Transport times and retention as tools to understand temporal and spatial nitrogen dynamics in catchments

Dissertation

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Abstract

Excess nitrogen (N) deteriorates water quality and causes eutrophication of surface waters. Regulations to reduce anthropogenic 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 soils (biogeochemical legacy) and groundwater (hydrological legacy). However, due to the high complexity of interacting hydrological and biogeochemical processes in catchments, legacy stores are poorly understood. This PhD project aims to advance the knowledge about these N legacy stores across a large variety of European catchments.

The main objective was a quantification and separation of N retention mechanisms in catchments: legacy stores and removal via denitrification, to contribute to a more effective and science-based water quality management. To this end, the PhD work was designed in three studies. Although facing differences in data availability and testing different methods, all studies associated long-term N inputs with observed riverine nitrate concentrations and loads. A key method applied here, was the adaption of the travel time concept (Kirchner et al., 2000) to infer catchment-scale N transport times from time series of diffuse N input and riverine N output.

The first study (Study 1) focused on the Central German Holtemme catchment, which is divided into three nested subcatchments with an increasing agricultural impact. Due to this gradient and an agricultural history with strong temporal shifts in fertilizer usage, the catchment was well suited to enable a better process understanding of N transport through subcatchments.

In the second study (Study 2) long-term data from 16 French catchments were investigated to determine legacy stores and their controls. Study 2 used the Generalized Likelihood Uncertainty Estimation (GLUE) approach for the quantification in the hydrologic N transport timescales.

By merging findings and methods from Study 1 and 2, Study 3 advanced the knowledge about the temporal and spatial variation of N retention mechanisms. In a large-scale set-

ting, retention mechanisms and their dominant controls were analyzed across 238 diverse western European catchments.
The catchment in Study 1 showed an overall N retention of 88 %. The log-normal transfer functions, fitted to the input-output data from different subcatchments and seasons, yielded highest N exports 7–22 years after the N input. In line with an inter-annual shift in concentration-discharge relations observed in the stream, Study 1 concluded a dominant hydrologic legacy. The temporal riverine N dynamics were dominantly shaped by a seasonally changing activation of differently loaded subsurface flow paths. Based on the identified dominance of hydrologic N legacy, the study suggested measures that trigger denitrification to avoid future massive release of N that is still present in the groundwater.
In the western French catchments (Study 2), 45–88 % of the diffuse N input was retained within the catchments, two-thirds of which were attributed to storage in the topsoil. Although this biogeochemical legacy in the soil was different to the hydrologic N legacy in the Holtemme catchment (Study 1), the overall high retention was comparable in both studies. While differences in N retention between the catchments could be explained by differences in average runoff, the varying peak exports (2–14 years after N input) were partly attributable to spatial differences in the lithology. Due to the N accumulation in the soil, the study suggested that catchment management should address the recycling of the stored soil N through agroecosystem practices.
The large-scale analysis in Study 3, conducted across diverse catchment settings, showed a median of peak exports of 5 years after the input (up to 34 years) with longer transport times being evident in catchments with high potential evapotranspiration and low precipitation seasonality. On average, almost three quarters of the diffuse N input were retained in the catchments with a retention efficiency that was specifically high in catchments with low specific discharge and thick, unconsolidated aquifers. This study confirmed a widespread presence of strong N retention across western European catchments. Given the overall short transport times but high retention of N, Study 3 concluded a dominance of biogeochemical legacy rather than groundwater N storage or substantial N removal via denitrification in catchments across western Europe. In line with Study 2, management should aim to recycle accumulated soil N to prevent long-term leaching, which poses a risk to aquatic ecosystems.
In summary, the three studies advanced the knowledge of the N dynamics and their spatial variation at catchment scale, relevant to management. By the use of differing and partly refined methods, the data driven input-output-assessment highlighted the interplay

between biogeochemical processes, hydrological transport and anthropogenic activities. This improved knowledge on catchment response and its controls is useful in developing strategies for more effective water quality management. Along those lines, this PhD project proposed methods to assess the most promising locations for the implementation of measures. Based on this, catchment managers can develop science-based concepts to efficiently tackle the N legacy components and to curb current N losses to rivers.

Zusammenfassung

Massive Stickstoff-Einträge (N) belasten die Wasserqualität unserer Trinkwasserressourcen und verursachen die Eutrophierung von Oberflächengewässern. Zahlreiche Regelungen zur Reduzierung des anthropogenen N-Eintrags in die Biosphäre zeigen oft keine oder nur verzögerte Effekte in den Oberflächengewässern, was auf ein großes, gespeichertes N-Vermächtnis in Böden (biogeochemisches Vermächtnis) und im Grundwasser (hydrologisches Vermächtnis) schließen lässt. Aufgrund der komplexen Interaktionen zwischen hydrologischen und biogeochemischen Prozessen in Einzugsgebieten sind solche Vermächtnisse bisher wenig verstanden. Die vorliegende Dissertation erweitert das Wissen über diese Vermächtnisse über eine große Bandbreite an europäischen Einzugsgebieten.
Ein Hauptziel der Arbeit war eine Quantifizierung und Differenzierung der Retentionsmechanismen, die zusätzlich zu den beiden Vermächtnissen im Boden und Grundwasser auch die N-Freisetzung mittels Denitrifikation umfassen. Diese Ergebnisse sollen zu einem effektiveren Wasserqualitätsmanagement beitragen. Die kumulative Dissertation umfasst drei wissenschaftliche Studien. Trotz der unterschiedlichen Methoden und verfügbaren Daten vergleichen alle drei Studien Langzeitdaten von N-Einträgen mit Nitratkonzentrationen und -exporten im Fluss. Eine wichtige Methode, die hier angewandt wurde, war die Übertragung des Verweilzeitenkonzepts (Kirchner et al., 2000), um aus Zeitreihen des diffusen N-Eintrags und des flussgebundenen N-Austrags auf die N-Transportzeiten im Einzugsgebiet zu schließen.
Die erste Studie (Studie 1) untersucht das mitteldeutsche Holtemme-Einzugsgebiet, welches in drei verschachtelte Teileinzugsgebiete mit zunehmender landwirtschaftlicher Nutzung gegliedert ist. Aufgrund dieses Gradienten und starker zeitlicher Variationen im Düngemitteleinsatz ist das Einzugsgebiet gut geeignet, um ein besseres Prozessverständnis des N-Transports durch die Teileinzugsgebiete zu ermöglichen.
In der zweiten Studie (Studie 2) werden Langzeitdaten aus 16 französischen Einzugsgebieten verwendet, um die Art des Vermächtnisses und deren Einflussfaktoren zu bestimmen.

Für die Quantifizierung des N-Transports dient der Ansatz der Generalized Likelihood Uncertainty Estimation (GLUE).
Durch die Zusammenführung von Erkenntnissen und Methoden aus beiden vorangegangenen Studien erweitert Studie 3 das Wissen über die zeitliche und räumliche Variation der N-Retentionsmechanismen. In einer großräumigen Analyse werden diese und ihre dominanten Einflussfaktoren in 238 verschiedenen westeuropäischen Einzugsgebieten analysiert.
Studie 1 zeigt, dass 88 % der N-Einträge im Holtemme-Einzugsgebiet zurückgehalten wurden. Die log-normalen Transferfunktionen aus den drei Teileinzugsgebieten zu den unterschiedlichen Jahreszeiten ergaben die höchsten N-Exporte 7 bis 22 Jahre nach dem N-Eintrag. In Kombination mit inter-annualen Veränderungen der Konzentrations-Abfluss-Beziehungen schloss Studie 1 auf die Dominanz eines hydrologisches Vermächtnisses. Die saisonale N-Dynamik im Fluss wird maßgeblich durch die jahreszeitlich wechselnde Aktivierung von unterschiedlich stark belasteten Fließpfaden des Grundwassers geprägt. Basierend auf den Erkenntnissen über die Dominanz des hydrologischen Vermächtnisses wurden in der Studie denitrifikationsbegünstigende Maßnahmen vorgeschlagen, um einer zukünftigen massiven N-Freisetzung aus dem Grundwasser entgegenzuwirken.
In den westfranzösischen Einzugsgebieten (Studie 2) wurden 45–88 % des diffusen N-Eintrags in den Einzugsgebieten zurückgehalten, von denen zwei Drittel im Oberboden vermutet werden. Trotz des anderen Speicherorts im Gegensatz zu dessen aus Studie 1 konnte eine massive Retention des N-Eintrags bestätigt werden. Während die N-Retentionen mit den durchschnittlichen Abflüsssen korreliert waren, konnten die unterschiedlichen Zeitversätze des hydrologischen N-Exports (2–14 Jahre nach N-Eintrag) teilweise mit räumlichen Unterschieden in der Lithologie erklärt werden. Aufgrund der abgeleiteten N-Akkumulation im Boden könnte ein Einzugsgebietsmanagement den gespeicherten N durch effiziente Agrarökosystempraktiken sinnvoll recyceln.
Studie 3, die eine breite Variation an Einzugsgebietseigenschaften abdeckt, zeigte den Hauptexport im Fluss 5 Jahre (bis zu 34 Jahre) nach den Einträgen, wobei lange Versätze in Einzugsgebieten mit hoher potenzieller Evapotranspiration und geringer Niederschlagssaisonalität zu beobachten waren. Im Durchschnitt wurden fast drei Viertel des diffusen N-Eintrags in den Einzugsgebieten zurückgehalten, wobei Einzugsgebiete mit geringem spezifischem Abfluss und mächtigen, nicht konsolidierten Grundwasserleitern besonders effektiv N zurückhalten konnten. Darüber hinaus bestätigte auch diese Studie die massive Retention von N-Einträgen in westeuropäischen Einzugsgebieten. In Anbetracht der

kurzen Transportzeiten, der hohen Retentionen und der vorhandenen Einzugsgebietscharakteristika schloss Studie 3 auf eine weit verbreitete Dominanz des biogeochemischen Vermächtnisses, während dem hydrologischen Vermächtnis und der N-Freisetzung durch Denitrifikation nur untergeordnete Rollen zukamen. Wie in Studie 2 empfohlen, sollte das Einzugsgebietsmanagement darauf abzielen, den im Boden akkumulierten N zu recyceln, um eine langfristige Auswaschung zu verhindern, welche ihrerseits eine Gefahr für aquatische Ökosysteme darstellen würde.

Zusammenfassend haben die drei Studien das Wissen über N-Dynamiken und ihre räumliche Variation in Einzugsgebieten erweitert. Durch den Einsatz unterschiedlicher und überarbeiteter Methoden hat der datengetriebene Vergleich von N-Ein- und -Austrägen das Zusammenspiel zwischen biogeochemischen Prozessen, hydrologischem Transport und anthropogenen Aktivitäten näher beleuchtet. Dieses verbesserte Wissen über die Reaktion von Einzugsgebieten auf Änderungen im Eintrag ist nützlich für die Entwicklung von Strategien für ein effektiveres Wasserqualitätsmanagement. Hierfür wurden in dieser Dissertation Methoden zur Abschätzung der N-Retention sowie sinnvolle Orte für Maßnahmen aufgezeigt. Darauf aufbauend können Einzugsgebietsmanager wissenschaftsbasierte Konzepte entwickeln, um die bereits angesammelten N-Vermächtnisse schadensbegrenzend zu bewältigen und die Ausschwemmung aktueller N-Einträge in die Flüsse einzudämmen.

Chapter 1

Introduction

1.1 Importance of nitrogen and its cycle

For terrestrial, freshwater and marine ecosystems nitrogen (N) is an essential and frequently limiting nutrient (Webster et al., 2003). It plays a crucial role in the productivity, organization and functioning of ecosystems (Vitousek et al., 1997, 2002). Along with oxygen and carbon, N is essential for the living environment (Keeney and Hatfield, 2008) – indispensable for proteins, genetic material, chlorophyll and other key organic molecules (Vitousek et al., 1997). With its numerous mechanisms for interspecies conversion (Fig. 1) and the variety of environmental transport processes, N has the most complex cycle of all major elements (Galloway et al., 2004).

Although dinitrogen (N_2) constitutes 78 % of the Earth's atmosphere, it is not directly available to most plants and animals (Galloway et al., 2004). Apart of human activities, there are two processes that make atmospheric N_2 biologically available – (1) lightning with subsequent atmospheric deposition and (2) biological fixation, the latter being the dominant natural source of N to the landscape (Cleveland et al., n.d.; Galloway et al., 1995). Both processes provide reactive, inorganic N compounds such as nitrate (NO_3^-), other N-oxides, ammonium (NH_4^+; Bouwman et al., 2013) and ammonia (NH_3) in a bioavailable form.

During the last decades, anthropogenic activities have extended this natural N fixation through leguminous crop production, fertilizers and emissions from combusted fossil fuels, releasing annually as much reactive N as formed by natural processes (about 150 Mt N; Smil, 2011). Especially the fertilizer production, which grew exponentially from the 1940s on (Vitousek et al., 1997), caused massive anthropogenic N input to the terrestrial environment. Artificial N_2 fixation is the basis of industrial fertilizer production and was

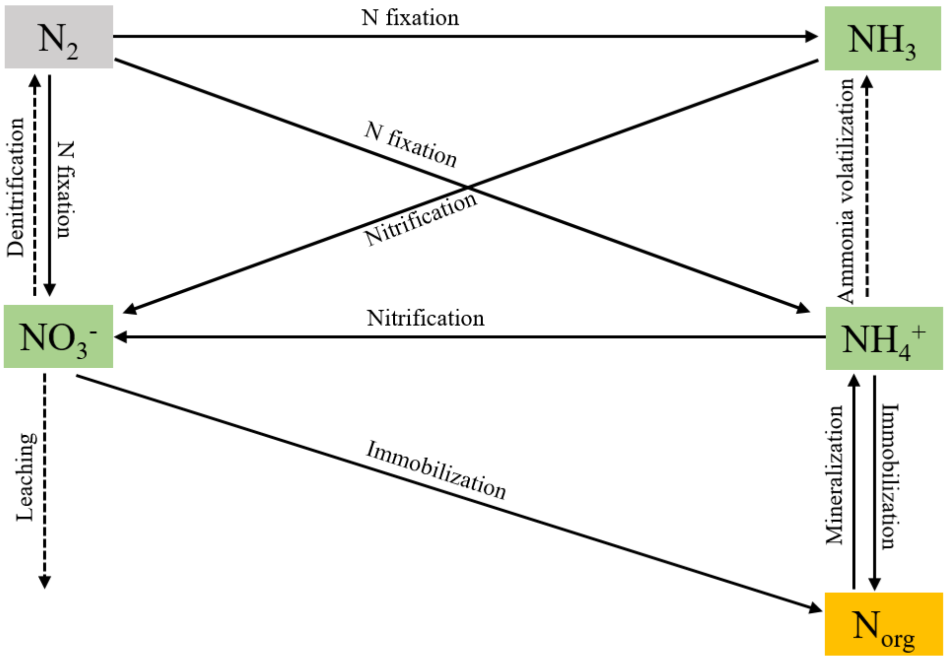

Figure 1: Overview of the described N pathways. The green boxes highlight the plant-available, inorganic N pool, while the yellow box highlights the organic N pool, which is unavailable for plants. The dashed lines show processes causing N loss from the catchment.

invented by Fritz Haber and Carl Bosch in the early 20th century. Smil (2011) estimated that by 2025 more than half of the world's food production will depend on this artificial N_2 fixation with rising rates for at least several more decades.

Fertilizers provide inorganic (from mineral fertilizers) and organic N (N_{org}; from manure) compounds to soils. While the mineral form is directly plant-available, the organic compounds need to be mineralized to NH_4^+ via decomposition by soil microbes to become available for crop growth (Ilampooranan, 2019; Vitousek et al., 1997). Mineralization is also needed to make abundant N from soil organic matter (e.g., rotten plants, animal remains) plant-available (Vitousek et al., 1997). As the bulk of the soil N stock is likely in organic form (Schulten and Schnitzer, 1998), mineralization is an indispensable conversion process to provide reactive N for plant uptake. The reverse process is the conversion of inorganic to organic forms by micro-organisms and is called immobilization (Burt and Pinay, 2005). Mineralization–immobilization dynamics are considered to be critical for accumulating N in soils (Chen et al., 2018). In general, soils are assumed as the largest pool of fixed and biologically available N (Bingham and Cotrufo, 2016).

Besides the constant cycling between organic and inorganic compounds (Galloway et al., 2004), internal inorganic conversions like the one from NH_3 or NH_4^+ via nitrite (NO_2^-) to NO_3^- in soils and water are possible. This process, known as nitrification, is dependent on aerobic environments – warm and moist conditions in well-aerated soils favoring nitrification (Johnson et al., 2005). The end product of nitrification (i.e., NO_3^-) is the most mobile form of N (Burgin and Hamilton, 2007), highly soluble, and therefore could potentially leach to groundwater (Benettin et al., 2020). This leached N constitutes one of three forms of N loss (Fig. 1, dashed line) in catchments.

Under anoxic conditions, microbial denitrification in soils or water bodies (e.g., groundwater or wetlands) reduces NO_3^- to NO_2^-, other gaseous N-oxides (like nitrous oxide: N_2O) and N_2 (Bouwman et al., 2013). Especially for agricultural soils, this N release by microbially facilitated, gaseous emissions is an important source for N loss – limiting crop production and emitting the long-living greenhouse gas N_2O on the one hand (Tiedje, 1988), but reducing the problem of a global N overload to the hydrological system on the other hand (Bouwman et al., 2013). The rates of denitrification are influenced by the availability of reactants (e.g., O_2, organic carbon, reduced iron) and environmental factors like moisture availability, ambient temperature as well as pH (Heinen, 2006; Kumar et al., 2020; Rivett et al., 2008). Although denitrification is highly variable over time and space (Oehler et al., 2007), decreasing NO_3^- concentrations with increasing groundwater depth or age are a commonly observed pattern (e.g., Rozemeijer and Broers, 2007; Visser et al., 2009; Zhang et al., 2009).

Besides leaching through runoff and denitrification, ammonia volatilization is an additional process that causes N losses in catchments (Hesser et al., 2010). Volatilization is responsible for large gaseous N losses from animal manure and all NH_3 fertilizers (Smil, 2011). This conversion of NH_4^+ to NH_3 gas increases with higher soil pH and conditions that favor evapotranspiration (e.g., hot, windy; Johnson et al., 2005).

The described N losses determine the N use efficiency in agricultural landscapes, hereby defined as “N output in useful products”. Oenema et al. (2009) modeled the increase in N use efficiency in the EU between 2000 and 2020. Over 20 years, they reported an increase by only 4 %, while at the same time in 2020 up to 52 % of the applied N were potentially lost unused. Traditional cultivation methods in China for rice production might have even higher N losses of more than 80 % (Fan et al., 2007). Besides decreased crop harvest, unintended N losses entail a number of human health and environmental concerns.

1.2 Nitrogen as a risk for human health and ecosystems

Different atmospheric N emissions (NO_x, NH_x) from agricultural sources and combustion contribute to air pollution (Bettez and Groffman, 2013), which in turn is associated with an increased risk of lung cancer and cardiopulmonary mortality (Pope et al., 2002).

In drinking water, excess NO_3^- causes methemoglobinemia ("blue-baby" syndrome) in infants (Kapoor, 1997) and may increase colorectal as well as bladder cancer risk (Jones et al., 2016; Temkin et al., 2019). For example, it is estimated that 40 % of monitoring wells in Denmark exceed the WHO recommended drinking water standard of $50\,mg\,l^{-1}$ NO_3^- (Hansen et al., 2017), while the problem affects 27 % of the wells in Germany (BMU, 2020). Throughout the EU, NO_3^- is the predominant groundwater pollutant stemming mainly from agriculture (European Environment Agency, 2018). As 75 % of the EU inhabitants depend on groundwater for their water supply (European Commission, 2008) thorough treatment of N polluted water for public supply is indispensable, but costly and complex.

Excess N emissions also cause global problems by contributing to climate change. For example, anthropogenic N_2O emissions are the most important ozone-depleting emissions (Ravishankara et al., 2009), with a global warming potential which is 298 times higher than that of carbon dioxide (IPCC, 2007). One hotspot for N_2O release are riverine environments due to microbially mediated denitrification (Marzadri et al., 2017) being supported by anthropogenic excess N input.

Furthermore, excess reactive N in the environment causes ecological degradation of freshwater and marine ecosystems (Ascott et al., 2017; Vitousek et al., 1997). In comparison to N export from pristine systems, Howarth (1998) stated that riverine N inputs to the ocean have increased by elevenfold in the North Sea region, by sixfold in Europe, and by threefold in North America due to human activities. Excess nutrient input can lead to excessive production of algae, also known as eutrophication in inland and coastal waters (Cai et al., 2011; Grant et al., 2018). Microbial processes, consuming the organic matter when the algae die off, lower the water's oxygen level and cause dead zones in coastal oceans as well as increasing acidity causing biodiversity loss (Cai et al., 2011; Diaz and Rosenberg, 2008; Galloway et al., 2004).

1.3 Regulations to prevent aquatic nitrate pollution

To reduce groundwater and surface water pollution by NO_3^-, several national, federal and international regulations have been implemented worldwide. As water sources are not restricted to national boundaries, the EU has agreed on a joint approach for improving water quality in all its member states. In three directives – the Nitrate Directive (EUR-Lex, 1991), the Water Framework Directive (EUR-Lex, 2000) and the Groundwater Directive (EUR-Lex, 2006) – protection from NO_3^- pollution is an integral part.
The first one aims explicitly at overcoming NO_3^- pollution from agricultural sources, which contribute 50 % of total N to surface waters (EUR-Lex, 1991). The directive considers several types of NO_3^-–polluted water bodies:

1. Surface freshwaters (especially those used for the abstraction of drinking water)
2. Groundwaters
3. Natural freshwater lakes or other freshwater bodies, estuaries, coastal waters and marine water

The European Commission (2010) reported that all its 27 member states developed more than 300 action programs including monitoring networks, N application limits and new technologies for nutrient processing to cut N pollution. The success of the Nitrate Directive regarding NO_3^- pollution is assessed in reports, published at the end of each four-year action program. For Germany, the current report (BMU, 2020) states that 27 % of the groundwater monitoring stations exceed the threshold of $50\,mg\,l^{-1}$ NO_3^- and miss the target of the Nitrate Directive. In comparison to the previous report time (2012–2015), the number of sampling sites with no to little pollution ($< 50\,mg\,l^{-1}$) remains almost the same, while NO_3^- concentrations have increased at 24 % of the sites.
Besides the EU-wide and national reports, several studies investigated the magnitude of improvement in water quality subsequent to implemented measures (e.g., Dupas et al., 2016; Fenton et al., 2011; Grimvall et al., 2000; Löfgren et al., 1999). An evaluation of long-term changes in nutrient concentrations revealed that the reduced N inputs from agricultural sources and nutrient point source emissions in large portions of the European territory are reflected only to a limited extent in an improved water quality (Bouraoui and Grizzetti, 2011). This is similar to studies in the U.S., Canada and China, where limited or delayed catchment responses to reduced N inputs have been observed (Chen et al., 2014; Sousa et al., 2013; Van Meter et al., 2018; Vero et al., 2018).

1.4 Time lags as an explanation for failed management goals

Grimvall et al. (2000) explained delayed responses with the inertia of aquatic and terrestrial systems that controls nutrient export from land to sea. This inertia is largely characterized by time lags, which are of critical importance from a catchment management perspective (Bain et al., 2012; Fenton et al., 2011). Those time lags are defined as time between the management change (modified agricultural practices) and improvement in the target water body (e.g., reduced riverine concentration levels) (Meals et al., 2010). The total time lag via subsurface pathways is determined by the required time of N transport through the root zone, unsaturated and saturated zone (Vero et al., 2018). In conjunction with this, time lags are attributed to the presence of two different types of legacy: biogeochemical legacy and hydrologic legacy (Van Meter et al., 2016).

Biogeochemical legacy describes the retention of N (likely as immobile N_{org}) in the root zone (Van Meter et al., 2016). Despite a temporal retention, a mineralization of this soil N pool can constitute a long-term source for leaching to subsurface and surface waters (Benettin et al., 2020; Löfgren et al., 1999; Van Meter et al., 2016). A review of long-term fertilization experiments showed that the turnover processes of N in soils operate on timescales of decades to centuries (Grimvall et al., 2000). A long-term tracer study covering three decades revealed that 12–15 % of the fertilizer-derived N was still residing in the soil organic matter, while 8–12 % leached to groundwater (Sebilo et al., 2013).

The time needed for dissolved N species to move from the point of application (e.g., agricultural field site) to the point of concern (e.g., sampling station), passing the unsaturated and saturated zone, is defined as hydrologic time lag (Van Meter et al., 2016) – a temporal storage of N predominantly in unsaturated zones (Ascott et al., 2017) or groundwater (Van Meter et al., 2016). Although NO_3^- is highly mobile and could be rapidly flushed out to the stream (in comparison to contaminants like phosphate), the scale of flushing depends on flow paths and residence times of storage reservoirs (Hamilton, 2012). Hydrologic time lags e.g., in drier climates with thick unsaturated zones, can be in the order of decades to a few centuries (Howden et al., 2011; McMahon et al., 2006). Therefore, both, underlying catchment hydrogeological attributes and overlying climate conditions, can greatly shape the subsurface travel pathways, and consequently may result in strongly delayed water quality improvements.

Quantifying delays by estimating N transport is challenging. In this PhD project, an approach which quantifies the time that rainfall travels through a catchment to the stream was adapted to quantify time lags for N transport. The diversity of subsurface flow paths that rain can take, is represented by a distribution of travel times (Kirchner et al., 2000). Besides information on flow paths, these distributions integrate information of timing, amount, storage and mixing of water (Botter et al., 2011, 2010; Harman, 2015; Heidbüchel et al., 2020; Rinaldo et al., 2011). The potential shapes of travel time distributions can be approximated by mathematical distribution functions as parametric forms (e.g., log-normal, gamma or exponential; Fiori et al., 2009; Godsey et al., 2010; Musolff et al., 2017) or non-parametric forms (Payn et al., 2008). By convolving these distributions with past tracer inputs, they serve as transfer functions between the incoming concentration of natural tracers in the rainfall and their subsequent concentration in the stream (e.g., Benettin et al., 2015; Harman, 2015; Heidbüchel et al., 2020; Kirchner et al., 2000).

1.5 Recognising time lags to improve catchment management

Due to the high complexity of hydrological and biogeochemical processes in catchments, N transport times (TT) in the pedosphere-hydrosphere system are poorly understood (Sebilo et al., 2013). Therefore, NO_3^- time lags as natural catchment behavior have rarely been considered in environmental water management (Wang et al., 2016), although it is highly recommended for its effectiveness to quantify them before implementing measures. Otherwise, improved water quality could be falsely attributed to the success of such measures instead of natural catchment response like shown in Dupas et al. (2016). They reported for an Eastern German catchment a five-year linear decrease in mean NO_3^--N concentrations after the implementation of mitigation measures, which was not the result of the changed management, but rather the natural response of the catchment to inter-annual precipitation dynamics.

Furthermore, legacy stores can buffer riverine effects to input changes, when export is limited by transport rather than by supply (Basu et al., 2010). In this case, water quality problems persist until the accumulated storage has been substantially depleted (Basu et al., 2010).

Nevertheless, a quantification of time lags as well as the separation of the responsible legacy stores are crucial to advance the understanding of N dynamics in catchments, especially now that the Nitrate Directive has been and is being violated in many parts of Europe e.g., in Germany (EUR-Lex, 2018) and France (EUR-Lex, 2013). The political need to recognise the legacy N stores for the affected countries, asks to overcome a recurring and essential problem – the data availability to reliably infer "hidden" subsurface N transport on a spatial and temporal perspective.

For a reliable N budgeting, continuous long-term series of N fluxes into and out of catchments should be available as well as data for soil and groundwater N fluxes. Only in recent times, these data have become more and more available. Therefore, only a few studies have been able to quantify retained N (includes legacy and denitrification) and conclude information on legacy stores, mainly for the U.S. (Van Meter et al., 2018, 2017) and Great Britain (Howden et al., 2010). Furthermore, data-driven studies focused either solely on quantifying retained N or on TTs, such that a joint-approach by investigating both has great potential for understanding N dynamics in catchments.

Clearly, a better knowledge of hydrological and biogeochemical functioning across multiple spatial and temporal scales is indispensable for restoring aquatic ecosystems under growing anthropogenic pressures (Abbott et al., 2016). An improved understanding of (1) spatially explicit flow paths, (2) water residence times and (3) biogeochemical transformation beyond site-specific heterogeneity could solve current ecohydrological concerns (Abbott et al., 2016). Investigating N dynamics with respect to legacies in the soil or groundwater is therefore urgently needed for catchment sciences and from a management perspective. Hereby, research on a catchment scale investigating N dynamics, as well as their spatial variation among different catchments contributes to a scientific progress.

Chapter 2

Thesis structure and objectives

2.1 Thesis structure

The introductory chapter (Chapter 1) identifies the role of N in catchments and the need for research on temporal and spatial N dynamics. Chapter 2 specifies the objectives of this PhD project as well as the research approach and methods in the three studies. The third chapter (Chapter 3) presents the key findings and conclusions from these studies. A synthesis of overall conclusions and potential research questions for follow-up studies are presented in Chapter 4. Following this, the manuscripts of the three individual studies are included.

2.2 Research objectives

The overall objective of the research was to advance the knowledge of temporal and spatial N dynamics in catchments in order to better understand and predict catchment behavior after input changes. Especially from a management perspective, a prediction of catchment response needs to be urgently addressed to understand the delay or absence of effects in streams to measures. Because this disconnection is largely driven by legacies in soils and groundwater, the objectives in this PhD project were to (Fig. 2):

1. Quantify N retention and TTs
2. Conclude potential processes in soils and groundwater to separate legacy stores in catchments
3. Better predict catchment response to input changes, contributing to a more effective water quality management

2.3 Workflow

To answer the three objectives, this PhD project followed a data-driven approach, which is illustrated in Fig. 2.

