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Using long time series of agricultural-derived nitrates for estimating catchment transit times

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SUMMARY

The estimation of water and solute transit times in catchments is crucial for predicting the response of hydrosystems to external forcings (climatic or anthropogenic). The hydrogeochemical signatures of tracers (either natural or anthropogenic) in streams have been widely used to estimate transit times in catchments as they integrate the various processes at stake. However, most of these tracers are well suited for catchments with mean transit times lower than about 4–5 years. Since the second half of the 20th century, the intensification of agriculture led to a general increase of the nitrogen load in rivers. As nitrate is mainly transported by groundwater in agricultural catchments, this signal can be used to estimate transit times greater than several years, even if nitrate is not a conservative tracer. Conceptual hydrological models can be used to estimate catchment transit times provided their consistency is demonstrated, based on their ability to simulate the stream chemical signatures at various time scales and catchment internal processes such as N storage in groundwater.

The objective of this study was to assess if a conceptual lumped model was able to simulate the observed patterns of nitrogen concentration, at various time scales, from seasonal to pluriannual and thus if it was relevant to estimate the nitrogen transit times in headwater catchments. A conceptual lumped model, representing shallow groundwater flow as two parallel linear stores with double porosity, and riparian processes by a constant nitrogen removal function, was applied on two paired agricultural catchments which belong to the Research Observatory ORE AgrHys. The Global Likelihood Uncertainty Estimation (GLUE) approach was used to estimate parameter values and uncertainties. The model performance was assessed on (i) its ability to simulate the contrasted patterns of stream flow and stream nitrate concentrations at seasonal and inter-annual time scales, (ii) its ability to simulate the patterns observed in groundwater at the same temporal scales, and (iii) the consistency of long-term simulations using the calibrated model and the general pattern of the nitrate concentration increase in the region since the beginning of the intensification of agriculture in the 1960s. The simulated nitrate transit times were found more sensitive to climate variability than to parameter uncertainty, and average values were found to be consistent with results from others studies in the same region involving modeling and groundwater dating.

This study shows that a simple model can be used to simulate the main dynamics of nitrogen in an intensively polluted catchment and then be used to estimate the transit times of these pollutants in the system which is crucial to guide mitigation plans design and assessment.

1. Introduction

The estimation of water and solute transit times in catchments is crucial for predicting the response of hydrosystems to external forcings (climatic or anthropogenic). As the hydrological and

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geochemical signatures of streams represent the integration of the various processes at stake (Aubert et al., 2013; Kirchner et al., 2001), they have been widely used to study hydrological processes and to estimate transit times in catchments. For example, many studies compute transit time distribution (TTD) by matching input (precipitation) and output (stream) time series of concentrations of natural tracers like stable isotopes ^{18}O and ^{2}H or chloride (McGuire et al., 2007). This method is well suited for catchments with mean transit times (MTT) lower than about 4–5 years (Hrachowitz et al., 2009; McDonnell et al., 2010), otherwise it can lead to large MTT underestimation (Stewart et al., 2010). However, it is more and more acknowledged that groundwater is playing a major role in nutrient transport in agricultural catchments leading to MTTs exceeding several years or decades, e.g. (Basu et al., 2012; Capell et al., 2012; Stewart et al., 2010). Several tracers of anthropogenic origin like ^{3}Hor CFCs can be used for estimating groundwater transit times spanning several decades, but the current decline in their concentration in the atmosphere increases the estimation uncertainty (Aquilina et al., 2012; Molénat et al., 2013; Stewart et al., 2010).

In many parts of the world, the intensification of agriculture led to dramatic increase of reactive nitrogen input to agricultural watersheds in the second half of the 20th century (Galloway et al., 2004). Agricultural inputs are known to be the main source of nitrogen in agricultural catchments (Dunn et al., 2012; Howden et al., 2011b; Wang et al., 2013; Worrall et al., 2012). This led to a general increase of the nitrogen load (mainly as nitrate) in many rivers of the world (Seitzinger et al., 2010; Green et al., 2014). However, using nitrogen for estimating catchment transit time is not straightforward as it is not a conservative tracer. Many studies on the impact of agriculture on stream nitrate concentration have enlightened the lack of correlation between estimated N inputs and outputs, but while part of them attribute this discrepancy mainly to N biotransformation, highlighting the attenuation potential of the system (Montreuil et al., 2010; Billen and Garnier, 1999), others suggest that it is mainly due to nitrate storage in the hydrosystem (vadose zone and groundwater) leading to response times exceeding several years even in very small catchments (Basu et al., 2012; Molenat et al., 2008; Owens et al., 2008; Ruiz et al., 2002a; Schilling and Spooner, 2006; Tomer and Burkart, 2003; Wriedt and Rode, 2006).

