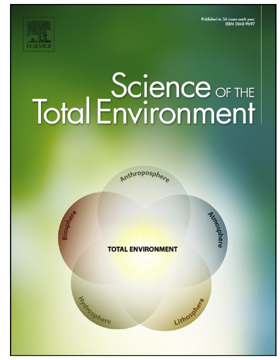
What do we need to predict groundwater nitrate recovery trajectories?

Camille Vautier, Tamara Kolbe, Tristan Babey, Jean Marçais, Benjamin W Abbott, Anniet M. Laverman, Zahra Thomas, Luc Aquilina, Gilles Pinay, Jean-Raynald de Dreuzy

Journal Pre-proof



What do we need to predict groundwater nitrate recovery trajectories?

Camille Vautier, Tamara Kolbe, Tristan Babey, Jean Marçais, Benjamin W. Abbott, Anniet M. Laverman, Zahra Thomas, Luc Aquilina, Gilles Pinay, Jean-Raynald de Dreuzy

PII: S0048-9697(21)02732-7

DOI: https://doi.org/10.1016/j.scitotenv.2021.147661

Reference: STOTEN 147661

To appear in: *Science of the Total Environment*

Received date: 2 March 2021

Revised date: 16 April 2021

Accepted date: 5 May 2021

What do we need to predict groundwater nitrate recovery trajectories?

Camille Vautier [a], Tamara Kolbe [b], Tristan Babey [c], Jean Marçais [d], Benjamin W. Abbott [e], Anniet M. Laverman [f], Zahra Thomas [g], Luc Aquilina [a], Gilles Pinay [h], Jean-Raynald de Dreuzy [a,i]*

[a] Univ Rennes, CNRS, Géosciences Rennes, UMR 6118, 35000 Rennes, France

[b] Chair of Hydrogeology and Hydrochemistry, Faculty of Geoscience, Geoengineering and Mining, Institute of Geology, Technische Universität Bergakademie Freiberg, 09599 Freiberg, Germany

[c] Department of Earth System Science, Stanford University, Stanford, CA 94305, USA

[d] Institut National de Recherche en Sciences et Technologies pour l'Environnement et l'Agriculture (Irstea), RiverLy, Centre de Lyon-Villeurbanne, 69625 Villeurbanne, France

[e] Department of Plant and Wildlife Sciences, Brigham Young University, Provo, UT 84602, USA

[f] Univ Rennes, CNRS, Ecobio, UMR 6553, 35000 Rennes, France

[g] Institut National de la Recherche Agronomique (INRA), Sol Agro et Hydrosystème Spatialisation, UMR 1069, Agrocampus Ouest, 35042 Rennes, France

[h] Environnement, Ville et Société, EVS - UMR5600 CNRS, Lyon France

[i] Univ Rennes, CNRS, OSUR (Observatoire des sciences de l'univers de Rennes), UMS 3343, 35000 Rennes, France

Highlights

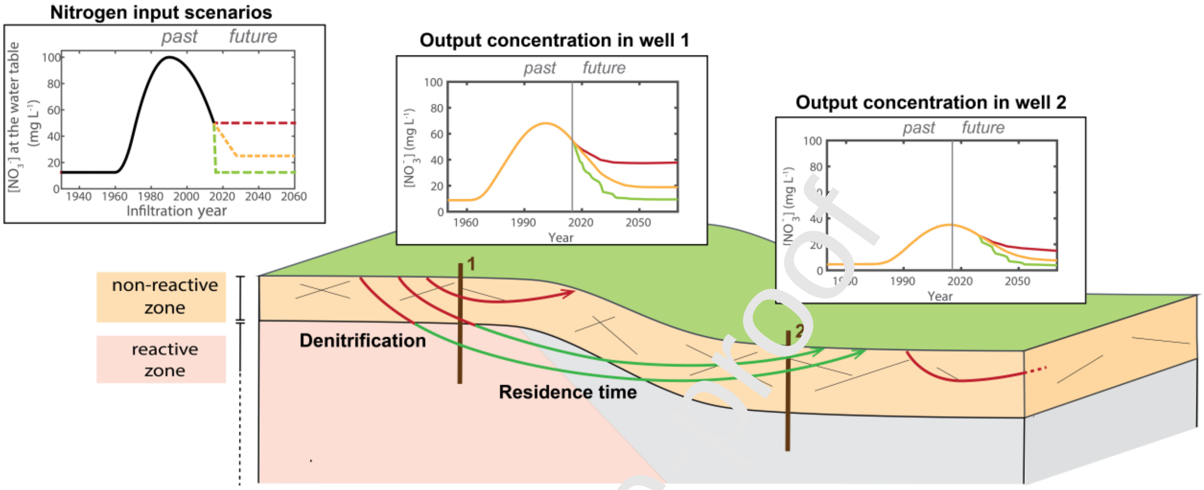
- Nitrate recovery trajectories were predicted based on a few key-parameters.
- Two age tracers are necessary to predict groundwater nitrate concentration.
- The stratification of denitrification controls the nitrate dynamic in the aquifer.
- Uncertainty about past nitrogen inputs may not alter the predictions.

Abstract

Nitrate contamination affects many of the Earth's aquifers and surface waters. Large-scale predictions of groundwater nitrate trends normally require the characterization of multiple anthropic and natural factors. To assess different approaches for upscaling estimates of nitrate recovery, we tested the influence of hydrological, historical, and biological factors on predictions of future nitrate concentration in aquifers. We tested the factors with a rich hydrogeological dataset from a heterogeneously fractured bedrock catchment in western France. A sensitivity analysis performed on a calibrated model of groundwater flow, denitrification, and nitrogen inputs revealed that trends in nitrate concentration can effectively be approximated with a limited number of key parameters. The total mass of nitrate that entered the aquifer since the beginning of the industrial period needs to be characterized, but the shape of the historical nitrogen input time series can be largely simplified without substantially altering the predictions. Aquifer flow and transport processes can be represented by the mean and standard deviation of the residence time distribution, offering a tractable scaling tool to make reasonable predictions at watershed or regional scales. Apparent sensitivity to denitrification rate was primarily attributable to time lags in oxygen depletion, meaning that denitrification can be simplified to an ON/OFF process, defined only by the time needed to transfer nitrate to the hypoxic reactive layer. Obtaining these key-parameters at large scales is still challenging with currently available information,

but the results are promising regarding our future ability to predict nitrate concentration with integrated monitoring and modeling approaches.

Graphical abstract



Key-words

Groundwater, nitrate, denitrification, eutrophication, residence time, predictions

1 Introduction

Human activity has more than doubled reactive nitrogen delivery to Earth's ecosystems, creating eutrophic (over-fertilized) conditions in aquatic and coastal environments around the world (Galloway et al. 2008; Kronvang et al. 2005). In the past several decades, widespread efforts have been made to reduce human nutrient loading to protect freshwater resources and ecosystems (Abbott et al. 2018; Boers 1996; Kronvang et al. 2008; Kronvang et al. 2005; Steffen et al. 2015). However, natural systems often respond to changes in nutrient inputs with a time lag, making recovery trajectories difficult to predict. This complicates the evaluation of mitigation strategies and can even imperil public and political support for investment in mitigation (Hamilton 2012; Kronvang et al. 2005; Meals et al. 2010; Van Meter and Basu 2015; Van Meter and Basu 2017). In many catchments, long time lags mean that the agricultural policies we choose today will affect nitrogen concentration in surface and groundwater for several decades (Ehrhardt et al. 2019; Thomas and Abbott 2018; Van Meter and Basu 2015). Thus, improving predictions of nutrient recovery timelines following different agricultural scenarios is an important ecological and socioeconomic goal (Kolbe et al. 2019; Le Moal et al. 2019; Marcais et al. 2018; Minaudo et al. 2019).

Nitrogen can be stored for several years to several decades in different compartments of surface and subsurface ecosystems, leading to what is called a nitrogen legacy (Ehrhardt et al. 2019; Hrachowitz et al. 2015; Van Meter et al. 2017; Van Meter et al. 2016). Apart from the soil (Sebilo et al. 2013), one of the main drivers of nitrogen legacy is groundwater. Because aquifers contain two orders of magnitude more water than all rivers and lakes (Abbott et al. 2019), groundwater nitrogen can be stored for decades before reaching the surface (Fenton et al. 2011; Wendland et al. 2002). However, because the major form of groundwater nitrogen is nitrate (NO_3^-), microbial activity during groundwater storage and transport can reduce nitrogen stocks via anaerobic catabolism (denitrification), which eventually transforms NO_3^- into N_2 gas (Green et al. 2016; Kolbe et al. 2019; Korom 1992). As a result, groundwater circulation exerts a dual control on NO_3^- pollution: it creates a delay or time lag between inputs and outputs and it directly reduces the NO_3^- stock in the system.

Predicting NO_3^- recovery trajectory for a given aquifer requires information about the past and future nitrogen inputs, the water residence times, and the rate of nitrate removal (Kolbe et al. 2019; Małoszewski and Zuber 1982; Van Meter and Basu 2015). Each of these three functions is defined by a set of parameters that need to be quantified. However, quantifying these functions is challenging because of a lack of data at appropriate spatiotemporal scales (Abbott et al. 2016; Frei et al. 2020; McDonnell et al. 2007). The information is only available in few study sites where measurements and modelling efforts have been coupled (Böhlke and Denver 1995; Green et al. 2016; Kolbe et al. 2019; Paradis et al. 2017; Singleton et al. 2007; Tesoriero and Puckett 2011). Because mitigation strategies are often decided and implemented at large scales such as regions or nations (Kronvang et al. 2005; US EPA 2008), large-scale predictions of removal and storage capacities are needed to set realistic expectations of mitigation actions and time frame of recovery and to predict ecosystem vulnerability to nutrient loading (Abbott et al. 2018; Pinay et al. 2015).

