Nitrate transport and retention in Western European catchments are shaped by hydroclimate and subsurface properties

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Abstract

Excess nitrogen (N) from anthropogenic sources deteriorates freshwater resources. Actions taken to reduce N inputs to the biosphere often show no or only delayed effects in receiving surface waters hinting at large legacy N stores built up in the catchments soils and groundwater. Here, we quantify transport and retention of N in 238 Western European catchments by analyzing a unique data set of long-term N input and output time series. We find that half of the catchments exhibited peak transport times larger than five years with longer times being evident in catchments with high potential evapotranspiration and low precipitation seasonality. On average the catchments retained 72% of the N from diffuse sources with retention efficiency being specifically high in catchments with low discharge and thick, unconsolidated aquifers. The estimated transport time scales do not explain the observed N retention, suggesting a dominant role of biogeochemical legacy in the catchments' soils rather than a legacy store in the groundwater. Future water quality management should account for the accumulated biogeochemical N legacy to avoid long-term leaching and water quality deteriorations for decades to come.

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Key Points:

- Time lags of nitrogen transport in Western European catchments were five years on average and mainly explained by hydroclimatic variability

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- Almost three-quarters of the diffuse N input was retained in the catchment, mainly controlled by subsurface parameters and specific discharge
- Biogeochemical legacy likely exceeded hydrologic legacy in most of the 238 analyzed catchments

Abstract

Excess nitrogen (N) from anthropogenic sources deteriorates freshwater resources. Actions taken to reduce N inputs to the biosphere often show no or only delayed effects in receiving surface waters hinting at large legacy N stores built up in the catchments' soils and groundwater. Here, we quantify transport and retention of N in 238 Western European catchments by analyzing a unique data set of long-term N input and output time series. We find that half of the catchments exhibited peak transport times larger than five years with longer times being evident in catchments with high potential evapotranspiration and low precipitation seasonality. On average the catchments retained 72% of the N from diffuse sources with retention efficiency being specifically high in catchments with low discharge and thick, unconsolidated aquifers. The estimated transport time scales do not explain the observed N retention, suggesting a dominant role of biogeochemical legacy in the catchments' soils rather than a legacy store in the groundwater. Future water quality management should account for the accumulated biogeochemical N legacy to avoid long-term leaching and water quality deteriorations for decades to come.

Plain language summary

Despite different regulations that limit anthropogenic nitrate input to the biosphere, there is in many cases no or only delayed improvement in groundwater or surface water contamination. One reason for this mismatch are legacies either by accumulated nitrate in the soil or nitrate with slow transport pathways in the groundwater to the river. We assessed long-term data covering nitrate in- and output for Western-European catchments to quantify (1) the needed transport time until reappearance in the river and (2) the quantity of reappeared nitrate.

The transport time through the catchment had its peak at 5 years and was mainly controlled by hydrological parameters as high seasonality in precipitation favored faster transports. Furthermore 72% of the nitrate was retained in the catchment, mainly controlled by subsurface characteristics as thick and unconsolidated material favored retention either by holding nitrate in the soil or by supporting a bacterial process that released nitrate to the atmosphere. We hypothesized that most of the retained nitrate is accumulated in the soil. This huge pool has on the one hand the potential of being recycled and on the other hand the danger of leaching slowly, which would constitute a future long-lasting contamination source for groundwater and surface waters.

1. Introduction

Nitrogen (N) can be a limiting nutrient in terrestrial, freshwater and marine ecosystems (Webster et al., 2003). However, the N cycling in these ecosystems is modified and disturbed by humans through inputs from atmospheric deposition, agricultural fertilizers and waste water. High N inputs especially in economically developed countries have led to increased riverine dissolved inorganic nitrogen (DIN) fluxes, causing ecological degradation in aquatic systems and posing a threat to drinking water safety (Dupas et al., 2016; Sebilo et al., 2013; Wassenaar, 1995). Diffuse agricultural sources (mineral fertilizer and manure) constitute most of the N emissions into waters in European countries (Bouraoui and Grizzetti, 2011; Dupas et al., 2013).

Several regulations at federal, national or international levels have been implemented e.g. the EU Nitrate Directive (CEC, 1991) or the Clean Water Act (EPA, 1972) in the US – aiming particularly at reducing N inputs to the terrestrial system. Despite the reduction in inputs, there is often no or only little improvement in water quality observed in many catchments (Meals et al., 2010; Bouraoui and Grizzetti, 2011; Vero et al., 2017). The inadequacy of implemented measures to improve water quality can be related to transport and retention in the catchments responding to changes in the nutrient inputs. The latter is closely connected to a legacy accumulation of N (e.g. Thomas & Abbott, 2018; Van Meter & Basu, 2015; Wang & Burke, 2017) - a buildup of large N stores in the catchment that are not or only slowly exported. This legacy acts

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as long-term memory of catchments and has been hypothesized to buffer stream concentration variability (Basu et al., 2010).

N legacies can be attributed to two major components: the biogeochemical and the hydrologic N storage. The first one is related to biogeochemical transformation processes of N in the unsaturated (vadose) zone, often leading to a large buildup of an organic N pool in the soil matrix and only slowly converting to mobile nitrate (NO_3; Van Meter & Basu, 2017). Hydrologic legacy describes the pool of dissolved N in the groundwater and unsaturated zone, subjected to very slow transport processes (Van Meter & Basu, 2015). This transport is controlled by the travel time, i.e., the time rainfall needs to travel through a catchment (Kirchner et al., 2000). The diversity of subsurface flow paths in a catchment creates a distribution of travel times (Kirchner et al., 2000) varying from days to decades (e.g. Howden et al., 2011; Jasechko et al., 2016; McMahon et al., 2006; Sebilo et al., 2013) also integrating information on timing, amount, storage and mixing of water and thus solutes (Heidbüchel et al., 2020). Therefore, slow travel times and a resulting temporary storage of reactive N in the unsaturated zone (Ascott et al., 2017; Ehrhardt et al., 2019), can create similar time lags as the biogeochemical legacy of N stored in the soil N pool (Bingham & Cotrufo, 2016; Bouwman et al., 2013; Sebilo et al., 2013). Due to the high complexity of hydrological and biogeochemical processes in catchments, a good understanding of the share of the two different legacy storages and the fate of N remains challenging.

Data-based joint quantification and characterization of N transport timescales and retention under different land-use and management practices can provide an evidence based entry point to better understand N trajectories for reactive N transport at catchment scale (e.g. Ehrhardt et al., 2019; Van Meter and Basu, 2015). More specifically, comparing quantity and temporal patterns of diffuse N input and riverine N concentrations from catchments allow to estimate N transport time (TT) scales as well as retention (Dupas et al., 2020; Ehrhardt et al., 2019). Retention is defined here as the "missing N" that is either stored in a catchment due to the buildup of legacies or permanently removed by denitrification. The estimated TT of N integrates time delays by biogeochemical immobilization and mobilization in the soils and the TT through the vadose zone and groundwater. So far, only a few studies investigated retention and TTs simultaneously as availability of long-term data often limits the number of studied catchments (e.g. Dupas et al., 2020; Ehrhardt et al., 2019; Howden et al., 2010; Van Meter et al., 2017; Van Meter et al., 2018) although the identification and quantification of legacy effects is of critical importance for predicting future N dynamics and for implementing effective restoration efforts (Bain et al., 2012). Here we analyze a large-sample database of 238 Western European catchments with different geophysical and hydro-climatological characteristics and at least 20 years of observations with regards to observed nitrogen (1) TT scales and (2) retention. Furthermore, we connect these results to catchment characteristics to discuss their (3) main controlling factors. These research objectives are used to improve the understanding of catchment responses to changes in input and the fate of retained N being associated with different legacy stores and/or denitrification.

2. Materials and Methods

2.1. Study area

For data on water quantity and quality, we relied on three national data sets. Water quality data for French catchments are publicly available at http://naiades.eaufrance.fr/, while water quantity data are available at http://hydro.eaufrance.fr/. For Germany, Musolff (2020) provided a database for water quality and water quantity.

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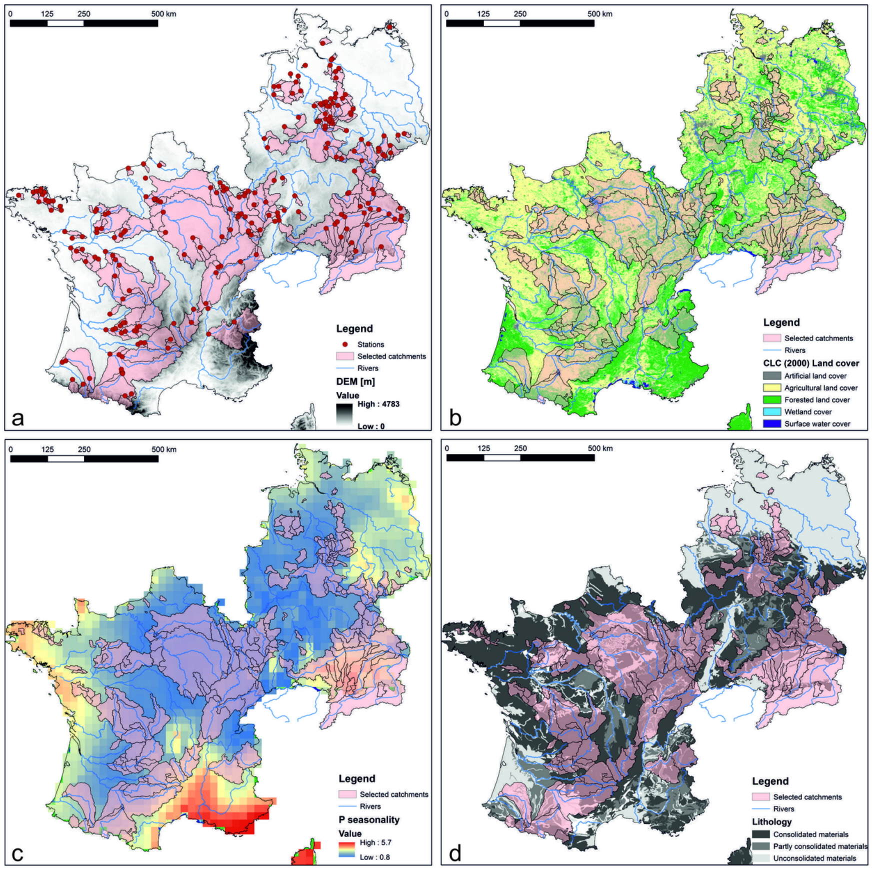

Figure 1 . Study catchments (n = 238) based on the quality criteria with selected catchment characteristics: a – Elevation (EEA, 2013), b – Land cover (CLC, 2000), c – Lithology (BCR & UNESCO, 2014), d – Depth to bedrock (Shangguan et al., 2017).