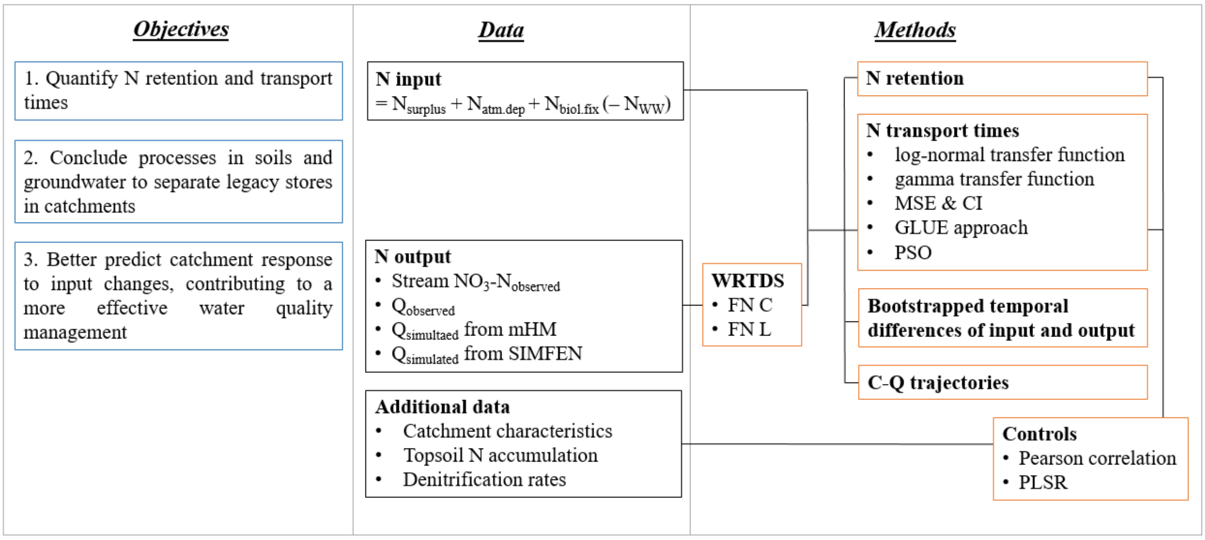

Figure 2: Workflow to investigate the objectives of the PhD project.

Diffuse N inputs were connected to riverine NO_3^--N concentrations by the use of long-term time series. These diffuse inputs covered excess N fluxes from agriculture ($N_{surplus}$), N input from atmospheric deposition ($N_{atm.dep}$) and biologically fixed N ($N_{bio.fix}$). For Study 1, additional data for N inputs stemming from two local wastewater treatment plants (N_{WW}) of the investigated Holtemme catchment were considered.
The riverine NO_3^--N observations were connected to discharge data (Q) to calculate riverine loads. Due to data gaps in the observed discharge time series, modelled discharge data from the mesoscale hydrologic Model (mHM; Kumar et al., 2013; Samaniego et al., 2010) for Germany and from the SIMFEN model (De Lavenne and Cudennec, 2019) for Brittany (France) were used. In order to focus on long-term N changes independent of inter-annual discharge variability, all studies applied a Weighted Regressions on Time, Discharge, and Season (WRTDS; Hirsch et al., 2010). This regression provides robust estimates of flow-normalized concentrations (FN C) and loads (FN L) that were used as output signal in the input-output-assessment. By comparing the latter with the diffuse N input,the sum of retained N was calculated, which was either stored as biogeochemical and hydrologic legacy or was removed via denitrification. Furthermore, the (predominantly hydrologic) N transport was quantified by fitting log-normal or gamma transfer functions between

input and output following the travel time approach of Kirchner et al. (2000). To derive measures for catchment response times, the mode TT, as representative for the peak N export of the mobile, inorganic N, was chosen. Parameters for these transfer functions were obtained by minimizing the sum of squared errors (MSE; Study 1) between observed and simulated N dynamics, obtained based on a generalized likelihood uncertainty estimation (GLUE; Beven and Freer, 2001; Study 2) approach or by obtaining the optimal MSE via a Particle Swarm Optimization (PSO; Zambrano-Bigiarini and Rojas, 2013; Study 3).
Further analyses such as a bootstrapped analysis of temporal differences of the N input and N output or concentration-discharge (C-Q) trajectories helped to evaluate catchment responses to changes and, in case of bootstrapping, to consider the uncertainty of the estimated temporal differences.
For the investigation of controls for retention and TTs, catchment characteristics (i.a., morphology, climate, geological properties and land use attributes) were associated to previous results (TT and retention) via a Pearson correlation or a Partial Least Squares Regression (PLSR). Additional data like topsoil N accumulation data helped to discuss potential soil and groundwater processes.

2.4 Study designs

Study 1: Trajectories of nitrate input and output in three nested catchments along a land use gradient

Focus: Process understanding of N transport in a mesoscale catchment with a nested subcatchment structure and development of methods to investigate the above mentioned objectives

The first study assessed long-term data of three nested subcatchments in the Holtemme catchment, being part of the Bode catchment that is one of the meteorologically and hydrologically best-equipped catchments in Germany (Wollschläger et al., 2017; Zacharias et al., 2011). Besides the comprehensive database for many environmental variables, two further aspects made the study catchment ideal for improving the understanding of N dynamics. First, the strong temporal change in fertilizer usage in East Germany before and after reunification and second, the strong spatial gradient with increasing anthropogenic impact from upstream to downstream. Study 1 addressed the following three research questions:

1. How high is the retention potential for N of the studied mesoscale catchment with a nested subcatchment structure and what are the consequences in terms of a potential buildup of an N legacy?

2. What are the characteristics of the transport time distribution (TTD) for N that links change in the diffuse anthropogenic N inputs to the geosphere and their observable effect in riverine NO_3^-– N concentrations?

3. What are the characteristics of a long-term trajectory of C–Q relationships? Is there an evolution to a chemostatic export regime that can be linked to a biogeochemical or hydrologic N legacy?

Study 1 provided a temporally and spatially detailed process-understanding of N transport from a well-instrumented catchment, which was supportive for discussing results in Study 2 and Study 3. Furthermore, Study 1 for the first time applied methods for quantifying retention and TTs that were further developed in Study 2 and Study 3.

Study 2: Long-term nitrogen retention and transit time distribution in agricultural catchments in western France

Focus: Determining N legacy stores and their controls

Study 2 addressed the first two research objectives of Study 1 in 16 nested and independent catchments in Brittany. This region is one of the emblematic areas for N-derived coastal eutrophication in Europe (Smetacek and Zingone, 2013), such that analysis for a better understanding of N dynamics and their potential storage is highly demanded for effective water quality management. In line with Study 1, the Brittany region has experienced large variations in the excess agricultural N input in the past few decades (Dupas et al., 2018), which further made it an interesting study area to understand catchment response to input changes.

Study 2 extended Study 1 by assessing additionally the controlling parameters for N retention and TTs via correlation analysis as well as by applying the GLUE approach for TT estimation. Furthermore, the analysis of Study 2 provided a necessary insight into the french database, which was needed to decide whether a joint assessment of Germany and France in Study 3 would be possible.

Study 3: Nitrate transport and retention in western European catchments are shaped by hydroclimate and subsurface properties

Focus: Temporal and spatial variation of N legacy stores and their controls

By collecting a unique data set providing long-term data for diffuse N input and N output, Study 3 aimed to contribute to a better understanding of temporal and spatial variation of legacy stores for 238 western European catchments, covering 38 % of the total land area of Germany and France.
Because Germany and France were found guilty of violating the Nitrate Directive (EUR-Lex, 2018, 2013), Study 3 aimed to quantify the retained N as potential cause for failing the EU goals. Furthermore, the study focused on differentiating the retention mechanisms and deriving TTs as well as associating both with a variety of geophysical and hydroclimatological characteristics. The identification of parameters that explain best the variability between catchments was regarded as a helpful tool for decision-makers to draw future realistic management plans.
Study 3 unified the objectives from Study 2 with a modified and merged methodological approach from Study 1 and Study 2 in order to acknowledge the large number of catchments and wide range of characteristics. The initial methods for estimating TTs were refined. Conclusions regarding legacy stores in connection with catchment response of both previous, small scale studies supported the interpretation of spatially varying TTs and retention investigated in Study 3.

Chapter 3

Key findings and conclusions

3.1 Study 1: Process understanding and method implementation

Study: Trajectories of nitrate input and output in three nested catchments along a land use gradient

Study 1 focused on the retention quantity and the type of dominant retention mechanism for the three nested catchments. The analysis of the transported N in the German Holtemme catchment indicated that only 12 % of the total excess N input (covering diffuse and wastewater sources) were exported at the catchment outlet over that period. Strong inter-annual changes in the export regime, revealed by C-Q trajectories, indicated that the retention of the remaining 88 % of N can be attributed to hydrologic legacy rather than being denitrified or stored as biogeochemical legacy. Basu et al. (2010) stated that catchments' memories can buffer biogeochemical variations. Consequently, Study 1 argue that a predominant biogeochemical legacy would have buffered the inter-annual variability of riverine concentrations which was not in accordance to the observed changes in C-Q behavior. The missing N, accumulating up to 1.7 t N ha^{-1}, represents a long-term challenge for future water quality management as the denitrification – a potential mechanism of N removal from the system – continues to play a minor role.
The significantly reduced N inputs after the reunification of Germany mitigated the legacy accumulation, as the Holtemme River exported only one fifth of the annual input during the last ten years of the time series (2005–2015). The ongoing over-fertilization constitutes non-sustainable management either in terms of a further growing N legacy store or exhausting the catchment's denitrification potential (Hannappel et al., 2018; Merz et al.,

2009; Wilde et al., 2017).
The analysis of the catchments' hydrological N transport revealed seasonally differing modes (peaks) of the TTDs ranging between 7 and 22 years that reflected a season-dependent activation of differently loaded subsurface flow paths. The latter contribute transferring the mobile N to streams, predominantly from the shallower flow paths during high flow seasons and from deeper paths during low flow seasons (Dupas et al., 2016; Musolff et al., 2016; Rozemeijer and Broers, 2007; Fig. 3a). The changing flow path activation among flow seasons in connection to the vertical location of the dominant N storage zone caused seasonally differing riverine NO^{3-}-N concentrations. With this improved knowledge on the activation of shallow flow paths during high flow events that favor young water ages (Birkel et al., 2015; Yang et al., 2018), the findings of Study 1 revealed the underlying differences among seasonal concentration patterns with export stemming from different past year contributions. Accordingly, the TTs were shaped by the lateral flow path connection and thus the possibilities for exporting the N load. The link between this activation-dependent load contribution and catchment response could only be disclosed by the investigation of TTs on intra-annual timescales. Two practical recommendations are suggested based on this finding: first, monitoring strategies should be maintained for a sufficient long period to catch peak TTs of potentially several decades, and second, they should cover an appropriate intra-annual resolution, containing different discharge conditions and hence able to distinguish different activation-dependent export contributions. A monitoring strategy focusing exclusively on inter-annual load differences could miss important information on catchments' N transport behavior.

The investigation of C-Q trajectories under abruptly reduced N inputs after the collapse of agriculture in the early 1990s in East Germany revealed unique information for the catchment's N export. The comparison of seasonally varying N transport among different years showed chemostatic export regimes (intra-annually lower concentration variability than discharge variability; Fig. 3a at $t_{1,3}$) in both catchments under intensive agricultural use, in line with previous findings (Basu et al., 2010; Dupas et al., 2016). In contrast to these previous studies, where N dynamics showed a monotonic evolution starting from the accretion pattern (highest concentration during high flows due to NO^{3-}-N mobilization from shallow depths by the activation of fast, shallow flow paths, Fig. 3a t_0), the Holtemme catchment showed an additional systematic shift to a dilution pattern (highest concentration during low flows due to NO^{3-}-N mobilization from deeper depths by the

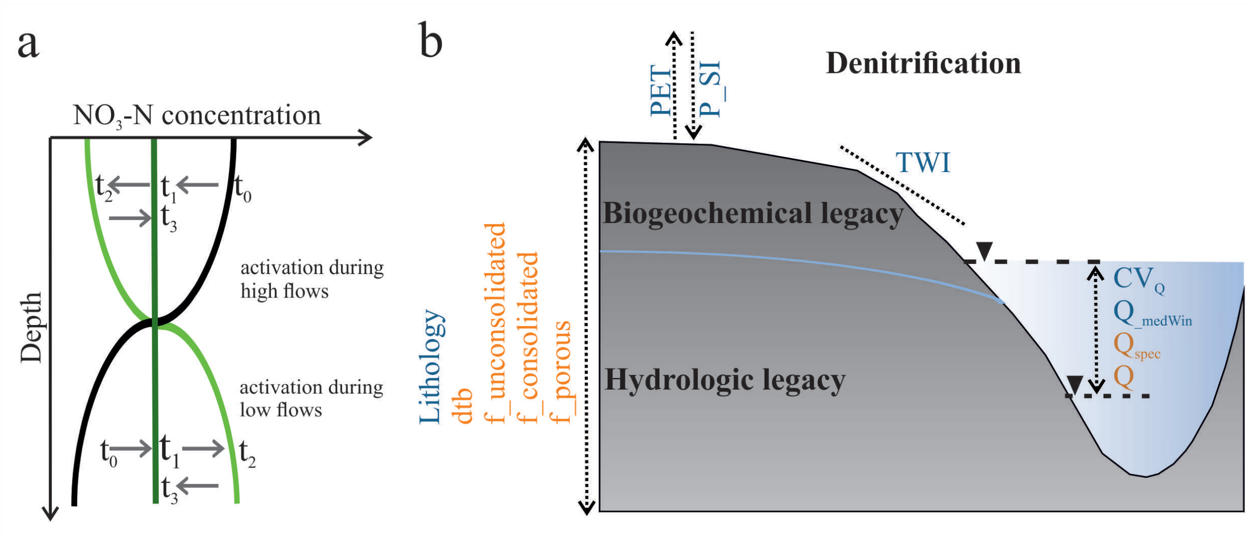

Figure 3: Overview of selected key findings from Study 1 and 3. a — Vertical migration of the dominant N storage zone over time (t) causing different export regimes (at t_0: chemodynamic regime with an accretion pattern, at $t_{1,3}$: chemostatic regime, at t_2: chemodynamic regime with a dilution pattern) b — Retention mechanisms (in bold) and their controlling predictors (orange variables) as well as controlling predictors for TTs (blue variables) from Study 2 and 3. Variable names (except for "Lithology" and "Q") are defined in Study 3 (p. **??**–**??**).

activation of deeper and thus older flow paths; Fig. 3a at t_2) over the observed decades before ending with the chemostatic regime (Fig. 3a at t_3). These fundamental regime shifts are largely due to a downward migration of the dominant N storage zone in the vertical soil–groundwater profile and the returning excess N input entering the profile in the late 1990s, which caused the final reappearance of the chemostatic regime. Nevertheless, this chemostatic endpoint in highly managed catchments should generally rather be referred to "pseudo-chemostatic" as it relies on a constant replenishment of the catchment's N store. Changing input conditions like after the collapse of agriculture (early 1990s) can entail a reappearance of a chemodynamic export regime by altering a homogenized vertical NO_3^--N profile. Accordingly besides legacy separation, investigating C-Q trajectories offered information on a catchment's vertical N homogenization and allowed predicting future concentrations following the observed systematic shift.

Overall, this study demonstrates that to overcome N pollution, local catchment management should focus on two aspects: first, a better management of fertilizer applications with a prevention of N losses from the root zone to avoid further buildup of the legacy, and second, diminishing past inputs by facilitating denitrification that may deplete the hydrologic N legacy.

3.2 Study 2: Determining legacy stores

Study: Long-term nitrogen retention and transit time distribution in agricultural catchments in western France

The estimation of TTs revealed an offset of 2 to 14 years between N input and its peak riverine export (mode TTDs), supporting earlier results for water TTs in the Brittany region using chemical tracers or physically-based modeling frameworks (Aquilina et al., 2012; Ayraud et al., 2008; Fovet et al., 2015; Martin et al., 2004; Molénat et al., 2002). Regarding controls for N transport, some of the inter-catchment TT variability could be explained by underlying lithology as catchments dominated by granite and mixed-lithology exhibited longer TTs than those noticed in schist dominated catchments.

In line with previous estimates for N retention in temperate regions (e.g., Billen et al., 2011; Boyer et al., 2002; Howarth et al., 2006), 45–88 % of the diffuse N was retained in the selected western French catchments.
The correlation analysis revealed runoff as a good predictor to explain retention variability among catchments ($r = -0.88$), indicating that wet areas decrease water residence times, which impedes N removal via denitrification or long-term accumulation of N in soils. While previous short-term studies (≤ 6 years; Dupas et al. 2015; Howarth et al. 2006) hypothesized the same relation, they could not exclude the presence of a transient state with wetter catchments responding faster to decreasing inputs. In comparison to this, the 40 years of observations could more reliably prove the relation between high runoff and low retention on decadal timescales due to the unfavorable conditions for denitrification and long-term accumulation.
The mean annual N accumulation in the topsoil (32 kg ha^{-1} yr^{-1}) over a 10-year period (2004–2014) constituted 64 % of the retained N (51 kg ha^{-1} yr^{-1}), which indicated a dominance of biogeochemical legacy rather than N removal via denitrification. Although a previous study (Dupas et al., 2018) did not show a decreasing seasonal variation of N concentrations in the same study catchments, the long-term accumulation of N in the soils during the study period is estimated to reach saturation in the future. At present, this accumulated N pool entails on the one hand a potential threat to aquatic ecosystems through prone to slow, long-term leaching, but provides on the other hand a potential resource for crops that could allow farmers to reduce fertilizer applications.

3.3 Study 3: Temporal and spatial variation of legacy stores and their controls

Study: Nitrate transport and retention in western European catchments are shaped by hydroclimate and subsurface properties

In this large-scale study, the time lags of the N transport in a diverse range of 238 West European catchments were first quantified. The modes of the N TTDs, connecting diffuse N input to riverine N output, ranged from less than a year to 34 years with a median of 5 years. As 70 % of the catchments had their peak export within 10 years after the N input, catchment managers need to be aware of this hydrological transport-dependent decrease in N concentrations – arising from (natural) catchment input/output response behavior – that should not be falsely only attributed to measures besides reducing the input.

In pursuit of identifying dominant controls on inferred TTs and retention capacity across the wide range of study catchments, the application of the PLSR revealed the importance of hydroclimatic variables (via potential evapotranspiration, precipitation seasonality, discharge variability and winter discharge) and morphology (via topographic wetness index; Fig. 3b, blue variables) for N transport, being in line and extending the correlation analysis from Study 2. These predictors explained nearly 49 % of the TT variability between catchments – leaving aside 51 % of the variability unexplained that underlines the need for more research in this direction. While high potential evapotranspiration was associated with longer TTs, high precipitation seasonality, discharge variability and high winter discharges favored short TTs. Based on the findings of Study 1, it was hypothesized that high flow events efficiently export young NO_3^--N from the shallow subsurface to the stream and thus shorten N TTs. Previous research (e.g., Birkel et al., 2015; Yang et al., 2018) has shown that high flow events favor young water ages, which our analysis supported by relating elevated N export (allowing for short TT estimates) to high winter discharge or to runoff events being reflected in "precipitation seasonality" as the predictor variable.

The median of the retained N over the 238 study catchments was almost three quarters of the diffuse N input. By covering 40 % of the country areas of Germany and France, this study showed a large-scale evidence for massive retention. The estimated N retentions with and without considering TTs were similarly high, leading to the conclusion that hydrologic legacy is a minor retention process in the majority of catchments. The variability in N retention among catchments was mainly explained by subsurface properties and the specific discharge (Fig. 3b, orange variables). Both highly influence the biogeochemical conditions favoring N storage as legacy and removal via denitrification. Low specific discharge and a high share of thick, unconsolidated aquifers in the catchments favored high retention. Unconsolidated deposits are often associated with iron sulfide minerals supporting denitrification under anaerobic conditions. Furthermore, higher degrees of silt and clay in these deposits are known for microaggregate formation and anion sorption, promoting N storage in the soil (Bingham and Cotrufo, 2016; Lützow et al., 2006). Vice versa, high discharge and consolidated aquifers are connected to short residence times in the root zone, aquifer and riparian zone, decreasing denitrification efficiency (e.g., Howarth et al., 2006; Kunkel and Wendland, 2006; Wendland et al., 2007) and favoring a wash-out of N before immobilization in the soil might be possible – both of these conditions resulting in low retention.

A comparative analysis of catchment response to N input changes between decades of 1980s and 2010s revealed a limited decrease in riverine N loads despite a significantly reduced diffuse N input in the recent decade. The buffered riverine response together with the predominant catchment characteristics that rarely met the specific biogeochemical conditions for effective denitrification, supports the hypothesis for the dominance of biogeochemical legacy for the majority of study catchments. This legacy acts as a buffer and often a secondary, delayed N source, constituting a system that is either inert or very slowly responding to decreasing N inputs. Hence, declining riverine concentrations after the peak TTs did neither imply that most of the N was already exported nor that restoration efforts can be reduced. Consequently and in line with Study 2, Study 3 recommended rather a recycling of the retained N or a fostering of denitrifying conditions to counteract the long-term leaching from the accumulated N pool in the soil.

Chapter 4

Synthesis and implications

4.1 Quantification of N retention and transport times

The three studies aimed to advance the knowledge of spatial and temporal N dynamics to better understand catchment response to changing inputs. These responses are often altered by legacy N stores in the soil or groundwater. One of the main objectives of this PhD project was devising an analysis approach for a proper quantification of the N retention and TTs across a wide variety of hydroclimatic settings.

The data-driven analyses presented here (Study 1, 2 and 3), covering in total more than 250 catchments in western Europe, revealed an overall N retention of around three-quarter (median: 72 %) of the N input.
An overview of the distribution of quantified retentions of all studies is shown in Fig. 4a. While the German Holtemme catchment (red, dashed lines) tends to have a slightly higher retention than the western European (green) average, the French catchments (yellow) show the opposite result with slightly smaller retentions. The slightly higher, but potentially more realistic retention estimates of the Holtemme catchment could be explained by the wastewater correction, attributing portions of N export to this point source rather than to legacy N export. Conversely, the other catchments could show a slight underestimation of retained N, due to exports incorrectly attributed to legacy depletion. Nevertheless, as all estimates are consistently high, and therefore almost independent from whether riverine concentrations were corrected by wastewater inputs (Study 1) or not (Study 2 and 3), a minor wastewater influence on the catchments' NO_3^--N budget can be concluded. Past and current excess agricultural N inputs are therefore the main driving factor for the nutrient-related water quality issues. This is in line with findings of the European

Commission (2010) that stated agricultural use of fertilisers as the major source for water pollution in Europe.

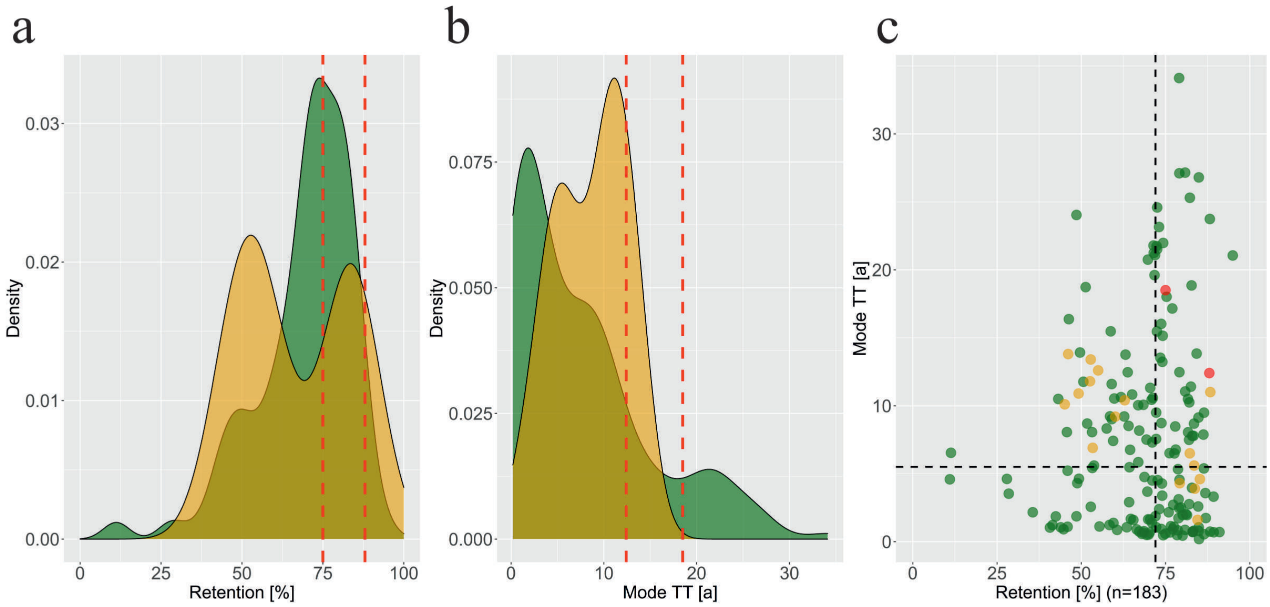

Figure 4: Overview of the PhD project's results regarding N TTs and retention. a – Histogram of the N retention of Study 2 (yellow) and Study 3 (green) with additional lines for the retention of the mid- and downstream subcatchments from Study 1 (red, dashed lines). b – Histogram of the mode TTs (same color scheme as in a) c – Scatter plot of the retention versus the mode TTs, with the corresponding medians for both measures of Study 3 (black, dashed lines). Additional dots for the corresponding results from Study 1 (red) and Study 2 (yellow). The figure is based on Fig. 2 from Study 3 (p. **??**). a and c exclude one outlier with negative retention from Study 3.

Almost all catchments have in common that they retain the majority of N inputs. However, the proportion between the three retention mechanisms (two legacy types + denitrification) can be assumed to differ. The timescale for N transport was quantified to partly reduce this inherent complexity. For this purpose, N dynamics in the riverine output were connected to dynamics in the N input through a transfer function based on log-normal or gamma distributions (results not discussed due to lower performance compared to log-normal transfer functions, see Study 3 for more information).

The synthesis of all investigated catchments (Fig. 4b) showed modes of the TTDs between less than a year and more than three decades. The majority of catchments had a mode TT below 10 years. Here, results from Study 1 show significantly longer mode TTs than the majority of catchments analysed in Study 2 and 3. The combination of above-average TTs and high retention yielded hitherto "hidden" information regarding the dominant retention mechanism, synthesized in the following section.

4.2 Conclude catchment processes in soils and groundwater to separate legacy stores

Dealing with different data availability among the studies, the PhD project's joint methodological approach made it possible to advance the knowledge about the interacting storage and transport processes in soils and groundwater (PhD project's second objective) that shape N dynamics in catchments. An estimate of the predicted N retention explained by hydrologic legacy was possible with the applied mathematical intersection of TT and retention.

A first intersection was applied in the German Holtemme catchment. From this approach, a large proportion of the retention could directly be assigned to a hydrologic legacy, despite the lack of explicit groundwater concentration and storage data. In this study area, non-hydrologic retention processes are affirmative the minor contributor to the N retention. Vice versa, the intersection of the overall large retention with the relatively short TTs in Study 3 assigned a minor role of hydrologic legacy for most of the western European catchments. This is in line with the predominant catchment characteristics: Hydroclimatic conditions that favor long TTs like low precipitation seasonality and low discharge variability are rarely found, since large portions of Europe exhibit a pronounced seasonality in precipitation (Zveryaev, 2004). Furthermore, the dominant (sub-)humid climate in (western) Europe rather supports hydrologic connectivity with shorter water transit times (Heidbüchel et al., 2020; Kumar et al., 2020) and thus faster N export instead of enabling a massive hydrologic legacy.

The TTs estimated between inputs and outputs characterize the effective transport, and accordingly, the approach assumes that N being denitrified or bypassing the station has no or only a minor effect on the shape of the TTDs. For quantifying the retention under consideration of the TTs (intersection), this simplification of transport can lead to an overestimation of future N release.

While the TT analysis along with the intersection approach, enabled insights into complex N dynamics operating at catchment scale, an extensive evaluation of the soil's N fate remained challenging in light of limited observational datasets on internal processes (like temporal dynamics of soil N storage or groundwater concentrations). A discrete separation into buildup of N legacy and permanent removal was not directly possible and needed to be approached using previous studies or additional data sources. While in Study 1, the two non-hydrologic retention processes could not be reliably delineated, N accumulation data from the topsoil in the French catchments in Study 2 directly supported the conclusion of a dominant biogeochemical legacy in these catchments.

Furthermore, the multivariate PLSR allows us to rank catchment characteristics that indirectly address different retention mechanisms. Accordingly, Study 3 exploited the potential of the large-sample database of catchment characteristics to provide further insights into related soil and groundwater processes across a wide variety of sites. The PLSR approach allows explaining variability of TTs and retention among catchments by associating predictors to favorable environmental and biogeochemical conditions for either accumulation or removal. The wide range of observed retentions and TTs (Fig. 4a,b,c) hints to potentially different underlying processes and controls covered in Study 3.
From subsurface composition (e.g., grain sizes, reactants), the probabilities for processes like sorption, aggregate formation or pyrite oxidation can be estimated (see Study 3 for further information). In connection with the average runoff and specific discharge, conclusions regarding biogeochemical contact time and reaction space can be drawn to hypothesize either N storage or removal processes.
To further assert the concluded dominating soil N storage, the comparison of bootstrapped temporal differences in input and output supported the assumption of a dominating soil N accumulation in most western European catchments (Study 2 and 3) acting as long-term N source, which increases the system's inertia to declining inputs. At the same time, Study 1 and Study 3 clearly indicated an ongoing anthropogenic excess N contribution, which still is a multiple of the riverine export, causing a further growth of the legacy store and/or an exhaustion of the catchment's denitrification potential (Hannappel et al., 2018; Merz et al., 2009; Wilde et al., 2017). Without the possibility yet to reliably assess the N storage capacity in all of the investigated catchments' soils, at least Study 2 suggests towards a possible storage saturation in the near future.

Besides using the PLSR, also the C-Q trajectories revealed information to conclude catchment processes that shape N dynamics. Temporal variations in N dynamics were partly associated with the vertical migration of the dominant N storage zone in the vertical soil-groundwater profile, which was corroborated by different analyses in Study 1 and Study 3. This evolution causes inter-annual (Fig. 3a, p. 22, different profiles) and intra-annual (Fig. 3a, p. 22, different depths) patterns of changing N load contributions with correspondingly differing impact on catchments' water quality.