In this context, we tested the sensitivity of NO_3^- recovery predictions based on simple but robust hydrological parameters in a well-studied unconfined fractured bedrock aquifer. We performed a sensitivity analysis to identify the key parameters, including both anthropic and natural drivers that need to be constrained to predict the future nitrate trajectories in the aquifer. Our immediate goals were to 1. forecast groundwater nitrate trajectories for different loading scenarios, 2. determine the dominant controls on groundwater nitrate concentration, and 3. assess how much hydrological detail is needed to make accurate predictions of large-scale biogeochemical patterns in space and time.

2 Material and methods

Based on a reference model including groundwater flow, nitrate degradation and reconstructed past nitrogen inputs, we predicted the evolution of nitrate concentration in 16 wells over a well-studied small agricultural catchment. We then performed a sensitivity analysis on the predicted concentrations to identify the primary controls on nitrate pollution in groundwater. Below, we describe the catchment, reference model, and methods used for the sensitivity analysis.

2.1 Field site

The study was conducted on a 35 km^2 agricultural catchment located near Pleine-Fougères, a small town in Brittany, France. The catchment is part of the Zone Atelier Armorique (Thomas et al. 2019), a Long Term Socio-Ecological Research site (LTSER) (www.lter-europe.net). Like in most of Brittany, the study area has been subject to high inputs of organic and mineral fertilizers since the 1960's (Aquilina et al. 2012; Dupas et al. 2018; Poisvert et al. 2016). After a peak of nitrogen inputs at the beginning of the 1990's, farmers slowly reduced their fertilizers use (Abbott et al. 2018).

Mean groundwater recharge was estimated at 167 mm y^{-1} using the ISBA model (Noilhan and Mahfouf 1996), slightly lower than the mean regional recharge of Brittany (Le Moigne 2009). Groundwater flows primarily through the weathered and fissured zones of a shallow, unconfined aquifer (Bernard-Griffiths et al. 1985; Wyns et al. 2004). Chlorofluorocarbons (CFCs) revealed typical mean residence times of several decades (~30 years), indicating a large-capacity aquifer relative to surface outflows (Kolbe et al. 2016; Marcais et al. 2018). However, the aquifer is marked by high spatial variability of residence and denitrification times, resulting in strong heterogeneity of groundwater NO_3^- concentration (Kolbe et al. 2019; Kolbe et al. 2016).

Data from the French geological survey indicate that the weathered zone thickness ranges from 0 to 40 m within the catchment area, with a mean depth of 9 m. The underlying fractured bedrock is less conductive but much thicker with a mean thickness of 48 m (Kolbe et al. 2016). The aquifer extends from a granitic intrusion in the south to a schist bedrock in the north, with groundwater flowing northward (Kolbe et al. 2016). A marked altitude difference of 90 m at the geological contact between schist and granite creates springs at the foot of the slope (Kolbe et al. 2016).

We used groundwater chemistry data from previous studies in the catchment. Specifically, 16 privately owned wells (28 m to 98 m deep) were sampled at three time-periods (December 2014, March 2015, and October 2015) to characterize the hydrochemistry of the aquifer (See Kolbe et al. 2016 for details).

2.2 Reference model

The nitrate concentration in the aquifer through time, $c(t)$, results from the convolution of the nitrate input time series at the water table c_0, the groundwater residence time distribution p, and the proportion of nitrate remaining after denitrification for a time τ in the saturated zone $r_{NO3}(\tau)$ (Małoszewski and Zuber 1982):

$$c(t) = \int_0^\infty c_0(t-\tau)\ p(\tau)\ r_{NO3}(\tau)\ d\tau \qquad (1)$$

2.2.1 Residence time distributions

We modelled groundwater circulation with a steady-state, three-dimensional, flow and transport model previously developed for the site by Kolbe et al. (2016) in the FEFLOW software environment (Diersch 2013). To limit boundary effects, the modeled zone was substantially larger (76 km^2) than the hydrological catchment (35 km^2). The mean annual recharge (167 mm/y) was applied uniformly on the top layer of the model. Flow lines were calculated using the particle tracking algorithm of FEFLOW (Diersch 2013). Hydraulic conductivity and effective porosity were calibrated using base-flow stream discharge and groundwater age data. The base flow stream discharge at the outlet of the catchment, interpreted as the catchment's mean annual groundwater discharge, was derived from hydrograph separation of long-term stream discharge time series. Groundwater discharge was estimated at 4.5 × 10^6 m^3 y^{-1}. Mean groundwater ages were determined in the sampling wells based on CFC-12, an anthropogenic gas used as age tracer for groundwater that infiltrated after 1950 (Ayraud et al. 2008; Busenberg and Plummer 1992). CFC-12 measurements were performed on grab samples in the CONDATE-EAU platform of the University of Rennes 1. For each of the 16 wells, residence time distributions of the groundwater were extracted from the calibrated model by intercepting the flow lines going through the full depth of the well handled as a fully penetrating well. Times were tracked from the water table of the aquifer to a sampling zone around the well. The sampling zone was chosen small enough to characterize the well capture and large enough to build representative residence time distributions. Representativity was reached for some 10^6 flow lines flux-weighted to the recharge (Kolbe et al., 2016). Well locations and parameters of the residence time distributions are given as supplementary material by Figure S1 and Table S1.

2.2.2 Denitrification

We applied a first order reaction to each flow line for oxygen (O_2) and NO_3^-. O_2 concentration at the water table, $O_{2\ water\ table}$, was set at 7 mg L^{-1}, corresponding to the concentration measured in shallow piezometers. O_2 consumption in the saturated zone was defined by an apparent degradation time τ_{O2} with $r_{O2}(t)$ the proportion of O_2 remaining after at time t:

$$r_{O2}(t) = \exp\left(-\frac{t}{\tau_{O2}}\right) \tag{2}$$

Because O_2 is a more powerful electron acceptor than NO_3^-, denitrification can start only after most O_2 has been consumed (Green et al. 2016; Kolbe et al. 2019; Korom 1992). Here we considered that denitrification started when O_2 concentration was below 2 mg L^{-1} ($O_{2\ threshold}$). Thus, the amount of remaining nitrate r_{NO3} is defined by two parameters: the time lag needed for the denitrification to begin, t_{lag}, which basically corresponds to the O_2 degradation time, and the denitrification time itself, τ_{NO3}, which described the rate of NO_3^- degradation once it has begun, that is after the $O_{2\ threshold}$.

$$r_{NO3}(t) = \begin{cases} 1 & for\ t < t_{lag} \\ \exp\left(-\frac{t - t_{lag}}{\tau_{NO3}}\right) & for\ t \geq t_{lag} \end{cases} \tag{3}$$

with:

$$t_{lag} = \tau_{O2} \ln\left(\frac{O_{2\ water\ table}}{O_{2\ threshold}}\right) \tag{4}$$

The chemical system is fully defined by the three equations (2), (3) and (4). The reaction times for O_2 and NO_3^- were calibrated from the sampled O_2, NO_3^- and N_2 concentrations (Kolbe et al. 2019). Values of t_{lag} and τ_{NO3} are given as supplementary materials by Table S1.

2.2.3 Past nitrogen inputs

The nitrogen input time series was reconstructed specifically for our catchment by Kolbe et al. (2019) from the 16 wells' NO_3^-, N_2, and groundwater age data. Denitrification produces N_2, creating an excess of dissolved N_2 relative to the atmosphere in groundwater, allowing estimation of the amount of degraded NO_3^- (Aeschbach-Hertig et al. 1999). The initial concentration of NO_3^- entering the saturated zone was calculated by adding the amount of degraded NO_3^- (estimated from the N_2 excess) to the current NO_3^- concentration. Though land use in particular plots over the last several decades has rotated (Barbe et al. 2019), the overall catchment land use revealed that nitrogen inputs can be considered as spatially uniform (Kolbe et al. 2019), allowing the determination of a single NO_3^- input time series for the whole catchment. Using initial NO_3^- concentration and the residence time distribution in each well, we used an inverse method to reconstruct the past NO_3^- concentration chronicle at the water table (i.e. until 2015). This time series corresponds to the amount of NO_3^- entering the saturated zone. Therefore, it accounts implicitly for potential biogeochemical uptake in the unsaturated zone (Thomas and Abbott 2018). Hence, our study focuses only on the processes occurring in the saturated zone, unlike traditional time series based on land use data and agronomic statistics, which provide nitrogen surpluses in the soil (Oenema et al. 2003; Parris 1998; Poisvert et al. 2016; Salo and Turtola 2006).

2.2.4 Future agricultural scenarios

To forecast the NO_3^- concentration, we extended the input time series c_0 into the future following three scenarios. The "reference" scenario followed the current decreasing trend until stabilizing at 25 mg NO_3^- L^{-1}. The "no decrease" scenario assumed the nitrate input stayed at its current value (50 mg L^{-1}), and the "immediate ban" scenario applied an immediate return to pre-industrial nitrate input (12.5 mg NO_3^- L^{-1}). Although unrealistic, this scenario highlights the nitrate legacy and its impact on future nitrate concentrations.

2.3 Sensitivity analysis

We performed a systematic sensitivity analysis on the future nitrate scenarios to evaluate the relative influence of residence time, denitrification, and past nitrogen input. As a sensitivity indicator, we used the nitrate concentration predicted for the year 2030 with a reference scenario assuming a progressive reduction of nitrogen inputs. We chose a 15-year period (2015 to 2030) to allow for the natural system to react to changes in nitrogen inputs, while still being short enough to be of interest for policy makers (Abbott et al. 2018; Choi et al. 2005). In the reference model, each of the parameters (residence time distribution, denitrification rate and duration, and nitrogen inputs) was modified individually in sequence.

For each of the 16 wells, we compared the concentration predicted under the reference model with all actual parameters and the concentration predicted with modified parameters.

