Response to Reviewers

Time lags of nitrate, chloride and tritium assessed by Dynamic Groundwater Flow Tracking in a Lowland Landscape

https://doi.org/10.5194/hess-2019-552

OVERALL RESPONSE: First we would like to thank the reviewers for again taking the time to review our manuscript and providing us with extensive and constructive reviews. Based on the reviewer's comments, we were able to significantly improve the manuscript.

The large changes to the manuscript are:

- The Introduction was rewritten.
- In the Methods section we improved the introduction of and reasoning behind the Scenario's that were applied.
- Several Figures were improved following the reviewers suggestions.

We will discuss the points raised by both reviewers step-wise below.

Anonymous Referee #1 Report #2

General comments:

This manuscript is coming together. There has been a definite improvement since the last revision. In particular the discussion section has gained a lot in terms of structure and readability. The addition of more detailed explanations and the more in-depth discussion makes the overall message and conclusions much clearer.
Still, I also have to mention the fact that reading the introduction I was not expecting a significant improvement of the revised paper. The introduction still lacks clarity and structure. For someone reading the text for the first time it is quite confusing (this gets much harder to realize if you have dealt with the paper yourself for such a long period of time).
So please consider my questions and comments below and give the first part of the manuscript another iteration in terms of structure and language. Shorter, more concise sentences in the right order and connected logically could be the way forward.
Concerning the research I would appreciate a clearer distinction between the methods the authors are applying and the recommendations they give. For example, the authors write that they derive backwards TTDs with a hydrologic model and a particle tracking routine. But do they also use those backward TTDs to convolve the input time series (or do they use forward TTDs for that)? The differentiation is often lacking throughout the text.
For me, this manuscript is on the right track but needs some further clarification.
RESPONSE: We would like to thank the reviewer for another constructive review. We are glad that the reviewer feels the paper is coming together.

Following the reviewers suggestion, we have considerably rewritten and improved the Introduction of the manuscript. We have clarified the methods that were used. We have further improved the different chapters and the figures following the reviewer's suggestions. All comments are addressed one by one below.

Specific comments:

Abstract

- Line 23: Which 'initial' model run? You did not mention it before.

RESPONSE: Agreed and changed.
Revised text: *"However, combining only TTDs and inputs underestimated the time lag "*

- Line 26-27: What is the difference between the 'long hydrological travel times' in line 26 and 'a long Mean Travel Time (MTT)' in line 27?

RESPONSE: Agreed this is not completely clear. We changed the 'long hydrological travel times' to also better reflect that the unsaturated zone adds to the travel time in the saturated zone.
Revised text: *"a thick unsaturated zone adding a certain travel time,"*

- Line 28: 'high' application areas? Also, the sentence is cut off after 'from'.

RESPONSE: Agreed. The sentence was not cut off but combined with the next point: "further away from-, or … close to- the stream or drainage network." We have rewritten this sentence.
Revised text: *"4) areas with a high application of nitrogen (agricultural fields) being located further away from the stream or drainage network, or 5)…"*

- Line 29: Please specify: Do you observe this lag only if the nitrate attenuating processes are located EXCLUSIVELY near the stream? What if nitrate attenuating processes are located everywhere – also near the stream or drainage network?

RESPONSE: Non exclusively, but higher close to the stream than in the rest of the catchment so that a larger amount of nitrate is removed from younger flowpaths (mainly originating close to the stream). This leads to the outflow of nitrate being dominated by older flowpaths. We have rewritten this line to better capture this.
Revised text: *"or 5) a higher presence of nitrate attenuating processes close to the stream or drainage network compared to the rest of the catchment. "*

Introduction

- Line 44-50: This paragraph is a good example for the language, structure and style issues that can be found throughout the introduction: First, flow paths are mentioned. In the next sentence these flow paths are referred to regarding their connection to nitrate concentrations. However, in the same sentence further controls are added (travel time and land use). In the next sentence it is explained why travel time and flow 'route' influence nitrate concentrations (but nothing about land use).
- It would be good to bring all these arguments into a comprehensive order and group them: Why are flow paths important for nitrate concentrations? Because they control travel times. Why are travel times important for nitrate concentrations? Because they have a large influence on biogeochemical reactions. Why is land use important? And so on…

RESPONSE: We agree with the reviewer that these paragraphs contained some repetition and were not clear enough to a first-time reader. We have rewritten large parts of the introduction to make the text more easy to read and clear.

