

Catchment tracers reveal discharge, recharge and sources of groundwater-borne pollutants in a novel lake modelling approach

General comments

I will give some more general comments in the following part while some further specific and technical aspects are listed below this section.

1. The introduction might need a bit more structure. There is a lack of background information especially on the functioning of the tracer methods and especially the model applied. It would be good to introduce the different tracers and their functioning in detection of groundwater-lake interactions in more detail. While the investigation of oxygen isotopes might be familiar to a lot of readers, the functions and applicability of the different DOC/DOC fractions as a tracer for groundwater interactions with lakes might be helpful to know. This is especially important for the development of the hypothesis/research question where the FDOM fraction plays an important role. Also, the reader might need more information about the meaning of WRTs in this context (elaborate this in more detail in Line 65).
Furthermore, the CATS model as the novelty in the study because it is applied for the first time in such a context, is not mentioned in the introduction at all. I feel that the quality of the manuscript would improve quite a bit if the authors try to step back from their own view and reflect the structure and the information given in the introduction from the point of the potential reader. Elaborate in more details the links between the different tracers, the WRT, the CATS model etc. Also, give a brief and general description of the study design and the methods applied in order to allow the reader to go for the details in the Material and Methods-section following.
2. Having said this, the authors start the method section by explaining groundwater sampling and sample/data analysis without introducing to the specific idea/concept/design of the study. This might be acceptable if the concept was already described in the introduction. However, as already mentioned above this is not the case which is why I strongly recommend adding the necessary information here.
Since the application of the CATS model is a crucial part of the study it should be already described in the introduction.
Also, since the reader until now is not aware of the concept of the study the headings "Groundwater recharge and areas of high recharge" (L132) is quite confusing since at first site such a differentiation does not make very much sense.
Similar to that the heading "Groundwater discharge and lake WRT" (L135) makes the reader wonder why these two aspects are looked at together.
3. About the CATS model:

- a. The model identifies those sites around the lake which contribute most significantly to the lake's tracer concentrations. From this, you conclude that at these sites most groundwater discharge takes place. However, if concentrations are high discharge volumes do not necessarily have to be large as well to influence the lake concentrations. For these kinds of approaches there are usually end-member-mixing models applied which I guess also the CATS model is of such a kind.
- b. L147: What are "entropy probability fractions of the groundwater..."
- c. L150f: "The model also predicts lambda values from the least squares regression explaining which tracers are most influential on the relative fractions of water originating from the groundwater well sites."

➔ I do not fully understand what that means. To me this implies that depending on the tracer looked at the model output differs, i. e. if you look at P there are different sites relevant for lake concentrations than compared to CDOM. And to me that totally makes sense because the concentrations may spatially vary a lot within the same or among different parameters. However, as already mentioned in 3a. the lake concentrations do not only depend on the concentrations but also on the volumes of groundwater discharge. But the discharge volume of a site is (to my understanding) completely independent from the parameter concentration which means that it is not possible to deduce discharge volumes/portions from parameter concentrations. By that the model does not give you any reliable output of relevant discharge sites.

- d. How is the water retention time implemented in the CATS model? I guess the CATS model initially didn't have such kind of parameter to be included in the algorithm.
- 4. About the results section: Provide more evidence for what you describe in the text by figures, or tables.
- 5. About the discussion: You start the section by phrasing three questions which are not all corresponding to the research questions phrased in the introduction. Try to be consistent here.

Specific comments

- L14 within 5-45 m **distance (?)** to the shore
- L17 What is WRT?
- L30 The sentence implies that nutrients such as P, N, and C are contaminants which is not necessarily true. See also Line 10 in the abstract.
- L45 The water does not leave the lake bottom but the lake via the lake bottom.
- L52 about environmental tracers: Besides atmospheric tracers: What about lithospheric or pedosphere tracers?

