Response to Reviewers

Aged streams: Time lags of nitrate, chloride and tritium assessed by Dynamic Groundwater Flow Tracking

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Anonymous Referee #1 Received and published: 11 December 2019

OVERALL RESPONSE: First we would like to thank the reviewer for their extensive and constructive review. Based on the reviewer's comments, we will rewrite large parts of the text, change some of the structure and add some extra analysis.
The large changes to the manuscript are:

- We will clearer articulate the innovative method that we use: this paper is one of the first to apply dynamic Travel Time Distributions to explore and interpret the processes driving observed water quality and isotopes dynamics.
- The sensitivity analysis has been renamed to an 'exploration of the model behaviour under different scenarios', which better reflects the aim of the analysis. Parts of the manuscript have been rewritten for this.
- The measurements of concentrations in-stream will get a more prominent place in the manuscript. They will now be presented in a new paragraph in the Results: "3.1. Water quality measurements of surface water" and more detail will be added on e.g. the time of observations, the resolution of the data and the amount of measurements. We will discuss the seasonal variability shown in the data and calculated by the model in more detail. Likewise, the constructed input curves are now added to the Results section.
- The way that the unsaturated zone was incorporated in the method is clarified and more extensively discussed.
- The discussion will be extended and rewritten to focus on the hydrological and chemical processes that occur in the breakthrough of agricultural solutes and the associated time lags, especially for nitrate. For instance, an extra scenario has been added in which a distinction is made between directly-available nitrogen and organic N that is more slowly leached towards the groundwater. We also intend to better define the concept of 'time lags' to avoid confusion over this term.
- Paragraph 4.4 on 'Improving and use of the model' for the study catchment, which included Figure 10 with the 'Best model fit' will be removed. This part of the manuscript was confusing and distracted from the overall aims of the manuscript. Relevant parts from this paragraph have been added elsewhere in the paper.

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

General comments:

Still the analysis/discussion of the results could use some more work. At the moment, results are reported but not discussed in sufficient depth concerning the potentially responsible hydrologic processes. Thus far the discussion can even be condensed as it contains several repetitions.

RESPONSE: Agreed. We will critically go through the discussion section and remove repetitions. Section 4.4, which discussed an attempt to improve the model fit, will be removed from the manuscript, as it does not add to, but actually distracts from the aim of the paper. Furthermore, we will add further discussion on the responsible hydrological processes that play a role. An extra scenario will be added to the exploration of the model behaviour, in which a distinction will be made between nitrogen that is directly available and leaching towards the groundwater and organic nitrogen that is only slowly transformed to nitrate and leached towards the groundwater (and thus creating a lag in the nitrate breakthrough). These processes will be discussed. Some of the text we added is:

Revised text: *"Aim of this study is to test whether the use of dynamic TTDs as derived from a groundwater flow model adds value to the understanding of the breakthrough pattern of solutes in a lowland stream. By combining the TTDs with input curves for solutes, we were able to calculate stream concentrations. The base model, which did not include time lags due to the unsaturated zone or chemical processes (except a simple correction for nitrate in the unsaturated zone), was able to calculate seasonality of chloride and nitrate as well as reasonably capture the long-term trend of chloride, thus adding confidence in the TTD approach. From this base model, we did an exploration of the model behaviour under different scenarios, to get more understanding of the effect of different processes on the long-term breakthrough of the solutes.*

In the discussion we will first focus on the effect of processes on the breakthrough of solutes, based on the exploration of the model behaviour under different scenarios. We will clarify the concept of time lags we proposed and will evaluate how unsaturated zone processes, advective saturated flow, the spatial source zones and temporal patterns of solute inputs and transformation processes such as denitrification all will influence these time lags in the receiving water body. Using our dynamic TTD model, we will then introduce 'contributing areas' to discuss the spatial and temporal effects of land-use and groundwater flow paths. We will subsequently discuss the case of the study area and take another look at the observed breakthroughs and time lags of the different solutes, varying different scenario and evaluating model behaviour and outputs. Lastly, we will discuss the implications of our findings for catchment management."

Also the model lacks measures to evaluate its performance/fit.