Revised text*: e.g.: "Land-use determines the timing and quantity of nitrate input as well as its spatial distribution (Boumans et al., 2008). For example, the input of nutrients is higher on fertilized agricultural fields than in forested areas. Nitrate leaches to the groundwater (Boumans et al., 2008; Wang et al., 2012) on locations with different land uses and distances to the stream, from where it is transported towards the streams through fast and slow groundwater flow paths. These flow paths reach certain depths, cross different geological formations taking a certain travel time from infiltration to exfiltration (Broers and van Geer, 2005; Howden et al., 2011b; van der Velde et al., 2010). Groundwater flow paths spatially connect infiltration areas and in-stream seepage zones (e.g. Ali et al., 2014; Birkel et al., 2015; McGuire and McDonnell, 2010). Groundwater flow paths also temporally connect changes in solute leaching for example due to land-use changes with a response in stream water concentrations that may occur many years later (e.g. Van Meter and Basu, 2017). Both flow paths and travel times also influence hydrochemical processes, as they determine which media are passed and the time that is available for (biogeo)chemical reactions. Nitrate concentrations may for instance decrease by denitrification when passing organic or pyrite-rich layers (e.g. Zhang et al., 2013). Consequently, all water particles may carry different nitrate concentrations depending on their place and time of infiltration, their flow paths and their travel times along their flow paths. Because groundwater flow path contributions to stream discharge are dynamic throughout the year, with activation/deactivation and changes in outflow locations, the delivery of nitrate from groundwater to surface waters also varies in time (Rozemeijer and Broers, 2007). Groundwater flow paths and travel times are thus an important control on the mean and variance of nitrate concentrations in groundwater and streams both in time and space (e.g. Musolff et al., 2017).*

- Further comments: Flow paths are not only the route that water particles travel through the subsoil (since surface flow paths also exist).

RESPONSE: Indeed, water flows through both subsurface and surface flow paths. We did not correctly capture this in Line 44 and have changed this sentence. We did not include surface flow paths in our study as we focus on groundwater flow paths which are more important for nitrate.

***Revised text**: "Groundwater flow paths are the routes that water particles travel through the subsoil,"*

- Why 'flow route', I thought you just introduced it as 'flow path'?

RESPONSE:Agreed and changed.
***Revised text**: "Both the flow paths and travel times influence hydrochemical processes, "*

- Line 62: Which approach? You did not describe an approach.

RESPONSE: We mean the approach of Kaandorp et al., 2018. Rewritten.
***Revised text**: "Using a groundwater model and particle tracking they calculated dynamic travel time distributions (TTDs) and showed how groundwater flow path contributions in these catchments vary in time. From this, they discussed differences in mixing processes between young and old groundwater in the streams with time. In this follow-up paper we used these previously calculated dynamic travel time distributions and the accompanying spatially explicit groundwater flow paths to carry inputs of tritium, chloride and nitrate towards the stream and compare simulated with observed concentrations in the Dutch Springendalse Beek stream from 1969 until present."*

- Line 66: 'while including the dynamic nature of catchments' - Details please. What does that mean? You already wrote that you will 'combine these dynamic travel time distributions with application rates…'! This is confusing and probably mixed up. Very hard to follow for the reader in any case.

RESPONSE: Agreed that this can be confusing. Removed this part of the sentence as it's described in the rest of the text.

- Line 85: 'and of different'?

RESPONSE: This is a typo, should be 'differences'. Corrected.
***Revised text**: "and of differences in the spatial input patterns "*

- Line 88: 'as a way forward'? In how far is the exploration of the effect of different processes on breakthrough patterns 'a way forward' in model calibration?

RESPONSE: Agreed that this is not clear. We have rewritten the sentence.
***Revised text**: "modelling of groundwater-fed catchments"*

Methods

- Line 107: 'The streambed of the stream…'?