- L58 I do not understand the last part of the sentence: What does “groundwater of different ages and origins” mean in the context of percolating groundwater?
- L60ff In this paragraph you are talking about the fate of inflowing components. However, (although for many readers probably quite obvious) you do not explain why this is important for your study.
- L74 Measurements were done not only around the lake but also in the lake, i. e. of the lake water, right?
- L74f Why are the existing approaches/tracers not sufficient? Maybe add something like “... to overcome....” to the first sentence of that paragraph.
- What methods/tracers do you actually combine and develop towards a new approach? Be more precise and at least list them here.
- L75ff Here you come up with a maximum entropy model which was not mentioned before. Is that the novel approach you are talking about before? So far, the reader might have considered the application of the tracers more or less described above to be the novel approach in this study.
- L77f What would be the benefit of a combined investigation of conservative and non-conservative tracers? And again: Which tracers will you use for this investigation?
- L78f Why are you interested in WRT? Where is the connection to the groundwater-lake interactions?
- L86 “to bypass water”: Is that surface runoff that is collected in the drainage channel?
- L93 Does “5-45 m” relate to the distance to the shore?
- L111 What exactly are the three steps of PARAFAC modelling?
- L111 What information do the “specific fluorescent components” provide? Be more specific here (and maybe introduce this background information on FDOM already in the introduction)
- L112 What is the “inner filter effect”?
- L113 “...which were measured spectrophotometrically ...” → does this refer to CDOM or FDOM and if it refers to CDOM it implies that the samples from each site were measured twice for CDOM (see L99f). Why was that?
- L117 How can the data be “Raman normalized” when the “Raman scattering” was “removed” from the data before?
- L129f “Changes in” This sentence was probably supposed to explain the concept of using oxygen isotopes as tracers for groundwater-lake interaction but in fact it does not. The authors should rework and complement the description of the use of O₂ isotopes (again, this general introduction of the approach should probably go to the introduction section of the manuscript).

- L130 “However, deviations from lake $\delta^{18}\text{O}$ concentration was not observed in areas with groundwater recharge due a sampling depth of 1.25 m close to the lake.” → I do not understand this sentence. $\delta^{18}\text{O}$ values in groundwater similar to lake water values indicate lake water infiltration into the aquifer which is why the sentence to me seems to be a circular reference. Also, I am not sure if the last part of the sentence refers to the sampling depth or the distance to the lake shore.
- L131 “Groundwater well sites which clustered with the lake were considered as being groundwater recharge sites and were removed for the later estimations of groundwater discharge sites.” → What does this sentence mean?
- L132f If I understand the meaning of the sentence and its link to the o_2 isotope section above correctly I would recommend modifying it as follows:
- “Hierarchical **Euclidean** clustering was also done for the fluorescence components from the PARAFAC modelling.”
- L133 This is not a complete sentence. It does not have a verb. I assume that the authors want to express that they applied two different tracers in the same way in order to validate their findings.
- L136ff This applies only in exclusively groundwater-fed lakes which should be indicated in this sentence.
- L138ff “Probabilities” of what?
- What are the “constraints” and the “linear features”? If possible try to explain these very abstract terms and relations a bit more. If this is not possible I would consider removing this sentence.
- L140f I assume that “species” are “plant species”?
- L142 At least give information on the meaning of the abbreviation of the R package mentioned.
- L143ff For which parameters/tracers have you run the CATS model? $\delta^{18}\text{O}_2$, N, P, CDOM, FDOM, DOC? And was the model run for each parameter separately or for all parameters simultaneously? In the first case: Would you not have to go for a more detailed discussion of the outcomes of the different model runs?
- L145ff Isn’t it more like the model identifies those sites along the lake which contribute most to the lake?
- L153 Is “equilibrium” the tracer concentration in the lake which would be the same as MIC in Eq. 1?
- L173ff “The combined summer UV-radiation and bacterial degradation rates of DOC and CDOM in groundwater from the dominating catchment vegetation type of the lake (MadsenØsterbye et al., 2017) were extrapolated to the rest of the year.”