2.3.1 Modification of residence time distributions

Natural residence time distributions may take a broad variety of shapes even when their mean and standard deviation are fixed (Engdahl and Maxwell 2014; Ginn 1999; Leray et al. 2016; Marcais et al. 2015). To test the sensitivity of the predictions to the shape of the residence time distributions, we replaced the complex distributions obtained from the calibrated simulations (Kolbe et al. 2016) with lumped parameter models (LPMs), that is with highly simplified analytical distributions. Two 1-parameter LPMs and four 2-parameters LPMs were tested (Table 1). The 1-parameter LPMs had the same mean as the actual distribution. The 2-parameter LPMs had the same mean and standard deviation as the actual distribution.

N	Lumped Parameter Model	Expression
1	Dirac (piston flow)	$p_T(t) = \delta(t - T)$
	Exponential (exponential)	$p_T(t) = \frac{1}{T} \exp\left(\frac{-t}{T}\right)$
2	Inverse Gaussian *(dispersion)*	$p_{T,Pe}(t) = \sqrt{\frac{T\,Pe}{2\,\pi\,t^3}} \exp\left(-\frac{Pe\,(t-T)^2}{2\,T\,t}\right)$
	Shifted exponential (exponential piston flow)	$p_{T,t_0}(t) = \begin{cases} 0 & for\quad t < T - t_0 \\ \frac{1}{t_0}\,exp\left(-\frac{t-(T-t_0)}{t_0}\right) & otherwise \end{cases}$
	Uniform (linear piston flow)	$p_{T,\varepsilon}(t) = \begin{cases} \frac{1}{\varepsilon} & for\ T - \frac{\varepsilon}{2} \leq t < T + \frac{\varepsilon}{2} \\ 0 & otherwise \end{cases}$
	Gamma	$p_{T,\alpha}(t) = \frac{t^{\alpha-1}}{\left(\frac{T}{\alpha}\right)^{\alpha}\,\Gamma(\alpha)} \exp\left(-\frac{\alpha\,t}{T}\right)$

Table 1. Lumped parameter models used in the sensitivity analysis. The left-hand column indicates the number of parameters (N). The names in brackets refer to those of Maloszewski and Zuber (1996). All LPM expressions involve the mean residence time *T*. Expressions of 2-parameters LPMs additionally introduce the Peclet number *Pe* for the inverse gaussian model, the time lag t_0 for the shifted exponential model, the range of explored times ε for the uniform model, and the shape factor α for the gamma model.

2.3.2 Modification of denitrification

We postulated that denitrification starts only when the O_2 concentration fell below 2 mg L^{-1}. Therefore, the denitrification function was defined by the time lag needed for denitrification to begin, t_{lag}, and the denitrification time itself, τ_{NO3} (equation 2). To test the impact of these two parameters on the nitrate concentration, we replaced the actual time lag t_{lag} and the actual denitrification rate τ_{NO3} determined for each well by their mean over the 16 wells. In the 16 wells, t_{lag} varied from 3 to 67 y (mean = 33 y) and τ_{NO3} varied from 1 to 20 y (mean = 4.7 y).

2.3.3 Modification of past nitrogen inputs

Regardless of the reconstruction method, nitrogen input time series contain uncertainties in their cumulated concentration (i.e. the total mass of nitrate that entered the system since the beginning of the industrial period) and in their shape, especially related to the position of the peak of nitrate inputs (Payraudeau et al. 2007). We analyzed model sensitivity to the total input mass by modifying the cumulated concentration between 1960 (beginning of the increase in the nitrate inputs) and 2015 (end of the sampling campaigns). We also tested the impact of the shape of the time series by simplifying it to a rectangular distribution (a plateau shape rather than curved).

3 Results

3.1 Nitrate concentrations predicted by the reference model

Groundwater nitrate concentration was predicted by the reference model for the three future loading scenarios presented in section 2.2.4. (Figure 1). Results are shown for the years 2020, 2030 and 2050, corresponding respectively to 5, 15 and 35 years ahead of the last measurement campaign (2015).

In three wells, the legacy effect is so strong that even with an “immediate ban” scenario, the nitrate concentration would increase between 2020 and 2030. On a time range of 15 years, their responses do not even depend on the evolution scenario and are only controlled by past inputs. Generally, differences between the three scenarios increase with time, as increasing quantities of water infiltrated after the beginning of the mitigation scenarios reach the wells.

Nevertheless, whatever the scenario, nitrate concentration is highly heterogeneous with a consistent spatial pattern throughout the catchment. In 2030, the concentration is close to 0 in some wells, while the maximum concentration is still higher than the guideline value of 50 mg L^{-1} recommended by the World Health Organization. The same nitrate input time series was applied to the whole catchment, so the heterogeneity in the output concentrations results from spatial variability of residence times and denitrification in the aquifer. This illustrates the wide range of residence times and denitrification rates existing in fractured bedrock aquifers such as the one studied here, and their impact on present and future nitrate concentration. Consequently, future nitrate concentrations in aquifers cannot be predicted straightforwardly from future agricultural scenarios. Predictions require not only to characterize past and future nitrate inputs, but also groundwater residence times and denitrification capacities.

To investigate the relative importance of anthropic and natural parameters, we further performed a sensitivity analysis on the concentrations predicted with the reference scenario in 2030 (enlarged map on Figure 1).

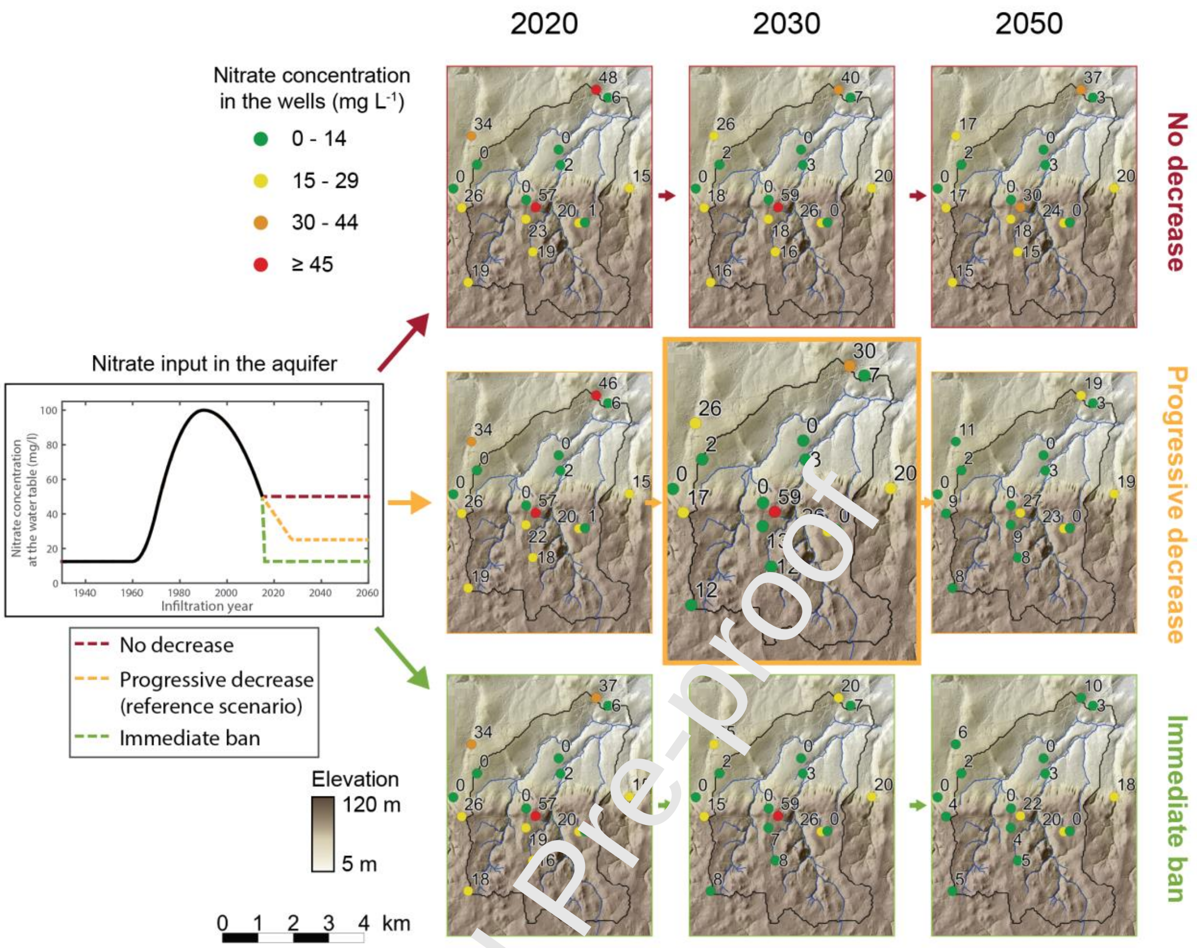


Figure 1. Predicted nitrate concentrations in the 16 wells following the three agricultural scenarios described in section 2.2.4 and recalled on the left. Concentrations were predicted for 2020, 2030 and 2050 using the reference model. The somewhat enlarged map in the middle displays the concentrations on which the sensitivity analysis was further performed, ie the concentrations predicted for 2030 with the reference scenario.

3.2 Sensitivity analysis

The primary results of the sensitivity analysis are presented in Figure 2 (additional details in Figure S2). For each tested parameter, the nitrate concentration predicted for 2030 in the 16 wells with the modified parameter are plotted against the nitrate concentration predicted for 2030 with the reference model. Deviation from the 1:1 line and systematic overprediction or underprediction indicate the degree of sensitivity of the predictions to the modified parameter. The larger the deviation, the higher the sensitivity. This analysis demonstrates the relative importance of biological activity, groundwater residence time, and nitrate input time series to future nitrate concentration.

