# Use of water isotopes and chemistry to infer the type and degree of exchange between groundwater and lakes in an esker complex of northeastern Ontario, Canada

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12	
13	Abstract
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15	Water chemistry and water isotopic composition were investigated in a set of 50 boreal lakes located
16	at different elevations in an esker system near Timmins, Ontario, as well as in local streams, groundwater
17	springs and information available from seasonal precipitation values. Insights gained from this study are
18	essential to develop a more detailed understanding on the local hydrology as the region has widespread
19	cottage development, mining activities and recreational fishing. Analyses focused on stable isotopic ratios
20	of hydrogen and oxygen, as well as specific conductance as indicators of the position of a lake with respect
21	to the influence of groundwater. Both isotopic composition and specific conductance distinguished higher
22	elevation groundwater recharge lakes from lower elevation groundwater discharge lakes. Groundwater
23	recharge lakes characterized by enriched isotopic values and low values of specific conductance are located
24	above the hydraulic midline elevation of the study lakes. In contrast, groundwater discharge lakes were
25	isotopically depleted and had higher values of specific conductance, and occurred below the hydraulic
26	midline of the study lakes. An intermediate group of lakes was also defined (termed seepage lakes) and
27	consisted of either recharge lakes that were alkaline, or discharge lakes that had no outlet. The seepage
28	lakes group had intermediate isotopic and water chemistry characteristics compared to recharge and
29	discharge lakes. A classification scheme for lakes was developed based on the specific conductivity, water
30	isotopic composition, the presence of an outlet, and other characteristics to define three types of recharge

- 31 lakes, and two types of discharge lakes.
- 32

Interannual (2013 and 2014) and summertime differences in water chemistry between early June and August revealed that upland groundwater recharge lakes showed evidence of evaporative drawdown, indicating sensitivity to short-term changes in climate, whereas the lower-elevation discharge lakes showed little variation between seasonal samples, and consequently would likely be affected only by hydroclimatological changes of greater duration and persistence.

38

#### 39 Keywords

- 40
- 41 Water balance, landscape limnology, groundwater, hydrochemistry, lake-water chemistry, stable isotopes
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#### 43 <u>1 Introduction</u>

44

45 Nearly all surface waters, including lakes, interact with groundwater to some extent (Winter et al., 46 1998). The degree to which lakes interact with groundwater strongly influences lake-water chemistry and water balance as well as aquatic biota and biochemical cycles (Rosenberry et al., 2015; Lewandowski et 47 48 al., 2015). These characteristics will influence the sensitivity and vulnerability of lakes to environmental stressors such as climate change, and other anthropogenic disturbances. Future climate change will likely 49 50 affect lakes differently depending on their connectivity to groundwater, further increasing our need to better 51 understand the relations between lake hydrology and lake water geochemistry. Further, understanding the 52 climatic controls on water balance and adverse impacts to aquatic ecosystems is essential for informed 53 ecosystem management and conservation practices (Winter et al., 1998).

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55 Groundwater-lake water interactions are an often poorly-studied component of lake hydrology. However, recent advances in isotopic techniques and modelling approaches have enabled researchers the 56 57 opportunity to better understand hydrological processes in lakes at a local to regional scale (Fleckenstein et 58 al., 2010; Rosenberry et al., 2015). This has included studies using numerical simulations (e.g. Winter et 59 al., 1998), as well as empirical studies at a range of different spatial and temporal scales. Studies at the 60 regional scale (e.g. Gorham et al., 1983; Webster et al., 2000) emphasize differences in climate and surface geology as being the important drivers of changes in lake-water chemistry. By contrast, empirical studies 61 62 performed at a local to regional scale (e.g. Webster et al., 1996; Quinlan et al., 2003; Martin and Soranno, 63 2006; Ala-aho et al., 2013) indicate the importance of landscape position and also lake morphology as being 64 important in understanding lake-groundwater interactions. At the scale of an individual lake, a number of 65 studies have shown that groundwater-lake water interactions can vary temporally according to changes in

66 seasonality and longer term changes in hydroclimatic conditions (e.g. Kenoyer and Anderson, 1989;

- 67 LaBaugh et *al.*, 1997; Sebestyen and Schneider, 2001; Schuster et *al.*, 2003; Arnoux et *al.*, 2017b).
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69 The vast majority of past empirical studies have relied on studying aspects of water chemistry (e.g. 70 dissolved ions), as an indicator of hydrological connectivity between lakes, since such approaches can 71 contain signals of important processes such as mineral weathering and dissolution (Bertrand et al., 2014). 72 Chemical tracers are often referred to as non-conservative tracers because their composition changes as 73 they react with catchment materials (Kendall and McDonnell, 1998). By contrast, other studies relied on 74 the isotopic composition of water as a hydrological tracer (e.g. Turner et al., 2010; Isokangas et al., 2015). The latter are labelled to as conservative tracers because they are relatively conservative in reactions with 75 catchment materials and retain their distinctive values until they mix with other water sources or they 76 77 evaporate (Kendall and McDonnell, 1998). In addition to being a good indicator of source water, stable 78 isotopes of water constitute an efficient and cost-effective means to quantify lake evaporation and water 79 balance status of water bodies using the Craig-Gordon model (Craig and Gordon, 1965), given that the 80 isotopic composition of lake-water and precipitation as well as air temperature and relative humidity are 81 known, or can be estimated (Gibson and Edwards, 2002). The Craig-Gordon model is well established and 82 has been used extensively to investigate the spatial and temporal variability in lake water balance in remote 83 boreal regions of Canada (e.g. Wolfe et al., 2007; Bouchard et al., 2013; Tondu et al., 2013; Turner et al., 84 2014a; Turner et al., 2014b). However, precipitation and groundwater often display similar isotopic 85 signatures as they both tend to retain their original isotopic composition because they undergo little to no evaporation (Gibson and Edwards, 2002; Gibson et al., 2008; Yi et al., 2008). This makes the distinction 86 87 of the relative influence of groundwater and precipitation in lake water balance challenging. Given this, the 88 combination of chemical and isotopic approaches has the ability to produce more reliable interpretations, 89 especially if the two approaches converge on a mutually reinforcing interpretation. Chemical and isotopic 90 tracers have been widely used together to investigate the connectivity between groundwater and lake water 91 within a single lake (e.g. Labaugh et al., 1997; Schuster et al., 2003; Rautio and Korkka-Niemi, 2011) or 92 for a cluster of a few selected lakes (e.g. Arnoux et al., 2017a; Arnoux et al., 2017b; Gurrieri and Furniss, 93 2004; Katz et al., 1997; Turner and Townley, 2006). Nonetheless, studies that have combined chemical and 94 isotopic approaches to investigate the connectivity between groundwater and lake water for a large cluster 95 of lakes at the scale of the landscape are lacking.

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97 The main objective of this study is to examine the importance of landscape position on groundwater 98 connectivity by scrutinising both water chemistry and isotopic composition of water in a boreal esker 99 complex in northeastern Ontario. Investigating such processes in the context of esker hydrology is 100 particularly relevant as eskers consist of porous and permeable materials that facilitate groundwater flows, 101 are widespread in boreal regions (Ala-aho et al., 2015) and constitute one of the most common type of 102 aquifers in boreal Canada (Cloutier et al., 2007). Results from the observations above, will be used to 103 develop a lake typology of hydrological connectivity based landscape position and lake characteristics 104 (Newton and Driscoll, 1990; Bertrand et al., 2014). The resultant typology will provide insights on lakes' 105 sensitivity and vulnerability to environmental stressors such as climate change, for water management and 106 conservation goals as the region is the site of cottage development, recreational fishing, mining activities 107 and aggregate extraction (Cochrane, 2006). Additionally, the typology will be used for site-selection and 108 interpretations of past hydrological changes from stratigraphic analysis of isotopic and geochemical 109 indicators in sediment cores from lakes. Finally, we will evaluate the sensitivity of the proposed typology, 110 by investigating if seasonal variations of lake-water characteristics are more readily detected in higherelevation groundwater recharge lakes (i.e. lakes that receive the majority of their water from precipitation 111 112 and feed the groundwater system) in comparison to lower elevation groundwater discharge lakes (*i.e.* lakes 113 that receive the majority of their water from groundwater).

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#### 115 <u>2 Study area</u>

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The study area is a portion of the Kettle Lake Esker between the southern shore of Frederick House 117 118 Lake, and the northern shore of Night Hawk Lake, a region located approximately 35-km east of Timmins, 119 Ontario, Canada (Fig. 1a). The Timmins region is characterized by a humid continental climate with a mean 120 annual temperature of 1.8°C and average precipitation of 835 mm (Environment Canada, 2015). The area 121 undergoes long cold winters and lakes are covered with ice from early November until early April. Summers 122 are usually wet and mean air temperatures are 17.5°C in July. Many of the study lakes and streams are 123 located within Kettle Lakes Provincial Park, as well as in lower elevation regions that have been moderately 124 influenced by human activities (Cochrane, 2006). The study region is covered with well drained orthic 125 humo-ferric podzols while surrounding clay plains are for the most part covered with moderately to poorly 126 drained orthic gray luvisols and gleyed gray luvisols (OMNDM, 2006). Jack pine, poplar, black spruce, 127 white birch, trembling aspen and balsam fir dominate the well-drained areas, with a dominance of spruce 128 in poorly drained regions.