From this joint database we selected catchments where the following conditions were given: riverine NO_3-N concentration observations available for at least 20 years of data with data gaps less than 2 years and the total number of observations being more than 150. Given these criteria, 238 catchments were selected (Figure 1a). The time series covered data between 1971 and 2015 with a median length of 30 years and in total 96,443 measurements for NO_3-N. Overall we covered 40% of the total land area of both countries (i.e., around 361,000 km^2, taking nested catchments into account). The selected catchments encompass contrasting settings in terms of morphology, climate, geological properties and land use attributes (Supporting Information Tables S1.1 and S1.2). More than half of the study catchments have a size of less than 1,000 km^2 (max. 62,500 km^2). The median altitude ranges from 15 m to 1848 m with a median slope of 3°. Climatic settings of the sites reach from Atlantic to Continental climate with aridity indices ranging between 0.4 and 1.5. The median annual precipitation across the sites is around 816 mm, and the estimated base flow index (BFI) ranges from 29% to 97% with a median of 65%.

Most catchments (> 90%) are dominated by sandy soils (median: 44.6%), with 18 of those located in northwestern Germany. The bedrock mainly covers fissured and hard rock geology with the latter being predominant in most of the catchments. The geology is characterized by crystalline rocks in the Armorican Massif, the Pyrenees and the Massif Central and in some of the German mountainous catchments; and younger sedimentary rocks in most parts of France and Germany (Allain, 1951; BGR & CGMW, 2005). Quaternary sediments are found in the Northern German Lowlands, the Alpine foothills and north of the Pyrenees (Allain, 1951; BGR & CGMW, 2005).

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Regarding land use, 87% of the catchments had at least one-third of their area covered by agriculture that mainly incorporates non-irrigated arable land and pastures (EEA, 2016; Figure 1b). Riverine NO_3-N concentrations in these areas are therefore predominantly impacted by diffuse agricultural N sources (EEA, 2018). The median share of forest cover across the study catchments is 37%. Although the fraction of artificial surfaces was small, the median population density with 92 inhabitants km^{-2} in the study catchments is almost three-times the average European value (Worldometers.info, 2020).

2.2. Nitrogen input

The N input was selected as diffuse N stemming from agricultural N surplus, atmospheric deposition and biological fixation in non-agricultural areas. The N surplus consists of agricultural N input that is in excess of crop and forage exports (also known as land nitrogen budget; de Vries et al., 2011). Here, we relied on two national scale data sets. Agricultural N contribution and atmospheric N deposition for the French catchments were provided by Poisvert et al. (2017). The annual agricultural N surplus for German catchments was provided by Bach and Frede (1998) as well as Häußermann et al. (2019). It basically consists of two data sets available at a (coarser) state level (NUTS2) for 1950–1999 and at finer county level (NUTS3) for 1995–2015. Both data sets were harmonized to produce a consistent long-term data set. The atmospheric N deposition for German catchments is based on Europe-wide gridded data from a chemical transport model of the Meteorological Synthesizing Centre-West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) (Bartnicky & Fagerli, 2006; Bartnicky & Benedictow, 2017).

In agricultural areas, biological fixation was already included in the N budgets. The biologically fixed N fluxes to non-agricultural land use types for France and Germany were calculated using the European Corine Land Cover data set from the year 2000 (EEA, 2020), which is most representative regarding the water quality time series. Terrestrial biological N mean uptake rates were set for forest (to 16.04 kg N ha^{-1} yr^{-1}; Cleveland et al., 1999), for natural and urban grassland (to 2.7 kg N ha^{-1}yr^{-1}; Cleveland et al., 1999) and other land use (wetlands, water bodies, open space with little or no vegetation to 0.75 kg N ha^{-1} yr^{-1}; Van Meter et al., 2017). A comparison of the two national long-term data sets for diffuse N with a Europe-wide benchmark estimation for 1997–2003 (West et al., 2014) indicated an acceptable offset (see Supporting Information S2 for further information).

Due to the lack of spatially and temporally reliable long-term data on N input by waste water, we did not consider this point source. For France, Dupas et al. (2015) estimated the contribution from point sources to total N flux to be 3% during the period 2005–2009, and we hypothesized that the negligible contribution of point sources also held for Germany.

2.3. Nitrogen output as riverine NO_3-N concentrations and loads

Gaps in the discharge time series at 30 runoff stations in Germany were filled through the support of simulations from the grid-based distributed mesoscale hydrological model mHM (Kumar et al., 2013; Samaniego et al., 2010). Here, only model simulations resulting in an R^2 greater than 0.6 when compared with the observed discharge were accepted. A piecewise linear regression was utilized to correct for potential biases in the modelled data. These bias-corrected modelled discharge data were finally used to gap-fill the original data to obtain a continuous daily time series. In France, no such national hydrological model existed and therefore, we only included catchments with nearly continuous daily discharge monitoring for which short gaps in the discharge (max. 7 days) were interpolated by a fixed-interval smoothing via a state-space model using the R software package “Baytrends”.

The irregularly sampled, riverine NO_3-N concentrations were used to estimate daily concentrations by using the software package*Exploration and Graphics for RivErTrends* (EGRET) in the R environment by Hirsch and DeCicco (2019). The applied *Weighted Regressions on Time, Discharge, and Season* (WRTDS) uses a flexible statistical representation for every day of the discharge record and has been proven to provide robust estimates (Hirsch et al., 2010; Van Meter & Basu, 2017). As we focus on changes in concentrations and fluxes independent of inter-annual discharge variability (Hirsch et al., 2010), we used flow-normalized concentrations and fluxes for further analyses. For each catchment median annual flow-normalized NO_3-N

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concentrations and annual summed NO_3-N fluxes were calculated and scaled to the catchment area.

2.4. Nitrogen transport time

Travel time distributions are commonly derived as the transfer function between rainfall concentration time series and stream concentrations of a conservatively transported solute or water isotope (e.g. Kirchner et al., 2000). We transfer this concept to reactive N transport with the N input as an incoming time series with annual resolution that is assumed to yield the median annual riverine NO_3-N concentration, when convolved with a fitted distribution. This transport time distribution (TTD) can be based on different theoretical probability distribution functions. To represent the long memory of past inputs, long-tailed distributions are most suitable at catchment scales (Kirchner et al., 2000). Therefore, the N input was convolved using a log-normal distribution (Equation 1; Ehrhardt et al., 2019; Musolff et al., 2017) to find the optimal fit to riverine NO_3-N concentrations. We alternatively used a gamma distribution (Equation 2; Godsey et al., 2010; Fiori et al., 2009; Kirchner et al., 2000) as a transfer function, and we compared the quality of fit (R^2) with both methods.

Equation 1 $f(t) = \frac{1}{\tau\sigma\sqrt{2\pi}}\ exp\left(-\frac{(ln\ t - u)^2}{2\sigma^2}\right)$

Equation 2 $f(t) = t^{-\alpha}\frac{\varepsilon^{-t/\beta}}{\beta^{\alpha}\ G(\alpha)}$

The two parameters mu (µ) and sigma (σ) for the log-normal and shape (α) and scale (β) for the gamma distribution, respectively, were calibrated through optimization based on minimizing the sum of squared errors between the normalized annual diffuse N input and normalized annual median riverine NO_3-N concentrations. For this purpose we used the Particle Swarm Optimization (using the R package "hydroPSO" by Zambrani-Bigiarini & Rojas, 2013) algorithm in 30 independent runs. We estimated the mode of the selected best fitted TTD (with max. R^2) to represent the peak TT and at the same time to resemble the peak N export of the mobile, inorganic N.

2.5. Nitrogen retention and its temporal change

The total cumulative diffuse N input load was compared to the respective riverine NO_3-N load (assumed as N load) to analyze the N retention in the catchment (Equation 3). The difference between the two is the load being retained in the catchment as biogeochemical legacy, as hydrologic legacy or being removed by denitrification. The cumulative flux differences were calculated based on two approaches: 1) using the annual frames of the overlapping years in in- and outflux, while disregarding time shifts; and 2) applying the derived TTs, to compare the convolved inputs with the corresponding annual exported load.

Equation 3 $Retention = 1 - \frac{\mathrm{Nout}}{\mathrm{Nin}} = 1 - \frac{\sum_{i=ts}^{\mathrm{te}} NO3-N\ Flux\ i}{\sum_{i=ts}^{\mathrm{te}}\ \mathrm{Ninput\ i}}$

To further characterize the catchment's reaction to N input changes, we compared the median diffuse N input in the 1980s (median year of max. N input: 1986) with the one in the last years of the time series ([?] 2010) for a subset of stations (n = 120) that sufficiently covered the 1980s and 2010s. The same was done with the exported riverine NO_3-N loads in the 1980s and the 2010s. To gain robust estimates for the size of difference, we calculated the bootstrapped (n = 10,000) median differences between the 1980s and 2010s (for N input and N output) with their corresponding 95% confidence intervals.

2.6. Statistical analysis for controls in catchment response and retention

We applied a Partial Least Squares Regression (PLSR) to identify the main factors controlling N TTs and N retention in a catchment. PLSR is an established multivariate regression approach to analyze data sets that are strongly correlated among predictors and noisy (Wold et al., 2001). The PLSR model finds the variables (catchment characteristics) that best predict the response variables (retention and TT; Ai et al., 2015). The importance of each predictor for the dependent variable is indicated by the measure *Variable Importance in the Projection*(VIP). Factors with VIPs larger than 1 are considered to be significantly important for explaining the dependent variable (Ai et al., 2015; Shi et al., 2013). The corresponding regression coefficient is used to explain the direction of influence of each independent variable (Shi et al., 2013). The predictor

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variables used in this study characterize the topography, land cover, climate, hydrology, lithology, soils and population density of the studied catchments (Supporting Information S1).

3. Results

3.1. Nitrogen transport time scales

Using the gamma distribution yielded comparable results to the results for log-normal distribution (both with median $R^2 = 0.8$), but less catchments with an acceptable fit (R^2 [?] 0.6) between the convolved annual N inputs and riverine concentrations. Therefore, we only report the results using a log-normal distribution as a transfer function.

