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Chemical and botanical indicators of groundwater inflow to *Sphagnum*-dominated peatlands

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Abstract

Knowledge of whether a peatland is fed by a surface aquifer or is providing water to the aquifer can lead to different aquifer and wetland management strategies. Few studies have been conducted to investigate aquifer-peatland connections, because flow connections are difficult to measure and can be spatially and temporally variable. was to combine chemical and botanical indicators of groundwater inflow to *Sphagnum*-dominated peatlands for a better classification of their water sources. Available knowledge of peatland geomorphic setting, water chemistry, and vegetation data for 12 aquifer-peatland systems of the Abitibi-Temiscamingue region and of the St. Lawrence Lowlands, two contrasting regions of southern Quebec (Canada), were used to derive indicators of groundwater inflow. Total dissolved solids (TDS) is identified as a comprehensive indicator of water mineralization. Threshold values of 16 mg/l (Abitibi-Temiscamingue) and 22 mg/l (St. Lawrence Lowlands) were found to indicate the presence of groundwater within the peatland. Results show that combining chemical (TDS) and botanical indicators can detect the presence of groundwater inflow into most of the studied peatlands. The indicators are more efficient on slope peatlands, where groundwater inflow is more substantial and less spatially variable, than in basin peatlands. A two-step approach is proposed: 1) identify the geomorphic setting of the peatland, and 2) estimate the chemical and botanical indicators. This approach is low-cost and easy to implement, and thus can be used on a large number of sites to assess the presence of groundwater inflow to peatlands.

Key words: Aquifer, peatland, connectivity, TDS, vegetation

1. Introduction

Peatlands are wetlands formed through the accumulation of partially decayed organic matter (peat), and represent 50 to 70% of global wetland resources (Chapman et al., 2003). They are of high conservation value due to the key ecological functions they provide and to their high level of biodiversity (Joosten and Clarke 2002; Moore 2002; Limpens et al. 2008). For example, as a result of their organic matter accumulation, peatlands play an important role in the global carbon cycle, having accumulated approximately 600 Gt C during the Holocene (Yu et al., 2010). They also constitute important freshwater reserves and help regulate regional hydrologic fluxes (Acreman et al., 2013).

Knowledge of whether a peatland is fed by a surface aquifer or is providing water to the aquifer can lead to different aquifer and wetland management strategies. For example, in a groundwater-fed peatland, a reduction in groundwater level can lead to a reduction of groundwater inflow to the peatland, in turn disrupting the peatland ecology. However, few studies have been conducted to investigate aquifer-peatland connections (some examples include Bourgault et al., 2014; Levison et al., 2014), probably because such flow connections are difficult to measure and can be both spatially and temporally variable. Approaches using the contrast between surface water and groundwater temperatures to identify groundwater inflows (e.g., House et al., 2015) are an interesting and relatively inexpensive alternative.

It is well known that different water sources provide distinct ions to a peatland. These ions give rise to the presence of different plant species and assemblages, plant communities or individual species, such as *Sarracenia purpurea* in bogs, which have been used to identify the origin of water flowing into peatlands (Wassen et al., 1988; Glaser et al., 1990; Goslee et al., 1997; Mouser et al., 2005; Munger et al., 2014). Much remains to be investigated to fully understand the limits of chemical and botanical indicators in a variety of situations (Lewis, 2012). Combining water chemistry and plant communities provides robust information to identify water source (Johnston and Brown, 2013). However, because they are more time and resource intensive, these methods are rarely used to determine which wetlands have the highest hydrological and ecological value. Based on the current state of knowledge, and considering the limited number of reference wetlands from which thorough understanding of peatland water sources can be identified throughout the world (Cole, 2006), there is a clear need for efficient wetland water source indicators.

Classifying peatland types according to their dominant water source (e.g., ombrotrophic peatlands are precipitation-dominated while minerotrophic peatlands are groundwater-dominated) provides a simplified classification scheme of wetland connections to the hydrosystem, which can be useful at the regional scale or as a first approximation. However, these simplifications may not be useful at the local scale, where connections can be discrete and variable in both space and time. In many cases, the peripheral wet zone, or lagg area, that tends to form at the edge of ombrotrophic peatlands is an expression of these connections (Langlois et al., 2015). Groundwater can feed *Sphagnum*-

dominated peatlands (poor fen to bog) both laterally and vertically (Drexler et al., 1999; Fraser et al., 2001), without obvious visible indices. Although it represents limited water volumes (e.g., Levison et al., 2014), groundwater inflow can play a crucial role in maintaining moisture conditions that are favorable for many plant species (Grootjans et al., 1988). Such inflow is rarely taken into consideration when assessing the hydrological functions of ombrotrophic peatlands, and yet the peatlands could be negatively impacted if groundwater levels were to be lowered (i.e., through pumping or groundwater extraction).

The objective of this study was to combine chemical and botanical indicators of groundwater inflow to *Sphagnum*-dominated peatlands for a better classification of their water sources. Available knowledge of peatland geomorphic setting and vegetation data for 12 aquifer-peatland systems of the Abitibi-Temiscamingue region, located 600 km northwest of Montreal, and of the St. Lawrence Lowlands in southern Quebec (Canada) is first described. This knowledge is used in tandem with new data on water geochemistry which is analyzed using principal component analysis. The combination of geomorphic setting, vegetation data, and water chemistry is used to derive a two-step approach to identify the presence of groundwater.

2. Methods

2.1 Study sites

Surficial geology in the Abitibi-Temiscamingue region (hereafter referred to as Abitibi) is characterized by an esker-moraine morphology, surrounded by an extensive

glaciolacustrine clay plain. Deposited when the region was submerged in the deep proglacial waters of Lake Barlow-Ojibway, this clay contributes to the highly productive aquifers found in eskers by retaining groundwater in the granular deposits (Nadeau et al., 2015). Approximately 19% of the region is covered by wetlands, most of which are peatlands (Ducks Unlimited Canada, 2009). The five *Sphagnum*-dominated peatlands selected in this study area are slope peatlands (as defined by NWWG, 1997) that have developed on esker slopes (Figure 1a). They are mostly formed of bogs, with marginally poor to moderate fens at their upgradient limit and fingering organic deposits that drain naturally into small streams at their outer edges. The uphill portion of the complexes are thus geogenous, i.e., they are open to outside hydrologic flows other than precipitation and are flow-through systems, as defined by Mitsch and Gosselink (2007). The following complexes were selected for study: La Belle (two transects: LB1 and LB2), La Coupe (LC), Saint-Mathieu-Berry (SMB), Sources Nord (SN), and Sources Sud (SS).

The geology of the Becancour watershed, which contains the studied St. Lawrence Lowlands peatlands, consists of a series of sedimentary and metamorphic rocks, overlain by tills and permeable Quaternary marine deposits that form surface and semi-confined aquifers. The low-permeability tills and Champlain Sea clay deposits that accumulated during and after the last glaciation have favored peat accumulation in topographic depressions (Godbout et al., 2011). Peatlands comprise approximately 6% of the studied watershed (Avard et al., 2013). The four peatlands selected for this study are basin bogs (as defined by NWWG, 1997) surrounded by a minerotrophic lagg, and are located at the head of small or intermediate watersheds (Figure 1b). All of the peatlands have more than

one small stream outflow, and most are drained by artificial ditches. The following St. Lawrence Lowlands peatlands were selected for study: Lac Rose (two transects: LR1 and LR2), Mer Bleue (MB; this peatland is different from the one with the same name located near Ottawa, Canada), Saint-Sylvère (SSY), and Villeroy (two transects: V1 and V2).

