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Hydrology and Earth System Sciences
Discussions

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

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Abstract. Surface waters are under pressure of diffuse pollution from agricultural activities and groundwater is known to be a connection between the agricultural fields and streams. We calculated in-stream concentrations by coupling input curves for tritium, chloride and nitrate with dynamic groundwater travel time distributions (TTDs) derived from a distributed, transient 3D groundwater flow model using forward particle tracking. We tested our approach in a lowland stream and found that the variable contribution of different groundwater flow paths to stream water quality reasonably explained the majority of long-term and seasonal variation in the measured stream nitrate concentrations. A sensitivity analysis was done to study the breakthrough of agricultural nitrate and it was found that an unsaturated zone, increased mean travel time and a longer distance between agricultural fields and stream cause a lag in the breakthrough of agricultural solutes. Similarly, the recovery of concentrations after measures that aim to reduce the solute inputs is determined by these parameters, with combinations of slow reduction rates and long MTT tending to result in considerable lag times after start of the reductions. We labelled the part of the catchment area where the seepage water infiltrated that contributes to stream discharge at a certain moment in time the 'groundwater contributing area'. This groundwater contributing area was shown to increase and shrink based on wetness conditions within the catchment. Especially the location of agricultural fields in the groundwater contributing area in relation to the catchments' drainage network was found to be an important factor that largely governs the travel times of the agricultural pollutants. We conclude that groundwater functions as a buffer on the effect of agricultural pollution, by distributing water in time and space and making it possible for different waters to mix.

1 Introduction

Diffuse pollution with nutrients is one of the main pressures on Europe's surface- and groundwaters (EEA, 2018). Intensive agricultural land-use and the accompanying use of manure and fertilizers have significantly increased the amount of nitrate in the hydrological system in the period after 1950 (Aquilina et al., 2012; Broers and van der Grift, 2004; Hansen et al., 2011; Worrall et al., 2015). Nitrate leaches to the groundwater (Boumans et al., 2008; Wang et al., 2012) from where it is transported

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

towards surface waters though fast and slow flow paths, creating a stress on surface water quality (Howden et al., 2011b; Kaandorp et al., 2018b; van der Velde et al., 2010).

Flow paths are the routes that water particles travel through the subsoil, crossing different geological formations and reaching certain depths, which takes a certain travel time from infiltration to exfiltration (Broers and van Geer, 2005; van der Velde et al., 2010). The nitrate concentration in groundwater and streams depends on these groundwater flow paths and travel times, as well as land-use. Both the route and travel time influence hydrochemical processes, as they determine which mediums are passed and the time that is allowed for (biogeo)chemical reactions. Nitrate concentrations may for instance decrease by denitrification when passing organic or pyrite-rich layers.

Land-use determines the nitrate input as well as the spatial distribution of the input (Boumans et al., 2008). Thus, all water particles may carry different nitrate concentrations depending on the source of infiltration, flow path and the travel time along the flow path. For example, the input of nutrients is higher on fertilized agricultural fields than in forested areas. In catchments, groundwater flow paths provide the hydrologic connection between infiltration areas and seepage zones in streams (e.g. Ali et al., 2014; Birkel et al., 2015; McGuire and McDonnell, 2010). Because groundwater flow paths are variable in time, the delivery of nitrate from groundwater to surface waters also varies in time (Rozemeijer and Broers, 2007).

In a recent paper, Kaandorp et al. (2018a) presented dynamic travel time distributions (TTDs) for lowland catchments in the Netherlands. They showed how groundwater flow paths in these catchments vary in time and discussed differences in mixing processes between young and old groundwater in the streams with time. In this paper we combine these dynamic travel time distributions with input curves for tritium, chloride and nitrate to reconstruct and forecast the historical and present concentrations in a Dutch stream, while including the dynamic nature of catchments both in time and space. Our aim was to test whether the use of dynamic travel time distributions as derived from a distributed, transient 3D groundwater flow model adds value to the understanding of the breakthrough pattern of groundwater derived solutes in a lowland stream. This work extends on recent advances of the groundwater contribution to streams (e.g. Engdahl et al., 2016; McDonnell et al., 2010; Morgenstern et al., 2010; Solomon et al., 2015; van der Velde et al., 2012), by combining transient TTDs from a forward particle tracking model with historical records of tritium, chloride and nitrate inputs.

Tritium and chloride were included as water tracers, where tritium is part of the actual water molecule and chloride was considered to be conservative while passing through the aquifer. Convolutions of the input curves with the modelled TTDs were compared with observed stream concentrations of tritium, chloride and nitrate, which opens the possibility of validation of the model-derived TTDs. We used the model to assess whether the fluctuation in flow paths and contributing areas explain the variability of stream water quality, as has been found in other studies (Musolff et al., 2016; Rozemeijer and Broers, 2007), and ran a sensitivity analysis of the parameters that determine lag times between recharge of the solutes and discharge in the stream, such as unsaturated zone delay, the distance between fields and the stream and the mean travel time of the system. Lastly, we explored the effects of input scenarios on the breakthrough of agricultural nitrate.

2. Methods

2.1. Study area

A lowland stream in the east of the Netherlands, the Springendalse Beek, was selected for this study because of its high nitrate concentrations and interesting differences between upstream and downstream parts of the catchment (Kaandorp et al., 2018b). The catchment has a temperate marine climate with a mean temperature of 9.6 °C and mean annual precipitation and evaporation of around 850 and 560 mm respectively. The size of the catchment is 4 km2 and the average discharge downstream is 0.043 m3/s with a baseflow index of 0.8 (Gustard et al., 1992).

The catchment is located on the flank of an ice-pushed ridge that was formed during the Saalien glaciation and has a maximum elevation of 75 m above sea level. Recent hydrogeological inventories strongly suggest a very complex ice-pushed structure, composed of a series of tilted slabs of Tertiary clays (Formation of Breda and older) intercalated with Pleistocene moderately coarse, organic poor sands and some gravel that were deposited by a braided river (Formation of Appelscha). These slabs roughly have a N-S strike direction, perpendicular to the receiving Springendalse Beek stream (pers. comm. Harting and Bakker, TNO Geological Survey of the Netherlands) and can hardly be passed by groundwater flow, leading to relatively high groundwater tables compared to more sandy ice-pushed ridges in the Netherlands. In general, the average depth of the water table is around 0.5 m below the surface in the downstream part of the catchment and up to about 3.0 meter below the surface in the highest parts of the upstream of the catchment, presumably concentrated at outcrops of the Pleistocene sands. The streambed of the stream is sandy with some occasional gravel, which represents material from the tilted Appelscha Formation.

The upstream part 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 of the catchment. These farmlands are often artificially drained by a system of tile drains and ditches. Due to its constant flow and permanent springs, the stream is known to have a high ecological value (e.g. Nijboer et al., 2003; Verdonschot et al., 2002).

2.2. Collecting water quality measurements of ground- and surface water

Surface water quality measurements were collected from various sources. First, historical data of chloride and nitrate concentrations was obtained from earlier studies (Dam et al., 1993; Higler et al., 1981; Hoek, 1992; Nijboer et al., 2003; van der Aa et al., 1999; Verdonschot and Loeb, 2008; Visser, 2001). This dataset was complemented with a 1985-present time series of Cl and NO_3 that was collected by the monitoring program of the local Waterboard Vechtstromen. We further extended

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

this dataset with field data of the period 2015-2018, determining NO_3 using a DR1900 HACH field spectrophotometer and laboratory analysis of NO_3 and Cl. For this, samples were filtered (0.45 µm) and stored cool in glass tubes and ion analysis was done within 48 hours using a Dionex ICS-1500. For tritium, 10 samples were taken over the period 2016 to 2018. These were stored in 1L plastic containers and measured at the Bremen mass spectrometric facility by degassing followed by analysis of ^3He with a Sectorfield mass-spectrometer (MAP 215-50) (Sültenfuß et al., 2009).

2.3. Groundwater Model and TTDs

The dynamic TTDs for the Springendalse Beek catchment were calculated using forward particle tracking on a high-resolution spatially distributed groundwater flow model following the method described by Kaandorp et al. (2018a). A concise description of the method is given here and more details are found in Kaandorp et al. (2018a). Groundwater flow was calculated using an existing finite-difference groundwater flow model (MODFLOW, Harbaugh, 2005) created and calibrated on groundwater heads and validated with both groundwater heads and river discharge in earlier studies (Hendriks et al., 2014; Kuijper et al., 2012). Groundwater flow was simulated with a monthly time step on a regional scale (total modelled area 58 by 45 km) with cells of 25*25 m. The top of the model followed the surface elevation and the model consisted of seven layers of variable thickness, based on the Dutch Geohydrological Information System (REGIS II, 2005). Figure 1 gives a 2D cross-section through the model's hydrogeological schematization of the subsurface, which is a gross simplification typical in regional groundwater flow models. Mean aquifer thickness in the model was approximately 18 m, but varied between 0.5 and 30 m. Transmissivity in the aquifers was approximately 40 m^2/day, porosity was assumed to be 0[illegible]nd some anisotropy was added in the ice pushed ridges (Kuijper et al., 2012). The entire drainage system in the catchment was modelled using the DRN and RIV MODFLOW packages (Harbaugh, 2005). Flow through the unsaturated zone was modelled using the MetaSWAP model for a seasonal representation of the groundwater recharge based on land-use (De Lange et al., 2014; van Walsum and Groenendijk, 2008; van Walsum and Veldhuizen, 2011). To allow for the calculation of long groundwater flow paths the model was run for the period of 1700-2017, repeating climate data from the period 1965-2017 (see Kaandorp et al., 2018a).