RESPONSE: The groundwater model itself was calibrated and validated using groundwater heads and discharges (discharge NSE 0.65), as discussed in Kaandorp et al., 2018 WRR. The model was not further calibrated as it is only used as a tool to investigate it's use for the particle tracking / Travel Time method. In the analysis done in the current paper the measured chloride, nitrate and tritium function as an added evaluation of the transient TTD model.

Likewise the sensitivity analysis does not include a comprehensive evaluation of the parameter importance.

RESPONSE: Agreed. The term 'sensitivity analysis' was a bit misleading for what we tried to do. We have changed this term throughout the manuscript to an 'exploration of the model behavior under different scenarios', to better represent the actual method and goal. The effect of the different parameters is discussed in section 4.1 (The effect of processes on modelled breakthroughs) and we will add a more comprehensive evaluation to this paragraph to indicate the importance of the different parameters and processes.

Addressing these issues would prevent the results and discussion to sound as vague as they currently still do. The overall conclusions are not that surprising and will benefit from a more in-depth discussion.

RESPONSE: Agreed. We will extent the discussion section with further discussion on the responsible hydrological processes that play a role. We will revise the conclusions to better represent the innovative parts of the manuscript. Additions to the text include:
Revised text: *"By making this connection between dynamic groundwater travel time distributions and in-stream concentration measurements, were able to show that the seasonal and long-term fluctuations of in-stream solute concentrations were mainly caused by the dynamic contribution of different groundwater flow paths."*
"We show that for most catchments, with a (close to) exponential TTD, a direct reaction of stream nitrate concentrations can be expected to reductions in the nitrogen inputs. Furthermore, we found that the breakthrough patterns of diffuse pollutants are largely governed by the spatial distribution (distance) of agricultural fields and the reactivity of the subsurface, which can both be tackled by creating riparian buffer zones."

The authors manage to write comprehensively and with a good overall structure. Just every now and then they should try to be more consistent when using short versions (Cl/NO3) or the words "chloride"/"nitrate".

RESPONSE: Thanks for the compliment regarding the comprehensiveness and structure. We now use 'chloride' and 'nitrate' consistently.
Revised text: *"chloride" and "nitrate"*

When reading the title of this manuscript I was hoping for more novelty in the results and discussion sections. Yes, the study is well-written and has a good structure, but somehow I feel that the authors do not go much beyond reporting the results. There is neither a lot of analysis nor discussion on which controls are important and specifically why they are more or most important. I like the modeling approach although it bothers me that it is purely a groundwater model without unsaturated zone processes. However, I believe that the authors can manage to add more analysis and discussion to merit and justify a publication in HESS.

RESPONSE: We agree with the reviewer. Especially the discussion and conclusions do not capture the innovative parts of the manuscript in the right way. Following the reviewers suggestions, we will critically go through the discussion section and add more discussion on the processes and controls. It is important to mention here that this paper is one of the first to couple measurement data of water quality and isotopes to Travel Time Distributions. Even though many recent papers suggest that this method holds a lot of potential, the papers which actually attempt to do so are absent or at least very scarce.

In this modelling study we focus on the groundwater system and indeed highly simplify the unsaturated zone. The unsaturated zone is included in the method in two ways: 1) the groundwater model is coupled with an unsatured zone model (MetaSWAP, see also Kaandorp et al., 2018 WRR) to provide a realistic groundwater recharge based on e.g. land-use; 2) the input curves include part of the unsaturated zone processes: before 2000 by using a nitrate transformation factor of 0.85 and after 2000 by using the concentrations of the shallow groundwater to construct the input curves. Thus, we take into account many of the unsaturated zone processes, just not the delay.

Furthermore, the relevance of the unsaturated zone also depends on the research area and the temporal scale of interest. In this case, the research area is a lowland groundwater-driven catchment with shallow groundwater levels and the focus is on seasonal changes in flow paths and solute concentrations in the stream. This can be well simulated with a simple representation of the unsaturated zone. In a more hilly catchment, or if we would want to simulate the concentration response to individual events, a more detailed representation of unsaturated zone hydrology would be required.

We will also highlight these more in the manuscript.

Specific comments:

Abstract: Try to underline the innovative parts of your study more. Think about more precise results (like TT results, R2) Isn't it important to at least name the investigation area?