In both regions, the peatlands are bordered by sand and gravel deposits that extend, at least partially, under the organic deposits. When located below the peatland, these permeable deposits are hereafter referred to as underlying mineral deposits. Regional aquifer characterization studies (Larocque et al., 2013; Cloutier et al., 2013) showed that sand thickness can vary from 1 to 20 m at the peatland border (near the surface aquifer), allowing lateral hydrogeological connectivity. Toward the center of the peatlands, the organic deposits sometimes directly overlie either clay or low permeability compact till. Vertical flows are therefore expected to be very limited in these areas.

2.2 Existing knowledge of aquifer-peatland connectivity at the study sites

Connection with surface aquifer

Field investigations, including monthly water level monitoring and continuous hydraulic head measurements using pressure transducers, were performed from May to November 2011 by Ferlatte et al. (2015). These authors reported that seven of the 12 transects (LB2, SMB, SN, SS, LR1, LR2, and MB) receive groundwater inflow from the surrounding surface aquifer (Figure 5 in Ferlatte et al., 2015). They identify two lateral flow patterns at the margin with the slope peatlands of the Abitibi sites: in the case of parallel inflow

(L_{par_in}), groundwater from the surface aquifer flows into the peatland, and peatland water flows in the same direction (LB2, SMB, SN, and SS); in the case of divergent flow (L_{div}), peatland water flows from a piezometric mound at station no. 2 into the surface aquifer and towards the peatland center (LB1 and LC). Ferlatte et al. (2015) also associated two lateral flow patterns within the basin bogs of the Becancour sites: in the case of convergent flow (L_{conv}), groundwater flows from the surface aquifer to the peatland, where it converges in the lagg with water flow from the peatland center to the peatland margin (LR1, LR2, and MB); in the case of parallel outflow (L_{par_out}), peatland water flows out of the organic deposits and into the surface aquifer (SSY, V1, and V2). Vertical hydraulic gradients suggest that water generally flows downward (i.e., from the peatland to the underlying mineral deposits). Some occurrence of vertical inflow (V_up) was identified during each of the seven head measurement campaigns at LB2, SMB, SS, LR1, LR2, SSY, V1, and V2 (Ferlatte et al., 2015).

Vegetation

Previous investigations (Munger et al., 2014) have identified the presence of two species (*Carex limosa* and *Sphagnum russowii*) and one combination of species (*Andromeda polifolia var. latifolia – Carex oligosperma*) that could be used as indicators of groundwater contribution to a given peatland (see Table A1, supplementary material, for more information). The same indicators were found when only lateral groundwater contributions were taken into account. In peatlands, these species are known to grow predominantly in minerotrophic habitats (moderate to poor fen) characterized by high Ca concentrations (Heinselman, 1970; Glaser et al., 1990; Vitt and Chee, 1990; Visser et al.,

2000; Gauthier, 2001). In the studied peatlands, Munger et al. (2014) also identified a gradient toward ombrotrophic plant communities as the distance from the peatland border increases. This reflects the presence of a minerogenous hydrological system in the lagg or marginal fen portion of the peatlands and an ombrogenous system towards the expanse of the peatland. On the other hand, three combinations of species were found to be indicators of vertical groundwater inflow: 1) *Chamedaphne calyculata – Larix laricina – Sphagnum capillifolium*, 2) *Eriophorum angustifolium – S. angustifolium*, and 3) *C. calyculata – Viburnum nudum* var. *cassinoides*. The complete methods used to identify indicator species and combinations of species are described in detail in Munger et al. (2014). Briefly, individual species indicative of the presence or absence of groundwater were determined by the IndVal method (Dufrêne and Legendre, 1997), while indicative combinations of species were determined using the extended IndVal method (De Cáceres et al., 2012; Bachand et al., 2014). It should be emphasized that the number of sites was relatively small, and that no species or combination of species had an indicator value of one, meaning that the indicator value is not perfect.

2.3 Sampling design

The sampling design used in this study was the same as that in Ferlatte et al. (2015). Only a brief description is provided here. One or two transects, depending on the peatland size, were positioned perpendicular to the peatland margin in each of the nine selected peatlands, for a total of 12 transects each including six piezometer stations, in the direction of potential lateral groundwater flow (Figure 2; see Ferlatte et al., 2015 for more details on site selection). For each transect, one piezometer was installed in the surface

aquifer station outside the peatland while nests of two piezometers (one shallow and one deep) were installed at each of the five peatland stations. The nests comprised a shallow piezometer, positioned at a maximum depth of 1.1 m in the peat, and a deep piezometer, positioned 40 cm below the mineral-peat interface (slotted section located in the underlying mineral deposits). There is no deep piezometer at stations where the underlying mineral deposit is clay (stations no.3, 4 and 5 in SMB, station no.6 in SSY, and station no.6 at V2). The shallow piezometer is considered to provide a reasonable estimate of water table depth. The deep piezometers reach 4.9 m on the SS transect (Abitibi) and 4.7 m on the SSY transect (Becancour). Each piezometer consisted of a 2.5 cm-ID-PVC pipe slotted over the lower 30 cm and sealed at the base. In the surface aquifer (station no. 1), the piezometers were installed sufficiently deep to ensure that they reached the water table, using an auger. The shallow piezometer in the surface aquifer was located within 10 m of the peatland margin; station no.2 was located close to the peatland margin, where peat thickness reaches 40 cm; station no.3 was located where change in vegetation was observed, likely indicating transition from fen vegetation to bog vegetation; stations no. 4, 5, and 6 were approximately 50, 100, and 300 m away from station no.3, respectively. This setup assumes that most exchanges between the surface aquifer and the peatland (both lateral and vertical) occur close to the peatland margin. The maximum peat thickness of the six Abitibi transects was 4.5 m, found at the SS site. The maximum peat thickness of the six Becancour transects was 4.3 m, found at the SSY site. Average water table depths ranged from 7 cm above the peat surface at the Becancour V2 site to 23 cm below the surface at the Abitibi LC site (Ferlatte et al.,

2015), but no systematic link was found between aquifer-peatland connectivity and water table depth.

2.4 Water chemistry

In 2011, two sampling campaigns were conducted in spring (May) and in late summer (Becancour: August; Abitibi: September). A total of 122 samples from the Abitibi region and 119 samples from the Becancour region were analyzed for barium (Ba^{2+}), calcium (Ca^{2+}), chloride (Cl^-), iron (Fe^{2+}), potassium (K^+), magnesium (Mg^{2+}), manganese (Mn^{2+}), sodium (Na^+), silicon (Si), strontium (Sr^{2+}), dissolved organic carbon (DOC), pH, nitrates (NO_3^-), sulphate (SO_4^{2-}), and total alkalinity (from which HCO_3^- was derived). The pH of water samples was measured *in situ*. Total dissolved solids (TDS) concentration was calculated as the sum of inorganic ions.

All piezometers were purged a week prior to sampling, to allow the recovery of water levels. Water was sampled using a peristaltic pump. Samples were taken in HDPE bottles for total alkalinity and anion analyses (60 ml), and for dissolved metals (30 ml). Samples for metals analysis were acidified with nitric acid. For DOC analysis, 4 ml glass vials were rinsed and combusted at 500 °C. A drop of mercuric chloride ($HgCl_2$) was added as a preservative. All samples were filtered to 0.45 μm in the field and refrigerated at 4˚C. Anions were analyzed by ion chromatography and metals by ICP-AES at the INRS-ETE laboratory (Quebec City, Canada). DOC was measured using a carbon analyzer (TOC-5000A Shimadzu) at the GEOTOP laboratory (UQAM, Montreal, Canada). Total alkalinity was determined by titration with acid for all samples with pH greater than 4.5.