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The eskers are the result of glaciofluvial, glaciolacustrine and related postglacial processes (Nadeau, 2011). The regional landscape is dominated by landforms and deposits of the Laurentide Ice Sheet during the last glacial maximum and deglaciation of the region was essentially complete approximately 10,000 years ago (Dyke, 2004). The ablation of the ice sheet was particularly dynamic and led to the formation of

- 134 relatively large eskers composed of coarse grained glaciofluvial sediments in deposits oriented in a north-135 south direction and mantling the crystalline bedrock (Cloutier et al., 2007). The retreat of the ice sheet was 136 accompanied by ponding of glacial meltwaters that led to the development of glacial Lake Ojibway that 137 submerged most of the region (Roy et al., 2011) and the widespread deposition of glaciolacustrine clay 138 (Nadeau, 2011), followed by the drainage of Lake Ojibway into Hudson Bay ~8,200 years ago (Roy et al., 139 2011). As Lake Ojibway levels dropped, wave action eroded the surface of the esker and redistributed some 140 sand materials on the flanks on the esker, forming lateral littoral sand units that drape the glaciolacustrine clavs (Cloutier et al., 2007) (Fig. 1b). The numerous kettle lakes on the esker formed once the glacial ice 141 142 trapped in the outwash materials melted (Nadeau, 2011).
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The esker stratigraphy ensures that its groundwater system is highly localized since the esker 144 generally have a high hydraulic conductivity due to their coarse texture. The esker is surrounded by 145 underlying bedrock and the adjacent fine-grained glaciolacustrine deposits, both characterized by very low 146 147 hydrological conductivity (Stauffer and Wittchen, 1992). As a consequence, the esker can be conceptually 148 partitioned into zones of unconfined aquifers in its center where coarse material is present at the surface 149 and zones of confined aquifers at its edges when fine-grained sediment mantles the core of the esker (Fig. **1b**) (Cloutier et al., 2007). Thus, the recharge of the esker will occur through infiltration of precipitation in 150 151 the unconfined aquifer and discharge will take place on the esker flanks at the contact of the clay, where 152 most groundwater springs emerge (Cloutier et al., 2007). Confined aquifers found on the surrounding clay 153 plain are often covered by peatlands and shallow lakes fed by groundwater springs on the edges of the esker 154 or by streams that drain the esker (Rossi et al., 2012). 155



Fig. 1: Location of the study area in north east Ontario near Timmins, Ontario (Based on: Richard and
 McClenaghan, 2000) (a) and conceptual geological transverse section of an esker complex (b) (Modified
 from: Veilette et *al.*, 2004)

#### 160 <u>3 Methods</u>

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#### 162 <u>3.1 Geomatic and lake morphometric data</u>

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164 Lakes and other geographic features were digitalized in ArcGIS 10.3 from Google Earth. Maximum 165 lake depths Z<sub>max</sub> were obtained from the Ontario Ministry of Natural Resources and Forestry (OMNRF, 166 2011). Digital Elevation Models (DEM) from the study area were obtained from Natural Resources Canada 167 with a spatial resolution of 20 m (NRC, 2013). Lake elevation values were calculated as the mean elevation of the lake in ArcGIS from the available DEM, and lake watershed slopes were calculated from the DEM 168 169 in ArcGIS in a 100 m buffer zone surrounding each lake. This approach was used because of the coarse 170 spatial resolution of the DEM and the close proximity of the lakes made clear individual lake watershed 171 delineation impossible. Since all lakes in the study area are kettles, which are characterized by steep slopes 172 on their shore over a small distance, buffer zone of different widths were produced and the 100 m showed 173 the best correlation with water tracers.

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#### 175 <u>3.2 Field measurements and water sample collection</u>

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Water samples were collected during three field campaigns (7-14 June 2013, 16-23 June 2014, and 12-19 August 2014). 50 lakes were sampled, as well as a number of streams (lake outlets and lake inlets) and groundwater springs. The lakes were chosen to achieve a wide spatial coverage over this region encompassing a gradient of lake elevation as well as lake types. A few lakes located in the area of interest could not be sampled due to poor accessibility. Groundwater springs and streams flowing into the study lakes were also sampled to characterize the local groundwater-surface water interactions.

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184 Temperature and specific conductance of the water (corrected to 25°C) at each site were measured 185 with an YSI Salinity Conductivity Temperature meter (accuracy  $\pm 0.1 \ \mu$ S/cm and  $\pm 0.1^{\circ}$ C). The pH was 186 measured with an UP-5 Denver Instrument pH meter calibrated before usage (accuracy  $\pm 0.1$ ). Water 187 samples were collected using 1 L Nalgene bottles that were tripled-rinse with distilled water prior to use 188 and again with sample water while sampling (Louiseize et al., 2014). To prevent cross-contamination, the 189 tripled-rinsing of bottles with sampling water was carried away from the final sampling point in the lake or 190 downstream of stream/spring sampling points. Bottles were completely filled in order to avoid headspace 191 air and subsequently filtered within 3 hours of sampling.

Samples collected for water stable isotope, dissolved ion analysis and dissolved inorganic nitrogen were vacuum filtered with 0.45 µm Millipore Isopore filters. Vacuum filtering apparati were triple-rinse with distilled water and the lake water before and after use for each sample. The filtrates were then poured and placed into pre-cleaned 20ml plastic scintillation vials. Three replicates were collected for each sample. All vials were previously rinsed with filtered sample water that was discarded. Vials were completely filled to avoid any headspace, sealed with Parafilm<sup>™</sup> to avoid evaporation, and kept cool and in the dark in a fridge prior to analysis.

200

201 Samples for total dissolved nitrogen (TDN), dissolved organic carbon (DOC) and dissolved inorganic 202 carbon (DIC) analysis were filtered on-site using a glass filtration and Whatman GF/F glass fiber filters to 203 avoid any ex situ carbon addition. Filters were pre-ashed at 550°C for two hours and wrapped with pre-204 ashed aluminum foil prior to utilization to eliminate any residual organic matter (Lamoureux and 205 Lafrenière, 2014). The glass filtration apparatus was triple-rinsed with distilled water and lake water before 206 and after use for each sample and was wrapped with new clean pre-ashed aluminum foil overnight. Filtrates 207 were then poured and stored into pre-cleaned 45 ml amber EPA vials with Teflon lined septa with no 208 headspace (Louiseize et al., 2014). Two replicates were collected for each sample. Vials were labelled and 209 were kept cool and in the dark in a fridge prior to analysis.

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#### 211 <u>3.3 Laboratory analysis</u>

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The stable isotope ratios of water ( $\delta^{18}$ O and  $\delta^{2}$ H) were measured using a Los Gatos Research Liquid– Water Isotope Analyzer (LGR), which vaporizes injected sample and measures its absorbance relative to Vienna Standard Mean Ocean (‰ V-SMOW). All runs contain 6 replicate analyses and 3 standards produced by Los Gatos bracketing every 3 samples (e.g. LGR1A,  $\delta^{18}$ O=-19.50‰ and  $\delta^{2}$ H=-154.3‰; LGR2A,  $\delta^{18}$ O=-16.14‰ and  $\delta^{2}$ H=-123.6‰; LGR3A,  $\delta^{18}$ O=-13.10‰ and  $\delta^{2}$ H=-96.4‰; LGR4A,  $\delta^{18}$ O=-7.69‰ and  $\delta^{2}$ H=-51.0‰; LGR5A,  $\delta^{18}$ O=-2.80‰ and  $\delta^{2}$ H=-9.5‰). Sample reproducibility (1 $\sigma$ ) based on repeated measurements of samples and standards was fixed at 0.25‰ for  $\delta^{18}$ O and at 1.5‰ for  $\delta^{2}$ H.

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Concentrations of inorganic ions (Ca, Mg, K, Na, Cl, SO<sub>4</sub>) were measured by liquid ion chromatography with a Dionex ICS-3000. Detection limits were as follows: 0.5ppm for Ca, 0.01ppm for Mg, 0.2ppm for K, 0.3ppm for Na, 0.05ppm for Cl and 0.1ppm for SO<sub>4</sub>). Concentrations of dissolved inorganic species (NO<sub>2</sub>-NO<sub>3</sub> and NH<sub>4</sub>) were measured by colorimetry using an Astoria Pacific FASPac II Flow Analyser (detection limits of 0.01ppm). Concentrations of DOC, DIC and TDN were measured by high temperature combustion and nondispersive infrared sensor and chemiluminescent detection using a Shimadzu TOC-VPCH/TNM equipped with a high sensitivity catalyst system (detection limits of 0.08ppm
for DOC and 0.015ppm for TN) (Louiseize et *al.*, 2014). Total dissolved carbon (TDC) was calculated as
the sum of DOC and DIC.

