Response to Reviewers

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

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OVERALL RESPONSE: First we would like to thank the reviewers for 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:

- Improved the manuscript by focusing on readability.
- Rewritten the Abstract and Conclusions.
- Improved the Introduction of the manuscript to make the aims more prominent. It is now much clearer from the beginning on why a model exploration was done.
- Added more explanation of the groundwater model and method that was used. Including discussion on the limitations.
- Large parts of the Discussion were rewritten. It is now much easier to follow and understand. We added some Figure panels and removed some Figures/Tables.
- Improved the paragraphs on the RCA and GCA to link it better with the rest of the manuscript.

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

Anonymous Referee #1 Report #2

General comments:

General comments:
The authors responded in detail to the comments written down in the review file and I appreciate the effort they put into implementing many of the suggested changes. However, none of the 57 comments I made in the annotated manuscript were (directly) addressed which makes it hard for me to fully evaluate the revised version. I would highly recommend to take these comments also into consideration.
Therefore, I included the annotated manuscript from the original submission again.
In addition I prepared a new annotated manuscript with comments on the revised version.
Also, I copied the comments from both annotated manuscripts to the end of this file.
The manuscript has already improved since the initial submission, still language and sentence structure would benefit from another round of careful checks.
The discussion needs more clarity and precision in explaining the processes, concepts, methods and results. The structure is also not that clear in certain places.
I was not able to follow some of the conclusions because there is not enough explanation on how they were drawn. For example, I understand that there will be an immediate decrease in solutes in the stream if we assume that the catchment TTD is exponential (this is trivial). Now why exactly does this immediate reduction not occur if the MTT is very large – this does not make sense to me – there should still be an immediate decrease, just a slower one. So there must be another process involved that turns the exponential TTD into a different kind of TTD (like, e.g., an exponential piston-flow TTD). It could be explained by making the difference between catchment and groundwater TTD more prominent (an exponential GW-TTD preceded by a constant time delay in the unsaturated zone is basically creating an overall exponential-piston flow TTD).
In the end I am still wondering about the exact results and conclusions that this study provides.
And although, as I said in the beginning, the manuscript has improved since the last round of reviews, in my opinion it requires another iteration.

RESPONSE: We would like to thank the reviewers for taking the time to provide us with another extended review.

In the previous iteration we did not notice that a supplement pdf file with annotations was provided and therefore only made revisions based on the published Referee Comment. We sincerely apologize for this! We have processed the comments from the previous pdf supplement as well as the newly supplied pdf file.

Overall, we have improved the manuscript by focusing on readability and clarity of explanations and discussions, as recommended by the reviewer. This included rewriting several paragraphs in the Discussion on the processes and concepts. The explanations should be easier to follow now, especially the part on the effect of a long MTT and slow decrease of input. We feel that the structure of the study, from the aims to the conclusions is much clearer now.

We have reviewed the comments in all the files that were provided by the reviewer, have made changes and answer them separately below.

Comments in the annotated manuscript of the original submission

• I do not understand the title. There is no specific focus or relation to 'aged streams' in the paper. The term is not even mentioned or explained anywhere. So why is this part of your title?

RESPONSE: Agreed and removed.
Revised text: "Time lags of nitrate, chloride and tritium in streams assessed by Dynamic Groundwater Flow Tracking in a lowland landscape"

• time series?

RESPONSE: Agreed, this was changed in the previous iteration.

• This last sentence makes me wonder what the actual novelty of this study is. You should definitely explain better what you mean by 'groundwater distributes water in time and space' and 'groundwater makes it possible for different waters to mix'.

RESPONSE: Agreed and changed in previous iteration.

• Mediums are actually persons who talk to ghosts. Media are substances that water passes through.

RESPONSE: Agreed and changed.
Revised text: *"as they determine which media are passed"*

• Maybe add some more details on the scenarios here?
RESPONSE: Agreed, this part of the introduction has been rewritten.

• Saalian

RESPONSE: Agreed and changed.
Revised text: *"Saalian"*

• was

RESPONSE: Agreed and changed.
Revised text: *"was"*

• Does 'the upstream' exist as a word?

RESPONSE: Agreed and changed in previous iteration.
Revised text: *"the upstream catchment"*

• Sampling surface and groundwater quality

RESPONSE: We did not only sample for water quality, but we collected measurement data from various sources.

• What does that mean exactly?

RESPONSE: Agreed and changed in previous iteration.
Revised text: *"First, historical data from 1969 onwards of chloride and nitrate concentrations was obtained from earlier studies "*

• m^3/m^3

RESPONSE: Agreed and changed.
Revised text: "*m^3/m^3"*

• Are you discussing the drawbacks of this method anywhere later in the manuscript?
RESPONSE: We discussed the drawbacks to some extent, but scattered through the manuscript. We have gathered this all in one paragraph.