The water samples were labeled according to water source, namely precipitation, peatland, underlying mineral deposits, surface aquifer (i.e., station no.1 from Ferlatte, 2014), and regional aquifer in the vicinity of the study sites (data from Cloutier et al., 2013 for the Abitibi region and from Larocque et al., 2013 for the Becancour region).

A principal component analysis (PCA) was conducted to identify the main variables underlying the peat water geochemistry variability. The analyses were performed for each region separately, by combining the May and late summer (August-September) results for 14 parameters (Ba, Ca, Cl, Fe, K, Mg, Mn, Na, Si, Sr, DOC, pH, SO_4, and NO_3). Total alkalinity was excluded from the PCA analysis because 39% of all samples were below the detection limit. Because of its additive nature, TDS was also excluded from the PCA. Data preparation for the PCA was carried out following the methodology suggested by Cloutier et al. (2008), and the analyses were performed using Statistica version 12 (StatSoft, Inc., 2013). The chemical parameters were log-transformed to reduce the deviation from normality of their distribution. From the standardized geochemical dataset for Abitibi (122 samples) and for Becancour (119 samples), principal components (PCs) were extracted from their symmetrical correlation matrix computed for the 14 parameters. Based on the Kaiser criterion, components with eigenvalues greater than one were retained for interpretation (StatSoft, Inc., 2013). To maximize the variance of the principal axes, a Varimax normalized rotation was applied to the retained components to identify the parameters associated with each component (Esbensen et al., 2004).

2.5 Testing the indicators

Ferlatte et al. (2015) have shown that the geomorphic setting has a major effect on the aquifer-peatland flow connections. We therefore use this aspect as the first component in a two-step approach to identify the presence or absence of such connections. The second step consists in evaluating the chemical and botanical indicators. The chemical indicators were derived from the research presented herein, while the botanical indicators were identified by Munger et al. (2014). To estimate their reliability on each of the 12 transects, results from the indicators are compared to the lateral flow connections (L_{div}, L_{par_in}, L_{par_out}, L_{conv}) and vertical flow connections (V_{up} or no V_{up}) from Ferlatte et al. (2015). Each transect was classified in a checkerboard matrix according to its chemical indicator (below/above the threshold for the given region) and to the presence of vegetation indicators (presence/absence). The ideal indicator would classify each transect according to its known flow connections and all transects would be located in white boxes on the checkerboard. If an indicator provides a wrong identification of flow, the transect where it has been measured will be classified in a hatched box on the checkerboard. Horizontal groundwater flow connections are considered to affect indicators at station no.2 while vertical groundwater inflow is considered for stations no.2 to no.6.

3. Results

3.1 Water chemistry

The water sources can be defined by the dominant water type of each sample: $CaSO_4$ for precipitation, Ca-HCO_3 for the regional aquifer and the underlying mineral deposits, Ca-

HCO_3 to Ca-SO_4 for the surface aquifer, and Ca-Cl to Ca-HCO_3 for peatland (Figure 3). The major ion chemistry of the regional aquifer and the underlying mineral deposits was mostly of Ca-HCO_3 water type, typical of near-surface mineral weathering. The water chemistry of the surface aquifer (station no.1) samples ranged from Ca-HCO_3 to Ca-SO_4 water types which is characteristic of recharge water in the Quaternary sediments. The peatland samples range from Ca-Cl to Ca-HCO_3 water types, indicating that the major ion chemistry of peatland water could be a result of water mixing between precipitation, the surface aquifer, and the underlying mineral deposits.

Three main trends in average chemical properties were observed between samples from surface aquifers, underlying mineral deposits, and peatlands (see Table 1 for average results). The first trend showed a decrease in Cl, K, Mn, pH, NO_3, and SO_4 from the surface aquifer to the underlying mineral deposits to the peatland (Abitibi). However, when pooling the results from the two regions and the two sampling seasons, and applying a Tukey-Kramer test (α=0.95), there was only a statistically significant difference between the average values for the aquifer, the underlying mineral deposits, and the peatland for pH. The second trend showed a decrease in Ca, Fe, Mg, Na, Si, Sr, HCO_3, and TDS in the chemical signature from the underlying mineral deposits to the peatland. When pooled for the two regions, all these chemical parameters were significantly higher in the underlying mineral deposits than in the peatland (Tukey-Kramer test, α=0.95). It is interesting to note that the TDS in the surface aquifer was generally lower than the TDS in the underlying mineral deposits in both regions, which probably reflects the short residence times and high recharge rates in the surface aquifer

compared to the water which is found in the mineral deposits below the peatland. The third trend was observed for DOC, for which average concentrations increase from the surface aquifer to the underlying mineral deposits to the peatland. In this case, differences between the three averages were statistically significant (Tukey-Kramer test, α=0.95). There were no notable difference in the dissolved chemical compositions of water between sampling seasons (seasonal results not shown), probably reflecting the temporal similarity in hydraulic gradients at the twelve sites (Ferlatte et al., 2015).

For the Abitibi region, the first four PCs respected the Kaiser criterion and accounted for 77% of the total variance. For Becancour, the first three retained PCs had eigenvalues greater than one, and account for 70% of the total variance (see Table A2, supplementary material, for results). For both regions, the first component, PC1, explained 39% of the variance, accounting for the majority of the variance in the original dataset. PC1 is characterized by highly positive loading in Ba, Ca, Mg, Mn, Si, and Sr (Abitibi) and Ba, Ca, Mg, Mn, Sr, and pH (Becancour). Several terrestrial groundwater-sourced elements are thus common to the two regions (Ba, Ca, Mg, Mn, and Sr) and were found to be positively loaded in PC1. Si, a groundwater-sourced element, only appeared in PC1 for the Abitibi region, while pH stands out as part of PC1 in the Becancour region only. The distinctions between the two regions could be explained by regional geological dissimilarities and differences in the dissolution rates of mafic and aluminosilicate materials, since Si is the product of the geochemical mineral weathering (Shotyk, 1988; Bendell-Young, 2003). PC2 explained 16% of the variance in the two regions, and was characterized by highly positive loading of Cl and K (Abitibi), and Cl, K, and Na

(Becancour). PC3 explains 13% and 15% of the variance for Abitibi and Becancour, respectively, with high loading in DOC and SO_4 (Abitibi) and NO_3 and SO_4 (Becancour). PC3 therefore reflects redox conditions in the aquifer-peatland system. Finally, PC4 explains 9% of the variance in the original Abitibi dataset, and has highly positive loading of NO_3.

The principal component scores, representing the relative influence of the PCs, were used to relate the PCs and their geochemical interpretations to the different water sources; surface aquifer, underlying mineral deposits, and peatland. Figure A1 (supplementary material) presents the position of sample scores in the plane defined by the axes of PC1 and PC3. Since PC2 and PC3 explain a comparable percentage of the variance, PC3 scores were retained in Figure A1, as they were found to group samples more efficiently than PC2. Although the samples were more dispersed in the Becancour region than in the Abitibi region, peatland water dominates left of PC1=0 and was clearly differentiated from water in the underlying mineral deposits by the principal component scores for PC1 in both regions. Water from underlying mineral deposits dominated right of PC1=0, indicating a geological signature related to mineral weathering. Water from the surface aquifer dominated in the upper portion of the diagram and forms a distinct group along the axis of PC3, indicating oxidized conditions.

When combining all water samples for each region separately (i.e., the spring and late summer sampling campaigns, as well as all sample types for Abitibi and for Becancour separately), a strong exponential correlation was observed between TDS concentrations

and the PC scores for PC1 (Figure 4). In the two regions, the lowest TDS values were from peatland water and are associated with the lowest (negative) PC1 scores. On the other side of the range, the TDS values from the underlying mineral deposits were associated with the highest (positive) PC1 scores.