RESPONSE: We agree and we thank the reviewer for these suggestions and will rewrite the abstract to include more the innovative aspects and precise results. We added for instance:
Revised text: "*This paper is one of the first to calculate in-stream concentrations of tritium, chloride and nitrate using dynamic groundwater travel time distributions (TTDs) derived from a distributed, transient 3D groundwater flow model using forward particle tracking."*

"We tested our approach in the Springendalse Beek catchment, a lowland stream in the east of the Netherlands,"

"By making the connection between dynamic groundwater travel time distributions and in-stream concentration measurements, we provide a method for validating the travel time approach and make the step towards application in water quality modelling and management. Important conclusion for management is that although the effect of mitigation measures can generally be expected instantly, based on an almost exponential steady state distribution of travel times in a catchment, our model also showed that the spatial distribution of agriculture in catchments influence the response of stream concentrations to mitigation actions."

p.2, 33: "through" instead of "though"?

RESPONSE: Agreed and changed accordingly

Revised text: *"through"*

p.2, 38: how do you mean "land-use" in this context?

RESPONSE: We agree that this is not entirely clear. We mean for instance whether or not manure/fertilizers are used, we made this more clear in the text.
Revised text: *"depends on these groundwater flow paths and travel times, as well as on land-use (for instance use of manure and fertilizer)."*

p.2, 41: "Land-use determines the timing and quantity of nitrate input" would be more general

RESPONSE: Agreed and changed accordingly.

Revised text: *"Land-use determines the timing and quantity of nitrate input as well as its spatial distribution"*

p.2, 42: ".depending on the source and timing of infiltration"

RESPONSE: Agreed and changed accordingly.

Revised text: *"*depending on the source and timing of infiltration,"

p.2, 52: What time is meant by "historical"?

RESPONSE: We agree that this is not clear. We changed the text into:
Revised text: *"Therefore, we combine in this follow-up paper these dynamic travel time distributions with input curves for tritium, chloride and nitrate to reconstruct the concentrations in a Dutch stream from 1970 until present, while including the dynamic nature of catchments both in time and space."*

p.3, 74: If 20 % of the river are not baseflow, is this not an important NO3 source due to surface runoff with high solute concentrations?

RESPONSE: A baseflow index of 0.8 does not mean that the other 20% is surface runoff. In Dutch catchments, almost all water comes from discharge of groundwater, either through tile drains, in ditches, diffuse or springs.

Surface runoff has been observed in the catchment, but consists only of a small part of the discharge. Furthermore the surface runoff mostly transports phosphates, not nitrate (which is leached towards the groundwater).

p.3, 85: How big are the sub-catchments up- and downstream?

RESPONSE: Agreed that this is not clear, we will add a map which shows the sub-catchments, and added to the text:

Revised text: "*The upstream part (2 km^2) of the Springendalse Beek catchment has several spring areas and is mostly forested with some agricultural fields, while farmland is more abundant in the downstream part (2 km^2) of the catchment."*

p.3, 71: How can you differentiate between up- and downstream, when having only one gauging station?

RESPONSE: We agree that this is a bit unclear. Some data is available from older gauges and from field activities. However for the analysis in this paper we use the discharges calculated by the model (which were in the earlier paper (Kaandorp et al. 2018, WRR) compared with measured discharges). Surface water quality data is available for both the up- and downstream catchment.

p.3, 89: Do you know rates of drainage? How much percent of the agricultural area are artificially drained? What is the difference of these rates between up- and downstream? I think it's an important number as later on it seems to be a large factor (Fig.9).

RESPONSE: We agree that this is important information. Unfortunately, exact rates of subsurface drainage are not known, although some indication exists from the groundwater model and based on information from the catchment/water authorities. It is also important to know that in this part of the Netherlands generally all agricultural land has some form of artificial drainage (ditches or tile drains). Especially in the lower part of the catchment, which is flatter and has shallow groundwater tables, fields are drained using tile drains and ditches. The average distance to a drainage unit (ditch, stream or known tile drain) is about 132 m for the downstream and 174 m for the upstream catchment, reflecting the difference in drainage density. The exact amount of subsurface tile drainage is however now known. Available data indicates that the total area of the downstream catchment, 3% is drained using tile drainage, while this is 1% for the upstream catchment, but this seems to be an underestimation. Overall, based on available data, the drainage density is 20 to 30% lower in the upstream part. We added some this information to the text.