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231 <u>3.4 Water balance calculations</u>

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Monthly precipitation isotopic data are available from February, 1997 to November, 2010. Precipitation isotopic data were collected at Bonner Lake, about 100 km NNW of Timmins by the Canadian Network for Isotopes in Precipitation (CNIP) (Birks et *al.*, 2010). The general water (Eq. 1) and isotope balance (Eq. 2) of a well-mixed lake may be written respectively as follow (Darling et *al.*, 2005):

237

$$\frac{dV}{dt} = I - Q - E$$
 Eq. 1

238

$$\frac{Vd\delta_L + \delta_L dV}{dt} = I\delta_I - Q\delta_Q - E\delta_E$$
 Eq. 2

239

240 where V is the volume of the lake, t is time, dV is the change of volume over time dt, I is instantaneous inflow where  $I = I_F + I_G + P$  ( $I_F$  being surface inflow,  $I_G$  groundwater inflow and P precipitation on the 241 lake surface); Q is instantaneous outflow where  $Q = Q_R + Q_G (Q_R \text{ is surface outflow and } Q_G \text{ is groundwater})$ 242 243 outflow), E is evaporation; and  $\delta_L$ ,  $\delta_I$ ,  $\delta_Q$  and  $\delta_E$  are the isotopic compositions of the lake, inflow, outflow and evaporative flux respectively. Assuming (1) that the lake maintains a near-constant volume on the long-244 term (*i.e.*, dV = 0 and  $dt \rightarrow \infty$ ) (Darling et al., 2005) and (2) that physical outflow does not cause isotopic 245 fractionation (*i.e.*,  $\delta_0 = \delta_L$ ) (Gibson and Edwards, 2002; Yi et *al.*, 2008), Eq. 1 and 2 can be simplified and 246 247 rewritten as follows:

248

$$I = Q + E$$
 Eq. 3

249

$$I\delta_I = Q\delta_Q + E\delta_E$$
 Eq. 4

250

E can be related to *I* assuming that the lakes are in isotopic steady state. This assumption seems well justified as the lakes have had sufficient time in the past to reach their isotopic steady-state which is reflective of the local climate and their mean hydrological status, and can be defined by its water balance, which corresponds to the ratio of the total inflow to the evaporation rate (Isokangas et *al.*, 2015). The evaporation-to-inflow ratio of the lake  $E_L/I_L$  can be calculated by combining Eq. 3 and 4 (Gibson and Edwards, 2002; Yi et *al.*, 2008):

257

$$\frac{E_L}{I_L} = \frac{\delta_I - \delta_L}{\delta_E - \delta_L}$$
 Eq. 5

258

where  $\delta_l$  was computed as the intersection of the Local Meteoric Water Line (LMWL) with the Local Evaporation Line (LEL) (Gibson et *al.*, 1993; Yi et *al.*, 2008);  $\delta_L$  is the isotopic composition of the lake water sample and  $\delta_E$  was estimated using the Craig-Gordon model (Craig and Gordon, 1965) formulated by Gonfiantini (1986) as follows:

$$\delta_E = \frac{(\delta_L - \varepsilon^*)/\alpha^* - h\delta_A - \varepsilon_k}{1 - h + \varepsilon_k}$$
Eq. 6

263

where  $\delta_L$  is the isotopic composition of lake water,  $\varepsilon^*$  is the equilibrium isotopic separation term,  $\alpha^*$  is the liquid–vapour equilibrium fractionation factor, *h* is the relative humidity,  $\delta_A$  is the isotopic composition of the local atmospheric moisture, and  $\varepsilon_k$  is the kinetic separation term between the liquid and vapour phases. The  $\varepsilon^*$  and  $\alpha^*$  parameters which are temperature dependent can be calculated using empirical equations for  $\delta^{18}$ O as follows (Horita and Wesolowski, 1994):

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$$\varepsilon^* = -7.685 + 6.7123 \left(\frac{10^3}{T}\right) - 1.6664 \left(\frac{10^6}{T^2}\right) + 0.35041 \left(\frac{10^9}{T^3}\right)$$
 Eq. 7

270

$$\alpha^* = exp\left(-\frac{7.685}{10^3} + \frac{6.7123}{T} - \frac{1666.4}{T^2} + \frac{350410}{T^3}\right)$$
 Eq. 8

271

#### where T is the air temperature in Kelvins. $\varepsilon_k$ (Eq. 9) is expressed for $\delta^{18}$ O by (Gonfiantini, 1986):

273

$$\varepsilon_k = (0.0142 (1-h))1000$$
 Eq. 9

274

275 The equation for  $\delta_E$  was modified according to Gibson and Edwards (2002) to directly utilize isotopic data 276 in per mil rather than as a decimal fraction and expressed as follows:

277

$$\delta_E = \frac{\alpha^* \delta_L - h \delta_A - \varepsilon}{1 - h + 10^{-3} \varepsilon_k}$$
 Eq. 10

279 where  $\varepsilon$  is the total isotopic separation factor that includes both  $\varepsilon^*$  and  $\varepsilon_k$  expressed as:

280

$$\varepsilon = \varepsilon^* + \varepsilon_k$$
 Eq. 11

281

282  $\delta_A$  was originally estimated with the original model that assumes isotopic equilibrium between atmospheric 283 moisture and precipitation as follows (Gibson, 2002):

284

$$\delta_A = \frac{\delta_P - \varepsilon^*}{1 + 10^{-3} \varepsilon^*}$$
 Eq. 12

285

where  $\delta p$  was computed as the average isotopic composition of annual precipitation from February 1997 to November 2010 (data collected by CNIP). The same procedure was used to calculate E/I ratios of streams and groundwater springs.

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#### 290 <u>4 Results</u>

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#### 292 <u>4.1 Temperature and water stable isotopes</u>

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During the August 2014 field campaign, all types of bodies of water differed from one another by their temperature: springs are characterized by low temperatures (6 -12°C) whereas streams have slightly higher temperature (12 -16°C) and lakes ranged from (16 -18°C). It should be noted however that spring temperature is not an accurate indication of groundwater temperature due to alterations induced by the velocity of the discharging spring and the resulting warming of the discharging water as it reaches the surface.

300

Monthly precipitation isotopic data from CNIP from February, 1997 to November, 2010 from Bonner 301 302 Lake, about 100 km NNW of Timmins, show progressive enrichment in values between winter, spring, fall 303 and summer on the global and local meteoric water lines, which are similar (Fig. 2a). The water samples (*i.e.* groundwater springs, streams and lakes) displayed a wide range of water stable isotope values (-14.7%) 304 305 to -6.8‰ for  $\delta^{18}$ O and -105.5‰ to -68.6‰ for  $\delta^{2}$ H), which fell on a Local Evaporation Line (r = 0.99, p < 0.001) (Fig. 2b). Groundwater springs have isotopic values very similar to mean annual precipitation (-306 307 14.7% to -13.1% for  $\delta^{18}$ O and 105.5% to -96.0% for  $\delta^{2}$ H). Streams have comparable isotopic composition 308 to groundwater springs (-13.8% to -11.3% for  $\delta^{18}$ O, and -100.8% to -91.9% for  $\delta^{2}$ H). By contrast, lakes are characterized by large variations in water isotopic composition, ranging from values comparable to 309

- groundwater springs (*ca.* -14‰ for  $\delta^{18}$ O and -100‰ for  $\delta^{2}$ H) to more enriched values (*ca.* -6‰ for  $\delta^{18}$ O
- 311 and -70‰ for  $\delta^2$ H).
- 312



**Fig. 2**: Isotopic composition of precipitation in relation to the Global Meteoric Water and Local Meteoric Water lines ( $\mathbf{r} = 0.99$ ,  $\mathbf{n} = 166$ , p < 0.001) (a), and isotopic composition of collected water samples in relation to the Local Evaporitic Line ( $\mathbf{r} = 0.99$ ,  $\mathbf{n} = 68$ , p < 0.001) (b).

317

A significant correlation exists between  $\delta^{18}$ O and elevation (r = 0.53, n = 50, p < 0.001) (Fig. 3a), suggesting that elevation is a variable explaining lake-water isotopic composition in lakes. Lakes sampled at lower elevations are more depleted while lakes sampled at higher elevations are enriched in <sup>18</sup>O and <sup>2</sup>H.



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Fig. 3: Relation between  $\delta^{18}$ O in water samples and elevation ( $\mathbf{r} = 0.53$ ,  $\mathbf{n} = 50$ , p < 0.001) (a), and specific conductivity and elevation ( $\mathbf{r} = -0.67$ ,  $\mathbf{n} = 50$ , p < 0.001) (b). The horizontal dashed line indicates the position of a breakpoint analysis which occurs at an elevation of ~282 m asl, in both cases (**Tab. 1**)

Evaporation-to-inflow ratio calculations show that groundwater springs and streams have E/I ratios close to 0 due to their short residence times while lakes have E/I values ranging from values similar to groundwater springs and streams to above E/I ~ 1 owing to their longer residence times that expose them to evaporation (**Fig. 4a**).



331 332

**Fig. 4**: Relation between electrical conductance and calculated evaporation-to-inflow ratios. Lakes in panel b are coded according to a classification scheme developed in this paper

- 333 334
- 335 <u>4.2 Solutes and dissolved organic matter</u>
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337 As is the case with stable isotope values, water bodies reveal a wide range for non-conservative ions, and the overall sum of ions indicated by lake-water specific conductance, all of which are significantly 338 339 correlated (see correlation matrix **Tab. A1**). Groundwater springs have the highest specific conductance  $(300-550 \ \mu\text{S/cm})$  while streams have values *ca*. 300  $\mu\text{S/cm}$ . Lakes show a wide range of solute content and 340 341 values of specific conductance, from values similar to groundwater springs (ca. 400 µS/cm) to very low values similar to precipitation (as low as  $10 \ \mu\text{S/cm}$ ) (Fig. 3b). A significant correlation exists between the 342 specific conductance and elevation (r = -0.67, n = 50, p < 0.001), suggesting that elevation is a variable 343 explaining specific conductance in lakes. 344

345

Only 36 lakes were sampled for dissolved organic carbon (DOC) and nitrogen (TN). Unlike nonconservative ions and conservative isotopic tracers, no significant relation was found between dissolved organic elements and elevation ( $\mathbf{r} = -0.04$ ,  $\mathbf{n} = 36$ , p = 0.84 for DOC;  $\mathbf{r} = 0.05$ ,  $\mathbf{n} = 36$ , p = 0.77 for TN). However, significant, or marginally significant correlations were observed between DOC and mean lake depth, with deeper lakes having lower concentrations of DOC ( $\mathbf{r} = -0.58$ ,  $\mathbf{n} = 36$ , p = 0.11). A similar pattern was observed between TN and mean lake depth ( $\mathbf{r} = -0.71$ ,  $\mathbf{n} = 36$ , p = 0.02).