The transition point from negative to positive for the PC1 score was considered to correspond to the threshold TDS value indicative of groundwater inflow. When considering the mathematical relationship between TDS and PC1, the threshold is 16 mg/l and 22 mg/l for Abitibi and Becancour, respectively.

In the Abitibi region, peatland TDS values were below the identified groundwater contribution threshold at station no.2 for the LB1 and LC transects, which both have divergent groundwater flow identifying the absence of lateral groundwater inflow from the surface aquifer (Figures 5a and 5c). TDS was also below the threshold at SN even though parallel groundwater inflow exists at this site (Figure 5e). The LB2, SMB, and SS transects all have parallel groundwater inflow and show TDS exceeding the threshold at station no.2. In the Becancour region, peatland TDS at station no.2 was below the threshold at LR1, LR2, MB, and V1 (Figures 5g to 5l), even though only the V1 site was the only one without a convergent horizontal inflow. At sites SSY and V2 where the horizontal flow is out of the peatland, the threshold was exceeded at station no.2.

An upward vertical arrow at the bottom of the Figure 5 panels indicates the presence of an upward vertical gradient observed by Ferlatte et al. (2015) at least once during the

study period. Vertical groundwater inflows were reflected by above-threshold TDS concentrations at some stations in LB2, SMB, and SS in Abitibi. This was observed in SSY and V2 in Becancour. Threshold exceedance was observed at stations no.3 and 5 in SMB, in the absence of vertical inflow due to the presence of clay underneath the peatland. At station no.3, the high TDS could be linked to a strong lateral inflow at this site while at station no.5, it is possible that unmonitored vertical upflow close to the station influences the TDS.

3.4 Applying the chemical and botanical indicators to the studied peatlands

Horizontal groundwater inflow

In Abitibi, TDS values at station no.2 correctly identified five out of six horizontal groundwater inflow locations (Figure 6a; exception SN). Vegetation also correctly identified five out of six horizontal groundwater inflows, with the exception of transect LB1, for which the presence of vegetation indicators cannot be reconciled with observed flow directions. All horizontal groundwater inflows were identified by either TDS or vegetation.

In the Becancour region, peatland TDS values provided reliable information on lateral groundwater inflow at the V1 sites only (Figure 6a). Peatland TDS on the SSY and V2 transects, where there is no lateral inflow, was higher than the threshold, probably due to vertical inflows to the peatland at stations no.2 or 3. For the LR1, LR2, and MB transects, peatland TDS did not identify lateral groundwater inflows, probably due to the small groundwater inflow gradients (L_{conv}) observed at these two sites (Ferlatte et al., 2015).

Vegetation indicators correctly identified the type of lateral inflow for four out of six Becancour transects. Indicator species on the two transects where there is no lateral groundwater inflow (V1 and V2; L_{par_out}) were probably due to vertical inflows at stations no.2 or 3. Overall for the Becancour region, five out of six horizontal groundwater inflows were identified with either TDS or vegetation.

Vertical groundwater inflow

In Abitibi, peatland TDS values at stations no.2 to no.6 correctly identified the presence of vertical groundwater inflow conditions in any given station on all six transects (Figure 6b). Vegetation indicators correctly identified four out of six vertical groundwater inflows, LB2, SMB, SS, and LC. The presence of vegetation indicators at the SN transect might be related to the lateral groundwater inflow condition at this site, which could extend its impact beyond station no.2. There is no obvious explanation as to why vegetation indicators are present at the LB1 transect. Similarly to the results for lateral inflows, all vertical inflows were identified with either TDS or vegetation.

At three out of six Becancour sites (SSY, V2, and MB), peatland TDS values provided information that corresponds to the presence of vertical groundwater inflow (Figure 6b). TDS from transects LR1, LR2, and V1 have V_{up} conditions but TDS values were below the threshold. The MB transect showed TDS close to the threshold but no vertical inflow. It is possible that the vertical hydraulic gradient was not measured correctly at this transect. Vegetation indicators correctly identify the type of vertical inflow for four out of six transects. Indicator species were identified at one site (MB) where no vertical inflows

were observed, whereas they were absent on another site (SSY) where vertical inflows were observed. Overall for the Becancour region, all the vertical groundwater inflows were identified with either TDS or vegetation.

4. Discussion

4.1 Water chemistry

Average chemical parameter values were generally lower in the Abitibi region, for the surface aquifer, the underlying mineral deposits, and the peatland alike. This can be explained by the different sources of groundwater, from eskers in Abitibi, which are dynamic aquifers located in recharge conditions, and from water-rock interaction with Archean intrusive, plutonic, volcanic, and metasedimentary rocks of the Canadian Shield. In the Becancour region, interaction with sedimentary and metamorphic rocks, combined with recharge areas that can be much farther away, lead to longer groundwater residence times, resulting in higher mineralization.

These results show that peatland water can be characterized by low average values of pH, HCO_3 (most values being below detection limit), NO_3, SO_4, TDS, and most cations, and by the highest average values for DOC. The low HCO_3 concentrations of the peatland water, compared to the surface aquifer and the underlying mineral deposits, illustrates the limited buffering capacity of peatland water (Bendell-Young and Pick, 1997), where organic and carbonic acids induce low pH, leading to low HCO_3 concentrations. Since the capacity of HCO_3 to buffer the acidity of peatland water essentially comes from groundwater, peatland water samples having Ca-HCO_3 water types (Figure A1) support the hypothesis of groundwater inflows from the aquifer (Steinmann and Shotyk, 1997). It

is worth noting that in both regions the surface aquifers surrounding the peatlands are nutrient-poor, with low NO_3^- concentrations and almost no dissolved P (Cloutier et al., 2013; Larocque et al., 2013). Nitrate concentrations in the sampled peatland water are also very low, with average values of 0.20 and 0.21 mg N-NO_3/L for the Abitibi and Becancour regions, respectively (dissolved P was not analyzed in the current study). The low SO_4 concentrations in peatland and underlying mineral water, relative to the surface aquifer, can be explain by the reducing conditions prevailing in these environments.

4.2 Usefulness of the indicators

Although TDS was recommended by Adamus et al. (1991) as a geochemical tracer of wetland recharge and discharge, to our knowledge a threshold value for TDS has never before been defined. The relatively clear distinction between peatland and mineral water samples on either side of the PC1=0 line is an indication that the groundwater-sourced elements of PC1 constitute the major source of inorganic components in the studied pealand-aquifer system. The use of TDS has the advantage of smoothing background noise caused by variations in individual ion concentrations. It is important to highlight that all the samples were used in the PCA, including the high TDS values from the V2 transect. It is possible that this has resulted in an overestimation of the threshold for the Becancor region, and will be investigated further through the inclusion of additional peatlands in future work. The threshold values are interpreted as the TDS level indicative of a groundwater contribution, but are not absolute values distinguishing groundwater contribution from none at all. Although TDS thresholds similar to those identified here can be expected in other geological and climatic contexts, they could be different in other regions depending on the regional hydrogeology and on groundwater mineralization.

Overall, peatland TDS was slightly better able to identify vertical inflows than lateral inflows in the two regions. It is not clear why this is the case. Vegetation indicators perform slightly better to explain horizontal inflows than vertical inflows in Abitibi, while their performance is similar with the two types of inflow in Becancour. Munger et al. (2014) have shown that the identified species (or combinations of species) do not have a 100% indicator value. There is a clear tendency for the species to be indicative of groundwater inflow, but they are not perfect indicators since an indicator species can be found in a peatland where there is no groundwater inflow, and vice versa. This could be due to the relatively small number of sites available to identify the indicator species as part of the current work, especially for the lateral groundwater inflow of the Becancour region.