Backward groundwater travel times (TTs), that represent the age of the water that contributes to streamflow (Benettin et al., 2015; Harman, 2015; van der Velde et al., 2012), were calculated using a combination of forward particle tracking and volume "book keeping" (Kaandorp et al., 2018a). Using the flow velocities calculated by the groundwater flow model, particle tracking software MODPATH version 3 (Pollock, 1994) was used to calculate transient flow paths and TTs. Particles were released monthly at the water table at the center of each model cell and represented the volume equal to the total groundwater recharge of that month. Particles were released for the total model period spanning 317 years yielding a total of 3,804 particle tracking runs, which each had around 14 thousand particles. Particles were stopped at strong sinks or at weak sinks if the fraction of discharge to the sink was larger than 50% of the total inflow to the cell (Kaandorp et al., 2018a). To construct monthly TTDs, particles were collected on a monthly time scale at their endpoints in an area of interest (whole catchment or part of catchment).

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

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 our focus was on the groundwater TTs and time scales. Leaching of nitrate through the unsaturated zone was included in constructing the input curves.

2.4. Tritium input curve

Principally, a series of tritium measurements in streams can be used to derive (ground)water age distributions, assuming a certain lumped model (Broers and van Vliet, 2018a; Cartwright and Morgenstern, 2015; Duvert et al., 2016; Gusyev et al., 2014; Morgenstern et al., 2010; Solomon et al., 2015; Stewart et al., 2016). Here, we intend to use ^{3}H in an opposite approach; validating our dynamic groundwater model TTDs using a short series of ^{3}H measurements in the gaining stream. For the ^{3}H input into our model, we combined the monthly measurements of tritium in precipitation of the closest measurement stations Groningen (1970-2010) and Emmerich (1978-2016), taken from the GNIP Database of tritium activity in precipitation (IAEA/WMO, 2018). For months that both stations had measurements, we used the average concentration, as our study area is located approximately halfway between these two measurement stations. For months that measurements from both stations were not available, we adjusted the available data using a factor based on the average difference between the stations, following an approach similar to Meinardi (1994). Because the relation between the values measured at the two stations seemed to differ before and after 1997, we use two factors: before 1997, we used Emmerich = Groningen * 1.49. From 1997 onwards, we used Emmerich = Groningen * 1.03. For the period before 1970 we used adjusted measurements from Vienna and Ottawa, roughly following (Meinardi, 1994). Figure 2 shows the constructed input curve. Tritium in precipitation increased in the 1950s and 1960s following hydrogen bomb testing and has been returning to natural values since the 1980s (Figure 2). The monthly ^{3}H concentration in precipitation was fed directly into the modelled groundwater recharge, as tritium is part of the actual water molecule.

2.5. Land-use and chemical input curve

Two types of land-use were distinguished: farmlands and natural vegetation, which includes forests and heather (Figure 1). Concentrations of solutes reaching the water table below natural areas were assumed to be constant in time: 15 mg/L for chloride and 5 mg/L for nitrate, which are conservative estimates based on Kros et al. (2004) and Van Beek et al. (1994). For agricultural fields, a chemical input curve was constructed on an annual basis. For the period 2000 to 2017, we used the data for the Dutch sandy areas of the Dutch Minerals Policy Monitoring Programme (LMM), which includes monitored concentrations in the uppermost first meter below the water table at agricultural fields since 1991 (see e.g. Boumans et al., 2005; Fraters et al., 2015). For the period 1950 to 2000, we used the N and Cl surplus that was derived from historical bookkeeping records of minerals applied to farmlands and corrected for crop uptake (Broers and van der Grift, 2004; van den

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Open Access
Discussions

Brink et al., 2008; Visser et al., 2007). We combined this data with the 2000-2017 LMM data by fitting the overlap between 1991-2000 by adjusting the older data to correspond to a groundwater recharge of 0.35 m/year and a nitrate transformation factor of 0.85 in the unsaturated zone, which corresponds with Dutch data for soils with average water tables around 1 m depth (Steenvoorden et al., 1997; van den Brink et al., 2008). Chloride and nitrate increased from the 1950s until around 1985 due to intensification of agriculture (Figure 2). From 1985 concentrations from agricultural fields decreased as a result of national and European legislations (Dutch Manure Law, 1986; EU Nitrates Directive, 1991), that contain rules for the reduction of N applications in farming. Figure 1 shows the areas where the constructed agricultural input curve was used as input for the model, the other parts of the catchments were given the constant concentration of natural vegetation.

2.6. Water quality modeling

The dynamic TTD was combined with the input curves by assigning tritium, chloride and nitrate (Figure 2) to the particles based on their starting time and location (natural/agricultural). For each month the particles that contributed to stream discharge were combined, and their concentrations weighted based on their volumes to simulate the concentrations in the stream. Cl and NO_3 were assumed constant over a specific year, whereas monthly ^3H measurements were directly assigned to the particles in the start month. The model keeps trace of particles that are lost through evapotranspiration within the months after their initial start, thus effectively removing water and ^3H in periods of a precipitation deficit. For Cl and NO_3 the solute input is constant over the year and based on concentrations in the uppermost groundwater, thus there is no need to further account for evaporation for these solutes.

2.7. Sensitivity analysis

The initial run of the water quality model was based on the groundwater flow model that was made for other purposes, related to the quantification of water levels and flow of water, not solutes. Therefore, it had not been calibrated for transport of solutes. We did not intend to calibrate this model for this new purpose, instead we carried out a sensitivity analysis in order to increase understanding of the transport, and effectively revealing the uncertainties that are involved and the parameters that determine the outcomes. In the sensitivity analysis, we explored the effect of the following processes: 1) unsaturated zone delay, 2) increased travel times, 3) different input curves, 4) spatial differences in the input, and 5) denitrification (Table 1).

Base case:

The initial run of the model was based on land-use maps of the catchment of the year 2007 (Figure 1) and the constructed input curves (Figure 2) were used for the agricultural fields, with no further changes to the model. The model therefore did not consider an unsaturated zone or reactive processes such as denitrification.

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Open Access
Discussions

Set 1, unsaturated zone:

The initial model neglected transport time in the unsaturated zone, while it takes time for water to flow from the surface to the groundwater table. This creates a time delay in the order of months to multiple years (Green et al., 2018; Sprenger et al., 2016) and even decades (Wang et al., 2012), depending on the depth of the water table and soil characteristics. In our sensitivity analysis we applied a time delay of 5 years for all particles in our model, assuming that piston flow occurs through an unsaturated zone with an equal thickness everywhere in the catchment area. In reality, flow through the unsaturated zone is much more complicated due to e.g. macropores and chemical processes, but this was outside of the scope of the current study.

Set 2, increased travel times:

Next, we explored the effect of different travel times by applying a multiplication factor of 5 on all the calculated travel times of all flow paths. Increasing the ages of groundwater implies an increase in mean travel time (MTT), which could result from a different aquifer thickness, porosity, groundwater recharge or a change in drainage density (Broers, 2004; Duffy and Lee, 1992; Raats, 1978; van Ommen, 1986).

Set 3, differences in the input curve in time:

The input curve for Cl and NO3 was created on a regional scale and has been successfully used at a local scale in earlier studies (van den Brink et al., 2008; Visser et al., 2007). However, we explored the effect of a more delayed input curve, which could for instance be caused by slightly different local farming practices compared to the regional input curves. In addition, we explored the effect of a sharp decrease in the input by removing all agricultural application of N after the year 1985. In both scenarios the peak of the agricultural input curve for chloride and nitrate was kept at 1985, as this timing of the peak has been found all over the Netherlands (e.g. van den Brink et al., 2008; Visser et al., 2007; Zhang et al., 2013) and results from the EU milk quota legislations in 1984 and EU and Dutch manure laws (Dutch Manure Law, 1986; EU Nitrates Directive, 1991).

Set 4, differences in the input curve in space:

We explored the effect of different land-use configurations by moving the agricultural fields either away from the stream (towards longer travel times) or towards the stream (shorter travel times). A buffer zone of 200 m around the stream was used and two scenarios were tested. First the buffer zone was turned into an agricultural area, while all fields outside the buffer zone were turned into natural areas. Second, the reverse was done: the buffer zone was turned into natural areas with agricultural fields outside of the buffer zone. A ratio of 50% agriculture and 50% natural vegetation was used for the agricultural areas in

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Discussions

these scenarios to prevent excessive nitrate concentrations and to keep the total input in the system approximately equal as based on the land-use maps.