RESPONSE: Agreed that this does not fit in this paragraph. The information is not important for the manuscript and we decided to remove this sentence.

- Line 130: Better write 'exhibit' or 'show' instead of 'include'.

***Revised text**: "and show for instance seasonality…"*

- Line 148: Are there 'backward' travel times? I know there are backward TTDs, but backward TTs are the same as forward TTs, no?

RESPONSE: Agreed and changed.

***Revised text**: "Groundwater travel times (TTs), representing the age of the water that contributes to streamflow…"*

- Line 159: '… showed TTDs with exponential shapes…'. It's not just one TTD, it's a set of dynamic TTDs, no?

RESPONSE:The reviewer is right, we have corrected the sentence.
***Revised text**: "Using this model approach, Kaandorp et al. (2018) showed travel time distributions with an exponential- like shape. "*

- Line 161: Introducing Figure 3 before Figure 2?

RESPONSE: Thank you for pointing this out, this happened due to shifting of text and figures.
***Revised text**: "Figure 2"*

- Line 176: But you are reporting that 20% of the water in the creek has TTs of less than 1 year. How can you be sure if you haven't looked at anything shorter than 1 month? This could make up a large proportion of the outflowing water and increase your young water percentages significantly.

RESPONSE: The modelled discharge was compared with measured discharge (Kaandorp et al., 2018). We are not 'missing' significant amounts of water in the modelled discharge. Part of the water with travel times <1 month is labelled as having a travel time of 1 month. However, the reviewer is right that short peaks in discharge that were missed by the model (including e.g. overland flow) and have a travel time <1 month are not considered. Though it is not a large proportion of the overall outflow from the groundwater-fed catchment.
***Revised text**: "Several processes were not included in the modelling approach such as overland flow and re-infiltration of seeped water. Overland flow is not an important flow route in the catchment on a yearly basis and nitrate concentrations in overland flow are low due to little interaction with the soil. This manuscript thus focusses on longer groundwater TTs and time scales (>1 month)."*

- Line 216: I don't understand. Combining the input with the calculated dynamic TTDs or using your model? I thought you said dynamic TTDs but then you mention the model and assigning the input to particles.

RESPONSE: We calculated TTDs with the groundwater flow model + particle tracking. As we then know the age of the water that contributes to discharge at every moment in time, we can convolute the water quality input series to reconstruct stream water quality values. The water quality input is assigned to particles (post-processing after the particle tracking calculation based on the starting location of every particle (i.e. natural areas or agricultural fields). We refer to this combination of TTD model + 'tracking of water quality as the 'water quality model'. We have rewritten this paragraph to better describe the method that was used.
***Revised text**: "The calculated dynamic TTDs were combined with the input time series of solutes to create a water quality model. For this…"*

"In a similar way as the construction of the TTDs (Kaandorp et al., 2018a), particles that contributed to stream discharge were combined for each month and their concentrations weighted based on their volumes to simulate the concentrations in the stream. "

- Line 219: What is the constant concentration of natural vegetation?

RESPONSE: The input concentrations are given in paragraph 2.5, we added a reference to this paragraph.

- Line 223: What do you mean exactly by 'within the months after their initial start'?

RESPONSE: This sentence makes it sound more complicated than it is, the model corrects for the removal of water and tritium due to evapotranspiration. We removed this part of the sentence.

- Line 224-226: This is unclear to me: What about evapoconcentration of these solutes? What happens when particles that are assigned with nitrate evaporate out of the system?

RESPONSE: The input concentrations of nitrate and chloride are based on samples from the upper groundwater. This concentration in these time series are thus already leached beyond the influence of crops and vegetation and need no further correction.

- Line 229: How does the omission of chemical processes isolate input time series and groundwater travel time effects on stream concentrations? Travel time will always have effects on stream concentration, input time series (?) too. What do you mean? Please add more details to your explanation.

RESPONSE: Agreed that this formulated adds unnecessary complexity. Basically, we wanted to point out that the calculated concentrations are thus only based on these two factors. Sentence rewritten.
***Revised text**: "In the initial water quality model run, no chemical processes such as denitrification were implemented. Thus, in this model run the calculated stream solute concentrations are only based on the input time series and groundwater travel time. "*

- Line 230: What are 'catchment mechanisms'?