Revised text: *"The modelling assumptions and simplifications that were made have some drawbacks. As we started the particles at the water table, we effectively neglected the travel time through the unsaturated zone (e.g. Green et al., 2018; Sprenger et al., 2016; Wang et al., 2012), but this layer was generally thin in the study area (mostly <1 m) and is partly bypassed by preferential flow. Because particles were released monthly at the centre of each model cell, short travel times (<1 month) were not included at all and particles had to travel at least 12.5 m before reaching a next cell, causing further uncertainty to short travel times. Several processes were not included in the modelling approach such as overland flow and re-infiltration of seeped water. Because of these limitations, this manuscript focusses on longer groundwater TTs and time scales. Chemical processes in the unsaturated zone concerning nitrate were included in constructing the solute input curves. ."*

• What are strong and weak sinks? Why were the particles stopped there? Where they removed? What happened to the other 50%?
RESPONSE: These are terms used in groundwater modelling. A weak sink is a sink that does not take all the water that enters a model cell. We have further clarified the text and added an extra reference.
Revised text: *"Particles were stopped at sinks, such as wells, rivers or drains (Visser et al. 2009), when the fraction of discharge to the sink was larger than 50% of the total inflow to the cell (see also Kaandorp et al., 2018a)."*

• Are these subcatchment outlets?

RESPONSE: No, these are the end points of the particles itself, which can be anywhere in a catchment (seepage). They are collected for the whole area of a (sub)catchment.

• Can you estimate the TTs through this layer?

RESPONSE: We cannot make an estimate with our model, but generally travel times through the unsaturated zone is in the order of 1 meter per year in the Netherlands.

• How was this included?
RESPONSE: This is explained in section 2.5.

• Curve sounds awkward.
RESPONSE: Agreed. Changed to 'time series' throughout the manuscript.
Revised text: *"time series"*

• time-invariant?
RESPONSE: This sentence was changed in previous iteration.
Revised text: *"In principal, a series of tritium measurements in streams can be used to derive (ground)water age distributions"*

• Any ideas on why that could be?
RESPONSE: By using average values of the closest stations we aimed to construct the best possible 3H curve. In general with time the differences between Groningen, Koblenz and Emmerich became smaller and the overall 3H concentration lower. To account for this, we used the factors described in the manuscript, which we feel is the best method possible here.

• Why don't you show any of these dynamic TTDs (individually not like in Figure 3)?
RESPONSE: We have added a panel with the TTDs to Figure 3, so that the reader can see the shape of the TTD.
Revised text: *See addition to Figure 3.*

• What are possible implications?
RESPONSE: That this hydrological travel time through the unsaturated zone is only an approximation. In reality it can be long or shorter, with its own time-variability.

• You applied this factor where/when? During the model run? After the model run?
• You should achieve this by changing the model setup (different aquifer thickness, porosity , etc.) not by applying a factor.
RESPONSE: The factor was applied after the groundwater model and particle tracking calculations. Of course it would be even better to construct separate groundwater models for each scenario and repeat the particle tracking calculations. This would however require much more work and computational time. Here we only explore the effect of increased travel times.

• What delay? Some more years, months, days?
RESPONSE: We have rephrased these sentences in the revised version.
Revised text: "We explored the effect of a more delayed decrease in the solute input curve after 1985, which could for instance be caused by slightly different local farming practices compared to the regional input curves. For this, we added a linear decrease in time from the peak in 1985 (Figure 6a)."

• If the peak was kept in 1985, how did you achieve the delayed input function? Did you change the skewness, the variance?
RESPONSE: We added a linear decrease from the peak, as shown in Figure 6a. All values before 1985 were kept the same. See also textual change in previous reply.

• Does this not directly correspond to the fractions of agricultural land in the subcatchments? If not, why? Vegetation?
RESPONSE: Yes, we already added extra information in the revised manuscript.
Revised text: "because a slightly larger part of the streams capture zone in the downstream part of the catchment is used for agriculture"

• larger
RESPONSE: Sentence was removed in the revised manuscript.

• Why 'although'? The shorter the time series, the smaller the chance to not capture certain events...
RESPONSE: Sentence was removed in the revised manuscript.

• repetitive
RESPONSE: This paragraph was removed in the revised manuscript.

• superimposed
RESPONSE: Thank you for pointing this out.
Revised text: "superimposed".

• How was that done exactly? Was it added at the end? Was it done in the model? If so, how?
RESPONSE: We have added aa sentence to explain this to the Methods.
Revised text: "For this, the calculated travel times at the moment of discharge to the stream of all individual particles was multiplied by this factor during postprocessing."

• delete 'a'
• by
Revised text: "When all travel times were increased 5-fold the chloride and nitrate peaks shifted by approximately 10 years".

• Made it longer or thicker or both (added weight to the tail)?
RESPONSE: Both, part of the peak is removed and discharged later (mass-balanced).

Revised text: "increased the length and size of the tail of the peak (Figure 5b and c). ".

• no apostrophe (TTDs not TTD's)
RESPONSE: Changed in revised manuscript.
Revised text: "TTDs "

• The agricultural input to the GW? To the streams?
RESPONSE: To the stream, this was indeed to clear.
Revised text: "When fields are further away, the agricultural input to the stream is distributed more over time".

• Does that mean that nitrate was not removed at all for all other particles flowing only through shallower layers?
RESPONSE: Yes, that is indeed the case. We chose this approach as it was the most viable for use in our model and particle tracking results. We think that this is a good approach to demonstrate the effect of denitrification in deeper layers on the breakthrough pattern of nitrate.

• Is that because you assume that nitrate is not removed under unsaturated conditions?
RESPONSE: We have clarified this in the manuscript by naming the delay in this scenario a 'hydrological delay'.
Revised text: "unsaturated zone hydrological delay "

• nor
Revised text: "Areas that are neither groundwater- nor runoff contributing areas ".

