

General Comments

1. The authors need to spend more time on proofreading the manuscript. In its current state, the grammar does not hold up to the standards of Biogeosciences unfortunately. I have included a list of 27 items in technical corrections *for only the first five pages* of the manuscript. I encourage the authors to find a colleague to proofread or to use a reviewing service before the next submission

Dear referee

Thank you for taking your time to comment on this manuscript. First off, we are very sorry for the amount of technical errors in this manuscript! We have proofread the manuscript very carefully and hope that all the errors has been corrected. If the editor thinks that further proofreading could benefit the manuscript then we will have it proofread by a professional, when the final corrections has been added. We will address all the referee questions below.

2. In the paper, you are trying to combine several methods in a novel way to characterize the lake hydrology. Because of this, the methods must be clearer and not assume that the readers are familiar with the various components. The purpose of a certain method, the details of the models used, the interpretation of results needs to be more extensive. For example:

a. The PARAFAC analysis: How do you get?

PARAFAC modelling is a lengthy process involving many steps which is fully described in Murphy et al. (2013). We can add this to the manuscript if the editor believes it is of importance. To ease the understanding of PARAFAC modelling we have added a section regarding this to the introduction:

“Some non-conservative tracers such as fluorescent dissolved organic matter (FDOM), which can be determined using parallel factor analysis (PARAFAC), has been used to trace dissolved organic matter (DOM) in aquatic environments (He et al., 2014; Massicotte and Frenette, 2011; Stedmon et al., 2003; Stedmon and Markager, 2005b; Walker et al., 2009). PARAFAC analysis is a modelling tool which can separate multiple FDOM samples (emission and excitation matrices) into specific fluorescent components (Stedmon et al., 2003). The fluorescent components can be biological produced proteins derived from bacteria or molecules from the degradation of terrestrial organic material. These components has previously has been found visually using a single excitation emission matrix and the observed fluorescent peaks (Coble, 1996). The differentiation between the fluorescent components are both a strength and a weakness as we can isolate many different components, but all of them can differ in both degradation and production rate in the lake and groundwater. Furthermore, these FDOM components have not yet been investigated as tracers in groundwater fed lakes, as they, just as the rest of the non-conservative biological tracers, are volatile.”

What is the interpretation of the results in Figure 3?

Figure 3 provides a visual depiction of the fluorescent components found in the PARAFAC modelling. The interpretation of the results is described in the section named “Fluorescent DOM” where we explain the origin of the components and if they are degradable or not.

To ease the understanding of figure 3 we have added the following sentence to the result section:

“PARAFAC and split-half analysis modelling identified five distinct fluorescent DOM components (C1-C5, explained variance 96.79 %). The spectral properties of the five fluorophores (components) identified by the PARAFAC analysis (Fig. 3) revealed that the DOM pool had both terrestrial and microbial influence.”

b. The determination of WRT is unclear still. The text (Line 156) briefly describes that WRT was estimated through tracer concentrations if no degradation took place. There is no further mention beyond this paragraph and needs to be elaborated upon.

We have added the following to the introduction to describe “tracer concentrations if no degradation took place”:

“This is observed as a change in tracer concentrations (often a decrease) after the groundwater is discharged to the lake. The speed of which the change in concentration occur are typically related to seasonal variations (e.g. temperature, mixing of the water column and UV-radiation) and the WRT of the lake e.g. the amount of time the tracer has been the lake. The removal and degradation rates have been examined in many instances e.g. for phosphorus (Larsen and Mercier, 1976; Vollenweider, 1975), nitrate (Harrison et al., 2009; Jensen et al., 1995), CDOM and DOC (Madsen-Østerbye et al., 2017). In a modelling approach these rates are important as they provide information about the change in tracer concentration, from the time when the tracer entered the lake. From this, it is possible to back-calculate the mixed inflow concentration of specific tracers when they were discharged to the lake. These estimations are crucial when working with non-conservative tracers, as it enables a direct comparison between the tracer concentration found in the catchment and the estimated mixed lake concentration before degradation took place.”

