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Discussions

Landscape and groundwater controls over boreal lake water chemistry and water balance heterogeneity in an esker complex of northeastern Ontario, Canada

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Abstract

Water chemistry and water isotopic composition were investigated in a set of 50 boreal lakes located at different elevations in an esker system near Timmins, Ontario, as well as in local streams, groundwater springs and information available from seasonal precipitation values. Analyses focused on stable isotopic ratios of hydrogen and oxygen, as well as specific conductance as indicators of the position of a lake with respect to the influence of groundwater. Both isotopic composition and specific conductance distinguished higher elevation groundwater discharge lakes from lower elevation groundwater recharge lakes. Groundwater recharge lakes characterized by enriched isotopic values and low values of specific conductance are located above the hydraulic midline elevation of the study lakes. In contrast groundwater discharge lakes, were isotopically depleted and had higher values of specific conductance, and occurred below the hydraulic midline of the study lakes. An intermediate group of lakes was also defined (termed seepage lakes) and consisted of either recharge lakes that were alkaline, or discharge lakes that had no outlet. The seepage lakes group had intermediate isotopic and water chemistry characteristics compared to recharge and discharge lakes. A classification scheme for lakes was developed based on the specific conductivity, water isotopic composition, the presence of an outlet, and other characteristic to define three types of recharge lakes, and two types of discharge lakes.

Interannual (2013 and 2014) and seasonal 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 showed little variation between seasonal samples, and consequently would be affected by hydroclimatological changes of greater duration and persistence.

Keywords

Water balance, landscape limnology, groundwater, hydrochemistry, lake-water chemistry, stable isotopes

1 Introduction

Nearly all surface waters, including lakes, interact with groundwater to some extent (Winter et *al*., 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 *al*., 2015). These characteristics will influence the sensitivity and vulnerability of lakes to environmental stressors such as climate change, and other anthropogenic disturbances. The threat of future climate change will likely influence lakes differently depending on their connectivity to groundwater, further increasing our need to better relationships of lake hydrology, and changes in lake-water chemistry. Further, understanding the climatic controls on water balance and adverse impacts to aquatic ecosystems is essential for informed ecosystem management and conservation practices (Winter et *al*., 1998).

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 opportunity better understand hydrological processes in lakes at a local to regional scale (Fleckenstein et *al*., 2010; Rosenberry et *al*., 2015). This has included studies using numerical simulations (e.g. Winter et *al*., 1998), as well as empirical studies at a range of different spatial and temporal scales. Studies at the 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 performed at a local to regional scale (e.g. Webster et *al*., 1996; Quinlan et *al*., 2003; Martin and Soranno, 2006; Ala-aho et *al*., 2013) indicate the importance of landscape position and also lake morphology as being important in understanding lake-groundwater interactions. At the scale of an individual lake, a number of studies have shown that groundwater-lake water interactions can vary temporally according to changes in seasonality and changing longer term changes in hydroclimatic conditions (e.g. Kenoyer and Anderson, 1989; LaBaugh et *al*., 1997; Sebestyen and Schneider, 2001; Schuster et *al*., 2003; Arnoux et *al*., 2017b).

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The vast majority of past empirical studies have relied on studying aspects of water chemistry (e.g. dissolved ions), as an indicator of hydrological connectivity between lakes, as such approaches can contain signals of important processes such as mineral weathering and dissolution (Bertrand et *al*., 2014). By contrast, other studies relied on the isotopic composition of water as a hydrological tracers (e.g. Turner et *al*., 2010; Isokangas et *al*., 2015). In addition to being a good indicator of source water, stable isotopes of water constitute a time and cost-effective means to quantify lake evaporation and water balance status of water bodies using the Craig-Gordon model (Skrzypek et *al*., 2015), given that the isotopic composition of lake water and precipitation as well as air temperature and relative humidity are known, or can be estimated (Gibson and Edwards, 2002). The Craig-Gordon model is well established and has been used extensively to investigate the spatial and temporal variability in lake water balance in remote boreal regions of Canada (e.g. Wolfe et *al*., 2007; Bouchard et *al*., 2013; Tondu et *al*., 2013; Turner et *al*., 2014a; Turner et *al*., 2014b). However, only a very limited number of studies have combined chemical and isotopic approaches to investigate the connectivity between groundwater and lake water (e.g. Schuster et *al*., 2003; Rautio and Korkka-Niemi, 2011; Arnoux et *al*., 2017a; Arnoux et *al*., 2017b). Such an approach has the ability to produce more reliable interpretations if the two approaches converge on a mutually reinforcing interpretation.

The main objective of this study is to test the importance of landscape position on groundwater connectivity by examining both water chemistry and isotopic composition of water in a boreal esker complex in northeastern Ontario. Investigating such processes in the context of esker hydrology is particularly relevant as eskers are widespread in boreal regions (Ala-aho et *al*., 2015) and constitute one of the most common type of aquifers in boreal Canada (Cloutier et *al*., 2007). Results from the observations above, will be used to develop a lake typology of hydrological connectivity based landscape position and lake characteristics (Newton and Driscoll, 1990; Bertrand et *al*., 2014). The resultant typology will provide insights on lakes' sensitivity and vulnerability to environmental stressors such as climate change, for water management and conservation goals. Finally, we will evaluate the sensitivity of the proposed typology, by investigating if seasonal variations of lake-water characteristics are more readily detected in higher-elevation groundwater recharge lakes in comparison to lower elevation groundwater discharge lakes.