• ...and THUS removing this field only...
RESPONSE: Agreed and changed.
Revised text: "Therefore, in this example the groundwater contribution of the field close to the stream stops in the dry period and removing this field thus only affects stream nitrate concentrations during the wet period".

• Amount?
RESPONSE: Agreed and changed.
Revised text: ". The time series of discharge and solutes showed that the upstream area has less seasonal variation in the amount of discharge than the downstream catchment"

• Why? Maybe discuss it in more detail.
RESPONSE: We have rewritten this paragraph in the revised manuscript, the sentence is now followed by discussion.

• the majority of the yearly variation
RESPONSE: Agreed and changed.
Revised text: ", while the drained downstream part of the catchment causes the majority of the seasonal variation in stream concentrations."

• Could you derive it by combining tritium and NO3 measurements (transport through the unsaturated zone would cause more removal - lower peak concentrations - than transport through the saturated zone)?
RESPONSE: Agreed, but this part has been rewritten and this statement has been removed from the revised manuscript.

• Rephrase. The nitrate concentrations cannot be lower than the measurements, because you measured the measurements.
RESPONSE: Agreed and changed.

Revised text: "Denitrification does not seem to occur substantially in the upstream part of the study area as the modelled nitrate concentrations are generally already lower than the measurements."

• How does this promote denitrification?
RESPONSE: Denitrification can be promoted here by low redox conditions in the organic rich topsoil.

• What about changes to your denitrification calculations to improve model performance? I think this analysis falls a little short...
RESPONSE: Agreed, we have changed the overall structure of the manuscript. It is now more clear, that we use the model to explore the effect of different parameters and processes, and do not aim to have a perfectly fitted model. In rewriting, the section that is referred to here has been removed (although part of the text has been used in other sections).

• Why is it not possible? You should try it to provide a more complete analysis.
RESPONSE: In our model set-up, it was not possible to do this. However, this sentence has been removed in the revised manuscript.

• Can you quantify the uncertainty caused by the grid cell size?
RESPONSE: We have thought about this, but have not come up with a good method, yet. However, this paragraph has been removed from the revised manuscript.

• arguably
Revised text: "arguably"

• This does not correspond to any other shape in this figure.
• Are these urban areas?
• What is this? The hydrological base?
• I would label the individual panels.
RESPONSE: We have improved the Figure following suggestions from various reviewers. Individual panels are now labeled.

• I do not see a difference in the scale of the x-axes.
• fraction of area
RESPONSE: This should of course be the y-axes. Thanks for pointing out, we have changed the caption. We have also changed 'amount' to 'fraction'.
Revised text: "Figure 6. Panel a and b show the effect of two scenarios with changes in the nitrate input curve. Note the difference in scale of the y-axis between the left and right panels. Panels c and d show the effect of spatial changes in land-use on both chloride (c) and nitrate (d): only agriculture inside of a 200 m strip around the stream (Buffer scenario 1), and only agriculture outside of the same buffer strip (Buffer scenario 2). In both scenarios agricultural parts have 50% agriculture and 50% nature, so that the total fraction of fields is approximately equal to that in the real catchment."

<u>Comments in the annotated manuscript of the revised version</u>

• I still do not understand the title. There is still no specific focus or relation to 'aged streams' in the paper. The term is not even mentioned or explained anywhere. So why is this part of your title? I would remove it.
RESPONSE: Agreed and removed.
***Revised text:** "Time lags of nitrate, chloride and tritium in streams assessed by Dynamic Groundwater Flow Tracking in a lowland landscape"*

• limited to what?

RESPONSE: Agreed and changed.
Revised text: *"occurred after a time lag of 5-10 years"*

• does it depend on the travel time in the unsaturated zone or on the slow release of organic N or on the travel time in the unsaturated zone only if it includes slow release of organic N? This is not clear to me...
• not clear either
• Which processes?
• This list could use more explanation. How does the time lag change in response to the listed properties?
RESPONSE: Agreed, we have rewritten this part of the abstract.
Revised text: *"A time lag of several years and up to decades can occur due to 1) a thick unsaturated zone with long hydrological travel times, 2) persistent organic matter with a slow release of N in the unsaturated zone, 3) a long Mean Travel Time (MTT) compared to the rate of the reduction in nitrogen application, 4) high application areas (agricultural fields) being located further away from, or 5) the presence of nitrate attenuating processes close to the stream or drainage network."*

• You mean the location of delivery or the timing of delivery or the amount of delivery?
RESPONSE: All three actually, so the general delivery. When flow paths change, the location of delivery is also changed. With that, also the timing is changed, as some flow paths will fall dry or extent their pathway. Because of these changes, also the total amount of delivered nitrate is changed.

• ?
RESPONSE: Agreed, this sentence was not clear. Changed accordingly.
Revised text: ***"****In our study, tritium and chloride were included as water tracers. Tritium because it is part of the actual water molecule, chloride because it was considered to be a conservative tracer of manure and fertilizers when it passes through the aquifer. "*

• agricultural?
Revised text: *", the distance between agricultural fields and the stream and the mean travel time of the system"*

• Backward TTDs, to be precise.
RESPONSE: Agreed and added.
Revised text: ***"****Backward Travel Time Distributions"*

• Input curve sounds wrong. Input time series would be better.
RESPONSE: Changed throughout the manuscript.

