

Response to reviewer #2 comments on “Landscape and groundwater controls over boreal lake water chemistry and water balance heterogeneity in an esker complex of northeastern Ontario, Canada” by Boreux et al.

In black: reviewer’s comments.

In blue: our answers and/or what we propose to add or to change in the manuscript.

We thank the reviewer for the comments on our manuscript which will aid in improving a new version of the manuscript. We found the comments and suggestions useful and the majority of suggestions will be incorporated in the revised version of the manuscript.

Boreux et al. utilize lake water isotope and chemistry data to identify lake types in an esker complex in Ontario, and specifically characterize the role of groundwater and landscape position on lake conditions. I enjoyed reading the paper. This is an excellent dataset and, by and large, the interpretations appear to be sound and supported by the data. So, from an overall perspective, this paper will make for a useful contribution on lake hydrology. In particular, the links between water isotope composition and water chemistry serve as useful example of the strength in such an approach to characterize lake conditions at numerous locations across landscapes.

Thank you.

That being said, there are both analytical and structural issues with this manuscript that, in my view, should be addressed. I elaborate on these below.

1. Analytical. Specifically here, I refer to calculation of the isotope-inferred E/I ratios. If the authors intend on retaining this piece of the manuscript, much more detail needs to be provided as to how these calculations were performed. For instance, at the top of page 9 where the E/I ratio is provided, there is an incorrect definition of dE . Several of the papers listed in the reference utilize the Gonfiantini (1986) equation, but I do not know if the authors used this equation. Furthermore, there are no details provided regarding how they computed dA , or what they used for temperature or relative humidity. Fundamentally, insufficient text and details are provided, such that the calculations cannot be reproduced by a reader. So, much more needs to be provided here. But I wonder if this is even necessary? The E/I results are barely mentioned in the Discussion. It seems that, for the apparent purposes of this paper, the authors could simply get away with comments referring to differences in the degree of evaporative isotopic enrichment.

We agree after reading your comment that the calculations cannot be reproduced by a reader. We originally aimed at summarizing this as much as possible as this method has been used in several papers, but the external perspective of the reviewer made us realize this mistake. Thus, more text and details will be provided and the section will be rewritten.

δ_E was estimated using the Craig-Gordon model (Craig and Gordon, 1965) formulated by Gonfiantini (1986) as follows:

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

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

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

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

where T is the air temperature in Kelvins. ε_k (Eq. 8) is expressed for $\delta^{18}\text{O}$ by (Gonfiantini, 1986):

$$\varepsilon_k = (0.0142 (1 - h))1000$$

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

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

where ε is the total isotopic separation factor that includes both ε^* and ε_k expressed as:

$$\varepsilon = \varepsilon^* + \varepsilon_k$$

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

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

where δ_P was computed as the average isotopic composition of annual precipitation from February 1997 to November 2010 (data collected by CNIP). However, when reviewing this paper, we came across the publication of Gibson *et al.* (2015) which was published after the E/I calculations were done. This paper provides another formula where δ_A is estimated with a selected equilibrium applied to the average isotopic composition of annual precipitation as follows (Gibson *et al.*, 2015):

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

where k is a climate seasonality coefficient. Given this, we will test and address the sensitivity of the formula in a sensitivity analysis in the appendix.

References:

- Craig, H. and Gordon, L.I.: Deuterium and Oxygen-18 Variations in the Ocean and the Marine Atmosphere, in: *Stable Isotopes in Oceanographic Studies and Paleotemperatures*, edited by: Tongiorgi, E., Laboratorio di geologia nucleare, Pisa, Italy, 9–130, 1965.
- Gibson, J.J.: A new conceptual model for predicting isotope enrichment of lakes in seasonal climates, *PAGES News*, 10, 10-11, 2002.
- Gibson, J.J. and Edwards, T.W.D.: Regional surface water balance and evaporation–transpiration partitioning from a stable isotope survey of lakes in northern Canada, *Global Biogeochem. Cycles*, 16, 1-14, doi:10.1029/2001GB001839, 2002.
- Gibson, J.J., Birks, S.J. and Yi, Y.: Stable isotope mass balance of lakes: A contemporary perspective, *Quat. Sci. Rev.*, 131, 316–328, <https://doi.org/10.1016/j.quascirev.2015.04.013>, 2015.
- Gonfiantini, R: Environmental isotopes in lake studies, In: *Handbook of Environmental Isotope Geochemistry*, Vol. 2, *The Terrestrial Environment*, edited by: Fritz, B.P. and Fontes, J.C., Elsevier, Amsterdam, the Netherlands, 113–168, 1986.
- Horita, J. and Wesolowski, D.: Liquid-vapour fractionation of oxygen and hydrogen isotopes of water from the freezing to the critical temperature, *Geochim. Cosmochim. Acta*, 58, 3425–3437, doi:10.1016/0016-7037(94)90096-5, 1994.