RESPONSE: We mean the hydrological and hydrochemical processes. We have rewritten the sentence.
***Revised text**: "instead we aimed at understanding the hydrological and hydrochemical processes "*

- Line 240: How did the agricultural fields receive chloride and nitrate following the input time series AND calculated backward TTDs? Did you deconvolute the stream signal?

RESPONSE: Agreed, this is a textual mistake We have rewritten some sentences in the paragraph.
***Revised text**: "The initial run of the water quality model was only based on the constructed solute input time series and the dynamic TTDs derived from the calibrated groundwater flow model. In this model run, the spatial distribution of solute input (agricultural fields and natural areas) was based on the land-use map of the year 2007 (Figure 1). It was not further calibrated for solute transport, but instead we explored…"*

- Line 270: Suddenly Figure 6 pops up (before even Figure 2 was introduced).

RESPONSE: Agreed and removed.

Results

- Line 341-342: Please provide more details on how this agrees with the findings of Kaandorp et al. (2018).

RESPONSE: Agreed, we added more detail to this sentence.
***Revised text**: "Such a difference between the up- and downstream part of the catchment was also found by Kaandorp et al. (2018a), who reported that discharge as well as the contribution of different flow paths are more dynamic in the downstream part of the catchment."*

- Line 350-351: And what did you make of this finding that the original model underestimates the travel times? Do you have some suggestions on how to fix the original model? Or some thoughts on why this underestimation happens in the first place?

RESPONSE: The reviewer is right that this requires some more discussion. As discussed later in the text time lags are not directly coupled with (mean) travel times. Much text later in the manuscript (Paragraph 4.3) is focussed on the fit of the model and on the different reasons for time lags. We therefore decided to remove the sentence here. Focus in this paragraph is on the trend reversal.

- Line 375: What are physical explanations for the occurrence of your different scenarios? It would be beneficial to explain this in your methods section when you introduce the scenarios. For example, scenario 3 could be caused by a larger volume of the unsaturated zone or by a smaller amount of precipitation flowing through that volume.

RESPONSE: The scenarios are explaned in section 2.7 There something was mentioned also for Set 2, but we have now also indicated which way the paremeter should go (larger/smaller).
***Revised text**: "Increasing the ages of groundwater implies an increase in mean travel time (MTT), which could result from a larger aquifer thickness or porosity, smaller amount of groundwater recharge or a change in drainage density (Broers, 2004; Duffy and Lee, 1992; Raats, 1978; van Ommen, 1986)."*

- Line 394: The nitrate peak shifted in which direction to 1985?

RESPONSE: We have clarified this in the text.
***Revised text**: "the nitrate peak shifted back in time to 1985 "*

- Line 406: Why is that the case? I would assume that the longer flowpaths are the deeper flowpaths. Therefore the scenario where all nitrate that travels lower than 0.5 to 15 m is removed by a pyrite layer should have a lighter tail, no?

RESPONSE: The reviewer is correct that the scenario where nitrate is removed from deeper (and older) flow paths would have a lighter tail compared to the initial run. In the text we compared with the zero-order run, in which all nitrate is removed leading to lower concentrations on all flow paths. It is indeed better to compare with the initial run, we have rewritten the sentence and added some discussion on this to section 4.1.
***Revised text**: "This resulted in a rather steady decrease in nitrate concentrations in time, preserving the shape of the 1980s increase and subsequent decrease (Figure 7)."*

Discussion

- Line 414: Did you compute any efficiency measures (NSE, KGE)?

RESPONSE: The aim of the study is not to validate and further improve the model, but to use the model to gain a better understanding of the processes that may induce time lags in solute breakthrough. We could add RSME's or a similar number, but we feel this would not add much to the visual comparison that is done now.

- Line 461-462: If the mean travel time is long enough or the input decrease is gentle enough you will find that the peak of the resulting convolved output time series is shifted (disregarding the fact that you use an exponential distribution with an initial maximum value). So it's not that surprising after all. Oh, I just see that you describe exactly that in the next paragraph, so nevermind!

