterogeneous and range from  $5 \times 10^{-9} \text{ m.s}^{-1}$  to  
179 |  $7 \times 10^{-6} \text{ m.s}^{-1}$ . Confining zones have ~~been~~ previously been estimated using a 3D model of the  
180 | Quaternary sediment architecture, based on the thickness of the impermeable units. Results were  
181 | interpolated over 250 m x 250 m cells (see Figure 1b). Confined conditions were defined as when

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

187

## 188 **2.2 Previously available data**

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

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

205 the upgradient portion of the study area, to more than  $60\pm 3.2$  yrs in its downgradient portion  
206 (Saby et al., 2016). SF<sub>6</sub> residence times reported in Larocque et al. (2015) show values of a  
207 similar magnitude, between  $1\pm 0.5$  year upgradient of the study area, where the Quaternary  
208 deposit cover is thin and recharge is direct, and  $34\pm 5.6$  years downgradient. Saby et al. (2016)  
209 also calculated older <sup>14</sup>C groundwater ages, from  $280\pm 56$  to  $17050\pm 3410$  years. These results  
210 clearly indicate mixing between modern groundwater and a paleo-groundwater component  
211 circulating slowly in the deepest, less permeable layers of bedrock, creating this apparent  
212 contradiction in age (Vautour et al., 2015; Saby et al., 2016). Older groundwater likely infiltrated  
213 the bedrock aquifer through subglacial recharge when the Laurentide Ice Sheet covered the study  
214 area (Saby et al., 2016).

215 | Larocque et al. (2015) present a crop type map built from a database of insured crop acreage  
216 | crops (Martineau, 2014). A total of 48% of the studied surface ~~of the study~~ area is dedicated to  
217 | agriculture, mainly along the St. Lawrence River, while forest covers 45% of the area, principally  
218 | in the Appalachian piedmont (Figure 1c). Wetlands, urban areas, and surface water occupy 3.7%,  
219 | 2.0%, and 1.1% of the region respectively. A detailed description of the study area is found in  
220 | Larocque et al. (2015). Agriculture is dominated by cereal (54%) and hay (22%) production, with  
221 | a minor presence of mixed crops, vegetables, and small fruit production (3%) located mainly in  
222 | the lower part of the study area where the bedrock aquifer is covered by ~~the~~ Champlain Sea clay.  
223 | No information is available for the remaining 21% of the study area. ~~This~~ The study area is  
224 | considered to be among the most agriculturally productive in the province of Quebec (UPA,  
225 | 2012).

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

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

234 Larocque et al. (2015) computed the DRASTIC index (Aller et al., 1987) ~~on for~~  
235 500 m x 500 m cells for the bedrock aquifer of the study area using the usual parameters and  
236 associated parametric weights (see annex A1 for details of the method). Vulnerability values of  
237 the DRASTIC index for the bedrock aquifer vary from 24 to 185 for the study area. ~~The~~ Quebec  
238 legislation (Quebec, 2015) labels ~~as~~ “low vulnerability” regions as those where the DRASTIC  
239 index is below 100, ~~as~~ “medium vulnerability” regions as those where the DRASTIC index is  
240 between 100 and 180, and ~~as~~ “high vulnerability” regions as those with a DRASTIC index above  
241 180 (see Figure 1 in annex A1). Based on these categories, 28% of the study area ~~has-ais~~ low  
242 vulnerability and 72% ~~has-ais~~ medium vulnerability. Only 0.02% of the area ~~has-ais~~ high  
243 vulnerability. The medium and high vulnerability ~~values~~areas are located in the ~~Appalachian~~  
244 ~~area~~Appalachians, where recharge is high and sediment cover is thin. A vast portion of the central  
245 part of the study area is also characterised by ~~a~~ medium vulnerability, mainly because of the high  
246 water table and the high permeability of the ~~sediments~~sediment. The lower part and some areas  
247 around the Saint-François and Nicolet Rivers in the central section ~~have~~are of low vulnerability  
248 ~~values~~. The thick clay layer combined with low recharge rates ~~explain~~explain these low  
249 DRASTIC values.

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

256

### 257 3. METHODS

#### 258 3.1 Groundwater sampling and analysis

259 Between June and August 2013, 190 groundwater samples were collected from private wells (157  
260 wells), municipal wells (11 wells), 1" PVC observation wells (12 wells), and 6" steel tubing  
261 observation wells (10 wells) (see locations in Figure 1c and well ~~description~~descriptions in Table  
262 A1). Well depths range between 5 and 250 m for the 145 open borehole bedrock wells, and from  
263 1.2 to 50 m for the 45 wells tapping a granular aquifer (granular wells ~~are either~~ withhave a steel  
264 casing or are drive points). All samples were analyzed for nitrate and *E. coli*. Major ~~ion~~ion data  
265 ( $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ , and  $\text{HCO}_3^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^{-}$ ) are available for all the wells and are reported in  
266 Saby et al. (2016). In September 2014, 33 wells were ~~re-sampled~~resampled (six private wells,  
267 nine municipal wells, 11 1" PVC observation wells, and seven 6" steel tubing observation wells).  
268 This water was analyzed for 13 different PhAC compounds (antibiotics, beta-blockers, mood  
269 stabilizer and anticonvulsant, antilipemic agents, chemotherapy medication, and prescription and  
270 non-prescription non-steroidal anti-inflammatory agents) and 46 different pesticides (herbicides,  
271 fungicides, and insecticides) (~~see~~ see list of PhAC and pesticide molecules analyzed in Table A2).

272 All the wells were purged prior to sampling, and water was sampled prior to any treatment  
273 once the physiochemical parameters (pH, temperature, redox potential, and electric conductivity)  
274 measured in an air-tight cell had stabilized (MDDELCC, 2011). Groundwater was collected from  
275 the observation wells using a submersible pump with speed control (Redi-Flo2<sup>®</sup>), maintaining the  
276 whole sampling line under pressure to prevent water degassing. All samples were filtered in the  
277 field to 0.45 µm. Samples were kept at 4°C during storage and transport. Samples for PhACs and  
278 pesticides were collected in 1L Nalgene<sup>®</sup> bottles, and were sent to the Environmental  
279 Engineering Laboratory ~~at of the University of Sherbrooke University~~ for analysis. The samples  
280 were first extracted using a solid phase extraction procedure, ~~then~~ and the liquid phase was ~~then~~  
281 analyzed by liquid chromatography coupled with a triple ~~quadrupolesquadrupole~~ mass  
282 spectrometer (Ba et al., 2014; Haroune et al., 2014). The detection limit of the method for  
283 pesticides and PhACs was 5 ng.L<sup>-1</sup>. The calibration was validated by verifying the calculation of  
284 the deviation for each point (criteria < 20%). Each series of samples was validated for a spiked  
285 sample (recovering criteria ~~enbetween~~ 70% - 120%). No field blanks or duplicates were analyzed  
286 for ~~pestices and pesticides or~~ PhACs because of the high analytical cost. Groundwater for nitrate  
287 analysis was sampled in 125 ml Nalgene<sup>®</sup> bottles and analyzed by colorimetry in a private  
288 laboratory (ISO/CEI 17025), with a detection limit of 0.1 mg N-NO<sub>3</sub>.L<sup>-1</sup>. Laboratory blanks for  
289 nitrate analyses were done systematically for each sample, but no field blank ~~has been was~~ taken.  
290 A total of 10 duplicates ~~was were~~ sampled for the 190 samples analyzed for nitrate.

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

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

### 299 3.2 Anthropogenic Footprint Index (AFI) and Hydrogeochemical Vulnerability Index (HVI)

300 The Anthropogenic Footprint Index (AFI) developed in this study is derived from the farm  
301 density (FD) and anthropic activity density (AAD) data presented in Larocque et al. (2015). FD is  
302 the number of farm buildings per square kilometer. AAD is a weighted sum of risks per square  
303 kilometer. AAD takes into account the ~~typetypes~~ of anthropic ~~activitiesactivity~~ (punctual  
304 infrastructures) and their impact; in terms of groundwater pollution risks. This method was  
305 adapted from similar projects in the United States and elsewhere in the world (Foster and Hirata,  
306 1998; ~~EPA~~ Office of Water, 1991; SESAT, 2010). Each parameter is weighted following the  
307 methodology presented in Larocque et al. (2015), and the ~~globaloverall~~ impact is calculated as  
308 follows:

$$310 \quad AAD = (TC + CQ + IZA) \times RCD \quad (\text{eq. 1})$$

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

318 (CSST, 2007). The weight of the contaminant quantity is based on contaminant quantity and  
319 concentration for a given anthropogenic activity (modified from SESAT, 2010). The impacted  
320 area refers to the potential extent of the activity (punctual, local, or regional). Finally,  
321 contaminant discharge is either recurrent (systematic and linked to the activity itself), or  
322 accidental. Each parameter is evaluated qualitatively ~~with~~, assigned to one of four classes (low,  
323 moderate, high, very high) ~~),~~ and weighted following the tables available in Larocque et al.  
324 (2015). The parameters required to calculate the FD and AAD were extracted from a property  
325 assessment database describing the type of anthropic activity (MAMROT, 2010). The AAD  
326 values were computed for each point of anthropic activity on the land surface and ~~are~~were  
327 interpolated on a 250 m x 250 m grid.

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

332

$$333 \quad AFI = 100 \left( \frac{FD}{FD_{max}} + \frac{AAD}{AAD_{max}} \right) \quad (\text{eq. 2})$$

334

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

341 vulnerability at a regional scale. It is calculated by plotting  $(\text{Na}^+ - \text{Cl}^-)$  against  $(\text{Ca}^{2+} + \text{Mg}^{2+}) -$   
342  $(\text{HCO}_3^- + \text{SO}_4^-)$ . The HVI graphically illustrates how the groundwater chemical composition  
343 evolves from a (Ca, Mg)- $\text{HCO}_3$  type in the recharge area to a Na- $\text{HCO}_3$  type downgradient along  
344 a flow path. The HVI can vary between 0 (low vulnerability) and 10 (maximum vulnerability)  
345 along the linear regression from its orthogonal projection. In this study, the HVI was calculated  
346 using the major ion concentrations measured at the sampling points as reported in Saby et al.  
347 (2016).

348

### 349 3.3 Statistical analysis

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

364 “poorly drained” (from previous “very poorly drained,” “poorly drained,” and “imperfectly  
365 drained” categories). The aquifers tapped by the sampled wells were categorized as “unconfined,”  
366 “semi-confined,” and “confined.” Aquifer type was categorized as “granular” or “bedrock.”  
367 Recharge was divided into three categories: “low” for recharge values ~~below of less than~~  
368 100 mm.yr<sup>-1</sup>, “average” for recharge values between 100 and 200 mm.yr<sup>-1</sup>, and “high” for  
369 recharge values ~~larger of higher~~ than 200 mm.yr<sup>-1</sup>. The influence of water table depth and well  
370 depth was analyzed for all parameters and all contaminants, but results are not reported here since  
371 they were insignificant for all analyses.

372

## 373 4. RESULTS

### 374 4.1. Contaminant occurrence

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

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

387 concentrations exceeded the Canadian drinking water quality standards (MDDELCC, [20152011](#)).  
388 The highest total pesticide concentration was 692 ng.L<sup>-1</sup>, in [a](#) municipal well ~~tapping~~ tapping a  
389 semi-confined granular aquifer in the Appalachian piedmont (NSF177). None of the tested  
390 parameters (crop type, soil drainage, aquifer confinement, aquifer type, or recharge) explained  
391 the observed differences—~~observed~~ in pesticide concentrations between the sampled wells  
392 (Table A6). No clear link was observed between well depth and pesticide concentrations.

393 A total of 29 wells (15.3% of all sampled wells) ~~wells~~ had nitrate concentrations ~~above~~ higher  
394 ~~than~~ the natural background of 1 mg.L<sup>-1</sup> N-NO<sub>3</sub> (Dubrovsky et al., 2010) (Figure 2c and  
395 Table A2). The majority of the wells (62.6%) had ~~no~~ nitrate ~~above~~ in concentrations of less than  
396 the 0.1 mg.L<sup>-1</sup> N-NO<sub>3</sub> detection limit. The maximum nitrate concentration, 12 mg.L<sup>-1</sup> N-NO<sub>3</sub>, was  
397 measured in well NSF250, a granular well located upgradient in the Appalachian piedmont. This  
398 is the only well exceeding the drinking water quality standard of 10 mg.L<sup>-1</sup> N-NO<sub>3</sub> (Health  
399 Canada, 2014). The average nitrate concentration of all wells was 0.63 mg.L<sup>-1</sup> N-NO<sub>3</sub>. On  
400 average, wells near fields with hay crops had a significantly higher nitrate concentration  
401 (1.04 mg.L<sup>-1</sup> N-NO<sub>3</sub>) than those near fields which were not cultivated (0.16 mg.L<sup>-1</sup> N-NO<sub>3</sub>;  
402 p=0.0297) (Table A7). However, the simple presence of a crop near a well alone does not ~~itself~~  
403 explain nitrate concentrations (p>0.05). Well drained soils had significantly higher concentrations  
404 (1.01 mg.L<sup>-1</sup> N-NO<sub>3</sub>) than poorly drained soils (p=0.0241). The average nitrate concentration in  
405 wells tapping an unconfined bedrock aquifer (1.05 mg.L<sup>-1</sup> N-NO<sub>3</sub>) was significantly higher than  
406 that in wells in semi-confined conditions (0.21 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0022), and that in wells in  
407 confined conditions (0.16 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0017). The average nitrate concentration for wells  
408 in a granular aquifer (1.16 mg.L<sup>-1</sup> N-NO<sub>3</sub>) was significantly higher (~~p=0.0060~~) than for wells in

409 | the Ordovician bedrock aquifer (0.47 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0060). The three wells with nitrate  
410 | concentrations higher than 7 mg.L<sup>-1</sup> N-NO<sub>3</sub> were located in granular aquifers.

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

416 |

#### 417 | **4.2. AFI and HVI identified areas of contamination risk**

418 | The AFI was used to identify zones of potential contamination risk ~~linked with~~related to land  
419 | use (Figure 3). In the 190 wells sampled for nitrate and bacteria, the AFI varied between 1 and  
420 | 38%, with an average of 15%. The highest AFI values (i.e., the maximum value in the whole  
421 | study area; 42%) was observed in the intensive agricultural zones of the lower part of the study  
422 | area. The two largest municipalities in the study area, Victoriaville and Drummondville, also had  
423 | AFI values of 42%. The lowest AFI values were ~~found~~ mainly found in the forested zones  
424 | located in the central and upper ~~part~~parts of the study area.