Revised text: *"Many of these farmlands are artificially drained by a system of tile drains and ditches, especially in the downstream part of the catchment due to the flatter topography and more shallow groundwater tables compared to the upstream part of the catchment. Available data indicates that the drainage density is around 20-30% lower in the upstream part of the catchment than in the downstream part. "*

p3, 91: I cannot find groundwater data or cannot differentiate which collected data are from the surface and which are not.

RESPONSE: Agreed and clarified accordingly.

Revised text: *"2.2. Collecting water quality measurements of surface water "*

p3, 93: What time period is covered by "historical" data?

RESPONSE: Agreed and clarified accordingly.

Revised text: *"First, historical data from 1969 and onwards of chloride and nitrate concentrations was obtained from earlier studies"*

p.3, 96: Where is the first explanation of the abbreviation?

RESPONSE: We now use 'chloride' and 'nitrate' consistently.

Revised text: *"chloride" and "nitrate"*

p.3, 91- p.4, 101: As you join different data sources, it would be helpful to add a table consisting of the time of observation, the resolution of the data, the amount of measurements. . .

RESPONSE: Agreed. This will be added to the manuscript.

p.4, 102: Can you give more information on the "dynamic TTD"?

RESPONSE: Agreed that this should be introduced better. We have added the sentences below to the explanation in Section 2.3. More detail can be found in Kaandorp et al., 2018 (WRR).
Revised text: *"Travel Time Distributions describe the distribution of ages of the water that contributes to discharge in a catchment. Dynamic TTDs do this in a time-variable way and include for instance seasonality in the contribution of older and younger water. Dynamic TTDs for the Springendalse Beek catchment were calculated "*

p.5, 140: What are the distances of the two stations to the corresponding measurement station?

RESPONSE: For both stations the distance is around 80 to 90 km. We will add this information to the manuscript.

p.5, 148: "following Meinardi (1984)"

Revised text: *"following Meinardi (1994)"*

p.5, 154: How can you exclude land-use change?

RESPONSE: Land-use change will obviously affect the input of nitrate and we did not exclude this. Land use change is partly incorporated in the input curves. Furthermore, a large agricultural field in the upstream part of the catchment has been in use only since approximately 1985 and an agricultural field of approximately 7.5 ha was converted to natural vegetation in 1998. This was also considered when combining the TTDs and input curves. What was not considered is that small parts of the catchment changed from nature in agriculture and vice versa. This does not have a large effect on the downstream surface water concentrations. We simply do not have enough data to take small changes into account: -we do not have knowledge on the high detail and long term land-use changes (e.g. specific crops), and -farmer specific differences will affect the result (using maximum amount of fertilizer or not, etc). We do discuss the effects of this assumption later in the Discussion section.

Revised text: *"Land use change is partly incorporated in the input curves. Furthermore, a large agricultural field in the upstream part of the catchment has been in use only since approximately 1985 and an agricultural field of approximately 7.5 ha was converted to natural vegetation in 1998. This was also considered when combining the TTDs and input curves. What was not considered is that small parts of the catchment changed from nature in agriculture and vice versa. This does not have a large effect on the downstream surface water concentrations."*

p.5, 156: How can you assume NO3 to be constant over time although atm. N-deposition changed strongly within the last decades?

RESPONSE: We will gather more information and data on this and add to the manuscript where needed. Even though atmospheric inputs changed in the last decades, these are small effects compared with the inputs from fertilizers and manure in the Dutch agricultural catchments.

p.5, 159: What is the size and resolution of the data set? How did you manage data gaps?

RESPONSE: The size and resolution of the data set are: 1950 – 2017 with yearly values. Data gaps were filled using linear interpolation.

p.5, 160: Abbreviation of N?

Revised text: *"nitrogen (N)"*

p.5, 160: Later on you write about seasonal N contribution, which is highest in winter. Do you know the time of fertilizer application within the year? Are not the spring and potentially the fall also highly predestined to show N-peaks?