RESPONSE: Yes, the reviewer is correct! For many this is a difficult concept to understand, as it may feel counter-intuitive. In our last iteration we therefore added an extensive discussion about this to the manuscript (the next paragraph the reviewer refers to).

- Line 480: Better use 'longer' instead of 'higher' in combination with time.
- Line 480: In lower 'peak' concentrations – not in lower concentrations in general (or are you referring specifically to nitrate concentrations that experience degradation?).

RESPONSE: Thank you, we changed the sentence following the suggestions.
***Revised text**: "A longer MTT typically results in lower peak concentrations…"*

- Line 481: 'rate' not 'rage'.

RESPONSE: Haha, yes. Thanks for pointing this out.
***Revised text**: "rate"*

- Line 518-520: So the GCA changes because in certain periods in certain areas incoming precipitation is only turned into ET instead of ET and runoff? Would be good to mention why the area of the GCA changes in time.

RESPONSE: The GCA could change because at a certain location there is no groundwater recharge (e.g. due to ET). But more importantly, the GCA can change due to changes in groundwater flow paths based on wetness-conditions. This is discussed in the following sentences and Figure 10.
***Revised text**: ""*

- Line 571-572: This is unclear to me. Why would an overestimation of MTTs by the model cause higher tritium concentrations? Does the decay not compensate for that?

RESPONSE: This depends on the MTT, if the overestimation means that the model calculates that more water originates from the 1960-1970s when tritium input was high, it could lead to higher calculated concentrations. For instance, say water from 1965 with 1000 TU would be around 45 TU at this day. Water originating pre-1960s would indeed have very low tritium concentrations due to decay. We have clarified this in the text.
***Revised text**: "On the other hand, an overestimation of the mean water age by the model could also cause higher modelled tritium concentrations, if this means that the contribution of 1960s water is overestimated "*

- Line 540: This is the first time you mention 'forward' TTDs. So far you have only mentioned 'backward' TTDs. Why the change?
- Line 621, 631-635: You are writing about the usefulness of forward TTDs here. Yet, in your figures you are showing backwards TTDs. Why don't you also show the forward TTDs that you determined with your model? Or do you want to say that backward TTDs are just as useful (if so, how)?

RESPONSE: We used backward TTDs because we started from the point of the stream: the discharge consists of water of different ages which is described by the backward TTD. In our analysis, we explored the implications of spatial differences, and the setting of nitrate-contributing areas was found to be important for the breakthrough patterns in the catchment outflow.
L540 discussed when a time lag occurs, and Line 621 discussed how insight into the travel times flowing from a specific location towards the stream/outlet may be used in a vulnerability assessment. When looking into management options that are available, the concept of forward TTDs is more appropriate as it can be applied on specific locations in a catchment. So it depends on the question of view of a catchment manager: 1) what is the effect of input at this specific location (field -> stream) or 2) where are the inputs coming from that I measure at the stream/outlet (stream -> field)?

Figures:

- Figure 3: The MTT and MdTT in panel e) belong to which of the CDFs? Summer, winter, overall?

RESPONSE: The overall MTT and MdTT. We have added this to the caption.

***Revised text**: "and the overall Median and Mean TTs."*

- Figure 4: Put more information on the individual panels in the figure caption. Why not add the input curves for panels a) and b) too?

RESPONSE: We added some more information to the caption. We added the input curves for tritium.

***Revised text: "**Figure 4. Measurements, agricultural input time series and initial model results based on the TTDs from Kaandorp, et al. (2018) and the solute input time series in Figure 3. On the left tritium (a),*

chloride (c) and nitrate (e) for the upstream part of the catchment, on the right tritium (b), chloride (d) and nitrate (f) for the total catchment (downstream). Note that tritium samples were only available for the upstream part of the catchment (panel a). ”

- Figure 6: The legend is wrong. It says 4a) twice.

RESPONSE: Thank you, fixed.