In some catchments (n = 72) no acceptable fit of TTDs could be obtained. According to a Wilcoxon rank sum test, the variability in NO_3-N concentrations in these catchments (CV: 0.08) is significantly different (p [?] 0.01) to the ones in the other catchments (CV: 0.12 with n = 166). A low temporal variability in the input or output makes it challenging to derive a reliable transfer function connecting them.

The median mode (peak) of the TTs for the 166 selected catchments with an acceptable fit was 5.4 years (Supporting Information Table S3.). Although the mode ranged from 0.2 to 34.1 years, the majority (70%) had a mode TT less than 10 years (Figure 2c). Only a few catchments (10%) showed a mode of at least 20 years, most of them (11/17) located in the Massif Central (Figure 2a).

Although the TT derivation was not mass conform, on average across the study catchments, 75% (75%-percentile) of the N input should have been exported after 18 years (range: 1.4–38.2).

3. 2. Nitrogen retention

The median N retention of the selected catchments (n = 238) was 72% (sd: 16%; Supporting Information Table S3.; Figure 2b), meaning that a large part of N was retained as legacy or denitrified. Despite the wide range (-24–96%, with one negative outlier Figure 2b), 48% of the catchments had a retention between 50% and 75%. A convolution of the N inputs according to the corresponding TT resulted in a slightly lower retention with a median of 70% (n = 238; 71% with n = 166; Figure 2d).

N retention and TT did not correlate in the study catchments. Almost the same amount of catchments with retention above the median had TTs below and above the median (Figure 2e).

The median diffuse N input in the 1980s was 62.6 kg N ha^{-1} yr^{-1} (IQR: 42.0 kg N ha^{-1} yr^{-1}), decreasing by around 36%, when assuming the bootstrapped difference in medians of 22.6 kg N ha^{-1} yr^{-1} (95% CI: 20.5–25.6 kg N ha^{-1} yr^{-1}) in comparison to the 2010s. Diffuse N input in the 2010s was around 38.4 kg N ha^{-1} yr^{-1} (IQR: 23.1 kg N ha^{-1} yr^{-1}). The median N load in the 1980s was 12.4 kg N ha^{-1} yr^{-1} (IQR: 6.1 kg N ha^{-1} yr^{-1}) with a bootstrapped difference of medians of 1.2 kg N $ha^{-1}yr^{-1}$ (95% CI: 0.8–1.6 kg N $ha^{-1}yr^{-1}$) to the 2010s (median N load: 11.2 kg N ha^{-1} yr^{-1}; IQR: 5.7 kg N ha^{-1} yr^{-1}). The mismatch between N input and riverine N export decreased from an annual excess of 50.2 kg N ha^{-1} in the 1980s to 27.2 kg N ha^{-1}in the 2010s, also reflecting a decrease in apparent retention from 80% to 71%.

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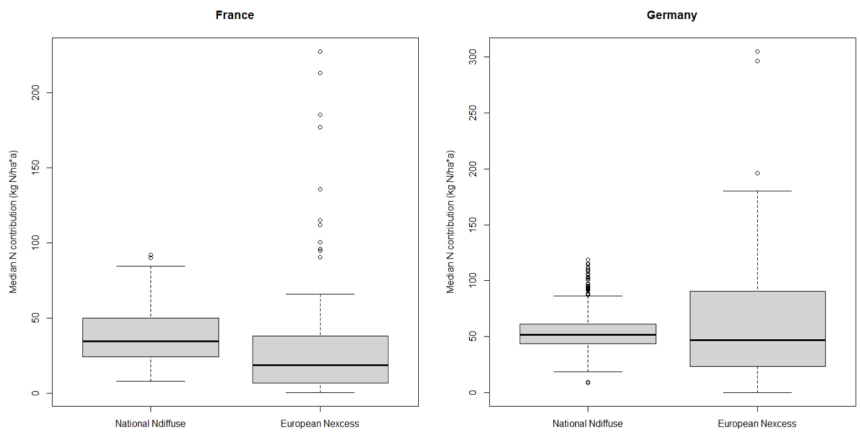

Figure 2 . a – Spatial variation of the TT modes in the 166 catchments with an $\mathbf{R^2}$ [?] 0.6. b – Spatial variation of the overlapping retention in all of the analyzed catchments (n = 238). c – Histogram of the mode TTs. d – Histogram of the retention for the overlapping time (beige curve) and the convolved retention (grey curve) with their corresponding medians (dashed lines). e – Scatter plot of the overlapping retention versus the mode TTs, with the corresponding medians for both measures (dashed lines). Excluding one outlier with negative retention.

3.3. Controls of catchment's response and retention

The PLSR for predicting the mode TTs in the selected catchments with a good fit (R^2 [?] 0.6) explained 49% of the total variance. Variables that are connected to the catchment's hydroclimatological characteristics were found to be most important (Supporting Information Figure S4.1.). Potential evapotranspiration (PET) was analyzed as the most important variable (VIP 2.1) indicating longer mode TTs with higher PET. The seasonality index of precipitation (P_SI, see Supporting Information S1 for detailed description) was with an almost same VIP value (2.10 vs. 2.07) the second most influential predictor (VIP = 2.1). The higher the mean difference between monthly P averages and the annual average, the shorter the mode TT. The other three most important parameters indicate shorter TT related with 1) higher coefficients of variation of discharge (VIP = 1.9), 2) higher topographic wetness indices (TWI; VIP = 1.5) and 3) higher median winter discharges (VIP = 1.3).

The N retention across the catchments was well predicted by the PLSR ($R^2 = 0.72$). Four of the five most important parameters (Supporting Information Figure S4.2.) referred to subsurface characteristics, while one predictor was a hydrological descriptor. High specific discharge was connected to low N retention and was the most important predictor (VIP = 2.3). Second most important factor for predicting retention was the depth to bedrock (VIP = 1.8). The positive coefficient indicated that a higher depth to bedrock is associated with a higher retention. Consolidated (VIP = 1.5) and porous aquifer materials (VIP = 1.4) were associated with low retention while vice versa unconsolidated aquifers (VIP = 1.4) favored higher retention.

4. Discussion

4.1. Nitrogen transport times and its controlling parameters

The high number of catchments showing a good fit between N input and riverine N export using a log-normal TTD indicate that the applied methodology is appropriate for the analyzed Western European catchments. This also shows that the temporal pattern of annual flow-weighted NO_3-N concentrations observed in the streams is mainly controlled by the pattern of the diffuse N input.

The PLSR that explained 49% of the variability of mode TTs between the catchments, reveals the importance of hydroclimatic variables (via PET, precipitation and discharge variability, winter discharge) and

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morphology (via TWI), which is partly in line with previous knowledge that stated recharge rate (besides aquifer porosity and thickness) as a major control for mean groundwater travel times (Haitjema, 1995). We note the close connection between hydroclimatic descriptors (e.g. between long-term mean precipitation, PET, discharge; Supporting Information Figure S5.; as established through the Budyko (1974) framework), but only discuss here the ones ranked as most important for TTs according to the PLSR.

Especially regions with highest intra-annual precipitation seasonality (Figure 1c) like in the Armorican Massif and the Alpine foothills showed short TTs with modes shorter than 5 years. Precipitation seasonality, entailing changing wetness conditions, can cause changing aquifer connectivity (Blume & Van Meerveld, 2015; Roa-Garcia & Weiler, 2010), which is known as a major control of NO_3 export from catchments (Molenat et al., 2008; Ocampo et al., 2006; Wriedt et al., 2007). In terms of hydrological connectivity, Birkel et al. (2015) and Yang et al. (2018) stated that the activation of shallow flow paths during runoff events favors young water ages. Hence, we hypothesize that these high-flow events efficiently export young NO_3 from the shallow subsurface to the stream and thus lowers N TT scales. High median winter discharge as another VIP, common in the Alpine foothills favoring short TTs, is in line with our hypothesis and the previous findings by Wriedt et al. (2007). The correlation between high TWI values and short TTs for N may be also attributed to a prevalence of N exports by shallow subsurface flow paths: lowland catchments, characterized by higher TWI's, show strong seasonal changes of discharging streams and the artificial drainage network (Van der Velde et al., 2009). As these drains favor rapid, shallow subsurface flows, their temporal connection during high-flow events favor short travel times (Van der Velde et al., 2009). Long N TTs were found in the western Massif Central and south of it where PET was highest among the study catchments and recharge likely low, corroborating Haitjema's (1995) finding for groundwater travel times.

The clear link between TTs for N and hydroclimatic settings make catchment N transport vulnerable to the changing future climate. Based on past observations since the 1960s, the intensity of extreme weather has been predicted to increase in most parts of Europe (EC, 2009). Hydroclimatic projection studies in general suggest drier conditions in Atlantic climatic zones in Europe in terms of longer drought durations and lower low flows under warming climates (Marx et al., 2018; Samaniego et al., 2018). Both extremes, heavy precipitation events and longer droughts, are more likely. According to the discussed influence of precipitation and discharge variability on N dynamics, TTs are supposed to decrease in the future. The stronger ET with increasing temperature (Donnelly et al., 2017) is counteracting this trend by favoring longer TTs. Since the climate is expected to manifest differently within Europe, reliable predictions on future N TTs on regional scales will need further research.

Despite a high number of catchments with a good fit using our TT estimations, we acknowledge the inherent uncertainties and limitations of the database as well as of the method itself. With better knowledge on the temporal evolution of waste water inputs and anthropogenic modifications in the catchment hydrology, like damming, more reliable TT estimations and a potentially better explainability among the catchments may have been possible. Furthermore the method, assuming a constant log-normal TTD, is only supposed to mirror the dominant long-term TT behavior, disregarding known temporal variability of water travel times in catchments (Benettin et al., 2013; Botter et al., 2011; Harman, 2015; Van der Velde et al., 2010). Moreover, we estimated TTs from the small fraction of total N inputs that left the catchment as NO_3-N (median 28%). Long-term tracer studies using labeled ^{15}N compounds (e.g. Sebilo et al., 2013) hold promising avenues for a more detailed and hedged evaluation of the fate of N.

4.2. Nitrogen retention and controlling parameters

According to the PLSR, the variability in retention among the catchments was mainly explained by subsurface properties that can be connected to biogeochemical conditions and the specific discharge. This finding was in line with Merz et al. (2009) and Nolan et al. (2002), who stated that spatial differences in NO_3 retention or contamination, respectively, result from a combination of the geochemical environment and the hydraulic conditions. We argue that the highly-ranked subsurface predictors describe favorable biogeochemical conditions for either permanent removal by denitrification or storage in the soils as biogeochemical

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legacy.