Perhaps it is just my weak understanding of statistics, but I would like to see a bit more background on the breakpoint analysis. This seems to be a very important part of the paper, as it apparently identifies 282 m (or is it 242 m? – both are listed, which added to my confusion) as the landscape position in which the role of groundwater changes. My limited understanding of breakpoint analysis is that it is used to detect when there is a change in a trend (often applied to time-series measurements), but it seems like this analysis is being applied differently here.

As the reviewer accurately mentioned, breakpoint analysis is used to detect when there is a change in a trend and it is often applied to time-series measurements. In our case, we have a gradient of lakes ranked according to elevation (thus a continuous series of data just like a time series) and we observed that lakes behaved isotopically and chemically differently in two groups according to elevation. A breakpoint analysis was done and indeed revealed that the breakpoint was significant for most variables at around the same elevation. We understand the use of breakpoint analysis is a little unusual in this context as clustering is usually the prefer method. Clustering would provide a grouping of the lakes but this method would not provide with a value of elevation that divides the two zones like the breakpoint analysis does. This is particularly relevant because: (1) the breakpoint line allows us to map what we believe to be the groundwater recharge and discharge zones; and (2) the elevation of the breakpoint line actually slightly varies according to the sampling campaign as does the water table level and allow us to track short term changes while the grouping of the lakes remains the same. The elevation of the breakpoint line is indeed 282 m, not 242 m. This is an unfortunate typo. Thank you for pointing this out.

2. Structural. In its present form, the manuscript imposes the lake classification scheme on the results, but it is only part-way through the Discussion where the rationale for the classification scheme is presented.

This creates a lot of awkwardness with the paper. The reader is quite literally forced to take the author's word for it that there is some basis for the classification scheme while they read the results (but they have no idea what that is). Since my expertise lies more with the isotope component of the paper, I kept wondering how the authors are going to distinguish the role of groundwater versus precipitation, since they often have very similar isotope compositions. It was only much later, in the Discussion, where I learned that the role of groundwater, in fact, is largely, maybe exclusively (?) based on the water chemistry. There needs to be some re-structuring of the manuscript, so that the reader can examine the results, unencumbered by the imposing of the classification scheme, and then use those results to develop the classification rationale. I think you are likely to end up with the same ultimate interpretations and conclusions, but the path to getting there needs refinement and re-organization so that it will be easier for the reader to digest.

We agree with the reviewer's diagnostic that: (1) the manuscript needs some restructuring so that the results and their interpretation are better distinguished; and that (2) some challenges such as the distinction between the roles of groundwater versus precipitation should be acknowledged and explained in the manuscript.

Other comments are listed below:

Thank you for the details comments, which will improve the quality and the clarity of the manuscript.

Line 17: Insert a sentence explaining why the study was conducted.

We will develop more on the relevance on the study (as also suggested by the reviewer's comments on line 600-602 below). The main reason for developing this study is to assess the lakes' sensitivity to changes in water balance which is necessary for an informed discussion of paleoenvironmental/climatic studies on a subset of these lakes, as well as to develop a more detailed understanding on the local hydrology (the region has a lot of mining activities and cottages).

Line 21-22: Interesting that evaporation did not lead to concentration of ions. Seems like an unexpected relation.

The reviewer is correct in stating that evaporation can lead to the evapoconcentration of ions but this doesn't really apply in this context because of the mesic climate in this region. In our case, water residence is low and the amount of solutes is a reflection of the rain water. Evaporation leads to changes in ion concentration for recharge lakes as showed in Fig. 7. Interestingly when we look at the percentage of change vs. the raw amount of change in electric conductance, the percentage is higher for recharge lakes. However, the amount of solutes in those lakes is so low that this enrichment in ions is insignificant. If the study area was more arid the results likely would be different.

Line 28: 'characteristics'

This will be corrected in the text.

Line 33: 'discharge lakes showed'

This will be adapted in the text as suggested.

Line 34: 'would only be likely affected'

This will be adapted in the text as suggested.

Line 64: delete 'changing'

We will adapt it to "interactions can vary temporally according to changes in seasonality and longer term changes in hydroclimatic conditions" as suggested by the other reviewer.

Line 84: replace 'to test' with 'examine'

This will be adapted in the text as suggested.

At this point, I'm wondering how the authors might distinguish influence of groundwater from precipitation since they often have similar isotopic signatures. Authors might want to acknowledge this challenge here, and may use this to also rationalize the combined use of water isotopes and chemistry.