Anonymous Referee #3 Report #1

General comments:

The authors obviously put efforts in revising the manuscript. I am still convinced about its value: A unique chance to bring together modelled travel times at catchment scale with observed output concentration changes of a conservative (Chloride) and a reactive (Nitrate) constituent. This touches the open issue of reasons for observed time lags for nitrate pollution and the potential buildup of legacies in soil and groundwater. Here, the travel time site can be largely fixed allowing for a detailed discussion on time lag reasons. Moreover this study can bridge between the spatially implicit travel time approach and the nitrate source location within the catchment with clear management implication. All this is somehow there in the paper but neither well introduced and referenced nor well discussed. The study builds partly on a scenario analysis that is, from my point of view, so simple that it can be left out. Adding a fixed time lag to all water ages to then state in the results and discussion that there is a fixed time lag in the model output does not make a story. Here, I strongly recommend to focus the scenarios on something with added value such as the spatial source arrangement and leave it to a verbal discussion on the observed Chloride and Nitrate behavior vs. modelled travel time that allows for the same conclusions. Or to enhance the scenarios with something more sophisticated than added time lags or multiplied travel times. Suggestions on that are given below in the detailed comments. However, this may not be needed for a good story.

RESPONSE: First, we thank the reviewer for another useful review. We feel that the manuscript has made good progress thanks to the previous and the current comments of the reviewer.

We have rewritten large parts of the Introduction to make the scope and aims more clear and focus better on the novelties in the manuscript. Following the reviewer's comments, we have taken a critical look at the methods and especially the scenario's that we applied. Parts of the methods section were rewritten to improve the introduction of the scenario's. We have rewritten parts of the methods to discussion to address some of the reviewer's comments, but disagree that the current scenario's do not add value to the discussion in the paper. We have decided to keep the scenario's in the manuscript, but have tried to better include them in the overall story of the manuscript.

All comments by the reviewer are addressed in detail below.

Detailed comments

Introduction:

- I still miss an introduction to the issue of spatial source arrangement and travel times.

RESPONSE: Agreed, we have rewritten parts of the introduction and have taken this comment into account.

Revised text: *"In catchments, groundwater flow paths thus provide the hydrologic connection between infiltration areas and seepage zones in streams (e.g. Ali et al., 2014; Birkel et al., 2015; McGuire and McDonnell, 2010) and therefore control the reaction of streams to the spatial distribution of and changes in land-use. "*

- L79ff: "Short" is a quite relative adjective. Short compared to what?

RESPONSE: Agreed and removed "short".

- Is this time lag of nitrate different from the mean TT derived from the conservative tracers? If yes, this should be mentioned here. Why else this may be "interestingly" if there is nothing

that deviates from other or previous knowledge. Is this a result of this study or can be referenced? This is a tricky point as you seem to need to state a result already to justify your methodology.

RESPONSE: For the upstream of the catchment there is indeed a difference between the time lag of nitrate and the time lag of chloride. We have rewritten the sentence to reflect this. Furthermore we agree that it is tricky that we have to mention this result here, but we feel this is needed to fully understand the aims of the paper.

Revised text: *"Interestingly, measurements show a time lag between the decrease in application and the peak concentration in the upstream of the Springendalse Beek that does not coincide for chloride and nitrate. The trend reversal of nitrate appears several years later. This time lag, defined as the time between the peak in solute application and the observed peak in the stream, was further studied using the model."*

Methods

- L142f: Can you spend one more sentence on the basis of recharge estimation? This is for most modellers a critical issue. Later in the text you mention ET and this would be the point to describe what you actually did.

RESPONSE: We added some more information about the unsaturated zone model.

Revised text*: "Flow through the unsaturated zone was modelled using the MetaSWAP model for a seasonal representation of the groundwater recharge (De Lange et al., 2014; van Walsum and Groenendijk, 2008; van Walsum and Veldhuizen, 2011). This unsaturated zone model consists of soil-column models and uses soil physical relationships to calculate water content profiles and water balances. It includes calculation of actual evaporation and transpiration based on land-use and vegetation type and considers evaporation and transpiration from groundwater."*

- L190: "seemed" sounds vague. Do they differ? There are statistical tests for that.

RESPONSE: Agreed, yes the relationship changes in time, with a step around 1997. For the purpose of our study this relatively simple correction by using two factors is acceptable. Note that concentrations after 1990 are very low (Figure 3).