4.3 Implications for management

The first two objectives of the PhD project contribute to a better understanding of the interplay between biogeochemical processes, hydrological transport and anthropogenic activities for long-term N transport and retention in catchments. This improved knowledge for catchment response can now be used for a more effective water quality management – in line with the third objective of the PhD project.

In general, catchment managers have the task to develop science-based concepts to alleviate negative effects of past, retained N inputs, e.g., by triggering denitrification (i.e., supporting riparian rehabilitation, decreasing land drainage or by increasing levels of bioavailable organic carbon; Abbott et al., 2018; Hunter et al., 2006), which at the same time can accelerate climate change, and, in cooperation with farmers, to curb current losses e.g., by examining potential recycling of topsoil N. Findings of this PhD project can help to assess the locations for effective measure implementation for short-term and long-term management.

The analyses of TTs and C-Q trajectories complement each other by distinguishing between transport-dependent (via TTs) and measure-dependent catchment responses. While Visser et al. (2009) predicted future N loads by combining extensive groundwater dating with groundwater concentrations, the less extensive investigation of C-Q trajectories provides promising results with comparable conclusions. Especially for effective water quality management, monitoring the vertical peak zone migration via C-Q trajectories, offers a great potential. For example, a high N contribution stemming from an already deeply migrated (and thus old) N peak zone will stay unaffected by recycling efforts of the stored N in the topsoil. Similarly, effective measures, like strongly reduced inputs, could be masked by massive N contribution from delayed responses of deeper aquifers.

In addition, evaluating C-Q trajectories is also recommended from an ecological perspective as C-Q shifts may also affect the functioning and health of aquatic ecosystems. Investigating seasonally differing N load contributions might be useful to understand changing ecosystem communities and the challenges they need to face when adapting to these fundamental inter-annual concentration shifts.

When the availability of long-term data for deriving TTs or investigating shifting C-Q trajectories is restricted, the selected catchment attributes and their underlying relationships to N transport characteristics as identified in Study 2 and 3 can be a useful approach and with moderate effort, they can enable a first-order estimation of a catchment's response behavior via estimates of TTs. A statistical technique (like PLSR) together with process understanding can allow uncovering catchment processes in soils and groundwater (e.g., lack of denitrification, long-term accumulation, migrating N storage zone, microaggregate formation) that may explain failed past management, and is beneficial for future realistic planning of appropriate measures. The use of this alternative estimate could be particularly valuable in the absence of long-term data.

On the basis of experience gained on the complexity of transport processes, I argue that the problem of deteriorated water quality can be solved by extending the responsibility from catchment managers themselves to three additional parties – farmers, politicians and consumers. First, farmers should realize a better site-dependent management of fertilizers by increasing the use efficiency. This includes not only reducing the required amount of fertilizers, but also the fertilization strategy (i.e., method, timing) to minimize N losses from the root zone. Second, the political decision-makers should reward sustainable agriculture, overcoming the usual dimensioning of subsidies based on farmed area. Subsidies should be linked to environmental standards, not only for maintaining ecosystem health but also to protect the end consumer from further increases in drinking water prices. Lastly, consumers should be willing to pay reasonable prices for agricultural products, waste less food and need to avoid products from unsustainable agriculture to accelerate a significant rethinking at the political level.

4.4 Further recommended investigations

In this project, the catchment was initially considered as a black box, from which only long-term data for N input and output were available. Using various analyses and other short-term data sources, an attempt was made to derive processes in the soil and groundwater that could explain the observed riverine N dynamics. In a future approach, it would be helpful to reliably constrain these potential processes in the "box". This would be conceivable with a combination of better data and mechanistic models. Reliable N data from soil and groundwater would be helpful for quantifying the fate of N with its various species.

A first progress could be achieved with a comprehensive soil database covering denitrification rates and soil N contents in catchments over time. As partly available in Study 2, the latter helped to quantify the share of biogeochemical legacy. Although being expected for the future, a precise quantification of soil N saturation or denitrification exhaustion was not possible. One of several challenges is the high temporal and spatial variation of soil properties (e.g., Green et al. 2016; Otero et al. 2009; Refsgaard et al. 2014), which makes an upscaling of local measurements to a catchment-scale estimation difficult. Nevertheless, a currently ongoing interdisciplinary approach of data-driven analyses and modeling frameworks at the Helmholtz Centre for Environmental Research aims at a closed catchment-scale and even national-scale N budgeting.

As N output was only considered at the catchment outlet, also the stream with its potential N conversion processes is part of the mentioned black box. Although N inputs from point sources can be crucial when budgeting N at catchment scales, wastewater data generally receive limited attention (only partly available in Study 1) as a source of N inputs, due to their infrequent availability. Especially longer time series of data, reflecting their contributions, are rarely available. While improved wastewater treatment during the last decades decreased the polluting impact on water quality in industrialized countries (Lofrano and Brown, 2010), a future application of the presented methodological approach in developing countries, which sometimes neither have safe drinking water nor sanitation (Lofrano and Brown, 2010), should consider N inputs from point sources. Moreover, for Study 2 and 3, riverine N exports in the earlier decades of the time series could falsely be attributed to a depletion of the legacy store instead of wastewater discharge, resulting in an underestimated N retention (as seen in 4.1). Methods to reconstruct a long-term trajectory of N inputs in industrialized countries as well as current point source inputs in developing countries would be an important improvement for more reliable retention estimates.

Lastly, to better understand the linkage between catchment response and management actions, the PhD project proposes the implementation of a European database, where catchment management efforts need to be registered. The assessment of mitigation measures at larger scales, where personal communication is not feasible, would largely profit from this database. Accordingly, the PhD project could only focus on explaining catchment response by diffuse N input dynamics, while it is possible that further actions such as constructed wetlands additionally altered the response.

References

Abbott, B. W., Baranov, V., Mendoza-Lera, C., Nikolakopoulou, M., Harjung, A., Kolbe, T., Balasubramanian, M. N., Vaessen, T. N., Ciocca, F., Campeau, A., Wallin, M. B., Romeijn, P., Antonelli, M., Gonçalves, J., Datry, T., Laverman, A. M., de Dreuzy, J.-R., Hannah, D. M., Krause, S., Oldham, C. and Pinay, G. (2016), 'Using multi-tracer inference to move beyond single-catchment ecohydrology', *Earth-Science Reviews* **160**, 19–42.

Abbott, B. W., Moatar, F., Gauthier, O., Fovet, O., Antoine, V. and Ragueneau, O. (2018), 'Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France', *Sci Total Environ* **624**, 845–858.

Aquilina, L., Vergnaud-Ayraud, V., Labasque, T., Bour, O., Molenat, J., Ruiz, L., de Montety, V., De Ridder, J., Roques, C. and Longuevergne, L. (2012), 'Nitrate dynamics in agricultural catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters', *Sci Total Environ* **435-436**, 167–78.

Ascott, M. J., Gooddy, D. C., Wang, L., Stuart, M. E., Lewis, M. A., Ward, R. S. and Binley, A. M. (2017), 'Global patterns of nitrate storage in the vadose zone', *Nature communications* **8**(1), 1–7.

Ayraud, V., Aquilina, L., Labasque, T., Pauwels, H., Molenat, J., Pierson-Wickmann, A.-C., Durand, V., Bour, O., Tarits, C., Le Corre, P., Fourre, E., Merot, P. and Davy, P. (2008), 'Compartmentalization of physical and chemical properties in hard-rock aquifers deduced from chemical and groundwater age analyses', *Applied Geochemistry* **23**(9), 2686–2707.

Bain, D. J., Green, M. B., Campbell, J. L., Chamblee, J. F., Chaoka, S., Fraterrigo, J. M., Kaushal, S. S., Martin, S. L., Jordan, T. E., Parolari, A. J., Sobczak, W. V., Weller, D. E., WolLheim, W. M., Boose, E. R., Duncan, J. M., Gettel, G. M., Hall, B. R., Kumar, P., Thompson, J. R., Vose, J. M., Elliott, E. M. and Leigh, D. S. (2012), 'Legacy Effects in Material Flux: Structural Catchment Changes Predate Long-Term Studies', *BioScience* **62**(6), 575–584.

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A. and Rao, P. S. C. (2010), 'Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity', *Geophysical Research Letters* **37**(23).

Benettin, P., Fovet, O. and Li, L. (2020), 'Nitrate removal and young stream water fractions at the catchment scale', *Hydrological Processes* **34**(12), 2725–2738.

Benettin, P., Kirchner, J. W., Rinaldo, A. and Botter, G. (2015), 'Modeling chloride transport using travel time distributions at Plynlimon, Wales', *Water Resources Research* **51**(5), 3259–3276.

Bettez, N. D. and Groffman, P. M. (2013), 'Nitrogen deposition in and near an urban ecosystem', *Environmental science technology* **47**(11), 6047–6051.

Beven, K. and Freer, J. (2001), 'Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology', *Journal of Hydrology* **249**(1-4), 11–29.

Billen, G., Silvestre, M., Grizzetti, B., Leip, A., Garnier, J., Voss, M., Howarth, R. W., Bouraoui, F., Lepisto, A., Kortelainen, P., Johnes, P., Curtis, C., Humborg, C., Smedburg, E., Kaste, O., Ganeshram, R., Beusen, A. H. and Lancelot, C. (2011), Nitrogen flows from European watersheds to coastal marine waters, Report.

Bingham, A. H. and Cotrufo, M. F. (2016), 'Organic nitrogen storage in mineral soil: Implications for policy and management', *Sci Total Environ* **551-552**, 116–26.

Birkel, C., Soulsby, C. and Tetzlaff, D. (2015), 'Conceptual modelling to assess how the interplay of hydrological connectivity, catchment storage and tracer dynamics controls nonstationary water age estimates', *Hydrological Processes* **29**(13), 2956–2969.

BMU, B. . (2020), Nitratbericht, Report.

Botter, G., Bertuzzo, E. and Rinaldo, A. (2010), 'Transport in the hydrologic response: Travel time distributions, soil moisture dynamics, and the old water paradox', *Water Resources Research* **46**(3).

Botter, G., Bertuzzo, E. and Rinaldo, A. (2011), 'Catchment residence and travel time distributions: The master equation', *Geophysical Research Letters* **38**(11).

Bouraoui, F. and Grizzetti, B. (2011), 'Long term change of nutrient concentrations of rivers discharging in European seas', *The Science of the total environment* **409**(23), 4899–4916.

Bouwman, A. F., Beusen, A. H., Griffioen, J., Van Groenigen, J. W., Hefting, M. M., Oenema, O., Van Puijenbroek, P. J., Seitzinger, S., Slomp, C. P. and Stehfest, E. (2013), 'Global trends and uncertainties in terrestrial denitrification and N(2)O emissions', *Philos Trans R Soc Lond B Biol Sci* **368**(1621), 20130112.

Boyer, E. W., Goodale, C., Jaworski, N. and Howarth, R. W. (2002), 'Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern U.S.A.', *Biogeochemistry* **57**, 33.

Burgin, A. J. and Hamilton, S. K. (2007), 'Have we overemphasized the role of denitrification in aquatic ecosystems? a review of nitrate removal pathways', *Front Ecol Environ* **5**(2), 8.

Burt, T. P. and Pinay, G. (2005), 'Linking hydrology and biogeochemistry in complex landscapes', *Progress in Physical Geography* **29**(3), 297–316.

Cai, W.-J., Hu, X., Huang, W.-J., Murrell, M. C., Lehrter, J. C., Lohrenz, S. E., Chou, W.-C., Zhai, W., Hollibaugh, J. T., Wang, Y., Zhao, P., Guo, X., Gundersen, K., Dai, M. and Gong, G.-C. (2011), 'Acidification of subsurface coastal waters enhanced by eutrophication', *Nature Geoscience* **4**(11), 766–770.

Chen, D., Hu, M. and Dahlgren, R. A. (2014), 'A dynamic watershed model for determining the effects of transient storage on nitrogen export to rivers', *Water Resources Research* **50**(10), 7714–7730.

Chen, D., Shen, H., Hu, M., Wang, J., Zhang, Y. and Dahlgren, R. A. (2018), *Legacy Nutrient Dynamics at the Watershed Scale: Principles, Modeling, and Implications*, Advances in Agronomy, pp. 237–313.

Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Howarth, R. W., Hedin, L. O., Perakis, S. S., Latty, E. F., Von Fischer, J. C., Elseroad, A. and Wasson, M. F.

(n.d.), ‘Global patterns of terrestrial biological nitrogen (N2) fixation in natural ecosystems’, *Global Biogeochemical Cycles* .

Commission, E. (2008), Groundwater Protection in Europe. THE NEW GROUNDWATER DIRECTIVE – CONSOLIDATING THE EU REGULATORY FRAMEWORK, Report.

Commission, E. (2010), The EU Nitrates Directive, Report.

De Lavenne, A. and Cudennec, C. (2019), ‘Assessment of freshwater discharge into a coastal bay through multi-basin ensemble hydrological modelling’, *Sci Total Environ* **669**, 812–820.

Diaz, R. J. and Rosenberg, R. (2008), ‘Spreading dead zones and consequences for marine ecosystems’, *Science* **321**(5891), 926–9.

Dupas, R., Delmas, M., Dorioz, J. M., Garnier, J., Moatar, F. and Gascuel-Odoux, C. (2015), ‘Assessing the impact of agricultural pressures on N and P loads and eutrophication risk’, *Ecological Indicators* **48**, 396–407.

Dupas, R., Jomaa, S., Musolff, A., Borchardt, D. and Rode, M. (2016), ‘Disentangling the influence of hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-hourly to decadal time scales’, *The Science of the total environment* **571**, 791–800.

Dupas, R., Minaudo, C., Gruau, G., Ruiz, L. and Gascuel-Odoux, C. (2018), ‘Multidecadal Trajectory of Riverine Nitrogen and Phosphorus Dynamics in Rural Catchments’, *Water Resources Research* **54**.

EUR-Lex, A. t. E. U. L. (1991), ‘COUNCIL DIRECTIVE of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources’.

EUR-Lex, A. t. E. U. L. (2000), ‘DIRECTIVE 2000/60/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 23 October 2000 establishing a framework for Community action in the field of water policy’.

EUR-Lex, A. t. E. U. L. (2006), ‘DIRECTIVE 2006/118/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of 12 December 2006 on the protection of groundwater against pollution and deterioration’.

EUR-Lex, A. t. E. U. L. (2013), 'Europäische Kommission gegen Französische Republik. Vertragsverletzung eines Mitgliedstaats - Richtlinie 91/676/EWG - Schutz der Gewässer vor Verunreinigung durch Nitrat aus landwirtschaftlichen Quellen - Ausweisung gefährdeter Gebiete - Überhöhter Nitratgehalt - Eutrophierung -Pflicht zur vierjährlichen Überprüfung. '.

EUR-Lex, A. t. E. U. L. (2018), 'Urteil des Gerichtshofs- „Vertragsverletzung eines Mitgliedstaats – Richtlinie 91/676/EWG – Art. 5 Abs. 5 und 7 – Anhang II Teil A Nrn. 1 bis 3 und 5 – Anhang III Nr. 1 Ziff. 1 bis 3 und Nr. 2 – Schutz der Gewässer vor Verunreinigung durch Nitrat aus landwirtschaftlichen Quellen – Unzulänglichkeit der geltenden Maßnahmen – Zusätzliche Maßnahmen oder verstärkte Aktionen – Fortschreibung des Aktionsprogramms – Begrenzung des Ausbringens – Ausgewogene Düngung – Zeiträume des Ausbringens – Fassungsvermögen von Behältern zur Lagerung von Dung – Ausbringen auf stark geneigten landwirtschaftlichen Flächen und auf gefrorenen oder schneebedeckten Böden“'.

European Environment Agency, E. (2018), European waters. Assessment of status and pressure, Report TH-AL-18-005-EN-N, European Environment Agency.

Fan, M., Lu, S., Jiang, R., Liu, X., Zeng, X., Goulding, K. W. T. and Zhang, F. (2007), 'Nitrogen input, 15N balance and mineral N dynamics in a rice–wheat rotation in southwest China', *Nutrient Cycling in Agroecosystems* **79**(3), 255–265.

Fenton, O., Schulte, R. P. O., Jordan, P., Lalor, S. T. J. and Richards, K. G. (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.

Fiori, A., Russo, D. and Di Lazzaro, M. (2009), 'Stochastic analysis of transport in hillslopes: Travel time distribution and source zone dispersion', *Water Resources Research* **45**(8).

Fovet, O., Ruiz, L., Faucheux, M., Molénat, J., Sekhar, M., Vertès, F., Aquilina, L., Gascuel-Odoux, C. and Durand, P. (2015), 'Using long time series of agricultural-derived nitrates for estimating catchment transit times', *Journal of Hydrology* **522**, 603–617.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R. and Vöosmarty, C. J. (2004), 'Nitrogen Cycles: Past, Present, and Future', *Biogeochemistry* **70**(2), 153–226.

Galloway, J. N., Schlesinger, W. H., Levy, H., Michaels, A. and Schnoor, J. L. (1995), 'Nitrogen fixation: Anthropogenic enhancement-environmental response', *Global Biogeochemical Cycles* **9**(2), 235–252.

Godsey, S. E., Aas, W., Clair, T. A., Wit, H. A. d., Fernandez, I. J., Kahl, J. S., Malcolm, I. A., Neal, C., Neal, M., Nelson, S. J., Norton, S. A., Palucis, M. C., Skjelkvåle, B. L., Soulsby, C., Tetzlaff, D. and Kirchner, J. W. (2010), 'Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions', *Hydrological Processes* **24**(12), 1660–1671.

Grant, S. B., Azizian, M., Cook, P., Boano, F. and Rippy, M. A. (2018), 'Factoring stream turbulence into global assessments of nitrogen pollution', *Science* **359**(6381), 1266–1268.

Green, C. T., Jurgens, B. C., Zhang, Y., Starn, J. J., Singleton, M. J. and Esser, B. K. (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.

Grimvall, A., Stalnacke, P. and Tonderski, A. (2000), 'Time scales of nutrient losses from land to sea - a European perspective', *Ecological Engineering* **14**(4), 363–371.

Hamilton, S. K. (2012), 'Biogeochemical time lags may delay responses of streams to ecological restoration', *Freshwater Biology* **57**, 43–57.

Hannappel, S., Köpp, C. and Bach, T. (2018), 'Charakterisierung des Nitratabbauvermögens der Grundwasserleiter in Sachsen-Anhalt', *Grundwasser* **23**(4), 311–321.

Hansen, B., Thorling, L., Schullehner, J., Termansen, M. and Dalgaard, T. (2017), 'Groundwater nitrate response to sustainable nitrogen management', *Sci Rep* **7**(1), 8566.

Harman, C. J. (2015), 'Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed', *Water Resources Research* **51**(1), 1–30.

Heidbüchel, I., Yang, J., Musolff, A., Troch, P., Ferré, T. and Fleckenstein, J. H. (2020), 'On the shape of forward transit time distributions in low-order catchments', *Hydrology and Earth System Sciences* **24**(6), 2895–2920.

Heinen, M. (2006), 'Simplified denitrification models: Overview and properties', *Geoderma* **133**(3-4), 444–463.

Hesser, F. B., Franko, U. and Rode, M. (2010), 'Spatially distributed lateral nitrate transport at the catchment scale', *J Environ Qual* **39**(1), 193–203.

Hirsch, R. M., Moyer, D. L. and Archfield, S. A. (2010), 'Weighted Regressions on Time, Discharge, and Season (WRTDS), with an Application to Chesapeake Bay River Inputs', *Journal of the American Water Resources Association* **46**(5), 857–880.

Howarth, R. W. (1998), 'An assessment of human influences on fluxes of nitrogen from the, journal = Nutrient Cycling in Agroecosystems', **52**(2/3), 213–223.

Howarth, R. W., Swaney, D. P., Boyer, E. W., Marino, R., Jaworski, N. and Goodale, C. (2006), 'The influence of climate on average nitrogen export from large watersheds in the Northeastern United States', *Biogeochemistry* **79**(1-2), 163–186.

Howden, N. J. K., Burt, T. P., Worrall, F., Mathias, S. and Whelan, M. J. (2011), 'Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater?', *Water Resources Research* **47**(6).

Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M. J. and Bieroza, M. (2010), 'Nitrate concentrations and fluxes in the River Thames over 140 years (1868-2008): Are increases irreversible?', *Hydrological Processes* **24**(18), 2657–2662.

Hunter, H., Fellows, C., Rassam, D., DeHayr, R., Pagendam, D., Conway, C., Bloesch, P. and N., B. (2006), Managing riparian lands to improve water quality: optimising nitrate removal via denitrification, Report.

Ilampooranan, I. (2019), Modeling Nutrient Legacies and Time Lags in Agricultural Landscapes: A Midwestern Case Study, Thesis.

IPCC (2007), Climate Change 2007: The Physical Science Basis. Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Report.

Johnson, C., Greg, A. and Ketterings, Q. (2005), 'Nitrogen-Basics - The Nitrogen cycle, Factsheet 2'.

Jones, R. R., Weyer, P. J., DellaValle, C. T., Inoue-Choi, M., Anderson, K. E., Cantor, K. P., Krasner, S., Robien, K., Freeman, L. E., Silverman, D. T. and Ward, M. H. (2016), 'Nitrate from Drinking Water and Diet and Bladder Cancer Among Postmenopausal Women in Iowa', *Environ Health Perspect* **124**(11), 1751–1758.

Kapoor, A.; Viraraghavan, T. (1997), 'Nitrate Removal from drinking water - review', *Journal of Environmental Engineering* **123**(4), 10.

Keeney, D. and Hatfield, J. (2008), *Chapter 1. The Nitrogen Cycle, Historical Perspective, and Current and Potential Future Concerns*, Elsevier, Amsterdam, Boston.

Kirchner, Feng and Neal (2000), 'Fractal stream chemistry and its implications for contaminant transport in catchments', *Nature* **403**(6769), 524–527.

Kumar, R., Hesse, F., Rao, P. S. C., Musolff, A., Jawitz, J. W., Sarrazin, F., Samaniego, L., Fleckenstein, J. H., Rakovec, O., Thober, S. and Attinger, S. (2020), 'Strong hydroclimatic controls on vulnerability to subsurface nitrate contamination across Europe', *Nat Commun* **11**(1), 6302.

Kumar, R., Samaniego, L. and Attinger, S. (2013), 'Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations', *Water Resources Research* **49**(1), 360–379.

Kunkel, R. and Wendland, F. (2006), 'Diffuse Nitrateinträge in die Grund- und Oberflächengewässer von Rhein und Ems- Ist-Zustands- und Maßnahmenanalysen', *Schriften des Forschungszentrums Jülich, Reihe Umwelt/ Environment* **62**, 143.

Lofrano, G. and Brown, J. (2010), 'Wastewater management through the ages: a history of mankind', *Sci Total Environ* **408**(22), 5254–64.

Löfgren, S., Gustafson, A., Steineck, S. and Stahlnacke, P. (1999), 'Agricultural development and nutrient flows in the Baltic states and Sweden after 1988', *Ambio* **28**(4), 320–327.

Lützow, M. v., Kogel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B. and Flessa, H. (2006), 'Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions - a review', *European Journal of Soil Science* **57**(4), 426–445.

Martin, C., Aquilina, L., Gascuel-Odoux, C., Molénat, J., Faucheux, M. and Ruiz, L. (2004), 'Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments', *Hydrological Processes* **18**(7), 1237–1254.

Marzadri, A., Dee, M. M., Tonina, D., Bellin, A. and Tank, J. L. (2017), 'Role of surface and subsurface processes in scaling N2O emissions along riverine networks', *Proc Natl Acad Sci U S A* **114**(17), 4330–4335.

McMahon, P. B., Dennehy, K. F., Bruce, B. W., Böhlke, J. K., Michel, R. L., Gurdak, J. J. and Hurlbut, D. B. (2006), 'Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States', *Water Resources Research* **42**(3).

Meals, D. W., Dressing, S. A. and Davenport, T. E. (2010), 'Lag Time in Water Quality Response to Best Management Practices: A Review', *J Environ Qual* **39**(1), 85–96.

Merz, C., Steidl, J. and Dannowski, R. (2009), 'Parameterization and regionalization of redox based denitrification for GIS-embedded nitrate transport modeling in Pleistocene aquifer systems', *Environmental Geology* **58**(7).

Molénat, J., Durand, P., Gascuel-Odoux, C., Davy, P. and Gruau, G. (2002), 'Mechanisms of Nitrate Transfer from Soil to Stream in an Agricultural Watershed of French Brittany', *Water, Air, and Soil Pollution* **133**(1/4), 161–183.

Musolff, A., Fleckenstein, J. H., Rao, P. S. C. and Jawitz, J. W. (2017), 'Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments', *Geophysical Research Letters* **44**(9), 4143–4151.

Musolff, A., Schmidt, C., Rode, M., Lischeid, G., Weise, S. M. and Fleckenstein, J. H. (2016), 'Groundwater head controls nitrate export from an agricultural lowland catchment', *Advances in Water Resources* **96**, 95–107.

Oehler, F., Bordenave, P. and Durand, P. (2007), 'Variations of denitrification in a farming catchment area', *Agriculture, Ecosystems Environment* **120**(2-4), 313–324.

Oenema, O., Witzke, H. P., Klimont, Z., Lesschen, J. P. and Velthof, G. L. (2009), 'Integrated assessment of promising measures to decrease nitrogen losses from agriculture in EU-27', *Agriculture, Ecosystems Environment* **133**(3-4), 280–288.

Otero, N., Torrentó, C., Soler, A., Menció, A. and Mas-Pla, J. (2009), 'Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain)', *Agriculture, Ecosystems Environment* **133**(1-2), 103–113.

Payn, R. A., Gooseff, M. N., Benson, D. A., Cirpka, O. A., Zarnetske, J. P., Bowden, W. B., McNamara, J. P. and Bradford, J. H. (2008), 'Comparison of instantaneous and constant-rate stream tracer experiments through non-parametric analysis of residence time distributions', *Water Resources Research* **44**(6), 718.

Pope, C. A., r., Burnett, R. T., Thun, M. J., Calle, E. E., Krewski, D., Ito, K. and Thurston, G. D. (2002), 'Lung cancer, cardiopulmonary mortality, and long-term exposure to fine particulate air pollution', *JAMA* **287**(9), 1132–41.

Ravishankara, A. R., Daniel, J. S. and Portmann, R. W. (2009), 'Nitrous oxide (N2O): the dominant ozone-depleting substance emitted in the 21st century', *Science* **326**(5949), 123–5.

Refsgaard, J. C., Auken, E., Bamberg, C. A., Christensen, B. S., Clausen, T., Dalgaard, E., Efferso, F., Ernstsen, V., Gertz, F., Hansen, A. L., He, X., Jacobsen, B. H., Jensen, K. H., Jorgensen, F., Jorgensen, L. F., Koch, J., Nilsson, B., Petersen, C., De Schepper, G., Schamper, C., Sorensen, K. I., Therrien, R., Thirup, C. and Viezzoli, A. (2014), 'Nitrate reduction in geologically heterogeneous catchments–a framework for assessing the scale of predictive capability of hydrological models', *Sci Total Environ* **468-469**, 1278–88.

Rinaldo, A., Beven, K. J., Bertuzzo, E., Nicotina, L., Davies, J., Fiori, A., Russo, D. and Botter, G. (2011), 'Catchment travel time distributions and water flow in soils', *Water Resources Research* **47**(7).

Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N. and Bemment, C. D. (2008), 'Nitrate attenuation in groundwater: A review of biogeochemical controlling processes', *Water Research* **42**(16), 4215–4232.

Rozemeijer, J. C. and Broers, H. P. (2007), 'The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, The Netherlands)', *Environ Pollut* **148**(3), 695–706.

Samaniego, L., Kumar, R. and Attinger, S. (2010), 'Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale', *Water Resources Research* **46**(5).

Schulten, H.-R. and Schnitzer, M. (1998), 'The chemistry of soil organic nitrogen: a review', *Biol Fertil Soils* **26**, 15.

Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G. and Mariotti, A. (2013), 'Long-term fate of nitrate fertilizer in agricultural soils', *Proceedings of the National Academy of Sciences of the United States of America* **110**(45), 18185–18189.

Smetacek, V. and Zingone, A. (2013), 'Green and golden seaweed tides on the rise', *Nature* **504**(7478), 84–88.

Smil, V. (2011), 'Nitrogen cycle and world food production', *World Agriculture* **2**(1), 4.

Sousa, M. R., Jones, J. P., Frind, E. O. and Rudolph, D. L. (2013), 'A simple method to assess unsaturated zone time lag in the travel time from ground surface to receptor', *J Contam Hydrol* **144**(1), 138–151.

Temkin, A., Evans, S., Manidis, T., Campbell, C. and Naidenko, O. V. (2019), 'Exposure-based assessment and economic valuation of adverse birth outcomes and cancer risk due to nitrate in United States drinking water', *Environ Res* **176**, 108442.

Tiedje, J. (1988), 'Ecology of denitrification and dissimilatory nitrate reduction to ammonium', *In A.J.B. Zehnder (ed), Environmental Microbiology of Anaerobes,* pp. 179–244.

Van Meter, K. J., Basu, N. B. and van Cappellen, P. (2017), 'Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins', *Global Biogeochemical Cycles* **31**(1), 2–23.

Van Meter, K. J., Basu, N. B., Veenstra, J. J. and Burras, C. L. (2016), 'The nitrogen legacy: Emerging evidence of nitrogen accumulation in anthropogenic landscapes', *Environmental Research Letters* **11**(3), 035014.

Van Meter, K. J., Van Cappellen, P. and Basu, N. B. (2018), 'Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico', *Science* **360**(6387), 427–430.

Vero, S. E., Basu, N. B., Van Meter, K., Richards, K. G., Mellander, P.-E., Healy, M. G. and Fenton, O. (2018), 'Review: the environmental status and implications of the nitrate time lag in Europe and North America', *Hydrogeology Journal* **26**(1), 7–22.

Visser, A., Broers, H. P., Heerdink, R. and Bierkens, M. F. P. (2009), 'Trends in pollutant concentrations in relation to time of recharge and reactive transport at the groundwater body scale', *Journal of Hydrology* **369**(3-4), 427–439.