2 Study area

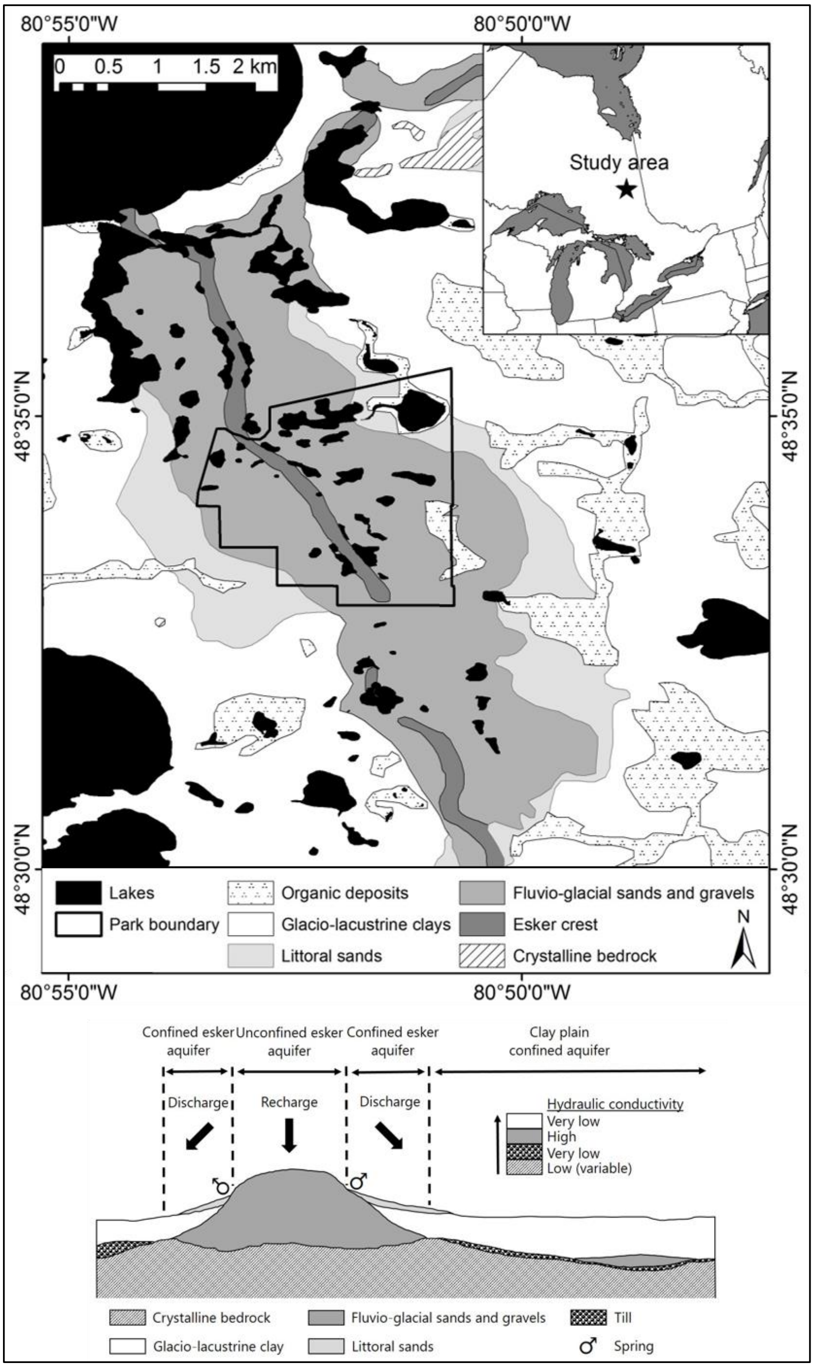

Fig. 1: Location of the study area in north east Ontario near Timmins, Ontario (Based on: Richard and McClenaghan, 2000) (a) and conceptual geological transverse section of an esker complex (b) (Modified from: Veilette *et al.*, 2004)

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

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 relatively large eskers composed of coarse grained glaciofluvial sediments in deposits oriented in a north-south direction and mantling the crystalline bedrock (Cloutier et *al*., 2007). The retreat of the ice sheet was accompanied by ponding of glacial meltwaters that led to the development of glacial Lake Ojibway that submerged most of the region (Roy et *al*., 2011) and the widespread deposition of glaciolacustrine clay (Nadeau, 2011), followed by the drainage of Lake Ojibway into Hudson Bay ~8,200 years ago (Roy et *al*., 2011). As Lake Ojibway levels dropped, wave action eroded the surface of the esker and redistributed some sand materials on the flanks on the esker, forming lateral sand units that drape the glaciolacustrine clays (Cloutier et *al*., 2007) (**Fig. 1b**). The numerous kettle lakes in on the esker formed once the glacial ice trapped in the outwash materials melted (Nadeau, 2011).

The esker stratigraphy ensures that its groundwater system is highly localized since the esker crests generally have a high hydraulic conductivity due to their coarse texture, the esker is surrounded by underlying bedrock and the adjacent fine-grained glaciolacustrine deposits, both characterized by very low hydrological conductivity (Stauffer and Wittchen, 1992). As a consequence, the esker can be conceptually partitioned into zones of unconfined aquifers in its center where coarse material is present at the surface and zones of confined aquifers in 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 the unconfined aquifer and discharge will take place on the esker flanks at the contact of the clay, where most groundwater springs emerge (Cloutier et *al*., 2007). Confined aquifers found on the surrounding clay plain are often covered by peatlands and shallow lakes fed by groundwater springs on the edges of the esker or by streams that drain the esker (Rossi et *al*., 2012).

3 Methods

3.1 Geomatic and lake morphometric data

Lakes and other geographic features were digitalized in ArcGIS 10.3 from Google Earth. Maximum depths Z_{max} were obtained from the Ontario Ministry of Natural Resources and Forestry (OMNRF, 2011). Digital Elevation Models (DEM) from the study area were obtained from Natural Resources Canada (NRC, 2013). Lake elevation values were calculated as the mean elevation of the lake in ArcGIS from the available DEM with a spatial resolution of 20 m, and lake watershed slopes were calculated from the DEM in ArcGIS in a 100 m buffer zone surrounding each lake.

3.2 Field measurements and water sample collection

Water samples were collected during three field seasons (7-14 June 2013, 16-23 June 2014, and 12-19 August 2014). Approximately 50 lakes were sampled, as well as a number of streams 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.

Temperature and specific conductance of the water (corrected to 25°C) at each site were measured with an YSI Salinity Conductivity Temperature meter (accuracy ±0.1 µS/cm and ±0.1°C). The pH was measured with an UP-5 Denver Instrument pH meter calibrated before usage (accuracy ±0.1). Water samples were collected using 1 L Nalgene bottles that were tripled-rinsed with distilled water prior to use and again with sample water (Louiseize et *al*., 2014). To prevent cross-contamination, bottles were tripled-rinsed with lake water away from the final sampling point in the lake or downstream of stream/spring sampling points. Bottles were completely filled in order to avoid headspace 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 apparatus were triple-rinsed with distilled water and the lake water before and after use for each sample. The filtrate were then poured and stored 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™ to avoid evaporation, and kept cool and in the dark in a fridge prior to analysis.

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

3.3 Laboratory analysis

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 (1σ) based on repeated measurements of samples and standards was fixed at 0.25‰ for $\delta^{18}O$ and at 1.5‰ for $\delta^{2}H$.

Concentrations of inorganic ions (Ca, Mg, K, Na, Cl, SO_4) were measured by liquid ion chromatography with a Dionex ICS-3000. Detections 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_4). Concentrations of dissolved inorganic species (NO_2-NO_3 and NH_4) were measured by colorimetry using an Astoria Pacific FASPac II Flow Analyser (detections limits of 0.01ppm). Concentrations of non-purgeable organic carbon or dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and total dissolved nitrogen (TDN) were measured by high temperature combustion and NDIR and chemiluminescent detection using a Shimadzu TOC-VPCH/TNM equipped with a high sensitivity catalyst system (detections 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. Carbonate species relative composition (H_2CO_3, HCO_3^- and CO_3^{2-}) was determined from TIC values using Bjerrum plot equations for carbonate systems.