Set 5, denitrification:

In the Netherlands, denitrification is known to remove nitrate from the groundwater, partly by oxidation of organic C or pyrite:

$$5C\ (s) + 4NO_3^- + 2H_2O\ \rightarrow\ 4HCO_3^- + CO_2(g) + 2N_2(g) \qquad (1)$$

$$5FeS_2\ (s) + 14NO_3^- + 4H^+ \rightarrow\ 5Fe^{2+} +\ 10SO_4^{2-} + 7N_2\ (g) + 2H_2O \qquad (2)$$

Oxidation of pyrite has been found to be the main nitrate reducing process in several studies (e.g. Broers and van der Grift, 2004; Postma et al., 1991; Prommer and Stuyfzand, 2005; Tesoriero et al., 2000; Visser et al., 2007; Zhang et al., 2009). To see the possible effects of different conceptualizations, denitrification and nitrate time lags were modelled in different ways. First, it was simulated as a kinetic zero order reaction following:

$$NO_3 = NO_3 - rate * travel\ time \qquad (3)$$

We used 10 mg NO3/L/year as the rate of denitrification, which is in the range of values reported by Van Beek et al. (1994) for the Netherlands. Second, denitrification was based on the occurrence of a pyrite layer at a certain depth, similar to the model of Zhang et al. (2013). All nitrate passing through the denitrifying pyrite layers was instantaneously removed.

3. Results

3.1. TTD modelling result

The model indicated that about 20% of discharge in the Springendalse Beek is water with a travel time less than 1 year, while about 15% of discharge has a travel time of more than 25 years (Figure 3a and b). The discharge in the Springendalse Beek thus consists mainly of medium aged water (1 – 25 years) and the mean travel time is approximately 11 years and median travel time around 4 years. Part of the discharge in the catchment originates from agricultural fields and part from natural areas. Based on the land-use map (Figure 1) and the particle tracking, we found that in the upstream part of the catchment between 15 and 25% of discharge infiltrated under agricultural fields (Figure 3c and d). For the total catchment this increases to about 25 to 35%, because a larger part of the downstream catchment is used for agriculture.

The contribution from agricultural fields shows a seasonal pattern especially for the total catchment (Figure 3d), with higher agricultural contributions during the wet winter. A larger fraction of discharge is young in winter compared to summer, especially in the downstream part of the catchment (Figure 3b). During this period, the activation of flow to tile drains and

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

towards adjacent ditches promotes the shallow flow paths resulting in a young water component (Rozemeijer and Broers, 2007; van der Velde et al., 2009).

3.2. Stream measurements and initial modelling results

We started sampling for 3H in 2016 because we anticipated that tritium could give an independent validation of our transient TTD model. Tritium concentrations were found to be around 5 TU (Figure 4a). Although the time series is relatively short, the model captures the variability of the actual 3H measurements well, though the modelled concentrations overestimate the measured concentrations by approximately 0.5 TU (Figure 4a). Based on experience in other catchments (Broers and van Vliet, 2018a; Morgenstern et al., 2010; Stolp et al., 2010) this might be caused by the model underestimating the mean age of water in our catchment.

The chloride and nitrate measurements show a clear trend reversal (Figure 4c-f) that resembles the trend reversal in the input curves (Figure 2). Chloride concentrations in the upstream part of the catchment increase from about 20 mg/L in the 1970s to up to 30 mg/L between 1990 and 1994 (Figure 4c), which is later than the peak in the input curve in 1985 (Figure 2). In the same period, the chloride concentrations measured at the outlet of the total catchment peak at a concentration up to about 42 mg/L (Figure 4d). After 1994, the chloride concentrations decrease both up- and downstream and have been approximately stable between 20 and 25 mg/L since the year 2000, similar to the trend in the chloride concentrations in the uppermost groundwater. The initial model run was based on the land-use and input curves described in paragraph 2.5 and included no further processes or changes to the original flow model. The modelled chloride concentrations gave a reasonable fit (Figure 4c and d), although the modelled concentrations were too low for the period between 1990 and 1995 and the chloride peak was simulated around 1985 instead of 1990.

The measured timing of nitrate at the outlet of the catchment (Figure 4f) is similar to chloride (figure 4d) with an increase up to 1994 when the maximum of 50 mg/L is reached. After that, nitrate concentrations have decreased but at a slower rate than chloride. While the measurements showed the nitrate peak around 1994 and 1997 for the total catchment and upstream respectively, the initial model run showed the nitrate peak around 1987 for both the total and upstream catchment. This may suggest that travel times were underestimated in the model, in correspondence with the results from 3H.

What is especially noticeable is that for the upstream part of the catchment, the timing of the chloride and nitrate peaks in the measurements do not coincide. This could be caused by processes that only affect nitrate and not the more conservative chloride, such as denitrification. The difference could also indicate that the ratio between chloride and nitrate have changed in the fertilizers used or suggest point source pollution disturbing the agricultural signal.

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

The measured chloride and nitrate measurements nicely reflect the seasonality in the contribution of water infiltrated below agricultural fields (Figure 3) by showing more variation in the downstream than in the upstream part of the catchment (Figure 4). Like the measurements, the initial model run showed higher chloride and nitrate concentrations in winter than in summer, and this seasonal variation was larger for the total catchment than the upstream catchment. This agrees with the measurements and conclusion of Kaandorp et al. (2018a) that the contribution of different flow paths differ between the two parts of the catchment.

3.3. Sensitivity analysis: Effects on the breakthrough of tritium, chloride and nitrate

Overall, the simulated tritium, chloride and nitrate concentrations in the stream did not completely fit the measurements, both in concentration and in the arrival in time of the agricultural peak (Figure 4). Instead of attempting to further adapt and calibrate the groundwater flow model, we ran a sensitivity analysis, exploring the parameters that might determine the apparent mismatch with the measured concentrations; thereby increasing our understanding of the flow and transport system in catchments in general.

3.3.1. Scenarios affecting the travel time distribution

Unsaturated zone

An unsaturated zone was added to the upstream catchment model with a travel time of 5 years, as a separate piston flow component superimposed on the groundwater system that was modelled.
This shifted the tritium peak in time and led to a decrease in the tritium concentrations because decay takes place while travelling through the unsaturated zone (Figure 5a). Because chloride and nitrate were not reactive, the unsaturated zone merely added a certain amount of time to the whole travel time distribution, simply shifting the chloride and nitrate output curves in time (Figure 5b and c).

Mean travel time

The application of a factor 5 on the mean travel times decreased the overall tritium concentrations due to the extra time for decay (Figure 5a). The input curves were distributed more in time and therefore lowered the chloride and nitrate peak and increased the tail of the peak (Figure 5b and c). When travel times were increased 5-fold the chloride and nitrate peaks shifted approximately 10 years.

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Open Access
EGU
Discussions

3.3.2. Scenarios affecting the input of solutes and the land-use specific TTD's

Time

We modelled two alternative input curves of agricultural fields. First, we used an input curve that has a slower decrease of nitrate in time after the 1985 peak (Figure 6a). This slower decrease resulted in a longer increase in nitrate extending also into the period when the input is already decreasing, followed by a slower decrease after that (Figure 6b). Second, we removed all agriculture after the 1985 nitrate peak (Figure 6a). This instantly lowered the stream nitrate concentrations, as the stream consists of a large amount of young water and after removal of agriculture is only affected by nitrate from older flow paths that started before 1986 (Figure 6b).

Space

The effect of spatial changes of the input was modelled in two scenarios: one scenario where a zone of 200 m around the stream was used for agriculture, and one scenario where agriculture took place outside of the same 200 m zone. With the agricultural fields directly around the stream (Buffer scenario 1), the nitrate peak shifted to 1985 (Figure 6c), which is the year of maximum input (Figure 2). With a natural buffer strip and the agricultural fields in the more upstream parts of the catchment (Buffer scenario 2), the nitrate peak shifted towards later in time and became flatter with a much slower decrease over time (Figure 6d). This results from the fact that the fields further away are connected with the stream by longer flow paths with longer travel times. In addition, the shape of the curve was changed based on the location of the fields: when fields are further away, the agricultural input is distributed more over time resulting in a lower peak but a longer tail with higher concentrations.

3.3.3. Scenarios affecting the transformation processes in the subsurface

Denitrification

Two denitrification scenarios were modelled, using different conceptualizations. Zero order denitrification with a rate of 10 mg/L per year resulted in continuously lower nitrate concentrations without a shift in time (Figure 7). In the other scenario, denitrification was modelled based on the depth that the particles flowed through, for which nitrate was removed from all particles travelling through deeper layers (> model layer 2, >0.5-15 m below surface). This also resulted in decreased nitrate concentrations, but with higher values in the concentration tail than in the zero order scenario (Figure 7).

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

4. Discussion

4.1. The effect of processes on modelled breakthroughs

Unsaturated zones led to a shift in time of the breakthrough of the nitrate curve while not affecting the concentration of nitrate (Figure 5; Table 2). 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). Storage of N in an area with a thick unsaturated zone can thus be large, but in a larger area with variations in the water table the outflow of N is often diluted by shallow flow paths contributing young water in downstream areas with shallow water tables or artificial drainage. In such an area the part of the catchment with thick unsaturated zones will create a longer tail in the nitrate concentrations.