When considered together, the success rate of the combined indicators are similar for horizontal and vertical inflows in Abitibi, and slightly better for vertical inflow than for horizontal inflow in Becancour. Overall, horizontal and vertical groundwater inflows were better identified on the slope peatlands of the Abitibi region than on the basin peatlands of the Becancour region. This is probably due to more substantial groundwater inflow in the Abitibi slope peatlands than in the Becancour basin peatlands. The combination of indicators is promising but needs to be tested on a large number of peatlands to ensure its validity in different environments.

4.4 Practical implication

The main practical implication of this research is with the development of a two-step approach to identify groundwater inflow to a peatland (Figure 7). The first step derives from the work of Ferlatte et al. (2015) and consists of determining the peatland geomorphic setting (slope peatland or basin peatland). Slope peatlands are considered to have a high probability of groundwater inflow, while groundwater inflow is often much more variable in *Sphagnum*-dominated basin peatlands (Ferlatte et al., 2015). Since each peatland type can be the host of lateral and/or vertical inflow connections with a surface aquifer or with the underlying mineral deposits, and because these exchanges are difficult to measure without extensive instrumentation, additional simple groundwater inflow indicators are required.

Once the geomorphic setting has been identified, the user can then go to step 2, i.e. chemical and botanical indicators can be used whether with both slope peatlands or basin peatlands. Here, the chemical and botanical indicators should be considered together. The recommended method is to first look for indicator plant species which can be identified through field investigation within the peatland. Where a vegetation indicator is observed, the TDS of the peatland water should be measured. It is recommended to measure TDS in different locations even if vegetation indicators are not observed since these indicators are not 100% effective. In this case, the presence of a TDS above the threshold would indicate possible groundwater inflow. Water sampling is ideally performed by inserting a 1 m long, 2.5 cm diameter slotted piezometer into the organic deposits. Peatland water TDS can be determined by having a this water sample analyzed for major ions content. Alternatively, TDS can also measured, although less precisely, *in situ* by lowering a

portable multi-meter within the piezometer. It is not recommended to measure TDS from a surface pond, since this water is exposed to the atmosphere (and thus to processes of evaporation, precipitation, etc.).

In the combined presence of vegetation indicators and above-threshold TDS concentration, there is a high probability of groundwater inflow. If the location is close to the peatland border, lateral inflow is expected, and if the location is further into the centre of the peatland, vertical groundwater inflow probably occurs. TDS values above the threshold without vegetation indicators should be considered indicative of the presence of groundwater. The combination of low TDS values and vegetation indicators could also indicate the presence of groundwater inflow. Low TDS and no vegetation indicators should be interpreted as a peatland where there is little to no groundwater inflow.

5. Conclusions

The objective of this study was to combine chemical and botanical indicators of groundwater inflow to *Sphagnum*-dominated peatlands for a better classification of their water sources. This was achieved through the use of peatland geomorphic setting, TDS, and vegetation indicators on 12 aquifer-peatland systems in two regions of southern Quebec (Canada). The combined indicator approach that was developed can easily be implemented, is cost- and labour-effective, and can thus be applied to a large number of peatlands. Results have shown that the approach is more efficient in slope peatlands, where groundwater inflow is relatively important, than in basin peatlands, where groundwater inflow tends to be less important and more spatially variable. Nevertheless,

the combination of TDS and vegetation indicators results in a relatively high rate of success on the 12 studied transects, providing a reasonable indication of the presence of groundwater inflow to a peatland. The approach now needs to be validated on a larger number of sites in southern Quebec, in other regions of North America and the world, and in other geological and climatic conditions.

The approach developed here provides information regarding whether or not *Sphagnum*-dominated peatlands are connected to surface aquifers through groundwater inflow. This knowledge is of critical importance when approving activities which could potentially lower groundwater levels in those surface aquifers. Beyond the current work, there is a need to develop a simple means to identify the peatlands which provide hydrogeological functions for surface aquifers and rivers. These functions include groundwater outflow from the peatland to the aquifer (from the peatland bottom or from its boundary), sustaining groundwater levels in the neighboring surface aquifer, and sustaining low flows in rivers. Continued development of a datasets on peatland-aquifer interactions is essential to increase the existing knowledge of these systems and to understand wetland functions.

Acknowledgements

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Figure captions

Figure 1. Locations of individual peatlands for the two study sites a) Abitibi, and b) Becancour.

Figure 2. Typical instrumented aquifer-peatland transect (from Ferlatte et al., 2015).

Figure 3. Piper diagrams of the water sampled in May 2011 for a) the Abitibi region and b) the Becancour region.

Figure 4. Scores of principal component 1 (PC1) from the principal component analysis for 14 parameters (Ba, Ca, Cl, Fe, K, Mg, Mn, Na, Si, Sr, DOC, pH, SO_4, and NO_3) as a function of total dissolved solids (TDS) concentrations for a) the Abitibi region, where PC1 represents high positive loading in Ba, Ca, Mg, Mn, Si, and Sr, and b) the Becancour region, where PC1 represents high positive loading in Ba, Ca, Mg, Mn, Sr, and pH

Figure 5. Evolution of total dissolved solids (TDS) concentrations along the transects. On panels a) through f): Abitibi sites, and on panels g) through l): Becancour sites. Upward vertical arrows indicate groundwater inflow as observed in Ferlatte et al. (2015) and * symbols represent stations where vegetation indicators of groundwater inflow were observed.

Figure 6. Testing the indicators for the Abitibi and Becancour transects for a) horizontal inflows and b) vertical inflows. Ineffective indicators are found in hatched boxes; L_{conv} is convergent horizontal inflow, L_{par_out} is parallel horizontal outflow, L_{par_in} is parallel horizontal inflow, and L_{div} is divergent horizontal flow (as described by Ferlatte et al., 2015); V_{up} is vertical groundwater inflow.

Figure 7. Schematic of the approach to identify groundwater inflow to peatlands for slope bogs and basin bogs. The first step in assessing groundwater inflow is to determine the peatland geomorphic setting. The second step applies to the two settings and depends on TDS values and on the presence/absence of vegetation indicators (VI).

Figure A1 (supplementary material). Principal components scores for PC1 and PC3 for a) the Abitibi region and b) the Becancour region.

Table 1. Average values of chemical parameters for the Abitibi and Becancour regions, as a function of the sampling context.

	ABITIBI			BECANCOUR		
	Aquifer	**UMD***	**Peatland**	**Aquifer**	**UMD**	**Peatland**
	(*n=10*)	**(*n=54*)**	**(*n=58*)**	**(*n=12*)**	**(*n=49*)**	**(*n=58*)**
Ba (mg/L)	0.01	0.01	0.01	0.05	0.07	0.02
Ca (mg/L)	1.70	3.08	1.35	1.85	10.77	2.91
Cl (mg/L)	0.88	0.65	0.48	2.32	0.79	0.64
Fe (mg/L)	0.35	2.21	0.47	1.73	4.91	0.90
K (mg/L)	0.51	0.48	0.32	0.73	0.59	0.47
Mg (mg/L)	0.37	0.47	0.26	0.28	0.75	0.25
Mn (mg/L)	0.07	0.03	0.01	0.52	0.07	0.02
Na (mg/L)	1.10	1.21	0.61	1.19	1.41	0.63
Si (mg/L)	3.38	6.88	3.27	3.51	6.68	2.89
Sr (mg/L)	0.01	0.02	0.01	0.02	0.19	0.04
DOC (mg/L)	3.18	17.00	19.63	5.52	17.42	24.72
pH	5.60	5.10	4.36	5.41	5.33	4.27
NO_3 (mg/L)	0.20	0.19	0.11	0.21	0.09	0.18
SO_4 (mg/L)	2.65	0.14	0.10	3.83	0.14	0.08
HCO_3 (mg/L)	8.36	16.95	2.50	7.23	39.43	6.89
TDS (mg/L)	20.70	34.93	10.59	25.10	68.43	17.36