3.4 Water balance calculations

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):

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

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

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 lake surface); Q is instantaneous outflow where $Q = Q_R + Q_G$ (Q_R is surface outflow and Q_G is groundwater outflow), E is evaporation; and $\delta_{L,}$ $\delta_{I,}$ δ_Q and δ_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-term (*i.e.*, $dV = 0$ and $dt \rightarrow \infty$) (Darling et *al*., 2005) and (2) that physical outflow does not cause isotopic fractionation (*i.e.*, $\delta_Q = \delta_L$) (Gibson and Edwards, 2002; Yi et *al*., 2008), Eq. 1 and 2 can be simplified and rewritten as follows:

$$I = Q + E \qquad \text{Eq. 3}$$

$$I\delta_I = Q\delta_Q + E\delta_E \qquad \text{Eq. 4}$$

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):

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

where δ_I was computed as the average isotopic composition of annual precipitation from February 1997 to November 2010 (data collected by CNIP); δ_L is the isotopic composition of the lake water sample and δ_E was computed as the difference between δ_I and δ_L. Surface water samples should be representative of the water column isotopic composition during spring overturn period.

4 Results

4.1 Temperature and water stable isotopes

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).

Monthly precipitation isotopic data from CNIP from February, 1997 to November, 2010 from Bonner Lake, about 100 km NNW of Timmins, show progressive enrichment in values between winter, spring, fall 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‰ to -6.8‰ for δ^{18}O and -105.5‰ to -68.6‰ for δ^2H), which fell on a Local Evaporitic Line (LEL) ($r^2 = 0.99$, $p < 0.001$) (**Fig. 2b**). Groundwater springs have isotopic values very similar to mean annual precipitation (-14.7‰ to -13.1‰ for δ^{18}O and 105.5‰ to -96.0‰ for δ^2H). Streams have comparable isotopic composition to groundwater springs (-13.8‰ to -11.3‰ for δ^{18}O, and -100.8‰ to -91.9‰ for δ^2H). By contrast, lakes are characterized by large variations in water isotopic composition, ranging from values comparable to groundwater springs (*ca*. -14‰ for δ^{18}O and -100‰ for δ^2H) to more enriched values (*ca*. -6‰ for δ^{18}O and -70‰ for δ^2H), with the more enriched values occurring in the higher elevation lakes, and the more depleted values in the lower elevation lakes.

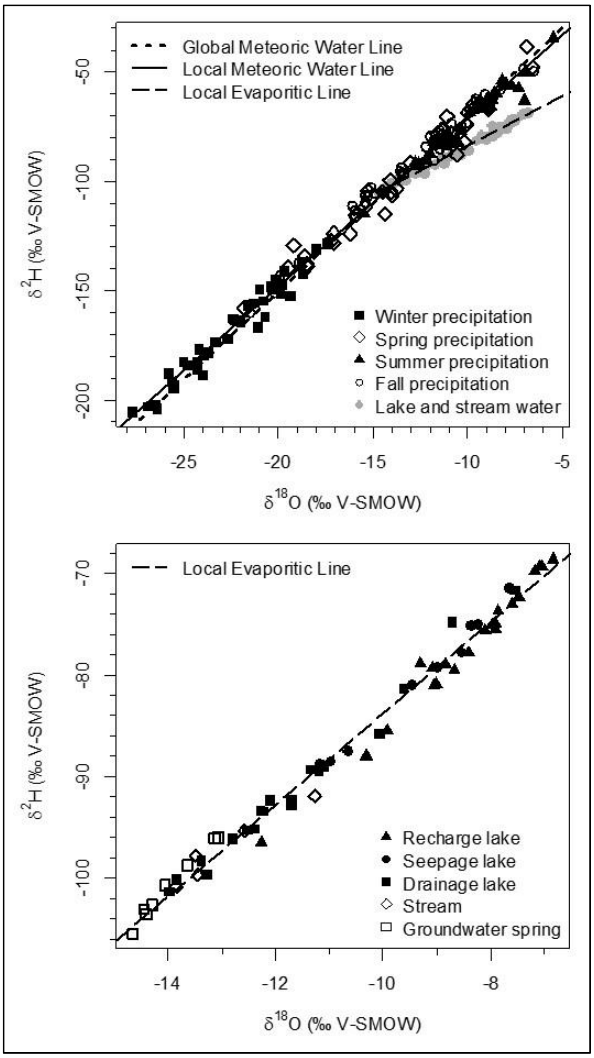

Fig. 2: Isotopic composition of precipitation in relation to the Global Meteoric Water and Local Meteoric Water lines ($r^2 = 0.99$, n = 166, $p < 0.001$) (a), and isotopic composition of collected water samples in relation to the Local Evaporitic Line ($r^2 = 0.99$, n = 68, $p < 0.001$) (b). Lakes are coded according to a classification scheme developed in this paper (please refer to **Fig. 6** and **7**).

A significant correlation exists between $\delta^{18}O$ and elevation ($r^2 = 0.53$, $p < 0.001$) (**Fig. 3a**), and between elevation and specific conductance ($r^2 = -0.67$, $p < 0.001$), indicating that the geographical position in the landscape is a variable explaining lake-water isotopic composition and specific conductance in lakes. Lakes sampled at lower elevations are more depleted while lakes sampled at higher elevations are enriched in ^{18}O and ^{2}H. Due to a strong correlation between $\delta^{18}O$ and $\delta^{2}H$, $\delta^{18}O$ is used as the primary variable reflecting isotopic composition.

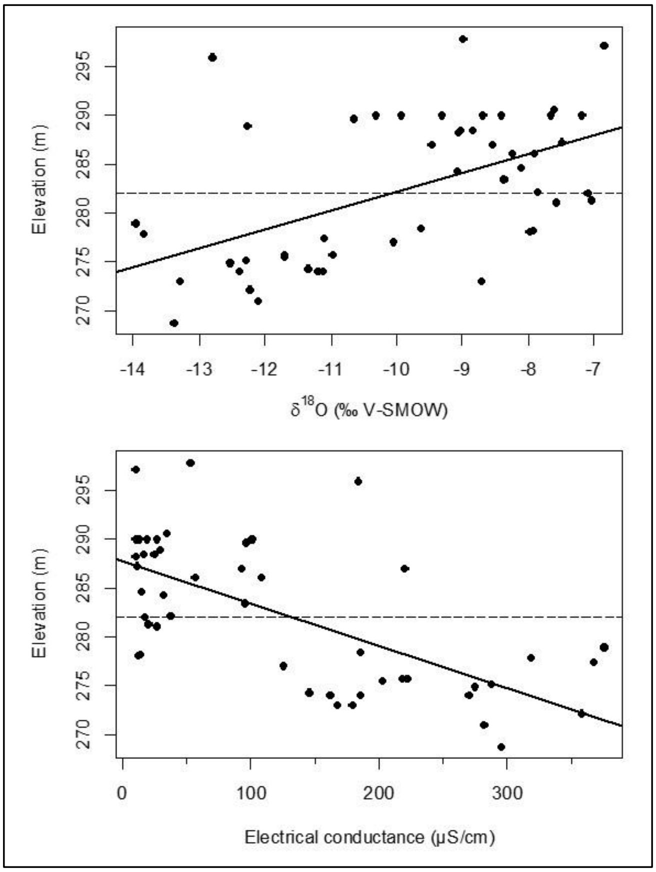

Fig. 3: Relation between $\delta^{18}O$ in water samples and elevation ($r^2 = 0.53$, n = 50, $p < 0.001$) (a), and specific conductivity and elevation ($r^2 = -0.67$, n = 50, $p < 0.001$) (b). The horizontal dashed line indicates the position of a breakpoint analysis which occurs at an elevation of ~282 m asl, in both cases (**Tab. 1**)

Evaporation-to-inflow ratio calculations indicate that groundwater springs and streams undergo minimal evaporation (E/I ~ 0) while lakes have high E/I values ranging from values similar to groundwater springs and streams to as high as almost E/I ~ 8 (**Fig. 4**), with the highest values in higher elevation lakes that were classified as groundwater recharge lakes (described later in this paper).