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

430 |

## 431 | **5. DISCUSSION**

432 **5.1. Groundwater contamination**

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

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

453 The measured concentrations of pesticides were below the Canadian drinking water quality  
454 standards (MDDELCC, ~~2015~~2011). The average total pesticide concentration was 67 ng.L<sup>-1</sup>,

455 which is lower than the European limit for cumulated pesticides, of 500 ng.L<sup>-1</sup> (CUE, 1998; there  
456 is no total pesticide water quality standard in Canada). The European limit was exceeded in one  
457 well (692 ng.L<sup>-1</sup>; NSF177, a municipal well ~~tapping~~ tapping a confined granular aquifer), and was  
458 near the European limit in another well (479 ng.L<sup>-1</sup>; NSF-R6, an observation well in the bedrock  
459 aquifer). These two wells are located upgradient, in the Appalachian piedmont, in areas where  
460 agricultural land surrounds the wells. The higher occurrence of pesticides in the tested wells  
461 (70%) compared to PhACs could be explained by more regionally distributed sources of the  
462 contaminant.

463 The measured nitrate concentrations are similar to those reported in other studies from  
464 southern Quebec (Carrier et al., 2013; Giroux and Sarrasin, 2011; Levallois et al., 1998;  
465 Meyzonnat et al., 2016; Quebec, 2004a). It is interesting to highlight that higher concentrations of  
466 nitrate, exceeding the drinking water quality standard (between 11 and 72 mg.L<sup>-1</sup> N-NO<sub>3</sub>), have  
467 been reported for shallow unconfined wells in a granular aquifer of the study area (e.g., BPR and  
468 Arrakis consultants, 2004). When comparing results from the current study with the previously  
469 available DRASTIC index values, the bedrock wells located in areas where the DRASTIC index  
470 was categorized as “medium” have significantly higher nitrate concentrations (0.52 mg.L<sup>-1</sup> N-  
471 NO<sub>3</sub>) than those located in areas where the DRASTIC index was categorized as “low-~~?”~~  
472 (≤0.001 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0278). Similar to these results, a study in the Lanaudiere region of  
473 southern Quebec showed a correlation between nitrate concentrations and the DRASTIC index  
474 (Quebec, 2004a), with stronger correlations for wells tapping granular aquifers than for deep  
475 bedrock wells. In the current study, the limited proportion of concentrations higher than the  
476 anthropogenic background could be related to the presence of agricultural drainage, which  
477 transports nitrate to surface water before it can infiltrate to groundwater (Thériault, 2013). Poorly

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

484 | The observed bacteria (*E. coli*) occurrence in 13.5% of the sampled wells was similar to that  
485 | reported by Leblanc et al. (2013) for the lower part of the Saint-Maurice River watershed in  
486 | southern Quebec (*E. coli* present in 12 % of all sampled wells). Considering the relatively short  
487 | residence time of *E. coli* in saturated conditions, Leblanc et al. (2013) concluded that bacterial  
488 | contamination was caused mainly by local processes, such as the proximity of a private sewage  
489 | system, or poor well construction or maintenance. Although the effect of aquifer type was not  
490 | clear in the current study, the Lanaudiere study (Quebec, 2004b) showed a higher occurrence of  
491 | *E. coli* in granular aquifers, with 49% of the granular wells having a positive detection. The  
492 | highly heterogeneous coverage of Quaternary post-glacial deposits in the study area could  
493 | explain the absence of significant correlations between the presence of bacteria and the tested  
494 | parameters. Interestingly, the average nitrate concentration in the wells where *E. coli* was  
495 | detected was significantly higher compared ~~to~~with the wells where no *E. coli* was detected  
496 | (1.61 mg.L<sup>-1</sup> N-~~NO<sub>3</sub>~~versus~~NO<sub>3</sub>~~ versus 0.44 mg.L<sup>-1</sup> N-NO<sub>3</sub> respectively; p=0.001). This could be  
497 | due to the combination of manure spreading with ~~fertilizers~~other fertilizer application in  
498 | agricultural areas.

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

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

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

524 | in one or more wells. The most frequently detected pesticides (kresoxim-methyl, in 9 wells;  
525 | trifloxystrobin, in 7 wells; piperonyl butoxide, in 7 wells) had log  $K_{ow}$  of equal to or higher than  
526 | 3.40.

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

535

## 536 | **5.2. Identifying contaminant sources with the Anthropogenic Footprint Index (AFI)**

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

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

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

567

### 568 5.3. Estimating aquifer vulnerability

#### 569 5.3.1. Aquifer recharge and groundwater dynamics

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

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

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

601

### 602 5.3.1 *Hydrogeochemical Vulnerability Index (HVI)*

603 The two wells with the highest total pesticide concentrations (NSFR6 and NSF177) also had  
604 among the highest HVI values (9.8 and 9.3 respectively) (Figure 6a). There was no apparent  
605 trend between PhAC concentrations and HVI. The comparison between nitrate concentrations  
606 and HVI (Figure 6b) showed that concentrations tended to be higher when the HVI was greater  
607 than 9 (maximum is 10), a result similar to that reported by Meyzonnat et al. (2016) in the  
608 neighboring Becancour watershed. Because it reflects the groundwater dynamics and the water-  
609 rock contact time, the HVI highlights flow conditions across different media and receiving  
610 infiltration from different land uses. The high HVI scores thus reflect the presence of  
611 groundwater near recharge areas with Ca,Mg-HCO<sub>3</sub>, Ca-HCO<sub>3</sub>, and Ca-SO<sub>4</sub> water types, while  
612 the low scores represent increasing confinement conditions and water type evolving to Na-HCO<sub>3</sub>  
613 and Na-Cl types. (Meyzonnat et al., 2016). The high HVI wells in recharge areas are also those  
614 where residence times are the shortest (Figure 5c), which explains their association with the  
615 highest nitrate concentrations. The weaker link observed between PhAC and the HVI, and, to a

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

621 | Results for the HVI ~~index~~ and ~~of~~ the DRASTIC ~~does~~index do not provide the same type of  
622 | spatial vulnerability information because of the differences inherent to the methods. The HVI  
623 | method provides information on groundwater flow paths, while DRASTIC focuses on vertical  
624 | flows from the surface to the water table. Thus, in the ~~studied~~study area, the DRASTIC and the  
625 | HVI indices ~~doesn't give~~do not provide the same results in comparison with ~~contaminants~~  
626 | ~~distribution~~contaminant distributions. The HVI index ~~better~~ correlates more strongly with  $\text{NO}_3$ ,  
627 | *E. coli*, and ~~pesticides~~pesticide occurrences than does DRASTIC. For PhACs, the correlation is  
628 | less clear for both DRASTIC and HVI. The ~~nitrate's~~ results for nitrate are similar to those of  
629 | Meyzonnat et al. (2016), who performed a complete comparison of the two methods on a  
630 | neighboring watershed ~~set in~~with similar geological conditions. These authors found that the  
631 | DRASTIC index was relatively ineffective ~~to evaluate~~in evaluating groundwater vulnerability,  
632 | while the HVI method showed a clear correlation with nitrate concentrations.

633

#### 634 | **5.4. Synthesis and recommendations**

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

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

644 | These results are expected to be of particular interest ~~for areas in similar post-glaciated glacial~~  
645 | environments and undergoing similar human ~~impact problems~~impacts elsewhere in the world,  
646 | such as Scandinavia, Denmark, Germany, and the USA (Harff et al., 2011; Scheck and Bayer,  
647 | 1999; Thomsen et al., 2004; Dyke, 2004). The results will also be useful for provincial and local  
648 | water management agencies, since it is the first time that regional-scale PhAC and pesticide  
649 | concentrations are measured in the province of Quebec. Although no measured concentration  
650 | ~~exceeding was found to exceed~~ drinking water standards ~~were detected~~ for pesticides (and no  
651 | standards exist for PhACs), the mere presence of PhACs and pesticides in groundwater used for  
652 | drinking is a public health concern and justifies long-term monitoring. This recommendation  
653 | stands for the study area, but also for ~~others~~surrounding regions ~~around~~ set in similar high  
654 | recharge post-glacial geological environments, and ~~face~~ingunder the same type of land uses.  
655 | Nitrate concentrations and the presence of *E. coli* have been a concern for some time, and should  
656 | be monitored so as to strengthen the implementation of better agricultural practices in general.  
657 | Measuring pollutant concentrations through time would also be useful ~~to link~~in linking their  
658 | presence to time-varying sources, such as the seasonality of recharge and of agricultural  
659 | contaminant input, an important factor of groundwater contamination which was not assessed  
660 | here. Long-term monitoring is especially important since PhAC and pesticide concentrations in  
661 | groundwater could increase in the next decades due to industrial and agricultural developments

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

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

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

Formatted: French (France)

Formatted: English (Canada)

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

692

## 693 6. CONCLUSIONS

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

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

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

716

#### 717 **ACKNOWLEDGMENTS**

718 | The authors would like to thank the Quebec Ministère du Développement durable, de  
719 | l'Environnement et de la Lutte contre les changements climatiques (Quebec Ministry of  
720 | Environment), the municipalities, and the watershed agencies (COGESAF and COPERNIC) who  
721 | contributed to the funding of this research, as well as the municipalities and private wells owners  
722 | who allowed access for water sampling.

723

724 **REFERENCES**

725 Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., Hackett, G., 1987. DRASTIC: A Standardized  
726 System for Evaluating Groundwater Pollution Potential Using Hydrogeologic Settings. EPA-  
727 600/2-87-035, 20 p.

728 American Public Health Association, American Water Works Association and Water  
729 Environment Federation. Standard Methods for the Examination of Water and Wastewater,  
730 22nd Edition, 2012.

731 Ba, S., Haroune, L., Cruz-Morató, C., Jacquet, C., Touahar, I.E., Bellenger, J.-P., Legault, C.Y.,  
732 Jones, J.P., Cabana, H., 2014. Synthesis and characterization of combined cross-linked  
733 laccase and tyrosinase aggregates transforming acetaminophen as a model phenolic  
734 compound in wastewaters. *Sci. Total Environ.* 487, 748-755.

735 Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., Barber, L.B., 2008. A  
736 national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the  
737 United States — I) Groundwater. *Sci. Total Environ.* 402(2-3), 192-200.

738 Bojórquez-Tapia, A., Cruz-Bello, G.M., Luna-González, L., Juárez, L., Ortiz-Pérez, M.A., 2009.  
739 V-DRASTIC: using visualization to engage policymakers in groundwater vulnerability  
740 assessment. *J. Hydrol.* 373, 242–255.

741 BPR and Arrakis consultants, 2004. Caractérisation des eaux souterraines de St-Albert-de-  
742 Warwick. Report written for the Quebec Ministry of Environment. 55 p.

743 Carrier, M.-A., Lefebvre, R., Rivard, C., Parent, M., Ballard, J.-M., Benoit, N., Vigneault, H.,  
744 Beaudry, C., Malet, X., Laurencelle, M., Gosselin, J.-S., Ladevèze, P., Thériault, R., Beaudin,  
745 Michaud, A., Pugin, A., Morin, R., Crow, H., Gloaguen, E., Bleser, J., Martin, A., Lavoie, D.,  
746 2013. Portrait des ressources en eau souterraine en Montérégie Est, Québec, Canada. Projet  
747 réalisé conjointement par l'INRS, la CGC, l'OBV Yamaska et l'IRDA dans le cadre du  
748 Programme d'acquisition de connaissances sur les eaux souterraines, rapport final INRS R-  
749 1433.

750 Cassidy, R., Comte, J.C., Nitsche, J., Wilson, C., Flynn, R., Ofterdinger, U., 2014. Combining  
751 multi-scale geophysical techniques for robust hydro-structural characterization in catchments  
752 underlain by hard rock in post-glacial regions. J Hydrol. 517, 715-731.

753 Chen, S.K., Jang, C.S., Peng, Y.P., 2013. Developing a probability-based model of aquifer  
754 vulnerability in an agricultural region. J. Hydrol. 486, 494–504.

755 Chowdhury, S.H., Kehew, A.E., Passero, R.N., 2003. Correlation between nitrate contamination  
756 and groundwater pollution potential. Ground water. 41, 735-745.

757 CLE (Communities, Lands and Environment) (2015). Pesticide Analysis for Drinking Water-  
758 Open data. [https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-](https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-open-data)  
759 [open-data](https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-open-data). (Accessed: June 2016)

760 CSST (Commission de la santé et de la sécurité du travail), 2007. Système d'information sur les  
761 matières utilisées au travail. [http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-](http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-toxicologique.aspx)  
762 [toxicologique.aspx](http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-toxicologique.aspx) (Accessed : July 2016)

763 CUE (Conseil de l'Union Européenne), 1998. Directive 98/83/CE du conseil relative à la qualité  
764 des eaux destinées à la consommation humaine. 23p.

765 Czekaj, J., Jakóbczyk -Karpierz, S., Rubin, H., Sitek, S., Witkowski, A.J., 2015. Identification of  
766 nitrate sources in groundwater and potential impact on drinking water reservoir  
767 (Goczalkowice reservoir, Poland). *Phys. Chem. Earth*. In press,  
768 doi:10.1016/j.pce.2015.11.005.

769  
770 Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton, P.A., Hitt, K.J.,  
771 Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr,  
772 N.E., Sprague, L.A., Wilber, W.G., 2010. The quality of our Nation's waters—nutrients in the  
773 Nation's streams and groundwater, 1992–2004. *U.S. Geological Survey Circular*, 1350, 174  
774 p.

775 Dyke, [A.S.](#), 2004. An outline of North American deglaciation with emphasis on central and  
776 northern Canada. [Dev. Quat. Sci. 2, 373-424.](#)

777 Environment Canada, 2012. Canadian climate normals 1971-2000 for Laurierville, Québec. On-  
778 line:[http://climate.weather.gc.ca/climate\\_normals/index\\_e.html](http://climate.weather.gc.ca/climate_normals/index_e.html)

779 ESRI (Environmental System Research Institute), 2016. ArcGIS Desktop. Release 10.3.1.  
780 Analysis Tools.

781 Evgenidou, E.N., Konstantinou, I.K., Lambropoulou, D.A., 2015. Occurrence and removal of  
782 transformation products of PPCPs and illicit drugs in wastewaters: a review. *Sci. Total*  
783 *Environ.* 505, 905-926.

784 Fatta-Kassinos, D., Vasquez, M.I., Kummerer, K., 2011. Transformation products of  
785 pharmaceuticals in surface waters and wastewater formed during photolysis and advanced

786 oxidation processes — degradation, elucidation of byproducts and assessment of their  
787 biological potency. *Chemosphere* 85, 693–709.

788 Fleckenstein, J.H., Niswonger, R.G., Fogg, G.E., 2006. River–aquifer interactions, geologic  
789 heterogeneity, and low-flow management. *Ground Water* 44, 837–852.

790 Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., 2008. A  
791 national reconnaissance for pharmaceuticals and other organic wastewater contaminants the  
792 United States — II) untreated drinking water sources. *Sci. Total Environ.* 402, 201–216.

793 Foster, S.S.D., Hirata, R., 1998. Groundwater pollution risk assessment. Pan American Center for  
794 Sanitary Engineering and Environmental Sciences, Lima.

795 Ghoshdastidar, A.J., Fox, S., Tong, A.Z. 2015. The presence of the top prescribed  
796 pharmaceuticals in treated sewage effluents and receiving waters in Southwest Nova Scotia,  
797 Canada. *Environ. Sci. Pollut. Res. Int.* 1, 689-700.