The reviewer raises an excellent point here. Indeed, as shown in Fig.2, the isotopic signature of groundwater and mean annual precipitation are very similar (which is not surprising). As accurately suggested, we will acknowledge this challenge and further support the rationale of using both water isotopes and chemistry in our study. However, given that: (1) our study was carried out on a small spatial scale (our study area consists basically of a rectangular zone of 12 km by 6 km); (2) the close proximity of the lakes; (3) the terrain homogeneity (with boreal forest as the dominant land cover); and (4) the limited topography, it is unlikely that there are significant differences in terms of precipitation patterns within our study area. Due to the particular setting of our study area, in this case, we believe this is a fair assumption that groundwater connectivity is the main control on lake water balance for our 50 lakes.

Line 91-92: re 'water management and conservation goals' . . . some mention of this applied aspect should be stated in the abstract, and furthermore, the abstract might relay more directly how the findings from this study contribute to these aspects

As suggested by the reviewer, we will mention the usefulness of this study in the abstract and how our findings and the developed typology can contribute to the conservation and the better management of the local environment.

Figure 1 caption: 'northeast'; label 'a' and 'b' on figure and label lakes and locations mentioned at the top of page 5

We will label part a and part b of Fig. 1 as suggested by the reviewer and label the mentioned locations on the map.

Line 107: delete 'the'

This will be adapted in the text as suggested.

Line 129: 'texture. The esker'

This will be adapted in the text as suggested.

Line 133: 'aquifers at its edges where'

This will be corrected in the text.

Line 153-154: Can you explain the three-time sampling rationale? This puzzled me a bit because the data are weighted to the early ice-free season, as mostly mean values are used, and there is very little mentioned about seasonal patterns in the data that are obtained.

There were 3 field campaigns to ensure the reproducibility of the data. Lakes were sampled mostly in the early ice-free season due to logistical reasons. The description of the observed changes between sampling campaigns are commented in the end of the manuscript in relation to the lake typology as the observed changes were specific to lake type.

Line 209: As stated above in my comments, I wonder if you even need to perform these calculations. If you would like to retain, more details are required as per comments above.

While we agree with the reviewer's previous statement that this study could be done with just the water stable isotope values, calculating the water balance gives us a better and more intuitive sense of the extent to which lakes are sensitive to evaporation. Thus, we took the above comments into consideration and added details to the calculation of E/I ratios.

Line 233: Another point of confusion for me was that dI was assumed to be the average of precipitation, and was assumed to be the same for all lakes. Yet knowing that the goal here is to detect influence from groundwater, I wondered then if there might be some variability in dI among your lakes. And, of course, I remained curious to know how groundwater influence might be distinguished from precipitation since they often have similar isotope signatures. I'm not sure any of this was ever explicitly discussed in the manuscript.

Even though δ_p is an approximation of δ_l (Gibson, 2002), we decided to estimate δ_l as the intersection of the LMWL with the LEL in the revised version as the latter method is more conventional (Gibson *et al.*, 1993; Yi *et al.*, 2008). While we agree with the challenge raised by the reviewer, the particularity of our study area (small spatial extend, homogeneity of land cover and limited differences in elevation), we assume that hypothesizing that δ_p is the same for all the lakes is a fair assumption as explained above. This is of course something that we will mention in the revised manuscript. We also recognize that δ_l can also be influenced by the isotopic composition of surface inflowing waters (which for the most part are groundwater springs and thus made up of groundwater). Only two lakes receive inflowing water from local streams (the volume of both of those is supposed to be small in comparison to the lake volume and those streams are intermittent in the sense that they were not flowing during each of the three field campaigns; the latter

observation was confirmed by local park officials). We thus assume that inflowing water can change the isotopic composition of a handful of lakes but this change is assumed to be limited. This limitation will be stated in the revised manuscript.

References:

Gibson, J.J.: A new conceptual model for predicting isotope enrichment of lakes in seasonal climates, PAGES News, 10, 10-11, 2002.

Gibson, J.J., Edwards, T.W.D., Burse, G.G., and Prowse, T.D.: Estimating evaporation using stable isotopes: quantitative results and sensitivity analysis for two catchments in northern Canada, Nord. Hydrol., 24, 79–94, 1993.

Yi, Y., Brock, B.E., Falcone, M.D., Wolfe, B.B. and Edwards, T.W.D.: A coupled isotope tracer method to characterize input water to lakes, J. Hydrol., 350, 1–13, doi:10.1016/j.jhydrol.2007.11.008, 2008.

