

## **Reviewer #1**

### *Summary*

Title: Novel Statistical Analysis Illustrates Importance of Flow Source for Extreme Variation in Dissolved Organic Carbon in a Eutrophic Reservoir in the Great Plains, by Baron et al.

Baron et al. present long-term (1990-2019) chemical and hydrological data from the Buffalo Pound Lake, a drinking water source lake in the Canadian prairie region. By using novel statistical analyses, they aimed to find drivers of DOC concentrations in the lake at various temporal scales. Upstream regulated flow and several chemical parameters accounted for most of the variation in lake DOC concentration. They conclude that both flow regulation and natural processes in the face of a changing climate pose important challenges for drinking water treatability.

### *Assessment*

This was an interesting read. Investigating drivers of DOC concentrations at short- and long-term scales is a recurrent but a relevant topic, more so in atypical areas such as the prairies. The manuscript is well-written, and appropriate and novel statistical methods have been used, which are well presented and justified. Yet, a few concerns and quite a few specific comments, which are probably not major overall, but would require some work before the manuscript can be accepted for publication. I therefore suggest the authors to consider my comments and amend the text accordingly or rebut.

Thanks for the encouraging feedback and ideas for improvements to the manuscript. We are glad you found this work interesting and easy to read.

### **General comments**

The hypothesis that “changes in lake water chemistry would impact DOC at shorter timescales” is ambiguous. Changes in lake water chemistry can relate to processes happening in the catchment, which would be the ones driving both overall lake water chemistry and lake DOC concentrations (these processes would relate more to allochthonous sources of DOC). But changes in lake water chemistry can also relate to internal processes in the lake, which in turn can drive DOC concentrations (these processes would relate more to autochthonous sources of DOC). I would like to see more explicit hypothesis considering whether both or one of the group of processes are expected to be important. I would also like to see this differentiation more explicitly made throughout the discussion.

Thanks for this feedback. We will revise our hypothesis to “changes in lake TP would impact DOC at shorter timescales” as our hypothesis to explore a direct link between autochthony and DOC. We will better differentiate internal vs external drivers elsewhere.

In relation to that and as much as I would think it should be the case, the lack of relevance of the local catchment flow (Q-LC) to explain DOC concentrations in the lake appears to imply that in-lake processes are more important (?). The authors should reconcile this observation with the explanations they provide that argue that catchment processes drive DOC concentrations in the lake under certain conditions.

Our analysis indicates that it is the role of flow (Q-LD) that emerges as dominant at long timescales, while at short timescales DOC was in phase with or lagging behind water chemistry predictors. While Q-LC was not significant, the analysis tells us that Q-LD has a flushing/dilution effect. While DOC coherence with Q-LC did not emerge in the analysis, we can expand on potential explanations for this in the text, including that these flows are intermittent, and when there is flow the magnitude of these is not always such that it can drive a substantive shift in the chemical state of the lake. We can't infer from this that in-lake processes are more important than the role of Q-LC; the evidence suggests that both will contribute to elevated DOC concentrations in the lake. We can add text to enhance clarity on this in the revised manuscript.

In relation to that, I am left unconvinced of the mechanisms/processes/situations that relate to high DOC concentrations in the lake. Indeed, the statistical methods that the authors use generally fail at the upper range of DOC concentrations. On one hand, I would like to see a more explicit explanation of the circumstances that lead to higher DOC concentrations, and on the other hand, the authors should acknowledge at this upper range their analyses did not provide a satisfactory answer.

We have included in the supporting information details on GAM performance (Figure S3), and this is in agreement with the reviewer concern about performance at the edges of observed ranges in DOC. In the revised manuscript we will utilize this figure better, to draw the reader to the limitations at these levels, despite overall satisfactory performance. We can also expand the discussion to draw on recent work examining the behaviour of this system, e.g. with respect to in-lake processes.