798 Giroux, I., 2003. Contamination de l’eau souterraine par les pesticides et les nitrates dans les  
799 régions en culture de pommes de terre, Direction du suivi de l’état de l’environnement,  
800 ministère de l’Environnement, Québec, envirodoq no ENV/2003/0233, 23 pages et 3 annexes.

801 Giroux, I., 2010. Présence de pesticides dans l’eau au Québec – Bilan dans quatre cours d’eau de  
802 zones en culture de maïs et de soya en 2005, 2006 et 2007 et dans des réseaux de distribution  
803 d’eau potable, ministère du Développement durable, de l’Environnement et des Parcs,  
804 Direction du suivi de l’état de l’environnement, 78 p.

805 | Giroux, I., ~~B.~~Sarrasin, B., 2011. Pesticides et nitrates dans l'eau souterraine près de cultures de  
806 | pommes de terre - Échantillonnage dans quelques régions du Québec en 2008 et 2009,  
807 | ministère du Développement durable, de l'Environnement et des Parcs, Direction du suivi de  
808 | l'état de l'environnement, Centre d'expertise en analyse environnementale du Québec, ISBN  
809 | 978-2-550-61396-1, 31 p.

810 | Globensky, Y., 1993. Lexique stratigraphique canadien. Volume V-B: région des Appalaches,  
811 | des Basses-Terres du Saint-Laurent et des Iles de la Madeleine. Ministère de l'Énergie et des  
812 | Ressources et Direction Générale de l'Exploration géologique et minérale, p. 327, DV 91e23.  
813 | (in French).

814 | Harff, J., Björk S., Hoth P., 2011. The Baltic Sea Basin, Central and Eastern European 3  
815 | Development Studies (CEEDES), Springer-Verlag Berlin Heidelberg, DOI 10.1007/978-3-  
816 | 642-17220-5\_1, C 2011

817 | Haroune, L., Saibi, S., Bellenger, J.-P., Cabana, H., 2014. Evaluation of the efficiency of  
818 | *Trametes hirsuta* for the removal of multiple pharmaceutical compounds under low  
819 | concentrations relevant to the environment. Bioresource Technol., 171, 199-202.

820 | Health Canada, 2014. Guidelines for Canadian drinking water quality: summary table. Federal–  
821 | Provincial–Territorial Committee on Drinking Water. [http://www.hc-sc.gc.ca/ewh-](http://www.hc-sc.gc.ca/ewh-semt/water-eau/drink-potab/guide/index-eng.php)  
822 | [semt/water-eau/drink-potab/guide/index-eng.php](http://www.hc-sc.gc.ca/ewh-semt/water-eau/drink-potab/guide/index-eng.php) (Accessed: March 2016)

823 | IRDA (Institut national de recherche et de développement en agroenvironnement), 2013. Études  
824 | pédologiques.[http://www.irda.qc.ca/fr/outils-et-services/informations-sur-les-sols/etudes-](http://www.irda.qc.ca/fr/outils-et-services/informations-sur-les-sols/etudes-pedologiques/)  
825 | [pedologiques/](http://www.irda.qc.ca/fr/outils-et-services/informations-sur-les-sols/etudes-pedologiques/) (Accessed: April 2016)

826 Jurado, A., Vázquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012.  
827 Emerging organic contaminants in groundwater in Spain: A review of sources, recent  
828 occurrence and fate in a European context. *Sci. Total Environ.* 440, 82-94.

829 Kleywegt, S., Smyth, S-A., Parrott, J., Schaefer, K., Lagacé, E., Payne, M., Topp, E., Beck, A.,  
830 McLaughlin, A., Ostapyk, K., 2007. Produits pharmaceutiques et produits d'hygiène  
831 personnelle dans l'environnement canadien : recherches et directives, série de rapports  
832 d'évaluation scientifique de l'INRE (Institut National de Recherche sur les Eaux), No 8, 61 p.

833 Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., de Alda, M.L., Barceló,  
834 D., 2014. Four-year advanced monitoring program of polar pesticides in groundwater of  
835 Catalonia (NE-Spain) *Sci. Total Environ.* 470–471, 1087–1098. Kolpin, D.W., Furlong, E.T.,  
836 Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., 2002. Pharmaceuticals, hormones,  
837 and other organic wastewater contaminants in U.S. Streams, 1999–2000: a national  
838 reconnaissance. *Environ. Sci. Technol.* 36, 1202–1211.

839 Kormos, J.L., Schulz, M., Kohler, H.P., Ternes, T.A., 2010. Biotransformation of selected  
840 iodinated X-ray contrast media and characterization of microbial transformation pathways.  
841 *Environ. Sci. Technol.* 44, 4998–5007.

842 Kolpin, D.W., Skopec, M., Meyer, M.T., Furlong, E.T., Zaugg, S.D., 2004. Urban contribution of  
843 pharmaceuticals and other organic wastewater contaminants to streams during different flow  
844 conditions. *Sci. Total Environ.* 328(1–3), 119–130.

845 Lamothe, M., St-Jacques G., 2014. Géologie du Quaternaire des bassins versant des rivières  
846 Nicolet et Saint-François, Québec. Ministère Energies et Ressources Naturelles Report, 34 p.

Formatted: English (Canada)

- 847 Lamothe, M. 1989. A new framework for the Pleistocene stratigraphy of the central St. Lawrence  
848 Lowland, southern Quebec. *Géogr. Phys. Quatern.* 43, 119-129.
- 849 Lapworth, D., Baran, N., Stuart, M., Ward, R., 2012. Emerging organic contaminants in  
850 groundwater: a review of sources, fate and occurrence. *Environ. Pollut.* 163, 287-303.
- 851 Larocque, M., Gagné, S., Barnetche, D., Meyzonnat, G., Graveline, M.-H., Ouellet, M.A., 2015.  
852 *Projet de connaissance des eaux souterraines du bassin versant de la zone Nicolet et de la*  
853 *partie basse de la zone Saint-François – Rapport final. Report presented to the MDDELCC,*  
854 *258 p.*
- 855 Larocque, M., Gagné, S., Tremblay, L., Meyzonnat, G., 2013. *Projet de connaissance des eaux*  
856 *souterraines du bassin versant de la zone Bécancour et de la MRC Bécancour – Rapport final.*  
857 *Report presented to the MDDEFP, 219 p.*
- 858 Leblanc, Y., Légaré, G., Lacasse, K., Parent, M., Campeau, S., 2013. *Caractérisation*  
859 *hydrogéologique du sud-ouest de la Mauricie. Rapport déposé au ministère du*  
860 *Développement durable, de l'Environnement, de la Faune et des Parcs dans le cadre du*  
861 *Programme d'acquisition de connaissances sur les eaux souterraines du Québec. Département*  
862 *des sciences de l'environnement, Université du Québec à Trois-Rivières, 134 p.*
- 863 Levallois, P., Thériault, M., Rouffignat, J., Tessier, S., Landry, R., Ayotte, P., Girard, M.,  
864 Gingras, S., Gauvin, D., Chiasson, C., 1998. Groundwater contamination by nitrates  
865 associated with intensive potato culture in Québec. *Sci. Total Environ.* 217(1-2), 91-101.
- 866 ~~L.~~Liao, ~~C.F.L.~~ Green, ~~B.A.C.T.~~ Bekins, ~~J.K.B.A.~~ Bohlke, ~~J.K.~~, 2012. Factors controlling  
867 nitrate fluxes in groundwater in agricultural areas. *Water Resour. Res.*, 48-(2012), p., W00109.

Formatted: Indent: Left: 0 cm,  
Hanging: 0.6 cm

868 Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide  
869 survey of polar organic persistent pollutants in European river waters. *Environ. Pollut.* 157(2),  
870 561–568.

871 | Loos, R., Locoro, G., Comero, S., 2010. Pan-European survey of the occurrence of selected polar  
872 organic persistent pollutants in groundwater. *Water Resour.* 44, 4115-4126.

873 Lopez, B., Ollivier, P., Togola, A., Baran, N., Ghestem, J.P., 2015. Screening of French  
874 groundwater for regulated and emerging contaminants. *Sci. Total Environ.* 518, 562-573.

875 | Ma, Y., Li, M., Wu, M., Li, Z., Liu, X., 2015. Occurrences and regional distributions of 20  
876 antibiotics in water bodies during groundwater recharge. *Sci. Total Environ.* 518-519, 498-  
877 506.

878 MAMROT (Ministère des Affaires municipales, des Régions et de l'Occupation du territoire),  
879 2010. Localisation des immeubles. Ministère des affaires municipales, des régions et de  
880 l'occupation du territoire. Direction du bureau municipal, de la géomatique et de la statistique.  
881 1 p.

882 Mansoor, A., Baloch, M.A., Sahar, L., 2014. Development of a Watershed-Based Geospatial  
883 Groundwater Specific Vulnerability Assessment Tool. *Ground water* 52, 137-147.

884 Marsalek, J., 2008. Pharmaceuticals and personal care products (PPCP) in Canadian urban water:  
885 A management perspective. In *Dangerous pollutants (xenobiotics) in urban water cycle* (pp.  
886 117-130). Springer Netherlands.

887 | Martineau, J.-F., 2014. Direction principale des ressources informationnelles et du soutien à  
888 | l'optimisation des processus. Base de données des cultures assurées. Financière agricole du  
889 | Québec. Guide technique BDCA 2014, Québec.  
890 | <http://www.fadq.qc.ca/en/documents/data/insured-crop-database> (Accessed: July 2016)

891 | MDDELCC (Ministère du Développement durable, de l'Environnement et de la Lutte contre les  
892 | changements climatiques), 2011. Guide de référence du Règlement sur les exploitations  
893 | agricoles, ministère du Développement durable, de l'Environnement et de la Lutte contre les  
894 | changements climatiques, ISBN 978-2-550-74799-4, 190 p.

895 | Meyzonnat, G., Larocque, M., Barbecot, F., Gagné, S., Pinti, D.L., 2016. The potential of major  
896 | ion chemistry to assess groundwater vulnerability of a regional aquifer in southern Quebec  
897 | (Canada). Environ. Earth Sci. 75, 68, doi 10.1007/s12665-015-4793-9.

898 | Murgulet, D., ~~and~~, Tick, G.R., 2013. Understanding the sources and fate of nitrate in a highly  
899 | developed aquifer system. J. Contam. Hydrol. 155, 69-81.

900 | Murgulet, D., ~~and~~ Tick, G.R., 2015. Effect of variable-density groundwater flow on nitrate flux to  
901 | coastal waters. Hydrol. Process. Online: DOI: 10.1002/hyp.10580.

902 | Office of Water – United States Environmental Protection Agency, 1991. Managing groundwater  
903 | contamination sources in wellhead protection areas: a priority setting approach. WH-550,  
904 | EPA 570/9-91-023, 286 p.

905 | Oregon Government – Department of Environment Quality – Water Quality, 1996. Wellhead  
906 | Protection Program – Guidance Manual. <http://www.deq.state.or.us/wq/whpguide/ch4.htm>  
907 | (Accessed: July 2016)

908 Pérez-Martin, M., Estrela, T., del-Amo, P., 2016. Measures required to reach the nitrate  
909 objectives in groundwater based on a long-term nitrate model for large river basins (Juncar,  
910 Spain). *Sci. Total Environ.* 566, 122-133.

911 Pisciotta, A., Cusimano, G., Favara, R., 2015. Groundwater nitrate risk assessment using intrinsic  
912 vulnerability methods: a comparative study of environmental impact by intensive farming in  
913 the Mediterranean region of Sicily, Italy. *J Geochem. Explor.* 156, 89-100.

914 Poissant, L., Beauvais, C., Lafrance, P., Deblois, C., 2008. Pesticides in fluvial wetlands  
915 catchments under intensive agricultural activities. *Sci. Total Environ.* 404(1), 182-195.

916 Prosser, R.S., Sibley P.K., 2015. Human health risk assessment of pharmaceuticals and personal  
917 care products in plant tissue due to biosolids and manure amendments, and wastewater  
918 irrigation. *Environ. Int.* 75, 223-233.

919 Quebec, 2015. Loi sur la qualité de l'environnement. Règlement sur le prélèvement des eaux et  
920 leur protection. Chapitre Q2, r. 35.2.

921 Quebec, 2004a. Étude sur la qualité de l'eau potable dans sept bassins versants en surplus de  
922 fumier et impact potentiel sur la santé - Influence de la vulnérabilité des aquifères sur la  
923 qualité de l'eau des puits individuels dans la MRC de Montcalm. *Envirodoq ENV/2004/0313*,  
924 150 p.

925 Quebec, 2004b. Étude sur la qualité de l'eau potable dans sept bassins versants en surplus de  
926 fumier et impact potentiel sur la santé - Étude du risque de gastro-entérite chez les familles  
927 utilisant l'eau d'un puits domestique. Direction risques biologiques, environnementaux et  
928 occupationnels. Institut nationale de santé publique du Québec et Unité de recherche en santé

929 publique du Centre de recherche du CHUL (CHUQ). Envirodoq ENV/2004/0317 (in French),  
930 165 p.

931 Rodriguez-Galiano, V., Mendes, M.P., Garcia-Soldado, M.J., Chica-Olmo, M., Ribeiro, L., 2014.  
932 Predictive modeling of groundwater nitrate pollution using Random Forest and multisource  
933 variables related to intrinsic and specific vulnerability: A case study in an agricultural setting  
934 (Southern Spain). *Sci. Total Environ.* 476, 189–206.

935 Rojas Fabro, A.Y., Pacheco Avila, J.G., Esteller Alberich, M.V., Cabrera Sansores,  
936 S.A., Camargo-Valero, M.A., 2015. Spatial distribution of nitrate health risk associated with  
937 groundwater use as drinking water in Merida, Mexico. *Appl. Geogr.* 65, 49 - 57. ISSN 1873-  
938 7730.

939 Saby, M., Larocque, M., Pinti, D.L., Barbecot, F., Sano, Y., Castro, M.C., 2016. Linking  
940 groundwater quality to residence times and regional geology in the St. Lawrence Lowlands,  
941 southern Quebec, Canada. *Appl. Geochem.* 65, 1-13.

942 Salgado, R., Pereira, V.J., Carvalho, G., Soeiro, R., Gaffney, V., Almeida, C., Cardoso, V.V.,  
943 Ferreira, E., Benoliel, M.J., Ternes, T.A., Oehmen, A., 2013. Photodegradation kinetics and  
944 transformation products of ketoprofen, diclofenac and atenolol in pure water and treated  
945 wastewater. *J. Hazard. Mater.* 244, 516–527.

946 SAS Institute, 2012. JMP® software, Version 12. SAS Institute Inc. Cary. NC. 1997-2016

947 | Scheck, M., Bayer U., 1999. Evolution of the Northeast German Basin: inferences from a 3D  
948 structural model and subsidence analysis. *Tectonophysics* 313,145–168.

949 Schulz, M., Loeffler, D., Wagner, M., Ternes, T.A., 2008. Transformation of the X-ray contrast  
950 medium lopromide in soil and biological wastewater treatment. *Environ. Sci. Technol.* 42,  
951 7207–7217.