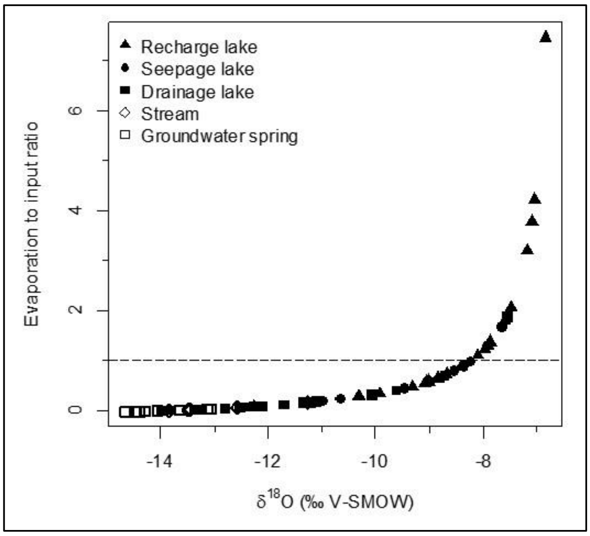

Fig. 4: Relation between δ^{18}O and calculated evaporation-to-inflow ratios. Lakes are coded according to a classification scheme developed in this paper (please refer to **Fig. 6** and **7**)

4.2 Solutes and dissolved organic matter

As it 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 correlated (see correlation matrix **Tab. A1**). Groundwater springs have the highest specific conductance (300-550 µS/cm) while streams have values *ca.* 300 µS/cm. Lakes show a wide range of solute content and 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 µS/cm) (**Fig. 3b**).

Only 36 lakes were sampled for dissolved organic carbon (DOC) and nitrogen (TN). Unlike non-conservative ions and conservative isotopic tracers, no significant relationship was found between dissolved organic elements and elevation ($r^2 = -0.2$, n = 36, $p = 0.84$ for DOC; $r^2 = 0.22$, 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 ($r^2 = -0.58$, n = 36, $p = 0.11$) and with a similar pattern between TN and mean lake depth ($r^2 = -0.71$, n = 36, $p = 0.02$).

4.3 Correlations between water tracers

There is a strong and significant correlation between lake water isotopic values and specific conductance ($r^2 = 0.63$, $n = 50$, $p < 0.001$). 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**).

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

Environmental Variable	Mean Elevation	Lower Elevation	Upper Elevation
IC	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^2H	282.0	279.9	284.1
d	282.2	280.3	284.1
$d^{18}O$	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		

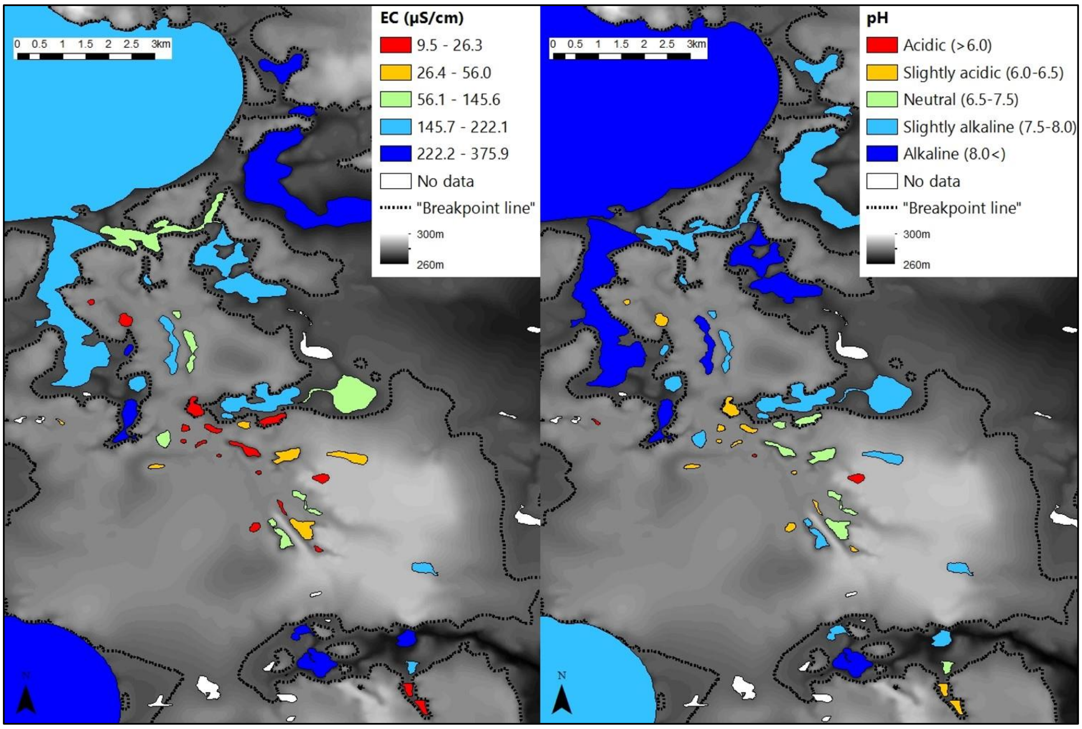

Fig. 5: Spatial depiction between elevation and lake-water specific conductance (μS/cm) (a), and lake-water pH (b). The elevation of the breakpoint line (284 m) is shown as a dashed line

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 242 m coded as groundwater recharge lakes, and lakes below 242 m coded as groundwater discharge lakes, indicating good separation of the groups based on water geochemistry (**Fig. 6a**). Using other lake characteristics, a third group of lakes was distinguished, that plots intermediate between the higher elevation (groundwater recharge) sites, and the lower elevation (groundwater discharge sites) that was developed later in this paper (**Fig. 6b** and **Tab. A2**).

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 the contribution of infer water chemistry variables, individual ANOVAs were undertaken for all lake-water variables that were above detection limits. 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 242 m asl. This was also the case of the isotopic variables. Variables that were not significantly different

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included: temperature, forms of nitrogen, the C/N, and lake depth. Similar results were found when lakes are separated into recharge, discharge and seepage lakes (**Tab. A3**).