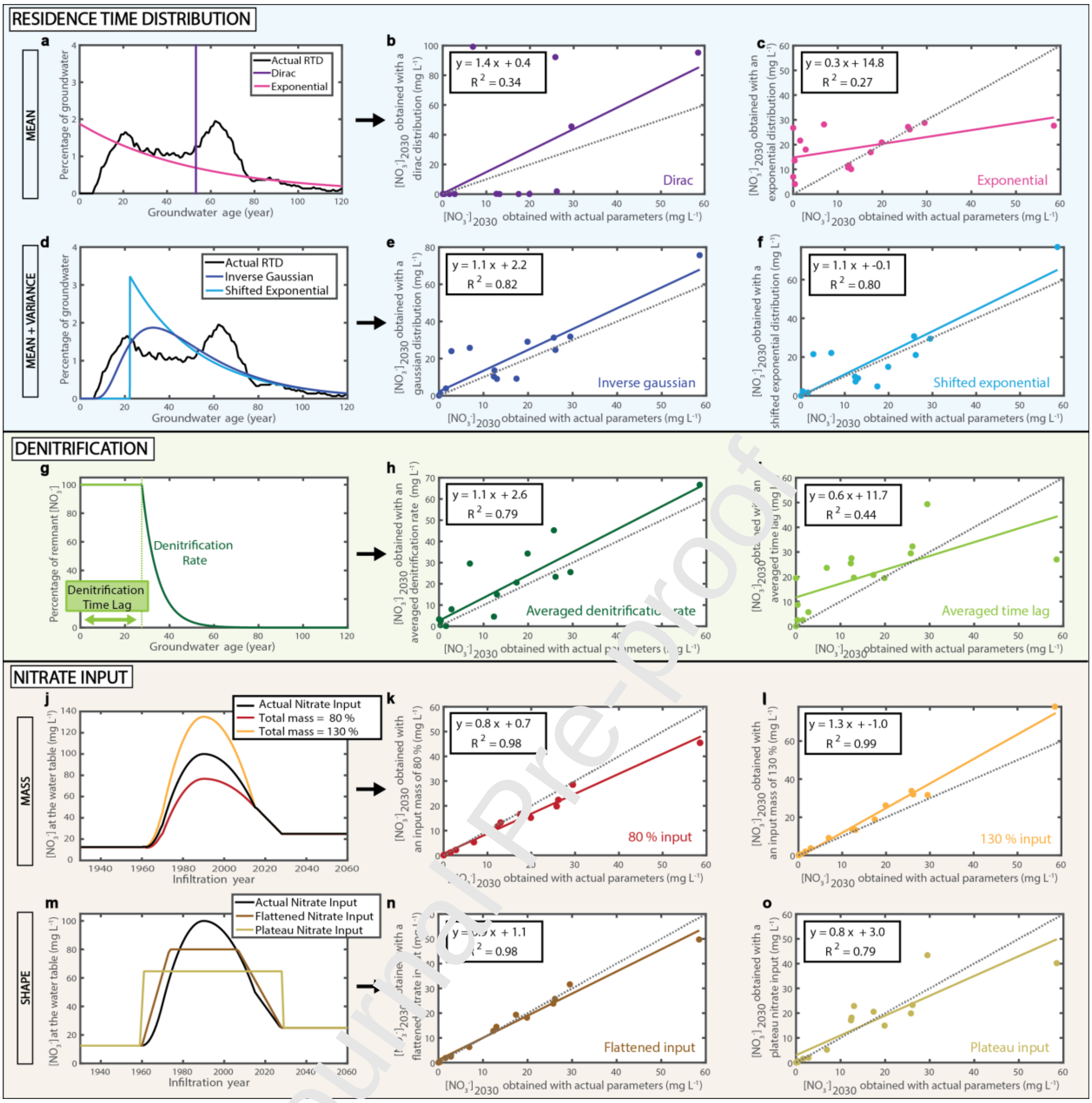

RESIDENCE TIME DISTRIBUTION
MEAN
MEAN + VARIANCE
DENITRIFICATION
NITRATE INPUT
MASS
SHAPE
Actual RTD
Dirac
Exponential
Inverse Gaussian
Shifted Exponential
Groundwater age (year)
Percentage of groundwater
y = 1.4 x + 0.4
R 2 = 0.34
y = 0.3 x + 14.8
R 2 = 0.27
y = 1.1 x + 2.2
R 2 = 0.82
y = 1.1 x + -0.1
R 2 = 0.80
y = 1.1 x + 2.6
R 2 = 0.79
y = 0.6 x + 11.7
R 2 = 0.44
y = 0.8 x + 0.7
R 2 = 0.98
y = 1.3 x + -1.0
R 2 = 0.99
R 2 = 0.98
y = 0.8 x + 3.0
R 2 = 0.79
Inverse gaussian
Shifted exponential
Denitrification Rate
Denitrification Time Lag
Percentage of remnant [NO3-]
Averaged time lag
Actual Nitrate Input
Total mass = 80 %
Total mass = 130 %
80 % input
130 % input
Flattened Nitrate Input
Plateau Nitrate Input
Flattened input
Plateau input
Infiltration year
[NO3-] at the water table (mg L-1)
[NO3-]2030 obtained with actual parameters (mg L-1)

Figure 2. Results of the sensitivity analysis were performed according to the reference model including the references for the residence time distribution, denitrification rate and duration, and nitrogen inputs. Subplots on the left illustrate the parameters and functions tested. For the 10 other subplots, on the middle and on the right, the nitrate concentration predicted for 2030 with the reference model is represented on the x-axis, while the y-axis represents the nitrate concentration predicted for 2030 with one modified parameter. Each dot corresponds to a well. Solid lines come from linear regressions and are described by the equation and associated R^2 coefficients in the top right frame. The 1:1 trend is displayed by a dashed line. Basically, the closer the regression line is to the dashed line and the smaller the dispersion is, the less the predictions are sensitive to the parameter tested. Note that the analysis is only weakly sensitive to any of the wells even though some points look like outliers as the well with the highest concentration on Figures 2c and 2i, where more than half of the other nitrate concentrations are significantly overpredicted.

3.2.1 Sensitivity to residence time distribution

The sensitivity analysis revealed that the mean residence time was insufficient on its own to make predictions of future nitrate concentration (Figure 2 a-c). A Dirac distribution, corresponding to a piston-flow model where the age of the whole water mass is equal to the mean residence time, created a binary response, where denitrification occurred either on all flow lines or not at all (Figure 2 b). Alternatively, an exponential distribution, corresponding to well-mixed flows, led to a homogenization of the nitrate concentration towards intermediate values that did not reflect the spatial heterogeneity of the catchment (Figure 2 c). Nitrate concentrations are strongly overestimated for almost half of the wells. For both 1-parameter LPMs, the correlation coefficient of the linear regression between the concentrations predicted by the reference model and the concentration predicted by the modified model is lower than 0.35 (Figure 2 b-c). Thus, despite their convenience, 1-parameter LPMs have very poor predictive capacities of nitrate concentrations.

Integrating information of both the mean and standard deviation of the residence time distribution allowed reasonable prediction of future nitrate concentration. Indeed, predictions obtained with the 2-parameters LPMs (Inverse Gaussian, Shifted exponential, Gamma and Uniform models) showed better agreement with the reference predictions (Figure 2 e-f and Figure S2). The slopes of the regression lines were close to 1 (~1.1), their intercepts were lower than 3, and the associated correlation coefficients (R^2) were above 0.8.

3.2.2 Sensitivity to denitrification

To predict future nitrate concentration, it mattered more to know the time needed for the denitrification to start, t_{lag}, than the precise rate of the denitrification once it began, τ_{NO3} (Figure 2 g-i). Indeed, replacing actual denitrification rates τ_{NO3} by the average denitrification rate of the catchment did not bias significantly the predictions of future nitrate concentration (Figure 2 h). The slope of the regression line between the concentration predicted using actual parameters and the concentration predicted using an average denitrification rate was close to 1 (1.1), and the intercept value was low (2.6), showing little systematic bias. On the contrary, replacing actual denitrification time lags t_{lag} by the average time lag over the 16 wells significantly biased the predictions of future nitrate concentrations (Figure 2 i). Most of the nitrate concentrations are overpredicted. We thus conclude that, in the saturated zone of the investigated aquifer, the nitrate concentration appears to be primarily controlled by the time needed for the denitrification to start, which is much longer than the actual time of reaction. This suggests that denitrification can virtually be considered as an ON/OFF system, in which the important point to set is whether it has begun or not.

3.2.3 Sensitivity to the past nitrogen inputs

As expected, the total mass of nitrate that entered the aquifer since the beginning of the industrial period impacted the absolute values of the output nitrate concentration in groundwater (Figure 2 k-l). A change in the input mass had a proportional effect on the aquifer concentration predictions. More surprisingly, uncertainties in the shape of the nitrate input time series did not substantially bias predictions (Figure 2 m-o). If the peak was flattened to a plateau that lasts 20 years, the output concentration remained very close to the actual concentration, with a slope of 0.9 and an R^2 of 0.98. If the time series was simplified to the extreme (i.e. a unique plateau lasting from the beginning of the industrial period to the return to a stable concentration), the predicted concentration was still relatively close to actual concentration, with a slope of 0.8 and a R^2 of 0.79. Thus, a first-order reconstruction of the nitrate input time series, based only on the starting time of input and the total mass of nitrate that entered the aquifer, already yielded reasonable predictions of nitrate concentrations in groundwater (Figure 2 n). If an additional evaluation of the period during which the input concentration reached its maximum was made, then, the predictions became very accurate (Figure 2 o). The low sensitivity to the shape of the input time series can be explained from the natural mixing of groundwater flow lines, which spreads the residence time distributions and flattens the nitrate time series.

4 Discussion

4.1 Local hydrogeomorphic and biogeochemical conditions induce a high variability on nitrate concentrations

The nitrate input reduction scenarios revealed large local variations in groundwater's nitrate concentration response despite identical initial input. In some of the wells, 5 to 15 years after a sudden stop of the nitrogen inputs, groundwater pollution was still almost as high as if the input had not decreased (Figure 1). However, in the same 35 km^2 catchment, other wells showed a nitrate concentration close to 0 mg/L, even in the worse input scenario (Figure 1). This underlines how strongly the small-scale variability of hydrogeomorphic and biogeochemical conditions affect nitrate concentrations in fractured-bedrock aquifers. More generally, the observed water quality state and recovery rate for a given catchment depends on both the degree of nutrient loading and the overall retention and removal capacity, which can vary substantially in both surface and subsurface environments (Cheng et al. 2020; Frei et al. 2020) .