952 Scott, T.M., Rose, J.B., Jenkins, T.M., Farrah, S.R., Lukasik, J., 2002. Microbial source tracking:  
953 current methodology and future directions. *Appl. Environ. Microb.* 68(12), 5796–5803.

954 SESAT, 2010. Gouvernance des eaux souterraines de l’Abitibi-Témiscamingue – État de  
955 situation 2010. Société de l’eau souterraine Abitibi-Témiscamingue (SESAT). 262 p.

956 Shrestha, S., Semkuyu, D.K., Pandey, V.P., 2016. Assessment of groundwater vulnerability and  
957 risk to pollution in Kathmandu Valley, Nepal. *Sci. Total Environ.* 556, 23-35.

958 Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Goody, D.C., Bell, R.A.,  
959 Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants  
960 in urban groundwater sources in Africa. *Water Res.* 72, 51-63.

961 Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging  
962 contaminants in UK groundwater. *Sci. Total Environ.* 416, 1–21.

963 Thériault, R., 2013. Identification des sources de nitrate et des facteurs contrôlant sa distribution  
964 dans les sols agricoles et les eaux souterraines des bassins versants Ewing et Walbridge  
965 (Montérégie est). Masters thesis, Institut national de la recherche scientifique, Quebec,  
966 Canada, 179 p.

967 | Thomsen, R., Sondergaard V.H., Sørensen K.I., 2004. Hydrogeological mapping as a basis for  
968 | establishing site-specific groundwater protection zones in Denmark. *Hydrogeol J.* 12(5), 550–  
969 | 562.

970 | UNEP (United Nations Environment Programme), 2003. Groundwater and its susceptibility to  
971 | degradation: A global assessment of the problem and options for management, ISBN: 92-807-  
972 | 2297-2. 140 p.

973 | UPA (Union des Producteurs Agricoles), 2012. UPA Centre-Du-Québec  
974 | <http://www.centre-du-quebec.upa.qc.ca/fr/Federation/Federation.html> (Accessed: January  
975 | 2016)

976 | USDA (United States Department of Agriculture), 2009. The Pesticides Properties Database,  
977 | Agricultural Research Service <http://www.ars.usda.gov/Services/docs.htm?docid=14199>  
978 | (Accessed: January 2016)

979 | US EPA (United States Environmental Protection Agency) 1993. A review of methods for  
980 | assessing aquifer sensitivity and groundwater vulnerability to pesticide contamination. EPA-  
981 | 813-R-93002, 147 p.

982 | Vautour, G, Pinti, D.L., Méjean, P., Saby, M., Meyzonnat, G., Larocque, M., Castro, M.C., Hall,  
983 | C.M., Boucher, C., Roulleau, E., Barbecot, F., Takahata, N., Sano, Y., 2015.  $^3\text{H}/^3\text{He}$ ,  $^{14}\text{C}$  and  
984 | (U-Th)/He groundwater ages in the St. Lawrence Lowlands, Quebec, Eastern Canada. *Chem.*  
985 | *Geol.* 413, 94-106, 10.1016/j.chemgeo.2015.08.003.

- 986 | Vogel, J.C., ~~A.S.~~Talma, ~~T.H.E.~~A.S., Heaton, T.H.E., 1981. Gaseous nitrogen as evidence for  
987 | denitrification in groundwater. *J. Hydrol.* 50-(1–3), 191–200.
- 988 | Woudneh, M.B., Ou, Z., Sekela, M., Tuominen, T., Gledhill, M., 2009. Pesticide multiresidues in  
989 | waters of the Lower Fraser Valley, British Columbia, Canada Part I. Surface water. *J.*  
990 | *Environ. Qual.* 38(3), 940–947.
- 991 | Zhao, Y., Pei, Y., 2012. Risk evaluation of groundwater pollution by pesticides in China: a short  
992 | review. *Procedia Environ. Sci.* 13, 1739–1747. doi: 10.1016/j.proenv.2012.01.167
- 993 | Zhou, J., Li, Q., Guo, Y., Guo, X., Li, X., Zhao, Y., Jia, R., 2012. VLDA model and its  
994 | application in assessing phreatic groundwater vulnerability: a case study of phreatic  
995 | groundwater in the plain area of Yanji County, Xinjiang, China. *Environ. Earth Sci.* 67,  
996 | 1789–1799.

997 **Figure captions**

998 **Figure 1.** Study area in the Nicolet and Lower Saint-François watersheds of southern Quebec  
999 (Canada); a) piezometric map, b) [Mapmap](#) of the bedrock confinement zones, and c) sampling  
1000 locations (wells), sample type, and land use. Data for the piezometric map, geology, and land use  
1001 are from Larocque et al. (2015).

1002 **Figure 2.** Pollutant concentrations in the study area; a) pharmaceutically active compound  
1003 (PhAC) concentrations (33 sampled wells), b) pesticide concentrations (33 sampled wells), and c)  
1004 nitrate concentrations and presence of *E. coli* (190 sampled wells).

1005 **Figure 3.** Spatial distribution of the Anthropogenic Footprint Index (AFI) in the study area.

1006 **Figure 4.** The Anthropogenic Footprint Index (AFI) in the study area as an explanatory variable  
1007 for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and  
1008 total pharmaceutically active compounds (PhAC) concentrations.

1009 **Figure 5.** Recharge in [the](#) study area as an explanatory variable for a) nitrate concentrations and  
1010 occurrence of *E. coli*, b) total pesticide concentrations and total concentrations of  
1011 pharmaceutically active compounds (PhACs), and c) groundwater residence time.

1012 **Figure 6.** The Hydrogeochemical Vulnerability Index (HVI) in the study area as an explanatory  
1013 variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide  
1014 concentrations and total concentrations of pharmaceutically active compounds (PhACs).

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

3

4 Marion SABY<sup>1\*</sup>, Marie LAROCQUE<sup>1</sup>, Daniele L. PINTI<sup>1</sup>, Florent BARBECOT<sup>1</sup>, Sylvain  
5 GAGNÉ<sup>1</sup>, Diogo BARNETCHE<sup>1</sup>, Hubert CABANA<sup>2</sup>

6

7

8 <sup>1</sup> GEOTOP and Département des sciences de la Terre et de l'atmosphère, Université du Québec à  
9 Montréal, CP8888 succ. Centre-Ville, Montréal, QC, Canada

10 <sup>2</sup> Département de génie civil, Université de Sherbrooke, 2500 boul. de l'Université, Sherbrooke,  
11 QC, Canada

12 \* Corresponding author: marion.saby23@gmail.com

13

14

15

16

17 **Abstract**

18 There is growing concern worldwide about the exposure of groundwater resources to  
19 pharmaceutically active compounds (PhACs) and agricultural contaminants, such as pesticides,  
20 nitrate, and Escherichia coli. For regions with a low population density and an abundance of  
21 water, regional contamination assessments are not carried out systematically due to the typically  
22 low concentrations and high costs of analyses. The objectives of this study were to evaluate  
23 regional-scale contaminant distributions in untreated groundwater in a rural region of Quebec  
24 (Canada). The geological and hydrogeological settings of this region are typical of post-glacial  
25 regions around the world, where groundwater flow can be complex due to heterogeneous  
26 geological conditions. A new spatially distributed Anthropogenic Footprint Index (AFI), based  
27 on land use data, was developed to assess surface pollution risks. The Hydrogeochemical  
28 Vulnerability Index (HVI) was computed to estimate aquifer vulnerability. Nine wells had  
29 detectable concentrations of one to four of the 13 tested PhACs, with a maximum concentration  
30 of 116 ng.L<sup>-1</sup> for benzafibrate. A total of 34 of the 47 tested pesticides were detected in  
31 concentrations equal to or greater than the detection limit, with a maximum total pesticide  
32 concentration of 692 ng.L<sup>-1</sup>. Nitrate concentrations exceeded 1 mg.L<sup>-1</sup> N-NO<sub>3</sub> in 15.3% of the  
33 wells, and the Canadian drinking water standard was exceeded in one well. Overall, 13.5% of the  
34 samples had detectable E. coli. Including regional-scale sources of pollutants to the assessment of  
35 aquifer vulnerability with the AFI did not lead to the identification of contaminated wells, due to  
36 the short groundwater flow paths between recharge and the sampled wells. Given the occurrence  
37 of contaminants, the public health concerns stemming from these new data on regional-scale  
38 PhAC and pesticide concentrations, and the local flow conditions observed in post-glacial  
39 terrains, there is a clear need to investigate the sources and behaviours of local-scale pollutants.

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

## 42 1. INTRODUCTION

43 As groundwater pollution increases worldwide (UNEP, 2003), assessing aquifer vulnerability  
44 to contamination is a priority for governmental agencies at all levels. Groundwater pollution from  
45 pharmaceutically active compounds (PhACs), pesticides, nitrate, and bacteria can originate from  
46 various sources (e.g., inorganic and organic fertilizers, individual septic systems, wastewater  
47 collection pipes, landfills). The presence of certain types of molecules in groundwater has already  
48 been linked to the leakage of buried infrastructure, among other determinants (Evgenidou et al.,  
49 2015; Ghoshdastidar et al., 2015; Marsalek, 2008). Because PhACs and pesticides are typically  
50 detected in low concentrations in groundwater, and have high analytical costs, regional-scale  
51 assessments of their presence in aquifers are rarely available. As these compounds are not often  
52 analyzed in routine groundwater monitoring, and because it is often difficult to identify their  
53 origins and locations of influx into the aquifer, their potential contributions to aquifer  
54 contamination and vulnerability are often poorly understood.

55 PhACs have been increasingly detected in groundwater around the world over the past  
56 decades (US EPA, 1993; Ma et al., 2015; Lopez et al., 2015). Among others, these include  
57 molecules that compose sleeping pills, painkillers, contraceptives, and anti-depressants  
58 (Lapworth et al., 2012; Sorensen et al., 2015). PhACs are associated with urban areas or  
59 wastewater treatment zones, and can also be linked to agricultural activity (e.g., pharmaceuticals  
60 from animal feedlots, biosolid application, etc.; Prosser and Sibley, 2015). Pesticides are  
61 increasingly detected in groundwater from a variety of environments (Köck-Schulmeyer et al.,  
62 2014; Lopez et al., 2015; Zhao and Pei, 2012). These can be from agricultural sources, but can  
63 also originate from municipal or residential water uses (e.g., golf courses, parks, and residential  
64 gardening). PhAC and pesticide molecules are typically difficult to trace in groundwater.  
65 Sorption to organic matter and clay minerals, ion exchange in the soil and aquifer, and microbial

66 degradation can modify PhAC and pesticide concentrations in groundwater (Lapworth et al.,  
67 2012). Studies carried out in the USA (Barnes et al., 2008; Focazio et al., 2008; Kolpin et al.,  
68 2004) and in European countries (Jurado et al., 2012; Loos et al., 2010, 2009; Stuart et al., 2012)  
69 have shown the ubiquitous presence of PhACs and pesticides in groundwater in a wide variety of  
70 geological and climatic conditions. This situation, in combination with the limited understanding  
71 of their cumulative, chronic, and long-term effects on humans and ecosystems (see references in  
72 Barnes et al., 2008), make assessing their current concentrations urgent.

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

83 Groundwater vulnerability assessment methods include the DRASTIC index (Aller et al.,  
84 1987), the AQUIPRO method (Chowdhury et al., 2003), the LHT method (Mansoor et al., 2014),  
85 and, more recently, methods based on groundwater isotopic (Murgulet and Tick, 2013) and major  
86 ion geochemistry (Meyzonnat et al., 2016). These semi-quantitative methods are often used as  
87 first assessment in groundwater resource management, and generally do not indicate specific  
88 potential contaminant sources. Different studies have attempted to improve these methods by  
89 identifying a link between land use, contaminant sources, and groundwater contamination (e.g.,

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

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

108 In cold and humid climates, such as southern Quebec (Canada), where water sources are  
109 abundant, groundwater contamination from anthropogenic sources in aquifers often remains  
110 relatively poorly understood. There are very few studies on emerging groundwater contaminants  
111 in Quebec, but research in other Canadian provinces has shown that PhACs can be found in wells  
112 and treated sewage effluents (Evgenidou et al., 2015; Ghoshdastidar et al., 2015; Kleywegt et al.,  
113 2007). Although few studies have focused on the presence of pesticides in groundwater in

114 Canada, this is becoming a concern in some parts of the country (CLE, 2015; Environment  
115 Canada, 2012; Giroux and Sarrasin, 2011; Giroux, 2010; Woudneh et al., 2009). Pesticides and  
116 their metabolites have also been identified in fluvial wetlands near intensive agricultural activity  
117 (Poissant et al., 2008). The presence of nitrate in Quebec groundwater has certainly been the most  
118 frequently investigated contaminant, generally revealing low concentrations (Carrier et al., 2013;  
119 Giroux and Sarrasin, 2011; Giroux 2003; Levallois et al., 1998; Meyzonnat et al., 2016; Quebec,  
120 2004a), which nonetheless often exceed the natural (non-anthropogenic) background of 1 mg N-  
121  $\text{NO}_3\cdot\text{L}^{-1}$  (Dubrovsky et al., 2010).

122 The objective of this study was to evaluate the distribution of PhACs, pesticides, nitrate, and  
123 bacteria in untreated groundwater in the low population density Centre-du-Quebec region of the  
124 St. Lawrence Lowlands (Quebec, Canada), as an example of contaminant distribution in post-  
125 glacial regions around the world. This research was carried out as part of a regional-scale aquifer  
126 characterization study on the Nicolet River watershed and on the lower portion of the Saint-  
127 François River watershed, both located in the Centre-du-Quebec region (Larocque et al., 2015).  
128 Related geological contexts, aquifer confinement, soil and crop types, spatially distributed  
129 recharge, major ion analyses (fully described in Saby et al., 2016), and a DRASTIC index map  
130 are also included in the Larocque et al. (2015) report. Presented here are results from  
131 groundwater sampling undertaken to assess the presence of nitrates, bacteria (*E. coli*), pesticides,  
132 and PhACs. A new Anthropogenic Footprint Index (AFI) was developed, based on the estimated  
133 density of agricultural and urban areas, both considered to be potential sources of contamination.  
134 The Hydrogeochemistry Vulnerability Index (HVI), developed recently by Meyzonnat et al.  
135 (2016), was used to provide an alternate estimate of aquifer vulnerability, based on major ion  
136 analyses reported by Saby et al. (2016). Statistical analyses were performed to assess explanatory  
137 factors for the water quality results, using the spatially distributed data reported in Larocque et al.

138 (2015) for presence of a crop, crop type, soil drainage, aquifer confinement, aquifer type, and  
139 recharge.

140

## 141 **2. STUDY AREA**

### 142 **2.1 Geology and hydrogeology**

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

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

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

162 30 km along the St. Lawrence River (Lamothe and St-Jacques, 2014). This clay creates confining  
163 conditions for the underlying fractured bedrock aquifer. Further upgradient, a flat area composed  
164 of sand, patches of clay, and shale induces a heterogeneous and semi-confined hydrogeological  
165 context, while still further upgradient, the outcropping of reworked till and bedrock leaves the  
166 fractured aquifer unconfined in its main recharge area (Figure 1b).