RESPONSE: We do not know the exact time of application of fertilizers, but it will be between spring and autumn (growing season), within the time permitted by EU legislations. In the Netherlands this is between half February until September. The timing differs per crop: grassland gets some after each grass harvest, arable land usually most in spring. However, we seldomly see these inputs causing high nitrate concentrations in streams directly (only sometimes in cold/wet conditions in February). The nutrients stay in the soil because of the precipitation deficit. Nitrate is leached to the upper groundwater during winter, and lateral transport is activated by rising groundwater levels (see e.g. Rozemeijer et al., 2009). The seasonal differences in the input will thus be averaged in the unsaturated zone and groundwater system. The contribution to stream discharge of groundwater that infiltrated on agricultural fields is higher in winter (Figure 3), but this water will no longer contain the seasonal signal of the input but instead an averaged value, as we use in the model here.

p.6, 175: Cl and NO3 concentrations or input? When did the concentration change then, at January 1st or when fertilizer application (e.g. April) would be realistic?

RESPONSE: The chloride and nitrate concentrations of the input (infiltrated water). The concentration changes at January 1st, which is a choice we made for simplicity. See also previous comment: the concentrations in upper groundwater don't change immediately after applying manure. They change when a precipitation surplus in fall/winter leaches salts down from the soil to the groundwater. It could be argued that the start of the growing season would be more realistic, but we did not focus on such short-term changes in the input (as described in the comment above).

Revised text: *"The input concentrations of chloride and nitrate were assumed constant over a specific year, "*

p.6, 178: What is the resolution of N input in the model? How can it be constant over the year?

RESPONSE: As described above we use yearly-average values, which are available from the different data sources. This reflects the concentration of the upper most groundwater. See also comments above.

p.6, 190-191: Could you revise this sentence? It is hard to understand.

RESPONSE: Agreed and changed accordingly.

Revised text: *"The initial run of the model used the land-use map of the catchment for the year 2007 (Figure 1) where the agricultural fields received chloride and nitrate following the constructed input curves (Figure 2)."*

p.7, 195-206: Does it makes sense to test for these parameters? What is the innovation?

RESPONSE: The change to the model itself is very simplistic here (adding to or multiplying the TTD). This exercise however gives understanding into the effect of such changes on the output concentrations in the receiving stream. And from that, it gives an idea of the performance of our model and which changes would improve the result of the model. It for instance indicated that we underestimate the average travel time in the catchment (due to e.g. unsaturated zone). Studying the effect of the mean TT is also interesting for comparison with other studies, which often use mean TTs.

p.8, 228: "partly by oxidation of organic C (1) or pyrite (2)". So it is easier for the reader to assign the two equations.

RESPONSE: Agreed and changed accordingly.

Revised text: *"partly by oxidation of organic C (Equation 1) or pyrite (Equation 2):"*

p.8, 236: It is also assumed as a first-order decay (e.g. van Meter et al., 2017) in literature. Why do you assume zero-order?

RESPONSE: Much literature exists on this matter and we considered using a first-order decay equation as well. However for simplicity, we decided to only use the zero-order decay and the complete decay at specific depth here.

p.8, 240: Do you have information about the denitrification potential assuming it as a finite process?

RESPONSE: In this scenario we assume the reactivity potential of the subsurface to be an infinite process. This complete decay at depth is in correspondence with literature from the Netherlands (Zhang et al., 2013; Visser et al., 2009) and Denmark (Jessen et al., 2017; Koch et al., 2019).

p.8, 249: Figure 3d as well? In the following sentence, I propose to add "Figure 3d".

RESPONSE: Agreed, we changed the text according to the reviewers suggestion.

p.8, 252: Highest contribution in winter although highest N inputs can be assumed in spring and are washed out until winter? And how can you see seasonal NO3 patterns assuming constant NO3 input over the year? So I think "agricultural contribution" (assumed as constant) is not the appropriate wording, perhaps NO3 transport/mobilization?

RESPONSE: The text here and Figure 3c and d, refer to the origin of water, i.e. infiltrated on agricultural fields. We will make this clearer in the text.

p.9, 268 I cannot associate the word "later" with the mentioned years.