Areas with a high depth to bedrock and an unconsolidated aquifer (Figure 1d), which showed retention above 75%, were particularly common in the Northern German Lowlands and in the Alpine foothills. This is in line with Ebeling et al. (2020), who attributed areas with large depth to bedrock and unconsolidated (sedimentary) aquifers to natural attenuation or retention processes based on riverine NO_3-N concentration-discharge relationships. Unconsolidated deposits in the terrestrial subsurface, like in the Northern German Lowlands, are often associated with iron sulphide minerals (pyrite; Bouwman et al., 2013). The pyrite oxidation acts as electron donor for denitrification under anaerobic conditions (Zhang et al., 2009). For the unconsolidated aquifers in northern Germany, a recent study (Knoll et al., 2020) connected the high denitrification potential to strongly anaerobic redox conditions in the groundwater. Although denitrification permanently removes N from the catchment, it can be a source for N_2O, an important greenhouse gas, being 300-fold more effective in trapping heat than carbon dioxide (Griffis et al., 2017). Lastly, long-term consumption of reactants via denitrification can alter the reduction capacity of the aquifer (Merz et al., 2009), decreasing the catchment's N retention over time.

In contrast to northern Germany, for the unconsolidated sediments in the Alpine foothills different studies (BMU, 2003; Knoll et al., 2020) proposed aerobic subsurface conditions, hindering denitrification. Also Ebeling et al. (2020) found in this area evidence for a lack of denitrification. Excluding denitrification and long TTs (see Section 4.1.), we hypothesize biogeochemical legacy as a likely process of the high retention in the Alpine foothills. In comparison to northern Germany, soils here contain higher degrees of silt and clay. These grain sizes are prone to microaggregate formation and anion sorption, both sequestering organic N in the mineral subsoil for long periods of time (Bingham & Cotrufo, 2016; Von Lutzow et al., 2006). Also mineral N fixed on clays can make a significant contribution to the soil N stock (Allred et al., 2007; Stevenson, 1986).

In contrast, areas with a high share of consolidated subsurface materials and a small depth to bedrock, like the Armorican Massif, parts of the Massif Central or the Harz Mountains showed N retention below 75%. In general, denitrification and biogeochemical legacies can only evolve if favorable biogeochemical conditions in soils and groundwater are abundant in the catchment. An important part for denitrification is the contact area and contact time with organic-rich soils (Bouwman et al., 2013). Due to abundant crystalline rocks, water moves along fissures in the weathered zone (Wyns et al., 2004), while it is dependent on joints and fractures in deeper depth (Wendland et al., 2007). Hence, there is only a limited reactive surface for NO_3 within the areas dominated by consolidated materials (Wendland et al., 2007). Furthermore, Knoll et al. (2020) showed oxic conditions in consolidated units for Germany that do not allow for denitrification in groundwater.

The only hydrological predictor for N retention was the specific discharge. High specific discharges were found in the Armorican Massif, the western part of the Massif Central, in the Harz Mountains and the southern Alpine foothills, were often spatially connected to areas with consolidated subsurface materials and had N retention below 75%. High discharge areas connect to short residence times in the catchment compartments like root zone, aquifer or riparian zone and therefore decreases denitrification efficiency through a reduced contact time (e.g. Howarth et al., 2006; Kunkel & Wendland, 2006; Wendland et al., 2007). This assumption is in line with a recent study by Dupas et al. (2020), arguing that higher runoff lowers denitrification. Tesoriero et al. (2017) and Knoll et al. (2020) stated high recharge rates as important predictors for aerobic conditions. Furthermore, high discharge may be driven by a high degree of shallow flow paths (Birkel et al., 2015; Yang et al., 2018), favoring a fast wash-out of N or an export before immobilization, thus decreasing retention as well.

With regard to climate change, the increase in European rainfall erosivity is estimated in the range from 10 to 15% until 2050 (Panagos et al., 2015). Especially in southern France and Germany, this may cause soil loss in arable lands up to 10 t $ha^{-1}yr^{-1}$ (Panagos et al., 2015). We argue that such mobilization of soils with high biogeochemical legacy (e.g. Alpine foothills) can contribute to further deterioration of downstream river water quality.

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4.3. Joint analysis of nitrogen transport times and retention

The joint analyses of N TT estimations and N retention (Figure 2e) revealed a discrepancy between the two in the studied catchments. The rather observed short TTs indicate that the largest part (75th-percentile) of N input should have been exported after at least 20 years. In contrast, the observed retention indicates that 72% of total N input was not exported. The retention was similarly high (70%) when convolving N input taking into consideration estimated TTs. The missing relation between TTs and retention as well as the different predictors for both through the PLSR, indicate that hydrologic legacies of N alone could not explain the failure of measures to improve water quality in Western European catchments (e.g. Bouraoui & Grizzetti, 2011), despite decreasing N-inputs. We rather assume a dominance of non-hydrologic retention, namely biogeochemical legacy and denitrification.

After the implementation of regulations such as the EU Nitrate Directive (CEC, 1991), the diffuse N input decreased between the 1980s and 2010s by more than 20 kg N ha^{-1} yr^{-1}(36%) in the studied Western European catchments. The responses of riverine N loads to this decrease in input was limited ($<$ 1.5 kg N ha^{-1} yr^{-1}). Hence, the retention decreased but catchments still received (in the 2010s) excess N of almost 30 kg N ha^{-1} every year, which is two-thirds of the diffuse input.

Besides failure to implement good agricultural practices, these results imply either a hindered substantial exploitation of the (already massive) biogeochemical legacy by mineralization and/or an ongoing exhaustion of the catchment's denitrification potential.

According to the discussed subsurface and hydrological catchment characteristics favoring biogeochemical legacy, and due to the specific conditions required for effective denitrification that are only fulfilled in a few areas, we argue that biogeochemical legacy is the dominant retention process in most of the study catchments. We explain the missing catchment response for decreasing N inputs with the buffer effect stemming from the accumulated biogeochemical legacy acting as a secondary source and constituting a system inert to decreasing N inputs. A biogeochemical dominance was also found in a recent study for catchments in northwestern France (Dupas et al., 2020). They concluded two-third of the retention being stored in the subsoil with the potential to recycle this N in the agroecosystem. Also Ascott et al. (2017) concluded that the vadose zone is globally a significant NO_3 store. If not being recycled and in light of limited denitrification potential, the stored N would further leach to the deeper subsurface (or groundwater), when being mineralized again (Van Meter & Basu, 2015). The missing export of three-quarters of the past N inputs in the study catchments therefore constitutes a huge challenge for efforts to reach effective water quality improvements now and in the future.

5. Conclusions and implications

In this study we used long-term time series of N input and riverine NO_3-N output from 238 Western European catchments to estimate the N TTs, retention amount as well as the controlling catchment characteristics for both.

The analysis of catchment responses revealed peak TTs around 5 years with 70% of the catchments showing a peak export within the first 10 years after N enters the system. Hence, when assessing the effectiveness of measures, catchment managers have to be aware of the hydrological transport dependent decrease in N concentrations after around 5 years that should not falsely be attributed to successfully taken measures. Conversely, assessing the effect of regulations on the N input before the arrival of needed peak TTs, is not recommended.

- Our analyses indicate a minor role of hydrologic legacy meaning that storage of NO_3 in groundwater is not the dominant process explaining 72% of ingoing N being retained. We rather see evidence for a widespread biogeochemical legacy of N, while biogeochemical conditions for a permanent removal by denitrification are only rarely achieved. Therefore, decreasing concentrations within the first 10 years mean neither that most of the N was already exported nor that restoration efforts can be reduced. Management in such cases would need rather long-term strategies to reduce ongoing leaching from soil

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N pools, for example by recycling the retained N within the soil or by fostering denitrifying conditions.
- While TTs were mainly controlled by hydroclimatic parameters with low PET and high precipitation seasonality favoring more rapid transport of N to the streams, retention was mainly controlled by specific discharge and subsurface parameters as low specific discharge and a high share of thick, unconsolidated aquifers in the catchments favor high retention. Thus, catchment managers can estimate from subsurface and hydroclimatic data, the natural conditions for retention and the dimension of TTs, which can be a helpful tool to explain the failure of measures or to advise a realistic management plan.
- From a management perspective, a better spatial and temporal knowledge of denitrification efficiency at larger scales should be aimed at. Being associated with this, research on long-term changes of N storage capacities in agricultural soils is required. These data-driven analyses can be used to support or compliment modelling approaches assisting different large scale water quality management activities.

Data

Please note that the used data base adheres to Enabling FAIR Data Project requirements and is referenced in the manuscript linking to the data bases and repositories.

Water quality data for France is publicly available at*http://naiades.eaufrance.fr/* . Water quantity data for France are available at *http://hydro.eaufrance.fr/* . Diffuse N input data for France were derived from Poisvert et al. (2017).

Water quality and quantity data for Germany are available at*https://www.hydroshare.org/resource/a42addcbd59a466a9aa5647*
2020).

Catchment characteristics for Germany and France are available at https://www.hydroshare.org/resource/c7d4df3ba74647f0aa83ae92be2e294b/ (Ebeling & Dupas, 2020).

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Nitrate transport and retention in Western European catchments are shaped by hydroclimate and subsurface properties

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Key Points:

- Time lags of nitrogen transport in Western European catchments were five years on average and mainly explained by hydroclimatic variability
- Almost three-quarters of the diffuse N input was retained in the catchment, mainly controlled by subsurface parameters and specific discharge
- Biogeochemical legacy likely exceeded hydrologic legacy in most of the 238 analyzed catchments

Abstract

Excess nitrogen (N) from anthropogenic sources deteriorates freshwater resources. Actions taken to reduce N inputs to the biosphere often show no or only delayed effects in receiving surface waters hinting at large legacy N stores built up in the catchments' soils and groundwater. Here, we quantify transport and retention of N in 238 Western European catchments by analyzing a unique data set of long-term N input and output time series. We find that half of the catchments exhibited peak transport times larger than five years with longer times being evident in catchments with high potential evapotranspiration and low precipitation seasonality. On average the catchments retained 72% of the N from diffuse sources with retention efficiency being specifically high in catchments with low discharge and thick, unconsolidated aquifers. The estimated transport time scales do not explain the observed N retention, suggesting a dominant role of biogeochemical legacy in the catchments' soils rather than a legacy store in the groundwater. Future water quality management should account for the accumulated biogeochemical N legacy to avoid long-term leaching and water quality deteriorations for decades to come.