• What do you mean by 'adding curves to the flow paths'?
RESPONSE: We mean that we combine the input curves with the flowpaths to calculate water quality.
Revised text: ***"****By combining the input curves of tritium, chloride and nitrate with the calculated flow paths it is possible to calculate the water quality of the catchment's streams."*

• 'principally' is not equal to 'in principle'
Revised text: ***"****In principle"*

• Do you mean time invariant? Also, do you mean backwards TTDs?
RESPONSE: No we do not mean time invariant: the dynamic time-variant TTDs are not changed for the Base case (initial run). We do mean backwards TTDs. We have rewritten the sentence.
Revised text: ***"****and the calculated backward TTDs"*

• What does that mean? A short explanation of the nitrate transformation factor method would be nice.

RESPONSE: We have further clarified this in the text.
Revised text: *"and to represent (part of) the nitrate transformation processes in the unsaturated zone we used a nitrate transformation factor of 0.85. This factor represents an average retention (e.g. denitrification) in the unsaturated zone and the value used here corresponds with Dutch data for soils with average water tables around 1 m depth (Steenvoorden et al., 1997; van den Brink et al., 2008)."*

• although
Revised text: *"although"*

• While
Revised text: *"while"*

• This is not a result of your modeling study. Just a description of your input.
• Again, this is not a result of your modeling study but rather a description of the measurements you use. It would be a results section if you described how your model was or was not able to reproduce certain parts of the measured time series.
RESPONSE: Agreed, however we feel that it is a result of our study, as we collected and combined different datasets which have not been analyzed in this way. How we did that is described in the Methods, here we present the results. In addition, it also improves the readability and structure of the manuscript to have this as the first paragraphs of the result section.

• This should be named figure 3.
RESPONSE: Some shifting of paragraphs has been done and the figures are now correctly numbered in the order of mentioning in text.

• You mean the input of solutes to the stream?
RESPONSE: Yes, that is correct.
Revised text: ***"****The input of solutes towards the stream was distributed more in time"*

• 'also' used twice
RESPONSE: Thank you for pointing out. We removed one 'also'.

• This entire section needs some careful language/sentence structure editing. It is sometimes hard to understand what you want to express. I recommend more consistency in your terminology - always refer to the same processes, solutes, methods, concepts with the exact same name.
RESPONSE: We have edited paragraph 4.1 to improve readability.

• higher/older/greater
• Be more specific, please.
Revised text: ***"****The scenario in which the TTD was multiplied by a factor 5 lowered the nitrate peak because the greater age of the discharging groundwater"*

• This is one of the sentences that are quite imprecise in their terminology. What change in what input? Which stream concentrations? What reduction rates in which input?
RESPONSE: Agreed, not clear. We have removed this sentence as it was not needed.

• Is that addition necessary?
RESPONSE: Agreed and removed.

• If the TTD is exponential there should never be a time lag in the arrival of the peak (because the maximum of each exponential TTD is always at the beginning). How exactly do you explain the observed time lag? It must come from something else in the model structure.
• Why? This does not make sense to me? Please explain this behavior.
• This is where it becomes interesting and therefore it needs more explanation/analysis.

RESPONSE: We have carefully rewritten these paragraphs to give a better explanation of what we found and the processes that are involved. What is happening is that the contribution of seeping groundwater with long travel times and still increasing concentrations exceeds the decrease of concentration in the seeping groundwater with short travel times. In other words, the input is still higher than the output, and thus the output keeps increasing.

• Why do you spell out Travel Time distribution and Mean Travel Time and reintroduce abbreviations (MTTs) here?
RESPONSE: Agreed and removed.

• But you are not looking at catchments with an exponential TTD. You are looking at a catchment with an exponential groundwater TTD. Adding a lag for the transport through the unsaturated zones makes the total catchment TTD become a piston flow-exponential TTD.
RESPONSE: We have clarified this in the text.
Revised text: *"This analysis shows that in the general case of a catchment with an exponential groundwater TTD the effect of measures on the solute input towards groundwater can be expected to show directly…"*

• Isn't this a different effect from the one you describe above? You say that if denitrification occurs predominantly close to the stream the time lag would increase. But is this not more a function of where the nitrate input takes place? Closer to the stream or farther away? I can imagine that the amount of damping is also influenced by these scenarios.
RESPONSE: In the end it depends on the concentrations that are assigned to a groundwater flow paths with a specific age. Either the input can be focused on younger or older flow paths, or the denitrification can take place on older or younger flow paths. We have clarified this further in the text.
Revised text: *"Such a spatial effect was also shown by the model scenario in "*

• This should be expressed more precisely and with more details:
    • Longer MTTs in the unsaturated zone cause a larger time lag...
    • Which combinations of MTT and solute input reduction cause which dynamics in the time lag?
    • ...and so on...
RESPONSE: This paragraph was removed in rewriting. Part was reused for the conclusions.

• I do not understand this new definition. '...where water entering the groundwater-flow system is discharged' Is this water entering or being discharged? Maybe a figure would help.
RESPONSE: This is a citation from Barlow et al. 2018. The water enters the groundwater system on one side, and discharge towards the surface (water) at the other side.

• I do not understand your point here. How are the two contributing areas different?
RESPONSE: We have rewritten this paragraph to make it clearer and make a better connection to the earlier parts of the manuscript.