The statistical methods were well-presented and justified. Yet, their results are difficult to follow at times. I would appreciate if the authors provide more analogies to how results would be presented when using more common methods. For example, how do predictors of DOC relate to DOC? Are they “positively” related, “negatively” related, something else? This is not clear in the text. Maybe an extra column specifying this in Table 2 would help?

We appreciate this question, and will be clearer in articulating that directionality of relationships is not available from this coherence analysis (as in correlation analyses). As such, this is not a detail that can be added.

In some parts, the connection of the discussion to the actual results was not fully clear. Please, consider making clearer links in this regard.

Yes, we will enhance the clarity here, and we will explore the suggestion that analogies can be applied to help provide clarity for the reader in this regard.

### **Specific comments**

Title

Shouldn't it be “Novel Statistical Analysis Illustrates the Importance of Flow Source for Extreme Variation in Dissolved Organic Carbon in a Eutrophic Reservoir in the Great Plains”. That is, please include “the” in front importance.

We will revise the title to include ‘the’.

## Abstract

L. 9. It would make sense to clarify that these trends have been overwhelmingly positive trends.

We can clarify that these trends have been mostly positive.

L. 10. They might not be universal, but I think there is little doubt that the prevailing driver was the decline in sulfur deposition and consequent increase in organic matter solubility.

We can be more explicit in our description of the importance of sulphate decline as a driver of increasing DOC trends via OM solubility, and that they have not been observed universally across regions.

## 1 Introduction

L. 25-38. When describing “the debate over the factors that govern DOC concentrations”, one must consider that such drivers operate on varying temporal and spatial scales (see e.g. Clark et al., 2010, doi: 10.1016/j.scitotenv.2010.02.046). Thus, drivers are not necessarily exclusive, they might just be dominant at different temporal and spatial scales. Elaborating on my previous point, there is little doubt that, at the long-term scale, increasing DOC trends observed across vast regions in the Northern hemisphere affected by acid deposition were driven by, indeed, reductions in sulfur emissions. This is especially true in smaller, forest headwater catchments. Areas affected by varying chloride or nitrogen deposition (mentioned in the paragraph) would behave similarly as they would trigger the same chemical effect on organic matter solubility and I therefore would consider them as analogous, not differentiated, drivers. Areas less affected by acid deposition of any kind where other drivers might come into play might of course show other patterns.

Thanks for this comment. We will revise the text to highlight the dominant role of changing acid deposition on DOC concentration patterns observed in industrial regions. We will better contrast these situations, with those without a history of high levels of acidic deposition of industrial origin, such as the study system we investigate herein where changing DOC levels have not been linked to regional scale behaviour across many acid-sensitive water bodies.

L. 45-46. Here you use both, catchment (rather UK English) and watershed (rather American English). Just use one of the two here and throughout the manuscript (it appears that you mainly use catchment so use that at every instance).

We will revise to only use catchment throughout.

L. 47. Are you referring to DOC exports or to concentrations here? You already mentioned before that “DOC export is highly correlated with precipitation and annual runoff”, which is true and rather uninteresting because it is self-evident given that  $\text{export} = \text{runoff} \times \text{concentration}$ , and runoff generally varies across a much wider range of values than concentration does.

Yes, we refer to DOC exports, and can revise the text to characterize this as a dependence, rather than correlation, for improved clarity. We will revise the introduction following from reviewer 2 to better situate the uniqueness of the landscape, as a contrast to the systems where much of the DOC research (that documenting decadal scale trends) has been conducted. This will better highlight the uniqueness of this landscape, the importance of few water bodies in the context of water security, and our relatively nascent knowledge of controls on wide temporal fluctuations in DOC concentration, e.g. directly through DOC export from the landscape, and indirectly via nutrient runoff.

L. 51-53. This is a very important point that I was eager to see. Do you have a reference to back this up? My perception of this system is that most of the area is hydrologically non-effective, i.e. I find half to be a low estimate.