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There is a strong and significant correlation between lake water isotopic values and specific conductance ( $\mathbf{r} = 0.80$ ,  $\mathbf{n} = 50$ , p < 0.001). However, the slopes of the linear regressions for the water  $\delta^{18}$ O (**Fig. 3a**) and specific conductance (**Fig. 3b**) do not match the data points perfectly as there seem to be a distinct transition between similar values found in higher- and lower-elevation lakes, which was further examined using a breakpoint analysis of the lake water properties. Nine available environmental variables had a statistically significant breakpoint when regressed over elevation and significant breakpoints were within a narrow range of elevation with a mean of 282.4 m asl (**Tab. 1**).

364

365	Tab. 1: Results showing significant breakpoints in nine water chemistry variables and lake elevation
366	(lower and upper elevation ranges calculated from the standard deviation)

` II	0		,
Environmental Variable	Mean Elevation	Lower Elevation	Upper Elevation
DIC	281.5	279.6	283.4
$K^+$	281.8	278.2	285.4
TC	281.8	280.2	283.4
$Mg^{2+}$	282.0	280.3	283.7
d <sup>2</sup> H	282.0	279.9	284.1
$d^*$	282.2	280.3	284.1
d <sup>18</sup> O	282.2	280.2	284.2
EC	284.0	281.4	286.6
$Ca^{2+}$	284.2	281.9	286.5
Breakpoint line	282.4		
	*d corresponds to	deuterium excess	

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369 370 371 372

Fig. 5: Spatial depiction between elevation and lake-water specific conductance (μS/cm) (a), and lake-water δ<sup>18</sup>O (‰) (b). The elevation of the breakpoint line (284 m) is shown as a dashed line

To further assess differentiation of the lakes in terms of conservative and non-conservative water tracers, a non-metric multidimensional scaling (NMDS) based on these factors was undertaken, with lakes above an elevation of 282 m coded as groundwater recharge lakes, and lakes below 282 m coded as groundwater discharge lakes, indicating good separation of the groups based on water geochemistry (**Fig. 6a**).

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The existence of two distinctive types of lakes was used to develop a lake typology to explain changes in water biogeochemistry across the studied lakes. In order to better understand how water tracers vary in those two zones, individual ANOVAs were undertaken for all lake-water variables that were above detection limits (**Tab. A2**). All anion and cations (and correlated variables including specific conductance), with the exception of nitrogen species, individually were significantly different above and below an elevation of 282 m asl. This was also the case of the isotopic variables. Variables that were not significantly different included: temperature, forms of nitrogen, the C/N, and lake depth.



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Fig. 6: Non-metric multidimensional scaling (NMDS) applied to conservative and non-conservative water
tracers. Lakes that occurred at an elevation of greater than 282 m asl are labelled as 'recharge' lakes,
whereas lakes as located at an elevation of less than 282 m are labelled as 'discharge' lakes (a). A third
group of lakes (labelled 'seepage') is further discerned based on chemical and isotopic characteristics (b).
Stress value for the NMSD is low (stress = 0.023)

#### 94 <u>4.4 Short-term evolution of water tracers</u>

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Short-term water balance variability was observed towards the end of the growing season (**Fig. A1b,d**) and between years (**Fig. A2a,c**). Lakes located at an elevation greater than 282 m asl underwent marked changes in water balance during the three sampling campaigns whereas lakes located below 282 m asl underwent little or no change, especially the lower lakes (**Fig. A2a,b**). Similarly, the water chemistry gradient between upland solute-poor lakes and lowland solute-rich lakes changed seasonally and between years. Lakes above 282 m asl did not respond chemically to short-term hydroclimatic change while lakes below 282 m asl displayed significant solute changes (**Fig. A2c,d**).

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#### 404 <u>5 Discussion</u>

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#### 406 <u>5.1 Interpretation of water tracers</u>

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The wide range of lake isotopic values and E/I ratios suggest that lakes on the esker are heterogeneous in terms of water balance and hydrological characteristics. Groundwater springs have the most depleted isotopic values because their water residence times are short and they only undergo limited evaporation 411 (Gazis and Feng, 2004). Streams display isotopic values similar to groundwater springs since they originate 412 from groundwater and experience relatively low evaporation rates due to more continuous water flow. The 413 wide range of isotopic values for lakes can be explained by their position in the landscape, particularly 414 relative to their location in the esker aquifer system for which elevation appears to be a good proxy. This 415 suggests that lowland lakes are primarily fed by groundwater inflow while upland lakes receive a much 416 lower contribution from the local groundwater in their respective water budgets. Nonetheless, it is 417 challenging to distinguish the influence of groundwater from precipitation in lake water balance as they both have similar isotopic signatures (Fig. 2b) (Gibson and Edwards, 2002; Gibson et al., 2008; Yi et al., 418 419 2008). Yet, given that i) our study was carried out on a small spatial scale (*i.e.* a rectangular zone of  $\sim 12$ 420 km by  $\sim 6$  km); ii) the close proximity of the lakes; iii) the terrain homogeneity (with boreal forest as the 421 dominant land cover); iv) the limited topography; and v) the good correlation between water isotopes and 422 specific conductance (r = 0.63, n = 50, p < 0.001), it is unlikely that there are significant differences in terms of precipitation patterns within our study area. Therefore, it is a reasonable assumption that 423 424 groundwater connectivity is the main control on lake water balance. Lake isotopic values can also be 425 influenced by the isotopic composition of surface inflowing waters. But those are for the most groundwater 426 springs (which are made up of groundwater), their volume is supposed to be small in comparison to the 427 lake volume and, some of those streams are intermittent in the sense that they were not flowing during each 428 of the three field campaigns. Thus, it can reasonably be assumed that this influence is limited.

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430 Similar patterns are observed with the major ions in water. Groundwater springs have the highest 431 solute load likely due to chemical processes associated with mineral surface exchanges and weathering 432 (Ala-aho et al., 2013). Lakes, however, displayed a wide range of water chemistries, and range from high 433 solutes characteristic of groundwater to values close to zero, typical of precipitation (Fig. 2), suggesting 434 that the heterogeneity of lakes on the esker are a result to the degree to which they interact with groundwater. 435 As it is the case for isotopic values, chemical composition of a given lake depends on elevation. Lakes 436 sampled at lower elevation are higher in solutes; this indicates that lowland lakes reflect interaction with 437 intermediate or regional groundwater flows subject to more mineral weathering and dissolution (Tóth, 1963). Upland lakes on the other hand reflect interaction with local groundwater flow paths with 438 439 correspondingly reduced mineral weathering and dissolution (Tóth, 1963). There are only minor differences 440 in terms of the relative solute composition among the samples suggesting that the esker subsurface material is geochemically relatively homogeneous and reflects the carbonate-rich nature of the glaciofuvial outwash 441 442 that makes up the esker (Cummings et al., 2011). The carbonate-rich sediment originates from Paleozoic 443 carbonates of the Hudson sedimentary Platform ca. 150 km to the north and is localized to glacial surficial 444 sediments (Roy et al., 2011).

region, while lake water temperature varies strongly with season. There is little differences of temperature between lakes and the latter are mainly the result of lake morphology than their connection with cool groundwater as lakes of smaller volumes have a lower thermal inertia than larger ones. Differences in dissolved organic content between the lakes is also a result of lake morphology as smaller lakes tend to have higher concentrations as they mix more easily and receive greater inputs due to their high catchment

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#### 456 <u>5.2 Lake hydrological classification</u>

likely due to their higher water residence times.

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The correlation between lake water  $\delta^{18}$ O and specific conductance (r = 0.80, n = 50, *p* < 0.001) shows there is a clear relation between conservative water tracers (which are indicative of water source and evaporation) and non-conservative water tracers (which are indicative of water flow paths), signifying that lowland lakes will receive a significant portion of their water as groundwater flows and will geochemically reflect this origin, while upland lakes will receive most of their water through precipitation and will be geochemically dilute.