• models
Revised text: *"models"*

• Why not call it 'recharge area' if you're using this term to explain it?
RESPONSE: We agree that this added confusion, thus removed.

• How about calling it subsurface flow contributing area and overland (or surface) flow contributing area? In the end your groundwater contributing area is also contributing to the runoff in the stream.
RESPONSE: These names would not capture what we are trying to say. Best is to think of the particle tracking that was used: particles have a starting point where groundwater is recharged, and an ending point where discharge is generated from seeping groundwater. In a steady state situation this would be clear, representing runoff generating areas (seepage locations) and infiltration areas (recharge areas). However, adding

seasonality and a varying drainage network add much complexity which we try to capture in the terms and figures introduced in this paragraph.

• nor
Revised text: *"nor"*

• Which consequences does this have on your model results? What about particles that reinfiltrate after seeping out?
RESPONSE: We did not include reinfiltration in the model but tried to include it in this figure, as obviously it occurs in reality. We have added more discussion on limitations of the model to the Methods section.

• Hey, but above you said that the lag to the peak is extended for some scenarios. How does that fit together?
• Again, you should be more precise. It is a trivial result (and not surprising at all) that there is an immediate reduction if the catchment TTD is exponential. But were you even looking at that or were you also exploring the lag caused by the unsaturated zone?
• To me this is not a convincing argument, because you give too little information on the specific processes that cause your conclusions.
RESPONSE: Agreed, the wording in this paragraph was poorly chosen, only repeated earlier findings and it didn't contribute much to the manuscript. We have decided to remove this paragraph.

• I would like to see a summary on how exactly each of these parameters influences the time lag. (Not just a statement that they can influence the time lag).
RESPONSE: We have rewritten this part of the Conclusions to summarize how the parameters influence the time lag.

• Again, if you expect an exponential TTD then you always expect an immediate reduction.
RESPONSE: We removed these sentences in rewriting the Conclusions.

• You didn't show them in enough detail or with enough explanation.
RESPONSE: We removed this sentence in rewriting the Conclusions.

• What about the blue line on panel c? Should also be mentioned in the captions.
RESPONSE: Agreed and added.
Revised text*: "Figure 5. The effect on tritium (a), chloride (b) and nitrate (c) in the upstream part of the catchment of a scenario with a 5-year delay due to an unsaturated zone, a scenario where all travel times where increased by a factor 5 and a scenario where part of the input of N was delayed"*

Anonymous Referee #3 Report #1

General comments:

General comment

Dear authors,

this is an interesting explorative study, highly relevant for managing diffuse nitrate pollutions at catchment scale. It is one of the rare examples implementing nitrate transport at catchment scale using the lumped travel time distributions. This is fits very well the scope of HESS. While I like the general idea of the manuscript, I see several issues in the way the authors justify, implement and discuss their research. Note that I was not reviewer in the first round which is surely not easy for the authors as I may raise issues that have not been asked for earlier. I tried to not be influenced by the first round of review.

Here are my major points (that are also addressed in more detail in the specific comments below): The authors are not very clear in the introduction of the manuscript that this is mainly an explorative study not aiming at fitting the observed concentrations. Readers, same as me, may expect that "fitting". I thus would like to see the explorative character to be made clear earlier on. The authors stress the role of dynamic TTDs but mostly discuss and validate the long-term average behavior of concentrations. The intra-annual variability is discussed later on but not well embedded in the introduction and result sections. I found some justification of scenarios poor. Here I think the beauty of this exploratory approach lies in the interplay of those scenario components in a realistic and justified range to come up with kind of a ranking of factors influencing the observed input-output time lag. The discussion of runoff contributing area and groundwater contributing area not well embedded in the overall story.

RESPONSE: First we would like to thank the reviewer for the kind words and taking the time to review our manuscript. We have used the Reviewers comments to significantly improve the manuscript.

As suggested by the reviewer, we rewrote parts of the Introduction of the manuscript to make it clear why a model exploration was done instead of 'fitting' on the measurements. We also made this clearer throughout the manuscript. To make the choice of scenarios more logical, we introduce the observed time lag in the measurements earlier on in the manuscript and shifted some paragraphs between Methods and the Results. We have rewritten some sentences on the 'dynamics' and added a Figure showing the dynamic TTDs that were calculated. Furthermore, we have improved the paragraphs on the RCA and GCA to link it better with the rest of the manuscript.

All comments by the reviewer are addressed in detail below.

Specific comments

Abstract
L17: It should be chloride and nitrate "concentrations", right?
RESPONSE: Indeed, we added "concentrations".
Revised text: *"for which we collected long time series of chloride and nitrate concentrations (1969-2018). "*

L25: "absence of these processes" has an unclear meaning as e.g. 2) (L23-24) cannot be absent. Consider rewording.
RESPONSE: Agreed, we have rewritten this part of the abstract.