Furthermore, we have also added information regarding the determination of WRT in the materials and method section:

“WRT of the lake were found using traditional hydrological methods combined with non-conservative tracer concentrations which were related to their degradation rates to form a proxy for the maximum WRT. Previous hydrological models suggested that the lake had a WRT between 0.4 and 3.3 years. To further narrow this range, we estimated the WRT by relating the concentrations found in the lake to their respective degradation rates related to increasing WRT e.g. by adding the estimated removed tracer since the groundwater entered the lake to the measured concentration in the lake. This enabled us to narrow the span of the WRT based on the estimated mixed inflowing tracer concentration related to the actual catchment concentrations. E.g. if the estimated inflow concentration of a tracer is $100 \mu\text{mol l}^{-1}$, at a WRT of 2 years, and the highest catchment

tracer concentrations is $50 \mu\text{mol l}^{-1}$ then the catchment do not support a WRT of 2 years.”

3. I have some reservations on the approach taken with determining the groundwater discharge areas and lake WRT (section starting from line 215) or the methods have not been described adequately. I appreciate that this section was added but it is still not clear. When reading the methods, the reader needs to be able to see how you took your data and processed it, and arrive at the resulting figure or results. Additionally, I am not convinced that the equations used in this section were used correctly (see specific comments below).

Thank you for addressing this. We have added a flow diagram to the manuscript which we hope will improve the understanding of the different aspects in the material and method section. Furthermore, we have changed and streamlined the section so it now reads:

“In this instance, we estimated lake tracer concentrations of TN, TP, CDOM and DOC for WRTs from 0.25 to 3.5 years in 0.25 year increments following Eq. (1):

$$MIC = \frac{tr_{lake}}{ret(frac)}, \quad (1)$$

where MIC is the mixed inflow concentration, tr_{lake} is the tracer concentration found in the lake and $ret(frac)$ is the retention fraction of the tracer at a known WRT. Retention models used in this study were based on the lake type as well as the geographical location of our lake. As there is not one model that can provide removal rates across all lakes we encourage the readers to find models related to their specific lake type. Thus, phosphorus equilibrium concentration in this study were found using Eq. (2) modified from Larsen and Mercier (1976) which describes phosphor retention in lakes with low productivity:

$$retP(frac) = 1 - \frac{1}{1 + \sqrt{WRT}}, \quad (2)$$

where $retP(frac)$ is the retention fraction of phosphorus and WRT is the water retention time in the lake.

Similarly, nitrate inflow concentration were estimated using a modified Danish nitrate removal model derived from Jensen et al. (1995) describing retention for shallow lakes with a short WRT (0-6 years) Eq. (3):

$$retN(frac) = \frac{59 \cdot WRT^{0.29}}{100}, \quad (3)$$

where $retN(frac)$ is the retention fraction of nitrate and WRT is the water retention time in the lake. The corresponding retention fractions removed at different WRT were related to the lake concentrations to estimate what the mixed inflow concentration must have been to produce the present lake concentration. The combined summer UV-radiation and bacterial degradation rates of DOC and CDOM in groundwater from the dominating catchment vegetation type of the lake (Madsen-Østerbye et al., 2017) were extrapolated to the rest of the year. This was done by relating the degradation rates to the mean monthly UV-index (DMI, 2015) while assuming a linear relationship between the UV-index and degradation rates. Thus, enabling us to estimate the specific removal of DOC and CDOM on a monthly basis related to the concentration measured in the lake at the time of sampling following Eq. (4):

$$tr_{lake} = tr_{lakepm} - tr_{lakepm} \cdot degra(frac) - tr_{lakepm} \cdot mf + tr_{inflow} \cdot mff, \quad (4)$$

Where tr_{lake} is the lake concentration in the specific month, tr_{lakepm} is the lake tracer concentration in the previous month, mff is the monthly flushing fraction ($mff = 1/WRT/12$), $degra(frac)$ is the degradation fraction

in present month related to UV-radiation and tr_{inflow} is the inflowing tracer concentration. Eq. 4 was solved for tr_{inflow} and calculated using the same WRTs as the nitrate and phosphorus models.”

Specific Comments

Line 111 - The PARAFAC analysis was described as a three - way modelling tool but it is not clear between what three things

This sentence has been moved from the materials and methods section to the introduction and now reads:

“PARAFAC analysis is a modelling tool which can separate multiple FDOM samples (emission and excitation matrices) into specific fluorescent components (Stedmon et al., 2003). “

Line 149 – What are the lambda values here? You should briefly comment on what this is

This sentence has been added to the materials and method section:

“The model also computes lambda values from the least squares regression measuring which tracers are most influential on the relative fractions of water originating from the groundwater well sites. Lambda values therefore quantifies how much the relative contribution from the sites change when one tracer is changed a unit while the rest of the tracers are kept constant.”