We will supplement this with citations (Godwin and Martin 1975: Calculation of gross and effective drainage areas for the Prairie Provinces; PFRA 2008: Prairie farm rehabilitation administration (PFRA) watershed project— areas of non-contributing drainage) and additional detail. Yes, the majority is non-effective, and this can vary tremendously at local scales, which we will describe more thoroughly as improved context for those less familiar with the region.

L. 70-71. But changes in lake water chemistry are concomitant to changes in DOC and therefore not necessarily drivers of DOC in the lake, i.e. they also depend on hydrological connectivity with the landscape and upstream sources, on processes occurring in the catchment, etc. Or you mean that in-lake processes are important for driving DOC concentrations?

We will clarify that we mean DOC concentration here, and cite work by Baron (2022) to describe that in-lake processes can affect DOC concentrations by  $\sim 1 \text{ mg L}^{-1}$  as water transits through this system.

## 2 Methods

L. 78. This is just out of curiosity for my own understanding. Can the climate of a region that receives only about 300 mm of annual precipitation still be classified as “subhumid”. I would consider that in the range of arid or semi-arid regions. But probably the evapotranspiration is very low too despite the warm summers?

Thank you for raising this question. It is more accurate to classify the local climate of the study site as semi-arid. We will differentiate this from the regional climate which is described as sub-humid to semi-arid climate.

L. 86-87. Interesting and important remark. However, I find the sentence oddly constructed (“contributes flow in 1:2 runoff years”). Can you rephrase?

Yes, this can be revised to be clearer using a description that is accessible to non-hydrologists (e.g., “contributes flow in one out of two years on average over the long-term (median flow)”).

L. 95-97. Can Lake Diefenbaker keep up with the demands from Buffalo Pound Lake under all circumstances?

Yes, the volume of Lake Diefenbaker is  $\sim 100$  times greater than that of Buffalo Pound Lake, and receives continuous flow sourced from the Canadian Rockies. We will add this detail.

L. 100. In Figure 1, I assume Ridge Creek is a small tributary into the Qu’Appelle River (you also describe it in the text as such). It would therefore be helpful to represent it in the figure as a lotic water system the same as e.g. Iskwao Creek, i.e. with a blue line.

We have used the best available hydrometric layer available for the region, which unfortunately does not capture the (intermittent) flow path of Ridge Creek (or the entire flow path of Iskwao). We believe this is an important reminder of the complex hydrological regime of the system, and will provide additional description to the text so that the role of Ridge and Iskwao Creeks is not ambiguous.

L. 109-123. I assume water samples are filtered before they are chemically analysed. What is the pore size of the filter?

Pore size used is 0.7 micron. This detail will be added to the text.

L. 125-126. Required a complete record at what temporal scale? Monthly, as implicitly suggested? Please, specify.

We can specify that complete record here means 360 monthly averages of samples collected weekly.

L. 137-174. I very much appreciate the effort to get the hydrology right and the consideration of water mass balances and catchment (effective) contributing areas. There is just one thing I am not sure I understand. How come Q-BP (the inflow to the lake) that is very much influenced by Q-LD (the outflow from Lake Diefenbaker, which is outside the catchment area of BP) is included in equation 4 that attempts to estimate only the local catchment flows? Shouldn't Q-BP be Q-U (the ungauged portion) in this equation?

Thanks for catching this. Equation 4 has not been expressed quite accurately. The local catchment flow is estimated using a combination of ungauged flows from the local catchment (which was mistakenly expressed as a second Q-BP term) and gauged (Q-RC, Q-IC) flows from the local catchment but does not explicitly include Q-LD flows that contribute to the flow at QBP. We will revise this equation and supporting text. The equation will read as  $Q-LC \approx Q-RC + Q-IC + Q-UC$ .

L. 176-179. Perhaps, remind the reader here that, for this analysis, you are using the monthly values that you estimated earlier.