*: UMD = Underlying mineral deposits

Figure 1

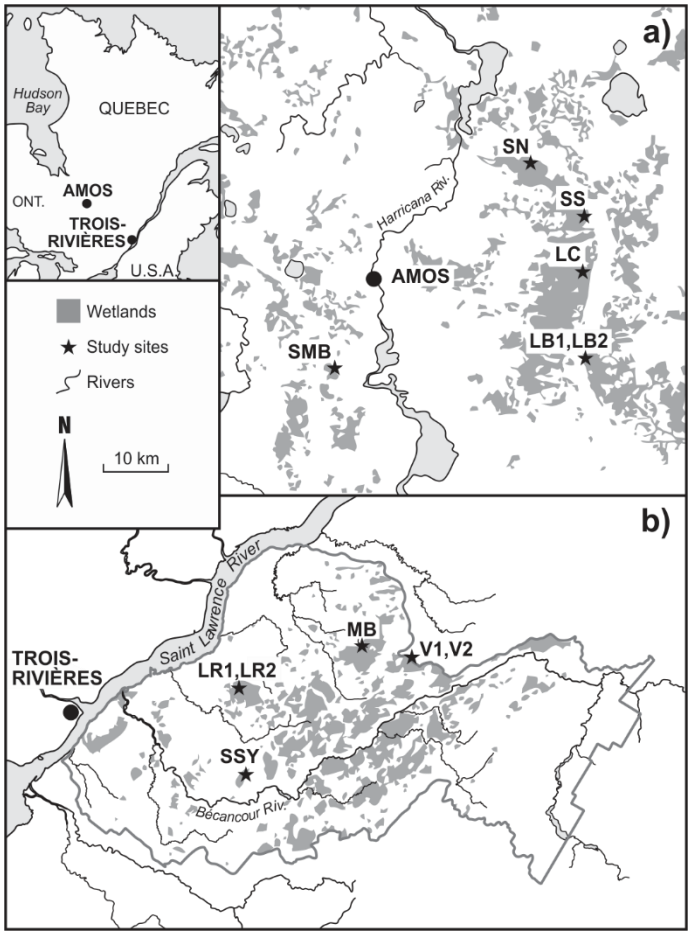

Figure 1

Larocque et al 2015

Ecological Indicators

Figure 2

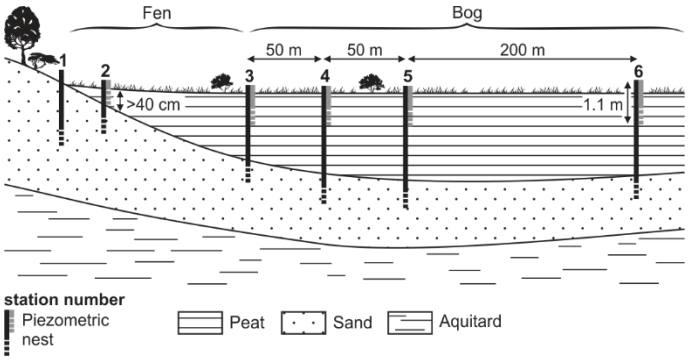

Figure 2

Larocque et al 2015

Ecological Indicators

Figure 3

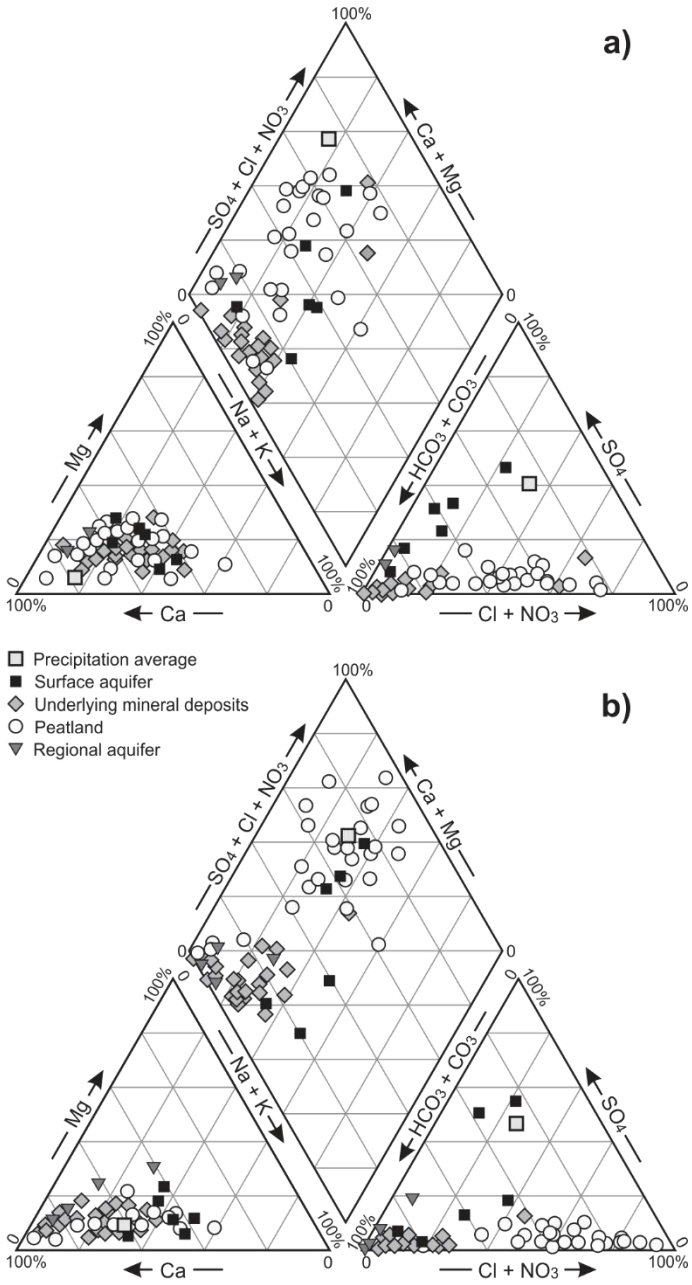

Figure 3

Larocque et al 2015

Ecological Indicators

Figure 4

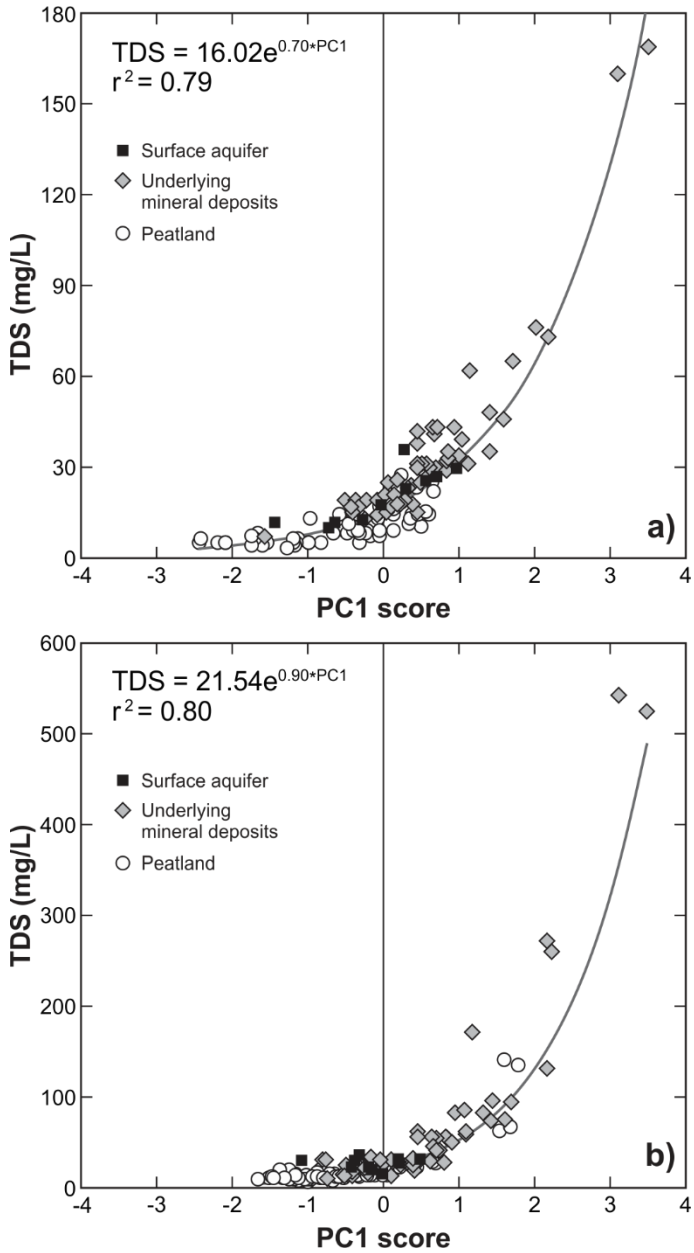

Figure 4

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Ecological Indicators

Figure 5

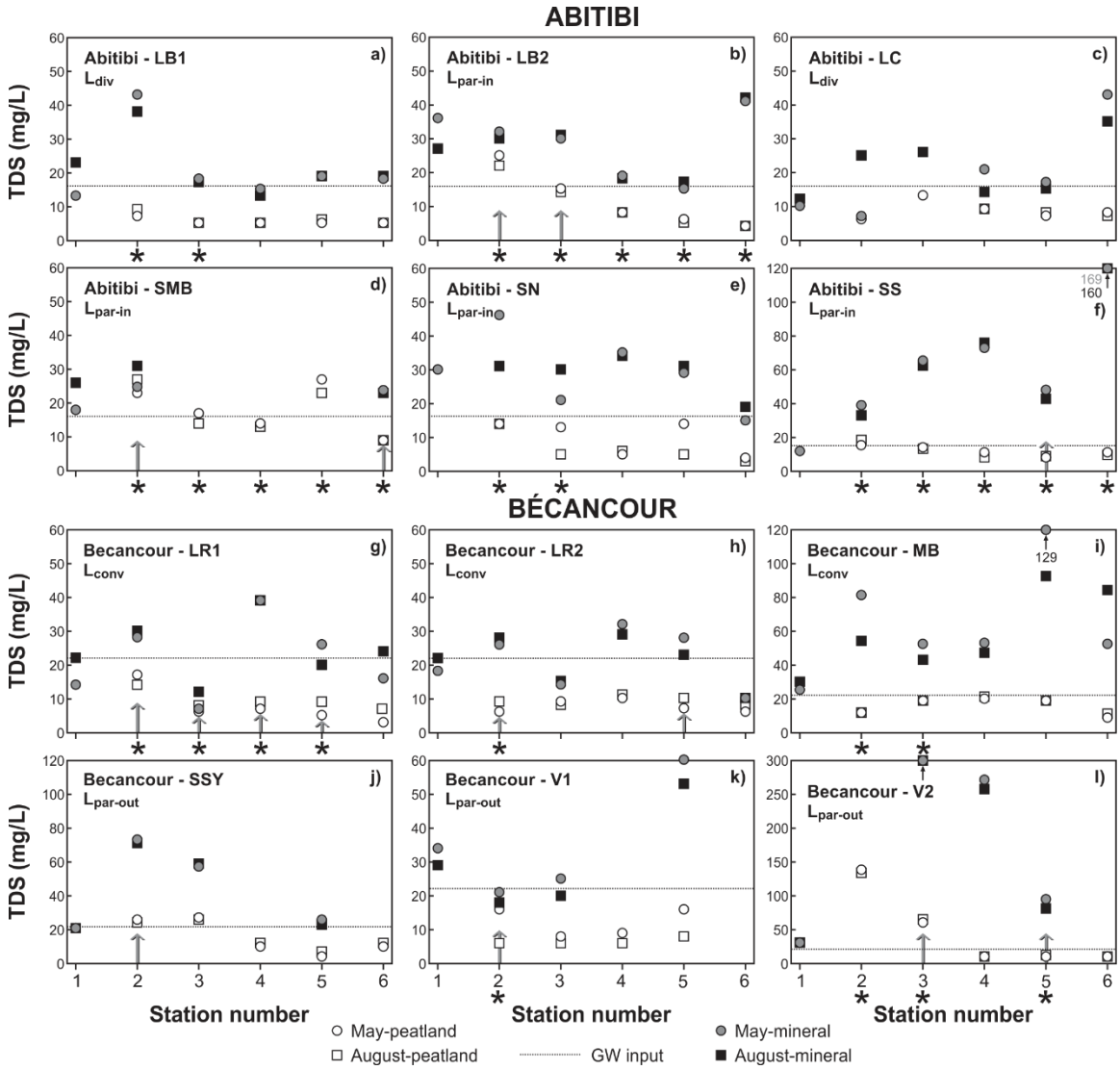


Figure 5

Larocque et al 2015

Ecological Indicators

Figure 6

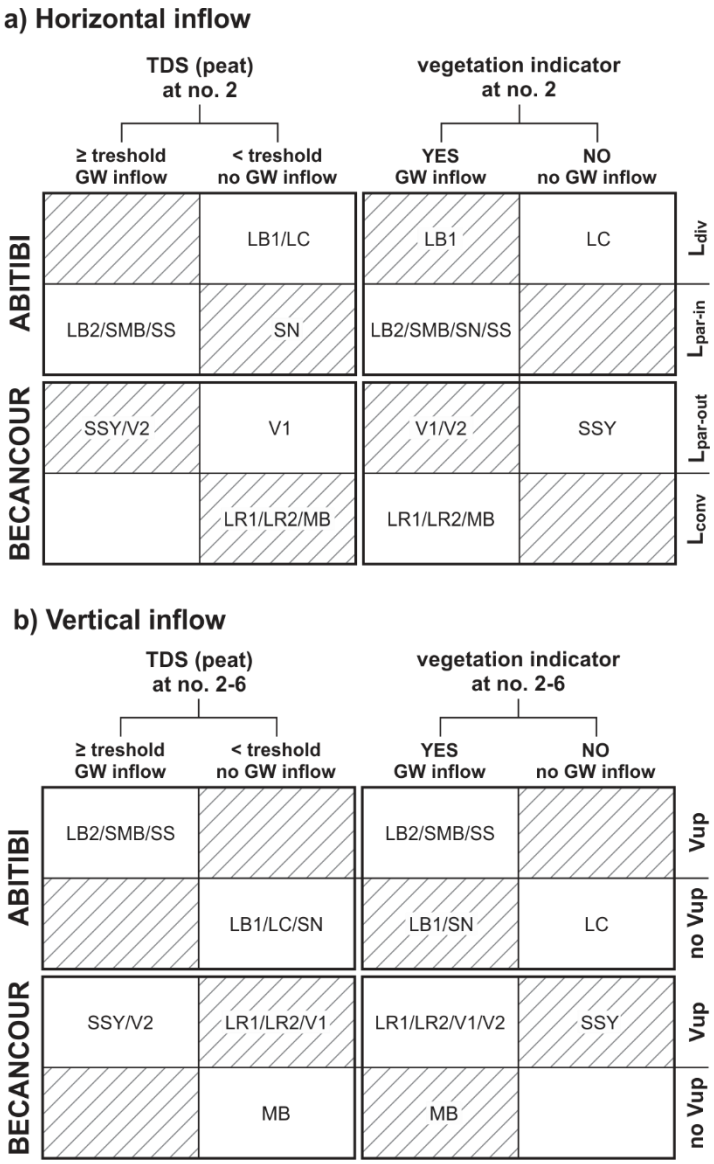


Figure 6

Larocque et al 2015

Ecological Indicators

Figure 7

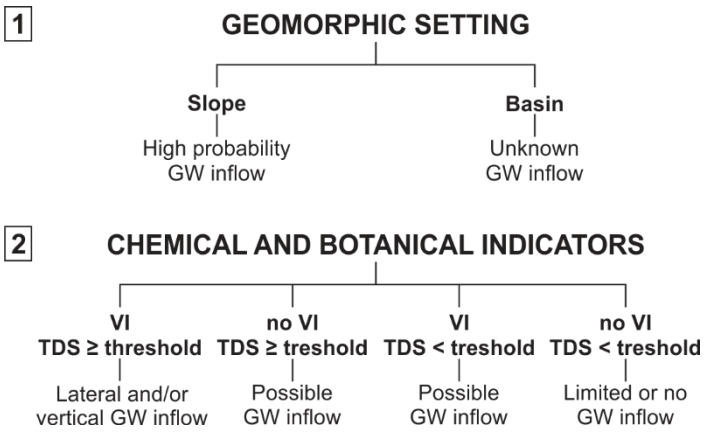
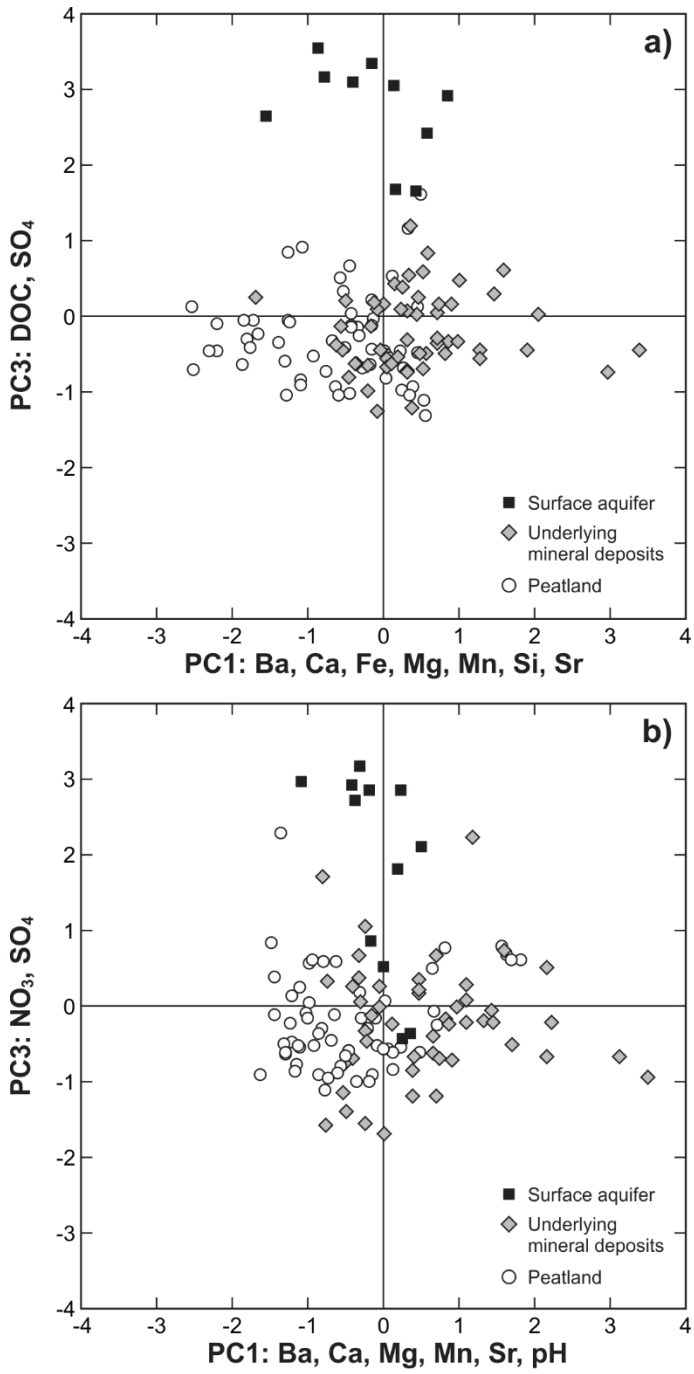


Figure 7

Larocque et al 2015

Ecological Indicators



Supplementary material - Figure A1

Larocque et al 2015

Ecological Indicators