Line 153 – The text is describing the degradation of tracer concentrations in the previous sentence. Then it is followed by “This equilibrium estimations” ... Is this referring to equilibrium concentrations? Degradation rates?

This sentence has been removed.

Line 165 – The Vollenweider equation that you provide as equation 2 is not the form provided in the 1975 paper you cite and has been used erroneously. From a mass balance approach, the mass fraction that is exported ($C_{outflow} / C_{initial}$) = $1/(1+k*WRT)$

- If you have decided to replace the removal rate constant k with $WRT^{0.5}$, you need to justify this with further literature

- The general form of the equation that is presented in your paper looks to be the percent *expor*, rather than percent *retention*. You will have to use $1 - (1/(1+k*WRT))$ to get retention

- In fact, the form given in this manuscript shows that the percent retained increases with decreasing WRT.

Thank you for addressing this. Unfortunately, the wrong reference was added to the equation. This has been corrected and the equation has been modified to ease the reading of the material and methods section. The

sentence now reads:

“Retention models used in this study were based on the lake type as well as the geographical location of our lake. As there is not one model that can provide removal rates across all lakes we encourage the reader to find models related to the specific lake type. Thus, phosphorus equilibrium concentration in this study were found using Eq. (2) modified from Larsen and Mercier (1976) which describes phosphor retention in lakes with low productivity:

$$retP (frac) = 1 - \frac{1}{1+\sqrt{WRT}}, \quad (2)$$

where *retP* (frac) is the retention fraction of phosphorus and *WRT* is the water retention time of the lake.”

Line 169 – I find it difficult to see how equation 3 is applicable. The equation only applies for lakes that have a WRT of approximately 0 – 6.2 years (and I agree the study site fits inside this range). However, the source that was cite for this equation is in a Danish report published over twenty years ago and is not easily accessible. As an empirical equation, it is extremely difficult for the reader to understand the limitations, assumptions and the overall validity of this equation for this study (e.g. anyone trying to replicate your methods).

We have added further description regarding the choice of models used for N and P removal estimates. We believe that specific models used to described specific lakes should be chosen based on lake-type, WRT, catchment and climate. Following this we have added these sentences to the materials and methods section:

“Retention models used in this study were based on the lake type as well as the geographical location of our lake. As there is not one model that can provide removal rates across all lakes we encourage the reader to find models related to the specific lake type. Thus, phosphorus equilibrium concentration in this study were found using Eq. (2) modified from Larsen and Mercier (1976) which describes phosphor retention in lakes with low productivity.”

“Similarly, nitrate inflow concentrations were estimated using a modified Danish nitrate removal model derived from Jensen et al. (1995) describing retention for shallow lakes with short WRT 0-6 years Eq. (3):”

Line 178 – It is unclear if the authors developed equation 4 on their own or was from literature and thus should be clarified. Regardless, it appears that this equation is not internally consistent with respect to units. The monthly flushing rates are in units of 1/Time; thus the first two terms on the right hand side of the equation are in concentration units, whereas the last two term s are in concentration/time

We have changed the sentence to clarify that the monthly flushing units are not 1/time, but the fraction water removed from the lake each month. This enables the calculation of tr_{lake} (the lake tracer concentration) on a monthly basis.

We have changed the sentence and have pointed out that the second part of the equation is not 1/time but the fraction of water flushed from the lake:

“Thus, enabling us to estimate the specific removal of DOC and CDOM on a monthly basis related to the concentration measured in the lake at the time of sampling following Eq. (4):

$$tr_{lake} = tr_{lakepm} - tr_{lakepm} \cdot degra(frac) - tr_{lakepm} \cdot mf + tr_{inflow} \cdot mff, \quad (4)$$

Where tr_{lake} is the lake concentration in the specific month, tr_{lakepm} is the lake tracer concentration in the previous month, mff is the monthly flushing fraction ($mff = 1/WRT/12$), $degra(frac)$ is the degradation fraction in present month related to UV-radiation and tr_{inflow} is the inflowing tracer concentration. Eq. 4 was solved for tr_{inflow} and calculated using the same WRTs as the nitrate and phosphorus models.”