Line 234-235: Incorrect calculation of δE . Very puzzled by this statement.

Indeed, this is an incorrect calculation of δE . This is obviously a major typo. The right formula was inserted in the rewriting of that section (see above).

Line 242-244. I gather you are summarizing here, but you have two springtime samples and one late summer sample, which makes this a bit awkward.

Temperature was only measured during the August 2014 field campaign. Thus we are only comparing samples collected during the same week.

Line 250: ‘Local Evaporation Line’

This will be corrected in the text.

Line 251-252: Concern about overlapping isotope signatures of gw and precip confirmed!

This justified concern was addressed above.

Line 256-257: Awkward incorporation of elevation here. Seems like this should be saved for the next paragraph.

We agree with the reviewer that the incorporation of elevation should be done in the following paragraph. We will change this accordingly.

Figure 2b: Label your figures ‘a’ and ‘b’. First awkward imposing of lake type here, without rationale being provided.

Labels a and b will be added to Figure 2. As to not impose the lake typology early in the manuscript, we will aggregate all the lake water samples as one category.

Line 266: A small thing but I would replace ‘indicating’ with ‘suggesting’. Of course, this may be just one factor driving the water balance. At this point in the article, it seems the authors are overly anxious to get to the conclusion without proper development of the results and interpretation.

This will be adapted in the text as suggested. We agree with the reviewer that the result section should only state the results and that interpretation should be withheld at this point.

Figure 3: I don’t understand the application of the breakpoint analysis.

Please see our response to your earlier comment.

Line 278: delete ‘high’

This will be adapted in the text as suggested.

Line 279: An E/I ratio of ‘8’ cannot be quoted so directly if using a steady-state model.

We agree with the reviewer that an E/I ratio of 8 shouldn’t be quoted directly due to the limitations of the Craig-Gordon model and we will delate the quotation.

Line 280: More awkward imposing of lake types without rationale. Same with Figure 4, which isn’t a very effective way of presenting E/I ratios, as they are calculated from the isotope measurements.

We agree about the non-effectiveness of Fig.4 as E/I is indeed computed from $\delta^{18}\text{O}$ (and we realized this beforehand). The original goal of this figure was to show the reader the range of E/I that exist in our data set. We will thus plot E/I and the electrical conductance instead.

We also agree that we awkwardly impose our lake typology but at the same time adding the typology adds more information to the figure and allows the reader to infer the importance of lake type on lake E/I as she or he reads further in the manuscript. The details related to the lake typology was advised in the figure caption. In order to take the reviewer’s concern into account, we will duplicate this figure as Fig. 4a (without the lake typology, which will be referred to in the result section) and Fig. 4b (with the lake typology, which will be referred to in the discussion).

Line 296: Are they really conservative isotope tracers if they are changing as a consequence of evaporation?

The reviewer is correct to challenge the conservativeness of isotope tracers as they indeed change as a consequence of evaporation. We did label isotope tracers as conservative in comparison to chemical tracers because isotopes are relatively conservative in reactions with catchment materials and retain their distinctive values until they mix with water of different isotopic composition (Kendall and McDonnell, 1998). We acknowledge that this terminology can be a little confusing and we will include a small definition of what we mean by conservative and non-conservative tracers.

Reference: Kendall, C. and Caldwell, E.A.: Fundamentals of Isotope Geochemistry. In: “Isotope Tracers in Catchment Hydrology”, Edited by: Kendall, C. and McDonnell J.J., Elsevier Science B.V., Amsterdam, pp. 51-86, 1998.

Table 1. More confusion about the breakpoint analysis, confounded by listing of ‘282’ m in the table and ‘242’ m on p. 14 and elsewhere.

The elevation is 282 m, not 242 m. A previous typo earlier in the manuscript made it confusing. This will be corrected.

Lines 323 to the end of this section: Again, imposing the lake types here is simply not warranted. Extremely confusing to the reader. Data needs to be presented first. Then it can be interpreted. Then a classification system can be developed. P. 15. At this point in the paper, I had too many questions to be able to critically evaluate further. But as I say in my opening comments, I believe the story may largely be ok, it is just the development of that story that really needs to be overhauled.

As commented earlier in our response, we agree with the reviewer’s diagnostic that the manuscript could be structurally improved so that the results are stated first, then interpreted, after which the typology can be developed and explained.

Figure 7. First (and perhaps only) characterization and use of the seasonal differences (although literal use of the very elevated E/I ratios is beyond the limitations of the model). Difficult to detect if this is really utilized in the Discussion. Is it relevant? Or can more be made of it? But again, as written, the reader is forced to accept the lake type classification.