Vitousek, P., Aber, C., Howarth, R. W., Likens, G. E., Matson, P., Schindler, D., Schlesinger, W. H. and Tilman, G. (1997), 'Human Alteration of the Global Nitrogen Cycle: Causes and Consequences', *Ecological Applications* **7(3)**, 17.

Vitousek, P. M., Hattenschwiler, S., Olander, L. and Allison, S. (2002), 'Nitrogen and nature', *Ambio* **31**(2), 97–101.

Wang, L., Stuart, M. E., Lewis, M. A., Ward, R. S., Skirvin, D., Naden, P. S., Collins, A. L. and Ascott, M. J. (2016), 'The changing trend in nitrate concentrations in major aquifers due to historical nitrate loading from agricultural land across England and Wales from 1925 to 2150', *The Science of the total environment* **542**, 694–705.

Webster, J. R., Mulholland, P. J., Tank, J. L., Valett, H. M., Dodds, W. K., Peterson, B. J., Bowden, W. B., Dahm, C. N., Findlay, S., Gregory, S. V., Grimm, N. B., Hamilton, S. K., Johnson, S. L., Marti, E., McDowell, W. H., Meyer, J. L., Morrall, D. D., Thomas, S. A. and Wollheim, W. M. (2003), 'Factors affecting ammonium uptake in streams - an inter-biome perspective', *Freshwater Biology* **48**(8), 1329–1352.

Wendland, F., Blum, A., Coetsiers, M., Gorova, R., Griffioen, J., Grima, J., Hinsby, K., Kunkel, R., Marandi, A., Melo, T., Panagopoulos, A., Pauwels, H., Ruisi, M., Traversa, P., Vermooten, J. S. A. and Walraevens, K. (2007), 'European aquifer typology: a practical framework for an overview of major groundwater composition at European scale', *Environmental Geology* **55**(1), 77–85.

Wilde, S., Hansen, C. and Bergmann, A. (2017), 'Nachlassender Nitratabbau im Grundwasser und deren Folgen – abgestufte modellgestützte Bewertungsansätze', *Grundwasser* **22**(4), 293–308.

Wollschläger, U., Attinger, S., Borchardt, D., Brauns, M., Cuntz, M., Dietrich, P., Fleckenstein, J. H., Friese, K., Friesen, J., Harpke, A., Hildebrandt, A., Jäckel, G., Kamjunke, N., Knöller, K., Kögler, S., Kolditz, O., Krieg, R., Kumar, R., Lausch, A., Liess, M., Marx, A., Merz, R., Mueller, C., Musolff, A., Norf, H., Oswald, S. E., Rebmann, C., Reinstorf, F., Rode, M., Rink, K., Rinke, K., Samaniego, L., Vieweg, M., Vogel, H.-J., Weitere, M., Werban, U., Zink, M. and Zacharias, S. (2017), 'The Bode hydrological observatory: A platform for integrated, interdisciplinary hydro-ecological research within the TERENO Harz/Central German Lowland Observatory', *Environmental Earth Sciences* **76**(1), 725.

Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F. and Fleckenstein, J. H. (2018), 'Exploring the Dynamics of Transit Times and Subsurface Mixing in a Small Agricultural Catchment', *Water Resources Research* **54**(3), 2317–2335.

Zacharias, S., Bogena, H., Samaniego, L., Mauder, M., Fuß, R., Pütz, T., Frenzel, M., Schwank, M., Baessler, C., Butterbach-Bahl, K., Bens, O., Borg, E., Brauer, A., Dietrich, P., Hajnsek, I., Helle, G., Kiese, R., Kunstmann, H., Klotz, S., Munch, J. C., Papen, H., Priesack, E., Schmid, H. P., Steinbrecher, R., Rosenbaum, U., Teutsch, G. and Vereecken, H. (2011), 'A Network of Terrestrial Environmental Observatories in Germany', *Vadose Zone Journal* **10**(3), 955.

Zambrano-Bigiarini, M. and Rojas, R. (2013), 'A model-independent Particle Swarm Optimisation software for model calibration', *Environmental Modelling Software* **43**, 5–25.

Zhang, Y.-C., Slomp, C. P., Broers, H. P., Passier, H. F. and Cappellen, P. V. (2009), 'Denitrification coupled to pyrite oxidation and changes in groundwater quality in a shallow sandy aquifer', *Geochimica et Cosmochimica Acta* **73**(22), 6716–6726.

Zveryaev, I. I. (2004), 'Seasonality in precipitation variability over Europe', *Journal of Geophysical Research* **109**(D5).

Study 1: Trajectories of nitrate input and output in three nested catchments along a land use gradient

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SE carried out the analysis, interpreted the data and wrote the paper. AM designed the study and co-wrote the paper. RK contributed discharge modeling results and atmospheric deposition and co-wrote the paper. All authors contributed to the study design and helped finalize the paper.

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Trajectories of nitrate input and output in three nested catchments along a land use gradient

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Abstract. Increased anthropogenic inputs of nitrogen (N) to the biosphere during the last few decades have resulted in increased groundwater and surface water concentrations of N (primarily as nitrate), posing a global problem. Although measures have been implemented to reduce N inputs, they have not always led to decreasing riverine nitrate concentrations and loads. This limited response to the measures can either be caused by the accumulation of organic N in the soils (biogeochemical legacy) – or by long travel times (TTs) of inorganic N to the streams (hydrological legacy). Here, we compare atmospheric and agricultural N inputs with long-term observations (1970–2016) of riverine nitrate concentrations and loads in a central German mesoscale catchment with three nested subcatchments of increasing agricultural land use. Based on a data-driven approach, we assess jointly the N budget and the effective TTs of N through the soil and groundwater compartments. In combination with long-term trajectories of the C–Q relationships, we evaluate the potential for and the characteristics of an N legacy.

We show that in the 40-year-long observation period, the catchment ($270\,km^2$) with 60 % agricultural area received an N input of 53 437 t, while it exported 6592 t, indicating an overall retention of 88 %. Removal of N by denitrification could not sufficiently explain this imbalance. Log-normal travel time distributions (TTDs) that link the N input history to the riverine export differed seasonally, with modes spanning 7–22 years and the mean TTs being systematically shorter during the high-flow season as compared to low-flow conditions. Systematic shifts in the C–Q relationships were noticed over time that could be attributed to strong changes in N inputs resulting from agricultural intensification before 1989, the break-down of East German agriculture after 1989 and the seasonal differences in TTs. A chemostatic export regime of nitrate was only found after several years of stabilized N inputs. The changes in C–Q relationships suggest a dominance of the hydrological N legacy over the biogeochemical N fixation in the soils, as we expected to observe a stronger and even increasing dampening of the riverine N concentrations after sustained high N inputs. Our analyses reveal an imbalance between N input and output, long time-lags and a lack of significant denitrification in the catchment. All these suggest that catchment management needs to address both a longer-term reduction of N inputs and shorter-term mitigation of today's high N loads. The latter may be covered by interventions triggering denitrification, such as hedgerows around agricultural fields, riparian buffers zones or constructed wetlands. Further joint analyses of N budgets and TTs covering a higher variety of catchments will provide a deeper insight into N trajectories and their controlling parameters.

1 Introduction

In terrestrial, freshwater and marine ecosystems nitrogen (N) species are essential and often limiting nutrients (Webster et al., 2003; Elser et al., 2007). Changes in strength of their different sources like atmospheric deposition, wastewater inputs and agricultural activities caused major changes in the N cycle (Webster et al., 2003). In particular, two major innovations from the industrial age accelerated anthropogenic inputs of reactive N species into the environment: artificial

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N fixation and the internal combustion engine (Elser, 2011). Therefore the amount of reactive N that enters into the element's biospheric cycle has been doubled in comparison to the preindustrial era (Smil, 1999; Vitousek et al., 1997). However, the different input sources of N show diverging rates of change over time and space. While the atmospheric emissions of N oxides and ammonia have strongly declined in Europe since the 1980s (EEA, 2014), the agricultural N input through fertilizers declined but is still at a high level (Federal Ministry for the Environment and Federal Ministry of Food, 2012). In the cultural landscape of western countries, most of the N emissions in surface and groundwater bodies stem from diffuse agricultural sources (Bouraoui and Grizzetti, 2011; Dupas et al., 2013).

The widespread consequences of these excessive N inputs are significantly elevated concentrations of dissolved inorganic nitrogen (DIN) in groundwater and connected surface waters (Altman and Parizek, 1995; Sebilo et al., 2013; Wassenaar, 1995), leading to increased riverine DIN fluxes (Dupas et al., 2016) and causing the ecological degradation of freshwater and marine systems. This degradation is caused by the ability of N species to increase primary production and to change food web structures (Howarth et al., 1996; Turner and Rabalais, 1991). In particular, the coastal marine environments, where nitrate (NO_3) is typically the limiting nutrient, are affected by these eutrophication problems (Decrem et al., 2007; Prasuhn and Sieber, 2005).

Several initiatives in the form of international, national and federal regulations have been implemented, aiming at an overall reduction of N inputs into the terrestrial system and its transfer to the aquatic system. In the European Union, guidelines are provided to its member states for national programs of measures and evaluation protocols through the Nitrate Directive (CEC, 1991) and the Water Framework Directive (CEC, 2000).

The evaluation of interventions showed that policy-makers still struggle to set appropriate goals for water quality improvement, particularly in heavily human-impacted watersheds. Studies in Europe and the United States showed that interventions like reduced N inputs mainly in agricultural land use do not immediately result in declining riverine NO_3–N concentrations (Bouraoui and Grizzetti, 2011; Sprague et al., 2011; Howden et al., 2011) and fluxes (Worrall et al., 2009), although fast responding headwaters have been reported as well (Rozemeijer et al., 2014).

In Germany considerable progress has been achieved in the improvement of water quality, but the diffuse water pollution from agricultural sources continues to be of concern (Wendland et al., 2005). This limited response to mitigation measures can partly be explained by nutrient legacy effects, which stem from an accumulation of excessive fertilizer inputs over decades creating a strongly dampened response between the implementation of measures and water quality improvement (van Meter and Basu, 2015). Furthermore, the multi-year travel times (TTs) of nitrate through the soil and groundwater compartments cause large time lags (Howden et al., 2010; Melland et al., 2012) that can substantially delay the riverine response to applied management interventions. For a targeted and effective water quality management, we therefore need a profound understanding of the processes and controls of time lags of N from the source to groundwater and surface water bodies. Bringing together N balancing and accumulation with estimations of N TTs from application to riverine exports can contribute to this lack of knowledge.

Estimation of the water or solute TTs is essential for predicting the retention, mobility and fate of solutes, nutrients and contaminants at catchment scale (Jasechko et al., 2016). Time series of solute concentrations and loads that cover both input to the geosphere and the subsequent riverine export can be used not only to determine TTs (van Meter and Basu, 2017), but also to quantify mass losses in the export as well as the behavior of the catchment's retention capacity (Dupas et al., 2015). Knowledge on the TT of N would therefore allow understanding on the N transport behavior, defining the fate of injected N mass into the system and its contribution to riverine N response. The mass of N being transported through the catchment storage can be referred to as hydrological legacy. Data-driven or simplified mechanistic approaches have often been used to derive stationary and seasonally variable travel time distributions (TTDs) using input and output signals of conservative tracers or isotopes (Jasechko et al., 2016; Heidbüchel et al., 2012) or chloride concentrations (Kirchner et al., 2000; Bennettin et al., 2015). Recently, van Meter and Basu (2017) estimated the solute TTs for N transport at several stations across a catchment located in Southern Ontario, Canada, showing decadal timelags between input and riverine exports. Moreover, systematic seasonal variations in the NO_3–N concentrations have been found, which were explained by seasonal shifts in the N delivery pathways and connected time lags (van Meter and Basu, 2017). Despite the determination of such seasonal concentration changes and age dynamics, there are relatively few studies focussing on their long-term trajectory under conditions of changing N inputs (Dupas et al., 2018; Howden et al., 2010; Minaudo et al., 2015; Abbott et al., 2018). Seasonally differing time shifts, resulting in changing intra-annual concentration variations are of importance to aquatic ecosystems' health and their functionality. Seasonal concentration changes can also be directly connected to changing concentration–discharge (C–Q) relationships – a tool for classifying observed solute responses to changing discharge conditions and for characterizing and understanding anthropogenic impacts on solute input, transport and fate (Jawitz and Mitchell, 2011; Musolff et al., 2015). Investigations of temporal dynamics in the C–Q relationship are a valuable addition to approaches based on N balancing only (e.g., Abbott et al., 2018), when evaluating the effect of management interventions.

The C–Q relationships can be on the one hand classified in terms of their pattern, characterized by the slope b of the ln(C)–ln(Q) regression (Godsey et al., 2009): with enrichment ($b > 0$), dilution ($b < 0$) or constant ($b \approx 0$) patterns (Musolff et al., 2017). On the other hand, C–Q relationships can be classified according to the ratio between the coefficients of variation of concentration (CV_C) and of discharge (CV_Q; Thompson et al., 2011). This export regime can be either chemodynamic (CV_C / $CV_Q > 0.5$) or chemostatic, where the variance of the solute load is more dominated by the variance in discharge than the variance in concentration (Musolff et al., 2017). Both patterns and regimes are dominantly shaped by the spatial distribution of solute sources (Seibert et al., 2009; Basu et al., 2010; Thompson et al., 2011; Musolff et al., 2017). High source heterogeneity and consequently high concentration variability is thought to be characteristic for nutrients under pristine conditions (Musolff et al., 2017; Basu et al., 2010). It was shown in Germany and the United States that catchments under intensive agricultural use evolve from chemodynamic to more chemostatic behavior regarding nitrate export (Thompson et al., 2011; Dupas et al., 2016). Several decades of human N inputs seem to dampen the discharge-dependent concentration variability, resulting in chemostatic behavior, where concentrations are largely independent of discharge variations (Dupas et al., 2016). Also Thompson et al. (2011) stated observational and model-based evidence of an increasing chemostatic response of nitrate with increasing agricultural intensity. This shift in the export regimes is caused by a long-term homogenization of the nitrate sources in space and/or at depth within soils and aquifers (Dupas et al., 2016; Musolff et al., 2017). However, effective denitrification in the subsurface can create concentration variability over depths and flow path age and thus has been shown to result in chemodynamic exports even with intensive agriculture (van der Velde et al., 2010; Musolff et al., 2017). Long-term N inputs lead to a loading of all flow paths in the catchment with mobile fractions of N and by that the formation of a hydrological N legacy (van Meter and Basu, 2015) and chemostatic riverine N exports. On the other hand, excessive fertilizer input is linked to the above-mentioned buildup of legacy N stores in the catchment, changing the export regime from a supply- to a transport-limited chemostatic one (Basu et al., 2010). This legacy is manifested as a biogeochemical legacy in the form of increased, less mobile, organic N content within the soil (Worral et al., 2015; van Meter and Basu, 2015; van Meter et al., 2017a). This type of legacy buffers biogeochemical variations, so that management measures can only show their effect if the buildup source gets substantially depleted (Basu et al., 2010).

Depending on the catchment configuration, both forms of legacy – hydrological and biogeochemical – can exist with different shares of the total N stored in a catchment (van Meter et al., 2017a). However, biogeochemical legacy is hard to distinguish from hydrological legacy when looking at time lags between N input and output or at catchment-scale N budgets only (van Meter and Basu, 2015). One way to better disentangle the N legacy types is applying the framework of C–Q relationships as defined by Jawitz and Mitchell (2011) and Musolff et al. (2015, 2017). In the case of a hydrological legacy, strong changes in fertilizer inputs (such as increasing inputs in the initial phase of intensification and decreasing inputs as a consequence of measures) will temporarily increase spatial concentration heterogeneity (e.g., comparing young and old water fractions in the catchment storage), and therefore also shift the export regime to more chemodynamic conditions. On the other hand, a dominant biogeochemical legacy will lead to sustained concentration homogeneity in the N source zone in the soils and to an insensitivity of the riverine N export regime to fast changes in inputs.

Common approaches to quantify catchment-scale N budgets and to characterize legacy or to derive TTs are either based on data-driven (Worral et al., 2015; Dupas et al., 2016) or on forward-modeling (van Meter and Basu, 2015; van Meter et al., 2017a) approaches. So far, data-driven studies focused either solely on N budgeting and legacy estimation or on TTs. Here, we conducted a joint data-driven assessment of the catchment-scale N budget, the potential and characteristics of an N legacy, and the estimation of TTs of the riverine exported N. We utilized the trajectory of agricultural catchments in terms of C–Q relationships, their changes over longer timescales and their potential evolution to a chemostatic export regime. The novel combination of the long-term N budgeting, TT estimation and C–Q trajectory will help understanding of the differentiation between biogeochemical and hydrological legacy, both reasons for missed targets in water quality management. This study will address the following research questions:

1. How high is the retention potential for N of the studied mesoscale catchment and what are the consequences in terms of a potential buildup of an N legacy?

2. What are the characteristics of the TTD for N that links change in the diffuse anthropogenic N inputs to the geosphere and their observable effect in riverine NO_3–N concentrations?

3. What are the characteristics of a long-term trajectory of C–Q relationships? Is there an evolution to a chemostatic export regime that can be linked to a biogeochemical or hydrological N legacy?

To answer these questions, we used time series of water quality data over four decades, available from a mesoscale German catchment, as well as estimated N input to the geosphere. We linked N input and output on annual and intra-annual timescales through consideration of N budgeting and the use of TTDs. This input–output assessment uses time series of the Holtemme catchment (270 km^2) with its three nested subcatchments along a land use gradient from pristine mountainous headwaters to a lower basin with intensive agriculture and associated increases in fertilizer applications. This catchment, with its pronounced increase in anthropogenic impacts from up- to downstream, is quite typical for many mesoscale catchments in Germany and elsewhere. Moreover, this catchment offers a unique possibility to analyze the system response to strong changes in fertilizer usage in East Germany before and after reunification. Thereby, we anticipate that our improved understanding gained through this study in these catchment settings is transferable to similar regions. In comparison to spatially and temporally integrated water quality signals stemming solely from the catchment outlet, the higher spatial resolution with three stations and the unique length of the monitoring period (1970–2016) allow for a more detailed investigation about the fate of N, and consequently findings may provide guidance for effective water quality management.

2 Data and methods

2.1 Study area

The Holtemme catchment ($270\,km^2$) is a subcatchment of the Bode River basin, which is part of the TERENO (TERrestrial ENvironmental Observatories) Harz/Central German Lowland Observatory (Fig. 1). The catchment, as part of the TERENO project, exhibits strong gradients in topography, climate, geology, soils, water quality, land use and level of urbanization (Wollschläger et al., 2017). Due to the low water availability and the risk of summer droughts that might be further exacerbated by a decrease in summer precipitation and increased evaporation with rising temperatures, the region is ranked as highly vulnerable to climate change (Schröter et al., 2005; Samaniego et al., 2018). With these conditions, the catchment is representative of other German and central European regions showing similar vulnerability (Zacharias et al., 2011). The observatory is one of the meteorologically and hydrologically best-equipped catchments in Germany (Zacharias et al., 2011; Wollschläger et al., 2017) and provides long-term data for many environmental variables including water quantity (e.g., precipitation, discharge) and water quality at various locations.

The Holtemme catchment has its spring at 862 m a.s.l. in the Harz Mountains and extends to the northeast to the central German lowlands with an outlet at 85 m a.s.l. The long-term annual mean precipitation (1951–2015) shows a remarkable decrease from a colder and humid climate in the Harz Mountains (1262 mm) down to the warmer and dryer climate of the central German lowlands on the leeward side of the mountains (614 mm; Rauthe et al., 2013; Frick et al., 2014). Discharge time series, provided by the State Office of Flood Protection and Water Management (LHW) of Saxony-Anhalt show a mean annual discharge at the outlet in Nienhagen of $1.5\,m^3\,s^{-1}$ (1976–2016), corresponding to $172\,mm\,a^{-1}$.

The geology of the catchment is dominated by late Paleozoic rocks in the mountainous upstream part that are largely covered by Mesozoic rocks as well as Tertiary and Quaternary sediments in the lowlands (Frühauf and Schwab, 2008; Schuberth, 2008). Land use of the catchment changes from forests in the pristine, mountainous headwaters to intensive agricultural use in the downstream lowlands (EEA, 2012). According to Corine Land Cover (CLC) from different years (1990, 2000, 2006, 2012), the land use change over the investigated period is negligible. Overall 60 % of the catchment is used for agriculture, with a crop rotation of wheat, barley, triticale, rye and rapeseed (Yang et al., 2018b), while 30 % is covered by forest (EEA, 2012). Urban land use occupies 8 % of the total catchment area (EEA, 2012) with two major towns (Wernigerode, Halberstadt) and several small villages. Two wastewater treatment plants (WWTPs) discharge into the river. The town of Wernigerode had its WWTP within its city boundaries until 1995, when a new WWTP was put into operation about 9.1 km downstream in a smaller village, called Silstedt, replacing the old WWTP. The WWTP in Halberstadt was not relocated but renovated in 2000. Nowadays, the total nitrogen load (TNb) in cleaned water is approximately $67.95\,kg\,d^{-1}$ (WWTP Silstedt: NO_3–N load $55\,kg\,d^{-1}$) and $35.09\,kg\,d^{-1}$ (WWTP Halberstadt: NO_3–N load $6.7\,kg\,d^{-1}$; mean daily loads 2014; Müller et al., 2018). Referring to the last 5 years of observations, NO_3–N load from wastewater made up 17 % of the total observed NO_3–N flux at the midstream station (see below) and 11 % at the downstream station. Despite this point source N input, the major nitrate contribution is due to inputs from agricultural land use (Müller et al., 2018), which is predominant in the mid- and downstream part of the catchment (Fig. 1).

The Holtemme River has a length of 47 km. Along the river, the LHW of Saxony-Anhalt maintains long-term monitoring stations, providing the daily mean discharge and the biweekly to monthly water quality measurements covering roughly the last four decades (1970–2016). Three of the water quality stations along the river were selected to represent the characteristic land use and topographic gradient in the catchment. From up- to downstream, the stations are named Werbat, Derenburg and Nienhagen (Fig. 1) and in the following are referred to as upstream, midstream and downstream. The pristine headwaters upstream represent the smallest (6 % of total catchment area) and the steepest area among the three selected subcatchments with a mean topographic slope about 3 times higher than the downstream parts (DGM25; Table 1). According to the latest Corine Land Cover dataset (CLC, 2012; EEA, 2012), the land use is characterized by forest only. The larger midstream subcatchment that represents one-third of the total area is still dominated by forests, but with growing anthropogenic impact due to increasing agricultural land use and the town of Wernigerode. More than half of the agricultural land in this subcatchment is artificially drained with open ditches (midstream: 38 %, downstream: 82 %) and tube drains (midstream: 62 %, downstream: 18 %; LHW, 2011; Table 1; Fig. S1.1 in the Supplement). The largest subcatchment (61 %) constitutes the downstream lowland areas which are predominantly covered

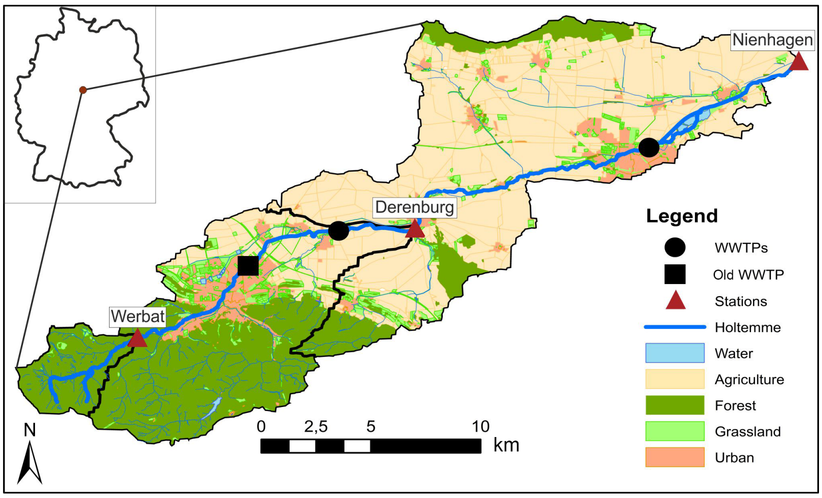

Figure 1. Map of the Holtemme catchment with the selected sampling locations. Map created from ATKIS data.

by Chernozems (Schuberth, 2008), representing one of the most fertile soils within Germany (Schmidt, 1995). Hence, the agricultural land use in this subcatchment is the highest (81 %) in comparison to the two upstream subcatchments (EEA, 2012).

2.2 Nitrogen input

The main N sources were quantified over time, assisting the data-based input–output assessment to address the three research questions regarding the N budgeting, effective TTs and C–Q relationships in the catchment.

A recent investigation in the study catchment by Müller et al. (2018) showed that the major nitrate contribution stems from agricultural land use and the associated application of fertilizers. The quantification of this contribution is the N surplus (also referred to as agricultural surplus) that reflects N input that is in excess of crop and forage needs. For Germany there is no consistent dataset available for the N surplus that covers all land use types and is sufficiently resolved in time and space. Therefore, we combined the available agricultural N input (including atmospheric deposition) dataset with another dataset of atmospheric N deposition rates for the nonagricultural land.

The annual agricultural N input for the Holtemme catchment was calculated using two different datasets of agricultural N surplus across Germany provided by the University of Gießen (Bach and Frede, 1998; Bach et al., 2011). Surplus data (kg N ha^{-1} a^{-1}) were available at the federal state level for 1950–2015 and at the county level for 1995–2015, with an accuracy level of 5 % (see Bach and Frede, 1998, for more details). We used the data from the overlapping time period (1995–2015) to downscale the state-level data (state: Saxony-Anhalt) to the county level (county: Harzkreis). Both (the state level and the aggregated county to state level) datasets show high correspondence with a correlation (R^2) of 0.85, but they differ slightly in their absolute values (by 6 % of the mean annual values). The mean offset of 3.85 kg N ha^{-1} a^{-1} was subtracted from the federal state level data to yield the surplus in the county before 1995.

Both of the above datasets account for the atmospheric deposition, but only on agricultural areas. For other nonagricultural areas (forest and urban landscapes), the N source stemming from atmospheric deposition was quantified based on datasets from the Meteorological Synthesizing Centre – West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP). The underlying dataset consists of gridded fields of EU-wide wet and dry atmospheric N depositions from a chemical transport model that assimilates different observational records on atmospheric chemicals (e.g., Bartnicky and Benedictow, 2017; Bartnicky and Fagerli, 2006). This dataset is available with annual time-steps since 1995, and with data every 5 years between 1980 and 1995. Data between the 5-year time steps were linearly interpolated to obtain annual estimates of N deposition between 1980 and 1995. For years prior to 1980, we made use of global gridded estimates of atmospheric N deposition from the three-dimensional chemistry-transport model (TM3) for the year 1860 (Dentener, 2006; Galloway et al., 2004). In absence of any other information, we performed a linear interpolation of the N deposition estimates between 1860 and 1980.

To quantify the net N fluxes to the soil nonagricultural land use types, the terrestrial biological N fixation had to be added to the atmospheric deposition. Based on a global inventory of terrestrial biological N fixation in natural ecosystems, Cleveland et al. (1999) estimated the mean uptake for temperate (mixed, coniferous or deciduous) forests and (tall/medium or short) grassland as 16.04 kg N ha^{-1} a^{-1} and

Table 1. General information on the study area, including input–output datasets; n – number of observations, Q – discharge.

	Upstream	Midstream	Downstream
n Q	16 132	–	12 114
n nitrate–N (NO_3–N)	646	631	770
Period of NO_3–N time series	1972–2014	1970–2011	1976–2016
Subcatchment area (km^2)	15.06	88.50	165.22
Cumulative catchment area (km^2)	15.06	103.60	268.80
Stream length (km)	1.5	19.3	24.4
Mean topographic slope (°)	9.82	7.52	2.55
Mean topographic slope in nonforested area (°)	–	3.2	1.9
Land use (Corine Land Cover; EEA, 2012)			
Forest land use (%)	100	56	11
Urban land use (%)	–	17	8
Agricultural land use (%)	–	27	81
Fraction of agricultural area artificially drained (%)	–	59.1	20.5

2.7 $kg\,N\,ha^{-1}\,a^{-1}$, respectively. The atmospheric deposition and biological fixation for the different nonagricultural land uses were added to the agricultural N surplus to achieve the total N input per area. In contrast to the widely applied term net anthropogenic nitrogen input (NANI), we do not account for wastewater fluxes in the N input but rather focus on the diffuse N input and connected flow paths, where legacy accumulation and time lags between input and output potentially occur.

2.3 Nitrogen output

2.3.1 Discharge and water quality time series

Discharge and water quality observations were used to quantify the N load and to characterize the trajectory of NO_3–N concentrations and the C–Q trajectories in the three subcatchments.

The data for water quality (biweekly to monthly) and discharge (daily) from 1970 to 2016 were provided by the LHW of Saxony-Anhalt. The biweekly to monthly sampling was done at gauging stations defining the three subcatchments. The datasets cover a wide range of instream chemical constituents including major ions, alkalinity, nutrients and in situ measured parameters (pH, O_2, water temperature, electrical conductivity). As this study only focuses on N species, we restricted the selection of parameters to nitrate (NO_3; Fig. 2), nitrite (NO_2; Fig. S1.2.2) and ammonium (NH_4; Fig. S1.2.1).

Discharge time series at daily timescales were measured at two of the water quality stations (upstream, downstream; Fig. 2). Continuous daily discharge series are required to calculate flow-normalized concentrations (see the following Sect. 2.3.2 for more details). To derive the discharge data for the midstream station and to fill measurement gaps at the other stations (2 % upstream, 3 % downstream), we used simulations from a grid-based distributed mesoscale hydrological model mHM (Samaniego et al., 2010; Kumar et al., 2013). Daily mean discharge was simulated for the same time frame as the available measured data. We used a model setup similar to Müller et al. (2016) with robust results capturing the observed variability of discharge in the nearby studied catchments. We note that the discharge time series were used as weighting factors in the later analysis of flow-normalized concentrations. Consequently it is more important to capture the temporal dynamics than the absolute values. Nonetheless, we performed a simple bias correction method by applying the regression equation of simulated and measured values to reduce the simulated bias of modeled discharge. After this revision, the simulated discharges could be used to fill the gaps of measured data. The midstream station (Derenburg) for the water quality data is 5.6 km upstream of the next gauging station. Therefore, the nearest station (Mahndorf) with simulated and measured discharge data was used to derive the bias correction equation that was subsequently applied to correct the simulated discharge data at the midstream station, assuming the same bias between modeled and observed discharges at the gauging station.