The time lag of measurable impacts of nitrate input mitigation strategies depends on local groundwater flowpaths. Hence, there is an urge to be able to characterize both local heterogeneity and the time lag of the response of aquifers to restoration measures to set realistic management targets (Dupas et al. 2018). Indeed, no clear decrease in nitrate concentrations after several years of stringent mitigation efforts could simply indicate that improvements have not yet propagated through the system (Sebilo et al. 2013). A lack of consideration of these time lags could discourage farmers and politicians and could provoke fines and penalties for nonattainment of water quality goals despite real progress if they were set on an unrealistic time scale (Meals et al. 2010).

4.2 Residence times: a single age tracer is not enough

In many studies, the residence time distribution is constrained by natural tracers (Ayraud et al. 2008; Böhlke and Denver 1995; Visser et al. 2013). Here we found that both the mean and the standard deviation of the groundwater residence time distribution were necessary, and sufficient, to make predictions of future nitrate concentrations (Figure 2). Thus, a single age tracer, giving a single apparent age, does not allow adequate prediction of future groundwater nitrate concentration. The distribution should not be reduced to a Dirac distribution where the only parameter would be altogether the mean and apparent ages. Therefore, accurate predictions require to constrain the standard deviation of the residence time distribution either by measuring an additional age tracer, or by using a model. Our finding is consistent with Marcais et al. (2015), who used results from groundwater flow models to show that two independent age tracers interpreted with a priori relevant LPM models are enough to constrain key quantiles of the residence time distribution. It also agrees with Eberts et al. (2012), who found evidence that lumped parameter models calibrated with two or three age tracers can be as efficient as particle tracking models to assess the vulnerability of wells to contamination.

Measuring the first two moments (mean and standard deviation) of the RTD requires two independent age tracers, which is often challenging. One way to circumvent the problem could be found in recent studies that demonstrate the linkage between geology, topography and residence times (McGuire et al. 2005; Soulsby and Tetzlaff 2008; Starn and Belitz 2018; Tetzlaff et al. 2009). Correlating the mean age and the variability of RTD with geomorphological characteristics, such as the total volume and the heterogeneity of the aquifer, is increasingly investigated on the basis of local to regional groundwater flow and transport models (Starn et al., 2021; Gauvain et al., 2021). Simulation results are handled either to determine generic rules or as an input to machine learning algorithms to eventually upscale residence times and nitrate predictions on the basis of widely available geological and topographic data.

4.3 Denitrification: the time to start is more important than the reaction rate

When considering denitrification, it is essential to distinguish the time needed for the reaction to start from the time needed for the reaction itself (Kolbe et al., 2019). Our study confirmed that the denitrification time lag is the primary control of nitrate concentration in groundwater, rather than variation in denitrification rate itself (Figure 2). Once O_2 has been sufficiently depleted, nitrate reduction is very fast compared to the denitrification time lag. The characteristic denitrification time is thus only a secondary control.

Oxygen and nitrate reduction require the availability of electron donors (Korom 1992), typically organic matter or pyrite (Hosono et al. 2013; Pauwels et al. 2000). In our system, organic carbon is mostly consumed in the soil and is not abundant in the saturated zone of the aquifer. Thus, in the aquifer, oxygen and nitrate degradation depend on the availability of mineral electron donors such as pyrite (Bochet et al. 2020). Kolbe et al. (2019) proposed a conceptual framework in which the aquifer is divided into a shallow, non-reactive zone that lacks available electron donors, and a deep, reactive zone, with available electron donors. After leaching from the soil, the groundwater first flows through the non-reactive zone, where neither O_2 nor NO_3^- is degraded. As soon as the groundwater enters the deep reactive zone, where electron donors are again available, O_2 is quickly consumed, followed by NO_3^-. Thus, the denitrification time lag is mainly controlled by the time needed for the nitrate to reach the reactive zone of the aquifer. This framework is consistent with piezometer profiles established by Postma et al. (1991) in an unconfined sandy aquifer, showing that oxygen and nitrate concentrations suddenly decrease at a depth that coincides with the apparition of pyrite. Kolbe et al. (2019) additionally correlated the depth of the reactive zone with the thickness of the geologically weathered zone. They proposed that geological weathering alters reduced minerals, inducing a stratification of biogeochemical activity.

Results from Böhlke and Denver (1995) in a well-instrumented sedimentary aquifer also suggested a stratification of denitrification related to the stratification of sedimentary layers. Our results, combined with the concept of stratified reactivity, suggest that the key parameter of denitrification could be characterized based on weathering profiles of the aquifer. Such profiles can be obtained by geophysical prospecting such as seismic imaging (Holbrook et al. 2014; Parsekian et al. 2015; Pasquet et al. 2015; St. Clair et al. 2015).

4.4 The interplay between residence times and denitrification controls nitrate concentration

Finally, the nitrate concentration in the aquifer is controlled by the proportion of water younger than the denitrification time lag (Figure 3). This young water did not encounter the reactive zone at all, meaning that it has the same nitrate concentration as the saturated zone input. Groundwater older than the denitrification time lag is almost fully denitrified and contains a very small amount of NO_3^-. Because the denitrification time lag is directly related to the time needed for oxygen to be consumed, O_2 concentration could be used as a proxy for the proportion of water younger than the denitrification time lag. Our results support Green et al. (2016), who proposed to use O_2 measurements to characterize denitrification processes. O_2 can be cheaply and reliably measured via routine laboratory and field methods, though care must be taken to avoid reaeration or degassing during sampling. Using groundwater oxygen concentration would greatly increase our capacity to predict nitrate removal at large scales.

The interplay between residence times and denitrification can be illustrated by looking at the NO_3^- trajectories in three wells with very distinctive flows and reactive conditions of the aquifer (Figure 3). The well that contains the largest fraction of water younger than the time needed for denitrification to start (t_{lag}) displays the highest NO_3^- concentration (well 1). The presence of very short flowpaths also leads to a rapid response to agricultural changes and allows the difference between the three input scenarios to be seen immediately. In the well with a smaller amount of water younger than t_{lag}, the NO_3^- concentration is lower (well 2). However, the absence of very short flowpaths delays the response to nitrate input decrease scenarios. For more than 10 years after a ban of nitrogen input, the concentration remained as if no change had been made. In the last well, the combination of a short denitrification time lag and the absence of very young flowpaths leads to a zero NO_3^- concentration, because only denitrified flow paths reach the well (well 3). Since the whole water mass is older than the denitrification time lag, this well is not vulnerable to NO_3^- pollution and its concentration is insensitive to any other parameter. These case studies highlight that the NO_3^- trajectories are governed by the fraction of groundwater younger than the denitrification time lag. This fraction is defined by the interplay between the mean and the standard deviation of the residence time distribution, and the denitrification time lag. The heterogeneity of these key parameters induces a spatially variable vulnerability to NO_3^- pollution over the aquifer.

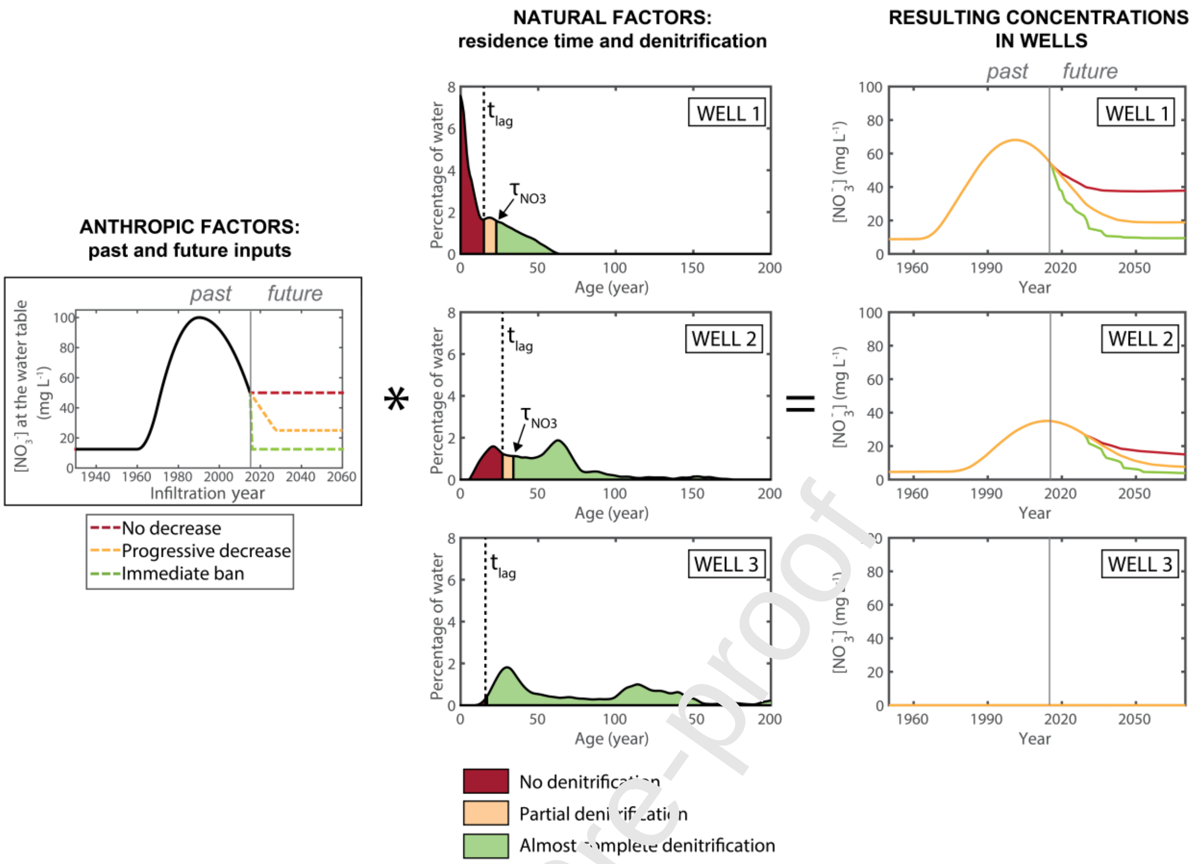


Figure 3. Prediction of the nitrate trajectories in three wells, following the three scenarios presented in section 2.2.3. The NO_3^- concentration in the wells (on the right panels) results from the convolution of the anthropic factors (on the left panel) and the natural factors (on the middle panels). The natural factors are themselves a combination of hydrogeology (residence time distribution) and biogeochemistry (denitrification). The denitrification time lag, t_{lag}, (dashed line) and the characteristic reaction time, τ_{NO3} (arrow) are indicated in the middle pannels.