Plain language summary

Despite different regulations that limit anthropogenic nitrate input to the biosphere, there is in many cases no or only delayed improvement in groundwater or surface water contamination. One reason for this mismatch are legacies either by accumulated nitrate in the soil or nitrate with slow transport pathways in the groundwater to the river. We assessed long-term data covering nitrate in- and output for Western-European catchments to quantify (1) the needed transport time until reappearance in the river and (2) the quantity of reappeared nitrate.

The transport time through the catchment had its peak at 5 years and was mainly controlled by hydrological parameters as high seasonality in precipitation favored faster transports. Furthermore 72% of the nitrate was retained in the catchment, mainly controlled by subsurface characteristics as thick and unconsolidated material favored retention either by holding nitrate in the soil or by supporting a bacterial process that released nitrate to the atmosphere. We hypothesized that most of the retained nitrate is accumulated in the soil. This huge pool has on the one hand the potential of being recycled and on the other hand the danger of leaching slowly, which would constitute a future long-lasting contamination source for groundwater and surface waters.

1. Introduction

Nitrogen (N) can be a limiting nutrient in terrestrial, freshwater and marine ecosystems (Webster et al., 2003). However, the N cycling in these ecosystems is modified and disturbed by humans through inputs from atmospheric deposition, agricultural fertilizers and waste water. High N inputs especially in economically developed countries have led to increased riverine dissolved inorganic nitrogen (DIN) fluxes, causing ecological degradation in aquatic systems and posing a threat to drinking water safety (Dupas et al., 2016; Sebilo et al., 2013; Wassenaar, 1995). Diffuse agricultural sources (mineral fertilizer and manure) constitute most of the N emissions into waters in European countries (Bouraoui and Grizzetti, 2011; Dupas et al., 2013).

Several regulations at federal, national or international levels have been implemented e.g. the EU Nitrate Directive (CEC, 1991) or the Clean Water Act (EPA, 1972) in the US – aiming particularly at reducing N inputs to the terrestrial system. Despite the reduction in inputs, there is often no or only little improvement in water quality observed in many catchments (Meals et al., 2010; Bouraoui and Grizzetti, 2011; Vero et al., 2017). The inadequacy of implemented measures to improve water quality can be related to transport and retention in the catchments responding to changes in the nutrient inputs. The latter is closely connected to a legacy accumulation of N (e.g. Thomas & Abbott, 2018; Van Meter & Basu, 2015; Wang & Burke, 2017) - a buildup of large N stores in the catchment that are not or only slowly exported. This legacy acts as long-term memory of catchments and has been hypothesized to buffer stream concentration variability (Basu et al., 2010).

N legacies can be attributed to two major components: the biogeochemical and the hydrologic N storage. The first one is related to biogeochemical transformation processes of N in the unsaturated (vadose) zone, often leading to a large buildup of an organic N pool in the soil matrix and only slowly converting to mobile nitrate (NO_3; Van Meter & Basu, 2017). Hydrologic legacy describes the pool of dissolved N in the groundwater and unsaturated zone, subjected to very slow transport processes (Van Meter & Basu, 2015). This transport is controlled by the travel time, i.e., the time rainfall needs to travel through a catchment (Kirchner et al., 2000). The diversity of subsurface flow paths in a catchment creates a distribution of travel times (Kirchner et al., 2000) varying from days to decades (e.g. Howden et al., 2011; Jasechko et al., 2016; McMahon et al., 2006; Sebilo et al., 2013) also integrating information on timing, amount, storage and mixing of water and thus solutes (Heidbüchel et al., 2020). Therefore, slow travel times and a resulting temporary storage of reactive N in the unsaturated zone (Ascott et al., 2017; Ehrhardt et al., 2019), can create similar time lags as the biogeochemical legacy of N stored in the soil N pool (Bingham & Cotrufo, 2016; Bouwman et al., 2013; Sebilo et al., 2013). Due to the high complexity of hydrological and biogeochemical processes in catchments, a good understanding of the share of the two different legacy storages and the fate of N remains challenging.

Data-based joint quantification and characterization of N transport timescales and retention under different land-use and management practices can provide an evidence based entry point to better understand N trajectories for reactive N transport at catchment scale (e.g. Ehrhardt et al., 2019; Van Meter and Basu, 2015). More specifically, comparing quantity and temporal patterns of diffuse N input and riverine N concentrations from catchments allow to estimate N transport time (TT) scales as well as retention (Dupas et al., 2020; Ehrhardt et al., 2019). Retention is defined here as the "missing N" that is either stored in a catchment due to the buildup of legacies or permanently removed by denitrification. The estimated TT of N integrates time delays by biogeochemical immobilization and mobilization in the soils and the TT through the vadose zone and groundwater. So far, only a few studies investigated retention and TTs simultaneously as availability of long-term data often limits the number of studied catchments (e.g. Dupas et al., 2020; Ehrhardt et al., 2019; Howden et al., 2010; Van Meter et al., 2017; Van Meter et al., 2018) although the identification and quantification of legacy effects is of critical importance for predicting future N dynamics and for implementing effective restoration efforts (Bain et al., 2012). Here we analyze a large-sample database of 238 Western European catchments with different geophysical and hydro-climatological characteristics and at least 20 years of observations with regards to observed nitrogen (1) TT scales and (2) retention. Furthermore, we connect these results to catchment characteristics to discuss their (3) main controlling factors. These research objectives are used to improve the understanding of catchment responses to changes in input and the fate of retained N being associated with different legacy stores and/or denitrification.

2. Materials and Methods

2.1. Study area

For data on water quantity and quality, we relied on three national data sets. Water quality data for French catchments are publicly available at http://naiades.eaufrance.fr/, while water quantity data are available at http://hydro.eaufrance.fr/. For Germany, Musolff (2020) provided a database for water quality and water quantity.

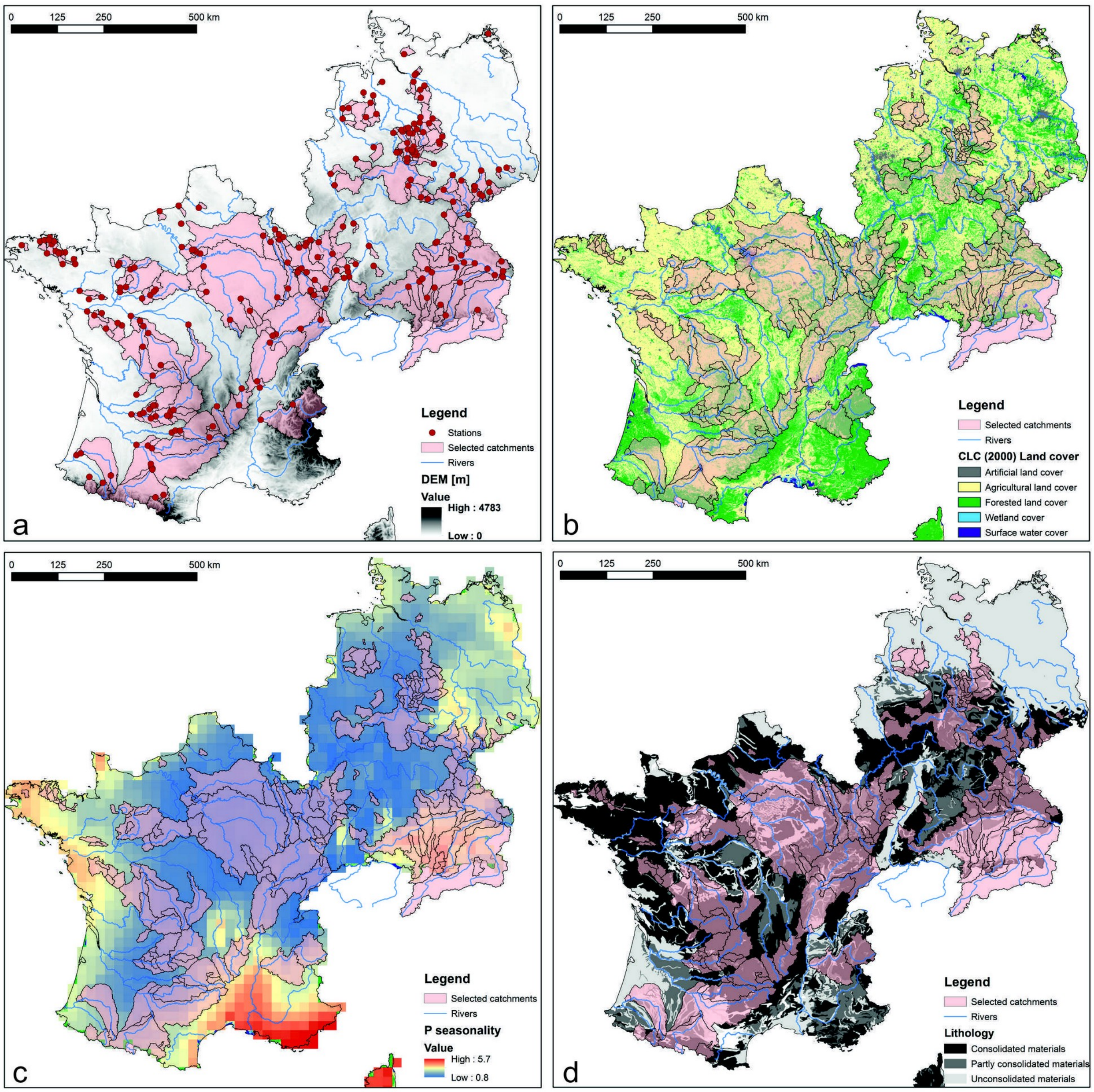

Figure 1. Study catchments (n = 238) based on the quality criteria with selected catchment characteristics: a – Elevation (EEA, 2013), b – Land cover (CLC, 2000), c – Lithology (BCR & UNESCO, 2014), d – Depth to bedrock (Shangguan et al., 2017).

From this joint database we selected catchments where the following conditions were given: riverine NO_3-N concentration observations available for at least 20 years of data with data gaps less than 2 years and the total number of observations being more than 150. Given these criteria, 238 catchments were selected (Figure 1a). The time series covered data between 1971 and 2015 with a median length of 30 years and in total 96,443 measurements for NO_3-N. Overall we covered 40% of the total land area of both countries (i.e., around 361,000 km², taking nested catchments into account). The selected catchments encompass contrasting settings in terms of morphology, climate, geological properties and land use attributes (Supporting Information Tables S1.1 and S1.2). More than half of the study catchments have a size of less than 1,000 km² (max. 62,500 km^2). The median altitude ranges from 15 m to 1848 m with a median slope of 3°. Climatic settings of the sites reach from Atlantic to Continental climate with aridity indices ranging between 0.4 and 1.5. The median annual precipitation across the sites is around 816 mm, and the estimated base flow index (BFI) ranges from 29% to 97% with a median of 65%.