Multiplication of the MTT lowered the nitrate peak because the larger age of the discharging groundwater results in a larger contribution of pre-1950 water, which has been less influenced by agricultural activities. Because the ages of the younger flow paths are increased, the agricultural peak from the 80s is distributed over a larger amount of time, resulting in a shift in arrival of the peak and a slower decrease of concentrations after the maximum stream concentration has been reached (Figure 5; Table 2). The factor 5 we multiplied the MTT with in our results clearly shows the effect on the breakthrough but is a very extreme case, as it represents a system with an aquifer that is also 5 times as thick or has a porosity 5 times higher given the same groundwater recharge rate (van Ommen, 1986; Vogel, 1967).

Changing the shape of the input curve led to a similar change in stream concentrations. In the case we presented, this was a slower decrease after the concentration peak (Figure 6a). There was no shift of the peak because the peak in the input was kept at the same moment in time as we have strong indications that the peak in Dutch agriculture occurred during the same year in all of the Netherlands, due to the strict measures taken around 1985 (van den Brink et al., 2008; Visser et al., 2007). It seems obvious that the input curve and its uncertainty have a large effect on the stream concentrations (Howden et al., 2011a). In a scenario where all agriculture was removed from the year 1986, an instant decrease of nitrate concentrations in the stream was found. This follows from the large amount of young water in our catchment. Van Ommen (1986) used a conceptual case to illustrate the same: in catchments with an exponential TTD (or in our case close to exponential TTD; Kaandorp et al., 2018a), a change in the input directly affects stream concentrations for all MTTs. The response differs with MTT when the reduction in inputs is more gradual. A delay of the arrival of the peak is possible when the MTT is rather long and the input decreases slowly or a combination of those (see Supplement).

Zero order denitrification removed nitrate from the model and thus lowered nitrate concentrations while not changing the timing of the peak (Table 2). Zhang et al. (2013) and more recently Kolbe et al. (2019) showed that varying denitrification with depth has a major influence on nitrate delivered to streams via groundwater. Our scenarios were relatively simple with equal denitrification rates and depths throughout the catchment. It is however know that there is a large variability in the reactivity of for instance organic matters (e.g. Hartog et al., 2004; Middelburg, 1989; Postma et al., 1991), which could lead to spatial differences in denitrification and therefore a change in the nitrate breakthrough similar to the scenarios where the spatial input was changed.

4.2. Contributing area of streams

Recently Barlow et al. (2018) restated the definition of the 'contributing area' as "the two-dimensional areal extent of that portion of a capture zone that intersects the water table and surface-water features where water entering the groundwater-flow system is discharged". They did this for groundwater wells, but streams also have a contributing area, which is not the same as the catchment. The catchment of a stream is the area in which all water finally ends up in the stream.
It is also not to be confused by the 'contributing area' or 'upslope area' used in many distributed hydrologic modes by catchment scientists, which is the runoff-generating area, i.e. the parts of the catchment where seepage and overland flow occur (e.g. Ambroise, 2004; Beven and Wood, 1983; Beven and Kirkby, 1979; Mcglynn and Seibert, 2003; Yang et al., 2018). To avoid further confusion, we introduce the terms 'groundwater contributing area' and 'runoff contributing area'. The groundwater contributing area (GCA) is defined as the area where the water that is actively contributing to streamflow at a certain moment of time through active flow paths entered the coupled groundwater-surface water system as precipitation (recharge area). The runoff contributing area (RCA) is defined as the area where at a certain moment in time water is discharged from the catchment storage as seepage or overland flow, and thus is the area where runoff is generated (Figure 8). Areas that are neither groundwater- or runoff contributing areas are inactive and do not actively influence streamflow at that specific moment in time. In our particle tracking method, the GCA is the starting point and the RCA is the ending point of a particle (Figure 9).

As older flow paths generally originate from a larger distance from the stream (e.g. Modica et al., 1998), there is a difference in the travel time of water from different parts of the groundwater contributing area. Because of this, the location of agricultural fields in the groundwater contributing area affects the breakthrough of tritium, chloride and nitrate. The buffer scenarios showed that the arrival of the nitrate peak shifts in time and changes shape if the fields are further away from the stream (Figure 6c and d), which is a result of the difference in travel time of the flow paths from the fields around the stream and the fields more upstream (e.g. Musolff et al., 2017).

Because flow paths change based on wetness conditions (e.g. Kaandorp et al., 2018a; Rozemeijer and Broers, 2007; Yang et al., 2018) the groundwater contributing area also shifts through the seasons. This includes the disappearance of flow through shallow flow paths towards e.g. drainage pipes and ditches in dry periods, which leads to the non-linear reaction in the dynamic TTD. In our results, the discharge originating from agricultural fields changes in time as a result of this variation in contributing area (Figure 3 and 9). Because of this, the seasonal variation in flow paths and thus the groundwater contributing area also

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Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Open Access
Discussions

leads to fluctuations in the concentrations of nitrate in the stream (e.g. Figure 4). Figure 8 illustrates how the groundwater contributing area may shift based on wetness conditions: in the wet period all flow paths are active while during the dry period only the older flow paths are active, and flow through shallow short flow paths has ceased. 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. This concept extents on the ideas presented by Rozemeijer and Broers (2007), by adding the spatial dimension and groundwater contributing area to their concept of variation in the contribution of flow paths with depth. Similarly, Musolff et al. (2017) showed that both seasonal and long-term concentration-discharge relationships strongly depend on spatial source patterns. Spatial differences in reactivity (e.g. Kolbe et al., 2019) can further cause spatial variability between solute concentrations of water in different flow paths.

The location of agricultural fields in relation to the catchments' drainage network, and more precisely the location of high loading is thus an important factor that largely governs the travel times of the agricultural solutes. This means that in modelling not only the location of fields must be known but also more information of leaching towards the groundwater at every field, as there can be significant difference in the use of manure and fertilizers due to for instance differences in crops. However, for our catchment national and EU regulations put strong constraints on the application of nitrogen, thus levelling differences in inputs to farmlands (e.g. Oenema et al., 1998; Schroder et al., 2007). Effectively, soil properties and groundwater levels determine the areas with strongest leaching towards the groundwater as those factors determine the potential for unsaturated zone denitrification.

4.3. Understanding nitrate in the Springendalse Beek catchment

The increase in old water contribution during dry periods has been found in several studies and is called the 'inverse storage effect' (e.g. Benettin et al., 2017; Harman, 2015). Seasonally, the upstream catchment shows less variation in discharge than the downstream catchment, as well as less variation in the contribution from agricultural fields and in the stream concentrations of chloride and nitrate (Figures 3 and 4). The fact that our groundwater-based model was able to simulate the seasonal variation in chloride and nitrate concentrations shows that this variation can largely be explained by variations in the contribution of different groundwater flow paths originating from different locations in the catchment, as was also concluded by e.g. Martin et al. (2004), Musolff et al. (2016), Rozemeijer and Broers (2007) and van der Velde et al. (2010a). High chloride and nitrate concentrations from agricultural activities are mostly present in the shallower layers (e.g. Bohlke and Denver, 1995; Broers and van der Grift, 2004; Rozemeijer and Broers, 2007; Zhang et al., 2013). Especially in the downstream part of the catchment, with its larger drainage density from the many (shallow) agricultural tile drains and ditches, these shallow flow paths have a larger contribution in the wet period with high groundwater tables than in the dry period (Kaandorp et al., 2018a). Similar to our model, van der Velde et al. (2010) and Wriedt et al. (2007) were able to model seasonality of in-stream nitrate concentrations using only groundwater dynamics, and concluded it to be an important process that is further superposed by

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Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
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Discussions

denitrification and variability in loading. We conclude that the upstream part of the Springendalse Beek catchment with its relatively stable year-round discharge, provides the lower limit of the NO3 concentrations in the catchment, while the drained downstream part of the catchment causes the yearly variation in stream concentrations.

Tritium concentrations were overestimated by approximately 0.5 TU in the initial model run (Figure 4a). Because the tritium concentrations can only be lowered by increasing the TTD, both an unsaturated zone or an increase of MTT could improve the fit of tritium. We cannot derive from the tritium measurements whether the catchment should have an unsaturated zone time delay or increased MTT, because no earlier measurements of tritium are available for the Springendalse Beek. In our catchment, unsaturated zones are relatively thin in the downstream part of the catchment (maximum a few meters, but mostly <1 m) and slightly thicker in the upstream part (up to 3 meters), and thus only a maximum shift of a few years would be realistic. Due to the complex hydrogeology of the ice pushed ridge, especially in the upstream part of the catchment, there is quite some uncertainty in the exact depths and volumes of the aquifers that are present within the ice-pushed ridge. In the regional groundwater flow model, this complex geology was highly simplified based on the version of the hydrogeological schematization of REGIS (REGIS II, 2005) that was available when building the flow model. The complex geological structure of the ice-pushed ridge makes it difficult to exactly pinpoint the position of the tilted Pleistocene sand layers that probably form the main pathways to the stream, as the tilted slabs of Tertiary clays form hydraulic barriers for groundwater flow (pers. comm. Harting, TNO Geological Survey of the Netherlands). Given the approximate N-S strike direction of the sandy intercalations, this may have influence on the distinct farmlands that contribute to the nitrate concentrations in the stream, that may be positioned further away than the modelled schematization might allow in the regional groundwater flow model. It might also affect the mean travel times in the groundwater system as a larger aquifer volume would result in overall longer travel times (Vogel, 1967; van Ommen, 1986). Moreover, thicker than average unsaturated zones within the sandy outcrops may also delay the propagation of nitrate and chloride peaks towards the stream, following the conceptualization presented.