167 The study area is divided into two main aquifer systems, further described in Larocque et al.  
168 (2015): the shallower Quaternary aquifers of relatively limited thickness and extent, and the  
169 underlying Paleozoic fractured bedrock aquifer, composed of sedimentary rocks. Hydraulic  
170 conductivities in the fractured bedrock aquifer are heterogeneous and range from  $5 \times 10^{-9} \text{ m.s}^{-1}$  to  
171  $7 \times 10^{-6} \text{ m.s}^{-1}$ . Confining zones have previously been estimated using a 3D model of the  
172 Quaternary sediment architecture, based on the thickness of the impermeable units. Results were  
173 interpolated over 250 m x 250 m cells (see Figure 1b). Confined conditions were defined as when  
174 either more than 3 m of clay or more than 5 m of compact till were present. Semi-confined  
175 conditions corresponded to areas where 1 to 3 m of clay or 3 to 5 m of compact till were found.  
176 Unconfined conditions referred to areas where less than 1 m of clay and less than 3 m of compact  
177 till were found. Unconfined zones were found to represent 55% of the studied surface area, while  
178 semi-confined and confined zones represent 18% and 27% respectively (Larocque et al., 2015).

179

## 180 **2.2 Previously available data**

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

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

193 Groundwater geochemistry evolves from a  $\text{Ca-HCO}_3$  water type at recharge, which  
194 corresponds mainly to the Appalachian piedmont, to a  $\text{Na-HCO}_3$  water type downgradient, closer  
195 to the St. Lawrence River. Geology and rock-water interactions control the regional evolution of  
196 groundwater chemistry (Saby et al., 2016).  $^3\text{H}/^3\text{He}$  groundwater ages range from  $4.8 \pm 0.4$  years in  
197 the upgradient portion of the study area, to more than  $60 \pm 3.2$  yrs in its downgradient portion  
198 (Saby et al., 2016).  $\text{SF}_6$  residence times reported in Larocque et al. (2015) show values of a  
199 similar magnitude, between  $1 \pm 0.5$  year upgradient of the study area, where the Quaternary  
200 deposit cover is thin and recharge is direct, and  $34 \pm 5.6$  years downgradient. Saby et al. (2016)  
201 also calculated older  $^{14}\text{C}$  groundwater ages, from  $280 \pm 56$  to  $17050 \pm 3410$  years. These results  
202 clearly indicate mixing between modern groundwater and a paleo-groundwater component  
203 circulating slowly in the deepest, less permeable layers of bedrock, creating this apparent  
204 contradiction in age (Vautour et al., 2015; Saby et al., 2016). Older groundwater likely infiltrated  
205 the bedrock aquifer through subglacial recharge when the Laurentide Ice Sheet covered the study  
206 area (Saby et al., 2016).

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

210 piedmont (Figure 1c). Wetlands, urban areas, and surface water occupy 3.7%, 2.0%, and 1.1% of  
211 the region respectively. A detailed description of the study area is found in Larocque et al.  
212 (2015). Agriculture is dominated by cereal (54%) and hay (22%) production, with a minor  
213 presence of mixed crops, vegetables, and small fruit production (3%) located mainly in the lower  
214 part of the study area where the bedrock aquifer is covered by Champlain Sea clay. No  
215 information is available for the remaining 21% of the study area. The study area is considered to  
216 be among the most agriculturally productive in the province of Quebec (UPA, 2012).

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

225 Larocque et al. (2015) computed the DRASTIC index (Aller et al., 1987) for  
226 500 m x 500 m cells for the bedrock aquifer of the study area using the usual parameters and  
227 associated parametric weights (see annex A1 for details of the method). Vulnerability values of  
228 the DRASTIC index for the bedrock aquifer vary from 24 to 185 for the study area. Quebec  
229 legislation (Quebec, 2015) labels “low vulnerability” regions as those where the DRASTIC index  
230 is below 100, “medium vulnerability” regions as those where the DRASTIC index is between  
231 100 and 180, and “high vulnerability” regions as those with a DRASTIC index above 180 (see  
232 Figure 1 in annex A1). Based on these categories, 28% of the study area is low vulnerability and  
233 72% is medium vulnerability. Only 0.02% of the area is high vulnerability. The medium and high

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

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

246

## 247 **3. METHODS**

### 248 **3.1 Groundwater sampling and analysis**

249 Between June and August 2013, 190 groundwater samples were collected from private wells (157  
250 wells), municipal wells (11 wells), 1" PVC observation wells (12 wells), and 6" steel tubing  
251 observation wells (10 wells) (see locations in Figure 1c and well descriptions in Table A1). Well  
252 depths range between 5 and 250 m for the 145 open borehole bedrock wells, and from 1.2 to 50  
253 m for the 45 wells tapping a granular aquifer (granular wells either have a steel casing or are drive  
254 points). All samples were analyzed for nitrate and *E. coli*. Major ion data ( $\text{Ca}^{2+}$ ,  $\text{Na}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^{+}$ ,  
255 and  $\text{HCO}_3^{-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^{-}$ ) are available for all the wells and are reported in Saby et al. (2016). In  
256 September 2014, 33 wells were resampled (six private wells, nine municipal wells, 11 1" PVC  
257 observation wells, and seven 6" steel tubing observation wells). This water was analyzed for 13

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

262 All the wells were purged prior to sampling, and water was sampled prior to any treatment  
263 once the physiochemical parameters (pH, temperature, redox potential, and electric conductivity)  
264 measured in an air-tight cell had stabilized (MDDELCC, 2011). Groundwater was collected from  
265 the observation wells using a submersible pump with speed control (Redi-Flo2<sup>®</sup>), maintaining the  
266 whole sampling line under pressure to prevent water degassing. All samples were filtered in the  
267 field to 0.45  $\mu\text{m}$ . Samples were kept at 4°C during storage and transport. Samples for PhACs and  
268 pesticides were collected in 1L Nalgene<sup>®</sup> bottles, and were sent to the Environmental  
269 Engineering Laboratory of the University of Sherbrooke for analysis. The samples were first  
270 extracted using a solid phase extraction procedure, and the liquid phase was then analyzed by  
271 liquid chromatography coupled with a triple quadrupole mass spectrometer (Ba et al., 2014;  
272 Haroune et al., 2014). The detection limit of the method for pesticides and PhACs was 5  $\text{ng}\cdot\text{L}^{-1}$ .  
273 The calibration was validated by verifying the calculation of the deviation for each point (criteria  
274 < 20%). Each series of samples was validated for a spiked sample (recovering criteria between  
275 70% - 120%). No field blanks or duplicates were analyzed for pesticides or PhACs because of the  
276 high analytical cost. Groundwater for nitrate analysis was sampled in 125 ml Nalgene<sup>®</sup> bottles  
277 and analyzed by colorimetry in a private laboratory (ISO/CEI 17025), with a detection limit of  
278 0.1  $\text{mg N}\cdot\text{NO}_3\cdot\text{L}^{-1}$ . Laboratory blanks for nitrate analyses were done systematically for each  
279 sample, but no field blank was taken. A total of 10 duplicates were sampled for the 190 samples  
280 analyzed for nitrate.

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

### 288

### 289 **3.2 Anthropogenic Footprint Index (AFI) and Hydrogeochemical Vulnerability Index (HVI)**

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

$$298$$
$$299 \text{ AAD} = (\text{TC} + \text{CQ} + \text{IZA}) \times \text{RCD} \quad (\text{eq. 1})$$

300

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

305 type of activity and depends on the toxicity classification of the Workplace Hazardous Materials  
306 Information System (WHMIS) (CSST, 2007). The weight of the contaminant quantity is based on  
307 contaminant quantity and concentration for a given anthropogenic activity (modified from  
308 SESAT, 2010). The impacted area refers to the potential extent of the activity (punctual, local, or  
309 regional). Finally, contaminant discharge is either recurrent (systematic and linked to the activity  
310 itself), or accidental. Each parameter is evaluated qualitatively, assigned to one of four classes  
311 (low, moderate, high, very high), and weighted following the tables available in Larocque et al.  
312 (2015). The parameters required to calculate the FD and AAD were extracted from a property  
313 assessment database describing the type of anthropic activity (MAMROT, 2010). The AAD  
314 values were computed for each point of anthropic activity on the land surface and were  
315 interpolated on a 250 m x 250 m grid.

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

320

$$321 \quad AFI = 100 \left( \frac{FD}{FD_{max}} + \frac{AAD}{AAD_{max}} \right) \quad (\text{eq. 2})$$

322

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

329 vulnerability at a regional scale. It is calculated by plotting  $(\text{Na}^+ - \text{Cl}^-)$  against  $(\text{Ca}^{2+} + \text{Mg}^{2+}) -$   
330  $(\text{HCO}_3^- + \text{SO}_4^-)$ . The HVI graphically illustrates how the groundwater chemical composition  
331 evolves from a (Ca, Mg)- $\text{HCO}_3$  type in the recharge area to a Na- $\text{HCO}_3$  type downgradient along  
332 a flow path. The HVI can vary between 0 (low vulnerability) and 10 (maximum vulnerability)  
333 along the linear regression from its orthogonal projection. In this study, the HVI was calculated  
334 using the major ion concentrations measured at the sampling points as reported in Saby et al.  
335 (2016).

336

### 337 **3.3 Statistical analysis**

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

353 “unconfined”, “semi-confined”, and “confined”. Aquifer type was categorized as “granular” or  
354 “bedrock”. Recharge was divided into three categories: “low” for recharge values of less than  
355 100 mm.yr<sup>-1</sup>, “average” for recharge values between 100 and 200 mm.yr<sup>-1</sup>, and “high” for  
356 recharge values of higher than 200 mm.yr<sup>-1</sup>. The influence of water table depth and well depth  
357 was analyzed for all parameters and all contaminants, but results are not reported here since they  
358 were insignificant for all analyses.

359

## 360 **4. RESULTS**

### 361 **4.1. Contaminant occurrence**

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

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

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

379 A total of 29 wells (15.3% of all sampled wells) had nitrate concentrations higher than the  
380 natural background of 1 mg.L<sup>-1</sup> N-NO<sub>3</sub> (Dubrovsky et al., 2010) (Figure 2c and Table A2). The  
381 majority of the wells (62.6%) had nitrate in concentrations of less than the 0.1 mg.L<sup>-1</sup> N-NO<sub>3</sub>  
382 detection limit. The maximum nitrate concentration, 12 mg.L<sup>-1</sup> N-NO<sub>3</sub>, was measured in well  
383 NSF250, a granular well located upgradient in the Appalachian piedmont. This is the only well  
384 exceeding the drinking water quality standard of 10 mg.L<sup>-1</sup> N-NO<sub>3</sub> (Health Canada, 2014). The  
385 average nitrate concentration of all wells was 0.63 mg.L<sup>-1</sup> N-NO<sub>3</sub>. On average, wells near fields  
386 with hay crops had a significantly higher nitrate concentration (1.04 mg.L<sup>-1</sup> N-NO<sub>3</sub>) than those  
387 near fields which were not cultivated (0.16 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0297) (Table A7). However, the  
388 simple presence of a crop near a well alone does not explain nitrate concentrations (p>0.05). Well  
389 drained soils had significantly higher concentrations (1.01 mg.L<sup>-1</sup> N-NO<sub>3</sub>) than poorly drained  
390 soils (p=0.0241). The average nitrate concentration in wells tapping an unconfined bedrock  
391 aquifer (1.05 mg.L<sup>-1</sup> N-NO<sub>3</sub>) was significantly higher than that in wells in semi-confined  
392 conditions (0.21 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0022), and that in wells in confined conditions (0.16 mg.L<sup>-1</sup>  
393 N-NO<sub>3</sub>; p=0.0017). The average nitrate concentration for wells in a granular aquifer (1.16 mg.L<sup>-1</sup>  
394 N-NO<sub>3</sub>) was significantly higher than for wells in the Ordovician bedrock aquifer (0.47 mg.L<sup>-1</sup> N-  
395 NO<sub>3</sub>; p=0.0060). The three wells with nitrate concentrations higher than 7 mg.L<sup>-1</sup> N-NO<sub>3</sub> were  
396 located in granular aquifers.

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

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

402

#### 403 **4.2. AFI and HVI identified areas of contamination risk**

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

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

416

## 417 **5. DISCUSSION**

### 418 **5.1. Groundwater contamination**

419 The drinking water quality standards were exceeded in only a limited number of wells (i.e.,  
420 13.5% of the wells for *E. coli*, one well for nitrate, and in none of the sampled wells for  
421 pesticides; there are no drinking water quality standards for PhACs). However, the results  
422 presented here have shown that groundwater in the study area is affected by all four contaminant  
423 types. This ubiquitous presence of PhAC and pesticides is similar to that reported in other studies

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

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

438 The measured concentrations of pesticides were below the Canadian drinking water quality  
439 standards (MDDELCC, 2011). The average total pesticide concentration was  $67 \text{ ng.L}^{-1}$ , which is  
440 lower than the European limit for cumulated pesticides, of  $500 \text{ ng.L}^{-1}$  (CUE, 1998; there is no  
441 total pesticide water quality standard in Canada). The European limit was exceeded in one well  
442 ( $692 \text{ ng.L}^{-1}$ ; NSF177, a municipal well tapping a confined granular aquifer), and was near the  
443 European limit in another well ( $479 \text{ ng.L}^{-1}$ ; NSF-R6, an observation well in the bedrock aquifer).  
444 These two wells are located upgradient, in the Appalachian piedmont, in areas where agricultural  
445 land surrounds the wells. The higher occurrence of pesticides in the tested wells (70%) compared  
446 to PhACs could be explained by more regionally distributed sources of the contaminant.

447 The measured nitrate concentrations are similar to those reported in other studies from  
448 southern Quebec (Carrier et al., 2013; Giroux and Sarrasin, 2011; Levallois et al., 1998;  
449 Meyzonnat et al., 2016; Quebec, 2004a). It is interesting to highlight that higher concentrations of  
450 nitrate, exceeding the drinking water quality standard (between 11 and 72 mg.L<sup>-1</sup> N-NO<sub>3</sub>), have  
451 been reported for shallow unconfined wells in a granular aquifer of the study area (e.g., BPR and  
452 Arrakis consultants, 2004). When comparing results from the current study with the previously  
453 available DRASTIC index values, the bedrock wells located in areas where the DRASTIC index  
454 was categorized as “medium” have significantly higher nitrate concentrations (0.52 mg.L<sup>-1</sup> N-  
455 NO<sub>3</sub>) than those located in areas where the DRASTIC index was categorized as “low”  
456 (<0.1 mg.L<sup>-1</sup> N-NO<sub>3</sub>; p=0.0278). Similar to these results, a study in the Lanaudiere region of  
457 southern Quebec showed a correlation between nitrate concentrations and the DRASTIC index  
458 (Quebec, 2004a), with stronger correlations for wells tapping granular aquifers than for deep  
459 bedrock wells. In the current study, the limited proportion of concentrations higher than the  
460 anthropogenic background could be related to the presence of agricultural drainage, which  
461 transports nitrate to surface water before it can infiltrate to groundwater (Thériault, 2013). Poorly  
462 drained soils with high organic contents could also be more anoxic, and thus produce nitrate-  
463 reducing conditions (Vogel et al., 1981; Liao et al., 2012). Denitrification tends to happen more  
464 often in soils and aquifers with high organic carbon content, and therefore can sometimes be an  
465 important factor for nitrate removal. However, the sampling density combined with the relatively  
466 low nitrate concentrations in groundwater makes it difficult to assess this effect in the study area.