Most catchments (> 90%) are dominated by sandy soils (median: 44.6%), with 18 of those located in northwestern Germany. The bedrock mainly covers fissured and hard rock geology with the latter being predominant in most of the catchments. The geology is characterized by crystalline rocks in the Armorican Massif, the Pyrenees and the Massif Central and in some of the German mountainous catchments; and younger sedimentary rocks in most parts of France and Germany (Allain, 1951; BGR & CGMW, 2005). Quaternary sediments are found in the Northern German Lowlands, the Alpine foothills and north of the Pyrenees (Allain, 1951; BGR & CGMW, 2005).

Regarding land use, 87% of the catchments had at least one-third of their area covered by agriculture that mainly incorporates non-irrigated arable land and pastures (EEA, 2016; Figure 1b). Riverine NO_3-N concentrations in these areas are therefore predominantly impacted by diffuse agricultural N sources (EEA, 2018). The median share of forest cover across the study catchments is 37%. Although the fraction of artificial surfaces was small, the median population density with 92 inhabitants km^{-2} in the study catchments is almost three-times the average European value (Worldometers.info, 2020).

2.2. Nitrogen input

The N input was selected as diffuse N stemming from agricultural N surplus, atmospheric deposition and biological fixation in non-agricultural areas. The N surplus consists of agricultural N input that is in excess of crop and forage exports (also known as land nitrogen budget; de Vries et al., 2011). Here, we relied on two national scale data sets. Agricultural N contribution and atmospheric N deposition for the French catchments were provided by Poisvert et al. (2017). The annual agricultural N surplus for German catchments was provided by Bach and Frede (1998) as well as Häußermann et al. (2019). It basically consists of two data sets available at a (coarser) state level (NUTS2) for 1950–1999 and at finer county level (NUTS3) for

1995–2015. Both data sets were harmonized to produce a consistent long-term data set. The atmospheric N deposition for German catchments is based on Europe-wide gridded data from a chemical transport model of the Meteorological Synthesizing Centre-West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) (Bartnicky & Fagerli, 2006; Bartnicky & Benedictow, 2017).
In agricultural areas, biological fixation was already included in the N budgets. The biologically fixed N fluxes to non-agricultural land use types for France and Germany were calculated using the European Corine Land Cover data set from the year 2000 (EEA, 2020), which is most representative regarding the water quality time series. Terrestrial biological N mean uptake rates were set for forest (to 16.04 kg N ha^{-1} yr^{-1}; Cleveland et al., 1999), for natural and urban grassland (to 2.7 kg N ha^{-1} yr^{-1}; Cleveland et al., 1999) and other land use (wetlands, water bodies, open space with little or no vegetation to 0.75 kg N ha^{-1} yr^{-1}; Van Meter et al., 2017). A comparison of the two national long-term data sets for diffuse N with a Europe-wide benchmark estimation for 1997–2003 (West et al., 2014) indicated an acceptable offset (see Supporting Information S2 for further information).
Due to the lack of spatially and temporally reliable long-term data on N input by waste water, we did not consider this point source. For France, Dupas et al. (2015) estimated the contribution from point sources to total N flux to be 3% during the period 2005–2009, and we hypothesized that the negligible contribution of point sources also held for Germany.

2.3. Nitrogen output as riverine NO_3-N concentrations and loads

Gaps in the discharge time series at 30 runoff stations in Germany were filled through the support of simulations from the grid-based distributed mesoscale hydrological model mHM (Kumar et al., 2013; Samaniego et al., 2010). Here, only model simulations resulting in an R^2 greater than 0.6 when compared with the observed discharge were accepted. A piecewise linear regression was utilized to correct for potential biases in the modelled data. These bias-corrected modelled discharge data were finally used to gap-fill the original data to obtain a continuous daily time series. In France, no such national hydrological model existed and therefore, we only included catchments with nearly continuous daily discharge monitoring for which short gaps in the discharge (max. 7 days) were interpolated by a fixed-interval smoothing via a state-space model using the R software package "Baytrends".
The irregularly sampled, riverine NO_3-N concentrations were used to estimate daily concentrations by using the software package *Exploration and Graphics for RivErTrends* (EGRET) in the R environment by Hirsch and DeCicco (2019). The applied *Weighted Regressions on Time, Discharge, and Season* (WRTDS) uses a flexible statistical representation for every day of the discharge record and has been proven to provide robust estimates (Hirsch et al., 2010; Van Meter & Basu, 2017). As we focus on changes in concentrations and fluxes independent of inter-annual discharge variability (Hirsch et al., 2010), we used flow-normalized concentrations and fluxes for further analyses. For each catchment median annual flow-normalized NO_3-N concentrations and annual summed NO_3-N fluxes were calculated and scaled to the catchment area.

2.4. Nitrogen transport time

Travel time distributions are commonly derived as the transfer function between rainfall concentration time series and stream concentrations of a conservatively transported solute or water isotope (e.g. Kirchner et al., 2000). We transfer this concept to reactive N transport with the N input as an incoming time series with annual resolution that is assumed to yield the median annual riverine NO_3-N concentration, when convolved with a fitted distribution. This transport time distribution (TTD) can be based on different theoretical probability distribution functions. To represent the long memory of past inputs, long-tailed distributions are most suitable at catchment scales (Kirchner et al., 2000). Therefore, the N input was convolved using a log-normal distribution (Equation 1; Ehrhardt et al., 2019; Musolff et al., 2017) to find the optimal fit to riverine NO_3-N concentrations. We alternatively used a gamma distribution (Equation 2; Godsey et al., 2010; Fiori et al., 2009; Kirchner et al., 2000) as a transfer function, and we compared the quality of fit (R^2) with both methods.

Equation 1

$$f(t) = \frac{1}{t\sigma\sqrt{2\pi}} \exp\left(\frac{-(\ln t - \mu)^2}{2\sigma^2}\right)$$

Equation 2

$$f(t) = t^{-\alpha} \frac{\varepsilon^{-t/\beta}}{\beta^{\alpha}\,\Gamma(\alpha)}$$

The two parameters mu (μ) and sigma (σ) for the log-normal and shape (α) and scale (β) for the gamma distribution, respectively, were calibrated through optimization based on minimizing the sum of squared errors between the normalized annual diffuse N input and normalized annual median riverine NO_3-N concentrations. For this purpose we used the Particle Swarm Optimization (using the R package “hydroPSO” by Zambrani-Bigiarini & Rojas, 2013) algorithm in 30 independent runs. We estimated the mode of the selected best fitted TTD (with max. R^2) to represent the peak TT and at the same time to resemble the peak N export of the mobile, inorganic N.

2.5. Nitrogen retention and its temporal change

The total cumulative diffuse N input load was compared to the respective riverine NO_3-N load (assumed as N load) to analyze the N retention in the catchment (Equation 3). The difference between the two is the load being retained in the catchment as biogeochemical legacy, as hydrologic legacy or being removed by denitrification. The cumulative flux differences were calculated based on two approaches: 1) using the annual frames of the overlapping years in in- and outflux, while disregarding time shifts; and 2) applying the derived TTs, to compare the convolved inputs with the corresponding annual exported load.

Equation 3

$$Retention = 1 - \frac{Nout}{Nin} = 1 - \frac{\sum_{i=ts}^{te} NO3-N\,Flux\,i}{\sum_{i=ts}^{te} Ninput\,i}$$

To further characterize the catchment’s reaction to N input changes, we compared the median diffuse N input in the 1980s (median year of max. N input: 1986) with the one in the last years of the time series (≥ 2010) for a subset of stations (n = 120) that sufficiently covered the 1980s and 2010s. The same was done with the exported riverine NO_3-N loads in the 1980s and the 2010s. To gain robust estimates for the size of difference, we calculated the bootstrapped (n = 10,000) median differences between the 1980s and 2010s (for N input and N output) with their corresponding 95% confidence intervals.

2.6. Statistical analysis for controls in catchment response and retention

We applied a Partial Least Squares Regression (PLSR) to identify the main factors controlling N TTs and N retention in a catchment. PLSR is an established multivariate regression approach to analyze data sets that are strongly correlated among predictors and noisy (Wold et al., 2001). The PLSR model finds the variables (catchment characteristics) that best predict the response variables (retention and TT; Ai et al., 2015). The importance of each predictor for the dependent variable is indicated by the measure *Variable Importance in the Projection* (VIP). Factors with VIPs larger than 1 are considered to be significantly important for explaining the dependent variable (Ai et al., 2015; Shi et al., 2013). The corresponding regression coefficient is used to explain the direction of influence of each independent variable (Shi et al., 2013). The predictor variables used in this study characterize the topography, land cover, climate, hydrology, lithology, soils and population density of the studied catchments (Supporting Information S1).

3. Results

3.1. Nitrogen transport time scales

Using the gamma distribution yielded comparable results to the results for log-normal distribution (both with median $R^2 = 0.8$), but less catchments with an acceptable fit ($R^2 \geq 0.6$) between the convolved annual N inputs and riverine concentrations. Therefore, we only report the results using a log-normal distribution as a transfer function.
In some catchments (n = 72) no acceptable fit of TTDs could be obtained. According to a Wilcoxon rank sum test, the variability in NO_3-N concentrations in these catchments (CV: 0.08) is significantly different ($p \leq 0.01$) to the ones in the other catchments (CV: 0.12 with n = 166). A low temporal variability in the input or output makes it challenging to derive a reliable transfer function connecting them.
The median mode (peak) of the TTs for the 166 selected catchments with an acceptable fit was 5.4 years (Supporting Information Table S3.). Although the mode ranged from 0.2 to 34.1 years, the majority (70%) had a mode TT less than 10 years (Figure 2c). Only a few catchments (10%) showed a mode of at least 20 years, most of them (11/17) located in the Massif Central (Figure 2a).
Although the TT derivation was not mass conform, on average across the study catchments, 75% (75%-percentile) of the N input should have been exported after 18 years (range: 1.4–38.2).

3. 2. Nitrogen retention

The median N retention of the selected catchments (n = 238) was 72% (sd: 16%; Supporting Information Table S3.; Figure 2b), meaning that a large part of N was retained as legacy or denitrified. Despite the wide range (-24–96%, with one negative outlier Figure 2b), 48% of the catchments had a retention between 50% and 75%. A convolution of the N inputs according to the corresponding TT resulted in a slightly lower retention with a median of 70% (n = 238; 71% with n = 166; Figure 2d).