***Revised** text: "An exploration of the model behaviour under different scenarios was done to study the observed time lag between the peak in nitrogen input and the following trend reversal of nitrate in the stream. A time lag of several years and up to decades can occur due to …"*

I miss some key numbers in the abstract. Eg. on mean travel time in groundwater and in the unsat. zone. I can imagine this makes the abstract a bit stronger and easier to digest for the readers.
RESPONSE: Agreed and more information added.
***Revised text**: e.g. "trend reversal in the stream occurred after a time lag of 5-10 years" and "A time lag of several years and up to decades can however occur"*

Introduction

L39f: Do you mean nitrate concentration dynamic in time or in space or the general concentration levels? You could also use "mean and variance" or moments of the probability distribution. Would be worth to note that here even if you mean all that aspects of concentrations.
RESPONSE: Agreed and rewritten.
***Revised text: "**The mean and variance of nitrate concentrations in groundwater and streams both in time and space depend on…"*

L48f: That is unclearly formulated. Do you mean the travel time along the flow path or activation/ deactivation/ changes of flow paths itself? Dynamic in surface water may also be just a translation of the dynamic in N inputs (on longer time scales).
RESPONSE: Agreed and reformulated.
***Revised text: "**Because groundwater flow paths 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)."*

L54: What is "hydrologic approach" referring to?
RESPONSE: We agree that 'hydrologic' may only add confusion and have therefore removed this word.
***Revised text: "**approach"*

L61: Typo "onf"
RESPONSE: Thank you for poining this out.
***Revised text: "**recent advances in research on..."*

L65f: The lack of input and validation data is, from my perspective, not the main reason for the lack of application cases. Isn't it rather still a lack of knowledge on subsurface nitrate storage (organic N), removal (denitrification) and on catchment scale heterogeneity in these processes?
RESPONSE: Agreed for storage and denitrification and added to the text. Spatial heterogeneity is not an important factor when considering travel time distributions (Duffy and Lee 1992, Broers 2004). This is because the recharge flux is the overriding factor; it averages these heterogeneities out, except for very extreme situations.
***Revised text**: "In addition the amount of subsurface nitrogen storage and denitrification capacities are generally unknown."*

L70: This sentence seems to miss some words at the end.
RESPONSE: We have removed the "and nitrate reactive'.

L75: Recharge of the solute is not clearly defined. Maybe it can be just input to the subsurface?
RESPONSE: Agreed, recharge is not the correct word. Changed and also added a better definition of 'time lag'.
***Revised text: "**Interestingly, measurements show a short time lag of 5-10 years between a decrease in the nitrogen application and the peak of nitrogen in the Springendalse Beek stream. 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

L170: Nitrate availability may change within the year. Can you shortly comment on the assumptions/ simplification you do here when assuming an annual constant input?

RESPONSE: Data on seasonal variations in upper groundwater are not available. Although these seasonal variations may be reflected in short travel time N inputs to streams, the seasonal variations will be averaged out in the longer subsurface transport routes.

L177: Can you specify what the nitrate transformation factor is? I suppose it represents an average retention (denitrification?) in the unsaturated zone.

RESPONSE: We have further clarified this in the text.

Revised text: *"and to represent (part of) the nitrate transformation processes in the unsaturated zone we used a nitrate transformation factor of 0.85. This factor represents an average retention (e.g. denitrification) in the unsaturated zone and the value used here corresponds with Dutch data for soils with average water tables around 1 m depth (Steenvoorden et al., 1997; van den Brink et al., 2008)."*

L197f: Hmm. To convincingly show that you meet the concentration dynamic you somehow need to acknowledge the reaction site too. Following the Damkoehler concept (or the first order reaction equation) load or concentration over time will depend on both, transport and reaction times. Especially if both are in a comparable range and the Damkoehler number is around 1. I think this needs to be explained in more detail. For me this is also related to the choice and parameter variations implemented in the scenarios. From my point of view you first need to pinpoint, best as you can, the processes as they are and, based on that, explore the different components in a scenario analysis. Here you jump in with a selection of scenarios that sometimes needs more background and justification (see comment on Set 1b below).

RESPONSE: We agree that our aim with the model exploration was not clear enough from the beginning of the manuscript and it should be more clearly introduced to the reader. For this, we have rewritten parts of the Introduction, Methods section 2.6 en 2.7 and the results.

Revised text: *"In the initial water quality model run, no chemical processes such as denitrification were implemented. With this approach, we isolate the input time series and groundwater travel time effects on the stream concentrations. We did not intend to add further local details to improve the model performance; instead we aimed at understanding the catchment mechanisms relevant for time lags between application of solutes and discharge in the stream, which is also useful outside our study catchment. For this, we explored the model behaviour under different scenarios of chemical and hydrological processes."*

L205ff: This is repetitive to L177.

RESPONSE: Agreed, we removed the text here and added further clarification to L177.

L213: 5 years seems long for that shallow zone. I know that this is a scenario to be translatable to other catchments. Still there are ways to estimate travel times in the unsaturated zone (Harmann et al. 2011 10.1029/2010wr010194; Sousa et al. 2013 10.1016/j.jconhyd.2012.10.007). This could be used to justify that you go 5-fold or 10-fold of that or whatever. But starting with 5 years out of nowhere seems not ok for me.

RESPONSE: We agree that 5 years is rather long. However, as we want to see a clear effect on the stream concentrations, we chose to pick this high value. A sentence has been added to the manuscript to clarify this.

Revised text: *"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."*

L220: Is there an evidence of that specific time lag or an accumulation in soils from the soil data you reference earlier in the manuscript (LMM)? That lag time seems to be long when considering a first order reaction transferring organic immobile to inorganic mobile N (e.g. taking mineralization rate in van der Velde et al. 2010).

RESPONSE: The fact that we chose 10 years is mostly to get a clear result, same as for the travel time through the unsaturated zone.