Other characteristics of the lake-water (temperature and dissolved organic matter) do not reflect the

changes seen in the stable isotopes and ionic concentration. Water temperatures of groundwater springs are

coolest because the temperature of groundwater is typically close to the mean annual temperature of the

size-lake volume ratios (Knoll et al., 2015). However, upland lakes tend to have slightly higher amounts

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465 Consequently, the observed breakpoint elevation appears to correspond to an effective hydraulic 466 separation between groundwater recharge and discharge areas (Winter et al., 1998). This contrast between 467 the contribution of groundwater flow is evident in the distribution of lake-water composition (Fig. 5, Fig. 468 A1). Lakes characterized by groundwater discharge are spatially distinct from higher elevation lakes in the 469 groundwater recharge zone. Lake position has been used as a classification criterion in several studies (e.g. Winter, 1997; Born et al., 1979). Thus, upland lakes in the recharge zone are known as groundwater 470 471 recharge lakes or recharge lakes and, conversely, lowland lakes in the discharge zone, also called underflow 472 zone, will be referred to as groundwater discharge lakes or discharge lakes (Fig. 7) (Winter et al., 1998). 473 Because discharge lakes receive a substantial amount of water from groundwater, they are considered to be 474 groundwater-fed or minerotrophic whereas recharge lakes which receive the majority of their water from 475 precipitation and feed the aquifer are said to be precipitation-fed or ombrotrophic (Webster et al., 1996). 476 NMDS (Fig. 6a) and ANOVA (Tab. A2) analysis showed that all conservative and non-conservative 477 tracers are statistically different between the discharge zone and the recharge zone, except for DOC, TN 478 and temperature. An analysis of similarity (ANOSIM) between of the recharge and discharge lakes shows

that within group similarity is significantly greater than between group similarity, as illustrated by a large and significant r value (r = 0.77, n = 50, significance = 0.001 on 1000 permutations).

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482 Nevertheless, a few solute-rich alkaline lakes are located in the groundwater recharge zone which is 483 supposed to be depleted in solutes (Fig. 5a). Furthermore, the two primary groups in ordinal space display 484 a small overlap (Fig. 6a), suggesting the existence a third category of hybrid lakes referred to as seepage 485 or flow-through lakes (Winter, 1976; Webster et al., 1996; Winter et al., 2003). In those lakes, water comes 486 in as groundwater in-seepage and is returned to the groundwater system as out-seepage (Anderson and 487 Munter, 1981). Seepage lakes can be found both in the recharge zone and the discharge zone and they can 488 be contribute a recharge or a discharge function (Anderson and Munter, 1981). In the groundwater recharge 489 zone, seepage lakes differ from recharge lakes by their pH, which is more alkaline while in the groundwater 490 discharge zone, seepage lakes differ from discharge lakes by the absence of an outlet, meaning they receive 491 less input than discharge lakes (Fig. 8). Lake water chemistry and the presence of outlets have been used 492 in several studies as a classification criterion (e.g. Newton and Driscoll, 1990; Winter, 1977). NMDS (Fig. 493 6b) and ANOVA (Tab. A3) analysis showed that all conservative and non-conservative tracers are 494 statistically different between the three types of lakes, except for DOC, TN and temperature.

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496 As noted earlier, lakes can first be classified according to their location within the groundwater 497 system, particularly above and below the hydraulic midline, in this case, at or near the 282 m elevation in 498 this study that indicated a breakpoint in the many isotopic and limnological variable (282.4 m) associated 499 with differences in hydrological inputs. In this study, elevation appears to be a proxy of the boundary 500 between the groundwater recharge and discharge zones on the esker. Seepage lakes, however, can be found 501 on each side of the hydraulic midline, thus generating additional classes of lakes (see conceptual diagram, 502 Fig. 7) distinguished from on the presence or absence of a lake outlet (Fig. A1) (Stauffer and Wittchen, 503 1992). Lakes with outlets were classified as "groundwater discharge lakes" and lakes without outlets as "discharge seepage lakes". 504

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Lakes with outlets are typically found at the contact between the impermeable glaciolacustrine clay plain and the permeable glaciofluvial esker sand contact where groundwater springs emerge (**Fig. 1b**). Furthermore, in the study area, there is a significant relation between elevation and lake watershed maximum slope (r = 0.75, n = 50, p < 0.001). Lithology is also a variable used as a classification criterion in several studies (Winter, 1997; Martin et *al.*, 2011). Lakes located at the edge of the esker tend to have steeper watershed slopes and have low elevations, which increases the likelihood of lakes to be in contact with deeper groundwater flows (Winter, 1976). These lakes receive a substantial inflow of groundwater due to their geological setting and their water isotopic and chemical composition is similar to the one of
groundwater springs and outlets (Ala-aho et *al.*, 2013).

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516 Only two lakes in the groundwater discharge zone are without outlets and are classified as discharge 517 seepage lakes. The following hypothesis could potentially explain the absence of outlet: the ability of the 518 lakes to lose water to groundwater, or a reduced input from groundwater or surface inflow. Yet, some lakes 519 with outlets, like Pit Lake, can be found at elevations corresponding to the groundwater recharge zone (Fig. 520 5). The presence of Pit Lake at a distinctly high elevation (296 m) is nonetheless explained by the location 521 of this lake at the clay-sand interface (Fig. 1b). This suggests that elevation is just a putative variable or, in 522 other words, a proxy of the actual hydraulic midline delineated by the clay-sand interface. This is confirmed 523 numerically by applying a logistic regression to the presence or absence of a lake outlet and lake elevation, which provided a poor relation (Mc-Fadden r = 0.40, n = 50, p < 0.01). On the other hand, the logistic 524 regression of the presence or absence of a lake outlet to the closest distance to the sand-clay contact provided 525 526 a better relation (Mc-Fadden r = 0.69, n = 50, p < 0.001), although it is challenging to find the real clay-527 sand interface as the lateral sands can mask the real exact location (Fig. 1b) and surficial geological maps 528 have errors in tens of meters in comparison to field observations.





Fig. 7: Illustration of a lake typology for the study lakes. Lake elevation was used as the primary factor in
 separating lakes, with elevation being an effective surrogate for dividing lakes based on contribution of

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groundwater flow to a lake. The lakes were then separated based on presence of an outlet, as well as lake water pH and other morphological characteristics of the lakes

- Some lakes in the recharge zone, called "recharge seepage lakes", have an alkaline or a circumneutral pH and higher solute content, signifying that they interact to some extent with groundwater. This could occur for a number of reasons related to the existence of significant groundwater input including: i) slightly steeper lake watershed slopes, ii) geographical proximity to the clay-sand interface, and iii) lake relative deepness allowing interactions with deeper groundwater flows, or a combination of those.
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542 Recharge lakes can be further subdivided into two types of recharge lakes: "classical" recharge lakes 543 and peat bogs (Fig. 7), adding a fifth type of lake in the typology (Newton and Driscoll, 1990). Sampled peat bogs are very small and shallow lakes rimmed by floating mats of vegetation (typically less than 1 ha 544 and 1 to 2 m deep), acidic, characterized by a very low amount of solutes (maximum 30 µS/cm), a relatively 545 high amount of dissolved organic carbon (above 10 ppm) and by water isotopic composition controlled by 546 547 short-term hydroclimatic conditions (enriched in heavy water isotopes during drier periods and similar to 548 the isotopic composition of precipitation during wet periods). This could result from relative hydrological 549 isolation from the groundwater system due to the thick layer of peat at their bottom formed by the successive 550 accumulation of sedge and sphagnum characterized by a low hydraulic conductivity (Newton and Driscoll, 551 1990). As a consequence, direct precipitation would be the predominant source of water, making these lakes 552 sensitive to hydroclimatic variability.

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A sixth type of lake can be added to the proposed lake typology: ephemeral kettle ponds, commonly called dry kettles, even though they are not lakes *per se*. They can be identified on geological maps, aerial photography and satellite imagery. Dry kettles consist of small kettle holes adjacent to the esker crest that are usually but not always too high in elevation and shallow to be connected to the water table and will be dry during the summer months and most of the year, creating patches of bare land or wetlands in the forested landscape.

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Based on this typology, 42% of the sampled lakes were recharge lakes, 20% seepage lakes and 38% discharge lakes. Other studies report slightly different proportions (e.g. Anderson and Munter, 1981) as might be expected based on the geographical location, the size of the study area, and other factors relative to the groundwater system. The subdivision of lakes into recharge and discharge lakes is consistent with Ala-aho et *al.* (2013) who worked in similar settings and established their classification based on water solutes. The three-fold typology compares well with Turner et *al.* (2010) who also established a three category lake typology although the terminology of the three lake types differ and E/I values were used as
the primary classification criteria. Hence, the threefold typology of Fig. 7 is particularly relevant for water
resources management in esker complexes as it uses readily available variables (*i.e.* elevation, specific
conductance/pH and presence/absence of an outlet).

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572 Discharge (ground-water discharge) lakes have the highest pH, and amounts of solutes, while the 573 opposite is observed for recharge lakes. Seepage lakes have intermediate values compared to the other two lake types. The same patterns are observed for isotopic values: recharge lakes tend to be enriched in heavier 574 575 water isotopes, discharge lakes tend to be depleted in heavier isotopes, and seepage lakes characterized by 576 intermediate values. This reinforces the interpretation that seepage lakes are a hybrid type between recharge 577 and discharge lakes. Seepage lakes thus tend to be closer to recharge lakes on an isotopic basis, but more 578 similar to discharge lakes on a chemical basis. This is explained by the fact that most sampled seepage lakes 579 are located in the recharge zone and those receive some intermediate groundwater flows.