Line 180 – Is the peak degradation through UV - radiation determined linearly from the UV - time relationship? I.e. is the peak degradation of 100% assumed to coincide with the peak UV radiation?

There is a clear relationship between the seasons and degradation of CDOM and DOC (see “Photodegradation of DOC in a shallow prairie wetland: evidence from seasonal changes in DOC optical properties and chemical characteristics MARLEY J. WAISER* and RICHARD D. ROBERTS”). This seasonal change is related to the UV-radiation which is absorbed by DOC and CDOM in the top layer of the lake. In this study, we assume peak degradation with maximum UV-radiation.

Line 200 – “... combination of peaks N and T produced biological (Coble, 1996).” does not make sense.

What Ns and Ts are you talking about?

We have rewritten the sentence and added it to the introduction to explain that “peaks” are observed fluorescent peaks seen in a single excitation emission matrix. The sentence now reads:

“The fluorescent components can be biological produced proteins derived from bacteria or molecules from the degradation of terrestrial organic material. These components has previously has been found visually using a single excitation emission matrix and the observed fluorescent peaks (Coble, 1996).”

What biological is produced?

Peaks N and T are produced biologically. We have changed the following sentence to explain that the peaks are actually components that is produced biologically:

“Component C4 is similar to component 5 found in Stedmon et al. (2003) and is believed to be a combination of fluorescent labile materials named peak N and T which are produced biologically associated with DOM degradation (Coble, 1996; Stedmon and Markager, 2005b).”

Line 218 – The conclusion that the concentrations of TDN do not support a WRT value of over 2 years is wholly dependent on the model you choose. With the limited support provided for the model, this claim is not strong.

We have added further information regarding the nitrate model used as well as a note that models should be

based on the lake in question. The following sentences has been changed and added:

“Similarly, nitrate inflow concentration were estimated using a modified Danish nitrate removal model derived from Jensen et al. (1995) describing retention for shallow lakes with a short WRT (0-6 years) Eq. (3):”

“Retention models used in this study were based on the lake type as well as the geographical location of our lake. As there is not one model that can provide removal rates across all lakes we encourage the reader to find models related to the specific lake type.

Line 297 – I do not think the manuscript does an adequate job in convincing the reader that this method can capture uncommon or stochastic events. It did not seem like the samples taken were taken at different times of the year when extreme conditions occur. Is there literature that supports your claim that these environmental tracers capture these stochastic events? Even so, how would a single sampling campaign be used to extrapolate beyond the timeframe or snapshot of when you sampled?

We have changed the sentence to clarify what our intentions were:

“The multi-tracer approach enables the determination of discharge areas much more precisely and on a temporal scale related to the WRT of the lake (in this instance the previous 3 to 24 months). The model is therefore able to track uncommon events such as heavy precipitation where large amount of water with different tracer concentrations is discharged to the lake during a short period. These events are often difficult to track as seepage meters needs to be deployed in this period as well as in the right place.”

Line 320 – I’m not sure that claiming the analysis remaining generally unchanged by running the CATS model with a 10% perturbation of tracer concentrations is sufficient. The tracer concentrations in your supplementary material show that TP, TN and DOC all can vary by an entire order of magnitude between sites. Can you be certain that they also cannot fluctuate by an order of magnitude throughout the year?

The differences in tracer concentration between sites are related to the catchment area and the percolating groundwater. We know the concentration within the groundwater wells fluctuates as well – often related to dry periods followed by rain events. We have seasonal measurements of the DOC and CDOM concentrations in a stationary groundwater well which, if the editor wants it, can be used as a proxy for changes in tracer concentrations. Samples taken after periods of drought followed by heavy rain can be removed from the dataset to calculate the yearly fluctuation in concentration which can be incorporated into the sensitivity analysis instead of a +/-10 % change.