For some locations this lag time could be realistic, as more persistent N is sometimes used in the Netherlands to improve soil structure and organic matter content, such as compost which has a 'werkingscoefficient' (mineralisation rate) of 10% per year (see: https://www.rvo.nl/sites/default/files/2019/01/Tabel-3-Werkingscoefficient-2019-2021.pdf).

L232: "slightly" seems an unnecessary word.
RESPONSE: Agreed and removed.

L246: Suggestion: As based on the present land-use maps.
RESPONSE: Agreed and changed.
Revised text: *"approximately equal as based on the present land-use maps."*

L257: Can you justify the use of the zero order kinetics?
RESPONSE: Much literature exists on this matter and we considered using a first-order decay equation as well. Zero or first order depends on the denitrification capacity and rate (N supply limited or reaction rate limited). However for simplicity, we decided to only use the zero-order decay and the complete decay at specific depth here. Zero order kinetics provides a simple and clear denitrification path that was easy to apply and understand. In addition, what is also important here is that neither zero order or first order would change the timing of the peak, which is what we are most interested in (and not the most realistic fit with measurements).

L260f: Is that a general statement or one specifically for the Dutch situation? If the former is the case the statement is fine as it is.
RESPONSE: We have clarified this in the text.
Revised text: *"Oxidation of pyrite has been found to be the main nitrate reducing process in several studies in the Netherlands (e.g. Broers and van der Grift, 2004; Postma et al., 1991; Prommer and Stuyfzand, 2005; Visser et al., 2007; Zhang et al., 2009) and in some other regions as reported by Tesoriero et al. (2000)."*

Results

L293ff: The age classes chosen seem arbitrary. Can you comment, even if it repeats former studies, on the shape of the travel time distribution? Is this rather an exponential or a more gamma shape? Something like that may help the readers understanding your system.
RESPONSE: We added a sentence on this and added a Figure with the shape of the cumulative TTD as panel 'e' to Figure 3.
Revised text: *"Using this model approach, Kaandorp et al. (2018) showed a travel time distribution with an exponential- like shape."*

L298: "stream's" capture zone?
RESPONSE: Agreed and changed.
Revised text: *"stream's capture zone"*

L307f: You mention measurements here. That seems to refer to water quality measurements although you wrote earlier that this is the first time to compare modelled travel times with water quality observations.
RESPONSE: Agreed and clarified.
Revised text: *"This agrees with the findings of Kaandorp et al. (2018a) that…"*

L310ff: Just visual model comparison are not really convincing. I think you need to add a measure of the quality of the modelled concentrations as well. If not you need to carefully justify as the aim of you entire study is to validate the modeled travel times with modeled vs. observed concentrations. Moreover, why do you comment on only that sparsely on the modeled nitrate concentration in this part of the manuscript?
RESPONSE: The aim of the study is not to validate the modelled travel times, but to use the model to gain a better understanding of the processes that may induce time lags in solute breakthrough. We have rewritten and clarified this throughout the manuscript (see other comments). 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.
We have added some extra information on NO3.
Revised text: *"The modelled trend reversal for nitrate thus occurs approximately 3 years after the trend reversal in the input, which is the same for the modelled chloride concentrations. "*

Fig. 4: Is there a specific reason for the inlets in panel a, d and f? At least in the results part I could not find a specific reference to that.
RESPONSE: They were added to give a better impression of the fit between the measurements and model, including the seasonality. Without the inset this is not clear, especially in panel a.

L320ff: See my comments above. I think this is a valid reasoning but needs to be introduced much earlier. You should than rather focus on the model exploration in the overall objectives than on the validation. Now I understand why you wrote "possibility of validation of the model-derived TTDs" in the objectives. I think you raise, at least with me, wrong expectations and need to address that more clearly and straightforwardly in the very beginning of the manuscript. Maybe the word "explorative" can already show up in the manuscript title.
RESPONSE: We agree that our aim with the model exploration was not clear enough from the beginning of the manuscript and it should be more clearly introduced to the reader. For this, we have rewritten parts of the Introduction, Methods section 2.6 en 2.7 and the results.
Revised text: *"In the initial water quality model run, no chemical processes such as denitrification were implemented. With this approach, we isolate the input time series and groundwater travel time effects on the stream concentrations. We did not intend to add further local details to improve the model performance; instead we aimed at understanding the catchment mechanisms relevant for time lags between application of solutes and discharge in the stream, which is also useful outside our study catchment. For this, we explored the model behaviour under different scenarios of chemical and hydrological processes."*

Fig. 5: All these scenarios are mass conserving, right? Does the overall much lower concentration of nitrate in 5c means that there is a considerable build-up of a nitrate legacy in groundwater?
RESPONSE: Indeed. The increase of all travel times means that much more nitrate was assigned to older flow paths.

L365f: I see this as a missed chance. For me, at least a first order kinetic is more realistic (and used in comparable studies with less physical basis such as van Meter et al. 2017 10.1002/2016gb005498 or Musolff et al. 2017 10.1002/2017GL072630) and would change the shape of the output concentration time series as well while zero order just lowers the concentrations.
RESPONSE: See answer on comment L257.