RESPONSE: Agreed and changed accordingly.

Revised text: *"which is about 5 to 10 years after the peak in the input (Figure 2). "*

p.9, 273: What is a reasonable fit? Do you have a measure for this, like R2?

RESPONSE: We will try to give it a measure to describe the fit.

p.10, 297: What is meant by "did not completely fit"? Think about using a measure to show the actual fit.

RESPONSE: See previous comment.

p.9, 284-286: Would not denitrification cause an earlier peak/decay than Cl instead of the surprisingly later peak. Is the changing N-Cl ratio not excluded by the input data of the farmer (chapter 2.5)? Do you have any hints for potential point sources? p.9, 286: What point sources are realistic in a non-urban area?

RESPONSE: We will more closely analyze and discuss the effects of denitrification and the difference in the breakthrough of different solutes. We will also look into potential point sources.

p.10, 295: Can you adjust the headings in this chapter or in the according method section so that it is easier to assign?

RESPONSE: Agreed. We will make this more consistent.

p.11,321: Think about adding (Figure 6, "red line") and later on (. . ., "green line"). Than it is easier to match. But this is probably a matter of taste.

RESPONSE: Agreed. We follow the suggestion by the reviewer and now mention the color of the line in the text.

p.12, 349-351: Do I need a larger area for N variations? Isn't it only caused by varying flow paths? And is "diluted" the appropriate wording? This implicates lower N concentrations in young water, which is often not the case.

RESPONSE: No, variation in N occurs in small areas due to varying flow paths, like the reviewer notes. This part of the text is not clear and will be rewritten. What we meant to describe is that the effect of unsaturated zones on the lag time can be large. But when looking at larger areas, this effect can be counteracted by parts of the area with more thin unsaturated zones.

Revised text: *"In catchments with thick unsaturated zones, the lag time due to unsaturated zones has been calculated to be up to decades such as for aquifers in the U.K. (Wang et al., 2012). The time lag introduced by the unsaturated zone is often averaged on a catchment scale, due to spatial variation in its thickness, although it can lead to long tails in the nitrate concentrations."*

p.12, 346-352: Did you consider a combination of unsaturated zone and denitrification, so not only delay but at the same time decay?

RESPONSE: No, we did not test this scenario and it would be interesting. Some decay is already included in the input curves by using a nitrate transformation factor. We will add more discussion on denitrification and chemical processes, and will add a scenario with more complex unsaturated zone and nitrogen related processes by making a distinction between directly available and organic N.

p.12, 356: Is it not "decreased" instead of "increased"?

RESPONSE: No it is increased because we multiplied all travel times with a certain value. E.g. for a factor 5, a travel time of 1 month would because 5 months and a travel time of 1 year would because 5 years.

p.12, 371: ". . .when the MTT is rather long or the input decreases slowly"

RESPONSE: Agreed. We followed the reviewers suggestion and changed the text.

p.12, 377: "It is however known"

Revised text: *"known"*

p.13. 379: Also "temporal" (temperature dependence), not only spatial differences?

RESPONSE: Agreed. This is true and we will add this to the text.

Revised text: *"spatial or temporal differences in denitrification"*

p.13, 408: Can you explain these non-linear reactions?

RESPONSE: Agreed that this was not clear from the text. When wetness conditions decrease, groundwater levels decrease, and drainage units fall dry. Consequently, the water that was flowing towards these drainage units suddenly stay in the aquifer and/or flows towards another drainage unit. When wetness conditions increase again, groundwater levels first have to rise to the point that they can activate these flow paths again. We added the following sentences:

Revised text: *"This includes the disappearance of flow through shallow flow paths towards e.g. drainage pipes and ditches in dry periods, which leads to a non-linear reaction in of the dynamic TTD to discharge. When wetness conditions decrease, groundwater levels decrease, and drainage units fall dry. Consequently, the water that was flowing towards these drainage units suddenly stay in the aquifer and/or flows towards another drainage unit. When wetness conditions increase again, groundwater levels first have to rise to the point that they can activate these flow paths again. This also (at least partly) explains why concentration-discharge relationships vary with the wetness of catchments."*

p.14, 441: So you assume transport limitation instead of source limitation, otherwise the wet period would cause dilution.