4.5 Nitrate inputs: uncertainty about the past does not hamper predictions of the future

Reconstructing nitrate input time series requires substantial resources and presents multiple challenges (Oenema et al. 2003; Payraudeau et al. 2007; Poisvert et al. 2016; Salo and Turtola 2006). Our study shows that in catchments without available nitrate input time series, a simplified time series allows reasonable estimations of future nitrate concentration in groundwater. Although the total mass of nitrate that entered the system since the beginning of the industrial period has to be estimated, the shape of the time series does not substantially affect predictions (Figure 2). Indeed, natural mixing of young and old groundwater smooths the nitrogen input time series in the aquifer (McDonnell et al. 2010). Regarding the state of current knowledge and the sensitivity of nitrate concentrations, it seems that larger gaps remain in the characterization of natural parameters of the groundwater system than on the reconstruction of the nitrate input time series.

5 Conclusion

Based on a calibrated model, we predicted the nitrate trajectories in 16 wells (28 to 98 m deep) of an unconfined fractured bedrock aquifer located in an agricultural area of Western France. Groundwater flow in the saturated zone was responsible for a marked nitrate legacy, delaying for several years the impact of mitigation strategies in some parts of the catchment. This highlights the need to determine where and when the results of mitigation efforts have a chance to be measurable. A sensitivity analysis on the predicted nitrate concentrations showed that the nitrate concentration in the aquifer can be predicted using a limited number of parameters:

1. the total mass of nitrate that entered the saturated zone in the past, which can be estimated with land use data.
2. the mean and the variance of the groundwater residence time distribution, which can be measured with a minimum of two age tracers. If only one age tracer is available, it must be combined with a model or an assumption on the residence time variance, that could be based on geomorphologic analysis.

3. the time needed for the groundwater to reach the reactive zone of the aquifer, which can be evaluated with groundwater dissolved oxygen concentration.

Other parameters, especially the precise shape of the nitrate input time series, have little impact on the recovery trajectory of the aquifer. At this point, we are able to evaluate these key parameters at a local scale, appropriate for policy implementations. Even if the path forward to upscale these parameters remains unclear, determining what information is most needed and valuable is the first step towards large scale predictions. The fact that the groundwater nitrate trajectories can be approached with a limited knowledge of the system is promising regarding our future ability to predict nitrate contamination of groundwater.

6 References

Abbott, B. W., V. Baranov, C. Mendoza-Lera, M. Nikolakopoulou, A. Harjung, T. Kolbe, M. N. Balasubramanian, T. N. Vaessen, F. Ciocca, A. Campeau, M. B. Wallin, P. Romeijn, M. Antonelli, J. Gonçalves, T. Datry, A. M. Laverman, J.-R. de Dreuzy, D. M. Hannah, S. Krause, C. Oldham & G. Pinay, 2016. Using multi-tracer inference to move beyond single-catchment ecohydrology. Earth-Science Reviews 160:19-42 doi:10.1016/j.earscirev.2016.06.014.

Abbott, B. W., K. Bishop, J. P. Zarnetske, C. Minaudo, F. S. Chapin, S. Krause, D. M. Hannah, L. Conner, D. Ellison, S. E. Godsey, S. Plont, J. Marçais, T. Kolbe, A. Huebner, R. J. Frei, T. Hampton, S. Gu, M. Buhman, S. Sara Sayedi, O. Ursache, M. Chapin, K. D. Henderson & G. Pinay, 2019. Human domination of the global water cycle absent from depictions and perceptions. Nature Geoscience 12(7):533-540 doi:10.1038/s41561-019-0374-y.

Abbott, B. W., F. Moatar, O. Gauthier, O. Fovet, V. Antoine & O. Ragueneau, 2018. Trends and seasonality of river nutrients in agricultural catchments: 18years of weekly citizen science in France. The Science of the total environment 624:845-858 doi:10.1016/j.scitotenv.2017.12.176.

Aeschbach-Hertig, W., F. Peeters, U. Beyerle & R. Kipfer, 1999. Interpretation of dissolved atmospheric noble gases in natural waters. Water Resources Research 35(9):2779-2792 doi:10.1029/1999wr900130.

Aquilina, L., V. Vergnaud-Ayraud, T. Labasque, O. Bour, J. Molenat, L. Ruiz, V. de Montety, J. De Ridder, C. Roques & L. Longuevergne, 2012. Nitrate dynamics in agricultural catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters. The Science of the total environment 435-436:167-78 doi:10.1016/j.scitotenv.2012.06.028.

Ayraud, V., L. Aquilina, T. Labasque, H. Pauwels, J. Molenat, A.-C. Pierson-Wickmann, V. Durand, O. Bour, C. Tarits, P. Le Corre, E. Fourre, P. Merot & P. Davy, 2008. Compartmentalization of physical and chemical properties in hard-rock aquifers deduced from chemical and groundwater age analyses. Applied Geochemistry 23(9):2686-2707 doi:https://doi.org/10.1016/j.apgeochem.2008.06.001.

Barbe, L., A. Prinzing, C. Mony, B. Abbott, M. Santonja, K. Hoeffner, S. Guillocheau, D. Cluzeau, A. J. Francez, N. Bris & V. Jung, 2019. Opposing Effects of Plant-Community Assembly Maintain Constant Litter Decomposition over Grasslands Aged from 1 to 25 Years. Ecosystems:1-13 doi:10.1007/s10021-019-00392-8.

Bernard-Griffiths, J., J. J. Peucat, S. Sheppard & P. Vidal, 1985. Petrogenesis of Hercynian leucogranites from the southern Armorican Massif: contribution of REE and isotopic (Sr, Nd, Pb and O) geochemical data to the study of source rock characteristics and ages. Earth and Planetary Science Letters 74(2):235-250 doi:https://doi.org/10.1016/0012-821X(85)90024-X.

Bochet, O., L. Bethencourt, A. Dufresne, J. Farasin, M. Pédrot, T. Labasque, E. Chatton, N. Lavenant, C. Petton, B. W. Abbott, L. Aquilina & T. Le Borgne, 2020. Iron-oxidizer hotspots formed by intermittent oxic–anoxic fluid mixing in fractured rocks. Nature Geoscience 13(2):149-155 doi:10.1038/s41561-019-0509-1.

Boers, P. C. M., 1996. Nutrient emissions from agriculture in the Netherlands, causes and remedies. Water Science and Technology 33(4-5):183-189 doi:10.2166/wst.1996.0503.

Böhlke, J. K. & J. M. Denver, 1995. Combined Use of Groundwater Dating, Chemical, and Isotopic Analyses to Resolve the History and Fate of Nitrate Contamination in Two Agricultural Watersheds, Atlantic Coastal Plain, Maryland. Water Resources Research 31(9):2319-2339 doi:doi:10.1029/95WR01584.

Busenberg, E. & L. N. Plummer, 1992. Use of chlorofluorocarbons (ccl3f and ccl2f2) as hydrologic tracers and age dating tools - the alluvium and terrace system of central oklahoma. Water Resources Research 28(9):2257-2283 doi:10.1029/92wr01263.

Cheng, F. Y., K. J. Van Meter, D. K. Byrnes & N. B. Basu, 2020. Maximizing US nitrate removal through wetland protection and restoration. Nature 588(7839):625-630 doi:10.1038/s41586-020-03042-5.

Choi, B. C., T. Pang, V. Lin, P. Puska, G. Sherman, M. Goddard, M. J. Ackland, P. Sainsbury, S. Stachenko, H. Morrison & C. Clottey, 2005. Can scientists and policy makers work together? J Epidemiol Community Health 59(8):632-7 doi:10.1136/jech.2004.031765.

Diersch, H. J. G., 2013. FEFLOW—Finite Element Modeling of Flow, Mass and Heat Transport in Porous and Fractured Media. Springer Science & Business Media.

Dupas, R., C. Minaudo, G. Gruau, L. Ruiz & C. Gascuel-Odoux, 2018. Multidecadal Trajectory of Riverine Nitrogen and Phosphorus Dynamics in Rural Catchments. Water Resources Research 54(8):5327-5340 doi:10.1029/2018wr022905.

Eberts, S. M., J. K. Böhlke, L. J. Kauffman & B. C. Jurgens, 2012. Comparison of particle-tracking and lumped-parameter age-distribution models for evaluating vulnerability of production wells to contamination. Hydrogeology Journal 20(2):263-282 doi:10.1007/s10040-011-0810-6.

Ehrhardt, S., R. Kumar, J. H. Fleckenstein, S. Attinger & A. Musolff, 2019. Trajectories of nitrate input and output in three nested catchments along a land use gradient. Hydrology and Earth System Sciences 23(9):3503-3524 doi:10.5194/hess-23-3503-2019.

Engdahl, N. B. & R. M. Maxwell, 2014. Approximating groundwater age distributions using simple streamtube models and multiple tracers. Advances in Water Resources 66:19-31 doi:https://doi.org/10.1016/j.advwatres.2014.02.001.