Table A1. Indicator species of groundwater inflows in peatlands of Abitibi and Becancour. The specificity (A), sensitivity (B), indicator value (IV) of each indicator, and significance (*p*) are presented.

Indicator	A	B	IV	*p*
Groundwater inflows				
Andromeda polifolia var. latifolia + Carex	0.87	0.63	0.74	0.001
Carex limosa	0.90	0.44	0.63	0.008
Sphagnum russowii	0.86	0.34	0.53	0.036
Lateral groundwater inflows				
Andromeda polifolia var. latifolia + Carex	0.88	0.62	0.74	0.006
Carex limosa	0.91	0.48	0.66	0.014
Sphagnum russowii	0.83	0.38	0.56	0.027
Vertical groundwater inflows				
Chamaedaphne calyculata + Larix laricina + Sphagnum capillifolium	0.66	0.60	0.63	0.039
Eriophorum angustifolium + Sphagnum	0.78	0.40	0.56	0.038
Chamaedaphne calycultata + Viburnum nudum var. *cassinoides*	0.76	0.40	0.55	0.011

Supplementary material
Larocque et al., 2015
Ecological Indicators

Table A2. PC loadings and explained variance for the first four components (Abitibi) and first three components (Becancour), with Varimax normalized rotation (values in bold are loadings exceeding 0.70)