Context will be added to note that this analysis is using monthly values.

### 3 Results

L. 265. Aren't both lakes covered with ice?

Yes, but flow continues through control structures during winter months. We can clarify this.

L. 263-272. Are typical peaks across the three Q generally associated with snowmelt events, or also with rainfall events?

Peaks at Q-BP and Q-LC are typically associated with snowmelt events, however heavy rainfall events do also contribute to peaks, particularly for Q-LC, albeit these are rare and typically smaller in magnitude than spring freshet. Detail to describing the timing of peak flows (e.g. top 5%) can be added to this paragraph or shown as a supporting figure.

L. 302-303. Are all these significantly coherent relationships found analogous to positive correlations or there are any negative correlations too? Is this something that can be said at all at this point? Either way, I think it is important to specify this for the reader.

Great question. Context will be added to indicate that, at this stage, positive or negative relationships can not be specified. Coherence relationships are analogous to the correlation strength (in terms of absolute value) but do not provide information on direction of the relationship. This is the primary reason GAM was used along with wavelet analysis. We will provide context to better link the wavelet and GAM results and clarify, where necessary, the limitations of each, and provide analogies to correlation strength and direction where appropriate.

#### 4 Discussion

L. 359-360. How is climate having an overriding influence on DOC concentration? You have not analysed any climatic variable.

We are referring to prolonged periods of drought in the region that are often followed by years with heavy rains. We will be more precise in our description by articulating this, and that these climatic patterns influence flow management for Buffalo Pound Lake.

L. 355-388. This section makes an interesting description of the general context of BPL, but how does it relate to your results? I fail to see the connection.

Given the uniqueness of our region and study system, this context is an important precursor to the discussion that follows later. We can include in this text more explicit pointing to our results to better solidify the basis for the statements we offer in this section.

L. 390-405. Let me see if I understand this correctly. Q-LD would have a “negative” relationship with DOC concentrations at BPL, meaning that when it is the prevailing source of water to the lake (that is when the catchment is generally hydrologically disconnected), DOC concentrations are generally low. By contrast, when the catchment does hydrologically connect to the lake via the activation of e.g. Ridge Creek and Iskwao Creek, you would expect to have higher DOC concentrations from organic matter-rich catchment sources. However, you were not able to see this through your analyses. Is my interpretation correct? And if so, how is all of this reconciled?

Yes, your interpretation is correct. We reconcile this in that Q-LC does not emerge as a more dominant driver as this flow is transient, and much smaller in magnitude than that of Q-LD, so not all catchment flow events are large enough to drive meaningful change in the lake. One way to think of this is more limited power to detect the role of the catchment as a driver on the lake. We can expand our discussion to speak to these challenges and also include information demonstrating the relationship between Q-LC and Q-LD that further support conclusions about the importance of local catchment flow (When Q-LC is very high, Q-LD is decreased by water managers).

L. 406-412. I would appreciate here if you'd explicitly mention whether these synchronous or lagging patterns imply, in each specific case, that DOC and the corresponding chemical parameter both increase, both decrease, or they go in opposite directions at the time scales considered.

We will rewrite this text, to allow us to better link hypothesized mechanisms to the patterns (synchronous, lagging, positive, negative) by breaking down the individual areas for discussion and mechanisms - this will also involve some revisions to the text that follows (which we referred to as 'see below'), because we can now see it is challenging to follow.

L. 411-412. Still, local catchment flow was not a predictor of DOC concentrations in BPL.

Correct. We note that local catchment flows can be large but are often intermittent, thus signals from this water source are not clear. We can clarify that despite this, nutrient delivery from the local catchment still appears to be important because water from Q-LD is typically not nutrient-rich.

L. 415-416. Following a previous comment, it can be that DOC concentration in BPL is linked to other chemical constituents in the lake, but is it really driven by in-lake chemistry itself? On the other hand, you did not find a relationship with Q-LC. All to say that I am having difficulties reconciling all these results so I would appreciate if you can make it clearer.