Land-use changes have occurred in the study area over the past few decades. For instance, 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. On top of this, more manure may have been imported from areas with a manure surplus towards the study area since 2000, which has been found to be the case for other catchments in the region (Roelsma et al., 2011). Obviously, this complexity in the input curves in time and space was too detailed for our model and beyond the scope of our analysis. However, the scenarios in which we shifted the location of agricultural fields and changed the input curves were an attempt to infer the effect of such land-use changes.

Denitrification does not seem to occur substantially in the upstream part of the study area as the nitrate concentrations are generally already lower than the measurements. This is confirmed by the oxic nature of the sandy sediments that the groundwater discharges from (Kaandorp et al., under revision for publication in JoH), the presence of oxygen and lack of iron

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Discussions
Open Access

in the discharge water (data not shown). Although the upstream part of the catchment contains less agriculture than the downstream part (Figure 3), the nitrate concentrations in the stream are comparable. This may be an indication of denitrification in the downstream part of the catchment where water levels are close to the root zone, promoting shallow denitrification, which could be a reason for the overestimation of nitrate (Figure 4f).

4.4. Improving and use of the model

The groundwater flow model that we used was calibrated on groundwater heads and validated using stream discharge (Kaandorp et al., 2018a), which is common practise for groundwater models. By combining TTDs with input curves for solutes, we were able to further validate the model using water quality measurements. This way, the model is not only validated on celerities, but also on water velocities (Beven, 1981; McDonnell and Beven, 2014). Although our model performed well on celerities (groundwater heads and stream discharge), it showed considerable mismatch for water velocities (solutes) even considered that it did not include reactive processes. Instead of completely adapting the model, we chose to run a sensitivity analysis to understand the reasons for the apparent mismatch, thus elucidating important transport factors in our study catchment, that are of general use in transport modelling studies for non-point sources in catchments worldwide.

To illustrate whether it is possible to match the model to the measured concentrations, we adapted some of the parameters that are most sensitive and somewhat most realistic. This is by no means a calibration effort, because that would require a significant change to the complete set up of both the hydrogeological part of the model, the unsaturated zone conceptualization and/or the introduction of time changing position of agricultural fields. The result depicted in Figure 10 is meant to show that a different parameterization is possible, adapting part of the uncertain parameters.

For the improved model run, we mainly focussed on the upstream part of the catchment, as the concentrations there also influence the stream concentrations in the downstream part. Especially the late arrival of the nitrate peak in the upstream area is exceptional for the Netherlands. To improve the model, we needed to delay the arrival of the chloride and nitrate peaks and provoke a slower decrease after the arrival of the peaks. For this, the spatial layout of agricultural fields was changed by removing the (few) fields close to the stream and increasing the amount of agriculture outside of a 200 m buffer. Considering that land-use has changed in the past decades and that the geology on the ice-pushed ridge is known to be much more complicated than the conceptualization in the model, the change made to the spatial input for this model run was deemed realistic. Additionally, based on the mismatch with tritium, we added an unsaturated zone with a travel time of 3 years. Note that an unsaturated zone of 3 years is not realistic for most of the downstream area as that part of the catchment has shallow groundwater levels. However, it is currently not possible in our method to add an unsaturated zone in the upstream area and not in the downstream at the same time. These two changes together resulted in a better fit with the tritium, chloride and nitrate measurements (Figure 10), especially for nitrate in the upstream area. For the measurements made downstream between 1985 and 1990 a better fit was not possible with realistic model changes.

Further calibration of the model, to use it for e.g. the calculation of the effects of certain management measures, would require much more changes to the model. It would be required to conceptually change the way the unsaturated zone is accounted for at this moment, it requires much more detail in the hydrogeology of especially the upstream part of the catchment on the ice-pushed ridge, and it requires knowledge of the location of all farmlands both in time and space. This was however outside of the scope of the current paper. The presented method has some further limitations: a large amount of computer power required for calculation of the dynamic TTDs, there is uncertainty in the short travel times due to the grid cell size in the groundwater model and processes such as overland flow and in-stream denitrification are not included.

4.5. Management implications

Removing the source of diffuse pollution led to an immediate decrease in concentrations in the studied stream (Figure 6b), due to the large fraction of younger water in the TTD. Thus, managing the input of agricultural pollutants is a good management option with direct benefits, except when decreases are very slow or the MTT is very large. Also, after an immediate decrease, the legacy from older flow paths leads to a slow further decrease in time. According to scenarios modelled by Tufford et al. (1998) the management of stream water quality is most effectively done at riparian and adjacent lands. Johnes and Heathwaite (1997) suggested to move agricultural fields to the locations with the highest potential for nutrient retention. We saw that the location of agricultural fields in a catchment is indeed an important factor in the effect of agricultural pollution. Not only does the location of the fields affect the time lag and shape of the breakthrough curve of stream concentrations, longer flow paths from the fields further away from the stream also have more time for processes such as denitrification. In fact, the scenario with the 200 m agricultural-free zone around the stream can be compared with a natural riparian zone, on which much research has been done (e.g. Anderson et al., 2014; Feld et al., 2018; Hefting and Klein, 1998; Hill, 1996; Ranalli and Macalady, 2010). These studies show that riparian zones positively affect stream water quality because of their high rate of denitrification. Our results show that in addition to this, the longer length of the groundwater flow paths lags the arrival of and dampens the nitrate peak. In fact, as denitrification rates are highly variable (e.g. Tesoriero and Puckett, 2011; Van Beek et al., 1994) and riparian zones can be by-passed by deeper groundwater flows (Bohlke and Denver, 1995; Flewelling et al., 2012; Hill, 1996; O'Toole et al., 2018; Ranalli and Macalady, 2010), the longer distance and thus distribution through time is at some locations and/or moments arguable the more important effect of riparian buffer zones. Although positively affecting water quality of the stream by decreasing concentrations, longer travel times also lead to a longer tail and thus invoke a longer lasting effect with lower concentrations of polluting stressors.

5. Conclusions

Dynamic travel time distributions based on a high-resolution spatially distributed groundwater flow model were combined with input curves for tritium, chloride and nitrate to calculate their concentrations in a Dutch lowland stream. The groundwater dynamics were shown to largely cause the seasonal and long-term fluctuations in stream concentrations, indicating the importance of the dynamic contribution of different groundwater flow paths.

The model was calibrated on celerities (pressure wave propagation) in earlier research and it was therefore not surprising that a mismatch existed for the results that we obtained for solutes, which depend on velocities. Instead of completely adapting the model, we ran a sensitivity analysis and scenarios to understand the reasons for the mismatch and clarifying the important transport factors. We found that the time of arrival of the nitrate peak shifted due to addition of an unsaturated zone, multiplication of the MTT and spatial changes of the input, as well as a slow decrease of the input combined with a relatively long MTT. The location of agricultural fields in relation to the catchments' drainage network was found to be an important factor that largely governs the travel times of the agricultural leachate. It was also shown that the 'groundwater contributing area' of a stream, that is the catchment area where the discharging water infiltrated, increases and shrinks based on wetness conditions.

The model for the presented case was improved by shifting the location of agricultural fields and adding the time delay of an unsaturated zone. Further improvements would require much more detail on the complex hydrogeology and historical land-use changes. A limited amount of stream tritium measurements proved to be a valuable indication of an unsaturated zone time delay and/or higher MTT. The method presented in this paper can be used to validate calculated TTDs and provides an opportunity to validate groundwater models not only on celerities, but also on water velocities.

Overall it was found that groundwater distributes water in time and space and makes it possible for water from different sources to mix and consequently groundwater functions as a buffer on the effect of (diffuse) pollution. The results of this study are interesting for water managers of catchments with diffuse pollution from agriculture, as it gives an insight into the possible parameters to steer on. For instance, in catchments with a (close to) exponential TTD and a limited unsaturated zone, a direct reaction of stream nitrate concentrations to reductions in the nitrogen inputs can often be expected when agricultural fields are close to the streams. Further research could be aimed on application of the same method in other catchments and focus on gathering further knowledge on dynamic contributing areas in other hydrogeochemical and topographical settings.

Competing interests

The authors declare that they have no conflict of interest.