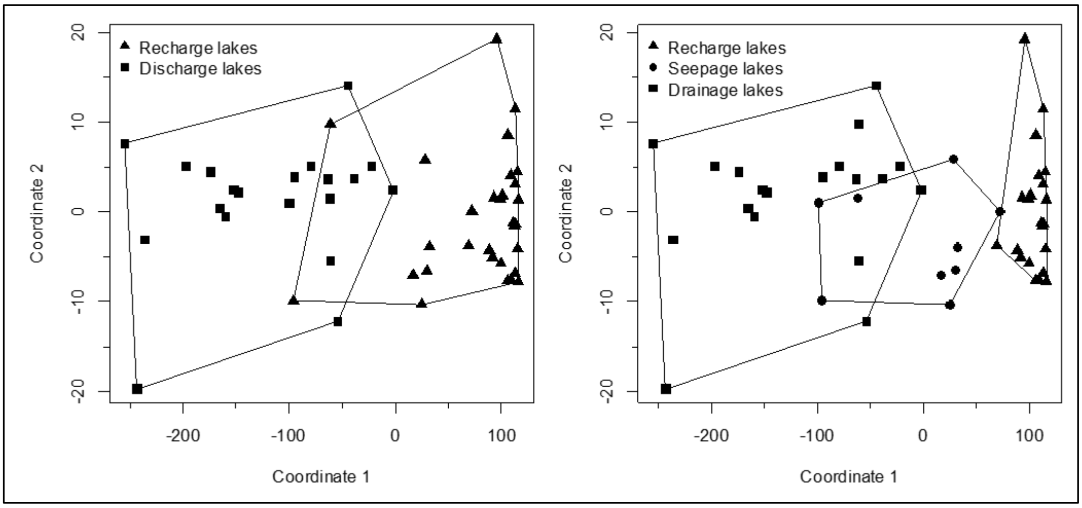

Fig. 6: Non-metric multidimensional scaling (NMDS) applied to conservative and non-conservative water tracers. Lakes that occurred at an elevation of greater than 242 m asl are labelled in red as 'recharge' lakes, whereas lakes as located at an elevation of less than 242 m are labelled as 'discharge' lakes. A third group of lakes (labelled 'seepage') is further discerned based on chemical and morphological characteristics. Stress value for the NMSD is low (stress = 0.023)

4.4 Short-term evolution of water tracers

Short-term water balance variability was observed seasonally and between years (**Fig. 7b**). Lakes located at an elevation greater than 242 m asl (recharge lakes) underwent marked changes in water balance during the three sampling seasons whereas discharge lakes and seepage lakes underwent little or no change, especially discharge lakes. Similarly, the water chemistry gradient between upland solute-poor lakes and lowland solute-rich lakes changed seasonally and between years. Recharge lakes did not respond chemically to short-term hydroclimatic change while seepage and drainage lakes displayed significant solute changes (**Fig. 7b**).

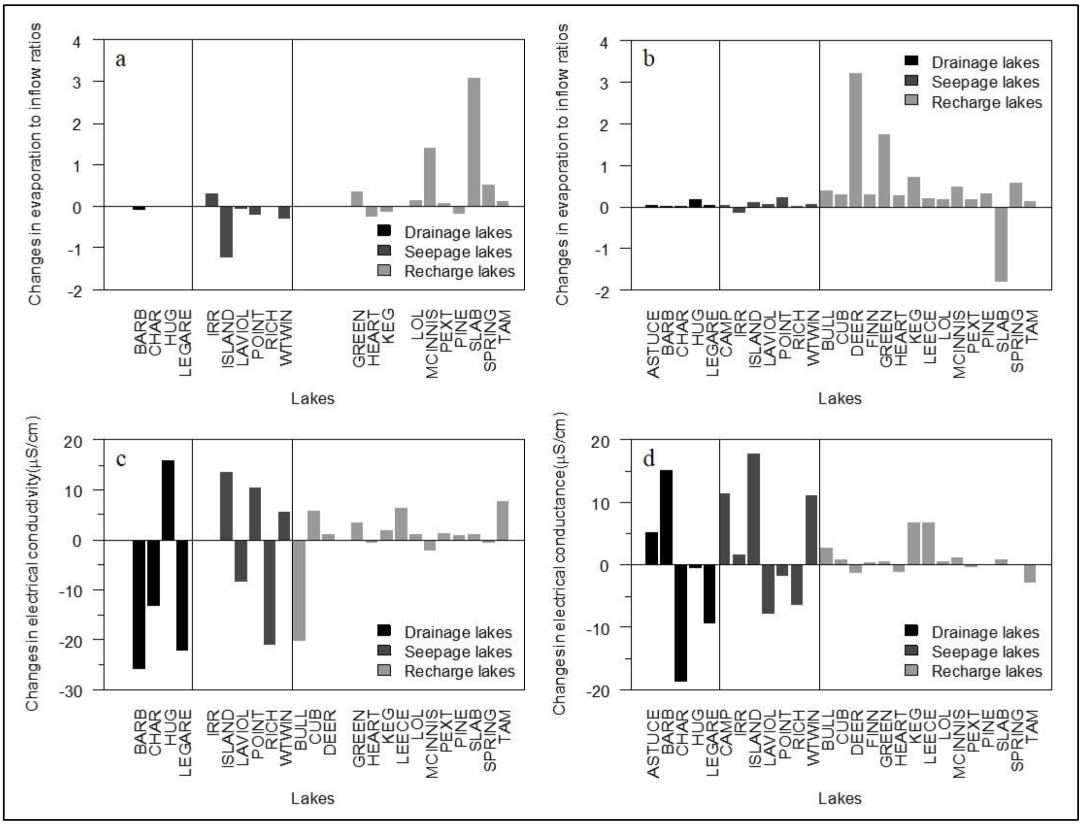

Fig. 7: Changes in E/I between June 2013 and June 2014 (E/I 2014 – E/I 2013) (a) and changes in E/I between August 2014 and June 2014 (E/I Aug – E/I Jun) (b), and changes in specific conductance between June 2013 and June 2014 (EC 2014 – EC 2013) (c) and changes in electrical conductance between August 2014 and June 2014 (EC Aug – EC Jun) (d)

5 Discussion

5.1 Interpretation of water tracers

The wide range of lake isotopic values and E/I 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 high and they only undergo limited evaporation (Gazis and Feng, 2004). Streams display isotopic values similar to groundwater springs since they originate from groundwater and experience relatively low evaporation rates due to more continuous water flow. The wide range of isotopic values for lakes can be explained by their position in the landscape, particularly relative to their location in the esker aquifer system for which elevation appears to be a good proxy. This suggests that lowland lakes are primarily fed by groundwater inflow while upland lakes receive a much lower contribution from the local groundwater in their respective water budgets.