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581 Recharge lakes contain higher amounts of dissolved organic matter likely due to substantial water 582 residence times, whereas seepage lakes and discharge lakes can have sustained inflow of groundwater that 583 decreases water residence times. The concentration of DOC in discharge lakes is relatively higher than 584 expected as groundwater usually contain limited organic matter. This is likely an artefact of lake 585 morphology and anthropogenic activities. Indeed, values of DOC for discharge lakes display a high 586 standard deviation due to a subgroup of smaller lakes that are relatively deep and without cottages, 587 combined with another group of larger lakes that are relatively shallow with the presence of cottages. 588 Relatively shallow lakes are known to have significantly higher amounts of DOC than deeper ones as a 589 result of smaller volumes relative to inputs, and potential reworking of bottom organic matter and nutrients 590 due to the shallow water columns. DOC values for discharge lakes also contain two sizeable outliers that 591 skew the average and median: Nighthawk Lake and Frederick House Lake, both of which are two regional 592 high-order and large lakes (10,701 ha and 3,888 ha respectively) that are relatively shallow (maximum 593 depth of 4.6 m and 12.0 m respectively) and are heavily used for recreational purposes.

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5.3 Lake morphometry and water geochemistry

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597 There are additional morphometric factors that influence lake water isotopic composition in these 598 settings. Evaporation over a water body is enhanced when there is a strong gradient of temperature and 599 water vapour pressure between the lake water and the adjacent air. Assuming that there is no large 600 microclimate differences within the esker complex, evaporation rates are influenced by: i) the lake fetch 601 (Granger and Hedstrom, 2011); ii) relative depth; and iii) the steepness of the slopes surrounding the lake.
602 In the case of the latter, steep slopes tend to reduce evaporation rates by blocking air flows over the lake,
603 thus reducing wind speed, water-air temperature and water vapour pressure contrasts.

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605 Lake-water chemistry can also be influenced by lake morphometry. Lake depth has been known to 606 play a role (Winter, 1976). It seems that a priori there is no relation between lake maximum depth and 607 specific conductance ( $\mathbf{r} = 0.00$ ,  $\mathbf{n} = 50$ , p = 0.64). However, to determine whether the relation between 608 specific conductance and lake maximum depth varied with lake landscape position, two separate 609 regressions analyses were carried out for recharge ( $\mathbf{r} = 0.01$ ,  $\mathbf{n} = 50$ , p = 0.66) and discharge lakes ( $\mathbf{r} = 0.30$ , 610 n = 50, p = 0.05). The two regressions show that maximum depth can acts as a control on specific conductance only in lakes in the discharge zone: the deeper the lake, the deeper solutes-rich groundwater 611 612 flows seep into the lake. It is also expected that small lakes with a large ratio of perimeter to surface area (r 613 = 0.24, n = 48, p < 0.001) will have a higher amounts of solutes as the majority of groundwater seepage 614 into the lake is typically localised near the shoreline (Rosenberry et al., 2015).

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Given this, it can be argued that lake morphometry can play a significant role on lake-water
geochemistry and introduce some complexity in the lake typology. As a fact, some lake typologies
incorporate morphometric features as defining characteristics (e.g. Knoll et *al.*, 2015; Martin et *al.*, 2011;
Winter, 1977)). Nevertheless, water tracers show a stronger correlation with elevation than with
morphometric features, implying that elevation accounts for much more variance in isotopic composition
and specific conductance and trumps the influence of variations in evaporation between lake basins.

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#### 623 5.4 Implications for water balance, hydrochemistry and response to external stressors

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625 Results from the study show that the water balance of individual lakes is highly dependent on the 626 nature of their interactions with groundwater that is in turn determined by landscape position at highly 627 localized scale. Discharge lakes undergo minimal changes in water balance (usually E/I ~ 0) as the continuous flow of isotopically light groundwater masks evaporative enrichment whereas recharge lakes 628 629 are highly sensitive to evaporation (in most cases E/I > 1) as they rely on precipitation as their primary 630 source of water. Seepage lakes constitute a hybrid between recharge and discharge and their water balance is between the other two lake types (typically 0 < E/I < 1) (Fig. 4b). Consequently, upland recharge lakes 631 632 will be more prone to evaporative drawdown and therefore more sensitive to short-term climate change and 633 droughts, while discharge lakes will be buffered by groundwater inflow and affected by 634 hydroclimatological changes of greater duration and persistence that alter water table position (Fig. 8).

Seepage lakes will presumably be sensitive to drought but not to the same extent as recharge lakes as they are have stronger interactions with groundwater (**Fig. 8**). Under extreme hydroclimatic conditions, seepage lakes can become recharge lakes or discharge lakes (Anderson and Munter, 1981), suggesting that the esker hydrological system can respond to a large-scale hydroclimatic forcing (e.g. prolonged drought) in a manner that affects individual lakes differently. The degree of interaction with groundwater by an individual lake will also dictate the response to strong hydroclimatic forcings and introduce time lags (Webster et *al.*, 2000).



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Fig. 8: Changes in E/I between June 2013 and June 2014 (E/I 2014 – E/I 2013) (a) and changes in E/I between August 2014 and June 2014 (E/I Aug – E/I Jun) (b), and changes in specific conductance between June 2013 and June 2014 (EC 2014 – EC 2013) (c) and changes in electrical conductance between August 2014 and June 2014 (EC Aug – EC Jun) (d) by lake type

648 Similarly, the water-chemistry gradient between upland solute-poor lakes and lowland solute-rich 649 lakes could make recharge lakes more vulnerable to acidification than seepage and discharge lakes. The 650 effects of changing hydroclimatic conditions on lake-water chemistry across the landscape observed during 651 successive sampling in June 2013, June 2014 and August 2014 resulted in heterogeneous pattern depending 652 on the lake type similar to the findings of Webster et al. (1996). Recharge lakes did not respond chemically 653 to short-term hydroclimatic change as they feed the groundwater system by lake out-seepage thus producing 654 no net change in solutes, while seepage and discharge lakes displayed significant solute changes. Based on 655 the limited sampling frequency, it is difficult to draw conclusions on which of the seepage or discharge lake 656 types undergo the most chemical variation. However, Webster et al. (1996) suggest that discharge lakes 657 and seepage lakes respond chemically to evaporative drawdown in opposite ways, with seepage lakes 658 showing a decline in solutes during droughts as inputs from groundwater diminish due to the lowering of 659 the water table. By contrast, discharge lakes have been noted as susceptible to evaporative enrichment of 660 solutes and increased relative contribution of solute-rich groundwater during drought periods (Kratz et al., 1997). For these reasons, Webster et al. (1996) suggested that climate change could amplify anthropogenic 661 662 impacts and make lakes more vulnerable to other stressors, such as lake acidification.

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664 Due to their varied hydrological characteristics, the lake types identified in this study will have a 665 different susceptibility to direct anthropogenic impacts. Because recharge lakes have lower groundwater 666 inflow, they are characterized by relatively long water residence times, making them highly vulnerable to 667 inputs in comparison to seepage lakes and discharge lakes that tend to have a greater watershed, which 668 results in increased flushing. However, it can be argued that differences in material permeability between 669 the esker and the clay plain can produce the opposite effect. Sand extraction and mining activities in the 670 groundwater discharge zone could potentially influence the water levels of upland lakes in the recharge 671 zone (Klove et al., 2011). This potential was acknowledged by an impact study undertaken for an aggregate 672 pit project in the study area, and one recommendation was the construction of an engineered frozen earth barrier to prevent ground water flow into the proposed pit in order to minimize the effects on the water table 673 674 and surrounding lake levels (Cochrane, 2006).

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676 Finally, when considering groundwater-fed lakes for the purposes of paleohydrological 677 reconstruction (e.g. Laird et al., 2012), it is critical to explore their modern hydrology to be able to correctly 678 interpret the probable causes of isotopic, chemical, and biological change and variability recorded in the 679 sediment through time along with their potential hydroclimatic drivers. Because the degree to which lakes 680 interact with groundwater produces differences in hydrologic response to a same hydroclimatic forcing, the interpretation of paleolimnological records can be complex (Fritz, 2000) and multiple site selection seem 681 therefore necessary as a discharge lake may show long-term stability while a recharge lake may display 682 683 significant short-term and long-term variability (Bennett et al., 2007).

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- **6** Conclusion 686
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688 Lakes located in an esker complex in northeast Ontario showed strong systematic and localized 689 differences in terms of water balance and hydrochemistry, similar to other esker complexes in other settings. 690 Results from this study indicated that elevation is a critical factor explaining water chemistry and water 691 balance across the landscape. As eskers are structurally complex and often characterized by high hydraulic 692 conductivity, groundwater interactions are an important component of lake water hydrology. Low elevation 693 lakes are likely interconnected with solute-rich intermediate and regional groundwater flowpaths while 694 upland lakes are only interacting with local solute-poor groundwater flowpaths. This threshold in water 695 chemistry is also accompanied by strong contrasts in lake-water balance. Upland lakes tend to be 696 isotopically-enriched and more sensitive to evaporation, while lowland lakes are more depleted and subject 697 to groundwater inflows. Limnological variables including lake depth, DOC and forms of nitrogen were a 698 bit related to elevation, and likely influenced by lake morphometry and watershed activities. Thus, these 699 results confirm other studies that indicate that at the local scale, landscape position is the main control on 700 lake water chemistry and balance.

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The physical and chemical characteristics of lake water allowed the development of a lake typology 703 that is made up of three main types of lakes: i) higher elevation groundwater recharge lakes essentially fed 704 by precipitation and characterized by higher evaporations rates and lower amounts of solutes; ii) seepage 705 lakes that both gain and lose water to the groundwater characterized by intermediate rates of evaporation 706 and amounts of solutes; and iii) lower elevation groundwater discharge lakes, that are continuously fed by 707 groundwater inflow and characterized by almost no evaporation rates and higher amounts of solutes. The 708 obtained typology provides insights about lake vulnerability to environmental stressors, particularly short-709 and long-term hydroclimatic change. Recharge lakes will be more prone to evaporative drawdown and 710 therefore more sensitive to short-term droughts, while discharge lakes will be buffered by groundwater 711 inflow and affected by hydroclimatological changes of greater persistence. Similarly, recharge lakes will 712 likely be more subject to other anthropogenic impacts, in comparison to discharge lakes.