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Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Discussions

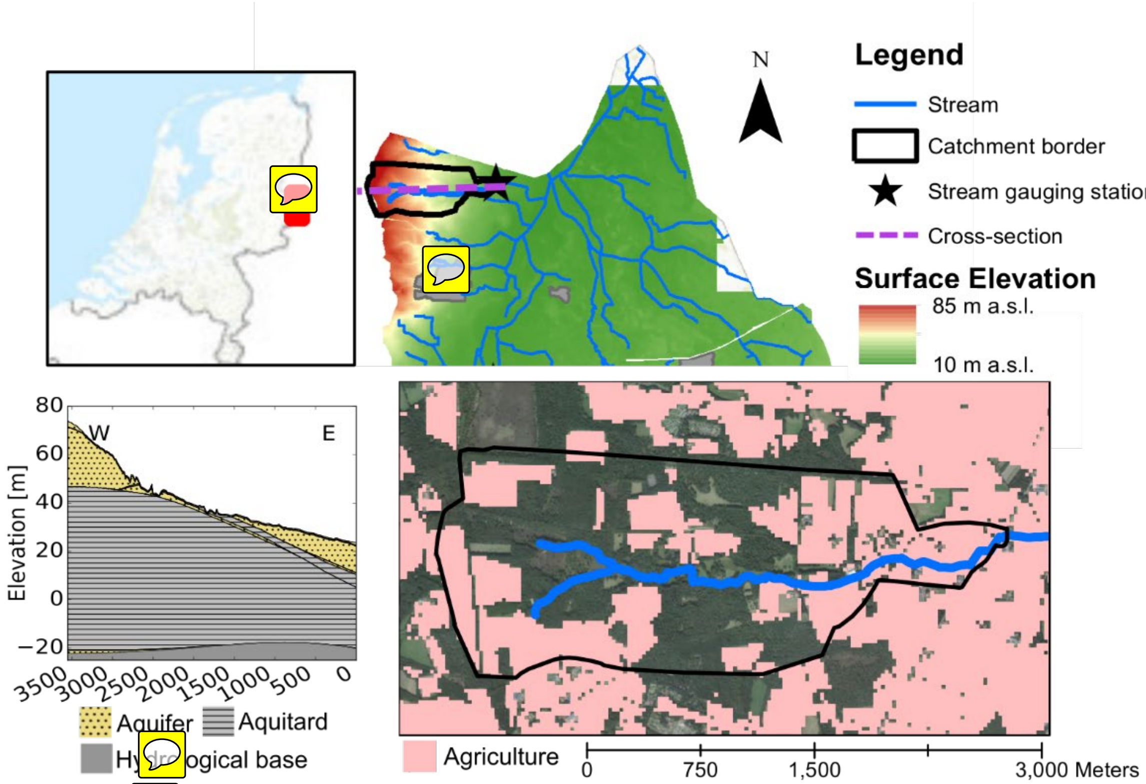

Figure 1: Location of the study area, model conceptualization, and the location of agricultural fields in the year 2007. ***Background maps and DEM from PDOK (PDOK.nl/datasets).***

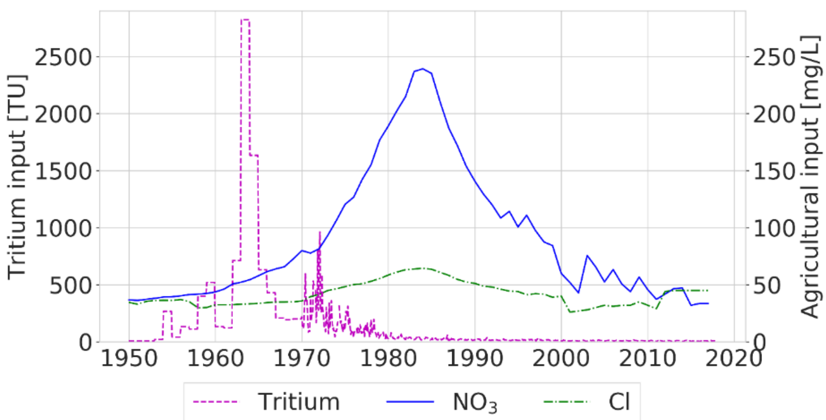

Figure 2. Input curves for tritium (left axis) and the estimated concentrations of nitrate and chloride under farmland (right axis). The tritium input curve is based on precipitation measurements at stations Groningen and Emmerich. The 1985 peak in Cl and NO_3 coincides with the start of the legislations from the Dutch Manure Law that placed restrictions on the applications of N in agriculture.

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

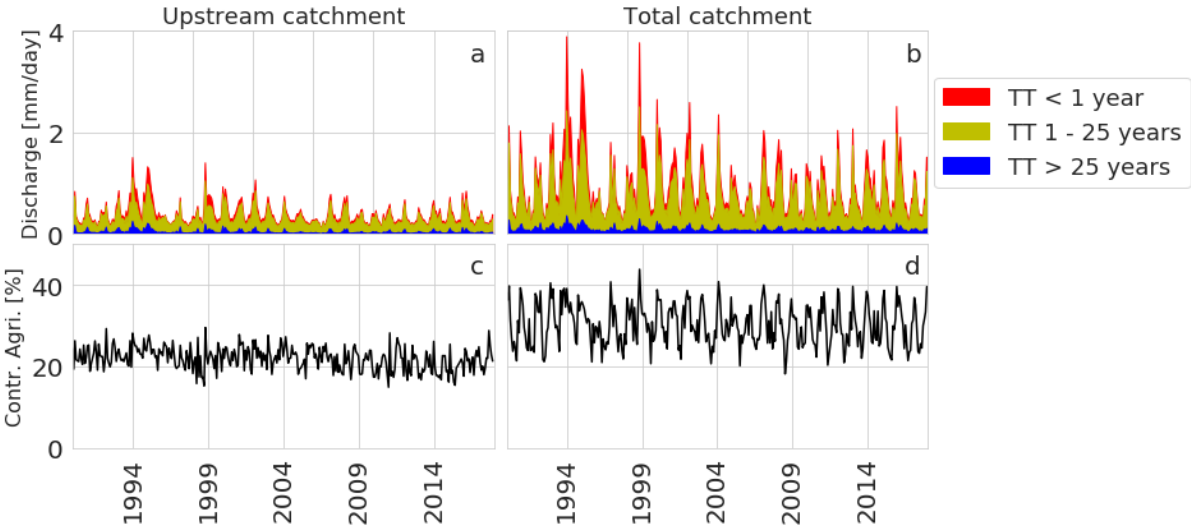

Figure 3. Three age classes of the travel time distributions of the discharge in the Springendalse Beek for the upstream part of the catchment (a) and the total catchment (b). The lower panels show the percentage of discharge originating from agricultural fields for the upstream part of the catchment (c) and the total catchment (d).