Similar patterns are observed with the major ions and cations in water. Groundwater springs have the highest solute load likely due to chemical processes associated with mineral surface exchanges and weathering (Ala-aho et *al*., 2013). Lakes however, displayed a wide range of composition, and range from high solutes characteristic of groundwater to values close to zero, typical of precipitation (**Fig. 2**), suggesting that the heterogeneity of lakes on the esker are a result to the degree to which they interact with groundwater. As it is the case for isotopic values, chemical composition of a given lake depends on landscape position and elevation. Lakes sampled at lower elevation are higher in solutes and suggests that lowland lakes reflect interaction with intermediate or regional groundwater flows (longer than *ca.* 1 km) subject to more mineral weathering and dissolution, while upland lakes are reflect interaction with local groundwater flow paths (less than *ca.* 1 km long) with correspondingly reduced mineral weathering and dissolution (Tóth, 1963). There are only minor differences 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 that makes up the esker (Cummings et *al*., 2011). The carbonate-rich sediment originates from Paleozoic carbonates of the Hudson sedimentary Platform *ca*. 150 km to the north and is localized to glacial surficial sediments (Roy et *al*., 2011).

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 region, while lake-water temperature varies strongly with season. There is little difference between lake-water temperature and those differences 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, reflecting greater inputs from the catchment relative to lake volume. However, upland lakes tend to have slightly higher amounts likely due to their higher water residence times.

5.2 Lake hydrological classification

The correlation between lake water δ^{18}O and specific conductance (r = 0.80, n = 50, $p < 0.001$) shows there is a clear relation between conservative water tracers (water source) and non-conservative water tracers (which are indicative of water flow paths), suggesting 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.

Consequently, the observed breakpoint elevation appears to correspond to an effective hydraulic separation between groundwater recharge and discharge (Winter et *al*., 1998). This contrast between the contribution of groundwater flow is evident in the distribution of lake-water composition (**Fig. 5**). Lakes characterized by groundwater discharge are spatially distinct from higher elevation lakes in the groundwater recharge zone. Thus, upland lakes in the recharge zone are known as groundwater recharge lakes or perched lakes and, conversely, lowland lakes in the discharge zone, also called underflow zone, will be referred to as groundwater discharge lakes or drainage lakes (Winter et *al*., 1998). Because discharge lakes receive a substantial amount of water from groundwater, they are considered to be groundwater-fed or minerotrophic whereas recharge lakes which receive the majority of their water from precipitation and feed the aquifer are said to be precipitation-fed or ombrotrophic (Webster et *al*., 1996). NMDS (**Fig. 6a**) and ANOVA (**Tab. A2**) analysis showed that all conservative and non-conservative tracers are statistically different between the discharge zone and the recharge zone, except for DOC.

Nevertheless, the recharge zone contains a few solute-rich alkaline lakes (**Fig. 5**) and the two primary groups in ordinal space (**Fig. 6a**) display a small overlap, suggesting the existence a third category of hybrid lakes referred to as seepage or flow-through lakes (Winter, 1976; Webster et *al*., 1996; Winter et *al*., 2003). In seepage lakes, groundwater seeps delivery water and outflow is also by seepage (Anderson and Munter, 1981). Seepage lakes can be found both in the recharge zone and the discharge zone and they can be contribute a recharge or a discharge function (Anderson and Munter, 1981). An analysis of similarity (ANOSIM) between of the recharge and discharge lakes, an analysis complimentary to the NMDS, 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).

Lakes can first be classified according to their location within the groundwater system, particularly above and below the hydraulic midline, in this case, at or near the 282 m elevation in this study that indicated a breakpoint in the many isotopic and limnological variable (282.4 m) associated with differences in hydrological inputs. In this study, elevation appears to be a proxy of the boundary between the groundwater recharge and discharge zones on the esker. Seepage lakes, however, can be found on each side of the hydraulic midline, thus generating additional classes of lakes (see conceptual diagram, **Fig. 8**) distinguished from on the presence or absence of a lake outlet (Stauffer and Wittchen, 1992). Lakes with outlets were classified as "groundwater discharge lakes" and lakes without outlets as "discharge seepage lakes".

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**). The impermeable clay acts as a hydraulic stagnation point and result in lakes with limited leakage, and which constitute discharge points of the esker groundwater flow system (Winter, 1976). Furthermore, in the study area, there is a significant relationship between elevation and lake watershed maximum slope ($r = 0.75$, $n = 50$, $p < 0.001$). 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 substantial inflow of groundwater due to their geological settings and watershed characteristics, their water isotopic and chemical composition is within the same range as groundwater and outlets (Ala-aho et *al*., 2013).

Only two lakes in the discharge zone are without outlets and are classified as discharge seepage lakes. The following hypothesis could potentially explain the absence of outlet: i) lake shallowness, ii) gentle slopes in the watershed, iii) relatively high elevation in the discharge zone and iv) the absence of inlet flowing from an adjacent lake with outlet. Yet, some lakes with outlets, like Pit Lake, can be found at elevations corresponding to the groundwater recharge zone (**Fig. 5**). The presence of Pit Lake at a distinctly high elevation (296 m) is nonetheless explained by the border of this lake at the clay-sand interface (**Fig. 1b**). This seems to indicate that elevation is just a putative variable or, in other words, a proxy of the actual hydraulic midline delineated by the clay-sand interface. This is confirmed 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 $r^2 = 0.16$, $n = 50$, $p < 0.01$). On the other hand, the logistic regression of the presence or absence of a lake outlet to the closest distance to the sand-clay contact provided a better relation (Mc-Fadden $r^2 = 0.48$, $n = 50$, $p < 0.001$), although it is challenging to find the real clay-sand interface as the lateral sands can mask the real exact location (**Fig. 1b**) and surficial geological maps have errors in tens of meters in comparison to field observations. Although elevation is just a proxy of the actual location of the clay-sand interface, the hydraulic midline determined by breakpoint analysis and the clay-sand interface are fairly positioned close to one another in the esker landscape and is considered to be a good indicator of the location of the midline.

In the recharge zone, mounded recharge lakes were distinguished from recharge seepage lakes based on their pH. Alkaline lakes (pH > 7.5) were classified as recharge seepage lakes while acidic and circumneutral lakes (pH < 7.5) were classified as mounded recharge lakes. The generally flat topography of the recharge zone on the esker is characterized by gentle slopes, likely resulting in low hydraulic gradients and slow groundwater movement, which tends to increase the tendency of the upland recharge lakes to only interact with local groundwater flow systems (Winter, 1976). Given that the crest of the esker is composed of sand and gravel, lakes readily contribute to the groundwater. Mounded recharge lakes will typically be lower in pH, as a result of being perched or mounded above the local water table (Newton and Driscoll, 1990) (**Fig. 8**).

Some lakes in the recharge zone, called recharge seepage lakes, have an alkaline 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 midline, iii) lake relative deepness allowing interactions with deeper groundwater flows, iv) the location at lower elevations in the recharge zone far enough from hydraulic heads to receive longer solute-rich flows for eskers in the area both have longitudinal and transversal flows (Bolduc et *al*., 2004), or a combination of those.