2.3.2 Weighted regression on time, discharge, and season (WRTDS) and wastewater correction

The software package "Exploration and Graphics for RivEr Trends" (EGRET) in the R environment by Hirsch and DeCicco (2019) was used to estimate daily concentrations of NO_3–N utilizing "Weighted Regressions on Time, Discharge, and Season" (WRTDS). The WRTDS method allows the interpolation of an irregularly sampled concentration to a regular series at a daily timescale using a flexible statistical representation for every day of the discharge record and proved to provide robust estimates (Hirsch et al., 2010; van Meter and Basu, 2017). In brief, a regression model based on the predictors discharge and time (to represent long-term

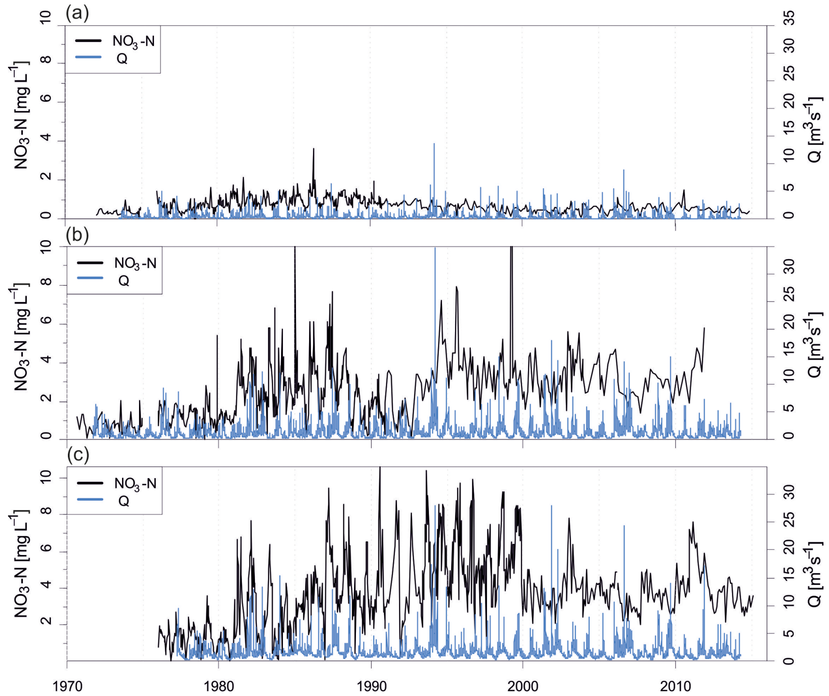

Figure 2. NO_3–N concentration and discharge (Q) time series: upstream **(a)**, midstream **(b)** and downstream **(c)**.

trend and seasonal component) is fitted for each day of the flow record with a flexible weighting of observations based on their time, seasonal and discharge "distance" (Hirsch et al., 2010). Results are daily concentrations and fluxes as well as daily flow-normalized concentrations and fluxes. Flow normalization uses the probability distribution of discharge of the specific day of the year from the entire discharge time series. More specifically, the flow-normalized concentration is the average of the same regression model for a specific day applied to all measured discharge values of the corresponding day of the year. While the non-flow-normalized concentrations are strongly dependent on the discharge, the flow-normalized estimations provide a more unbiased, robust estimate of the concentrations with a focus on changes in concentration and fluxes independent of interannual discharge variability (Hirsch et al., 2010). To account for uncertainty in the regression analysis of annual and seasonal flow-normalized concentration and fluxes, we used the block bootstrap method introduced by Hirsch et al. (2015). We derived the 5th and 95th percentile of annual flow-normalized concentration and flux estimates with a block length of 200 d and 10 replicates. The results are utilized to communicate uncertainty in both the N budgeting and the resulting TT estimation.

The study of Müller et al. (2018) indicated the dominance of N from diffuse sources in the Holtemme catchment but also stressed the impact of wastewater-borne nitrate during low-flow periods. Because our purpose was to balance and compare N input and outputs from diffuse sources only, the provided annual flux of total N from the two WWTPs was therefore used to correct flow-normalized fluxes and concentrations derived from the WRTDS assessment. We argue that the annual wastewater N flux is robust enough to correct the flow-normalized concentrations, but it does not allow for the correction of measured concentration data on a specific day. Both treatment plants provided snapshot samples of both NO_3–N and total N fluxes to derive the fraction of N that is discharged as NO_3–N into the stream. This fraction is 19 % for the WWTP Halberstadt (384 measurements between January 2014 to July 2016) and 81 % for Silstedt (eight measurements from February 2007 to December 2017). We argue that the fraction of N leaving as NH_4, NO_2 and N_{org} does not interfere with the NO_3–N flux in the river due to the limited stream length and therefore nitrification potential of the Holtemme River impacted by wastewater (see also Sect. S1.2.3). We related the wastewater-borne NO_3–N flux to the flow-normalized daily flux of NO_3–N from the WRTDS method to get a daily fraction of wastewater NO_3–N in the river that we used to correct the flow-normalized concentrations. Note that this correction was applied to the midstream station from 1996 on, when the Silstedt treatment plant was taken to operation. In the downstream station, we additionally applied the correction from the Halberstadt treatment plant, renovated in the year 2000. Before that, we assume that wastewater-borne N dominantly leaves the treatment plants as NH_4-N (see also Fig. S1.2.1).

Based on the daily resolved flow-normalized and wastewater-corrected concentration and flux data, descriptive statistical metrics were calculated on an annual timescale. Seasonal statistics of each year were also calculated for winter (December, January, February), spring (March, April, May), summer (June, July, August) and fall (September, October, November). Note that statistics for the winter season incorporate December values from the calendar year before.

Following Musolff et al. (2015, 2017), the ratio of $\mathrm{CV}_C / \mathrm{CV}_Q$ and the slope (b) of the linear relationship between $\ln(C)$ and $\ln(Q)$ were used to characterize the export pattern and the export regimes of NO_3–N along the three study catchments.

2.4 Input–output assessment: nitrogen budgeting and effective travel times

The input–output assessment is needed to estimate the retention potential for N in the catchment as well as to link temporal changes in the diffuse anthropogenic N inputs to the observed changes in the riverine NO_3–N concentrations. The stream concentration of a given solute, e.g., as shown by Kirchner et al. (2000), is assumed at any time as the convolution of the TTD and the rainfall concentration throughout the past. This study applies the same principle for the N input as incoming time series that, when convolved with the TTD, yields the stream concentration time series. We selected a log-normal distribution function (with two parameters, μ and σ) as a convolution transfer function, based on a recent study by Musolff et al. (2017), who successfully applied this form of a transfer function to represent TTs. The two free parameters were obtained through optimization based on minimizing the sum of squared errors between observed and simulated N exports. The form of selected transfer function is in line with Kirchner et al. (2000) stating that exponential TTDs are unlikely at catchment scale, but rather a skewed, long-tailed distribution would be likely. Note that we used the log-normal distribution as a transfer function between the temporal patterns of input (N load per area) and flow-normalized concentrations on an annual timescale only and not as a flux-conservative transfer function. TTDs were inferred based on median annual and median seasonal flow-normalized concentrations and the corresponding N input estimates. To account for the uncertainties in the flow-normalized concentration input, we additionally derive TTDs for the confidence bands of the concentrations (5th and 95th percentile) estimated through the bootstrap method (see Sect. 2.3.2 for more details). Here, we assumed that the width of the confidence bands provided for the annual concentrations also applies to the seasonal concentrations of the same year.

3 Results

3.1 Input assessment

In the period from 1950 to 2015, the Holtemme catchment received a cumulative diffuse N input (excluding the wastewater point sources) of 80 055 t with the majority of this associated with agriculture-related N application (74 %). Within the period when water quality data were available, the total sum is 63 396 t (1970–2015), with 76 % agricultural contribution. The N input showed a remarkable temporal variability (see Fig. 6; purple, dashed line). From 1950 to 1976, the input was characterized by a strong increase (slope of linear increase = 2.4 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$ per year) with a maximum annual, agricultural input of 132.05 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$ (1976), which is 20 times the agricultural input in 1950. After more than 10 years of high but more stable inputs, the N surplus dropped dramatically with the peaceful reunification of Germany and the collapse of the established agricultural structures in East Germany (1989–1990; Gross, 1996). In the time period afterwards (1990–1995), the N surplus was only one-sixth (20 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$) of the previous input. After another 8 years of increased agricultural inputs (1995–2003) of around 50 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$, the input slowly decreased, with a mean slope of -0.8 $\mathrm{kg\,N\,ha^{-1}\,a^{-1}}$ per year, but showed distinctive changes in the input between the years.

The median N input upstream (53 $\mathrm{t\,a^{-1}}$) is less than 7 % of the total catchment input (760 $\mathrm{t\,a^{-1}}$). Hence, the input to the upstream area was only minor in comparison to the ones further downstream that are dominated by agriculture.

As land use change over the investigated period is negligible, the N input from biological fixation stayed constant.

3.2 Output assessment

3.2.1 Discharge time series and WRTDS results on decadal statistics

Discharge was characterized by a strong seasonality throughout the entire data record, which divided the year into a high-flow season (HFS) during winter and spring, accounting for two-thirds of the annual discharge and a low-flow season (LFS) during summer and fall. Average discharge in the subcatchments is mainly a reflection of the strong spatial precipitation gradient across the study area being on the leeward side of the Harz Mountains. The upstream subcatchment contributed 21 % of the median discharge measured at the downstream station (Table 2). The midstream station, representing the cumulated discharge signal from the up- and midstream subcatchments, accounted for 82 % of the median annual discharge at the outlet. Although the upstream subcatchment had the highest specific discharge, the major fraction of total discharge (61 %) was generated in the midstream subcatchment. The seasonality in discharge was also dominated by this major midstream contribution, especially

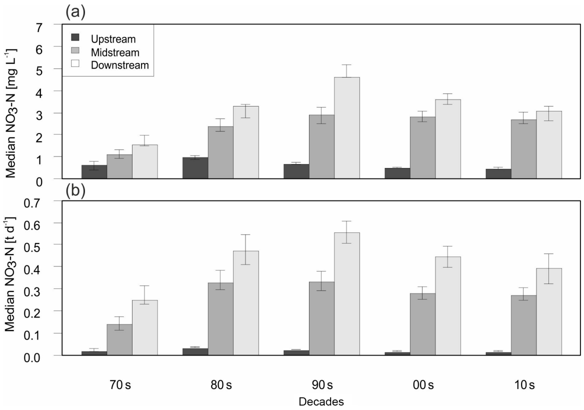

Figure 3. Flow-normalized median NO_3–N concentrations **(a)** and NO_3–N loads **(b)** for each decade of the time series and the three stations. Whiskers refer to the 5th and 95th percentiles of the WRTDS estimations.

during high-flow conditions, and vice versa: especially during HFSs, the median downstream contribution was less than 10 %, while during low-flow periods, the downstream contribution accounted for up to 33 % (summer).

The flow-normalized NO_3–N concentrations in each subcatchment showed strong differences in their overall levels and temporal patterns over the four decades (Fig. 3a; see also Figs. 2 and 6 for details). The lowest decadal concentration changes and the earliest decrease in concentrations were found in the pristine catchment. Median upstream concentrations were highest in the 80s (1987), with a reduction of the concentrations to about one-half in the latter decades. Over the entire period, the median upstream concentrations were smaller than 1 mg L^{-1}, so that the described changes are small compared to the NO_3–N dynamics of the more downstream stations. High changes over time were observed in the two downstream stations with a tripling of concentrations between the 1970s and 1990s, when maximum concentrations were reached. While median concentrations downstream decreased slightly after this peak (1995/1996), the ones at the midstream station (peak: 1998) stayed constantly high. At the end of the observation period, at the outlet (downstream), the median annual concentrations did not decrease below 3 mg L^{-1} of NO_3–N, a level that was exceeded after the 1970s. The differences in NO_3–N concentrations between the pristine upstream and the downstream station evolved from an increase by a factor of 3 in the 1970s to a factor of 7 after the 1980s.

Calculated loads (Fig. 3b) also showed a drastic change between the beginning and the end of the time series. The daily upstream load contribution was below 10 % of the total annual export at the downstream station in all decades and then the estimates decreased from 9 % (1970s) to 4 % (2010s). The median daily load between the 1970s and 1990s tripled at the midstream station (0.1 to 0.3 t d^{-1}) and more than doubled downstream (0.2 to 0.5 t d^{-1}). In the 1990s, the Holtemme River exported on average more than 0.5 t d^{-1} of NO_3–N, which, related to the agricultural area in the catchment, translates into more than 3.1 kg N km^{-2} d^{-1} (maximum 13.4 kg N ha^{-1} a^{-1} in 1995).

3.3 Input–output balance: N budget

We jointly evaluated the estimated N inputs and the exported NO_3–N loads to enable an input–output balance. This comparison on the one hand allowed for an estimation of the catchment's retention potential and on the other hand enabled us to estimate future exportable loads.

The load stemming from the most upstream, pristine catchment accounted for less than 10 % of the exported riverine load at the outlet. To focus on the anthropogenic impacts, the data from the upstream station are not discussed on its own in the following. At the midstream station, a total sum of input of 16 441 t compared to 4109 t of exported NO_3–N for the overlapping time period of input and output was analyzed (1970–2011). The midstream subcatchment received 73 % (Table 3) more N mass than it exported at the same time. Note that the exported N is not necessarily the N applied in the same period due to the temporal offset, as is discussed later in detail. With the assumption that 43 % (agricultural N input of subcatchment N input) of the diffuse input resulted from agriculture, the subcatchment exported 616 kg N ha^{-1} (537–719 kg N ha^{-1}) from agricultural areas. The cumulated N input from the entire catchment (measured downstream) from 1976 to 2015 (overlapping time of input and output) was 53 437 t, while the riverine export in the same time frame was only 12 % (6 kg N ha^{-1} a^{-1}; 11 %–14 %), implying an agricultural export of 370 kg N ha^{-1} (325–415 kg N ha^{-1}; Fig. 4). This mass discrepancy between input and output translates into a retention rate in the entire Holtemme catchment of 88 % (86 %–89 %). In relation to the entire subcatchment area (not only agricultural land use), the annual retention rate of NO_3–N was around 28 kg N ha^{-1} a^{-1} (27–30 kg N ha^{-1} a^{-1}) in the midstream subcatchment and 59 kg N ha^{-1} a^{-1} (59–59 kg N ha^{-1} a^{-1}) in the flatter and more intensively cultivated downstream subcatchment.

3.4 Effective TTs of N

We approximated the effective TTs for all seasonal NO_3–N concentration trajectories at the midstream and downstream stations by fitting the log-normal TTDs (Fig. 5; Table 4). Note that the upstream station was not used here due to the lack of temporally resolved input data on the atmospheric N deposition (estimated linear input increase between 1950 and 1979). In general, the optimized distributions were able to sufficiently capture the time lag and smoothing between the input and output concentrations ($R^2 \geq 0.72$; see also Figs. S2.1 and S2.2). Systematic differences between stations

Table 2. Descriptive statistics on discharge at the three observation points; LFS – low-flow season (June–November), HFS – high-flow season (December–May).

	Upstream	Midstream	Downstream
Median discharge ($m^3\,s^{-1}$)	0.23	0.9	1.1
Mean specific discharge ($mm\,a^{-1}$)	768	411	178
LFS subcatchment contribution (%)	17	53	30
HFS subcatchment contribution (%)	21	69	10

Table 3. Nitrogen retention potentials derived for the midstream and downstream subcatchment based on flow-normalized fluxes. Numbers in brackets refer to the 5th and 95th percentiles of the WRTDS flux estimation.

	Midstream	Downstream
Retention cumulative (%)	75 (71–78) (Up- + midstream)	88 (86–89) (Up- + mid- + downstream)
Retention subcatchment (%)	73 (68–76)	94 (94–95)
Retention per year ($N\,kg\,a^{-1}$)	251 589 (235 778–263 833)	917 823 (968 085–979 679)
Retention per area ($N\,kg\,a^{-1}\,ha^{-1}$)	28.43 (26.64–29.81)	58.82 (58.60–59.30)

and seasons can be observed, best represented by the mode of the distributions (peak TTs). The average deviation between the best- and worst-case estimation of the fitted TTDs from their respective average value was only 4 % with respect to the mode of the distributions (Table 4).

The TTDs for all seasons taken together showed longer TTs for the midstream in comparison to the downstream station. The comparison of the TTD modes for the different seasons at the midstream station showed distinctly differing peak TTs between 11 years (spring) and 22 years (fall), which represented a doubling of the peak TT. The fastest times appeared in the HFSs while modes of the TTDs appeared longer in the LFSs. Note that the shape factor σ of the effective TTs also changed systematically: the HFS spring exhibited a higher shape factor than those of the other seasons. This refers to a change in the coefficient of variation of the distributions at the midstream station from 0.6 in spring to 0.2 in fall.

The modes of the fitted distributions for the downstream station for each season were shorter than the ones at the midstream station. The mode of the TTs ranged between 7 years (spring) and 15 years (winter, fall). The shape factors of the fitted TTDs ranged between 0.8 (spring) and 0.3 (summer) for the downstream station. In summary, HFS spring in both subcatchments had shorter TTDs than the other seasons and the midstream subcatchment showed longer TTDs than downstream.

3.5 Seasonal NO_3–N concentrations and C–Q relationships over time

As described above, the Holtemme catchment showed a pronounced seasonality in discharge conditions, producing the HFS in December–May (winter + spring) and the LFS in June–November (summer + fall). Therefore, changes in the seasonal concentrations of NO_3–N also reflect in the annual C–Q relationship. Analyzing the changing seasonal dynamics therefore provide a deeper insight into N trajectories in the Holtemme catchment.

In the pristine upstream catchment, no temporal changes in the seasonal differences of riverine NO_3–N concentrations could be found (Fig. 6a). Also the C–Q relationship (Fig. 6d) showed a steady pattern (moderate accretion), with the highest concentrations in the HFSs, i.e., winter and spring. The ratio of $CV_C\,/\,CV_Q$ indicates a chemostatic export regime and changed only marginally (amplitude of 0.2) over time.

At the midstream station (Fig. 6b), the early 1970s showed an export pattern with highest concentration during HFSs similar to the upstream catchment, but with a general increase in concentrations from 1970 to 1995. During the 1980s, the increase in concentrations in the HFS was faster than in the LFS, which changed the C–Q pattern to a strongly positive one ($b_{max} = 0.42$, 1987; red to orange symbols in Fig. 6e). This development was characterized by a tripling of intra-annual amplitudes (C_{spring}–C_{fall}) of up to $2.4\,mg\,L^{-1}$ (1987). With a lag of around 10 years, in the 1990s the LFSs also exhibit a strong increase in concentrations ($C_{max} = 3.1\,mg\,L^{-1}$, 1998, Fig. 6b). The midstream concentration time series shows bimodality. The C–Q relationships (Fig. 6e) evolved from an intensifying accretion pattern in the 1970s and 1980s (red to orange symbols in Fig. 6e) to a constant pattern between C and Q in the 1990s and afterwards (yellow symbols). The $CV_C\,/\,CV_Q$ increased during the 1970s and strongly decreased afterwards by 0.4 between 1984 and 1995, showing a trajectory starting from a more chemostatic to a chemodynamic and then back to a chemostatic export regime.

At the downstream station (Fig. 6c) the concentrations in the HFSs were found to be comparable to the ones observed

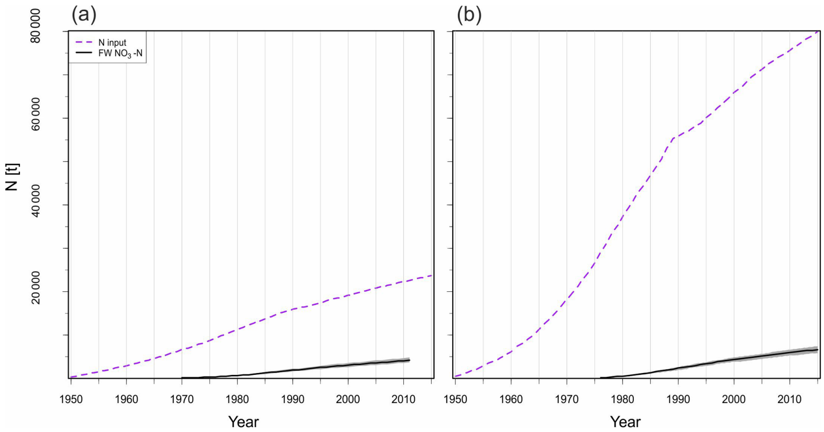

Figure 4. Cumulative annual diffuse N inputs to the catchment and measured cumulative NO_3–N exported load over time for mid-stream **(a)** and downstream **(b)** stations. Shaded grey confidence bands refer to the 5th and 95th percentile of the WRTDS flux estimation.

Table 4. Best-fit parameters of the log-normal TTDs for the N input and output responses. Parameters in brackets are derived by using the 5th and 95th percentiles of the bootstrapped flow-normalized concentration estimates.

	Parameter	All seasons	Winter	Spring	Summer	Fall
Midstream	μ	3.0 (3.0–3.1)	3.0 (3.0–3.1)	2.7 (2.7–2.7)	3.0 (3.0–3.1)	3.1 (3.1–3.2)
	σ	0.3 (0.3–0.4)	0.3 (0.3–0.4)	0.6 (0.6–0.6)	0.3 (0.3–0.4)	0.2 (0.1–0.3)
	Mode (years)	18.5 (16.7–20.5)	17.8 (16.0–20)	11.1 (10.3–10.3)	18.9 (17.1–20.8)	21.9 (20.8–23.9)
	R^2	0.93 (0.91–0.91)	0.88 (0.83–0.86)	0.81 (0.72–0.80)	0.91 (0.90–0.90)	0.87 (0.86–0.86)
Downstream	μ	2.8 (2.8–2.9)	3.0 (3.0–3.0)	2.6 (2.7–2.7)	2.7 (2.7–2.7)	2.9 (2.9–2.9)
	σ	0.6 (0.5–0.6)	0.5 (0.5–0.5)	0.8 (0.7–0.8)	0.3 (0.2–0.3)	0.5 (0.5–0.5)
	Mode (years)	12.4 (12.1.–13.1)	15.1 (14.7–16.4)	7.4 (7.9–8.3)	13.8 (13.6–14.2)	14.7 (14.1–14.9)
	R^2	0.94 (0.89–0.92)	0.92 (0.82–0.92)	0.84 (0.83–0.92)	0.90 (0.84–0.88)	0.81 (0.72–0.77)

at the midstream station. As seen at the midstream station, the N concentrations during the LFSs peaked with a delay compared to those of the HFSs. The resulting intra-annual amplitude showed a maximum of 2.4 mg L^{-1} in the 1980s (1983–1984), with strongly positive C–Q patterns (b_{max} = 0.4, 1985; red symbols in Fig. 6f). In contrast to the bimodal concentration trends in the mid- and downstream HFSs, the LFSs downstream showed an unimodal pattern peaking around 1995–1996 with concentrations above 6 mg L^{-1} NO_3–N (C_{max} =6.9 mg L^{-1}). In the 1990s, the concentrations in the LFSs were higher than those noticed in the HFSs, causing a switch to a dilution C–Q pattern (orange symbols in Fig. 6f). Due to the strong decline of LFS concentrations after 1995 (Fig. 6c), the dilution pattern evolved to a constant C–Q pattern (yellow symbols in Fig. 6f) from the 2000s onward. After an initial phase with chemostatic conditions (1970s), the CV_C / CV_Q strongly increased to a chemodynamic export regime in the 1980s (max. CV_C / CV_Q = 0.8, 1984). Later on CV_C / CV_Q declined by 0.8 between 1984 and 2001 (min. CV_C / CV_Q = 0.03), which indicates the C–Q trajectory is coming back to a chemostatic export nitrate regime.

4 Discussion

4.1 Catchment-scale N budgeting

Based on the calculated budgets of N inputs and riverine N outputs for the three subcatchments within the Holtemme catchment, we discuss here differences between the subcatchments and potential main reasons for the missing part in the N budget: (1) permanent N removal by denitrification or (2) the buildup of N legacies.

The N load stemming from the most upstream, pristine catchment accounted for less than 10 % of the exported annual load over the entire study period. This minor contribution can be attributed to the lack of agricultural and urban land use as dominant sources for N. Consequently, the N export from the upstream subcatchment was dominantly controlled by N inputs from atmospheric deposition and biological fixation.

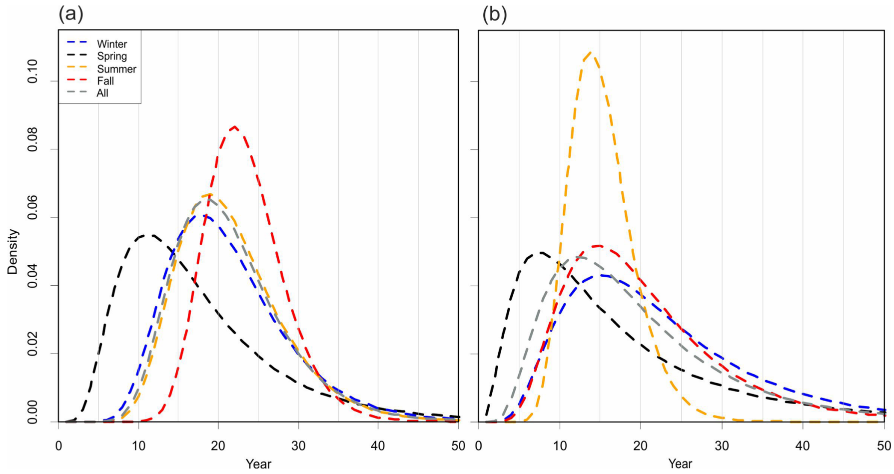

Figure 5. Seasonal variations in the fitted log-normal distributions of effective travel times between nitrogen input and output responses for midstream **(a)** and downstream **(b)** stations.

The total input over the whole catchment area was quantified as more than 53 000 t N (1976–2015) and, compared to the respective output over the same time period, yielded export rates of 25 % (22 %–29 %) at the midstream and 12 % (11 %–14 %) at the downstream station (Table 3), respectively. There can be several reasons for the difference in export rates between the two subcatchments. The most likely ones are due to differences in discharge, topography and denitrification capacity among the subcatchments, which are discussed in the following.

Load export of N from agricultural catchments is assumed to be mainly discharge-controlled (Basu et al., 2010). Many solutes show a lower variance in concentrations compared to the variance in streamflow, which makes the flow variability a strong surrogate for load variability (Jawitz and Mitchell, 2011). This can also be seen in the Holtemme catchment, which evolved over time to a more chemostatic export regime with high N loads (Fig. 6b). The highest N export and lowest retention were observed in the midstream subcatchment, where the overall highest discharge contribution can be found.

Besides discharge quantity, we argue that the midstream subcatchment favors a more effective export of NO_3–N. The higher percentage of artificial drainage by tiles and ditches (59 % vs. 21 %; Sect. S1.1) as well as the steeper terrain slopes (3.2° vs. 1.9°) in the nonforested area of the midstream catchment promotes rapid, shallow subsurface flows. These flow paths can more directly connect agricultural N sources with the stream and in turn cause elevated instream NO_3–N concentrations (Yang et al., 2018a). In addition, the steeper surface topography suggests a deeper vertical infiltration (Jasechko et al., 2016) and therefore a wider range of flow paths of different ages than those observed in the flatter terrain areas, and vice versa: fewer drainage installations, a flatter terrain and thus in general shallower flow paths may decrease the N export efficiency (increase the retention) potential downstream.

The only process able to permanently remove N input from the catchment is denitrification in soils, aquifers (Seitzinger et al., 2006; Hofstra and Bouwman, 2005), and at the stream-aquifer interface such as in the riparian (Vidon and Hill, 2004; Trauth et al., 2018) and hyporheic zones (Vieweg et al., 2016). As the riverine exports are signals of the catchment or subcatchment processes, integrated in time and space, separating a buildup of an N legacy from a permanent removal via denitrification is difficult. A clear separation of these two key processes, however, would be important for decision makers as both have different implications for management strategies and different future impacts on water quality. Even if groundwater quality measurements that indicate denitrification were available, using this type of local information for an effective catchment-scale estimation of N removal via denitrification would be challenging (Green et al., 2016; Otero et al., 2009; Refsgaard et al., 2014). Therefore, we discuss the denitrification potential in the soils and aquifers of the Holtemme catchment based on a local isotope study and a literature review of studies in similar settings. A strong argument against a dominant role of denitrification is provided by Müller et al. (2018) for the study area. On the basis of a monitoring of nitrate isotopic compositions in the Holtemme River and in tributaries, Müller et al. (2018) stated that denitrification played no or only a minor role in the catchment. However, we still see the need to carefully check the potential of denitrification to explain the input–output imbalance considering other studies.