	ABITIBI ***(n=122)***				**BECANCOUR** ***(n=119)***		
	PC1	**PC2**	**PC3**	**PC4**	**PC1**	**PC2**	**PC3**
	(39%)	**(16%)**	**(13%)**	**(9%)**	**(39%)**	**(16%)**	**(15%)**
Ba	**0.70**	0.26	-0.11	0.16	**0.86**	0.09	0.23
Ca	**0.90**	0.09	0.03	-0.05	**0.90**	0.10	0.13
Cl	0.14	**0.86**	0.09	0.14	-0.08	**0.78**	0.41
Fe	0.67	0.06	-0.53	-0.07	0.68	0.08	-0.28
K	0.25	**0.87**	-0.05	-0.08	0.09	**0.74**	0.09
Mg	**0.86**	0.12	0.03	0.04	**0.90**	0.18	0.11
Mn	**0.74**	0.20	0.19	0.01	**0.72**	0.26	0.37
Na	0.62	0.60	0.08	0.21	0.59	**0.70**	0.09
Si	**0.78**	0.15	-0.02	0.26	0.52	0.64	-0.11
Sr	**0.92**	0.17	0.02	0.12	**0.91**	0.01	0.08
DOC	-0.09	0.18	**-0.83**	0.37	-0.23	-0.00	-0.64
pH	0.68	0.22	0.46	0.20	**0.80**	0.20	0.33
NO_3	0.19	0.05	0.00	**0.91**	0.16	0.07	**0.71**
SO_4	0.05	0.30	**0.73**	0.36	-0.07	0.28	**0.72**

Supplementary material
Larocque et al., 2015
Ecological Indicators