713

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995	
996	Author contributions
997	
998	Maxime Boreux collected data in the field and processed samples in the lab, conducted data analysis and
999	interpretation (with input from all authors), generated figures and tables. Scott Lamoureux provided
1000	guidance, funding, reviewed and edited the manuscript in his function as supervisor, as did Brian Cumming.
1001	The manuscript was written by Maxime Boreux with input from all authors.
1002	
1003	Data availability
1004	
1005	The data can be made available by contacting the corresponding author.
1006	
1007	Competing interests
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1009	The authors declare that they have no conflict of interest.
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1019 Appendix

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Tab. A1a: Correlation matrix between hydrological tracers and morphometric variables

	EC	pН	Т	Ca <sup>2+</sup>	$Mg^{2+}$	$\mathbf{K}^+$	Na <sup>+</sup>	Cl	$SO_4^{2-}$	NO <sub>3</sub> -	$\mathrm{NH_{4}^{+}}$	$\delta^{18}O$	$\delta^2 H$
EC	1.00	0.73	-0.22	0.97	0.93	0.73	0.60	0.62	0.36	-0.13	-0.18	-0.80	-0.75
pН	0.73	1.00	-0.05	0.76	0.73	0.41	0.29	0.29	0.20	-0.15	-0.18	-0.47	-0.41
Т	-0.22	-0.05	1.00	-0.24	-0.25	-0.32	0.06	0.05	-0.12	0.19	-0.16	0.34	0.33
$Ca^{2+}$	0.97	0.76	-0.24	1.00	0.94	0.66	0.43	0.48	0.40	-0.12	-0.18	-0.83	-0.78
$Mg^{2+}$	0.93	0.73	-0.25	0.94	1.00	0.72	0.36	0.37	0.26	-0.12	-0.18	-0.77	-0.73
$K^+$	0.73	0.41	-0.32	0.66	0.72	1.00	0.56	0.49	0.37	-0.01	0.05	-0.55	-0.51
$Na^+$	0.60	0.29	0.06	0.43	0.36	0.56	1.00	0.95	0.12	-0.06	-0.07	-0.31	-0.29
Cl-	0.62	0.29	0.05	0.48	0.37	0.49	0.95	1.00	0.06	-0.06	-0.04	-0.35	-0.33
$SO_4^{2-}$	0.36	0.20	-0.12	0.40	0.26	0.37	0.12	0.06	1.00	0.03	-0.05	-0.33	-0.30
$NO_3^-$	-0.13	-0.15	0.19	-0.12	-0.12	-0.01	-0.06	-0.06	0.03	1.00	0.04	0.16	0.16
$\mathrm{NH_{4}^{+}}$	-0.18	-0.18	-0.16	-0.18	-0.18	0.05	-0.07	-0.04	-0.05	0.04	1.00	0.14	0.16
$\delta^{18}O$	-0.80	-0.47	0.34	-0.83	-0.77	-0.55	-0.31	-0.35	-0.33	0.16	0.14	1.00	0.99
$\delta^2 H$	-0.75	-0.41	0.33	-0.78	-0.73	-0.51	-0.29	-0.33	-0.30	0.16	0.16	0.99	1.00
d	0.84	0.53	-0.34	0.87	0.82	0.59	0.33	0.37	0.35	-0.16	-0.11	-0.99	-0.96
E/I	-0.49	-0.40	0.35	-0.50	-0.46	-0.32	-0.21	-0.21	-0.15	0.12	-0.04	0.68	0.69
TC	0.96	0.75	-0.43	0.96	0.95	0.74	0.59	0.42	0.36	-0.17	-0.03	-0.88	-0.85
DOC	-0.12	-0.25	-0.05	-0.09	-0.19	0.26	0.00	-0.14	0.59	-0.03	0.50	-0.06	-0.08
DIC	0.96	0.81	-0.38	0.95	0.97	0.62	0.56	0.44	0.16	-0.16	-0.21	-0.82	-0.79
TN	-0.22	-0.30	-0.09	-0.21	-0.29	0.16	0.00	-0.09	0.44	-0.06	0.53	0.08	0.06
C/N	-0.13	-0.21	0.28	-0.10	-0.10	0.12	-0.10	-0.20	0.35	0.04	0.17	-0.07	-0.08
Н	-0.67	-0.57	0.04	-0.69	-0.72	-0.55	-0.31	-0.28	-0.25	0.08	0.16	0.53	0.49
Ζ	0.09	0.20	0.17	0.06	0.18	0.06	-0.01	0.00	-0.18	0.08	0.01	0.01	0.05
S	0.51	0.50	-0.04	0.52	0.53	0.45	0.22	0.16	0.39	-0.10	-0.24	-0.33	-0.27
А	0.35	0.40	0.23	0.37	0.38	0.32	0.20	0.17	0.18	-0.06	-0.08	-0.24	-0.21
Р	0.42	0.53	0.25	0.45	0.45	0.35	0.21	0.17	0.24	-0.07	-0.13	-0.29	-0.27
P/A	-0.48	-0.73	-0.28	-0.48	-0.49	-0.29	-0.29	-0.23	-0.40	0.00	0.21	0.10	0.02

1022 Note: electrical conductance (EC) is expressed in  $\mu$ S/cm, temperature (T) in °C, dissolved ions (Ca<sup>2+</sup>,

 $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_2^{-}$ - $NO_3^{-}$ ,  $NH_4^+$ ) in ppm, water stable isotopes ( $\delta^{18}O$ ,  $\delta^{2}H$ ) and deuterium excess 1024 (*d*) in V-SMOW, total carbon (TC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) 1025 and total nitrogen (TN) in ppm, elevation (H), lake maximum depth (Z) and perimeter (P) in m, maximum 1026 lake watershed slope (S) in % and area (A) in ha.

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**Tab.** A1b: Correlation matrix between hydrological tracers and morphometric variables (con't)

	d	E/I	TC	DOC	DIC	TN	C/N	Н	Z	S	A	P	P/A
EC	0.84	-0.49	0.96	-0.12	0.96	-0.22	-0.13	-0.67	0.09	0.51	0.35	0.42	-0.48
pН	0.53	-0.40	0.75	-0.25	0.81	-0.30	-0.21	-0.57	0.20	0.50	0.40	0.53	-0.73
Т	-0.34	0.35	-0.43	-0.05	-0.38	-0.09	0.28	0.04	0.17	-0.04	0.23	0.25	-0.28
$Ca^{2+}$	0.87	-0.50	0.96	-0.09	0.95	-0.21	-0.10	-0.69	0.06	0.52	0.37	0.45	-0.48
$Mg^{2+}$	0.82	-0.46	0.95	-0.19	0.97	-0.29	-0.10	-0.72	0.18	0.53	0.38	0.45	-0.49
$\mathbf{K}^+$	0.59	-0.32	0.74	0.26	0.62	0.16	0.12	-0.55	0.06	0.45	0.32	0.35	-0.29
$Na^+$	0.33	-0.21	0.59	0.00	0.56	0.00	-0.10	-0.31	-0.01	0.22	0.20	0.21	-0.29
Cl	0.37	-0.21	0.42	-0.14	0.44	-0.09	-0.20	-0.28	0.00	0.16	0.17	0.17	-0.23
$SO_4^{2-}$	0.35	-0.15	0.36	0.59	0.16	0.44	0.35	-0.25	-0.18	0.39	0.18	0.24	-0.40
NO <sub>3</sub> -	-0.16	0.12	-0.17	-0.03	-0.16	-0.06	0.04	0.08	0.08	-0.10	-0.06	-0.07	0.00
$\mathrm{NH_{4}^{+}}$	-0.11	-0.04	-0.03	0.50	-0.21	0.53	0.17	0.16	0.01	-0.24	-0.08	-0.13	0.21
$\delta^{18}O$	-0.99	0.68	-0.88	-0.06	-0.82	0.08	-0.07	0.53	0.01	-0.33	-0.24	-0.29	0.10
$\delta^2 H$	-0.96	0.69	-0.85	-0.08	-0.79	0.06	-0.08	0.49	0.05	-0.27	-0.21	-0.27	0.02
d	1.00	-0.64	0.90	0.05	0.85	-0.11	0.05	-0.57	0.04	0.40	0.28	0.32	-0.20
E/I	-0.64	1.00	-0.60	-0.15	-0.53	-0.14	-0.03	0.39	-0.05	-0.13	-0.19	-0.23	-0.05
TC	0.90	-0.60	1.00	0.05	0.94	-0.05	0.01	-0.64	0.03	0.50	0.31	0.38	-0.27
DOC	0.05	-0.15	0.05	1.00	-0.29	0.93	0.66	-0.04	-0.29	0.08	0.00	-0.12	0.54
DIC	0.85	-0.53	0.94	-0.29	1.00	-0.37	-0.21	-0.60	0.12	0.45	0.29	0.39	-0.40
TN	-0.11	-0.14	-0.05	0.93	-0.37	1.00	0.40	0.05	-0.43	-0.03	-0.01	-0.10	0.60
C/N	0.05	-0.03	0.01	0.66	-0.21	0.40	1.00	-0.09	0.08	0.18	0.07	-0.03	0.03
Н	-0.57	0.39	-0.64	-0.04	-0.60	0.05	-0.09	1.00	-0.26	-0.77	-0.46	-0.50	0.53
Z	0.04	-0.05	0.03	-0.29	0.12	-0.43	0.08	-0.26	1.00	0.30	-0.02	0.04	-0.40
S	0.40	-0.13	0.50	0.08	0.45	-0.03	0.18	-0.77	0.30	1.00	0.33	0.35	-0.52
А	0.28	-0.19	0.31	0.00	0.29	-0.01	0.07	-0.46	-0.02	0.33	1.00	0.91	-0.49
Р	0.32	-0.23	0.38	-0.12	0.39	-0.10	-0.03	-0.50	0.04	0.35	0.91	1.00	-0.55
P/A	-0.20	-0.05	-0.27	0.54	-0.40	0.60	0.03	0.53	-0.40	-0.52	-0.49	-0.55	1.00