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences
Discussions

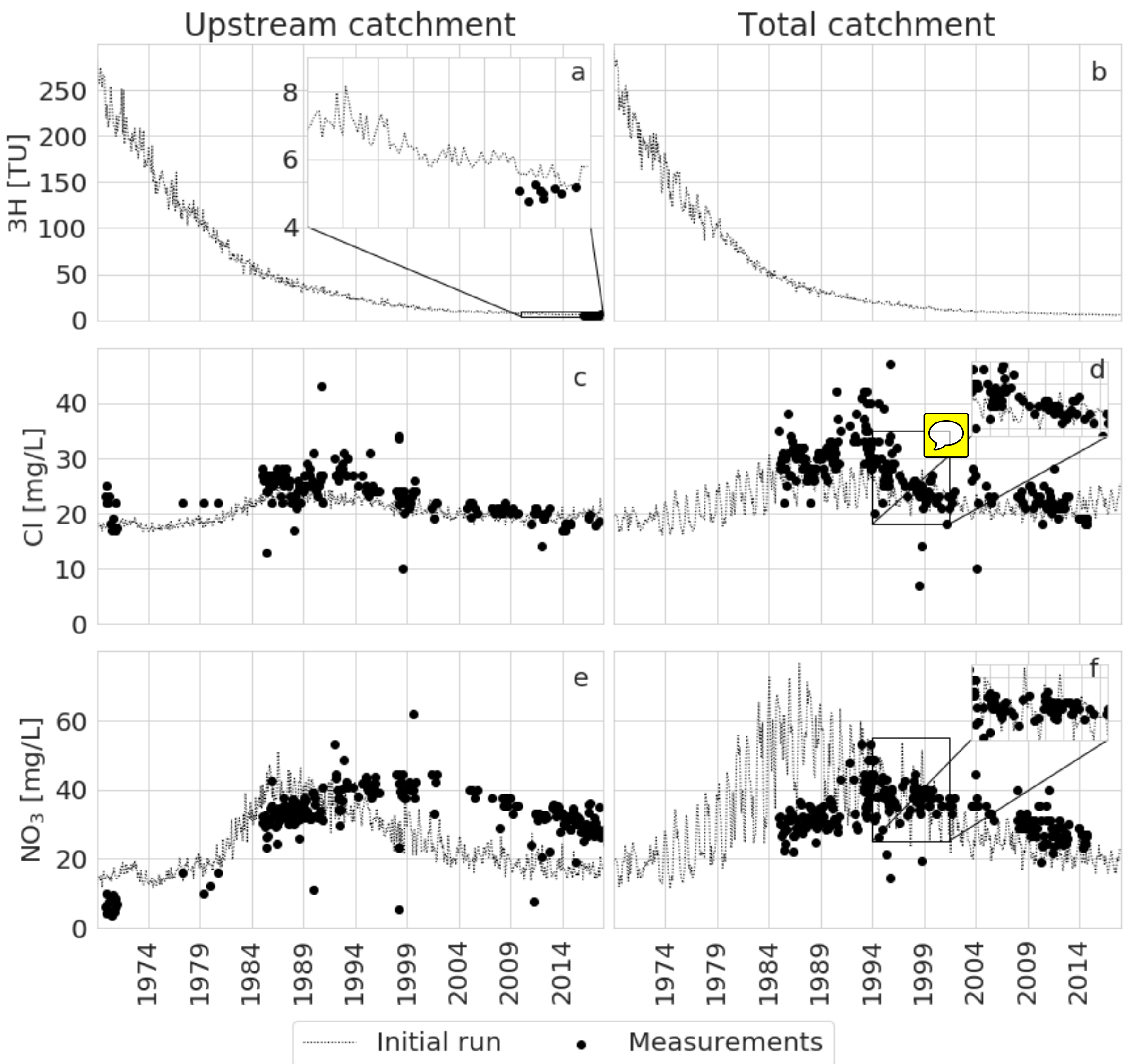

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Figure 4. Measurements and initial model results based on the TTDs from Kaandorp, et al. (2018) and the input curves in Figure 2. No further processes were added yet. Note that tritium samples were only available for the upstream part of the catchment (panel a).

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

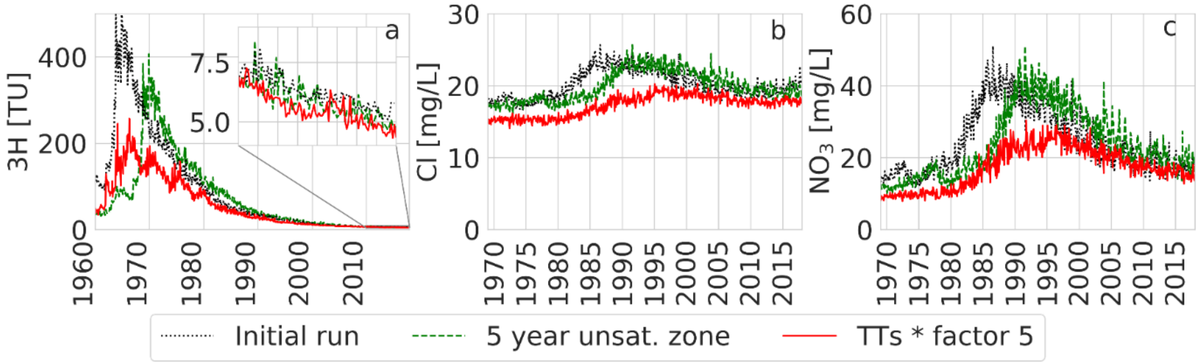

Figure 5. The effect on tritium (a), chloride (b) and nitrate (c) of a scenario with a 5-year delay due to an unsaturated zone and a scenario where all travel times where increased by a factor 5.

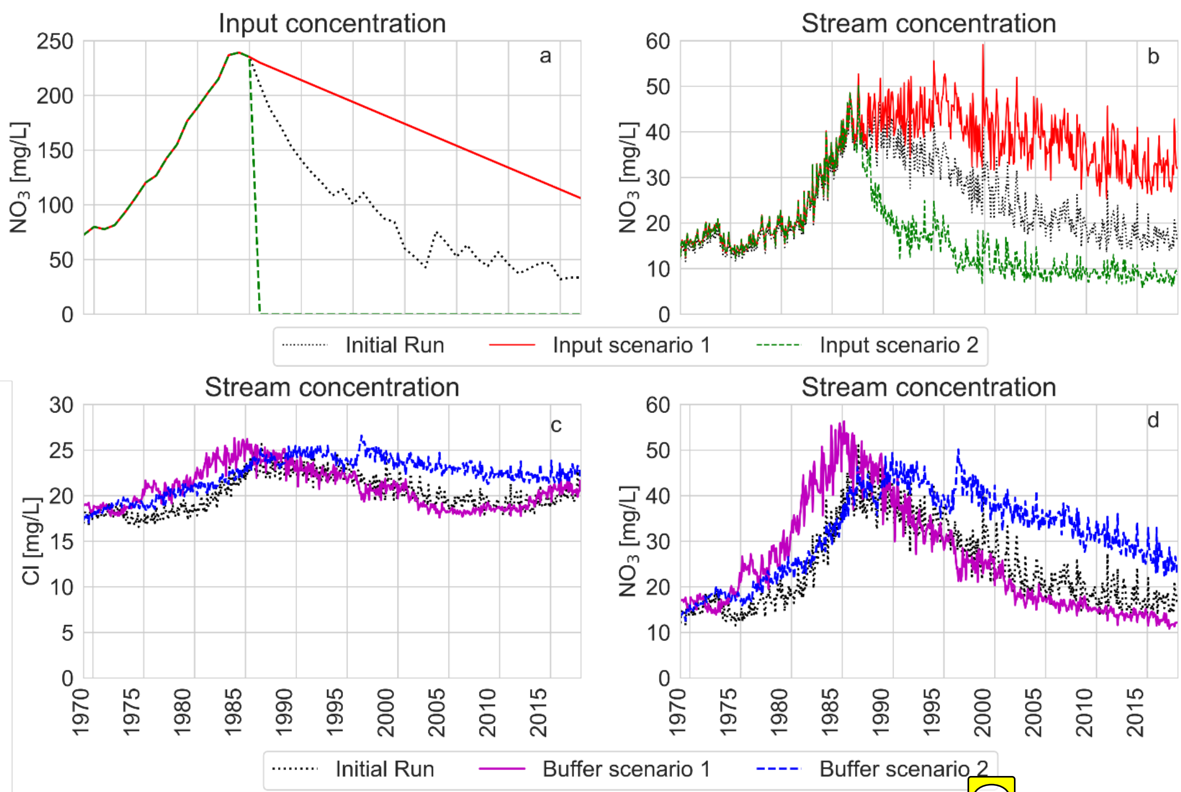

Figure 6. Panel a and b show the effect of two scenarios with changes in the nitrate input curve. [illegible]e the difference in scale of the x-axis between the left and right panels. Panels c and d show the effect of spatial changes in land-use on both chloride (c) and nitrate (d): only agriculture inside of a 200 m strip around the stream (Buffer scenario 1), and only agriculture outside of the sa[illegible]uffer strip (Buffer scenario 2). In both scenarios agricultural parts have 50% agriculture and 50% nature, so that the total [illegible]nt of fields is approximately equal to the that in the real catchment.

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Preprint. Discussion started: 5 November 2019

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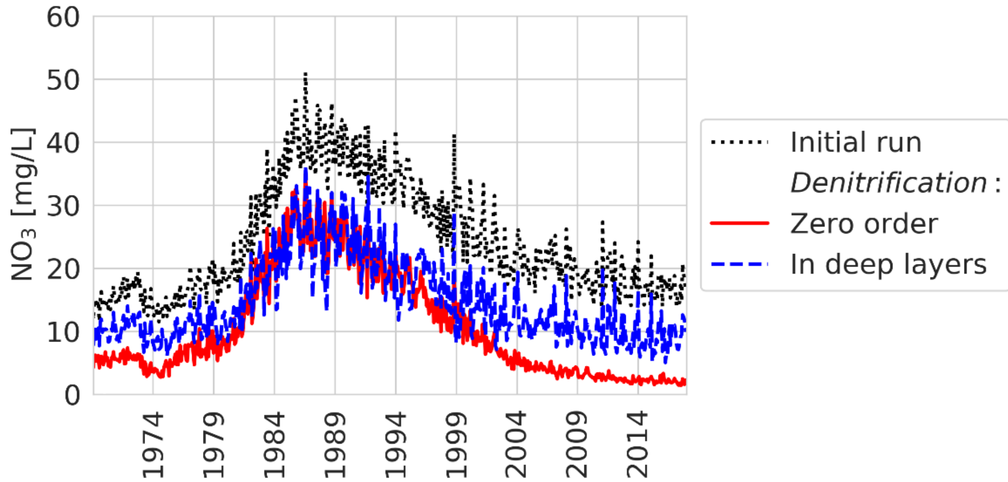

Figure 7. Effect of denitrification for the upstream part of the catchment using different conceptualizations: zero order denitrification and denitrification in deep layers.