- a. What does the vegetation type of the lake have to do with UV- and microbial degradation of C-fractions?
 - b. Why was it necessary to extrapolate to the rest of the year? To get the specific removal rates for month of the sampling?
- L174f “This was done by relating the rates to the mean monthly UV index (DMI, 2015) while assuming a linear relationship between the UV-index and degradation rates.” → Is there are literature reference which proves that this a legitimate way of doing this?
- L182f “Eq. 4 was solved **in relation** to tr_{inflow} and calculated using the same WRTs as the nitrate and phosphorus models.” → Do you mean “... was solved **for** tr_{inflow} ...”?
- L191 The split-half analysis modelling has never been mentioned before. What is that and what does it do?
- L192 “Component C1 was similar to previously **ly** found humic-like material...” → does this relate to material of this study site? Which one? Terrestrial, aquatic?
- L192ff “The component absorbs in the UV-C region which has low intensities at the ground surface (Diffey, 2002) and ~~are~~ **is** therefore expected to be photo-resistant (Ishii and Boyer, 2012).”
- a. Is “ground surface” = lake bottom?
 - b. I am not sure why you can conclude that the material is photo-resistant from the fact that UV-C has low intensities at the lake bottom.
- L199 “Component C3 may be an intermediate product since concentration changes even in open oceans”
- a. Intermediate product from what?
 - b. What do changes in concentrations in the open ocean imply?
- L200 “Component C4 was found to be similar to one in Stedmon et al. (2003) and ~~are~~ **is** believed to be a combination of peaks N and T produced biologically...”
- a. Please explain “peaks N and T produced biological”. Besides the fact that the sentence doesn’t seem to make sense grammatically it is also not clear what the peaks are and why they are able to biologically produce an FDOM component. Furthermore, T is not explained.
- L211f “Component C4 was chosen as a proxy for groundwater recharge as **the** concentration of the C4 component increase with biological activity and time in the groundwater.”
- a. How do you know that the concentration of C4 increases with biological activity and time in the groundwater? Since you have neither investigated biological activity nor groundwater residence times this information has to be from some literature. Please cite.

- b. I do not fully understand the conclusion, i.e. why you can conclude that C4 is suitable as a groundwater tracer because its concentrations increase with biological activity? Increased biological activities can be found in many environments and at very small scales (e.g., also in the lake sediments).
- L216 “Tracer concentrations **of the lake water** narrowed down the possible WRT of the lake.”
- L216ff “Equilibrium tracer concentrations of DOC, CDOM, TDP and TDN for water retention times between 0.25 and 3.5 years in 0.25 increments revealed that concentrations of TDN in the catchment are not high enough to support WRT-values over 2 years.”
- ➔ Does that mean that you calculated WRTs with each of the parameters individually and then picked the one most plausible? What is the range of results you got from those calculations? Show in table or graph and discuss why the same results differ (they shouldn't differ very much, right?).
- L220f “Groundwater discharge areas were found using the CATS model ~~combined with~~ **applied to (?)** nutrient concentrations and dissolved organic matter fractions estimated in relation to WRTs between 0.25 and 2 years.”
- L221f “The estimated phosphorus concentrations ranged from 46 to 80 $\mu\text{g P l}^{-1}$...”
- a. Does that refer to MIC in Eq. 1?
- b. I assume the given concentration range refers to the time increments for which you run the model. Is that correct?
- L224 Explain $A_{\text{CDOM}}(340)$ and be consistent in using the same way/units for this parameter throughout the whole manuscript.
- L228f “The model identified the sites 1, 9, 11, 13 and 14 as the possible groundwater discharge sites for all WRTs (Fig. 5).” ➔ Figure 5 does not show that. It shows modelling results for the sites mentioned but this does not show the results of the other sites.
- L236ff Add table or figure with lambda values
- L251 “... thus facilitating....” ➔ does that refer to the drainage channels? Should be “which facilitate ...” or something?
- L254ff “Sites resembling the fluorescence found in the lake will indicate flowing water, while a difference in components between lake and **groundwater** sites will indicate a lower flow rate where there is sufficient time for a significant modification of the components representing the DOM pool.”
- a. What is meant by flowing water? What is meant by differing between “flowing water” and “sites with lower flow rates”? Please be more specific and refer to the scientific correct terms.