Fenton, O., R. P. O. Schulte, P. Jordan, S. T. J. Lalor & K. G. Richards, 2011. Time lag: a methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. Environmental Science & Policy 14(4):419-431 doi:https://doi.org/10.1016/j.envsci.2011.03.006.

Frei, R. J., B. W. Abbott, R. Dupas, S. Gu, G. Gruau, Z. Thomas, T. Kolbe, L. Aquilina, T. Labasque, A. Laverman, O. Fovet, F. Moatar & G. Pinay, 2020. Predicting Nutrient Incontinence in the Anthropocene at Watershed Scales. Frontiers in Environmental Science 7 doi:10.3389/fenvs.2019.00200.

Galloway, J. N., A. R. Townsend, J. W. Erisman, M. Bekunda, Z. Cai, J. R. Freney, L. A. Martinelli, S. P. Seitzinger & M. A. Sutton, 2008. Transformation of the Nitrogen

Cycle: Recent Trends, Questions, and Potential Solutions. Science 320(5878):889-892 doi:10.1126/science.1136674.

Ginn, T. R., 1999. On the distribution of multicomponent mixtures over generalized exposure time in subsurface flow and reactive transport: Foundations, and formulations for groundwater age, chemical heterogeneity, and biodegradation. Water Resources Research 35(5):1395-1407 doi:10.1029/1999wr900013.

Green, C. T., B. C. Jurgens, Y. Zhang, J. J. Starn, M. J. Singleton & B. K. Esser, 2016. Regional oxygen reduction and denitrification rates in groundwater from multi-model residence time distributions, San Joaquin Valley, USA. Journal of Hydrology 543:155-166 doi:10.1016/j.jhydrol.2016.05.018.

Hamilton, S. K., 2012. Biogeochemical time lags may delay responses of streams to ecological restoration. Freshwater Biology 57:43-57 doi:10.1111/j.1365-2427.2011.02685.x.

Holbrook, S., C. S. Riebe, M. Elwaseif, J. Hayes, K. Basler-Reeder, D. Harry, A. Malazian, A. Dosseto, P. Hartsough & J. Hopmans, 2014. Geophysical constraints on deep weathering and water storage potential in the Southern Sierra Critical Zone Observatory. Earth Surface Processes and Landforms 39 doi:10.1002/esp.3502.

Hosono, T., T. Tokunaga, M. Kagabu, H. Nakata, T. Orishikida, I. T. Lin & J. Shimada, 2013. The use of delta15N and delta18O tracers with an understanding of groundwater flow dynamics for evaluating the origins and attenuation mechanisms of nitrate pollution. Water Res 47(8):2661-75 doi:10.1016/j.watres.2013.02.020.

Hrachowitz, M., O. Fovet, L. Ruiz & H. H. G. Savenije, 2015. Transit time distributions, legacy contamination and variability in biogeochemical 1/fα scaling: how are hydrological response dynamics linked to water quality at the catchment scale? Hydrological Processes 29(25):5241-5256 doi:10.1002/hyp.10546.

Kolbe, T., J. R. de Dreuzy, B. W. Abbott, L. Aquilina, T. Babey, C. T. Green, J. H. Fleckenstein, T. Labasque, A. M. Laverman, J. Marcais, S. Peiffer, Z. Thomas & G. Pinay, 2019. Stratification of reactivity determines nitrate removal in groundwater. Proc Natl Acad Sci U S A 116(7):2494-2499 doi:10.1073/pnas.1816892116.

Kolbe, T., J. Marçais, Z. Thomas, B. W. Abbott, J.-R. de Dreuzy, P. Rousseau-Gueutin, L. Aquilina, T. Labasque & G. Pinay, 2016. Coupling 3D groundwater modeling with CFC-based age dating to classify local groundwater circulation in an unconfined crystalline aquifer. Journal of Hydrology 543:31-46 doi:https://doi.org/10.1016/j.jhydrol.2016.05.020.

Korom, S. F., 1992. Natural denitrification in the saturated zone: A review. Water Resources Research 28(6):1657-1668 doi:10.1029/92wr00252.

Kronvang, B., H. E. Andersen, C. Børgesen, T. Dalgaard, S. E. Larsen, J. Bøgestrand & G. Blicher-Mathiasen, 2008. Effects of policy measures implemented in Denmark on nitrogen pollution of the aquatic environment. Environmental Science & Policy 11(2):144-152 doi:10.1016/j.envsci.2007.10.007.

Kronvang, B., E. Jeppesen, D. J. Conley, M. Søndergaard, S. E. Larsen, N. B. Ovesen & J. Carstensen, 2005. Nutrient pressures and ecological responses to nutrient loading reductions in Danish streams, lakes and coastal waters. Journal of Hydrology 304(1-4):274-288 doi:10.1016/j.jhydrol.2004.07.035.

Le Moal, M., C. Gascuel-Odoux, A. Menesguen, Y. Souchon, C. Etrillard, A. Levain, F. Moatar, A. Pannard, P. Souchu, A. Lefebvre & G. Pinay, 2019. Eutrophication: A new wine in an old bottle? The Science of the total environment 651(Pt 1):1-11 doi:10.1016/j.scitotenv.2018.09.139.

Le Moigne, P., 2009. SURFEX scientific documentation. 87:211.

Leray, S., N. B. Engdahl, A. Massoudieh, E. Bresciani & J. McCallum, 2016. Residence time distributions for hydrologic systems: Mechanistic foundations and steady-state analytical solutions. Journal of Hydrology 543:67-87 doi:10.1016/j.jhydrol.2016.01.068.

Maloszewski, P. & A. Zuber, 1996. Lumped parameter models for the interpretation of environmental tracer data. International Atomic Energy Agency (IAEA), 9-58.

Małoszewski, P. & A. Zuber, 1982. Determining the turnover time of groundwater systems with the aid of environmental tracers: 1. Models and their applicability. Journal of Hydrology 57(3):207-231 doi:https://doi.org/10.1016/0022-1694(82)90147-0.

Marcais, J., J. R. de Dreuzy, T. R. Ginn, P. Rousseau-Gueutin & S. Leray, 2015. Inferring transit time distributions from atmospheric tracer data: Assessment of the predictive capacities of Lumped Parameter Models on a 3D crystalline aquifer model. Journal of Hydrology 525:619-631 doi:10.1016/j.jhydrol.2015.03.055.

Marcais, J., A. Gauvain, T. Labasque, B. W. Abbott, G. Pinay, L. Aquilina, F. Chabaux, D. Viville & J. R. de Dreuzy, 2018. Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers. The Science of the total environment 636:260-272 doi:10.1016/j.scitotenv.2018.04.196.

McDonnell, J. J., K. McGuire, P. Aggarwal, K. J. Beven, D. Biondi, G. Destouni, S. Dunn, A. James, J. Kirchner, P. Kraft, S. Lyon, P. Maloszewski, B. Newman, L. Pfister, A. Rinaldo, A. Rodhe, T. Sayama, J. Seibert, K. Solomon, C. Soulsby, M. Stewart, D. Tetzlaff, C. Tobin, P. Troch, M. Weiler, A. Western, A. Wörman & S. Wrede, 2010. How old is streamwater? Open questions in catchment transit time conceptualization, modelling and analysis. Hydrological Processes 24(12):1745-1754 doi:10.1002/hyp.7796.

McDonnell, J. J., M. Sivapalan, K. Vache, S. Dunn, G. Grant, R. Haggerty, C. Hinz, R. Hooper, J. Kirchner, M. L. Roderick, J. Selker & M. Weiler, 2007. Moving beyond heterogeneity and process complexity: A new vision for watershed hydrology. Water Resources Research 43(7) doi:10.1029/2006wr005467.

McGuire, K. J., J. J. McDonnell, M. Weiler, C. Kendall, B. L. McGlynn, J. M. Welker & J. Seibert, 2005. The role of topography on catchment-scale water residence time. Water Resources Research 41(5) doi:10.1029/2004wr003657.

Meals, D. W., S. A. Dressing & T. E. Davenport, 2010. Lag Time in Water Quality Response to Best Management Practices: A Review. J Environ Qual 39(1):85-96 doi:10.2134/jeq2009.0108.

Minaudo, C., R. Dupas, C. Gascuel-Odoux, V. Roubeix, P.-A. Danis & F. Moatar, 2019. Seasonal and event-based concentration-discharge relationships to identify catchment controls on nutrient export regimes. Advances in Water Resources 131 doi:10.1016/j.advwatres.2019.103379.

Noilhan, J. & J. F. Mahfouf, 1996. The ISBA land surface parameterisation scheme. Global and Planetary Change 13(1):145-159 doi:https://doi.org/10.1016/0921-8181(95)00043-7.

Oenema, O., H. Kros & W. de Vries, 2003. Approaches and uncertainties in nutrient budgets: implications for nutrient management and environmental policies. European Journal of Agronomy 20(1-2):3-16 doi:10.1016/s1161-0301(03)00067-4.

Paradis, D., J.-M. Ballard, R. Lefebvre & M. M. Savard, 2017. Multi-scale nitrate transport in a sandstone aquifer system under intensive agriculture. Hydrogeology Journal 26(2):511-531 doi:10.1007/s10040-017-1668-z.

Parris, K., 1998. Agricultural nutrient balances as agri-environmental indicators: an OECD perspective. Environmental Pollution 102(1, Supplement 1):219-225 doi:https://doi.org/10.1016/S0269-7491(98)80036-5.

Parsekian, A. D., K. Singha, B. J. Minsley, W. S. Holbrook & L. Slater, 2015. Multiscale geophysical imaging of the critical zone. Rev Geophys 53(1):1-26 doi:10.1002/2014rg000465.

Pasquet, S., L. Bodet, L. Longuevergne, A. Dhemaied, C. Camerlynck, F. Rejiba & R. Guérin, 2015. 2D characterization of near-surface VP/VS: Surface-wave dispersion inversion versus refraction tomography. Near Surface Geophysics 13 doi:10.3997/1873-0604.2015028.