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

471 contamination was caused mainly by local processes, such as the proximity of a private sewage  
472 system, or poor well construction or maintenance. Although the effect of aquifer type was not  
473 clear in the current study, the Lanaudiere study (Quebec, 2004b) showed a higher occurrence of  
474 *E. coli* in granular aquifers, with 49% of the granular wells having a positive detection. The  
475 highly heterogeneous coverage of Quaternary post-glacial deposits in the study area could  
476 explain the absence of significant correlations between the presence of bacteria and the tested  
477 parameters. Interestingly, the average nitrate concentration in the wells where *E. coli* was  
478 detected was significantly higher compared with the wells where no *E. coli* was detected  
479 (1.61 mg.L<sup>-1</sup> N-NO<sub>3</sub> versus 0.44 mg.L<sup>-1</sup> N-NO<sub>3</sub> respectively; p=0.001). This could be due to the  
480 combination of manure spreading with other fertilizer application in agricultural areas.

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

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

495 was detected (in three wells). Counterintuitively, the PhAC mefenamic acid, which has the  
496 highest log  $K_{ow}$ , was detected in the highest number of wells (seven). Similarly to PhAC  
497 compounds, the low log  $K_{ow}$  pesticides were not the most frequently detected. Aldicarb-sulfone  
498 (log  $K_{ow}$  = -0.57) and imidacloprid (log  $K_{ow}$  = 0.57) were detected in only one well. Another  
499 soluble pesticide was not detected (dimethoate, log  $K_{ow}$  = 0.78) while chlotianidin (log  $K_{ow}$  =  
500 0.70) was detected in two wells. Permethrin, a pyrethroid compound frequently used in  
501 agriculture and for municipal uses, was detected in two wells (PZ2, a 9.1 m observation well in  
502 the unconfined surface sediments, and NSF177, a 39.0 m municipal well tapping a semi-confined  
503 granular aquifer). This was unexpected since this insecticide has the highest log  $K_{ow}$  of the tested  
504 pesticides (log  $K_{ow}$  = 6.50) and is generally considered to be highly adsorbed. All the pesticides  
505 with a log  $K_{ow}$  of higher than 4 were detected in one or more wells. The most frequently detected  
506 pesticides (kresoxim-methyl, in 9 wells; trifloxystrobin, in 7 wells; piperonyl butoxide, in 7  
507 wells) had log  $K_{ow}$  of equal to or higher than 3.40.

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

516

## 517 **5.2. Identifying contaminant sources with the Anthropogenic Footprint Index (AFI)**

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

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

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

548

### 549 **5.3. Estimating aquifer vulnerability**

#### 550 ***5.3.1. Aquifer recharge and groundwater dynamics***

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

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

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

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

580

### 581 *5.3.1 Hydrogeochemical Vulnerability Index (HVI)*

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

590 groundwater near recharge areas with Ca,Mg-HCO<sub>3</sub>, Ca-HCO<sub>3</sub>, and Ca-SO<sub>4</sub> water types, while  
591 the low scores represent increasing confinement conditions and water type evolving to Na-HCO<sub>3</sub>  
592 and Na-Cl types (Meyzonnat et al., 2016). The high HVI wells in recharge areas are also those  
593 where residence times are the shortest (Figure 5c), which explains their association with the  
594 highest nitrate concentrations. The weaker link observed between PhAC and the HVI, and, to a  
595 certain extent, pesticide concentrations and the HVI could be due to the small number of wells  
596 sampled for these contaminants ( $n = 33$ ). It could also be explained by PhAC and pesticide  
597 degradation in the unsaturated zone. Overall, the HVI appears to be a good indicator of aquifer  
598 contamination risk from agricultural sources, but the results are less conclusive for PhAC and  
599 pesticide sources.

600 Results for the HVI and the DRASTIC index do not provide the same type of spatial  
601 vulnerability information because of the differences inherent to the methods. The HVI method  
602 provides information on groundwater flow paths, while DRASTIC focuses on vertical flows from  
603 the surface to the water table. Thus, in the study area, the DRASTIC and the HVI indices do not  
604 provide the same results in comparison with contaminant distributions. The HVI index correlates  
605 more strongly with NO<sub>3</sub>, *E. coli*, and pesticide occurrences than does DRASTIC. For PhACs, the  
606 correlation is less clear for both DRASTIC and HVI. The results for nitrate are similar to those of  
607 Meyzonnat et al. (2016), who performed a complete comparison of the two methods on a  
608 neighboring watershed with similar geological conditions. These authors found that the  
609 DRASTIC index was relatively ineffective in evaluating groundwater vulnerability, while the  
610 HVI method showed a clear correlation with nitrate concentrations.

611

#### 612 **5.4. Synthesis and recommendations**

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

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

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

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

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

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

669

## 670 **6. CONCLUSIONS**

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

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

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

692

### 693 **ACKNOWLEDGMENTS**

694 The authors would like to thank the Quebec Ministère du Développement durable, de  
695 l'Environnement et de la Lutte contre les changements climatiques (Quebec Ministry of  
696 Environment), the municipalities, and the watershed agencies (COGESAF and COPERNIC) who  
697 contributed to the funding of this research, as well as the municipalities and private wells owners  
698 who allowed access for water sampling.

699

700 **REFERENCES**

- 701 Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., Hackett, G., 1987. DRASTIC: A Standardized  
702 System for Evaluating Groundwater Pollution Potential Using Hydrogeologic Settings. EPA-  
703 600/2-87-035, 20 p.
- 704 American Public Health Association, American Water Works Association and Water  
705 Environment Federation. Standard Methods for the Examination of Water and Wastewater,  
706 22nd Edition, 2012.
- 707 Ba, S., Haroune, L., Cruz-Morató, C., Jacquet, C., Touahar, I.E., Bellenger, J.-P., Legault, C.Y.,  
708 Jones, J.P., Cabana, H., 2014. Synthesis and characterization of combined cross-linked  
709 laccase and tyrosinase aggregates transforming acetaminophen as a model phenolic  
710 compound in wastewaters. *Sci. Total Environ.* 487, 748-755.
- 711 Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., Barber, L.B., 2008. A  
712 national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the  
713 United States — I) Groundwater. *Sci. Total Environ.* 402(2-3), 192-200.
- 714 Bojórquez-Tapia, A., Cruz-Bello, G.M., Luna-González, L., Juárez, L., Ortiz-Pérez, M.A., 2009.  
715 V-DRASTIC: using visualization to engage policymakers in groundwater vulnerability  
716 assessment. *J. Hydrol.* 373, 242–255.
- 717 BPR and Arrakis consultants, 2004. Caractérisation des eaux souterraines de St-Albert-de-  
718 Warwick. Report written for the Quebec Ministry of Environment. 55 p.
- 719 Carrier, M.-A., Lefebvre, R., Rivard, C., Parent, M., Ballard, J.-M., Benoit, N., Vigneault, H.,  
720 Beaudry, C., Malet, X., Laurencelle, M., Gosselin, J.-S., Ladevèze, P., Thériault, R., Beaudin,

721 Michaud, A., Pugin, A., Morin, R., Crow, H., Gloaguen, E., Bleser, J., Martin, A., Lavoie, D.,  
722 2013. Portrait des ressources en eau souterraine en Montérégie Est, Québec, Canada. Projet  
723 réalisé conjointement par l'INRS, la CGC, l'OBV Yamaska et l'IRDA dans le cadre du  
724 Programme d'acquisition de connaissances sur les eaux souterraines, rapport final INRS R-  
725 1433.

726 Cassidy, R., Comte, J.C., Nitsche, J., Wilson, C., Flynn, R., Ofterdinger, U., 2014. Combining  
727 multi-scale geophysical techniques for robust hydro-structural characterization in catchments  
728 underlain by hard rock in post-glacial regions. J Hydrol. 517, 715-731.

729 Chen, S.K., Jang, C.S., Peng, Y.P., 2013. Developing a probability-based model of aquifer  
730 vulnerability in an agricultural region. J. Hydrol. 486, 494–504.

731 Chowdhury, S.H., Kehew, A.E., Passero, R.N., 2003. Correlation between nitrate contamination  
732 and groundwater pollution potential. Ground water. 41, 735-745.

733 CLE (Communities, Lands and Environment) (2015). Pesticide Analysis for Drinking Water-  
734 Open data. [https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-](https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-open-data)  
735 [open-data](https://www.princeedwardisland.ca/en/service/pesticide-analysis-drinking-water-open-data). (Accessed: June 2016)

736 CSST (Commission de la santé et de la sécurité du travail), 2007. Système d'information sur les  
737 matières utilisées au travail. [http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-](http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-toxicologique.aspx)  
738 [toxicologique.aspx](http://www.csst.qc.ca/prevention/reptox/Pages/repertoire-toxicologique.aspx) (Accessed : July 2016)

739 CUE (Conseil de l'Union Européenne), 1998. Directive 98/83/CE du conseil relative à la qualité  
740 des eaux destinées à la consommation humaine. 23p.

741 Czekaj, J., Jakóbczyk -Karpierz, S., Rubin, H., Sitek, S., Witkowski, A.J., 2015. Identification of  
742 nitrate sources in groundwater and potential impact on drinking water reservoir

743 (Goczałkowice reservoir, Poland). *Phys. Chem. Earth*. In press,  
744 doi:10.1016/j.pce.2015.11.005.

745  
746 Dubrovsky, N.M., Burow, K.R., Clark, G.M., Gronberg, J.M., Hamilton, P.A., Hitt, K.J.,  
747 Mueller, D.K., Munn, M.D., Nolan, B.T., Puckett, L.J., Rupert, M.G., Short, T.M., Spahr,  
748 N.E., Sprague, L.A., Wilber, W.G., 2010. The quality of our Nation's waters—nutrients in the  
749 Nation's streams and groundwater, 1992–2004. U.S. Geological Survey Circular, 1350, 174  
750 p.

751 Dyke, A.S., 2004. An outline of North American deglaciation with emphasis on central and  
752 northern Canada. *Dev. Quat. Sci.* 2, 373-424.

753 Environment Canada, 2012. Canadian climate normals 1971-2000 for Laurierville, Québec. On-  
754 line:[http://climate.weather.gc.ca/climate\\_normals/index\\_e.html](http://climate.weather.gc.ca/climate_normals/index_e.html)

755 ESRI (Environmental System Research Institute), 2016. ArcGIS Desktop. Release 10.3.1.  
756 Analysis Tools.

757 Evgenidou, E.N., Konstantinou, I.K., Lambropoulou, D.A., 2015. Occurrence and removal of  
758 transformation products of PPCPs and illicit drugs in wastewaters: a review. *Sci. Total*  
759 *Environ.* 505, 905-926.

760 Fatta-Kassinos, D., Vasquez, M.I., Kummerer, K., 2011. Transformation products of  
761 pharmaceuticals in surface waters and wastewater formed during photolysis and advanced  
762 oxidation processes — degradation, elucidation of byproducts and assessment of their  
763 biological potency. *Chemosphere* 85, 693–709.

764 Fleckenstein, J.H., Niswonger, R.G., Fogg, G.E., 2006. River–aquifer interactions, geologic  
765 heterogeneity, and low-flow management. *Ground Water* 44, 837–852.

766 Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., 2008. A  
767 national reconnaissance for pharmaceuticals and other organic wastewater contaminants the  
768 United States — II) untreated drinking water sources. *Sci. Total Environ.* 402, 201–216.

769 Foster, S.S.D., Hirata, R., 1998. Groundwater pollution risk assessment. Pan American Center for  
770 Sanitary Engineering and Environmental Sciences, Lima.

771 Ghoshdastidar, A.J., Fox, S., Tong, A.Z. 2015. The presence of the top prescribed  
772 pharmaceuticals in treated sewage effluents and receiving waters in Southwest Nova Scotia,  
773 Canada. *Environ. Sci. Pollut. Res. Int.* 1, 689-700.

774 Giroux, I., 2003. Contamination de l’eau souterraine par les pesticides et les nitrates dans les  
775 régions en culture de pommes de terre, Direction du suivi de l’état de l’environnement,  
776 ministère de l’Environnement, Québec, enviropdoq no ENV/2003/0233, 23 pages et 3 annexes.

777 Giroux, I., 2010. Présence de pesticides dans l’eau au Québec – Bilan dans quatre cours d’eau de  
778 zones en culture de maïs et de soya en 2005, 2006 et 2007 et dans des réseaux de distribution  
779 d’eau potable, ministère du Développement durable, de l’Environnement et des Parcs,  
780 Direction du suivi de l’état de l’environnement, 78 p.

781 Giroux, I., Sarrasin, B., 2011. Pesticides et nitrates dans l’eau souterraine près de cultures de  
782 pommes de terre - Échantillonnage dans quelques régions du Québec en 2008 et 2009,  
783 ministère du Développement durable, de l’Environnement et des Parcs, Direction du suivi de  
784 l’état de l’environnement, Centre d’expertise en analyse environnementale du Québec, ISBN  
785 978-2-550-61396-1, 31 p.

786 Globensky, Y., 1993. Lexique stratigraphique canadien. Volume V-B: région des Appalaches,  
787 des Basses-Terres du Saint-Laurent et des Iles de la Madeleine. Ministère de l'Énergie et des  
788 Ressources et Direction Générale de l'Exploration géologique et minérale, p. 327, DV 91e23.  
789 (in French).

790 Harff, J., Björk S., Hoth P., 2011. The Baltic Sea Basin, Central and Eastern European 3  
791 Development Studies (CEEDES), Springer-Verlag Berlin Heidelberg, DOI 10.1007/978-3-  
792 642-17220-5\_1, C 2011

793 Haroune, L., Saibi, S., Bellenger, J.-P., Cabana, H., 2014. Evaluation of the efficiency of  
794 *Trametes hirsuta* for the removal of multiple pharmaceutical compounds under low  
795 concentrations relevant to the environment. *Bioresource Technol.*, 171, 199-202.

796 Health Canada, 2014. Guidelines for Canadian drinking water quality: summary table. Federal–  
797 Provincial–Territorial Committee on Drinking Water. [http://www.hc-sc.gc.ca/ewh-  
798 semt/water-eau/drink-potab/guide/index-eng.php](http://www.hc-sc.gc.ca/ewh-<br/>798 semt/water-eau/drink-potab/guide/index-eng.php) (Accessed: March 2016)

799 IRDA (Institut national de recherche et de développement en agroenvironnement), 2013. Études  
800 pédologiques. [http://www.irda.qc.ca/fr/outils-et-services/informations-sur-les-sols/etudes-  
801 pedologiques/](http://www.irda.qc.ca/fr/outils-et-services/informations-sur-les-sols/etudes-<br/>801 pedologiques/) (Accessed: April 2016)

802 Jurado, A., Vázquez-Suñé, E., Carrera, J., López de Alda, M., Pujades, E., Barceló, D., 2012.  
803 Emerging organic contaminants in groundwater in Spain: A review of sources, recent  
804 occurrence and fate in a European context. *Sci. Total Environ.* 440, 82-94.