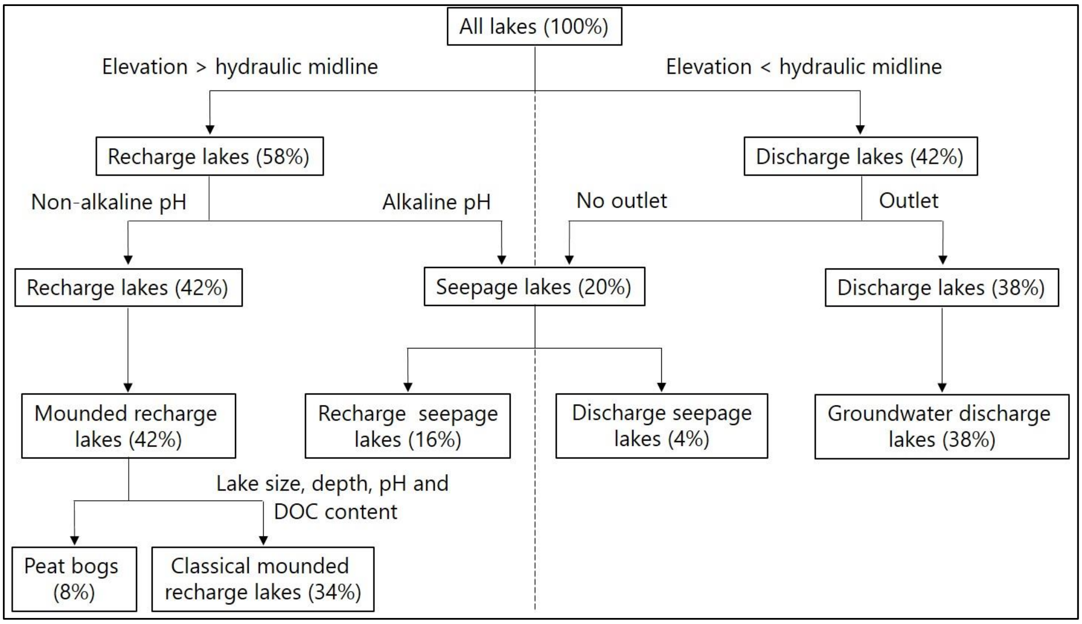

Fig. 8: Illustration of a lake typology for the study lakes. Lake elevation was used as the primary factor in separating lakes, with elevation being an effective surrogate for dividing lakes based on contribution of groundwater flow to a lake. The lakes were then separated based on presence of an outlet, as well as lake water pH and other morphological characteristics of the lakes

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The lakes identified as mounded recharge lakes can also be subdivided into two types of recharge lakes: “classical” mounded recharge lakes and peat bogs (**Fig. 8**), 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 and 1 to 2 m deep), acidic, characterized by a very low amount of solutes (maximum 30 µS/cm), a relatively high amount of dissolved organic carbon (above 10 ppm) and by water isotopic composition controlled by short-term hydroclimatic conditions (enriched in heavy water isotopes during drier periods and similar to the isotopic composition of precipitation during wet periods). This could result from relative hydrological isolation from the groundwater system due to the thick layer of peat at their bottom formed by the successive accumulation of sedge and sphagnum characterized by a low hydraulic conductivity (Newton and Driscoll, 1990). As a consequence, direct precipitation would be the predominant source of water, making these lakes sensitive to hydroclimatic variability.

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.

Based on this typology, 42% of the sampled lakes were mounded recharge lakes, 20% seepage lakes and 38% drainage 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.

Drainage (ground-water discharge) lakes have the highest pH, and amounts of solutes, while the 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 water isotopes, discharge lakes tend to be depleted in heavier isotopes, and seepage lakes characterized by intermediate values. This reinforces the interpretation that seepage lakes are a hybrid type between recharge and drainage lakes. Seepage lakes thus tend to be closer to recharge lakes on an isotopic basis, but more similar to discharge lakes on a chemical basis. This is explained by the fact that most sampled seepage lakes are located in the recharge zone and those receive some intermediate groundwater flows.

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

5.3 Lake morphometry and water geochemistry

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

Lake-water chemistry can also be influenced by lake morphometry. Lake depth has been known to play a role (Winter, 1976). It seems that *a priori* there is no relation between lake maximum depth and specific conductance ($r^2 = 0.00$, n = 50, $p = 0.64$). However, to determine whether the relationship between specific conductance and lake maximum depth varied with lake landscape position, two separate regressions analyses were carried out for recharge ($r^2 = 0.01$, n = 50, $p = 0.66$) and discharge lakes ($r^2 = 0.30$, 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 flows seep into the lake. It is also expected that small lakes with a large ratio of perimeter to surface area ($r^2 = 0.24$, n = 48, $p < 0.001$) will have a higher amounts of solutes as the majority of groundwater seepage into the lake is typically localised near the shoreline (Rosenberry et *al*., 2015).

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

Results from the study show that the water balance of individual lakes is highly dependent on the nature of their interactions with groundwater that is in turn determined by landscape position at highly localized scale. Drainage lakes undergo minimal evaporation (usually E/I ~ 0) as they are continuously fed by groundwater whereas groundwater recharge lakes are highly sensitive to evaporation (in most cases E/I > 1) as they rely on precipitation as their primary source of water. Seepage lakes constitute a hybrid between recharge and drainage and their water balance is between the other two lake types (typically 0 < E/I < 1) (**Fig. 4**). Consequently, upland recharge lakes will be more prone to evaporative drawdown and therefore more sensitive to short-term climate change and droughts, while discharge lakes will be buffered by groundwater inflow and affected by hydroclimatological changes of greater duration and persistence that alter water table position (**Fig. 7**). Seepage lakes will presumably be sensitive to drought but not to the same extend as recharge lakes as they are have stronger interactions with groundwater (**Fig. 7**). Under extreme hydroclimatic conditions, seepage lakes can become recharge lakes or drainage lakes (Anderson and Munter, 1981), suggesting that the esker hydrological system can respond to 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).

Similarly, the water-chemistry gradient between upland solute-poor lakes and lowland solute-rich lakes could make recharge lakes more vulnerable to acidification than seepage and discharge lakes. The effects of changing hydroclimatic conditions on lake-water chemistry across the landscape observed during successive sampling in June 2013, June 2014 and August 2014 resulted in heterogeneous pattern depending on the lake type similar to the findings of Webster et *al*. (1996). Recharge lakes did not respond chemically to short-term hydroclimatic change as they receive limited solutes from groundwater (**Fig. 8b**), while seepage and drainage lakes displayed significant solute changes. Based on the limited sampling frequency, it is difficult to draw conclusions on which of the seepage or discharge lake types undergo the most chemical variation. However, Webster et *al*. (1996) suggest that drainage lakes and seepage lakes respond chemically to evaporative drawdown in opposite ways, with seepage lakes showing a decline in solutes during droughts as inputs from groundwater diminish due to the lowering of the water table. By contrast, drainage lakes have been noted as susceptible to evaporative enrichment of 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 impacts and make lakes more vulnerable to other stressors, such as lake acidification.