Thank you for this comment. We can revise our use of drivers and instead use predictors.

L. 423-444. First, these are very high concentrations of sulfate compared to what I am used to in other natural environments. I assume this can only be explained by the geological settings of the region containing large amounts of gypsum and pyrite, i.e. the ultimate source of sulfate in the catchment and the lake should primarily be mineral weathering. If this is correct, please make it more explicitly clear in the text. Second, if I understood it right from section 3.3 and Figure 4d, sulfate has a complex relationship with DOC, where above certain threshold sulfate and DOC are “negatively” related and below this threshold they are “positively” related (excluding the upper sulfate concentration range where the model did not perform well). Is this correct and if so, how do you interpret it? I miss this explanation in this discussion.

Yes, this (1) is correct. We can add this detail to the discussion. In case 2, yes the relationship emerging in the GAM is complicated, and not one that is readily interpreted. Without stronger empirical evidence of any link between DOC and sulphate across the large range in sulphate concentrations presented here, we prefer to avoid speculation in any potential interpretation. There is likely to be very high spatial variability in sulfate in the catchment, which is contributing to this complex relationship.

L. 441-444. This might be the case, but how would this drive DOC concentrations in the lake? You need to provide support for in-lake control of DOC concentrations, if that’s one of your lines of argumentation, which is still not clear to me.

We can expand this discussion to include the work of a recent student who explored salinity/sulphate dynamics across a range of pothole wetland types. The patterns at the scale of individual wetlands seems to suggest activation and delivery of sulphate to surface waters consistent with the temporal dynamics on record at Buffalo Pound Lake. We will also rephrase to describe as ‘predictor’ rather than ‘driver’.

L. 449-450. But yet again, Q-LC was not related to DOC concentrations in BPL.

We can clarify here that nutrients delivered from local catchment are likely important despite intermittent catchment flows. From the collective comments from the reviewers, we also believe there is value in better explaining overall flow management, and that Q-LD is reduced with Q-LC is high. Adding these details will better prepare readers to navigate the analysis.

L. 451-473. Maybe these in-lake mechanisms are of greater importance than the catchment input mechanisms given the lack of relevance of Q-LC? I don’t know, I am sceptical about that, but I am worried about the lack of explanatory power of Q-LC. In any case, you should be more explicit in differentiating catchment processes that can drive DOC concentration in the lake via allochthonous sources, and in-lake processes that can drive DOC concentrations via autochthonous sources. And once you make that differentiation clear, it would be best if you argue for either one of them with more conviction.

We have touched on this point (Q-LC not emerging as dominant) above, and this will be expanded on in the discussion. Likewise we can describe further the potential role of in-lake processes, we believe this will confirm the reviewers skepticism that that would be an outsized role for in-lake DOC production or processing.

L. 480. This was not entirely clear to me according to your results.

We can expand the text to link major water quality events with the wet-dry state and catchment flows.

L. 475-510. What I take from here is that this is a very challenging system in which no scenario is easy to manage. Would you provide a more explicit description of the conditions that would be best for both ecology and industry, even if they are not “natural” and potentially infrequent?

Yes, in line with the suggestions of shifting the introduction to better emphasize flow management, we will expand the discussion here, and can use some flow regime examples to describe potential trade-offs.

## 5 Conclusions

L. 5113-514. I would very much agree with this a priori, but given the lack of explanatory power of Q-LC, can you still claim that “pulses of allochthonous DOC from the local catchment during wet periods are linked to higher DOC”?

Through the responses above, we can do this in a number of ways. We can also strengthen our descriptions, as there are two prevailing flows. If we know that Q-LD acts to flush the system, then it stands to reason that (in the absence of inordinate amounts of DOC production in-lake), that these dilute upstream flows are countering the behaviour of local flows. We can be more explicit here in the revision.