RESPONSE: Yes.

p.15, 445: Can you describe the changing discharge in Figure 3a still as “relatively stable year-round”? Are the NO3- differences caused by different Q ages (stable Q assumption, but different paths) or Q amounts (wet and dry period assumptions)?

RESPONSE: Most of the baseflow comes form the upper part of the catchment, so compared with that the discharge upstream is relatively stable. The differences in nitrate levels are caused by the activation of different flow paths (e.g. shallow flow paths fall dry during summer). Changes in the discharge through active paths is also considered, but as discussed in Kaandorp et al., 2018 (WRR) the difference in wetness between wet and dry periods seem to change the discharge through all active flow paths in a similar way, thus not affecting concentrations by such a large amount as the activation of flow paths. We will try to make this interpretation clearer in the discussion section here.

p.15, 466-473: This information could be also important earlier in the methods.

RESPONSE: As discussed in the response on the comment of p.5, 154, we do not have sufficient data to incorporate this in our model in an acceptable way. Therefore we do not consider land-use in the model, but discuss the effect of this assumption here in the Discussion using some of the results from the scenarios.

p.17, 510-511: How reliable is the model if you cannot constitute one (downstream) of two (up- and downstream) catchments?

RESPONSE: We agree with the reviewer that it is strange to present these results in this way. In rewriting, we have removed the part of the manuscript where this ‘best fit’ was presented. It did not add to the aims of the paper. Instead we focus on the actual processes and their effects on the variability of and breakthrough of solutes.

p.17, 522-540: Could you underline the innovative management implications?

RESPONSE: Agreed that this should be clearer. The innovative conclusions are: 1) Contrary to what is often thought, the response of measures through the groundwater system is instant in the general case that the TTD is exponential, even in areas with relative long MTT. We will extend the text to specifically address how the time lags between measures and effects in the receiving stream vary under different combinations of MTT and temporal and spatial patterns of solute inputs and transformation processes such as denitrification and slow N mineralization. Some of this work was already discussed in the appendix and we will extend the discussion part of the paper to address this in more detail, linking in to the results of the transient travel time modelling. 2) Location of agricultural fields has a large effect of stream concentrations and creating a (significant) riparian buffer zone lags and dampens the effect of agricultural pollution on surface water quality. Therefore, riparian buffers have a positive effect also when it is bypassed or the often assumed denitrification is low.

We will make these points clearer in the text.

Revised text: *“The exploration of the model behaviour indicated that removing the source of diffuse pollution leads to an immediate decrease of in-stream concentrations (Figure 6b), due to the large fraction of younger water in the TTD. Therefore, contrary to what is often thought, the response of measures through the groundwater system is instant in the general case that the TTD is (close to) exponential and thus managing the input of agricultural pollutants is a good management option with direct benefits, although the direct impact does not occur when decreases are very slow or the MTT is very large. After the immediate decrease, the legacy from older groundwater flow paths leads to a slow further decrease in time.”*

“Therefore, creating a (significant) riparian buffer zone lags and dampens the effect of agricultural pollution on surface water quality and riparian buffers have a positive effect even when it is bypassed or denitrification is low.”

p.18, 564-565: What is new in this statement?

RESPONSE: We agree with the reviewer that the current conclusions of the paper are too general and we will rewrite them to better reflect the innovative methods and findings of the paper (innovative method of TTD+solutes, processes affecting the breakthrough of agricultural solutes and innovative management implications).

Figures & Tables:

p.27, Figure 1: I miss an x-axis label for the figure bottom left. Think to add also a,b,c,d to the different plots. This would also benefit the figure caption. Where is the border between up- and downstream catchments in bottom right?

RESPONSE: Agreed. We will add these parts to the figure.

p.27, Figure 2: According to the caption, the tritium curve is based on measurements from Groningen and Emmerich, but isn’t this the case only for values later than 1970?

RESPONSE: Yes, before that the curve is based on Vienna and Ottawa, as described in the manuscript text. We will change the caption accordingly.