Technical Corrections

1. Line 17 – WRT has not been introduced yet, do not use abbreviation

This has been corrected

2. Line 17 – WRT was estimated to *be* 2 years

This has been corrected

3. Line 17 – Isolation of groundwater recharge areas *was*

This has been corrected

4. Line 18 - ... sites with *a* high degree of recharge *were*

This has been corrected

5. Line 29 - ... which to some *degree*

This has been corrected

6. Line 30 - ... the groundwater contributes nutrients

This has been corrected

7. Line 37 - ... *particularly* in small water bodies. *For example*

This has been corrected

8. Line 53 – 36 Cl

This has been corrected

9. Line 60 - You are talking about the nutrients (plural) so it should be “which *are* either remineralized when dying ...”. Also poorly phrased as nutrients (which is the subject of this sentence do not die)

This sentence has been completely rewritten

10. Line 66 – *fluorescent*

This has been corrected

11. Line 75 – use consistent style for lists throughout your paper. Either use (1) as you did in line 52 or keep to Also use a colon to introduce your lists, not a semicolon

This has been corrected throughout the manuscript

12. Line 84 – *Subularia aquatica*

The name has been changed to: “*Subularia aquatica*”

13. Line 90 – *preliminary work*

This has been corrected

14. Line 93 – within 5 - 45m of what?

The sentence has been changed to:

“A total of 30 groundwater samples were taken every 50 meters around the lake, within a distance of 5-45 m to the shore, in temporary groundwater wells at 1.25 meters of depth in February 2016”

15. Line 96 – *hermetically sealed*

This has been corrected

16. Line 100 – *quartz*

This has been corrected

17. Line 101 – $\delta^{18}\text{O}$ is a ratio, not a concentration, please fix this throughout your paper

This has been corrected and we generally use $\delta^{18}\text{O}$ ‰ to describe the isotope throughout the manuscript. Furthermore, we have added a sentence to the introduction explaining how $\delta^{18}\text{O}$ is presented:

“Precipitation-derived environmental tracers, such as the isotope $\delta^{18}\text{O}$ (reported in the Vienna-standard mean ocean water (SMOW) where $\delta_{\text{sample}} \text{‰} = 1000((R_{\text{sample}}/R_{\text{smow}})-1)$ and R is the $\delta^{18}\text{O}/\delta^{16}\text{O}$ ratio (Turner et al., 1987)), have been used to trace the interaction between ground and surface-water. As evaporation occurs in the surface water it becomes enriched with $\delta^{18}\text{O}$ producing a unique lake $\delta^{18}\text{O}/\delta^{16}\text{O}$ ratio which can be traced in the areas with groundwater recharge (Krabbenhoft et al., 1990).”

18. Line 107 – borate buffer *was*

This has been corrected

19. Line 117 – were subtracted ... *to remove*

This has been corrected

20. Line 117 is a run on sentence; separate is at “the data were then Raman normalized ...”

This has been corrected

21. Line 129 – *biologically inert*

This has been corrected

22. Line 134 is not a full sentence

This sentence has been complete rewritten

23. Line 137 – atmospheric *deposition*

This has been corrected

24. Line 139 – ... linear in features. What features are you talking about?

This sentence and paragraph has been completely rewritten and added to the introduction:

“As the concentrations of both conservative and non-conservative tracers in a groundwater fed lake correspond to the mixed concentrations of discharging groundwater, while taking degradation and atmospheric deposition into account, it is possible to utilize the Community Assembly via Trait Selection approach (CATS). This model has been used to predict the relative abundances of a set of species from measures of community-aggregated trait values (average leaf area, root length etc.) for all plant species at a site (Shiple, 2010; Shiple et al., 2006, 2011). The CATS model has three main parameters: (1) it models the probabilities (2) that maximize the entropy (3) based on a set of constraints (Laliberté and Shiple, 2011; Shiple et al., 2011). In reality, the model (1) predicts the relative abundances of species at a location from their (3) average traits values by (2) minimizing the number of species that explain the mean traits values. The maximum entropy (2) is the maximizing of “new knowledge gained”, related to plant communities this means that we are moving from “all species has the same relative abundances” to “a few species has a high relative abundance”. When applying the model to the lake-groundwater interaction we use the measured tracer concentrations at groundwater well sites around the lake as the individual plant species and the estimated mixed lake concentration before degradation took place as the community-aggregated trait values.”

25. Line 142 – What is the FD package?

It a R package which can be downloaded through the CRAN package repository. For more information please see <https://cloud.r-project.org>

26. Line 143 – In *the* present study

This has been corrected

27. Line 147 – The model outputs maximum entropy *probability* fractions

This has been corrected