805 Kleywegt, S., Smyth, S-A., Parrott, J., Schaefer, K., Lagacé, E., Payne, M., Topp, E., Beck, A.,  
806 McLaughlin, A., Ostapyk, K., 2007. Produits pharmaceutiques et produits d'hygiène

807       personnelle dans l'environnement canadien : recherches et directives, série de rapports  
808       d'évaluation scientifique de l'INRE (Institut National de Recherche sur les Eaux), No 8, 61 p.

809   Köck-Schulmeyer, M., Ginebreda, A., Postigo, C., Garrido, T., Fraile, J., de Alda, M.L., Barceló,  
810   D., 2014. Four-year advanced monitoring program of polar pesticides in groundwater of  
811   Catalonia (NE-Spain) *Sci. Total Environ.* 470–471, 1087–1098. Kolpin, D.W., Furlong, E.T.,  
812   Meyer, M.T., Thurman, E.M., Zaugg, S.D., Barber, L.B., 2002. Pharmaceuticals, hormones,  
813   and other organic wastewater contaminants in U.S. Streams, 1999–2000: a national  
814   reconnaissance. *Environ. Sci. Technol.* 36, 1202–1211.

815   Kormos, J.L., Schulz, M., Kohler, H.P., Ternes, T.A., 2010. Biotransformation of selected  
816   iodinated X-ray contrast media and characterization of microbial transformation pathways.  
817   *Environ. Sci. Technol.* 44, 4998–5007.

818   Kolpin, D.W., Skopec, M., Meyer, M.T., Furlong, E.T., Zaugg, S.D., 2004. Urban contribution of  
819   pharmaceuticals and other organic wastewater contaminants to streams during different flow  
820   conditions. *Sci. Total Environ.* 328(1–3), 119–130.

821   Lamothe, M., St-Jacques G., 2014. Géologie du Quaternaire des bassins versant des rivières  
822   Nicolet et Saint-François, Québec. Ministère Energies et Ressources Naturelles Report, 34 p.

823   Lamothe, M. 1989. A new framework for the Pleistocene stratigraphy of the central St. Lawrence  
824   Lowland, southern Quebec. *Géogr. Phys. Quatern.* 43, 119-129.

825   Lapworth, D., Baran, N., Stuart, M., Ward, R., 2012. Emerging organic contaminants in  
826   groundwater: a review of sources, fate and occurrence. *Environ. Pollut.* 163, 287-303.

- 827 Larocque, M., Gagné, S., Barnetche, D., Meyzonnat, G., Graveline, M.-H., Ouellet, M.A., 2015.  
828       Projet de connaissance des eaux souterraines du bassin versant de la zone Nicolet et de la  
829       partie basse de la zone Saint-François – Rapport final. Report presented to the MDDELCC,  
830       258 p.
- 831 Larocque, M., Gagné, S., Tremblay, L., Meyzonnat, G., 2013. Projet de connaissance des eaux  
832       souterraines du bassin versant de la zone Bécancour et de la MRC Bécancour – Rapport final.  
833       Report presented to the MDDEFP, 219 p.
- 834 Leblanc, Y., Légaré, G., Lacasse, K., Parent, M., Campeau, S., 2013. Caractérisation  
835       hydrogéologique du sud-ouest de la Mauricie. Rapport déposé au ministère du  
836       Développement durable, de l'Environnement, de la Faune et des Parcs dans le cadre du  
837       Programme d'acquisition de connaissances sur les eaux souterraines du Québec. Département  
838       des sciences de l'environnement, Université du Québec à Trois-Rivières, 134 p.
- 839 Levallois, P., Thériault, M., Rouffignat, J., Tessier, S., Landry, R., Ayotte, P., Girard, M.,  
840       Gingras, S., Gauvin, D., Chiasson, C., 1998. Groundwater contamination by nitrates  
841       associated with intensive potato culture in Québec. *Sci. Total Environ.* 217(1-2), 91-101.
- 842 Liao, L., Green, C.T., Bekins, B.A., Bohlke, J.K., 2012. Factors controlling nitrate fluxes in  
843       groundwater in agricultural areas. *Water Resour. Res.*, 48, W00109.
- 844 Loos, R., Gawlik, B.M., Locoro, G., Rimaviciute, E., Contini, S., Bidoglio, G., 2009. EU-wide  
845       survey of polar organic persistent pollutants in European river waters. *Environ. Pollut.* 157(2),  
846       561–568.
- 847 Loos, R., Locoro, G., Comero, S., 2010. Pan-European survey of the occurrence of selected polar  
848       organic persistent pollutants in groundwater. *Water Resour.* 44, 4115-4126.

849 Lopez, B., Ollivier, P., Togola, A., Baran, N., Ghestem, J.P., 2015. Screening of French  
850 groundwater for regulated and emerging contaminants. *Sci. Total Environ.* 518, 562-573.

851 Ma, Y., Li, M., Wu, M., Li, Z., Liu, X., 2015. Occurrences and regional distributions of 20  
852 antibiotics in water bodies during groundwater recharge. *Sci. Total Environ.* 518-519, 498-  
853 506.

854 MAMROT (Ministère des Affaires municipales, des Régions et de l'Occupation du territoire),  
855 2010. Localisation des immeubles. Ministère des affaires municipales, des régions et de  
856 l'occupation du territoire. Direction du bureau municipal, de la géomatique et de la statistique.  
857 1 p.

858 Mansoor, A., Baloch, M.A., Sahar, L., 2014. Development of a Watershed-Based Geospatial  
859 Groundwater Specific Vulnerability Assessment Tool. *Ground water* 52, 137-147.

860 Marsalek, J., 2008. Pharmaceuticals and personal care products (PPCP) in Canadian urban water:  
861 A management perspective. In *Dangerous pollutants (xenobiotics) in urban water cycle* (pp.  
862 117-130). Springer Netherlands.

863 Martineau, J.-F., 2014. Direction principale des ressources informationnelles et du soutien à  
864 l'optimisation des processus. Base de données des cultures assurées. Financière agricole du  
865 Québec. Guide technique BDCA 2014, Québec.  
866 <http://www.fadq.qc.ca/en/documents/data/insured-crop-database> (Accessed: July 2016)

867 MDDELCC (Ministère du Développement durable, de l'Environnement et de la Lutte contre les  
868 changements climatiques), 2011. Guide de référence du Règlement sur les exploitations  
869 agricoles, ministère du Développement durable, de l'Environnement et de la Lutte contre les  
870 changements climatiques, ISBN 978-2-550-74799-4, 190 p.

871 Meyzonnat, G., Larocque, M., Barbecot, F., Gagné, S., Pinti, D.L., 2016. The potential of major  
872 ion chemistry to assess groundwater vulnerability of a regional aquifer in southern Quebec  
873 (Canada). *Environ. Earth Sci.* 75, 68, doi 10.1007/s12665-015-4793-9.

874 Murgulet, D., Tick, G.R., 2013. Understanding the sources and fate of nitrate in a highly  
875 developed aquifer system. *J. Contam. Hydrol.* 155, 69-81.

876 Murgulet, D., Tick, G.R., 2015. Effect of variable-density groundwater flow on nitrate flux to  
877 coastal waters. *Hydrol. Process.* Online: DOI: 10.1002/hyp.10580.

878 Office of Water – United States Environmental Protection Agency, 1991. Managing groundwater  
879 contamination sources in wellhead protection areas: a priority setting approach. WH-550,  
880 EPA 570/9-91-023, 286 p.

881 Oregon Government – Department of Environment Quality – Water Quality, 1996. Wellhead  
882 Protection Program – Guidance Manual. <http://www.deq.state.or.us/wq/whpguide/ch4.htm>  
883 (Accessed: July 2016)

884 Pérez-Martin, M., Estrela, T., del-Amo, P., 2016. Measures required to reach the nitrate  
885 objectives in groundwater based on a long-term nitrate model for large river basins (Juncar,  
886 Spain). *Sci. Total Environ.* 566, 122-133.

887 Pisciotta, A., Cusimano, G., Favara, R., 2015. Groundwater nitrate risk assessment using intrinsic  
888 vulnerability methods: a comparative study of environmental impact by intensive farming in  
889 the Mediterranean region of Sicily, Italy. *J Geochem. Explor.* 156, 89-100.

890 Poissant, L., Beauvais, C., Lafrance, P., Deblois, C., 2008. Pesticides in fluvial wetlands  
891 catchments under intensive agricultural activities. *Sci. Total Environ.* 404(1), 182-195.

892 Prosser, R.S., Sibley P.K., 2015. Human health risk assessment of pharmaceuticals and personal  
893 care products in plant tissue due to biosolids and manure amendments, and wastewater  
894 irrigation. *Environ. Int.* 75, 223-233.

895 Quebec, 2015. Loi sur la qualité de l'environnement. Règlement sur le prélèvement des eaux et  
896 leur protection. Chapitre Q2, r. 35.2.

897 Quebec, 2004a. Étude sur la qualité de l'eau potable dans sept bassins versants en surplus de  
898 fumier et impact potentiel sur la santé - Influence de la vulnérabilité des aquifères sur la  
899 qualité de l'eau des puits individuels dans la MRC de Montcalm. *Envirodoq ENV/2004/0313*,  
900 150 p.

901 Quebec, 2004b. Étude sur la qualité de l'eau potable dans sept bassins versants en surplus de  
902 fumier et impact potentiel sur la santé - Étude du risque de gastro-entérite chez les familles  
903 utilisant l'eau d'un puits domestique. Direction risques biologiques, environnementaux et  
904 occupationnels. Institut nationale de santé publique du Québec et Unité de recherche en santé  
905 publique du Centre de recherche du CHUL (CHUQ). *Envirodoq ENV/2004/0317 (in French)*,  
906 165 p.

907 Rodriguez-Galiano, V., Mendes, M.P., Garcia-Soldado, M.J., Chica-Olmo, M., Ribeiro, L., 2014.  
908 Predictive modeling of groundwater nitrate pollution using Random Forest and multisource  
909 variables related to intrinsic and specific vulnerability: A case study in an agricultural setting  
910 (Southern Spain). *Sci. Total Environ.* 476, 189–206.

911 Rojas Fabro, A.Y., Pacheco Avila, J.G., Esteller Alberich, M.V., Cabrera Sansores,  
912 S.A., Camargo-Valero, M.A., 2015. Spatial distribution of nitrate health risk associated with

913 groundwater use as drinking water in Merida, Mexico. *Appl. Geogr.* 65, 49 - 57. ISSN 1873-  
914 7730.

915 Saby, M., Larocque, M., Pinti, D.L., Barbecot, F., Sano, Y., Castro, M.C., 2016. Linking  
916 groundwater quality to residence times and regional geology in the St. Lawrence Lowlands,  
917 southern Quebec, Canada. *Appl. Geochem.* 65, 1-13.

918 Salgado, R., Pereira, V.J., Carvalho, G., Soeiro, R., Gaffney, V., Almeida, C., Cardoso, V.V.,  
919 Ferreira, E., Benoliel, M.J., Ternes, T.A., Oehmen, A., 2013. Photodegradation kinetics and  
920 transformation products of ketoprofen, diclofenac and atenolol in pure water and treated  
921 wastewater. *J. Hazard. Mater.* 244, 516–527.

922 SAS Institute, 2012. JMP<sup>®</sup> software, Version 12. SAS Institute Inc. Cary. NC. 1997-2016

923 Scheck, M., Bayer U., 1999. Evolution of the Northeast German Basin: inferences from a 3D  
924 structural model and subsidence analysis. *Tectonophysics* 313,145–168.

925 Schulz, M., Loeffler, D., Wagner, M., Ternes, T.A., 2008. Transformation of the X-ray contrast  
926 medium lopromide in soil and biological wastewater treatment. *Environ. Sci. Technol.* 42,  
927 7207–7217.

928 Scott, T.M., Rose, J.B., Jenkins, T.M., Farrah, S.R., Lukasik, J., 2002. Microbial source tracking:  
929 current methodology and future directions. *Appl. Environ. Microb.* 68(12), 5796–5803.

930 SESAT, 2010. Gouvernance des eaux souterraines de l’Abitibi-Témiscamingue – État de  
931 situation 2010. Société de l’eau souterraine Abitibi-Témiscamingue (SESAT). 262 p.

932 Shrestha, S., Semkuyu, D.K., Pandey, V.P., 2016. Assessment of groundwater vulnerability and  
933 risk to pollution in Kathmandu Valley, Nepal. *Sci. Total Environ.* 556, 23-35.

934 Sorensen, J.P.R., Lapworth, D.J., Nkhuwa, D.C.W., Stuart, M.E., Goody, D.C., Bell, R.A.,  
935 Chirwa, M., Kabika, J., Liemisa, M., Chibesa, M., Pedley, S., 2015. Emerging contaminants  
936 in urban groundwater sources in Africa. *Water Res.* 72, 51-63.

937 Stuart, M., Lapworth, D., Crane, E., Hart, A., 2012. Review of risk from potential emerging  
938 contaminants in UK groundwater. *Sci. Total Environ.* 416, 1–21.

939 Thériault, R., 2013. Identification des sources de nitrate et des facteurs contrôlant sa distribution  
940 dans les sols agricoles et les eaux souterraines des bassins versants Ewing et Walbridge  
941 (Montérégie est). Masters thesis, Institut national de la recherche scientifique, Quebec,  
942 Canada, 179 p.

943 Thomsen, R., Sondergaard V.H., Sørensen K.I., 2004. Hydrogeological mapping as a basis for  
944 establishing site-specific groundwater protection zones in Denmark. *Hydrogeol J.* 12(5), 550–  
945 562.

946 UNEP (United Nations Environment Programme), 2003. Groundwater and its susceptibility to  
947 degradation: A global assessment of the problem and options for management, ISBN: 92-807-  
948 2297-2. 140 p.

949 UPA (Union des Producteurs Agricoles), 2012. UPA Centre-Du-Québec  
950 <http://www.centre-du-quebec.upa.qc.ca/fr/Federation/Federation.html> (Accessed: January  
951 2016)

952 USDA (United States Department of Agriculture), 2009. The Pesticides Properties Database,  
953 Agricultural Research Service <http://www.ars.usda.gov/Services/docs.htm?docid=14199>  
954 (Accessed: January 2016)

955 US EPA (United States Environmental Protection Agency) 1993. A review of methods for  
956 assessing aquifer sensitivity and groundwater vulnerability to pesticide contamination. EPA-  
957 813-R-93002, 147 p.

958 Vautour, G, Pinti, D.L., Méjean, P., Saby, M., Meyzonnat, G., Larocque, M., Castro, M.C., Hall,  
959 C.M., Boucher, C., Roulleau, E., Barbecot, F., Takahata, N., Sano, Y., 2015.  $^3\text{H}/^3\text{He}$ ,  $^{14}\text{C}$  and  
960 (U-Th)/He groundwater ages in the St. Lawrence Lowlands, Quebec, Eastern Canada. *Chem.*  
961 *Geol.* 413, 94-106, 10.1016/j.chemgeo.2015.08.003.