Revised text*: "Because the relation between the values measured at the two stations changes in time, we use two factors:"*

- L210: You may give the % in brackets to make fully clear that this is a minor part of the catchment only.

RESPONSE: Good suggestion, we have added this for the agricultural field on which agricultural activities were stopped. For the small areas we do not have a number as the information is not available at this detail (yearly changes, small areas).

Revised text*: "an agricultural field of approximately 7.5 ha (~2%)"*

- L223: So there is ET from the groundwater? That is not clear in the model description above.

RESPONSE: See comment on L142f.

- L226: Evaporation or evapotranspiration?

RESPONSE: Both, rewritten.

Revised text*: "thus there is no need to further account for evapo(transpi)ration for these solutes."*

- L243ff: I am still not fully convinced by that time lag. Why assuming a simple time shift? Effect will just by the addition of 5 years to all ages in the stream, right? Assuming an unsaturated TTD would make more sense for me. With the often used exponential forward TTD for unsaturated zones you don't even need an additional parameter than the mean.
- L253ff: Same as above. This just adds a constant time delay to each particle. This effect is implemented in models such as ELEMENT (van Meter et al). Slow mineralization can be represented by a simple first order reaction that just need one reaction rate constant as a parameter and you will create something more meaningful than a constant time lag.

RESPONSE: The reason we do these scenario's is to give the reader insights into the possible parameters that affect a time lag. Here we assume only piston flow through the unsaturated zone, as

that would induce a time lag, as opposed to an exponential TTD. We could implement more detailed processes, such as exponential TTDs or first or higher order reactions, but this is beyond the scope of the manuscript. We purposely use simple examples to show the effect that different changes can have on a time lag, also compared to other processes.

L260ff: This is not really an uncertainty assessment. Based on your modelling approach and the preceding papers: Is there any uncertainty assessment that you may use here? Just based on Darcy's law or Haitjema (1995): What would be a reasonable error in the recharge and what in the aquifer volume (depth, porosity)? This is something you may use.

RESPONSE: Agreed, uncertainty is not the right word to use for what we wanted to say. We merely want to explore the effect of changes in the saturated zone travel time, and use a very simple scenario with a high increase of TTs. We chose this to create a result with clear differences. The discussion section contains further discussion on realistic uncertainties in TTs.
***Revised text**: "Next, we explored the effect of the saturated zone travel time by applying a multiplication factor of 5 on all the calculated travel times of all flow paths. "*

- L294: I am not convinced here. To what I know, a first order reaction would change the age distribution of the remaining nitrate.

RESPONSE: The timing of the peak shouldn't change when the denitrification takes place equally along all flow paths. With zero or first order, denitrification doesn't distinguish between older or newer nitrate.

Results

- L330: The described behavior in the fig. 4 is hard to see. Esp. the peak times. I there a way to average the data to better see the long-term behavior within the inter-annual variation?

RESPONSE: We have added a rolling mean through the data.
***Revised text**: See new Figure 4.*

- L334: Would it make sense to state the resulting time lag in this chapter already?

RESPONSE: Yes, agreed that the description of the measurements in this paragraph can be clearer. We have rewritten several sentences in the paragraph.
***Revised text**: e.g. "Thus, for the upstream catchment there seems to be a time lag between the peak input and the following trend reversal that is several years longer than observed in the downstream catchment."*

- L346: The chloride input peak was around that time as well (1984). How can that fast peak be with a modelled median travel time of 4 and a mean travel time of 11 years? Nothing you need to comment on here - it just puzzles me. The difference between mean or median and first reaction to an input is obviously may be something different.

RESPONSE: Indeed, the median/mean travel time does not directly lead to a time lag in the response. This is extensively discussed in Paragraph 4.1.

- L348: Very old water may contribute tritium free water as well?

RESPONSE: That's true! Although it is not a major contributor in this catchment we added it to the sentence for completeness.
***Revised text**: "or an underestimation of the amount of younger or pre-1950s water (contributing water with low tritium concentrations)"*

- L361ff: This is largely as trivial as the scenario setup. I don't see the added value here of simulating that at all. This could be done in a verbal description only. Or consider to make the scenarios more interesting as suggested above.

RESPONSE: See response to L243.