If 88 % of the N input (53 437 t, dominantly agricultural input) to the catchment between 1976 and 2015 (39 years) were denitrified in the soils of the agricultural area (161 km^2), it

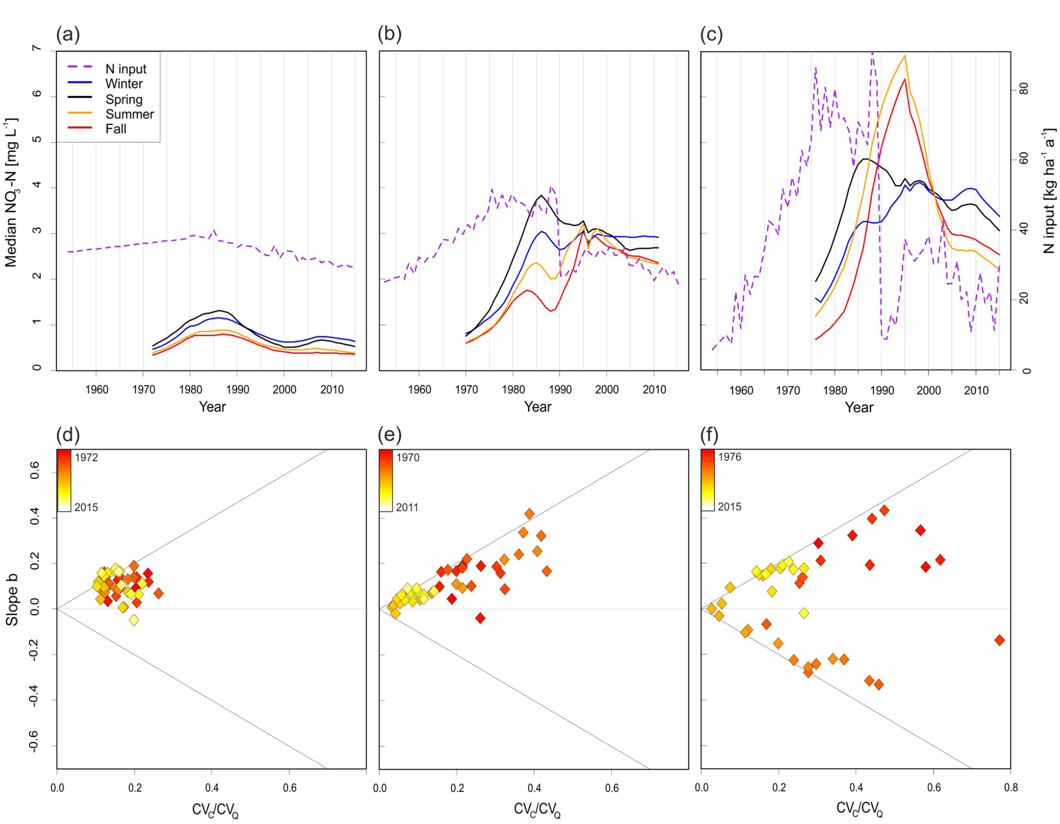

Figure 6. Annual N input (referring to the whole catchment, second y axis) to the catchment and measured median NO_3–N concentrations in the stream (first y axis) over time at three different locations: upstream **(a, d)**, midstream **(b, e)**, downstream **(c, f)**. Lower panels show plots of slope b vs. CV_C / CV_Q for NO_3–N for the three subcatchments following the classification scheme provided in Musolff et al. (2015). The x axis gives the coefficient of variation of concentrations (C) relative to the coefficient of variation of discharge (Q). The y axis gives the slope b of the linear ln(C)–ln(Q) relationship. Colors indicate the temporal evolution from 1970 to 2015 along a gradient from red to yellow.

would need a rate of 74.9 kg N ha^{-1} a^{-1}. Considering the derived TTs, denitrification of the convolved input would need a slightly lower rate (66.7 kg N ha^{-1} a^{-1}, 1976–2015). Denitrification rates in soils for Germany (NLfB, 2005) have been reported to range between 13.5 and 250 kg N ha^{-1} a^{-1}, with rates larger than 50 kg N ha^{-1} a^{-1} may be found in carbon-rich and waterlogged soils in the riparian zones near rivers and in areas with fens and bogs (Kunkel et al., 2008). As water bodies and wetlands make up only 1 % of the catchment's land use (Fig. 1; EEA, 2012), and consequently the extent of waterlogged soils is negligible, denitrification rates larger than 50 kg N ha^{-1} a^{-1} are highly unlikely. In a global study, Seitzinger et al. (2006) assumed a rate of 14 kg N ha^{-1} a^{-1} as denitrification for agricultural soils. With this rate only 19 % of the retained (88 %) study catchment's N input can be denitrified. On the basis of a simulation with the modeling framework GROWA-WEKU-MEPhos, Kuhr et al. (2014) estimate very low to low denitrification rates, of 9–13 kg N ha^{-1} a^{-1}, for the soils of the Holtemme catchment. Based on the above discussion we find for our study catchment, the denitrification in the soils, including the riparian zone, may partly explain the retention of NO_3–N, but there is unlikely to be a single explanation for the observed imbalance between input and output.

Regarding the potential for denitrification in groundwater, the literature provides denitrification rate constants of a first-order decay process between 0.01 and 0.56 a^{-1} (van Meter et al., 2017b; van der Velde et al., 2010; Wendland et al., 2005). We derived the denitrification constant by distributing the input according to the fitted log-normal distribution of TTs, assuming a first-order decay along the flow paths (Kuhr et al., 2014; Rode et al., 2009; van der Velde, 2010). The denitrification of the 88 % of input mass would require a rate constant of 0.14 a^{-1}. This constant is in the range of values reported by the abovementioned modeling studies. However, in a regional evaluation of groundwater quality, Hannappel et al. (2018) provide strong evidence that denitrification in the groundwater of the Holtemme catchment is not a dominant retention process. More specifically, Hannappel et al. (2018) assess denitrification in over 500 wells in the federal state of Saxony-Anhalt for nitrate, oxygen, iron concentrations and redox potential and connect the results to the hydrogeological units. Within the hard rock aquifers that are present in our study area, only 0 %–16 % of the wells showed signs of denitrification. Taking together the local evidence from the nitrate isotopic composition (Müller et al., 2018), the regional evidence from groundwater quality (Hannappel et al., 2018), and the rates provided in literature for soils and groundwater, we argue that the role of denitrification in groundwater is unlikely to explain the observed imbalance between N input and output.

Lastly, assimilatory NO_3 uptake in the stream may be a potential contributor to the difference between input and output. But even with maximal NO_3 uptake rates as reported by Mulholland et al. (2004; $0.14\,g\,N\,m^{-2}\,d^{-1}$) or Rode et al. (2016; max. $0.27\,g\,N\,m^{-2}\,d^{-1}$, estimated for a catchment adjacent to the Holtemme), the annual assimilatory uptake in the river would be a minor removal process, estimated to contribute only 3 % of the 88 % discrepancy between input and output. According to the rates reported by Mulholland et al. (2008; max. $0.24\,g\,N\,m^{-2}\,d^{-1}$), the Holtemme River would need an area 45 times larger to be able to denitrify the retained N. Therefore denitrification in the stream can be excluded as a dominant removal process.

In summary, the precise differentiation between the accumulation of an N legacy and removal by denitrification cannot be fully resolved on the basis of the available data. Also a mix of both may account for the missing 88 % (86 %–89 %, downstream) or 75 % (71 %–78 %, midstream) in the N output. Input–output assessments with time series from different catchments, as presented in van Meter and Basu (2017), covering a larger variety of catchment characteristics, hold promise for an improved understanding of the controlling parameters and dominant retention processes.

The fact that current NO_3 concentration levels in the Holtemme River still show no clear sign of a significant decrease calls for a continuation of the NO_3 concentration monitoring, best extended by additional monitoring in soils and groundwater. Despite strong reductions in agricultural N input since the 1990s, the annual N surplus (e.g., $818\,t\,a^{-1}$, 2015) is still much higher than the highest measured export ($load_{max} = 216\,t\,a^{-1}$, 1995) from the catchment. Hence, the difference between input and output is still high with a mean factor of 6 during the past 10 years (mean factor of 7 with the shifted input according to 12 years of TT). Consequently, either the legacy of N in the catchment keeps growing instead of getting depleted or the system relies on a potentially limited denitrification capacity. Denitrification may irreversibly consume electron donors like pyrite for autolithotrophic denitrification or organic carbon for heterotrophic denitrification (Rivett et al., 2008).

Based on the analyses and literature research, there is evidence but no proof of the fate of missing N, although a directed water quality management would need a clearer differentiation between N mass that is stored or denitrified. However, neither tolerating the growing buildup of legacies nor relying on finite denitrification represents sustainable and adapted agricultural management practices. Hence, future years will also face increased NO_3–N concentrations and loads exported from the Holtemme catchment.

4.2 Linking effective TTs, concentrations and C–Q trajectories with N legacies

Based on our data-driven analyses, we propose the following conceptual model (Fig. 7) for N export from the Holtemme catchment, which is able to plausibly connect and synthesize the available data and findings on TTs, concentration trajectories and C–Q relationships and allows for a discussion on the type of N legacy.

Over the course of a year, different subsurface flow paths are active, which connect different subsurface N source zones with different source strength (in terms of concentration and flux) to streams. These flow paths transfer water and NO_3–N to streams, predominantly from shallower parts of the aquifer when water tables are high during HFSs and exclusively from deeper groundwater during low flows in LFSs (Rozemeijer and Broers, 2007; Dupas et al., 2016; Musolff et al., 2016). This conceptual model allows us to explain the observed intra-annual concentration patterns and the distinct clustering of TTs into low-flow and high-flow conditions. Furthermore, it can explain the mobilization of nutrients from spatially distributed NO_3–N sources by temporally varying flow-generating zones (Basu et al., 2010). Spatial heterogeneity of solute source zones can be a result of downward migration of the dominant NO_3–N storage zone in the vertical soil–groundwater profile (Dupas et al., 2016). Moreover, a systematic increase in the water age with depths would, if denitrification in groundwater takes place uniformly, lead to a vertical concentration decrease. Based on the stable hydroclimatic conditions without changes in land use, topography or the river network during the observation period, long-term changes in flow paths in the catchment are unlikely. Assuming that flow contributions from the same depths do not change between the years, the observed decadal changes in the seasonal concentrations cannot be explained by a stronger imprint of denitrification with increasing water age. Under such conditions one would expect a more steady seasonality in concentrations and C–Q patterns over time with NO_3–N concentrations that are always similarly high in HFSs and similarly low in LFSs, which we do not see in the data. Additionally, previous findings have indicated no or only a minor role of denitrification in the catchment (Hannappel et al., 2018; Kunkel et al., 2008; Müller et al., 2018). In line with Dupas et al. (2016) we instead argue that the vertical migration of a temporally changing NO_3–N

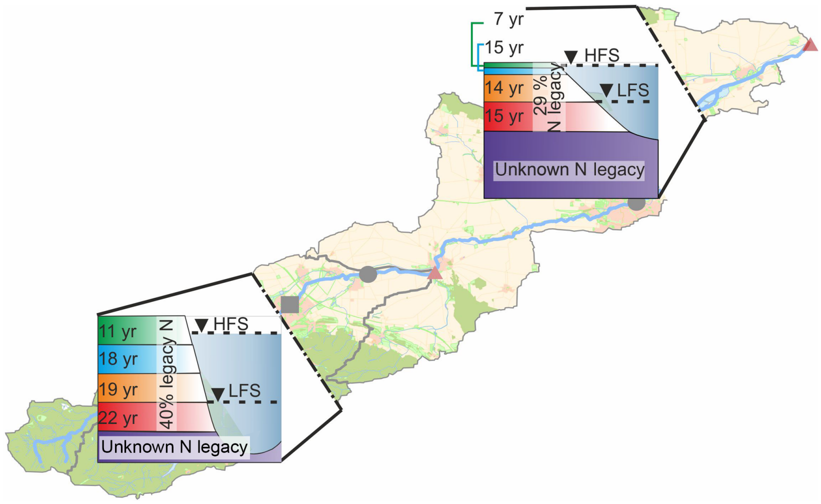

Figure 7. Conceptual model of nitrogen legacy and exports from the midstream and the downstream catchments. The four stacked boxes refer to the dominant source layer of nitrate that is activated with changing water level and catchment wetness during low-flow seasons fall (red) and autumn (orange) as well as high-flow seasons winter (blue) and spring (green). Numbers in the boxes refer to peak travel times of each season. The percentages refer to the N imbalance between input and output explainable by travel times (hydrological legacy). Background map created from ATKIS data.

input is one of the most likely plausible explanations for our observations with regard to N budgets, concentrations and C–Q trajectories.

The faster TTs observed at the midstream station during HFSs are assumed to be dominated by discharge from shallow (near-surface) source zones. This zone is responsible for the fast response of instream NO_3–N concentrations to the increasing N inputs (1970s to mid-1980s). This faster lateral transfer, especially in spring (shortest TT), may be also enhanced by the presence of artificial drainage structures such as tiles and ditches. In line with the longer TTs during the LFSs, low-flow NO_3–N concentrations were less impacted in the 1970s to mid-1980s as deeper parts of the aquifer were still less affected by anthropogenic inputs. With time and a downward migration of the high NO_3–N inputs before 1990, those deeper layers and thus longer flow paths also delivered increased concentrations to the stream (1990s). In parallel with the increasing low-flow concentrations (in the 1990s), the spring concentrations of NO_3 decreased, caused by a depletion of the shallower NO_3–N stocks (see also Dupas et al., 2016; Thomas and Abbott, 2018). This depletion of the stocks was a consequence of drastically reduced N input after the German reunification in 1989. This conceptual model of N trajectories is supported by the changing C–Q relationship over time. The seasonal cycle started with increasing NO_3–N maxima during high flows and minima during low flows, since shallow source zones were getting loaded with NO_3 first. Consequently, the accretion pattern was intensified in the first decades, accompanied by an increase in CV_C / CV_Q. The resulting positive C–Q relationship on a seasonal basis was found in many agricultural catchments worldwide (e.g., Aubert et al., 2013; Martin et al., 2004; Mellander et al., 2014; Rodríguez-Blanco et al., 2015; Musolff et al., 2015). However, after several years of deeper migration of the N input, the catchment started to exhibit a chemostatic NO_3 export regime (after the 1990s), which was manifested in the decreasing CV_C / CV_Q ratio. This stationarity could have been caused by a vertical equilibration of NO_3–N concentrations in all seasonally activated depth zones of the soils and aquifers after a more stable long-term N input after 1995. According to the 50th percentile of the derived TT, after 20 years only 50 % of the input had been released at the midstream station. Therefore without any strong changes in input, the chemostatic conditions caused by the uniform, vertical NO_3–N contamination will remain. At the same time, this chemostatic export regime supports the hypothesis of an accumulated N legacy rather than denitrification as the dominant reason for the imbalance between input and output.

At the downstream station, the riverine NO_3 concentrations during high flows were dominated by inputs from the midstream subcatchment, which explains the similarity with the midstream bimodality in concentrations as well as the comparable TTs. The reason for these dominating midstream flows is the strong precipitation gradient resulting in a runoff gradient on the leeward side of the mountains. During low flows, the downstream subcatchment can contribute much more to discharge and therefore to the overall N export. During the LFSs, we observed higher NO_3–N concentrations with a unimodal trajectory and shorter TTs compared to the midstream subcatchment. We argue that the lowland subcatchment supports higher water levels and thus faster TTs during the low flows. Greater prevalence of young streamflow in flatter lowland terrain was also described by Jasechko et al. (2016). But besides the earlier peak time during low flows, the concentration was found to be much higher than at the midstream station. To cause such high intra-annual concentration changes, the downstream NO_3–N load contribution, e.g., during the concentration peak of 1995–1996, had to be high: the summer season export was 46 t, which is more than twice the median contribution during summer (22 t). A more effective export from the downstream catchment happened mainly during LFSs, which is also supported by the narrower TTD (small shape factor σ) in the summer and fall (Fig. 5b). The difference between the 75th and 25th percentiles (5 years) was also the smallest of all seasons in the summer at the downstream station. This could be one reason for the high concentrations in comparison to the midstream catchment and during the HFSs.

In contrast to the midstream catchment, the C–Q trajectory in the downstream catchment temporarily switched from an enrichment pattern, dominated by the high concentration during high flows from the midstream catchment to a dilution pattern and a chemodynamic regime, when the high concentrations in the LFS from the downstream subcatchment dominated. Although the low-flow concentrations were slowly decreasing in the 2000s and 2010s, the downstream catchment also finally evolved to a chemostatic NO_3 export regime, as was noticed at the midstream station (Fig. 6f).

Our findings support the evolution from chemodynamic to chemostatic behavior in managed catchments, but also emphasize that changing inputs of N into the catchment can lead to fast-changing export regimes even in relatively slowly reacting systems. Our findings expand on previous knowledge (Basu et al., 2010; Dupas et al., 2016) as we could show systematic interannual C–Q changes that are in line with a changing input and a systematic seasonal differentiation of TTs. Although our study showed chemostatic behavior towards the end of the observation period (mid- and downstream; Fig. 6e–f), this export regime is not necessarily stable as it depends on a continuous replenishment of the legacy store. Changes in the N input translate to an increase in spatial heterogeneity in NO_3–N concentrations in soil water and groundwater with contrasting water ages. The seasonally changing contribution of different water ages thus results in more chemodynamic NO_3 export regimes. As described in Musolff et al. (2017), both export regimes and patterns are therefore controlled by the interrelation of TT and source concentrations. We argue that a hydrological legacy of NO_3 in the catchment has been established that resulted in the pseudo-chemostatic export behavior we observe nowadays. This supports the notion that a biogeochemical legacy corresponding to the buildup of organic N in the root zones of the soil (van Meter et al., 2016) is less probable. If we assume that all of the 88 % of the N input is accumulating in the soils, we cannot explain the observed shorter-term interannual concentration changes and trajectory in the C–Q relationships. We would rather expect a stronger and even growing dampening of the N input to the subsurface with the buildup of a biogeochemical legacy in the form of organic N. However, we cannot fully exclude the accumulation of a protected pool of soil organic matter with very slow mineralization rates as described in van Meter et al. (2017). Our conceptual model assigns the missing N to the long TTs of NO_3–N in soil water and groundwater and in turn to a pronounced hydrological legacy. In the midstream subcatchment, the estimated TTD explains 40 % of the retained NO_3–N, comparing the convolution of TTD with the N input time series to the actual riverine export. The remaining 60 % cannot be fully explained at the moment and may be assigned to a permanent removal by denitrification (see discussion above), to a fixation due to the biogeochemical legacy or to more complex (e.g., longer tailed) TTDs, which are not well represented by our assumed log-normal distribution. In the downstream subcatchment, our approach explains 29 % of the observed export. This could in principle be caused by the same processes as described for the midstream subcatchment. A hydrological legacy store in deeper zones without significant discharge contribution is also possible (Fig. 7). That mass of N is either bypassing the downstream monitoring station (note that the downstream station is still 3 km upstream of the Holtemme catchment outlet) or is affected by a strong time delay and dampening not captured by our approach. Consequently, future changes in N inputs will also change the future export patterns and regimes, since this would shift the homogeneous NO_3–N distributions in vertical soil and groundwater profiles back to more heterogeneous ones.

5 Conclusion

In the present study we used a unique time series of riverine N concentrations over the last four decades from a mesoscale German catchment as well as estimated N input to discuss the linkage between the two on annual and intra-annual timescales. From the input–output assessment, the buildup of a potential N legacy was quantified, effective TTs of nitrate were estimated and the temporal evolution to chemostatic NO_3–N export was investigated. This study provides four major findings that can be generalized and transferred to other catchments of similar hydroclimatic and landscape settings as well.

First, the retention capacity of the catchment for N is 88 % of the N input (input and output referring to 1976 to 2015), which either can be stored as a legacy or denitrified in the terrestrial or aquatic system. Although we could not fully quantify denitrification, we argue that this process is not the dominant one in the catchment to explain input–output differences. The observed N retention can be more plausibly explained by legacy than by denitrification. As a consequence, the hydrological N legacy, i.e., the load of nitrate still on the way to the stream, may have strong effects on future water quality and long-term implications for river water quality management. With a median export rate of 162 t N a^{-1} (1976–2016, downstream station, 6 kg N ha^{-1} a^{-1}), a depletion of this legacy (< 46 000 t N) via baseflow would maintain elevated riverine concentrations for the next few decades. Although N surplus strongly decreased after the 1980s, during the past 10 years there was still an imbalance between agricultural input and riverine export by a mean factor of 5 (assuming the temporal offset of peak TTs between input and output of 12 years). This is a nonsustainable condition, regardless of whether the retained nitrate is stored or denitrified. Export rates as well as retention capacity derived for this catchment were found to be comparable to findings of other studies in Europe (Worrall et al., 2015; Dupas et al., 2015) and North America (van Meter et al., 2016).

Second, we derived peak time lags between N input and riverine export between 7 and 22 years with systematic differences among the different seasons. Catchment managers should be aware of these long time frames when implementing measures and when evaluating them. This study explains the seasonally differing lag times and temporal concentration evolutions with the vertical migration of the nitrate and their changing contribution to discharge by seasonally changing aquifer connection. Hence, interannual concentration changes are not dominantly controlled by interannually changing discharge conditions, but rather by the seasonally changing activation of subsurface flows with differing ages and thus differing N loads. As a consequence of this activation-dependent load contribution, an effective, adapted monitoring needs to cover, different discharge conditions when measures shall be assessed for their effectiveness. In the light of comparable findings of long time lags (van Meter and Basu, 2017; Howden, 2011), there is a general need for sufficient monitoring length and appropriate methods for data evaluation like the seasonal statistics of time series.

Third, in contrast to a more monotonic change from a chemodynamic to a chemostatic nitrate export regime that was observed previously (Dupas et al., 2016; Basu et al., 2010), this study found a systematic change in the nitrate export regime from accretion over dilution to chemostatic behavior. Here, we can make use of the unique situation in East German catchments where the collapse of agriculture in the early 1990s provided a large-scale "experiment" with abruptly reduced N inputs. While previous studies could not distinguish between biogeochemical and hydrological legacy to cause chemostatic export behavior, our findings provide support for a hydrological legacy in the study catchment. The systematic interannual changes in C–Q relationships of NO_3–N were explained by the changes in the N input in combination with the seasonally changing effective TTs of N. The observed export regime and pattern of NO_3–N suggest a dominance of a hydrological N legacy over the biogeochemical N legacy in the upper soils. In turn, observed trajectories in export regimes of other catchments may be an indicator of their state of homogenization and can be helpful to classify results and predict future concentrations.

Fourth, although we observed long TTs, significant input changes also created strong interannual changes in the export regime. The chemostatic behavior is therefore not necessarily a persistent endpoint of intense agricultural land use, but depends on steady replenishment of the N store. Therefore, the export behavior can also be termed pseudo-chemostatic and may further evolve in the future (Musolff et al., 2015) under the assumptions of a changing N input. Depending on the legacy size, a significant reduction or increase in N input can cause an evolution back to more chemodynamic regimes with dilution or enrichment patterns. Simultaneously, input changes affect the homogenized vertical nitrate profile, resulting in larger intra-annual concentration differences and consequently chemodynamic behavior. Hence, chemostatic behavior and homogenization may be characteristics of managed catchments, but only under constant N input.

Recommendations for a sustainable management of N pollution in the studied Holtemme catchment, also transferable to comparable catchments, focus on the two aspects: depleting past inputs and reducing future ones.

Our findings could not prove a significant loss of NO_3–N by denitrification. To deal with the past inputs and to focus on the depletion of the N legacy, end-of-pipe measures such as hedgerows around agricultural fields (Thomas and Abbott, 2018), riparian buffers or constructed wetlands may initiate N removal by denitrification (Messer et al., 2012).

We could show that there is still an imbalance of agricultural N input and riverine export by a mean factor of 5. A reduced N input due to better management of fertilizer and the prevention of N losses from the root zone at the present time is indispensable to enable depletion instead of a further buildup or stabilization of the legacy.

The combination of N budgeting, effective TTs with long-term changes in C–Q characteristics proved to be a helpful tool to discuss the buildup and type of N legacy at catchment scale. This study strongly benefits from the availability of long time series in nested catchments with a hydroclimatic and land-use gradient. This wealth of data may not be available everywhere. However, we see the potential to transfer this approach to a much wider range of catchments with long-term observations for understanding the spatial and temporal variation and type of legacy buildup, denitrification and TTs as well as their controlling factors. Data-driven analyses of differing catchments covering a higher variety of characteristics may provide a more comprehensive picture of N trajectories and their controlling parameters. In addition to data-driven approaches emphasis should also be put on robust estimations of water TT in catchments to constrain reaction rates. Recent studies present promising approaches to derive TTs in groundwater (Marcais et al., 2018; Kolbe et al., 2019) and at catchment scale (Jasechko et al., 2016; Yang et al., 2018a)

Data availability. Discharge data (for all dates) and water quality data (from 1993) can be accessed on the websites of the State Office of Flood Protection and Water Management (LHW) of Saxony-Anhalt (http://gldweb.dhi-wasy.com/gld-portal/, LHW, 2017). Water quality data for nitrate (including those prior to 1993) are available at https://doi.org/10.4211/hs.9c57af9b5c1343bb840ba198a49ace1c (Ehrhardt, 2019). Atmospheric deposition data between 1995 and 2015 can be accessed on the website of the Meteorological Synthesizing Centre – West (MSC-W) of the European Monitoring and Evaluation Programme (EMEP) (http://www.emep.int/mscw/index_mscw.html, Norwegian Meteorological Institute, 2017), which is assigned to the Meteorological institute of Norway (MET Norway).

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Author contributions. SE carried out the analysis, interpreted the data and wrote the paper. AM designed the study and co-wrote the paper. RK contributed discharge modeling results and atmospheric deposition and co-wrote the paper. All authors contributed to the study design and helped finalize the paper.

Competing interests. The authors declare that they have no conflict of interest.

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References

Abbott, B. W., Moatar, F., Gauthier, O., Fovet, O., Antoine, V., and Ragueneau, O.: Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France, Sci. Total Environ., 624, 845–858, https://doi.org/10.1016/j.scitotenv.2017.12.176, 2018.

Altman, S. J. and Parizek, R. R.: Dilution of non-point source nitrate in ground water, J. Environ. Qual., 24, 11, 707–718, 1995.

Aubert, A. H., Gascuel-Odoux, C., Gruau, G., Akkal, N., Faucheux, M., Fauvel, Y., Grimaldi, C., Hamon, Y., Jaffrézic, A., Lecoz-Boutnik, M., Molénat, J., Petitjean, P., Ruiz, L., and Merot, P.: Solute transport dynamics in small, shallow groundwater-dominated agricultural catchments: insights from a high-frequency, multisolute 10 yr-long monitoring study, Hydrol. Earth Syst. Sci., 17, 1379–1391, https://doi.org/10.5194/hess-17-1379-2013, 2013.

Bach, M. and Frede, H. G.: Agricultural nitrogen, phosphorus and potassium balances in Germany-Methodology and trends 1979 to 1995, Z. Pflanzenernähr. Bodenk., 161, 385–393, 1998.

Bach, M., Godlinski, F., and Greef, J.-M.: Handbuch Berechnung der Stickstoff-Bilanz für die Landwirtschaft in Deutschland Jahre 1990–2008, in: Berichte aus dem Julius Kühn-Institut 159, edited by: Julius Kühn-Institut, Federal Research Centre for Cultivated Plants, 36, Braunschweig, Germany, 2011.

Bartnicky, J. and Benedictow, A.: Atmospheric Deposition of Nitrogen to OSPAR Convention waters in the period 1995–2014, in: EMEP MSC-W Report for OSPAR EMEP/MSC-W TECHNICAL REPORT 1/2017, edited by: Meteorological Synthesizing Centre-West (MSC-W) Norwegian Meteorological Institute, 112, Oslo, Norway, 2017.

Bartnicky, J. and Fagerli, H.: Atmospheric Nitrogen in the OSPAR Convention Area in the period 1990–2004, in: Summary Report for the OSPAR Convention, edited by: Meteorological Synthesizing Centre-West (MSC-W) of EMEP, Oslo, 66, Oslo, Norway, 2006.

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., Zanardo, S., Yaeger, M., Sivapalan, M., Rinaldo, A., and Rao, P. S. C.: Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity, Geophys. Res. Lett., 37, 1–5, https://doi.org/10.1029/2010gl045168, 2010.

Benettin, P., Kirchner, J. W., Rinaldo, A., and Botter, G.: Modeling chloride transport using travel time distributions at Plynlimon, Wales, Water Resour. Res., 51, 3259–3276, https://doi.org/10.1002/2014wr016600, 2015.

Bouraoui, F. and Grizzetti, B.: Long term change of nutrient concentrations of rivers discharging in European seas, Sci. Total Environ., 409, 4899–4916, https://doi.org/10.1016/j.scitotenv.2011.08.015, 2011.

CEC (Council of the European Communities): Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC), Official Journal of the European Communities, 34, 33, 1991.

CEC (Council of the European Communities): Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy, Official Journal of the European Communities, 43, 84, 2000.

Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Howarth, R. W., Hedin, L. O., Perakis, S. S., Latty, E. F., Von Fischer, J. C., Elseroad, A., and Wasson, M. F.: Global patterns of terrestrial biological nitrogen (N_2) fixation in natural ecosystems, Global Biogeochem. Cy., 13, 623–645, https://doi.org/10.1029/1999gb900014, 1999.

Decrem, M., Spiess, E., Richner, W., and Herzog, F.: Impact of Swiss agricultural policies on nitrate leaching from arable land, Agron. Sustain. Dev., 27, 243–253, https://doi.org/10.1051/agro:2007012, 2007.

Dentener, F. J.: Global Maps of Atmospheric Nitrogen Deposition, 1860, 1993, and 2050, Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, Tennessee, USA, 2006.

Dupas, R., Curie, F., Gascuel-Odoux, C., Moatar, F., Delmas, M., Parnaudeau, V., and Durand, P.: Assessing N emissions in surface water at the national level: comparison of country-wide vs. regionalized models, Sci. Total Environ., 443, 152–162, https://doi.org/10.1016/j.scitotenv.2012.10.011, 2013.

Dupas, R., Delmas, M., Dorioz, J.-M., Garnier, J., Moatar, F., and Gascuel-Odoux, C.: Assessing the impact of agricultural pressures on N and P loads and eutrophication risk, Ecol. Indic., 48, 396–407, https://doi.org/10.1016/j.ecolind.2014.08.007, 2015.

Dupas, R., Jomaa, S., Musolff, A., Borchardt, D., and Rode, M.: Disentangling the influence of hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-hourly to decadal time scales, Sci. Total Environ., 571, 791–800, https://doi.org/10.1016/j.scitotenv.2016.07.053, 2016.

Dupas, R., Minaudo, C., Gruau, G., Ruiz, L., and Gascuel-Odoux, C.: Multidecadal Trajectory of Riverine Nitrogen and Phosphorus Dynamics in Rural Catchments, Water Resour. Res., 54, 5327–5340, https://doi.org/10.1029/2018wr022905, 2018.