Pauwels, H., J.-C. Foucher & W. Kloppmann, 2000. Denitrification and mixing in a schist aquifer: influence on water chemistry and isotopes. Chemical Geology 168(3):307-324 doi:https://doi.org/10.1016/S0009-2541(00)00201-1.

Payraudeau, S., H. M. G. van der Werf & F. Vertès, 2007. Analysis of the uncertainty associated with the estimation of nitrogen losses from farming systems. Agricultural Systems 94(2):416-430 doi:10.1016/j.agsy.2006.11.014.

Pinay, G., S. Peiffer, J. R. De Dreuzy, S. Krause, D. M. Hannah, J. H. Fleckenstein, M. Sebilo, K. Bishop & L. Hubert-Moy, 2015. Upscaling Nitrogen Removal Capacity from Local Hotspots to Low Stream Orders' Drainage Basins. Ecosystems 18(6):1101-1120 doi:10.1007/s10021-015-9878-5.

Poisvert, C., F. Curie & F. Moatar, 2016. Annual agricultural N surplus in France over a 70-year period. Nutrient Cycling in Agroecosystems 107(1):63-78 doi:10.1007/s10705-016-9814-x.

Postma, D., C. Boesen, H. Kristiansen & F. Larsen, 1991. Nitrate Reduction in an Unconfined Sandy Aquifer: Water Chemistry, Reduction Processes, and Geochemical Modeling. Water Resources Research 27(8):2027-2045 doi:10.1029/91wr00989.

Salo, T. & E. Turtola, 2006. Nitrogen balance as an indicator of nitrogen leaching in Finland. Agriculture, Ecosystems & Environment 113(1-4):98-107 doi:10.1016/j.agee.2005.09.002.

Sebilo, M., B. Mayer, B. Nicolardot, G. Pinay & A. Mariotti, 2013. Long-term fate of nitrate fertilizer in agricultural soils. Proc Natl Acad Sci U S A 110(45):18185-9 doi:10.1073/pnas.1305372110.

Singleton, M. J., B. K. Esser, J. E. Moran, G. B. Hudson, W. W. McNab & T. Harter, 2007. Saturated Zone Denitrification: Potential for Natural Attenuation of Nitrate Contamination in Shallow Groundwater Under Dairy Operations. Environ Sci Technol 41(3):759-765 doi:10.1021/es061253g.

Soulsby, C. & D. Tetzlaff, 2008. Towards simple approaches for mean residence time estimation in ungauged basins using tracers and soil distributions. Journal of Hydrology 363(1-4):60-74 doi:10.1016/j.jhydrol.2008.10.001.

St. Clair, J., S. Moon, W. S. Holbrook, J. T. Perron, C. S. Riebe, S. J. Martel, B. Carr, C. Harman, K. Singha & D. d. Richter, 2015. Geophysical imaging reveals topographic stress control of bedrock weathering. Science 350(6260):534-538 doi:10.1126/science.aab2210.

Starn, J. J. & K. Belitz, 2018. Regionalization of Groundwater Residence Time Using Metamodeling. Water Resources Research 54(9):6357-6373 doi:10.1029/2017wr021531.

Steffen, W., K. Richardson, J. Rockstrom, S. E. Cornell, I. Fetzer, E. M. Bennett, R. Biggs, S. R. Carpenter, W. de Vries, C. A. de Wit, C. Folke, D. Gerten, J. Heinke, G. M. Mace,

L. M. Persson, V. Ramanathan, B. Reyers & S. Sorlin, 2015. Sustainability. Planetary boundaries: guiding human development on a changing planet. Science 347(6223):1259855 doi:10.1126/science.1259855.

Tesoriero, A. J. & L. J. Puckett, 2011. O2reduction and denitrification rates in shallow aquifers. Water Resources Research 47(12) doi:10.1029/2011wr010471.

Tetzlaff, D., J. Seibert & C. Soulsby, 2009. Inter-catchment comparison to assess the influence of topography and soils on catchment transit times in a geomorphic province; the Cairngorm mountains, Scotland. Hydrological Processes 23(13):1874-1886 doi:10.1002/hyp.7318.

Thomas, Z. & B. W. Abbott, 2018. Hedgerows reduce nitrate flux at hillslope and catchment scales via root uptake and secondary effects. Journal of Contaminant Hydrology 215:51-61 doi:https://doi.org/10.1016/j.jconhyd.2018.07.002.

Thomas, Z., P. Rousseau-Gueutin, B. W. Abbott, T. Kolbe, H. Le Lay, J. Marçais, F. Rouault, C. Petton, P. Pichelin, G. Le Hennaff, H. Squividant, T. Labasque, J.-R. de Dreuzy, L. Aquilina, J. Baudry & G. Pinay, 2019. Long-term ecological observatories needed to understand ecohydrological systems in the Anthropocene: a catchment-scale case study in Brittany, France. Regional Environmental Change 19(2):363-377 doi:10.1007/s10113-018-1444-1.

US EPA, 2008. Gulf Hypoxia Action Plan 2008 for Reducing, Mitigating, and Controlling Hypoxia in the Northern Gulf of Mexico and Improving Water Quality in the Mississippi River Basin. Mississippi River/Gulf of Mexico Watershed Nutrient Task Force.

Van Meter, K. J. & N. B. Basu, 2015. Catchment legacies and time lags: a parsimonious watershed model to predict the effects of legacy storage on nitrogen export. PLoS One 10(5):e0125971 doi:10.1371/journal.pone.0125971.

Van Meter, K. J. & N. B. Basu, 2017. Time lags in watershed-scale nutrient transport: an exploration of dominant controls. Environmental Research Letters 12(8) doi:10.1088/1748-9326/aa7bf4.

Van Meter, K. J., N. B. Basu & P. Van Cappellen, 2017. Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins. Global Biogeochemical Cycles 31(1):2-23 doi:10.1002/2016gb005498.

Van Meter, K. J., N. B. Basu, J. J. Veenstra & C. L. Burras, 2016. The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes. Environmental Research Letters 11(3) doi:10.1088/1748-9326/11/3/035014.

Visser, A., H. P. Broers, R. Purtschert, J. Sültenfuß & M. de Jonge, 2013. Groundwater age distributions at a public drinking water supply well field derived from multiple age tracers (^{85}Kr, ^{3}H/^{3}He, and ^{39}Ar). Water Resources Research 49(11):7778-7796 doi:10.1002/2013wr014012.

Wendland, F., R. Kunkel, A. Grimvall, B. Kronvang & D. I. Müller-Wohlfell, 2002. The SOIL-N/WEKU model system – a GIS-supported tool for the assessment and management of diffuse nitrogen leaching at the scale of river basins. Water Science and Technology 45(9):285-292 doi:10.2166/wst.2002.0260.

Wyns, R., J. M. Baltassat, P. Lachassagne, A. Legchenko, J. Vairon & F. Mathieu, 2004. Application of proton magnetic resonance soundings to groundwater reserve mapping in weathered basement rocks (Brittany, France). Bulletin De La Societe Geologique De France 175(1):21-34 doi:10.2113/175.1.21.

CRediT author statement

Camille Vautier : Conceptualization, Methodology, Formal analysis, Software, Writing - Review & Editing

Tamara Kolbe : Methodology, Investigation

Tristan Babey : Methodology, Investigation

Jean Marçais : Conceptualization, Methodology, Review & Editing

Benjamin W. Abbott : Writing - Review & Editing

Anniet M. Laverman : Conceptualization, Review & Editing

Zahra Thomas : Investigation, Review & Editing

Luc Aquilina : Conceptualization, Review & Editing

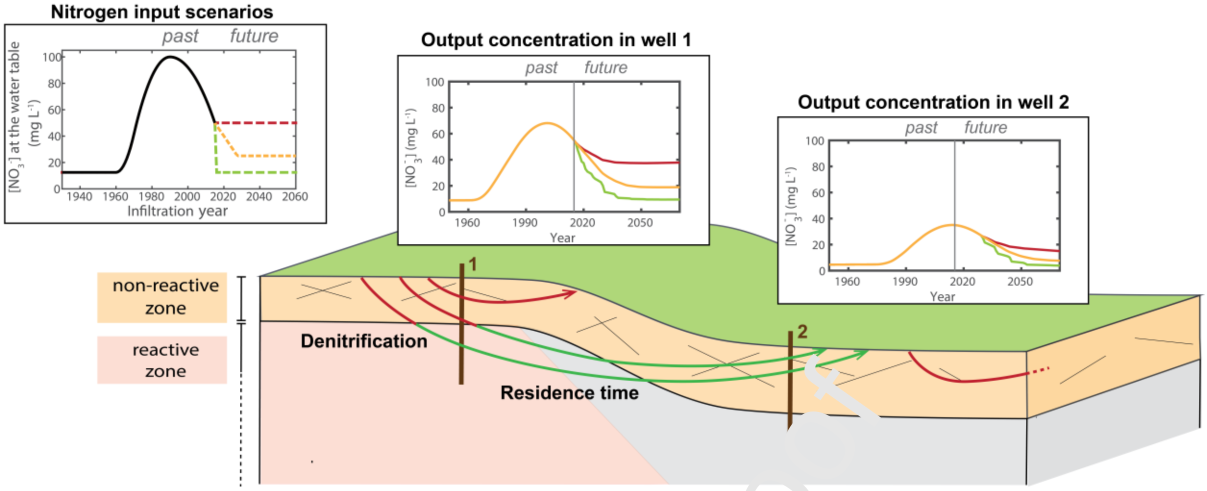
Gilles Pinay : Conceptualization, Writing - Review & Editing

Jean-Raynald de Dreuzy : Conceptualization, Methodology, Writing - Review & Editing

Declaration of interests

X The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



Highlights

- Nitrate recovery trajectories were predicted based on a few key-parameters.
- Two age tracers are necessary to predict groundwater nitrate concentration.
- The stratification of denitrification controls the nitrate dynamic in the aquifer.
- Uncertainty about past nitrogen inputs may not alter the predictions.