Discussion

- L427: This is not a good chapter name. What processes?

RESPONSE: Agreed this is vague. This chapter is tied with the sections '2.7. Exploration of the model behaviour under different scenarios' and '3.4. Exploration of model behaviour: Effects on the breakthrough of tritium, chloride and nitrate'. We changed the name of the paragraph to:
Revised text: *"Changes in breakthrough patterns of tritium, chloride and nitrate"*

- L428ff: This introduction to the unsaturated zone effects partly repeats what was written in further above in 2.7. Remove redundancies and rather hint to the text above.

RESPONSE: Agreed. We have removed all redundancies and rewritten and shortened this paragraph.
Revised text: *"The model exploration showed that unsaturated zones lead to a shift in time of the solute breakthrough as it takes time for water to percolate from the surface towards the groundwater (Figure 5; Table 3). This is purely a hydrological effect (scenario 1a). Biochemical processes in the unsaturated zone can also create time lags in the breakthrough of nitrate (scenario 1b). This not only lowers the height of the nitrate peak, but also leads to a time lag and elevated nitrate levels over a longer period of time. "*

The initial model neglected hydrological transport time in the unsaturated zone, although it takes time for water to flow from the surface to the groundwater table. This creates a time delay in the order of months to multiple years (Green et al., 2018; Sprenger et al., 2016) and even decades (Wang et al., 2012), depending on the depth of the water table and soil characteristics. In our model exploration we applied a time delay of 5 years for all particles in our model, assuming that piston flow occurs through an unsaturated zone with an equal thickness everywhere in the catchment area. In reality, flow through the unsaturated zone is much more complicated due to e.g. macropores, but this was outside of the scope of the current study. Note that the value of 5 years is not chosen to represent unsaturated zone travel times in this catchment as realistically as possible, but this rather high value only serves to clearly show the effect of such process on the time lag between input and stream concentration.

- The following text is all mainly stating the obvious which, from my point of view, is a result of the questionable scenario implementation.

RESPONSE: We have tried to sharpen paragraph 4.1 where needed. But overall feel that the discussion on the different scenario's adds value to the manuscript. The Discussion section was already considerably rewritten and improved in previous review iterations.

- L461f: This is unclearly phrased. How can a time lag occur before something?

RESPONSE: Agreed and rephrased.
Revised text: *"Surprisingly, a time lag occurred between peak input and the trend reversal, "*

- L510ff: The exploration of this aspect of spatial source arrangement and the introduction of new results in the discussion section is not justified. It is not clear why you come up with contributing areas here and where this is leading to.

RESPONSE: In the first sentence of the paragraph we state that we found that the spatial distribution of processes and inputs are an important factor. Therefore, in section 4.2 we describe the catchment using the GCA and RCA. These are not new results, but a different way of describing the catchment and spatial processes, which followed from the results and discussion in 4.1.
text: *"In the previous paragraph, we have seen that the spatial distribution of inputs and processes is an important factor in the breakthrough of agricultural solutes. The concept of contributing areas can be used as a different way of describing the catchment and spatial processes and their effect on stream chemistry."*

- L602f: This is a crucial point that should be focused on most in this chapter. You have the unique chance to compare a conservative tracer with a reactive constituent. From the differences in the model to the observed behavior you can discuss what reasons for time delay are most likely. This cannot be done in one sentence while the rest of chapter's text seems to be too long.

- L612ff: This exploration of TT-location-notion is very valuable but, again, not well introduced in the introduction.

RESPONSE: We have rewritten parts of the introduction to better reflect the spatial aspects.

Revised text: *"In catchments, groundwater flow paths thus provide the hydrologic connection between infiltration areas and seepage zones in streams (e.g. Ali et al., 2014; Birkel et al., 2015; McGuire and McDonnell, 2010) and therefore control the reaction of streams to the spatial distribution of and changes in land-use."*

"Consequently, all water particles may carry different nitrate concentrations depending on their place and time of infiltration,"

"application of dynamic TTDs for solute transport calculation, taking into account also the spatial aspects of flow paths and land-use."

"to explore the controls on time lags in the breakthrough of agricultural nitrate, such as … differences in the spatial input patterns."