Note: electrical conductance (EC) is expressed in  $\mu$ S/cm, temperature (T) in °C, dissolved ions (Ca<sup>2+</sup>,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ,  $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_2^{-}$ - $NO_3^{-}$ ,  $NH_4^+$ ) in ppm, water stable isotopes ( $\delta^{18}O$ ,  $\delta^{2}H$ ) and deuterium excess (d) in V-SMOW, total carbon (TC), dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and total nitrogen (TN) in ppm, elevation (H), lake maximum depth (Z) and perimeter (P) in m, maximum lake watershed slope (S) in % and area (A) in ha. 

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Tab. A2. Results of analysis of variance (ANOVA) of individual conservative and non-conservative hydrological tracers using the 2-class lake typology as the categorical variable. Non-significant *p*-values are indicated in bold. Lakes in the 'recharge' zone are defined as lakes above an elevation of 282 m asl, whereas lakes in the 'discharge' zone are defined as lakes located at an elevation of less than 282 m asl.

	Lakes in the	Lakes in the		
	recharge zone	discharge zone	ANOVA	analysis
Variable	Mean (SD)	Mean (SD)	F value	p-value
EC (µS/cm)	47.6 (53.5)	230.4 (88.4)	82.6	<i>p</i> < 0.001
pН	6.7 (0.9)	7.9 (0.4)	34.9	p < 0.001
T (°C)	17.0 (1.9)	16.5 (2.6)	0.7	0.409
Ca <sup>2+</sup> (ppm)	4.8 (6.6)	29.4 (10.7)	101.0	p < 0.001
Mg <sup>2+</sup> (ppm)	1.1 (1.4)	7.1 (3.1)	83.4	p < 0.001
K <sup>+</sup> (ppm)	0.4 (0.2)	1.0 (0.4)	28.0	p < 0.001
Na <sup>+</sup> (ppm)	0.8 (1.9)	5.3 (7.9)	8.9	0.005
Cl <sup>-</sup> (ppm)	1.1 (3.9)	9.5 (15.0)	8.3	0.006
SO <sub>4</sub> <sup>2-</sup> (ppm)	0.9 (0.8)	6.6 (13.9)	4.8	0.034
NO <sub>2</sub> <sup>-</sup> -NO <sub>3</sub> <sup>-</sup> (ppm)	0.0 (0.3)	0.0 (0.0)	0.9	0.339
NH <sub>4</sub> <sup>+</sup> (ppm)	0.0 (0.0)	0.0 (0.0)	2.1	0.159
δ <sup>18</sup> O (‰)	- 8.7 (1.4)	- 11.5 (1.6)	43.0	<i>p</i> < 0.001
δ <sup>2</sup> H (‰)	- 78.2 (7.1)	- 90.6 (7.6)	35.0	p < 0.001
<i>d</i> (‰)	- 8.5 (4.5)	1.7 (5.5)	52.3	p < 0.001
E/I	1.4 (1.6)	0.2 (0.4)	10.4	0.002
TC (ppm)	11.4 (5.9)	30.4 (8.7)	60.2	p < 0.001
DOC (ppm)	5.9 (3.2)	6.2 (4.9)	0.1	0.813
DIC (ppm)	5.5 (6.4)	24.2 (10.6)	44.2	p < 0.001
TN (ppm)	0.5 (0.2)	0.5 (0.3)	0.2	0.652
Atomic C/N	13.2 (3.3)	13.6 (4.0)	0.1	0.739
Elevation (m)	287.7 (4.8)	275.1 (2.8)	116.5	p < 0.001
Maximum depth (m)	12.4 (6.2)	13.2 (6.7)	0.2	0.694
Maximum lake watershed				
slope (%)	9.8 (6.9)	20.5 (5.7)	33.7	<i>p</i> < 0.001

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Tab. A3: Results of analysis of variance (ANOVA) of conservative and non-conservative hydrological
tracers using the 3 class lake typology as the categorical variable. Non-significant *p*-values are indicated
in bold. Lakes in the 'recharge' zone are defined as lakes above an elevation of 282 m asl and nonalkaline, lakes in the 'seepage' zone are defined as lakes above an elevation of 282 m asl and alkaline
whereas lakes in the 'discharge' zone are defined as lakes located at an elevation of less than 282 m asl.

	Recharge lakes	Seepage lakes	Discharge lakes	ANOVA	analysis
Variable	Mean (SD)	Mean (SD)	Mean (SD)	F value	p-value
EC (µS/cm)	20.5 (11.9)	135.9 (60.8)	233.2 (92.5)	114.4	<i>p</i> < 0.001
pН	6.2 (0.7)	7.8 (0.3)	7.9 (0.4)	88.4	<i>p</i> < 0.001
T (°C)	17.1 (2.0)	16.4 (1.7)	16.5 (2.8)	0.7	0.402
Ca <sup>2+</sup> (ppm)	1.4 (1.4)	16.8 (8.6)	29.5 (11.2)	130.3	<i>p</i> < 0.001
Mg <sup>2+</sup> (ppm)	0.4 (0.3)	3.5 (1.7)	7.2 (3.3)	95.2	<i>p</i> < 0.001
K <sup>+</sup> (ppm)	0.5 (0.3)	0.4 (0.1)	1.0 (0.4)	19.3	<i>p</i> < 0.001
Na <sup>+</sup> (ppm)	0.4 (0.7)	1.9 (2.9)	5.6 (8.3)	9.2	0.004
Cl <sup>-</sup> (ppm)	0.4 (1.3)	3.3 (6.5)	9.9 (15.7)	8.1	0.006
SO <sub>4</sub> <sup>2-</sup> (ppm)	0.7 (0.6)	1.7 (1.1)	7.0 (14.6)	4.7	0.035
NO <sub>2</sub> <sup>-</sup> -NO <sub>3</sub> <sup>-</sup> (ppm)	0.1 (0.4)	0.0 (0.0)	0.0 (0.0)	0.9	0.339
NH <sub>4</sub> <sup>+</sup> (ppm)	0.0 (0.0)	0.0 (0.0)	0.0 (0.00)	2.6	0.114
δ <sup>18</sup> O (‰)	-8.5 (1.3)	- 9.7 (1.6)	- 11.6 (1.7)	48.0	<i>p</i> < 0.001
δ <sup>2</sup> H (‰)	- 77.4 (6.8)	- 82.1 (7.8)	- 90.8 (8.0)	36.5	<i>p</i> < 0.001
<i>d</i> (‰)	- 9.6 (3.7)	- 4.5 (5.4)	1.9 (5.7)	64.6	<i>p</i> < 0.001
E/I	1.6 (1.8)	0.6 (0.5)	0.2 (0.4)	14.0	<i>p</i> < 0.001
TC (ppm)	8.7 (4.0)	19.9 (6.6)	30.8 (9.4)	74.7	<i>p</i> < 0.001
DOC (ppm)	6.7 (3.5)	3.9 (1.2)	6.7 (5.2)	0.1	0.733
DIC (ppm)	2.0 (1.3)	15.9 (7.2)	24.1 (11.5)	65.7	<i>p</i> < 0.001
TN (ppm)	0.6 (0.2)	0.4 (0.1)	0.5 (0.3)	0.9	0.341
Atomic C/N	14.1 (3.5)	11.1 (1.4)	14.0 (4.3)	0.1	0.784
Elevation (m)	287.0 (4.6)	286.7 (7.6)	275.1 (3.0)	37.0	<i>p</i> < 0.001
Maximum depth					
(m)	12.0 (6.6)	12.4 (5.7)	13.5 (6.8)	0.4	0.555
Maximum lake					
watershed slope					
(%)	10.2 (7.4)	11.3 (6.7)	19.9 (6.7)	19.1	<i>p</i> < 0.001



Fig. A1: Spatial depiction between elevation and lake-water pH (a) and lake type (b). The elevation of the breakpoint line (284 m) is shown as a dashed line 



Fig. A2: Changes in E/I between June 2013 and June 2014 (E/I 2014 – E/I 2013) (a) and changes in E/I
between August 2014 and June 2014 (E/I Aug – E/I Jun) (b), and changes in specific conductance
between June 2013 and June 2014 (EC 2014 – EC 2013) (c) and changes in electrical conductance
between August 2014 and June 2014 (EC Aug – EC Jun) (d). Lakes are organized along an elevation
gradient (lower to higher elevation).