- b. Which DOM pool do you refer to hear? Be more specific to facilitate easy understanding by the reader.
- L257ff I still do not necessarily see the link between microbial activity and the use of this component as indicator for groundwater discharge since microbial activity is not at all a process restricted to groundwater or aquifers.
- L264f “CDOM generally showed much lower absorbance at groundwater recharge sites than in the lake making it less suitable for estimating recharge areas.” → Maybe I missed it but I haven’t found this information in the results section.
- L267 “While component C1 was not particularly useful for estimating groundwater recharge, it could potentially be useful to estimate discharge sites.”
- This sentence sounds very vague (a lot of “could” “potentially” “estimate”). Consider rephrasing.
 - I do not follow the argumentation that C1 is a discharge indicator. Isn’t photo-resistance irrelevant in groundwater environments?
 - Also, when the component is photo-resistant and resistant to microbial degradation which other factors lead to a degradation which can be related to increased groundwater discharge at sites 9 and 11?
- L282 “...hinting that the lake is influenced by other water sources.” → What other sources could that be since the lake is solely groundwater fed? Besides atmospheric deposition there shouldn’t be any other options.
- L289f “Seepage meter measurements from this area showed both discharging and recharging of groundwater (Solvang, 2016).” → Which area are you referring to? From the sentence before it could be any.
- L291f “...indicating an influence of newly precipitated water or discharge and recharge of groundwater.” → Do the results indicate discharge or recharge? Indicating both at the same time is not possible.
- L298 Please elaborate how your approach is able to capture the dynamics you describe when you have only a single sampling date.
- L296 “because soils are generally wet at this time of year (Sand-Jensen and Lindegaard, 2004).”
- I recommend saying “saturated” instead of wet.
 - What does that imply? That samples are more representative? But that doesn’t go along with the findings that concentrations change during the year.
- L310 Did you show inter-annual DOC concentrations in the results? If yes refer to Figure, Table. If not provide evidence for the data you refer to.

L346f “Furthermore, huge reductions would occur for TP and TN, with a decrease of 82-96 % if diverting water from the eastern shore in contrast to the southern shore with a modelled decrease of 4-18 %.” → What do the 4-18% relate to?

Technical comments

L17 ... was estimated to **be** 2 years.

L17 ...Isolation of groundwater recharge areas **was** based on...

L18 ... sites with a high degree... **were** isolated... (I would also consider saying “identified” instead of “isolated”)

L36 I recommend substituting “changes” by “differences”

L37 ... **particularly** in small water...

L19 I recommend exchanging “Although” by “However”

L25 I recommend exchanging “in relation to lake water...” by “comparing to lake water...”

L30 “... groundwater contributes nutrients....” → skip “with”

L44 “... which **quantify**...”

L46 Exchange “although” by “However”

L50 “...to determine ~~the~~ groundwater input and influence.”

L59 “the fate **is** well known”

L60 “...which **are** either remineralized...”

L98 “...hermetically**ly** closed...”

L119 “...corrected for **the** inner filter effect.”

L122 “This allow**s for the** detection of components insufficient**ly** represented....”

L123 Reference to software (probably R) is missing

L124ff “A contour map showing the measured FDOM concentrations **s** in groundwater **was** plotted in ArcMap (ArcMap 10.4.1, ESRI, U.S.A) using the inverse distance weighted (IDW) function”

L144f “... the average trait value **of** all species...”

- L175ff “Thus, enabling estimations of the specific removal on a monthly basis related to the concentration measured in the lake at the sampling time following Eq. (4)” → This is not a complete sentence. Please add a verb.
- L192 “Component C1 was similar to previously found humic-like material...”
- L192ff “The component absorbs in the UV-C region which has low intensities at the ground surface (Diffey, 2002) and ~~are~~ **is** therefore expected to be photo-resistant (Ishii and Boyer, 2012).”
- L197f “The component absorbs in the UV-A region and ~~are~~ **is** susceptible to both microbial and photochemical degradation...”
- L208 “...with a low**est** value of ~~only~~ 0.1 R.U....”
- L209 “Component**s** C1, C2, and C3 had...”
- L210 “Concentrations of C4 **were** generally higher....”
- L253 “While $\delta^{18}\text{O}$ worked well as a general groundwater recharge estimator, *it does not indicate which sites deliver more water.*” → about the last part of the sentence: Consider rephrasing including “quantitative information”

After this, I have given up to comment on each of the technical errors.