Discussion
L372f: Well, the "dynamic" part of TTD have not been shown in its implication so far. The dynamic part is aiming at day-to-day or seasonal shifts in the TTD but you dominantly looked at the long-term effects of TTs on the output concentrations. I would therefore not stress the strength of the dynamic TTDs here but rather refer to TTDs in general.
RESPONSE: Agreed that we don't focus on day-to-day and seasonal shifts, we removed the word dynamic here. We have also added a panel to Figure 3 which shows the shape and (seasonal) dynamics of the TTD. We keep the name 'dynamic TTD' throughout the manuscript to stress that we did take into account the dynamics in the calculations instead of using just a single mean TTD for the catchment.
Revised text: *"Aim of this study is to test whether the use of TTDs as derived from a groundwater flow model helps us to understand the observed breakthrough pattern of solutes in a lowland stream . "*

L377: The simple correction does not create a time delay!
RESPONSE: Correct, thank you for pointing this out. We removed this part of the sentence.
Revised text: *"This base model, which did not include time delays due to the unsaturated zone or chemical processes, was able to reasonably capture the long-term trends of chloride and nitrate."*

L379: This has not been shown in the results above.
RESPONSE: It was, in Paragraph 3.2. We added a reference.

L382: Just as a remark: This argumentation can be a starter in in the introduction already. "We observe time lags between input and export here and elsewhere - here we use the strong physical basis of particle based dynamic TTDs to explore the controls of that time lag, e.g. biogeochemical legacy effects in the soil, TT in the unsat. zone, TT in groundwater, denitrification in soils and groundwater... We will also explore management scenarios such as reduction schemes of fertilizer inputs and land use arrangements".
RESPONSE: Agreed. We have moved part of this paragraph towards the Introduction.
Revised text: *"Interestingly, measurements show a short time lag of 5-10 years between a decrease in the nitrogen application and the peak of nitrogen in the Springendalse Beek stream. 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. …"*

L419: Why exponential? Also referring to my comment above on the overall shape of TTDs. For me this explorative analysis is surely valuable but also detaches from the study case. Surely, convolving to different function (input with TT) creates varying peaks that depends on both functions. Maybe this would be more telling if the TTD you use would be the long term average TTDs modeled in your catchment. But I do not insist on that if you earlier can show that exponential TT is a good approximation of your system (as literature is critical about that - see Kirchner et al. 2000, Nature).
RESPONSE: We have added a panel showing the shape of the TTDs to Figure 3 and added a sentence earlier in the manuscript.
Revised text: *"Using this model approach, Kaandorp et al. (2018) showed a travel time distribution with an exponential- like shape."*

L458ff: This is all justification for what you did earlier. Part of that may be shifted above.
RESPONSE: Agreed. We shifted parts to the Methods.

L473f: Basically you argue that a spatial map of forward TTD can be used for a vulnerability assessment, right?
RESPONSE: Indeed this would be very useful. We added a sentence to the management implications.
Revised text: *"The importance of the spatial setting of land-use in the landscape means that a map of forward TTDs combined with the locations of high solute input can be used for a vulnerability assessment of a catchment."*

L486: This spatial settings-issue may be also formulated as the difference in forward TT of nitrate-contributing areas to forward TT of the entire catchment? I am not insisting on a reformulation but try to understand your discussion points here.
RESPONSE: This is correct and a good way to look at it. We have added a similar sentence to Paragraph 4.2 as this observation links perfectly with the discussion on 'contributing areas'.
Revised text: *"Information about the GCA is important for solute transport, as time lags occur if there is a difference between the forward TTD of the nitrate-contributing areas and the forward TTD of the entire catchment."*

L502f: Maybe like this "area where at a certain moment in time water is leaving the subsurface domain to become discharge"? I find the naming of "groundwater contributing area" a bit misleading as it seems to indicate where groundwater contributes to the stream. What you mean seems similar to Yang et al. (2018), Fig. 9. Maybe "runoff generating area" vs. "runoff origin area"? I am not entirely convinced for myself here but wanted to raise that issue with the current naming.
RESPONSE: We thank the reviewer for suggesting a clearer definition. Naming is a bit difficult because it touches different disciplines. Comparison with the applied particle tracking method makes it extra clear, as mentioned in the text. Although not perfect, we feel that the current naming is suited.

Revised text: *"The runoff contributing area (RCA) is defined as the area where at a certain moment in time water is leaving the subsurface domain (catchment storage) to become discharge,"*

Fig. 11: The dots and colors are hard to see. Maybe increase dot size (a bit on the costs of spatial resolution of course). Esp. RCA in the dry situation is hard to be captured - I mainly see red dots. In the plot it is not clear which colors in the background map refer to agriculture.
RESPONSE: Detail would however be lost by increasing the size of the dots, also dots are sometimes stacked especially for the RCA. The current figure seems sufficient to show the overall patterns. Background is a standard topographic map: green is forest, yellowish is mostly agriculture.

L539ff: Again. This is a valuable discussion. However, you neither touched on seasonality or C-Q relationships in the introduction nor in the observed data description nor in the modeled concentration time series. So the whole idea of intra-annual concentration variability is not well embedded in the manuscript while the inter-annual idea seems to be well addressed.
RESPONSE: We covered seasonality in paragraphs 3.2 and 3.3.

L550f: As you discuss later on maybe the active aquifer volume in this specific hydrogeological situation is a bigger factor of uncertainty.
RESPONSE: Agreed and rewritten.
Revised text: *"this might be caused by the model underestimating the mean age of water in our catchment, for instance due to an underestimation of the aquifer volume caused by the complex geology in the area. "*