N retention and TT did not correlate in the study catchments. Almost the same amount of catchments with retention above the median had TTs below and above the median (Figure 2e).
The median diffuse N input in the 1980s was 62.6 kg N ha^{-1} yr^{-1} (IQR: 42.0 kg N ha^{-1} yr^{-1}), decreasing by around 36%, when assuming the bootstrapped difference in medians of 22.6 kg N ha^{-1} yr^{-1} (95% CI: 20.5–25.6 kg N ha^{-1} yr^{-1}) in comparison to the 2010s. Diffuse N input in the 2010s was around 38.4 kg N ha^{-1} yr^{-1} (IQR: 23.1 kg N ha^{-1} yr^{-1}). The median N load in the 1980s was 12.4 kg N ha^{-1} yr^{-1} (IQR: 6.1 kg N ha^{-1} yr^{-1}) with a bootstrapped difference of medians of 1.2 kg N ha^{-1} yr^{-1} (95% CI: 0.8–1.6 kg N ha^{-1} yr^{-1}) to the 2010s (median N load: 11.2 kg N ha^{-1} yr^{-1}; IQR: 5.7 kg N ha^{-1} yr^{-1}). The mismatch between N input and riverine N export decreased from an annual excess of 50.2 kg N ha^{-1} in the 1980s to 27.2 kg N ha^{-1} in the 2010s, also reflecting a decrease in apparent retention from 80% to 71%.

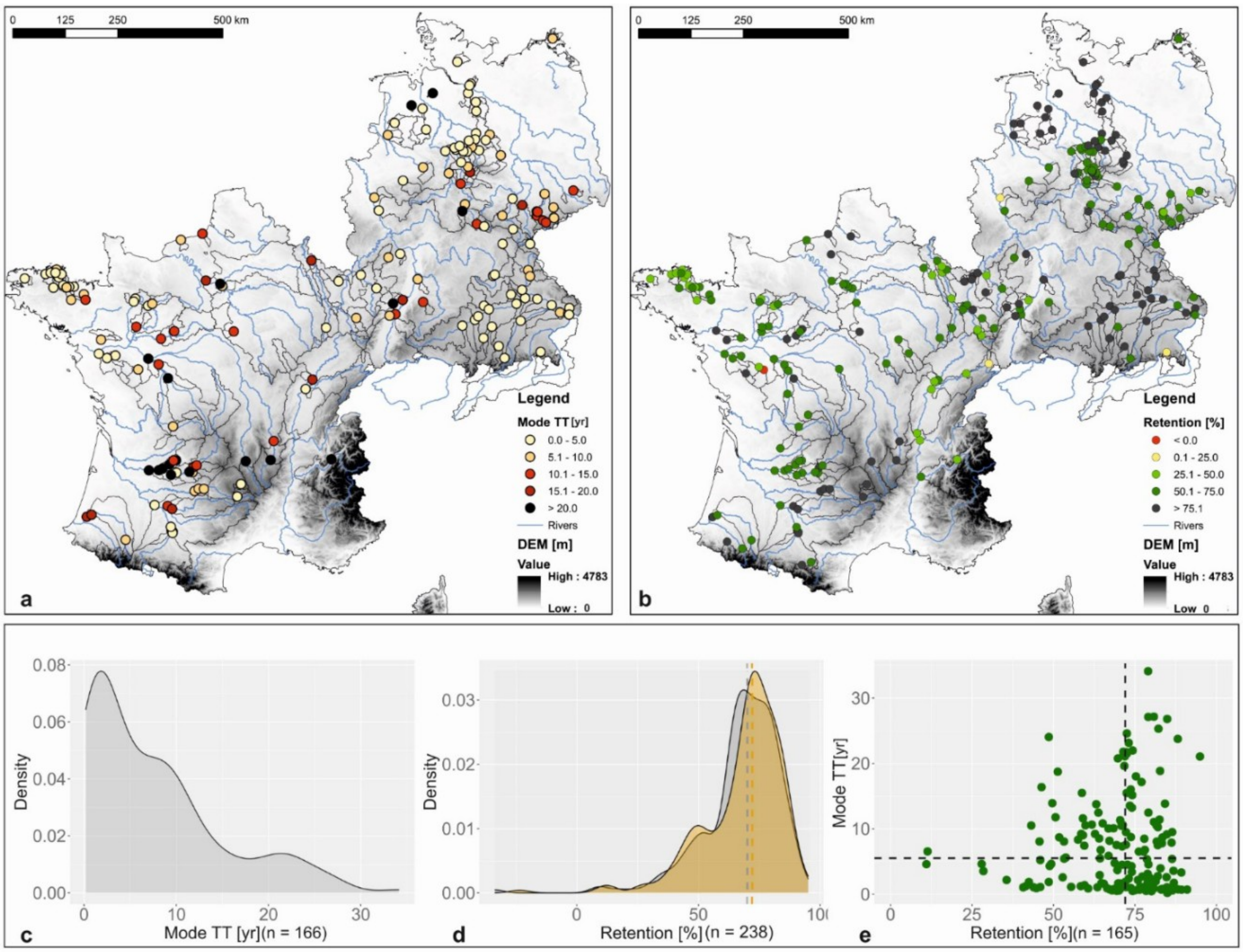

Figure 2. a – Spatial variation of the TT modes in the 166 catchments with an R² ≥ 0.6. b – Spatial variation of the overlapping retention in all of the analyzed catchments (n = 238). c – Histogram of the mode TTs. d – Histogram of the retention for the overlapping time (beige curve) and the convolved retention (grey curve) with their corresponding medians (dashed lines). e – Scatter plot of the overlapping retention versus the mode TTs, with the corresponding medians for both measures (dashed lines). Excluding one outlier with negative retention.

3.3. Controls of catchment's response and retention

The PLSR for predicting the mode TTs in the selected catchments with a good fit ($R^2 \geq 0.6$) explained 49% of the total variance. Variables that are connected to the catchment's hydroclimatological characteristics were found to be most important (Supporting Information Figure S4.1.). Potential evapotranspiration (PET) was analyzed as the most important variable (VIP 2.1) indicating longer mode TTs with higher PET. The seasonality index of precipitation (P_SI, see Supporting Information S1 for detailed description) was with an almost same VIP value (2.10 vs. 2.07) the second most influential predictor (VIP = 2.1). The higher the mean difference between monthly P averages and the annual average, the shorter the mode TT. The other three most important parameters indicate shorter TT related with 1) higher coefficients of variation of discharge (VIP = 1.9), 2) higher topographic wetness indices (TWI; VIP = 1.5) and 3) higher median winter discharges (VIP = 1.3).

The N retention across the catchments was well predicted by the PLSR ($R^2 = 0.72$). Four of the five most important parameters (Supporting Information Figure S4.2.) referred to subsurface characteristics, while one predictor was a hydrological descriptor. High specific discharge was connected to low N retention and was the most important predictor (VIP = 2.3). Second most important factor for predicting retention was the depth to bedrock (VIP = 1.8). The positive coefficient indicated that a higher depth to bedrock is associated with a higher retention. Consolidated (VIP = 1.5) and porous aquifer materials (VIP = 1.4) were associated with low retention while vice versa unconsolidated aquifers (VIP = 1.4) favored higher retention.

4. Discussion

4.1. Nitrogen transport times and its controlling parameters

The high number of catchments showing a good fit between N input and riverine N export using a log-normal TTD indicate that the applied methodology is appropriate for the analyzed Western European catchments. This also shows that the temporal pattern of annual flow-weighted NO_3-N concentrations observed in the streams is mainly controlled by the pattern of the diffuse N input.

The PLSR that explained 49% of the variability of mode TTs between the catchments, reveals the importance of hydroclimatic variables (via PET, precipitation and discharge variability, winter discharge) and morphology (via TWI), which is partly in line with previous knowledge that stated recharge rate (besides aquifer porosity and thickness) as a major control for mean groundwater travel times (Haitjema, 1995). We note the close connection between hydroclimatic descriptors (e.g. between long-term mean precipitation, PET, discharge; Supporting Information Figure S5.; as established through the Budyko (1974) framework), but only discuss here the ones ranked as most important for TTs according to the PLSR.

Especially regions with highest intra-annual precipitation seasonality (Figure 1c) like in the Armorican Massif and the Alpine foothills showed short TTs with modes shorter than 5 years. Precipitation seasonality, entailing changing wetness conditions, can cause changing aquifer connectivity (Blume & Van Meerveld, 2015; Roa-Garcia & Weiler, 2010), which is known as a major control of NO_3 export from catchments (Molenat et al., 2008; Ocampo et al., 2006; Wriedt et al., 2007). In terms of hydrological connectivity, Birkel et al. (2015) and Yang et al. (2018) stated that the activation of shallow flow paths during runoff events favors young water ages. Hence, we hypothesize that these high-flow events efficiently export young NO_3 from the shallow subsurface to the stream and thus lowers N TT scales. High median winter discharge as another VIP, common in the Alpine foothills favoring short TTs, is in line with our hypothesis and the previous findings by Wriedt et al. (2007). The correlation between high TWI values and short TTs for N may be also attributed to a prevalence of N exports by shallow subsurface flow paths: lowland catchments, characterized by higher TWI's, show strong seasonal changes of discharging streams and the artificial drainage network (Van der Velde et al., 2009). As these drains favor rapid, shallow subsurface flows, their temporal connection during high-flow events favor short travel times (Van der Velde et al., 2009). Long N TTs were found in the western Massif Central and south of it where PET was highest among the study catchments and recharge likely low, corroborating Haitjema's (1995) finding for groundwater travel times.

The clear link between TTs for N and hydroclimatic settings make catchment N transport vulnerable to the changing future climate. Based on past observations since the 1960s, the intensity of extreme weather has been predicted to increase in most parts of Europe (EC, 2009). Hydroclimatic projection studies in general suggest drier conditions in Atlantic climatic zones in Europe in terms of longer drought durations and lower low flows under warming climates (Marx et al., 2018; Samaniego et al., 2018). Both extremes, heavy precipitation events and longer droughts, are more likely. According to the discussed influence of precipitation and discharge variability on N dynamics, TTs are supposed to decrease in the future. The stronger ET with increasing temperature (Donnelly et al., 2017) is counteracting this trend by favoring longer TTs. Since the climate is expected to manifest differently within Europe, reliable predictions on future N TTs on regional scales will need further research.