EEA (European Environment Agency): Corine Land Cover, European Environment Agency, Copenhagen, available at: https://land.copernicus.eu/pan-european/corine-land-cover (last access: 19 October 2017), 2012.

EEA (European Environment Agency): Effects of Air Pollution on European Ecosystems, in: Past and future exposure of European freshwater and terrestrial habitats to acidifying and eutrophying air pollutants, EEA Technical report No. 11, 42, Copenhagen, Danmark, 2014.

Ehrhardt, S.: Nitrate Data for the Holtemme, https://doi.org/10.4211/hs.9c57af9b5c1343bb840ba198a49ace1c, 2019.

Elser, J. J.: A World Awash with Nitrogen, Science, 334, 1503–1504, https://doi.org/10.1126/science.1216124, 2011.

Elser, J. J., Bracken, M. E., Cleland, E. E., Gruner, D. S., Harpole, W. S., Hillebrand, H., Ngai, J. T., Seabloom, E. W., Shurin, J. B., and Smith, J. E.: Global analysis of nitrogen and phosphorus limitation of primary producers in freshwater, marine and terrestrial ecosystems, Ecol. Lett., 10, 1135–1142, https://doi.org/10.1111/j.1461-0248.2007.01113.x, 2007.

Federal Ministry for the Environment: Nature Conservation and Nuclear Safety and Federal Ministry of Food, Agriculture and Consumer Protection: Nitrates Report 2012, edited by: Keppner, L., Rohmoser, W., Wendang, J., and Fischer, D., 90, Bonn, Germany, 2012.

Frick, C., Steiner, H., Mazurkiewicz, A., Riediger, U., Rauthe, M., Reich, T., and Gratzki, A.: Central European high-resolution gridded daily data sets (HYRAS): Mean temperature and relative humidity, Meteorol. Z., 23, 15–32, https://doi.org/10.1127/0941-2948/2014/0560, 2014.

Frühauf, M. and Schwab, M.: Landschaftscharakter und Oberflaechengestalt, in: Geologie von Sachsen-Anhalt, Sect. 5.6.2, edited by: Bachmann, G. H., Ehling, B.-C., Eichner, R., and Schwab, M., 689, Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 2008.

Galloway, J. N., Dentener, F. J., Capone, D. G., Boyer, E. W., Howarth, R. W., Seitzinger, S. P., Asner, G. P., Cleveland, C. C., Green, P. A., Holland, E. A., Karl, D. M., Michaels, A. F., Porter, J. H., Townsend, A. R., and Vöosmarty, C. J.: Nitrogen Cycles: Past, Present, and Future, Biogeochemistry, 70, 153–226, https://doi.org/10.1007/s10533-004-0370-0, 2004.

Godsey, S. E., Kirchner, J. W., and Clow, D. W.: Concentration-discharge relationships reflect chemostatic characteristics of US catchments, Hydrol. Process., 23, 1844–1864, https://doi.org/10.1002/hyp.7315, 2009.

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

Gross, N.: Farming in former East Germany: Past policies and future prospects, Landscape Urban Plan., 35, 25–40, https://doi.org/10.1016/0169-2046(95)00215-4, 1996.

Hannappel, S., Köpp, C., and Bach, T.: Charakterisierung des Nitratabbauvermögens der Grundwasserleiter in Sachsen-Anhalt, Grundwasser, 23, 311–321, https://doi.org/10.1007/s00767-018-0402-7, 2018.

Heidbüchel, I., Troch, P. A., Lyon, S. W., and Weiler, M.: The master transit time distribution of variable flow systems, Water Resour. Res., 48, 2637, https://doi.org/10.1029/2011wr011293, 2012.

Hirsch, R. M. and DeCicco, L. A.: EGRET: Exploration and Graphics for RivEr Trends, R package version 3.0.2, 2019.

Hirsch, R. M., Moyer, D. L., and Archfield, S. A.: Weighted Regressions on Time, Discharge, and Season (WRTDS), with an Application to Chesapeake Bay River Inputs, J. Am. Water Resour. As., 46, 857–880, https://doi.org/10.1111/j.1752-1688.2010.00482.x, 2010.

Hirsch, R. M., Archfield, S. A. and DeCicco, L. A.: A bootstrap method for estimating uncertainty of water quality trends, Environ. Modell. Softw., 73, 148–166, 2015.

Hofstra, N. and Bouwman, A. F.: Denitrification in Agricultural Soils: Summarizing Published Data and Estimating Global Annual Rates, Nutr. Cycl. Agroecos., 72, 267–278, https://doi.org/10.1007/s10705-005-3109-y, 2005.

Howarth, R. W., Billen, G., Swaney, D., Townsend, A., Jaworski, N., Lajtha, K., Downing, J. A., Elmgren, R., Caraco, N., Jordan, T., Berendse, F., Freney, J., Kudeyarov, V., Murdoch, P., and Zhao-Liang, Z.: Regional nitrogen budgets and riverine N & P fluxes for the drainages to the North Atlantic Ocean: Natural and human influences, Biogeochemistry, 35, 75–139, https://doi.org/10.1007/bf02179825, 1996.

Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M. J., and Bieroza, M.: Nitrate concentrations and fluxes in the River Thames over 140 years (1868–2008): Are increases irreversible?, Hydrol. Process., 24, 2657–2662, https://doi.org/10.1002/hyp.7835, 2010.

Howden, N. J. K., Burt, T. P., Worrall, F., Mathias, S., and Whelan, M. J.: Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater?, Water Resour. Res., 47, 13 pp., https://doi.org/10.1029/2011wr010843, 2011.

Jasechko, S., Kirchner, J. W., Welker, J. M., and McDonnell, J. J.: Substantial proportion of global streamflow less than three months old, Nat. Geosci., 9, 126–129, https://doi.org/10.1038/ngeo2636, 2016.

Jawitz, J. W. and Mitchell, J.: Temporal inequality in catchment discharge and solute export, Water Resour. Res., 47, 16 pp., https://doi.org/10.1029/2010wr010197, 2011.

Kirchner, J. W., Feng, X., and Neal, C.: Fractal stream chemistry and its implications for contaminant transport in catchments, Nature, 403, 524–527, https://doi.org/10.1038/35000537, 2000.

Kolbe, T., de Dreuzy, J. R., Abbott, B. W., Aquilina, L., Babey, T., Green, C. T., Fleckenstein, J. H., Labasque, T., Laverman, A. M., Marcais, J., Peiffer, S., Thomas, Z., and Pinay, G.: Stratification of reactivity determines nitrate removal in groundwater, P. Natl. Acad. Sci. USA, 116, 2494–2499, https://doi.org/10.1073/pnas.1816892116, 2019.

Kuhr, P., Kunkel, R., Tetzlaff, B., and Wendland, F.: Räumlich differenzierte Quantifizierung der Nährstoffeinträge in Grundwasser und Oberflächengewässer in Sachsen-Anhalt unter Anwendung der Modellkombination GROWA-WEKU-MEPhos, edited by: Jülich, F., 218 pp., 2014.

Kumar, R., Samaniego, L., and Attinger, S.: Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations, Water Resour. Res., 49, 360–379, https://doi.org/10.1029/2012wr012195, 2013.

Kunkel, R., Eisele, M., and Wendland, F.: Evaluation of strategies to reduce nitrate pollution of groundwater – assessing the needs and efficiencies of agri-environmental measures for selected groundwater bodies in Germany, IWA World Water Congress, 2008.

LHW: Karte der potenziellen Entwässerungsbedürftigkeit landwirtschaftlicher Nutzfläche Sachsen-Anhalts, Landesbetrieb für Hochwasserschutz und Wasser-wirtschaft Sachsen-Anhalt, Halle/S, 2011.

LHW, Landesbetrieb für Hochwasserschutz und Wasserwirtschaft Sachsen-Anhalt: Datenportal Gewässerkundlicher Landesdienst, Fließgewässer und Seen, available at: http://gldweb.dhi-wasy.com/gld-portal/ (last access: 17 January 2018), 2017.

Marcais, J., Gauvain, A., Labasque, T., Abbott, B. W., Pinay, G., Aquilina, L., Chabaux, F., Viville, D., and De Dreuzy, J. R.: Dating groundwater with dissolved silica and CFC concentrations in crystalline aquifers, Sci. Total Environ., 636, 260–272, https://doi.org/10.1016/j.scitotenv.2018.04.196, 2018.

Martin, C., Aquilina, L., Gascuel-Odoux, C., Molénat, J., Faucheux, M., and Ruiz, L.: Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments, Hydrol. Process., 18, 1237–1254, https://doi.org/10.1002/hyp.1395, 2004.

Melland, A. R., Mellander, P.-E., Murphy, P. N. C., Wall, D. P., Mechan, S., Shine, O., Shortle, G., and Jordan, P.: Stream water quality in intensive cereal cropping catchments with regulated nutrient management, Environ. Sci. Policy, 24, 58–70, https://doi.org/10.1016/j.envsci.2012.06.006, 2012.

Mellander, P. E., Melland, A. R., Murphy, P., Wall, D., Shortle, G., and Jordan, P.: Coupling of surface water and groundwater nitrate-N dynamics in two permeable agricultural catchments, J. Agr. Sci.-Cambridge, 152, 18 pp., https://doi.org/10.1017/S0021859614000021 2014.

Messer, T. L., Burchell, M. R., Grabow, G. L., and Osmond, D. L.: Groundwater nitrate reductions within upstream and downstream sections of a riparian buffer, Ecol. Eng., 47, 297–307, https://doi.org/10.1016/j.ecoleng.2012.06.017, 2012.

Minaudo, C., Meybeck, M., Moatar, F., Gassama, N., and Curie, F.: Eutrophication mitigation in rivers: 30 years of trends in spatial and seasonal patterns of biogeochemistry of the Loire River (1980–2012), Biogeosciences, 12, 2549–2563, https://doi.org/10.5194/bg-12-2549-2015, 2015.

Mulholland, P. J., Valett, H. M., Webster, J. R., Thomas, S. A., Cooper, L. W., Hamilton, D. P., and Peterson, B. J.: Stream denitrification and total nitrate uptake rates measured using a field 15N tracer addition approach, Limnol. Oceanogr., 49, 809–820, 2004.

Mulholland, P. J., Helton, A. M., Poole, G. C., Hall, R. O., Hamilton, S. K., Peterson, B. J., Tank, J. L., Ashkenas, L. R., Cooper, L. W., Dahm, C. N., Dodds, W. K., Findlay, S. E. G., Gregory, S. V., Grimm, N. B., Johnson, S. L., McDowell, W. H., Meyer, J. L., Valett, H. M., Webster, J. R., Arango, C. P., Beaulieu, J. J., Bernot, M. J., Burgin, A. J., Crenshaw, C. L., Johnson, L. T., Niederlehner, B. R., O'Brien, J. M., Potter, J. D., Sheibley, R. W., Sobota, D. J., and Thomas, S. M.: Stream denitrification across biomes and its response to anthropogenic nitrate loading, Nature, 452, 202–205, https://doi.org/10.1038/nature06686, 2008.

Müller, C., Zink, M., Samaniego, L., Krieg, R., Merz, R., Rode, M., and Knoller, K.: Discharge Driven Nitrogen Dynamics in a Mesoscale River Basin As Constrained by Stable Isotope Patterns, Environ. Sci. Technol., 50, 9187–9196, https://doi.org/10.1021/acs.est.6b01057, 2016.

Müller, C., Musolff, A., Strachauer, U., Brauns, M., Tarasova, L., Merz, R., and Knöller, K.: Tomography of anthropogenic nitrate contribution along a mesoscale river, Sci. Total Environ., 615, 773–783, https://doi.org/10.1016/j.scitotenv.2017.09.297, 2018.

Musolff, A., Schmidt, C., Selle, B., and Fleckenstein, J. H.: Catchment controls on solute export, Adv. Water Resour. Res., 86, 133–146, https://doi.org/10.1016/j.advwatres.2015.09.026, 2015.

Musolff, A., Schmidt, C., Rode, M., Lischeid, G., Weise, S. M., and Fleckenstein, J. H.: Groundwater head controls nitrate export from an agricultural lowland catchment, Adv. Water Resour. Res., 96, 95–107, https://doi.org/10.1016/j.advwatres.2016.07.003, 2016.

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., and Jawitz, J. W.: Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments, Geophys. Res. Lett., 44, 4143–4151, https://doi.org/10.1002/2017gl072630, 2017.

NLfB (Niedersächsisches Landesamt für Bodenforschung): Bericht 2005 Grundwasser, Methodenbeschreibung, EG-WRRL Bericht 2005, 58, Niedersächsisches Landesamt für Bodenforschung, Niedersächsisches Landesamt für Ökologie, Bezirksregierung Hannover, Hannover, Germany, 2005.

Norwegian Meteorological Institute: Meteorological Synthesizing Centre-West of EMEP (MSC-W of EMEP), Oslo, Norway, available at: https://www.emep.int/mscw/index.html, last access: 1 November 2017.

Otero, N., Torrentó, C., Soler, A., Menció, A., and Mas-Pla, J.: Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Plana de Vic (Osona, Spain), Agr. Ecosyst. Environ., 133, 103–113, https://doi.org/10.1016/j.agee.2009.05.007, 2009.

Prasuhn, V. and Sieber, U.: Changes in diffuse phosphorus and nitrogen inputs into surface waters in the Rhine watershed in Switzerland, Aquat. Sci., 67, 363–371, https://doi.org/10.1007/s00027-005-0774-5, 2005.

Rauthe, M., Steiner, H., Riediger, U., Mazurkiewicz, A., and Gratzki, A.: A Central European precipitation climatology – Part I: Generation and validation of a high-resolution gridded daily data set (HYRAS), Meteorol. Z., 22, 235–256, https://doi.org/10.1127/0941-2948/2013/0436, 2013.

Refsgaard, J. C., Auken, E., Bamberg, C. A., Christensen, B. S., Clausen, T., Dalgaard, E., Efferso, F., Ernstsen, V., Gertz, F., Hansen, A. L., He, X., Jacobsen, B. H., Jensen, K. H., Jorgensen, F., Jorgensen, L. F., Koch, J., Nilsson, B., Petersen, C., De Schepper, G., Schamper, C., Sorensen, K. I., Therrien, R., Thirup, C., and Viezzoli, A.: Nitrate reduction in geologically heterogeneous catchments – a framework for assessing the scale of predictive capability of hydrological models, Sci. Total Environ., 468–469, 1278–1288, https://doi.org/10.1016/j.scitotenv.2013.07.042, 2014.

Rivett, M. O., Buss, S. R., Morgan, P., Smith, J. W. N., and Bemment, C. D.: Nitrate attenuation in groundwater: A review of biogeochemical controlling processes, Water Res., 42, 4215–4232, https://doi.org/10.1016/j.watres.2008.07.020, 2008.

Rode, M., Thiel, E., Franko, U., Wenk, G., and Hesser, F.: Impact of selected agricultural management options on the reduction of nitrogen loads in three representative meso scale catchments in Central Germany, Sci. Total Environ., 407, 3459–3472, https://doi.org/10.1016/j.scitotenv.2009.01.053, 2009.

Rode, M., Halbedel Née Angelstein, S., Anis, M. R., Borchardt, D., and Weitere, M.: Continuous In-Stream Assimilatory Nitrate Uptake from High-Frequency Sensor Measurements, Environ. Sci. Technol., 50, 5685–5694, https://doi.org/10.1021/acs.est.6b00943, 2016.

Rodríguez-Blanco, M. L., Taboada-Castro, M. M., Taboada-Castro, M. T., and Oropeza-Mota, J. L.: Relating nitrogen export patterns from a mixed land use catchment in NW Spain with rainfall and streamflow, Hydrol. Process., 29, 2720–2730, https://doi.org/10.1002/hyp.10388, 2015.

Rozemeijer, J. C., Klein, J., Broers, H. P., van Tol-Leenders, T. P., and van der Grift, B.: Water quality status and trends in agriculture-dominated headwaters, a national monitoring network for assessing the effectiveness of national and European manure legislation in the Netherlands, Environ. Monit. Assess., 186, 8981–8995, https://doi.org/10.1007/s10661-014-4059-0, 2014.

Rozemeijer, J. C. and Broers, H. P.: The groundwater contribution to surface water contamination in a region with intensive agricultural land use (Noord-Brabant, the Netherlands), Environ. Pollut., 148, 695–706, https://doi.org/10.1016/j.envpol.2007.01.028, 2007.

Samaniego, L., Kumar, R., and Attinger, S.: Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale, Water Resour. Res., 46, 25 pp., https://doi.org/10.1029/2008wr007327, 2010.

Samaniego, L., Thober, S., Kumar, R., Wanders, N., Rakovec, O., Pan, M., Zink, M., Sheffield, J., Wood, E. F., and Marx, A.: Anthropogenic warming exacerbates European soil moisture droughts, Nat. Clim. Change, 8, 421–426, https://doi.org/10.1038/s41558-018-0138-5, 2018.

Schmidt, R.: Böden, in: Physische Geographie Deutschlands, edited by: Liedke, H. and Marcinek, J., Gotha, 1995.

Schröter, D., Zebisch, M., and Grothmann, T.: Climate Change in Germany – Vulnerability and Adaptation of Climate-Sensitive Sectors, in: Research Report 201 41 253, Environmental Research of the Federal Ministry of the Environment, edited by: Environmental Research of the Federal Ministry of the Environment, Nature Conservation and Nuclear Safety, UBA-FB 000844/e, Dessau, Germany, 2005.

Schuberth, K.: Geomorphologischer Ueberblick, in: Geologie von Sachsen-Anhalt, edited by: Bachmann, G. H., Ehling, B.-C., Eichner, R., and Schwab, M., Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 689, 2008.

Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., and Mariotti, A.: Long-term fate of nitrate fertilizer in agricultural soils, P. Natl. Acad. Sci. USA, 110, 18185–18189, https://doi.org/10.1073/pnas.1305372110, 2013.

Seibert, J., Grabs, T., Köhler, S., Laudon, H., Winterdahl, M., and Bishop, K.: Linking soil- and stream-water chemistry based on a Riparian Flow-Concentration Integration Model, Hydrol. Earth Syst. Sci., 13, 2287–2297, https://doi.org/10.5194/hess-13-2287-2009, 2009.

Seitzinger, S. P., Harrison, J. A., Böhlke, J. K., Bouwman, A. F., Lowrance, R., Peterson, B. J., Tobias, C., and van Drecht, G.: DENITRIFICATION ACROSS LANDSCAPES AND WATERSCAPES: A SYNTHESIS, Ecol. Appl., 16, 2064–2090, https://doi.org/10.1890/1051-0761(2006)016[2064:DALAWA]2.0.CO;2, 2006.

Smil, V.: Nitrogen in Crop Production: An Account of Global Flows, Global Biogeochem. Cy., 13, 647–662, https://doi.org/10.1029/1999GB900015, 1999.

Sprague, L. A., Hirsch, R. M., and Aulenbach, B. T.: Nitrate in the Mississippi River and its tributaries, 1980 to 2008: are we making progress?, Environ. Sci. Technol., 45, 7209–7216, https://doi.org/10.1021/es201221s, 2011.

Thomas, Z. and Abbott, B. W.: Hedgerows reduce nitrate flux at hillslope and catchment scales via root uptake and secondary effects, J. Contam. Hydrol., 215, 51–61, https://doi.org/10.1016/j.jconhyd.2018.07.002, 2018.

Thompson, S. E., Basu, N. B., Lascurain, J., Aubeneau, A., and Rao, P. S. C.: Relative dominance of hydrologic versus biogeochemical factors on solute export across impact gradients, Water Resour. Res., 47, 20 pp., https://doi.org/10.1029/2010wr009605, 2011.

Trauth, N., Musolff, A., Knöller, K., Kaden, U. S., Keller, T., Werban, U., and Fleckenstein, J. H.: River water infiltration enhances denitrification efficiency in riparian groundwater, Water Res., 130, 185–199, https://doi.org/10.1016/j.watres.2017.11.058, 2018.

Turner, R. B. and Rabalais, N. N.: Changes in Mississippi River Water Quality this Century, BioScience, 41, 8, https://doi.org/10.2307/1311453, 1991.

van der Velde, Y., Rooij, G. H. D., Rozemeijer, J. C., van Geer, F. C., and Broers, H. P.: Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics, Water Resour. Res., 46, 1–17, https://doi.org/10.1029/2010wr009105, 2010.

van Meter, K. J. and Basu, N. B.: Catchment legacies and time lags: A parsimonious watershed model to predict the effects of legacy storage on nitrogen export, PloS one, 10, e0125971, https://doi.org/10.1371/journal.pone.0125971, 2015.

van Meter, K. J. and Basu, N. B.: Time lags in watershed-scale nutrient transport: An exploration of dominant controls, Environ. Res. Lett., 12, 084017, https://doi.org/10.1088/1748-9326/aa7bf4, 2017.

van Meter, K. J., Basu, N. B., Veenstra, J. J., and Burras, C. L.: The nitrogen legacy: Emerging evidence of nitrogen accumulation in anthropogenic landscapes, Environ. Res. Lett., 11, 035014, https://doi.org/10.1088/1748-9326/11/3/035014, 2016.

van Meter, K. J., Basu, N. B., and van Cappellen, P.: Two centuries of nitrogen dynamics: Legacy sources and sinks in the Mississippi and Susquehanna River Basins, Global Biogeochem. Cy., 31, 2–23, https://doi.org/10.1002/2016gb005498, 2017a.

van Meter, K. J., Basu, N. B., and van Cappellen, P.: Supplement-Two Centuries of Nitrogen Dynamics: Legacy Sources and Sinks in the Mississippi and Susquehanna River Basins, Global Biogeochem. Cy., 31, 22, https://doi.org/10.1002/2016GB005498, 2017b.

Vidon, P. G. F. and Hill, A. R.: Landscape controls on nitrate removal in stream riparian zones, Water Resour. Res., 40, 707, https://doi.org/10.1029/2003wr002473, 2004.

Vieweg, M., Kurz, M. J., Trauth, N., Fleckenstein, J. H., Musolff, A., and Schmidt, C.: Estimating time-variable aerobic respiration in the streambed by combining electrical conductivity and dissolved oxygen time series, J. Geophys. Res.-Biogeo., 121, 2199–2215, https://doi.org/10.1002/2016jg003345, 2016.

Vitousek, P. M., Aber, C. A., Howarth, R. W., Likens, G. E., Matson, P. A., Schindler, D. W., Schlesinger, W. H., and Tilman, G. D.: Human Alteration of the Global Nitrogen Cycle: Sources and Consequences, Ecol. Appl., 7, 737–750, https://doi.org/10.1890/1051-0761(1997)007[0737:HAOTGN]2.0.CO;2, 1997.

Wassenaar, L. I.: Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes, Appl. Geochem., 10, 391–405, https://doi.org/10.1016/0883-2927(95)00013-A, 1995.

Webster, J. R., Mulholland, P. J., Tank, J. L., Valett, H. M., Dodds, W. K., Peterson, B. J., Bowden, W. B., Dahm, C. N., Findlay, S., Gregory, S. V., Grimm, N. B., Hamilton, S. K., Johnson, S. L., Marti, E., McDowell, W. H., Meyer, J. L., Morrall, D. D., Thomas, S. A., and Wollheim, W. M.: Factors affecting ammonium uptake in streams – an inter-biome perspective, Freshwater Biol., 48, 1329–1352, https://doi.org/10.1046/j.1365-2427.2003.01094.x, 2003.

Wendland, F., Bogena, H., Goemann, H., Hake, J. F., Kreins, P., and Kunkel, R.: Impact of nitrogen reduction measures on the nitrogen loads of the river Ems and Rhine (Germany), Phys. Chem. Earth Pt. A/B/C, 30, 527–541, https://doi.org/10.1016/j.pce.2005.07.007, 2005.

Wollschläger, U., Attinger, S., Borchardt, D., Brauns, M., Cuntz, M., Dietrich, P., Fleckenstein, J. H., Friese, K., Friesen, J., Harpke, A., Hildebrandt, A., Jäckel, G., Kamjunke, N., Knöller, K., Kögler, S., Kolditz, O., Krieg, R., Kumar, R., Lausch, A., Liess, M., Marx, A., Merz, R., Mueller, C., Musolff, A., Norf, H., Oswald, S. E., Rebmann, C., Reinstorf, F., Rode, M., Rink, K., Rinke, K., Samaniego, L., Vieweg, M., Vogel, H.-J., Weitere, M., Werban, U., Zink, M., and Zacharias, S.: The Bode hydrological observatory: A platform for integrated, interdisciplinary hydro-ecological research within the TERENO Harz/Central German Lowland Observatory, Environ. Earth Sci., 76, 725, https://doi.org/10.1007/s12665-016-6327-5, 2017.

Worrall, F., Burt, T. P., Howden, N. J. K., and Whelan, M. J.: Fluvial flux of nitrogen from Great Britain 1974–2005 in the context of the terrestrial nitrogen budget of Great Britain, Global Biogeochem. Cy., 23, 13 pp., https://doi.org/10.1029/2008gb003351, 2009.

Worrall, F., Howden, N. J. K., and Burt, T. P.: Evidence for nitrogen accumulation: the total nitrogen budget of the terrestrial biosphere of a lowland agricultural catchment, Biogeochemistry, 123, 411–428, https://doi.org/10.1007/s10533-015-0074-7, 2015.

Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F., and Fleckenstein, J. H.: Exploring the Dynamics of Transit Times and Subsurface Mixing in a Small Agricultural Catchment, Water Resour. Res., 54, 2317–2335, https://doi.org/10.1002/2017wr021896, 2018a.

Yang, X., Jomaa, S., Zink, M., Fleckenstein, J. H., Borchardt, D., and Rode, M.: A New Fully Distributed Model of Nitrate Transport and Removal at Catchment Scale, Water Resour. Res., 54, 5856–5877, https://doi.org/10.1029/2017wr022380, 2018b.

Zacharias, S., Bogena, H., Samaniego, L., Mauder, M., Fuß, R., Pütz, T., Frenzel, M., Schwank, M., Baessler, C., Butterbach-Bahl, K., Bens, O., Borg, E., Brauer, A., Dietrich, P., Hajnsek, I., Helle, G., Kiese, R., Kunstmann, H., Klotz, S., Munch, J. C., Papen, H., Priesack, E., Schmid, H. P., Steinbrecher, R., Rosenbaum, U., Teutsch, G., and Vereecken, H.: A Network of Terrestrial Environmental Observatories in Germany, Vadose Zone J., 10, 955, https://doi.org/10.2136/vzj2010.0139, 2011.

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Trajectories of nitrate input and output in three nested catchments along a land use gradient

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Supplement

S1 Addition to material and methods

S**1.1 Catchment characteristics**

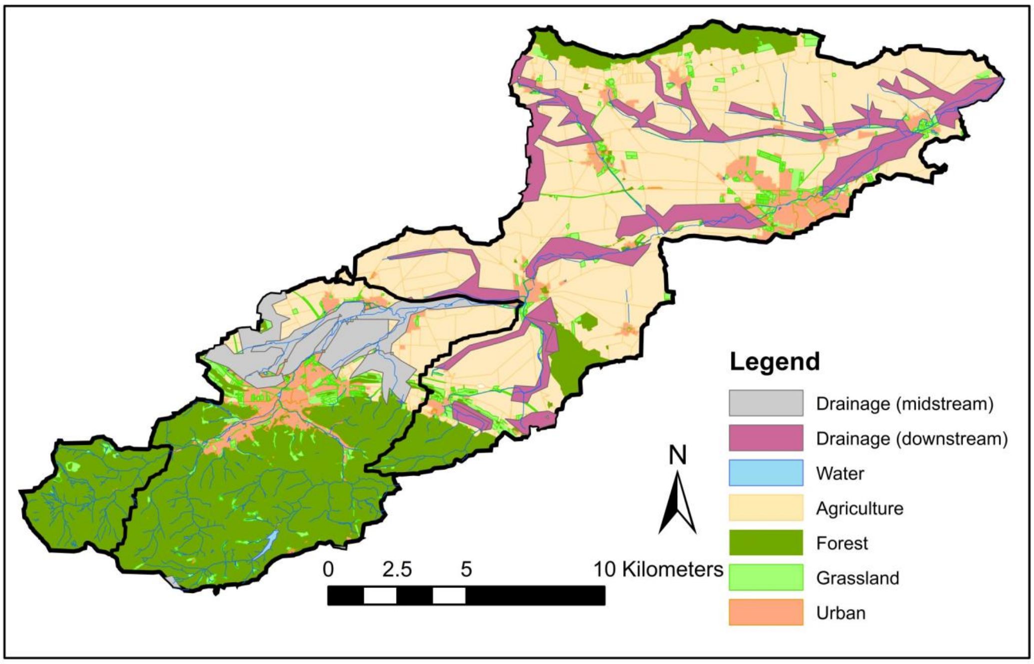

Figure S1.1: Map of the catchment highlighting the agricultural area that is artificially drained

1

S1.2 Water quality time series of NH_4-N and NO_2-N

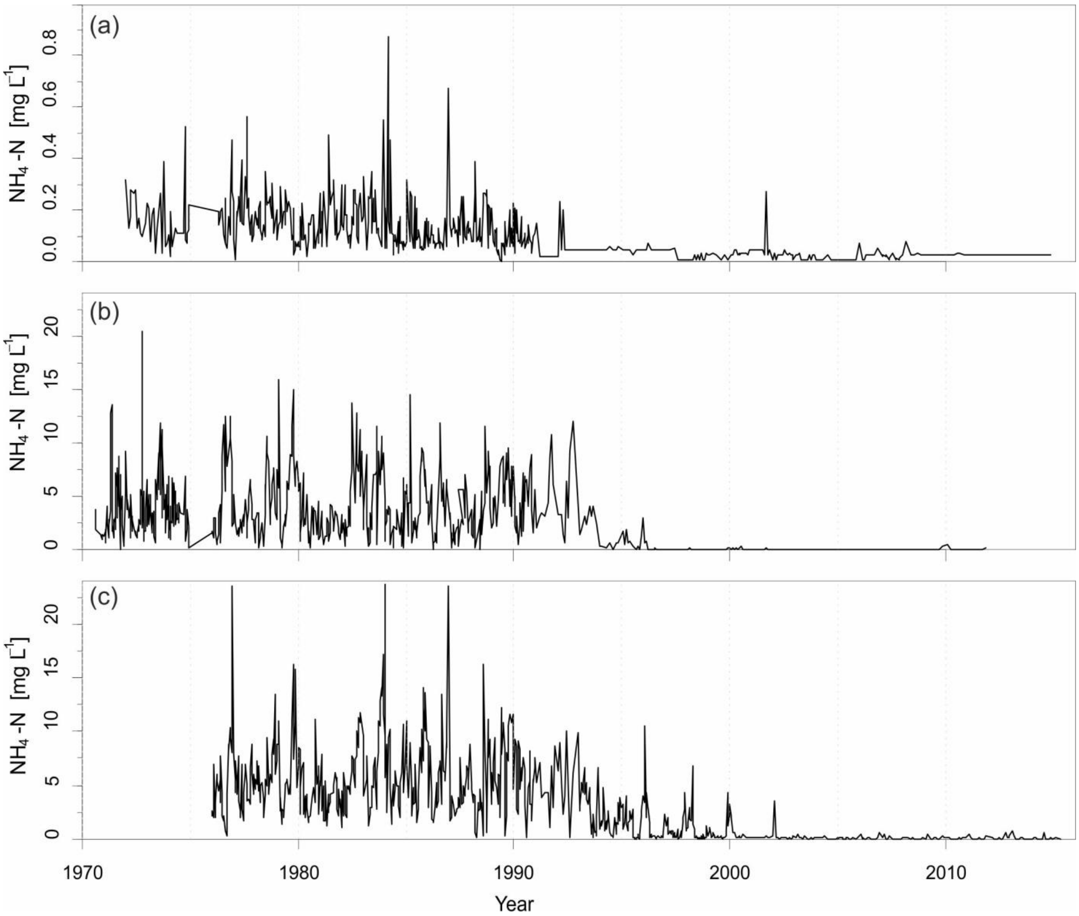

Figure S1.2.1: Time series of NH_4-N concentrations. (a) Upstream; (b) Midstream; (c) Downstream.