During the last 30 years, more and more complex hydrological models have been developed intending to simulate as accurately as possible the transformations and transfer of nitrogen in catchments, while accounting as much as possible for the spatial heterogeneity of the processes. However in models either semi-distributed, as INCA (Wade et al., 2002, 2001), SWAT (Arnold et al., 1998); or fully-distributed, as TNT2 (Beaujouan et al., 2001; Moreau et al., 2013);, MODFLOW-MT3D (McDonald and Harbaugh, 2003; Zheng et al., 2012) NitroScape (Duretz et al., 2011), the complexity brings a number of issues related to overparameterization, parameter uncertainty, and equifinality (Beven, 2006; Beven and Binley, 1992; Jakeman and Hornberger, 1993; Perrin et al., 2001). As a consequence, there is renewed interest for lumped conceptual models, as they are more parsimonious. However, the question remains if, while ignoring complexity and heterogeneity, such models are still able to mimic realistic catchment processes and to provide "the right answers for the right reasons" (Hrachowitz et al., 2013; Kirchner, 2006; Seibert and McDonnell, 2002).

A way to improve the realism of conceptual hydrological models is to make a better use of the available information while assessing model performances by not relying on stream data only but adding for example groundwater storage and chemical signature (Gupta et al., 2008; Seibert and McDonnell, 2002), although getting acceptable simulation on both stream flow and groundwater dynamics is not easy, even when considering only water (Fenicia et al., 2008; Gascuel-Odoux et al., 2010b; Molénat et al., 2005). Similarly, using the temporal variations of the hydrochemical signature of streams can help in designing better model structures (Hrachowitz et al., 2011; Woodward et al., 2013).

In temperate climates, nitrate concentrations in streams are characterized by different time scales of variability. At the subdaily scale, large variations can occur, which are linked either to hydrological events (storm events) or to diurnal biological processes. As groundwater is the main pathway for nitrate in agricultural catchments (Basu et al., 2012; Howden et al., 2011b; Molenat et al., 2008; Woodward et al., 2013) these variations are not likely to affect significantly the nitrate mean transit time. At the annual scale, seasonal cycles of nitrate concentrations are commonly described, either positively or negatively correlated with flow (Martin et al., 2006; Betton et al., 1991) and attributed mainly either to water mixing or to biological processes (e.g. Grimaldi et al., 2004; Martin et al., 2006; Woodward et al., 2013). Interannual variability reflects the combined influence of year-to-year variations of agricultural inputs and climate, the later determining the amount of water recharging the groundwater which impacts its transit times (Gascuel-Odoux et al., 2010a; Heidbüchel et al., 2013; Hrachowitz et al., 2009). On the long term (several decades), trends in nitrate concentration reflect the impact of agricultural system evolution. However, studies are generally focused on only one part of these temporal scales of variability. For example (Howden et al., 2011b) develop a model based on the long time series (140 years) of nitrate concentrations on the Thames River. The model is assessed on its ability to reproduce the dynamics of average yearly concentrations but without looking at the seasonal variations. Green et al. (2014) used simple models for simulated annual average nitrate concentrations over 10 catchments in USA and over the period 1964–2012, and estimated from the models the mean travel time of nitrogen in the catchments ranging between 0 and 19 years depending on the model and the catchment. However they did not consider seasonal pattern on the concentration too. Conversely, modeling seasonal variations of solute concentrations in streams is usually carried out using only one (Benettin et al., 2013) or a few (Woodward et al., 2013) water years.

The objective of this study was to assess if a conceptual lumped model was able to simulate the observed patterns of nitrogen concentration at various time scales from seasonal to pluriannual and thus if such a model was relevant to estimate the nitrogen transit time in headwater catchments. This was achieved using a 20 year time-series of stream base flow and nitrogen concentration on two paired agricultural catchments where a comprehensive survey of agriculture practices was available over the same period. The conceptual lumped model used (ETNA modified from (Ruiz et al., 2002b)) represents shallow groundwater flow as two parallel linear stores with double porosity, and riparian processes are represented by a constant nitrogen removal function. Parameter values and uncertainties were estimated using the Global Likelihood Uncertainty Estimation (GLUE) approach (Beven and Binley, 1992). The output variables of the model (water and nitrate output fluxes) were used to compute the nitrate residence times in both catchments. The model was assessed according to (i) its ability to simulate the contrasted patterns of stream flow and stream nitrate concentrations at seasonal and inter-annual time scales for the two catchments, (ii) its ability to simulate the patterns observed in groundwater (water level and chemistry) at the same temporal scales, and (iii) the consistency between the nitrate transit times resulting from the model calibration and the general pattern of the probable nitrate concentration evolution in the region since the beginning of the intensification of agriculture in the 1960s. Finally, the sensitivity of the simulated transit times to parameter