Despite a high number of catchments with a good fit using our TT estimations, we acknowledge the inherent uncertainties and limitations of the database as well as of the method itself. With better knowledge on the temporal evolution of waste water inputs and anthropogenic modifications in the catchment hydrology, like damming, more reliable TT estimations and a potentially better explainability among the catchments may have been possible. Furthermore the method, assuming a constant log-normal TTD, is only supposed to mirror the dominant long-term TT behavior, disregarding known temporal variability of water travel times in catchments (Benettin et al., 2013; Botter et al., 2011; Harman, 2015; Van der Velde et al., 2010). Moreover, we estimated TTs from the small fraction of total N inputs that left the catchment as NO_3-N (median 28%). Long-term tracer studies using labeled ^{15}N compounds (e.g. Sebilo et al., 2013) hold promising avenues for a more detailed and hedged evaluation of the fate of N.

4.2. Nitrogen retention and controlling parameters

According to the PLSR, the variability in retention among the catchments was mainly explained by subsurface properties that can be connected to biogeochemical conditions and the specific discharge. This finding was in line with Merz et al. (2009) and Nolan et al. (2002), who stated that spatial differences in NO_3 retention or contamination, respectively, result from a combination of the geochemical environment and the hydraulic conditions. We argue that the highly-ranked subsurface predictors describe favorable biogeochemical conditions for either permanent removal by denitrification or storage in the soils as biogeochemical legacy.

Areas with a high depth to bedrock and an unconsolidated aquifer (Figure 1d), which showed retention above 75%, were particularly common in the Northern German Lowlands and in the Alpine foothills. This is in line with Ebeling et al. (2020), who attributed areas with large depth to bedrock and unconsolidated (sedimentary) aquifers to natural attenuation or retention processes based on riverine NO_3-N concentration-discharge relationships. Unconsolidated deposits in the terrestrial subsurface, like in the Northern German Lowlands, are often associated with iron sulphide minerals (pyrite; Bouwman et al., 2013). The pyrite oxidation acts as electron donor for denitrification under anaerobic conditions (Zhang et al., 2009). For the unconsolidated aquifers in northern Germany, a recent study (Knoll et al., 2020) connected the high denitrification potential to strongly anaerobic redox conditions in the groundwater. Although denitrification permanently removes N from the catchment, it can be a source for N_2O, an important greenhouse gas, being 300-fold more effective in trapping heat than carbon dioxide (Griffis et al., 2017). Lastly, long-term consumption of reactants via denitrification can alter the reduction capacity of the aquifer (Merz et al., 2009), decreasing the catchment's N retention over time.

In contrast to northern Germany, for the unconsolidated sediments in the Alpine foothills different studies (BMU, 2003; Knoll et al., 2020) proposed aerobic subsurface conditions, hindering denitrification. Also Ebeling et al. (2020) found in this area evidence for a lack of denitrification. Excluding denitrification and long TTs (see Section 4.1.), we hypothesize biogeochemical legacy as a likely process of the high retention in the Alpine foothills. In comparison to northern Germany, soils here contain higher degrees of silt and clay. These grain sizes are prone to microaggregate formation and anion sorption, both sequestering organic N in the mineral subsoil for long periods of time (Bingham & Cotrufo, 2016; Von Lützow et al., 2006). Also mineral N fixed on clays can make a significant contribution to the soil N stock (Allred et al., 2007; Stevenson, 1986).

In contrast, areas with a high share of consolidated subsurface materials and a small depth to bedrock, like the Armorican Massif, parts of the Massif Central or the Harz Mountains showed N retention below 75%. In general, denitrification and biogeochemical legacies can only evolve if favorable biogeochemical conditions in soils and groundwater are abundant in the catchment. An important part for denitrification is the contact area and contact time with organic-rich soils (Bouwman et al., 2013). Due to abundant crystalline rocks, water moves along fissures in the weathered zone (Wyns et al., 2004), while it is dependent on joints and fractures in deeper depth (Wendland et al., 2007). Hence, there is only a limited reactive surface for NO_3 within the areas dominated by consolidated materials (Wendland et al., 2007). Furthermore, Knoll et al. (2020) showed oxic conditions in consolidated units for Germany that do not allow for denitrification in groundwater.

The only hydrological predictor for N retention was the specific discharge. High specific discharges were found in the Armorican Massif, the western part of the Massif Central, in the Harz Mountains and the southern Alpine foothills, were often spatially connected to areas with consolidated subsurface materials and had N retention below 75%. High discharge areas connect to short residence times in the catchment compartments like root zone, aquifer or riparian zone and therefore decreases denitrification efficiency through a reduced contact time (e.g. Howarth et al., 2006; Kunkel & Wendland, 2006; Wendland et al., 2007). This assumption is in line with a recent study by Dupas et al. (2020), arguing that higher runoff lowers denitrification. Tesoriero et al. (2017) and Knoll et al. (2020) stated high recharge rates as important predictors for aerobic conditions. Furthermore, high discharge may be driven by a high degree of shallow flow paths (Birkel et al., 2015; Yang et al., 2018), favoring a fast wash-out of N or an export before immobilization, thus decreasing retention as well.

With regard to climate change, the increase in European rainfall erosivity is estimated in the range from 10 to 15% until 2050 (Panagos et al., 2015). Especially in southern France and Germany, this may cause soil loss in arable lands up to 10 t ha^{-1} yr^{-1} (Panagos et al., 2015). We argue that such mobilization of soils with high biogeochemical legacy (e.g. Alpine foothills) can contribute to further deterioration of downstream river water quality.

4.3. Joint analysis of nitrogen transport times and retention

The joint analyses of N TT estimations and N retention (Figure 2e) revealed a discrepancy between the two in the studied catchments. The rather observed short TTs indicate that the largest part (75th-percentile) of N input should have been exported after at least 20 years. In contrast, the observed retention indicates that 72% of total N input was not exported. The retention was similarly high (70%) when convolving N input taking into consideration estimated TTs. The missing relation between TTs and retention as well as the different predictors for both through the PLSR, indicate that hydrologic legacies of N alone could not explain the failure of measures to improve water quality in Western European catchments (e.g. Bouraoui & Grizzetti, 2011), despite decreasing N-inputs. We rather assume a dominance of non-hydrologic retention, namely biogeochemical legacy and denitrification.

After the implementation of regulations such as the EU Nitrate Directive (CEC, 1991), the diffuse N input decreased between the 1980s and 2010s by more than 20 kg N ha^{-1} yr^{-1} (36%) in the studied Western European catchments. The responses of riverine N loads to this decrease in input was limited (< 1.5 kg N ha^{-1} yr^{-1}). Hence, the retention decreased but catchments still received (in the 2010s) excess N of almost 30 kg N ha^{-1} every year, which is two-thirds of the diffuse input.

Besides failure to implement good agricultural practices, these results imply either a hindered substantial exploitation of the (already massive) biogeochemical legacy by mineralization and/or an ongoing exhaustion of the catchment's denitrification potential.

According to the discussed subsurface and hydrological catchment characteristics favoring biogeochemical legacy, and due to the specific conditions required for effective denitrification that are only fulfilled in a few areas, we argue that biogeochemical legacy is the dominant retention process in most of the study catchments. We explain the missing catchment response for decreasing N inputs with the buffer effect stemming from the accumulated biogeochemical legacy acting as a secondary source and constituting a system inert to decreasing N inputs. A biogeochemical dominance was also found in a recent study for catchments in northwestern France (Dupas et al., 2020). They concluded two-third of the retention being stored in the subsoil with the potential to recycle this N in the agroecosystem. Also Ascott et al. (2017) concluded that the vadose zone is globally a significant NO_3 store. If not being recycled and in light of limited denitrification potential, the stored N would further leach to the deeper subsurface (or groundwater), when being mineralized again (Van Meter & Basu, 2015). The missing export of three-quarters of the past N inputs in the study catchments therefore constitutes a huge challenge for efforts to reach effective water quality improvements now and in the future.

5. Conclusions and implications

In this study we used long-term time series of N input and riverine NO_3-N output from 238 Western European catchments to estimate the N TTs, retention amount as well as the controlling catchment characteristics for both.

- The analysis of catchment responses revealed peak TTs around 5 years with 70% of the catchments showing a peak export within the first 10 years after N enters the system. Hence, when assessing the effectiveness of measures, catchment managers have to be aware of the hydrological transport dependent decrease in N concentrations after around 5 years that should not falsely be attributed to successfully taken measures. Conversely, assessing the effect of regulations on the N input before the arrival of needed peak TTs, is not recommended.
- Our analyses indicate a minor role of hydrologic legacy meaning that storage of NO_3 in groundwater is not the dominant process explaining 72% of ingoing N being retained. We rather see evidence for a widespread biogeochemical legacy of N, while biogeochemical conditions for a permanent removal by denitrification are only rarely achieved. Therefore, decreasing concentrations within the first 10 years mean neither that most of the N was already exported nor that restoration efforts can be reduced. Management in such cases would need rather long-term strategies to reduce ongoing leaching from soil N pools, for example by recycling the retained N within the soil or by fostering denitrifying conditions.
- While TTs were mainly controlled by hydroclimatic parameters with low PET and high precipitation seasonality favoring more rapid transport of N to the streams, retention was mainly controlled by specific discharge and subsurface parameters as low specific discharge and a high share of thick, unconsolidated aquifers in the catchments favor high retention. Thus, catchment managers can estimate from subsurface and hydroclimatic data, the natural conditions for retention and the dimension of TTs, which can be a helpful tool to explain the failure of measures or to advise a realistic management plan.
- From a management perspective, a better spatial and temporal knowledge of denitrification efficiency at larger scales should be aimed at. Being associated with this, research on long-term changes of N storage capacities in agricultural soils is required. These data-driven analyses can be used to support or compliment modelling approaches assisting different large scale water quality management activities.

Data

Please note that the used data base adheres to Enabling FAIR Data Project requirements and is referenced in the manuscript linking to the data bases and repositories.
Water quality data for France is publicly available at http://naiades.eaufrance.fr/. Water quantity data for France are available at http://hydro.eaufrance.fr/. Diffuse N input data for France were derived from Poisvert et al. (2017).
Water quality and quantity data for Germany are available at https://www.hydroshare.org/resource/a42addcbd59a466a9aa56472dfef8721/ (Musolff, 2020).
Catchment characteristics for Germany and France are available at https://www.hydroshare.org/resource/c7d4df3ba74647f0aa83ae92be2e294b/ (Ebeling & Dupas, 2020).

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