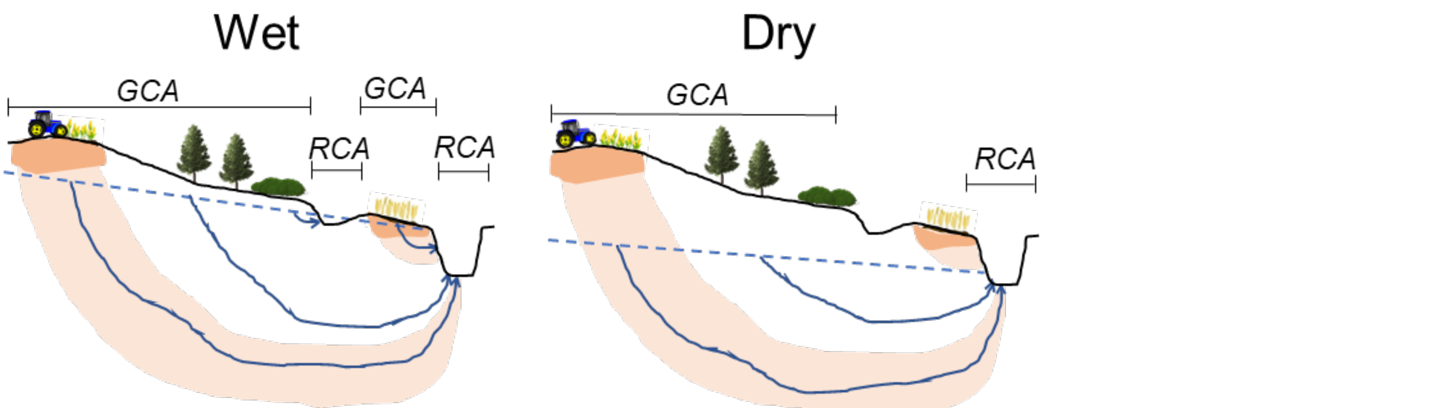

Figure 8. Contributing areas fluctuate with wetness conditions due to changing flow paths. GCA is the Groundwater Contributing Area which is where discharge was infiltrated and RCA is the Runoff Contributing Area which is where discharge is generated. Areas between the two different contributing areas are 'inactive' and do not actively influence stream discharge.

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

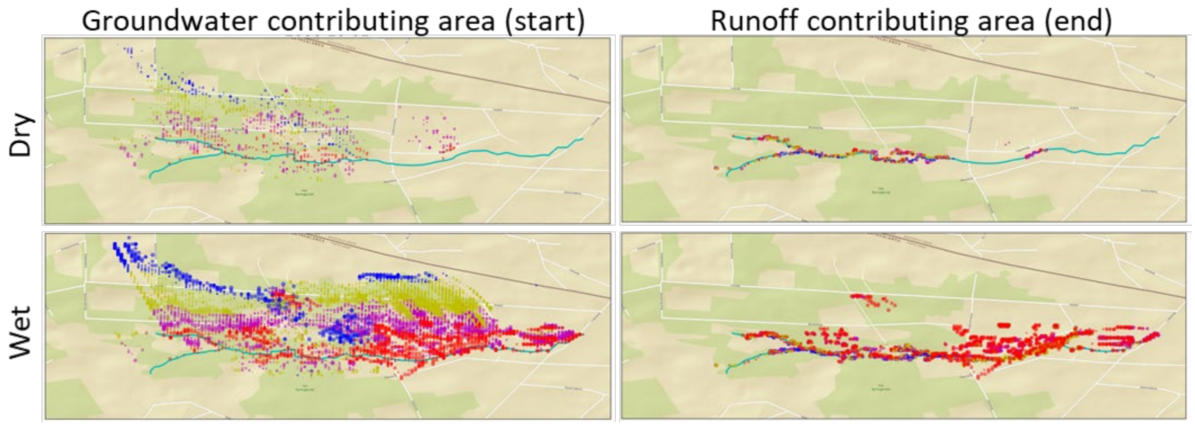

Figure 9. Contributing area in the model for a dry (top; summer 2006) and a wet (bottom; winter 2006/2007) period. Colors represent the travel time towards the stream with blue TT >25 year and red TT < 1 year (similar to Figure 3). Notice the large increase in the runoff contributing area in the downstream part of the catchment during wet periods which results from the extensive agricultural drainage system. ***Background map ESRI_StreetMap_World_2D, Sources: Esri, DeLorme, NAVTEQ, USGS, NRCAN, METI, iPC, TomTom, http://services.arcgisonline.com/ArcGIS/rest/services/ESRI_StreetMap_World_2D/MapServer.***

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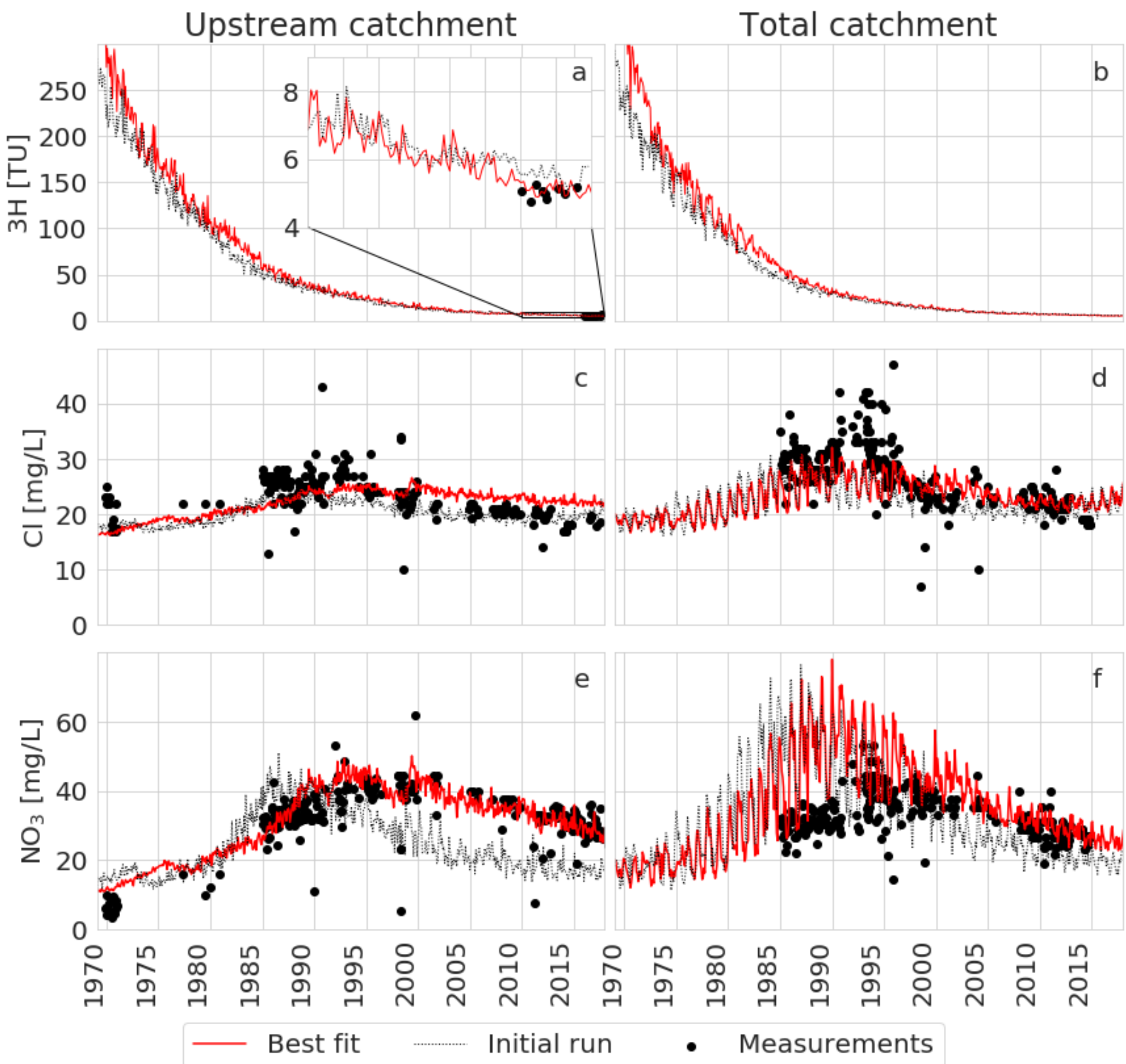

Figure 10. Best model fit using changed agricultural fields and an unsaturated zone of 3 years.

875

https://doi.org/10.5194/hess-2019-552
Preprint. Discussion started: 5 November 2019

Hydrology and Earth System Sciences Discussions

Table 1. Sensitivity analysis.

Set		Parameter
-	Base case. Variable input, no denitrification	
1	Unsaturated zone delay	Travel Time delay
2	Increased travel times	Mean Travel Time
3	Differences in the input curve in time	Input
4	Differences in the input curve in space	Input
5	Denitrification	Travel Time, depth

Table 2. Summarized results of the sensitivity analysis.

Set		Peak concentration change [mg/L]		Time to peak change [years]		Conc. in 2016 change [TU]
		Cl	NO_3	Cl	NO_3	Tritium
1	Unsaturated zone, 5 years	0	0	+5	+5	-0.29
2	Increased travel times, factor 5	-5	-20	+10	+10	-0.63
3	Differences in the input curve in time	0*	0*	0*	0*	0
4	Differences in the input curve in space 1	+1	+5	-1	-1	0
	Differences in the input curve in space 2	0	-1	+7	+4	0
5	Denitrification zero order	0	-15	0	0	0
	Denitrification deep layers	0	-15	0	0	0

*No changes because the peak was not changed.