962 Vogel, J.C., Talma, A.S., Heaton, T.H.E., 1981. Gaseous nitrogen as evidence for denitrification  
963 in groundwater. *J. Hydrol.* 50(1–3), 191–200.

964 Woudneh, M.B., Ou, Z., Sekela, M., Tuominen, T., Gledhill, M., 2009. Pesticide multiresidues in  
965 waters of the Lower Fraser Valley, British Columbia, Canada Part I. Surface water. *J.*  
966 *Environ. Qual.* 38(3), 940–947.

967 Zhao, Y., Pei, Y., 2012. Risk evaluation of groundwater pollution by pesticides in China: a short  
968 review. *Procedia Environ. Sci.* 13, 1739–1747. doi: 10.1016/j.proenv.2012.01.167

969 Zhou, J., Li, Q., Guo, Y., Guo, X., Li, X., Zhao, Y., Jia, R., 2012. VLDA model and its  
970 application in assessing phreatic groundwater vulnerability: a case study of phreatic  
971 groundwater in the plain area of Yanji County, Xinjiang, China. *Environ. Earth Sci.* 67,  
972 1789–1799.

973 **Figure captions**

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

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

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

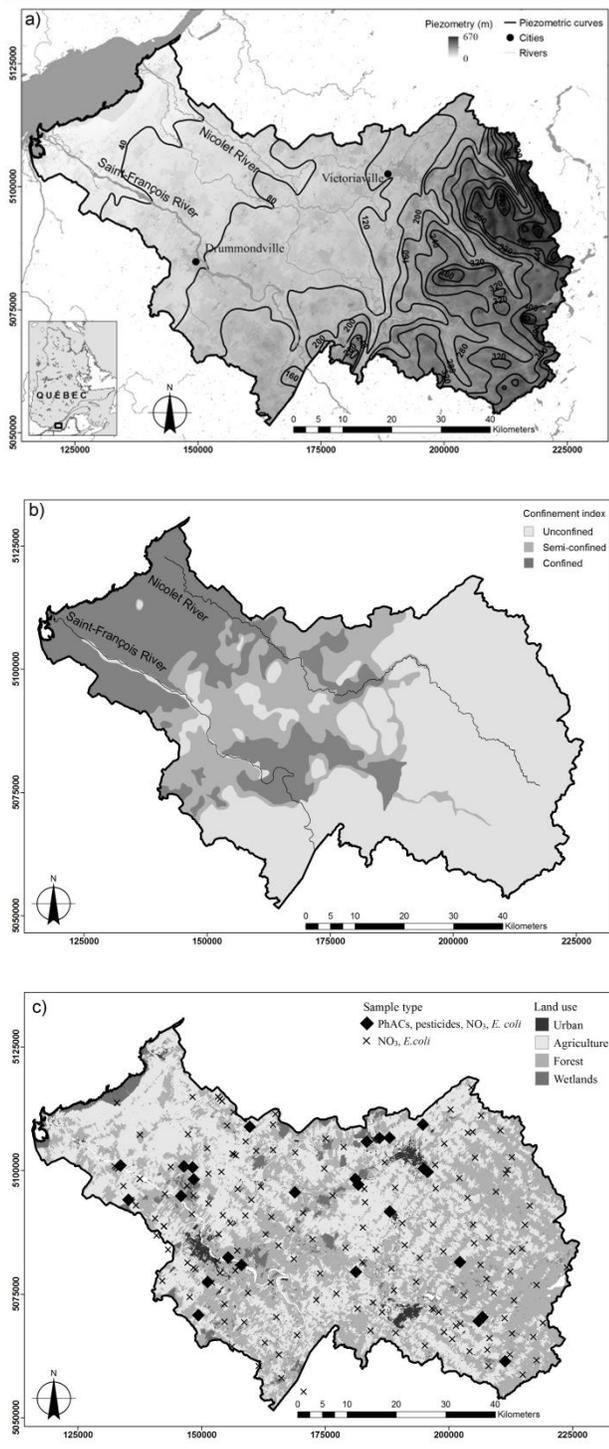
982 **Figure 4.** The Anthropogenic Footprint Index (AFI) in the study area as an explanatory variable  
983 for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide concentrations and  
984 total pharmaceutically active compounds (PhAC) concentrations.

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

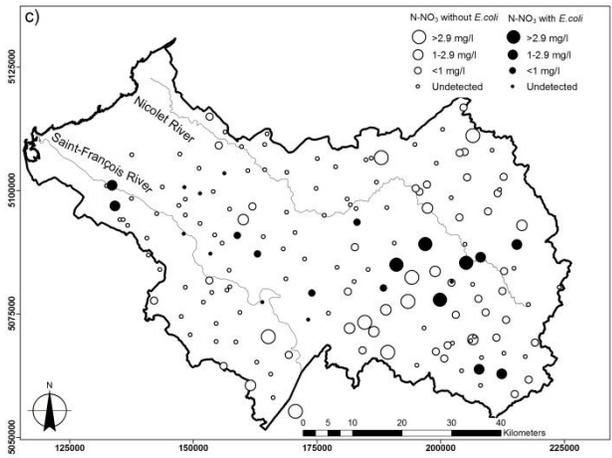
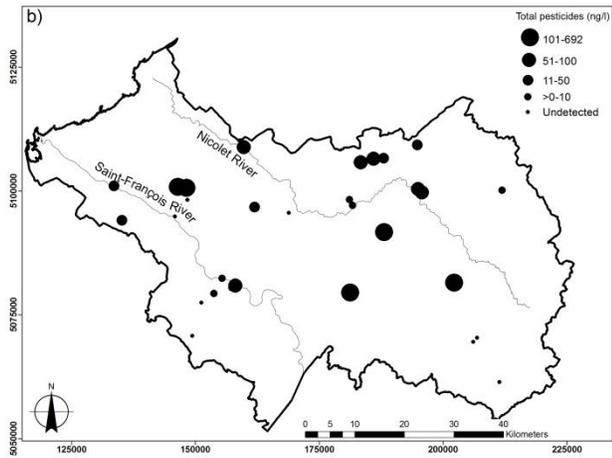
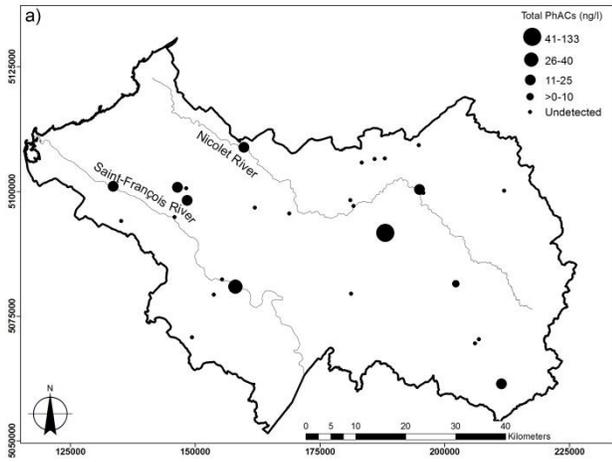
988 **Figure 6.** The Hydrogeochemical Vulnerability Index (HVI) in the study area as an explanatory  
989 variable for a) nitrate concentrations and occurrence of *E. coli*, and b) total pesticide  
990 concentrations and total concentrations of pharmaceutically active compounds (PhACs).

# Figure

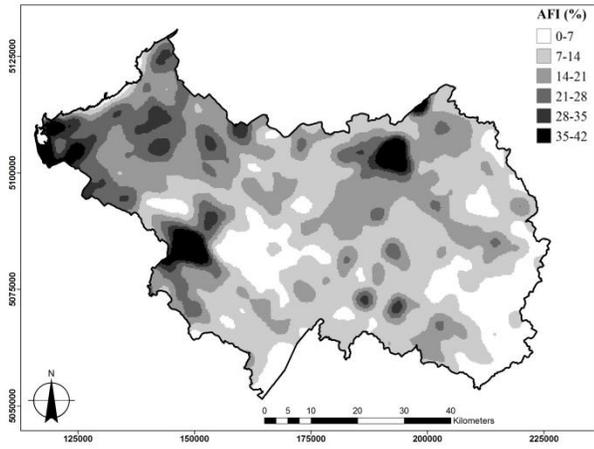
[Click here to download Figure: Figures\\_Saby\\_18oct2016.docx](#)



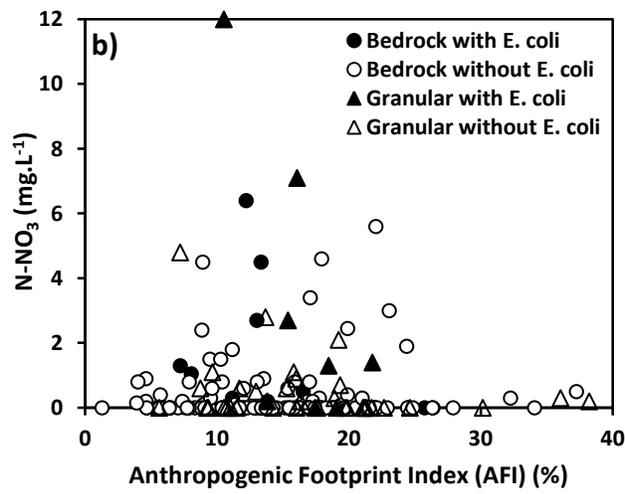
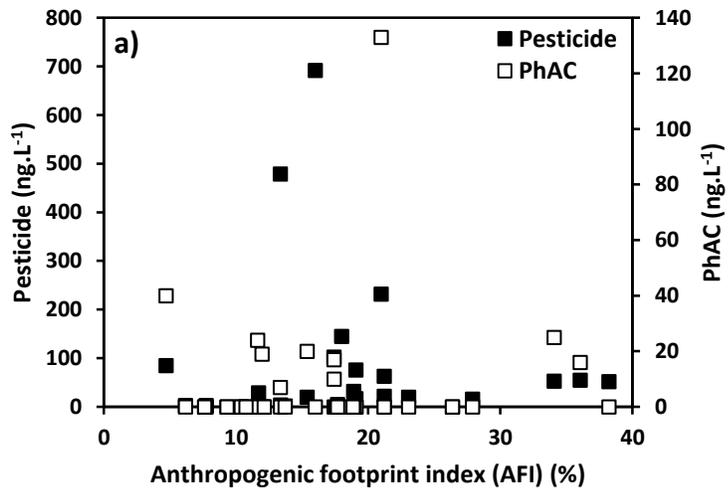
**Figure 1**  
**Saby et al 2016**  
**Science of the Total Environment**



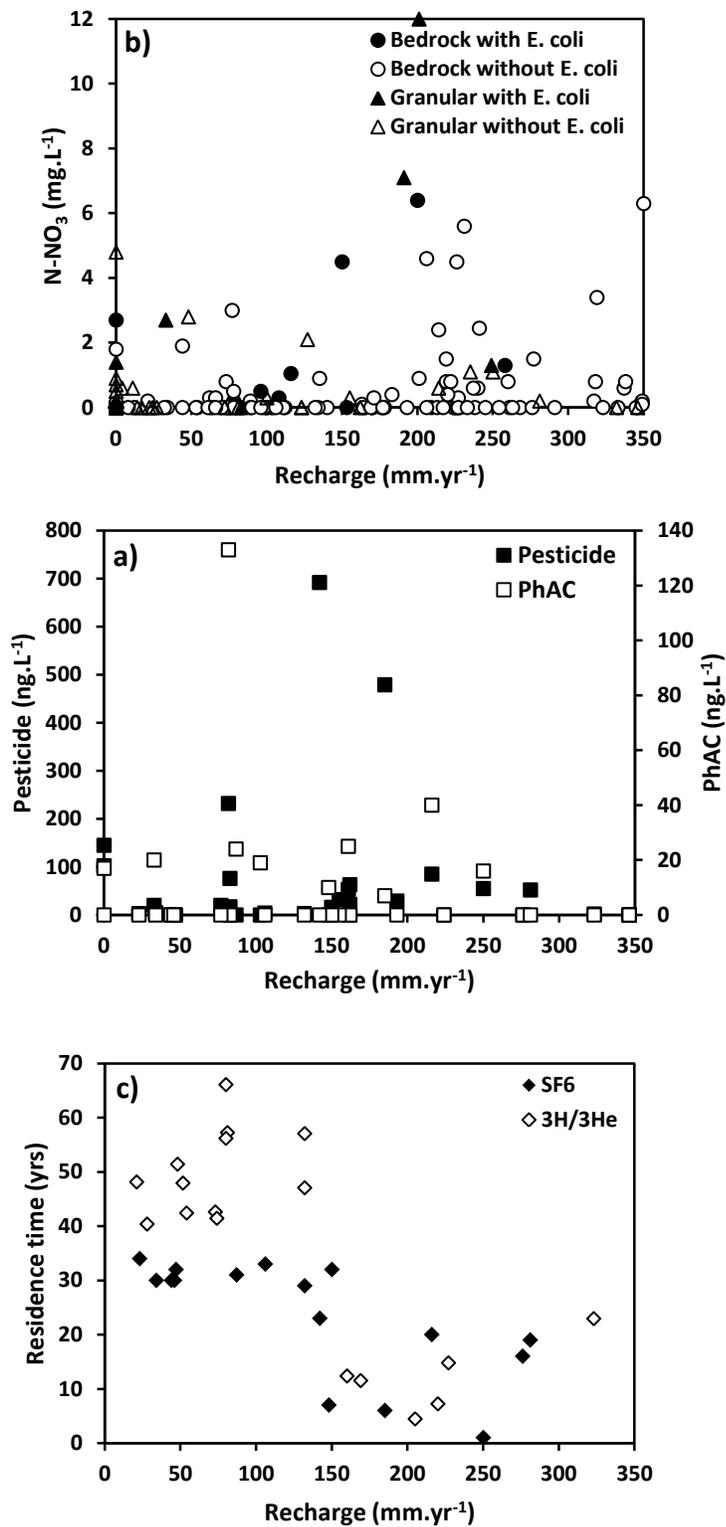
**Figure 2**  
**Saby et al 2016**  
**Science of the Total Environment**



**Figure 3**  
**Saby et al 2016**  
**Science of the Total Environment**



**Figure 4**  
**Saby et al 2016**  
**Science of the Total Environment**



**Figure 5**  
 Saby et al 2016  
 Science of the Total Environment



**Supplementary material for on-line publication only**

[Click here to download Supplementary material for on-line publication only: DRASTIC\\_18oct2016.docx](#)

**Supplementary material for on-line publication only**

[Click here to download Supplementary material for on-line publication only: Tables 1-3-5\\_Annex\\_Sab\\_18oct2016.xlsx](#)

**Supplementary material for on-line publication only**

**[Click here to download Supplementary material for on-line publication only: Tables 2-4-6-7-8\\_Annex\\_Saby\\_18oct2016.docx](#)**