Revised text: *“The tritium input curve is based on precipitation measurements at stations Vienna and Ottawa (before 1970) and Groningen and Emmerich (from 1970).“*

p.29, Figure 4: Think about plotting also an input curve in the same plots. This would make the in-output-comparison much easier.

RESPONSE: This is a good suggestion, although it might make the Figure harder to read. We will look into this and see if we can include the input curve.

p.30, Figure 6: Is there a superfluous “the” in the end of the caption?

RESPONSE: Yes, thanks for noticing. This has been removed.

p.31, Figure 8: I am surprised that the upper RCA does not contribute any water to the GCA. And in the text overland flow is also included in the RCA. Could you revise the figure to show that?

RESPONSE: This is a good point which is not clear from the current figure. Is it possible for a location to be both a RCA and GCA? We will adjust the figure accordingly.

p.32, Figure 9: When the colors are similar to Figure 3, where does the purple come from?

RESPONSE: Agreed that this may be confusing. We will add a legend to the figure.

Supplement

p.1, 24: I do not understand the “just”. Do I really need combinations of TTDs and reduction rates to determine a lag between in and output? I don’t think so. Perhaps in your special case, but not in general.

RESPONSE: What we attempt to illustrate in the Supplement is the importance of the reduction rate, and how that combined with the mean travel time of a catchment determines the lag time. Generally, in literature only the mean travel time (of generally an exponential TTD) is assumed. Obviously, our argumentation about the effects of temporal trends in the solutes input on the time lags should be clarified further and we intend to include this in the Discussion part of the paper. This will benefit from a better definition of groundwater induced time lags between measures and effects in receiving water which we will also provide. We believe that the example mentioned in the Appendix represents a general finding which is not limited to our special case or study area.

p.2, Table S1: What is the definition of the delay? The peak matching? In Figure S2 you write "time to peak". This could be helpful as a column in Table S1 too.

RESPONSE: Agreed. We will add 'time to peak' to the caption of the Table to make this clearer. Furthermore, we also intend to better define the concept of 'time lags' to avoid confusion over this term.

Revised text: *"Time to peak [years] of the output concentrations following a change in the input for different rates of changes and MTTs."*

p.3, Figure S2: The same colors as in Figure S1 but with different meanings are confusing. Think about another color or line code.

RESPONSE: Agreed. We will make the distinction clearer.

References:

Jessen, S., D. Postma, L. Thorling, S. Müller, J. Leskelä, P. Engesgaard ,2017. Decadal variations in groundwater quality: A legacy from nitrate leaching and denitrification by pyrite in a sandy aquifer, Water Resour. Res., 53, doi:10.1002/2016WR018995.

Kaandorp, V. P., de Louw, P. G. B., van der Velde, Y. and Broers, H. P.: Transient Groundwater Travel Time Distributions and Age-Ranked Storage-Discharge Relationships of Three Lowland Catchments, Water Resour. Res., 1–18, doi:10.1029/2017WR022461, 2018.

Koch, J., Stisen, S., Refsgaard, J.C., Ernstsen, V., Jakobsen, P.R., Højberg, A.L., 2019. Modelling depth of the redox interface at high resolution at national scale using Random Forest and residual Gaussian simulation. Water Resour. Res., https://doi.org/10.1029/2018WR023939 \

Rozemeijer, J. C., Broers, H. P., Geer, F. C. van and Bierkens, M. F. P.: Weather-induced temporal variations in nitrate concentrations in shallow groundwater, J. Hydrol., 378(1–2), 119–127, doi:10.1016/j.jhydrol.2009.09.011, 2009.

Visser, A., Broers, H. P., Heerdink, R. and Bierkens, M. F. P.: Trends in pollutant concentrations in relation to time of recharge and reactive transport at the groundwater body scale, J. Hydrol., 369(3–4), 427–439, doi:10.1016/j.jhydrol.2009.02.008, 2009.

Zhang, Y. C., Prommer, H., Broers, H. P., Slomp, C. P., Greskowiak, J., van der Grift, B. and Van Cappellen, P.: Model-based integration and analysis of biogeochemical and isotopic dynamics in a nitrate-polluted pyritic aquifer, Environ. Sci. Technol., 47(18), 10415–10422, doi:10.1021/es4023909, 2013.