Due to their varied hydrological characteristics, the lake types identified in this study will have a different susceptibility to direct anthropogenic impacts. Because recharge lakes have lower groundwater inflow, they are characterized by relatively long water residence times, making them highly vulnerable to inputs in comparison to seepage lakes and discharge lakes. Sand extraction and mining activities in the groundwater discharge zone could potentially influence the water levels of upland lakes in the recharge zone (Klove et *al*., 2011). This potential was acknowledged by an impact study undertaken for an aggregate 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 and surrounding lake levels (Cochrane, 2006).

Finally, when considering groundwater-fed lakes for the purposes of paleohydrological reconstruction (e.g. Laird et *al*., 2012), it is critical to explore the current landscape limnology of the study area to be able to correctly interpret the probable causes of isotopic, chemical, and biological change and variability recorded in the sediment through time and the potential hydroclimatic drivers. It is important to delimit groundwater recharge and discharge influences and lake typology, and multiple site selection seem therefore necessary (Bennett et *al*., 2007) as the degree to which lakes interact with groundwater produces differences in hydrologic response to environmental change and complicates the interpretation of paleolimnological records (Fritz, 2000).

6 Conclusion

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

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

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Author contributions

Maxime Boreux collected data in the field and processed samples in the lab, conducted data analysis and interpretation (with input from all authors), generated figures and tables. Scott Lamoureux provided guidance, funding, reviewed and edited the manuscript in his function as supervisor, as did Brian Cumming. The manuscript was written by Maxime Boreux with input from all authors.

Data availability

The data can be made available by contacting the corresponding author.

Competing interests

The authors declare that they have no conflict of interest.

Appendix

Tab. A1b: Correlation matrix between hydrological tracers and morphometric variables

	EC	pH	T	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	SO_4^{2-}	NO_3^-	NH_4^+	$\delta^{18}O$	δ^2H
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
pH	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
T	-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
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
δ^2H	-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
NPOC	-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
IC	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
H	-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
Z	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
A	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
P	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

Note: electrical conductance (EC) is expressed in µS/cm, temperature (T) in °C, dissolved ions (Ca^{2+}, Mg^{2+}, K^+, Na^+, Cl^-, SO_4^{2-}, NO_2^--NO_3^-, NH_4^+) in ppm, water stable isotopes ($\delta^{18}O$, δ^2H, *d*) in V-SMOW, total carbon (TC), non purgeable organic carbon (NPOC), inorganic carbon (IC) 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.

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

	d	E/I	TC	NPOC	IC	TN	C/N	H	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
pH	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
T	-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
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$_3^{-}$	-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
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
δ^{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
δ^{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
NPOC	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
IC	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
H	-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
A	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
P	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 µS/cm, temperature (T) in °C, dissolved ions (Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, SO$_4^{2-}$, NO$_2^{-}$-NO$_3^{-}$, NH$_4^{+}$) in ppm, water stable isotopes (δ^{18}O, δ^{2}H, *d*) in V-SMOW, total carbon (TC), non purgeable organic carbon (NPOC), inorganic carbon (IC) 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.

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 242 m asl, whereas lakes in the 'discharge' zone are defined as lakes located at an elevation of less than 242 m asl.

	Lakes in the recharge zone	Lakes in the 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	$p < 0.001$
pH	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^{2+} (ppm)	4.8 (6.6)	29.4 (10.7)	101.0	$p < 0.001$
Mg^{2+} (ppm)	1.1 (1.4)	7.1 (3.1)	83.4	$p < 0.001$
K^{+} (ppm)	0.4 (0.2)	1.0 (0.4)	28.0	$p < 0.001$
Na^{+} (ppm)	0.8 (1.9)	5.3 (7.9)	8.9	0.005
Cl^{-} (ppm)	1.1 (3.9)	9.5 (15.0)	8.3	0.006
SO_4^{2-} (ppm)	0.9 (0.8)	6.6 (13.9)	4.8	0.034
NO_2^{-}-NO_3^{-} (ppm)	0.0 (0.3)	0.0 (0.0)	**0.9**	**0.339**
NH_4^{+} (ppm)	0.0 (0.0)	0.0 (0.0)	**2.1**	**0.159**
$\delta^{18}O$ (‰)	- 8.7 (1.4)	- 11.5 (1.6)	43.0	$p < 0.001$
$\delta^{2}H$ (‰)	- 78.2 (7.1)	- 90.6 (7.6)	35.0	$p < 0.001$
d (‰)	- 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	$p < 0.001$
NPOC (ppm)	5.9 (3.2)	6.2 (4.9)	**0.1**	**0.813**
IC (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	$p < 0.001$

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 242 m asl and non-alkaline, lakes in the 'seepage' zone are defined as lakes above an elevation of 242 m asl and alkaline whereas lakes in the 'discharge' zone are defined as lakes located at an elevation of less than 242 m asl.

	Recharge lakes	Seepage lakes	Drainage 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	$p < 0.001$
pH	6.2 (0.7)	7.8 (0.3)	7.9 (0.4)	88.4	$p < 0.001$
T (°C)	17.1 (2.0)	16.4 (1.7)	16.5 (2.8)	**0.7**	**0.402**
Ca^{2+} (ppm)	1.4 (1.4)	16.8 (8.6)	29.5 (11.2)	130.3	$p < 0.001$
Mg^{2+} (ppm)	0.4 (0.3)	3.5 (1.7)	7.2 (3.3)	95.2	$p < 0.001$
K^+ (ppm)	0.5 (0.3)	0.4 (0.1)	1.0 (0.4)	19.3	$p < 0.001$
Na^+ (ppm)	0.4 (0.7)	1.9 (2.9)	5.6 (8.3)	9.2	0.004
Cl^- (ppm)	0.4 (1.3)	3.3 (6.5)	9.9 (15.7)	8.1	0.006
SO_4^{2-} (ppm)	0.7 (0.6)	1.7 (1.1)	7.0 (14.6)	4.7	0.035
NO_2^--NO_3^- (ppm)	0.1 (0.4)	0.0 (0.0)	0.0 (0.0)	**0.9**	**0.339**
NH_4^+ (ppm)	0.0 (0.0)	0.0 (0.0)	0.0 (0.00)	**2.6**	**0.114**
$\delta^{18}O$ (‰)	-8.5 (1.3)	- 9.7 (1.6)	- 11.6 (1.7)	48.0	$p < 0.001$
δ^2H (‰)	- 77.4 (6.8)	- 82.1 (7.8)	- 90.8 (8.0)	36.5	$p < 0.001$
d (‰)	- 9.6 (3.7)	- 4.5 (5.4)	1.9 (5.7)	64.6	$p < 0.001$
E/I	1.6 (1.8)	0.6 (0.5)	0.2 (0.4)	14.0	$p < 0.001$
TC (ppm)	8.7 (4.0)	19.9 (6.6)	30.8 (9.4)	74.7	$p < 0.001$
NPOC (ppm)	6.7 (3.5)	3.9 (1.2)	6.7 (5.2)	**0.1**	**0.733**
IC (ppm)	2.0 (1.3)	15.9 (7.2)	24.1 (11.5)	65.7	$p < 0.001$
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	$p < 0.001$
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	$p < 0.001$