We understand that it is confusing to impose the lake typology in the result section. To make things clearer and less confusing for the readers, we will move Fig. 7 to the discussion section (although introducing figures in the discussion is not ideal) and we will add a figure in the appendix that will be referred to in the result section with part a showing changes in water balance between the sampling campaigns for each lake ranked by elevation and with part b showing changes in water chemistry between the sampling campaigns for each lake ranked by elevation. The interpretation of those changes is mostly relevant when relating to the lake typology given that the observed changes were dependent on the lake typology. For this reason, we think this is relevant to include it in the manuscript.

Line 369: replace ‘high’ with ‘short’

This will be adapted in the text as suggested.

Line 373-374. So now we’re finally getting some explanation of the different lake types, but this is confusing too. How do you know that gw is causing the difference here (which is not explicitly stated)?

We already addressed those two concerns above: (1) the manuscript will be restructure as not to impose the lake typology too early to the reader; (2) we will address the issue of differencing the relative contribution of precipitation and groundwater to balance and the assumption that in our study area, groundwater is

causing the difference in water balance as precipitation is supposed to be uniform in our study area due to its small size.

Line 379: replace ‘composition’ with ‘water chemistries’

This will be adapted in the text as suggested.

Line 384, 386: How do you know the 1 km statements? Where does that come from? But here, I get the sense that the gw role is mainly based on the water chemistry differences, and less so on the isotope data.

The 1 km value was quoted from the literature (Bertrand *et al.*, 2011) as a typical example of spatial scale. However we acknowledge it can be hazardous to cite values that applies to general settings so we will delete this value. Because we labelled isotopes as conservative tracers and chemical tracers as non-conservative (with respect to their ability to react chemically with the watershed materials), we indeed rely on water chemistry to infer whether the flows are local or intermediate.

Reference: Bertrand, G., Goldscheider, N., Gobat, J.M. and Hunkeler, D.: Review: from multi-scale conceptualization to a classification system for inland groundwater-dependent ecosystems, *Hydrogeol. J.* 20, 5–25, 2012.

Line 404: This classification section has been pre-empted by all the comments before this point on lake types, which is the most awkward aspect of this paper. Sorry to keep emphasizing this. I’m sure it can be resolved!

As commented earlier in our response, we agree with the reviewer’s diagnostic that the manuscript could be structurally improved so that the results are stated first, then interpreted, after which the typology can be developed and explained and that the typology shouldn’t be imposed too early to the reader. Efforts will be made to restructure the manuscript to address this concern.

Line 407: ‘conservative water tracers (water source)’ – I am very confused by this terminology. The isotope data reflects more than just source water. It is modified by varying degrees of evaporative enrichment.

We agree with the reviewer that isotopic tracers reflect water sources and their level of evaporative enrichment as well. As mentioned above we defined conservative and non-conservative tracers with respect to their reactivity with the watershed materials, which will be specified earlier in the manuscript.

Line 428: Awkward sentence.

We agree with the reviewer that the sentence is awkwardly phrased and is confusing. We will rephrase it as: “In seepage lakes, water comes in as groundwater in-seepage and is returned to the groundwater system as out-seepage”.

Line 436- 437: 282? Or 242? But I still don’t understand how this elevation was defined.

The elevation is 282 m. A previous typo earlier in the manuscript made it confusing. The details of how it was estimated is provided above.

Line 451-453: Not a sentence.

We agree with the reviewer that those two lines didn't constitute a proper sentence. We will rephrase it as: "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".

Line 473: What is meant by the word 'mounded'?

Mounded lakes are lakes positioned above the water table that receive most of their water input from direct precipitation as defined by the ALSC Lake Classification System (Newton and Driscoll, 1990). The word mounded will be discarded following the comments of the other reviewer.

Reference: Newton, R.M. and Driscoll, C.T.: Classification of ALSC lakes, in: Adirondack Lakes Survey: An Interpretive Analysis of Fish Communities and Water Chemistry, 1984-87, Adirondack Lakes Survey Corporation, Ray Brook, NY., 2-70 to 2-91, 1990.

Line 545: 'those'?

Those will be changed to these.

Line 575: 'extent'

This will be corrected in the text.

Line 600-602: Interesting. Shouldn't these activities be mentioned in the Intro to help rationalize the study?

As suggested we will add this to the rationale in the introduction.

Line 632: Awkward phrasing.

We agree with the reviewer that the sentence is awkwardly phrased and is confusing, We will rephrase it as: "The physical and chemical characteristics of lake water allowed the development of a lake typology that is made up of three main types of lakes".

Line 635: delete 'are'

This will be corrected in the text.

I like the conclusion – well stated and summarized!

Thank you.