2

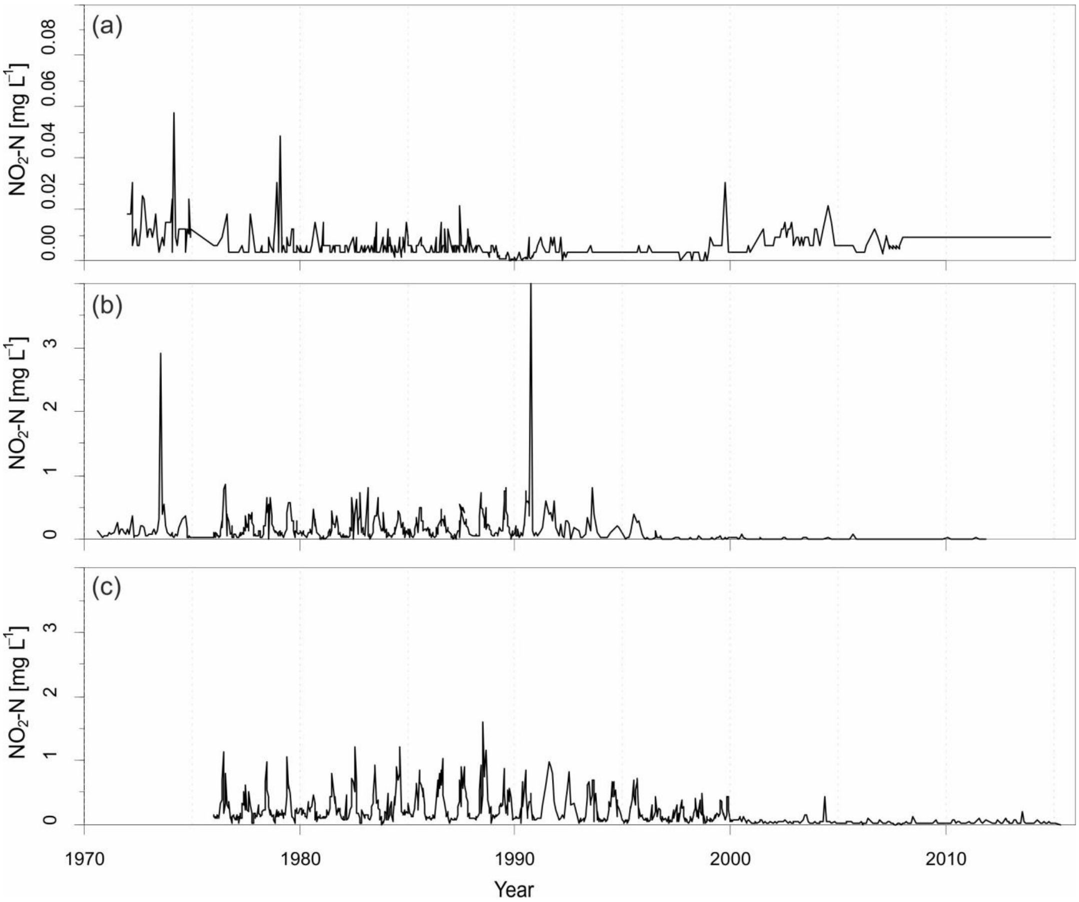

Figure S1.2.2: Time series of NO_2-N concentrations. (a) Upstream; (b) Midstream; (c) Downstream.

S.1.2.3 Estimation of NO_3-N contribution from wastewater borne NH_4-N

The assumption that agricultural, diffuse input was the main source of NO_3-N, needed an investigation of the possible amount of NO_3-N stemming from nitrified NH_4-N released by the WWTPs.

We estimated the maximal amount of waste water born NO_3-N from the highest nitrification rates taken from other studies (Webster et al., 2003; Mulholland et al., 2000, Tank et al., 2000). The highest rate was 0.19 g m^{-2} d^{-1} (Tank et al., 2000). Note that we assume that this rate is constant over the year and that NH_4-N was always unlimitedly available.

To calculate the river area, we used the stream length und mean stream width between the two WWTPs and corresponding stations Mid- and Downstream (Table S.1.2.3). This estimation took the relocation of the WWTP Wernigerode in 1995 into account. The estimation of waste water born NO_3-N revealed a maximal contribution of 5.2 % stemming from nitrification over the years. Hence, in-stream nitrification of NH_4-N release from point sources did not contributed significantly to riverine NO_3 loads or concentrations.

Table S.1.2.3: Estimation of NO_3-N contribution by in-stream nitrification of waste water born NH_4-N in the anthropogenically impacted subcatchments

	Midstream before 1995	Midstream after 1995	Downstream
NH_4-N uptake (Tank et al. 2000; g m^{-2} d^{-1})	0.19		
River area from WWTP to station (m^2)	58 456	12 431	46 092
Nitrified NH_4-N (t a^{-1})	4.1	0.9	3.2
Years of selected time series	1972–1995	1995–2011	1976–2011
Total uptake over time (t N)	107.0		111.9
Total NO_3-N export over time (t)	3 697		2 146
Total uptake according to export (%)	2.9		5.2

4

S2 Addition to results

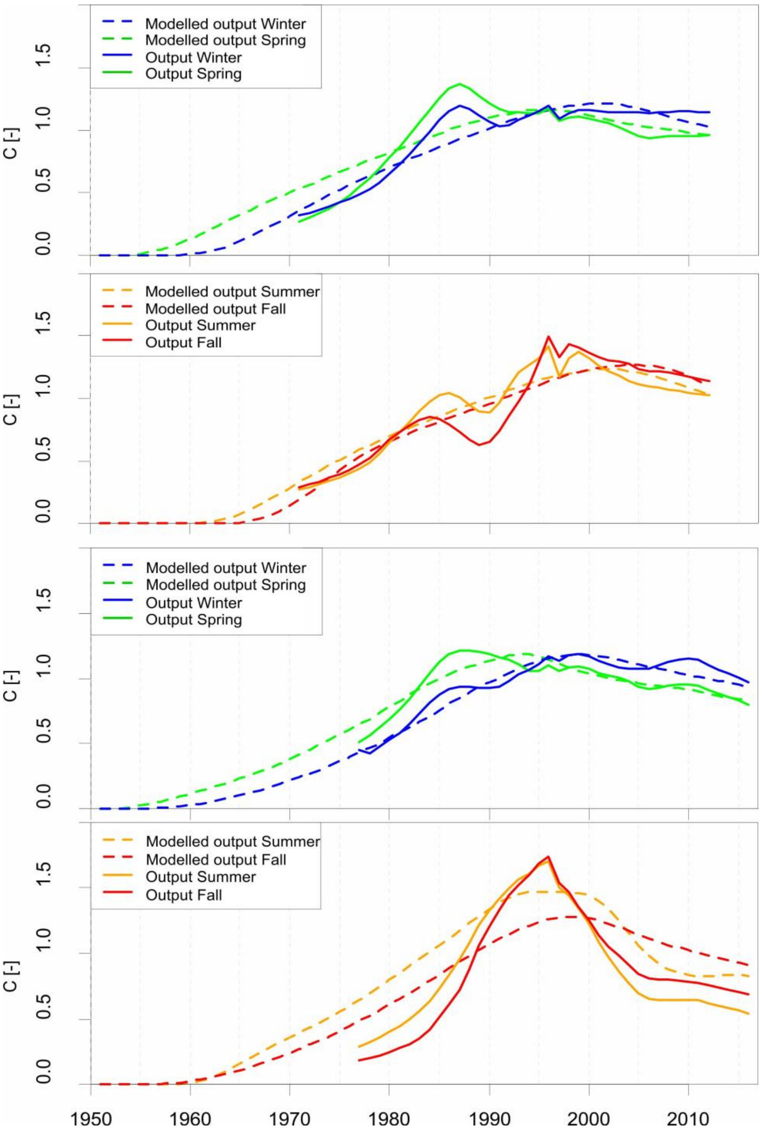

Figure S2.1: Modelled N-output concentrations derived from the N-input convolved with the log-normal travel time distributions (dashed lines) and the scaled observed flow-normalized seasonal NO_3-N concentrations (solid lines) over time.

5

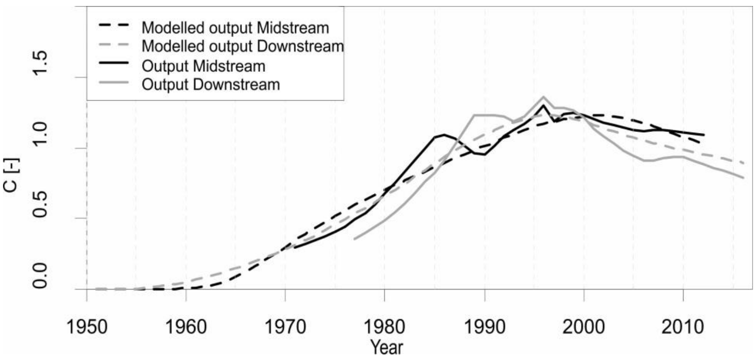

Figure S2.2: Modelled N-output concentrations derived from the N-input convolved with the log-normal travel time distributions (dashed lines) and the scaled observed flow-normalized annual NO_3-N concentrations (solid lines) over time.

Study 2: Long-term nitrogen retention and transit time distribution in agricultural catchments in western France

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RD and SE designed the study and carried out the analysis. RD wrote the paper. All authors discussed and interpreted the results and contributed to the text.

Own contribution:

- Study concept and design: 40 %
- Data analysis: 40 %
- Interpretation of the results: 40 %
- Preparation of the manuscript: 20 %

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PAPER

Long-term nitrogen retention and transit time distribution in agricultural catchments in western France

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Supplementary material for this article is available online

Abstract

Elevated nitrogen (N) concentrations have detrimental effects on aquatic ecosystems worldwide, calling for effective management practices. However, catchment-scale annual mass-balance estimates often exhibit N deficits and time lags between the trajectory of net N inputs and that of N riverine export. Here, we analyzed 40-year time series of N surplus and nitrate-N loads in 16 mesoscale catchments (104–10 135 km^2) of a temperate agricultural region, with the aim to (1) investigate the fate of the 'missing N', either still in transit through the soil—vadose zone—groundwater continuum or removed via denitrification, and (2) estimate the transit time distribution of N by convoluting the input signal with a lognormal model. We found that apparent N retention, the 'missing N', ranged from 45%–88% of then N net input, and that topsoil N accumulation alone accounted for ca. two-thirds of this retention. The mode of the nitrate-N transit time distribution ranged from 2–14 years and was negatively correlated with the estimated retention. Apparent retention was controlled primarily by average runoff, while the transit time mode was controlled in part by lithology. We conclude that the fate of the soil 'biogeochemical legacy', which represents much of the catchment-scale 'missing N', is in our hands, since the N accumulated in soils can still be recycled in agroecosystems.

1. Introduction

Excess reactive nitrogen (N) in the environment causes several detrimental effects, including acidification, climate change and eutrophication, particularly in marine ecosystems (Galloway *et al* 2003, Pinay *et al* 2017). Coastal and near-coastal eutrophication contributes to the formation of algal blooms and hypoxia, and these conditions threaten biodiversity, tourism, and fisheries (Turner *et al* 2008, Andersen *et al* 2017, Wang *et al* 2016). Besides alteration to ecosystem structure and function, massive algal blooms, also called 'green tides', can even result in a direct human health risk with documented cases of mortality due to exposure to toxic H_2S gas emissions resulting from decomposition of excess algae in shallow tidal areas (Smetacek and Zingone 2013, Le Moal *et al* 2019).

N inputs from agriculture represent most of the reactive N that enters streams and rivers, primarily as nitrate, in economically developed countries (Howarth and Marino 2006, De Vries *et al* 2011, Li *et al* 2019). Efforts to limit agricultural N losses to water include reduction of N surplus and maximization of N removal in natural and engineered wetlands (Seitzinger *et al* 2006). N mass-balance estimates at catchment and regional scales often reveal a N deficit, sometimes called 'missing N' (Van Breemen *et al* 2002), which commonly exceeds 50% of net inputs (Howarth *et al* 1996, Alexander *et al* 2002, Boyer *et al* 2002, Aquilina *et al* 2012, Lassaletta *et al* 2012, Ehrhardt *et al* 2019). Knowing the fate of this missing N has important implications for assessing trends in water quality and managing global and local N cycles. The missing N may have accumulated in the catchment, building a legacy source that causes a time lag in its transfer to surface water, or it may have been removed via denitrification (Chen *et al* 2018).

The N legacy of a catchment includes a 'biogeochemical legacy', when N accumulates in soil organic matter and may leach several years after on-field application, and a 'hydrological legacy', which corresponds to the transit time of water in catchments. Both types of legacies lead to time lags of several years to decades between implementation of measures to curb N losses and decreasing N concentrations in rivers (Van Meter and Basu 2017, Vero *et al* 2017). In a long-term tracer experiment, Sebilo *et al* (2013) observed that 12%–15% of isotopically labelled N still remained in an agricultural soil 30 years after application, 61%–65% having been taken up by plants and the rest emitted into the environment. Van Meter *et al* (2016) analyzed long-term soil N content in the Mississippi River Basin and estimated a net accumulation rate of 25–70 kg ha^{-1} yr^{-1}. On the other hand, N 'hydrological legacy' is assumed to follow the transit time distribution (TTD) of water, which can be investigated with conservative tracers and both empirical and numerical models (Fovet *et al* 2015, Hrachowitz *et al* 2016). Denitrification, the primary process by which N surplus can be permanently removed from a catchment, occurs in soils (Oehler *et al* 2007), groundwater (Kolbe *et al* 2019), wetlands (Montreuil *et al* 2010) and river networks (Pinay *et al* 2015). Denitrification produces both inert N_2 and the greenhouse gas N_2O. Multiple studies have observed denitrification at local scales, but upscaling to the catchment scale remains a challenge (Seitzinger *et al* 2006).

Few studies have simultaneously investigated both N retention and TTD, seemingly because doing so requires having detailed agricultural, soil and hydrological data to quantify budgets accurately and having these data over long periods. Such datasets have been rarely available until recently (Howden *et al* 2010, Van Meter *et al* 2017, 2018, Ehrhardt *et al* 2019). In this article, we analyzed long-term (1976–2015) data from previously estimated N surpluses (Poisvert *et al* 2017) and newly estimated riverine nitrate export and soil N content variation. The research objectives were to (1) estimate N retention and TTD and (2) relate these estimates to geographic variables (catchment area, annual runoff, lithology).

The study sites include 16 catchments in the Brittany region (western France), which is one of the emblematic areas for N-derived coastal eutrophication in Europe (Smetacek and Zingone 2013). It also has few N point sources (Gascuel-Odoux *et al* 2010), has experienced large variations in its N surplus in the past few decades (Dupas *et al* 2018) and has relatively quick catchment response times (Fovet *et al* 2015), which makes it an ideal study area for an empirical modeling study.

2. Materials and methods

2.1. Study area

Brittany is a 27 000 km^2 region located in the Armorican Massif of northwestern France (figure 1). Its geology is dominated by igneous and metamorphic rocks (granite, schist, micaschist), and its topography is relatively flat, with elevation ranging from 0–385 m above sea level (Gascuel-Odoux *et al* 2010). Its climate is temperate oceanic, with a mean annual temperature of 12 °C and a large rainfall gradient that increases from 700 to 1300 mm from east to west (Frei *et al* 2020). Its hydrology is characterized by shallow aquifers in weathered and fissured layers of bedrock, a high river density (1 km km^{-2}) and riparian wetlands (partly cultivated) that cover ca. 20% of the soil map (Aquilina *et al* 2012, Abbott *et al* 2018). Agriculture represents 80% of the land use and is dedicated mostly to animal production. Brittany contains 21%, 58%, 33% and 42% of France's dairy cows, pigs, layer chicken and broiler chicken, respectively, on only 6% of France's agricultural area (Agreste Bretagne 2019). Industrial agriculture began to develop there after 1945 and the European Union's Common Agricultural Policy (1962), this development was more rapid and intense there than in other French regions (Gascuel-Odoux *et al* 2010). The agricultural N surplus was only 33 kg ha^{-1} yr^{-1} in 1955, peaked at 104 kg ha^{-1} yr^{-1} in 1989 and decreased to 44 kg ha^{-1} yr^{-1} in 2015 (Poisvert *et al* 2017). Organic and mineral N fertilizers represented 69% of N inputs in 1955, 85% in 1989 and 80% in 2015. The rest came from biological fixation by legumes and atmospheric deposition.

2.2. Monitoring data and catchment characteristics

The study focused on 16 rivers in Brittany in which nitrate monitoring started in 1976 or earlier and in which nitrate was measured near a gauging station that provided daily discharge data (figure 1). Water quality was monitored on a regular interval (monthly to bimonthly): the number of years from 1976–2015 with at least six sampling dates ranged from 23–40 among the catchments. All nitrate and discharge data were collected by water authorities for regulatory purposes; they are publicly available at http://osur.eau-loire-bretagne.fr/ and http://hydro.eaufrance.fr/.

N surplus data were estimated by Poisvert *et al* (2017) based on agricultural statistics for each 'commune', a French administrative unit with a mean area of 15 km^2. Because the study catchments ranged from 104–10 135 km^2, we ignored uncertainties related to farms with fields in multiple communes or that transferred organic N to neighboring farms. Poisvert *et al* (2017) calculated the annual N surpluses using a land system budget (Oenema *et al* 2003, De Vries *et al* 2011). N inputs consist of mineral and organic fertilizer (farmyard manure and slurry), biological N fixation and atmospheric N deposition. N output are the sum of N exported by each crop type. In this study, N surplus was considered as a net diffuse N source for the catchments. We ignored point-source inputs because they represent a small percentage of total N fluxes in France (i.e. 2% from 2005–2009 (Dupas

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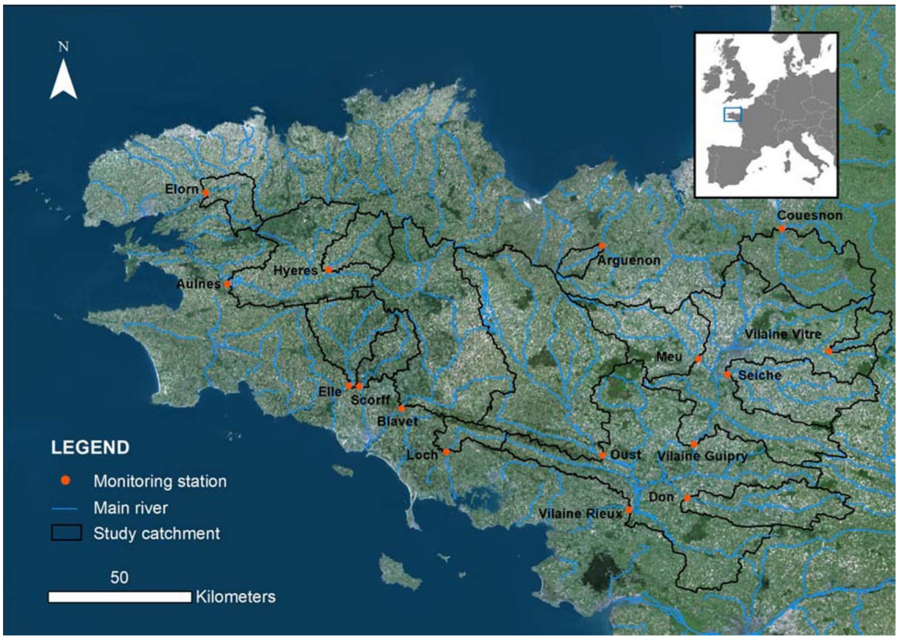

Figure 1. Locations of the 16 study catchments in the Brittany region.

et al 2015)) and no long-term point-source data were available.

The 16 catchments selected ranged from 104–10 135 km^2, had specific cumulative discharge of 195–689 mm yr^{-1} and a percentage of agricultural land use of 73%–92%. Two of them are dominated (i.e. >66%) by granite bedrock, nine are dominated by schist/mica-schist and five of them have mixed lithology (table 1).

2.3. Flux estimation and transit time modeling

We first filled data gaps in the discharge time series using the geomorphology-based SIMFEN model (de Lavenne and Cudennec 2019). Developed for Brittany, SIMFEN simulates discharge in ungauged catchments by transposing net rainfall from neighboring gauged 'donor' catchments and convoluting this net rainfall via a geomorphology-based transfer function. The percentage of discharge gaps ranged 1%–23% (median = 2%) and the Nash–Sutcliffe (NS) efficiency for catchments with >5% missing discharge ranged 0.73–0.84. We then interpolated the monthly concentration time series to a daily time step and then to annual time step using the 'Weighted Regressions on Time, Discharge, and Season' (WRTDS) provided by the EGRET package (Hirsch *et al* 2010, Hirsch and Decicco 2019) of R software. WRTDS is a load estimation method that use time, discharge and season as explanatory variables, and re-estimates statistical dependencies at each time step using the most relevant dates to represent the concentration dynamics and provide accurate load estimates (Zhang and Hirsch 2019).

Previous studies in Brittany have shown (1) large interannual variations in discharge, with annual discharge in a wet year up to three times that in a dry year (Gascuel-Odoux *et al* 2010), and (2) that nitrate concentrations increased in wet years, causing interannual variability in nitrate load to exceed that of discharge (Dupas *et al* 2018, Mellander *et al* 2018). The present study focused on long-term trends in nitrate loads due to changes in N surplus, not to interannual variations in the hydroclimate. Consequently, we considered the EGRET flow-normalized annual load rather than the actual estimated load. Using a flow-normalized load throughout this study was acceptable because, despite interannual variations, none of the 16 study catchments exhibited a long-term monotonous discharge trend from 1976–2015 (Mann–Kendall test, $p > 0.05$).

The input–output assessment considered N surplus as an input and flow-normalized nitrate flux as an output. N retention from 1976–2015 was estimated as:

$$Retention = 1 - \frac{\sum_{i=1976}^{2015} Flux\,i}{\sum_{i=1976}^{2015} Surplus\,i}$$

The estimated retention included both irreversible removal via denitrification and long-term reversible storage.

Table 1. Characteristics of the 16 catchments. Data sources: Corine Land Cover 2012, Sol de Bretagne 2010, BRGM 2019.

Catchment	Surface area (km^2)	Dominant lithology	Agricultural area (%)	Urban area (%)	Hydromorphic soils (%)	Mean slope (%)	River density (km/km^2)	Annual runoff (mm)
Arguenon	104	mixed	84.4	2.6	17.3	6.1	0.7	251.2
Aulne	1470	schist	80.5	2.2	22.8	8.3	0.8	589.9
Blavet	1934	mixed	81.4	3.5	20.9	6.9	1	450.4
Couesnon	859	mixed	90.3	4.3	23	4.6	1.2	292.4
Don	641	schist	90.1	3.6	35.8	2.7	0.9	209.7
Elle	577	mixed	80.5	2.1	24.1	8.2	1.1	585
Elorn	260	mixed	76.2	7	23.7	7	0.9	688.8
Hyeres	352	schist	87.4	2.9	19.9	8	0.8	546.2
Loch	184	granite	73.6	3.5	22.5	5.3	1.1	474.9
Meu	767	schist	83.5	4.5	22.5	3.6	0.8	213.9
Oust	2448	schist	82.3	3.5	20	5.7	0.9	313.1
Scorff	301	granite	73.4	1.9	19.5	8.5	1.2	534.3
Seiche	786	schist	90.9	5.9	23.8	3.4	0.9	195.4
Vilaine Guipry	4148	schist	83.7	7.4	23.5	3.8	0.9	236.2
Vilaine Rieux	10135	schist	82.6	5.3	25.1	4.2	0.9	236.2
Vilaine Vitre	149	schist	91.6	5.2	20.3	5.5	1	272.7

The TTD model consisted of a dynamic convolution model of the N surplus not retained in the catchments, on an annual time step. The mathematical function used was a lognormal distribution model with a mean (μ) and standard deviation (σ). Kirchner *et al* (2000) found that distributions with tails longer than those of exponential distributions (e.g. lognormal or gamma) were suitable for modeling solute transport in catchments, and Ehrhardt *et al* (2019) successfully fitted a lognormal distribution to long-term N surplus—N load data in a 270 km^2 temperate catchment. In essence, we fitted the TTD parameters so that the N surplus convolved with the optimal distribution matches the observed N loads at the outlets. We calibrated the TTD model in a generalized likelihood uncertainty estimation (GLUE) framework (Beven and Freer 2001). We performed 5000 model runs assuming a uniform distribution in the range [0:5] for log μ and [0:2] for log σ. We considered models that exceeded a NS efficiency coefficient of 0.60 to be 'behavioral', and calculated 5%–95% credibility intervals of outputs of the NS-weighted behavioral models.

Statistical analysis of TTD model outputs consisted of calculating correlations between estimated retention, transit time mode, transit percentiles (10%, 50% (median) and 90%) and selected catchment properties. The 10% transit time was selected as the time needed to detect a response to a change in N surplus, the 50% transit time represents the time needed to transfer half of the N surplus in a given year, and the 90% transit time represents the time needed to reach near-equilibrium. In statistical analyses of transit time percentiles, we considered the NS-weighted median of the behavioral models. The catchment properties selected were catchment area, dominant lithology and long-term runoff.

We assessed the fate of the retained N (i.e. removal via denitrification, or accumulation in soil, the vadose zone and groundwater) in relation to estimates of N accumulation from available soil N test data. Specifically, we compared total N content (modified Kjeldahl method ISO 11 261:1995) in the topsoil (0–30 cm) measured from 30 484 and 36 764 soil tests in Brittany from 2000–2004 and 2010–2014, respectively. Because these soil data are protected by statistical confidentiality, spatial coordinates of the sampling points were not available (Saby *et al* 2014). The objective of this approximate quantification was to compare the magnitudes of plausible N accumulation and quantified N retention during the study period.

All the statistical analyses and figures were done with the R software v. 3.5.1 (R Core Team 2019)

3. Results

3.1. Long-term nitrogen budget (1976–2015)

Cumulative N surplus inputs from 1976–2015 ranged from 1873–4424 kg N ha^{-1} among the 16 catchments, with a mean of 2960 kg N ha^{-1} (i.e. 74 kg ha^{-1} yr^{-1} on average for the 40-year period) (table 2). During the same period, cumulative N flux ranged from 398–1820 kg N ha^{-1}, with a mean of 911 kg N ha^{-1} (i.e. 23 kg ha^{-1} yr^{-1}). The coefficient of variation of cumulative flux exceeded that of cumulative surplus (42% and 26%, respectively), and the former was similar to that of long-term runoff (42%). Cumulative N flux was not correlated with cumulative N surplus, but it was positively correlated with long-term mean runoff ($r = 0.87$, $p < 0.05$). Cumulative N retention ranged from 45%–88% among catchments, with a mean of 67%. This retention represented a range of 864–3505 kg N ha^{-1}, with a mean of 2050 kg N ha^{-1} (i.e. 51 kg ha^{-1} yr^{-1} on average for the 40-year period).

Both the N surplus and the flow-normalized N flux varied by a factor of three during the study period (figure 2). The N surplus increased from 18–44 kg ha^{-1} yr^{-1} (mean of 34 kg ha^{-1} yr^{-1}) in 1976 to a maximum of 74–176 kg ha^{-1} yr^{-1} (mean of 113 kg ha^{-1} yr^{-1}) in 1988. It then decreased to 35–74 kg ha^{-1} yr^{-1} (mean of 49 kg ha^{-1} yr^{-1}) in 2015. The flow-normalized N flux increased from 2–23 kg ha^{-1} yr^{-1} (mean of 11 kg ha^{-1} yr^{-1}) in 1976 to a maximum of 12–57 kg ha^{-1} yr^{-1} (mean of 30 kg ha^{-1} yr^{-1}) in 1996. It then decreased to 11–41 kg ha^{-1} yr^{-1} (mean of 21 kg ha^{-1} yr^{-1}) in 2015.

The mean $\pm$ standard deviation of total N content measured in the topsoil was 2.20 $\pm$ 0.87 g kg^{-1} from 2000–2004 and 2.29 $\pm$ 0.77 g kg^{-1} from 2010–2014, indicating a statistically significant increase of 0.09 g kg^{-1} in a 10-year period (Student's t-test, $p < 0.05$). Assuming a typical soil bulk density of 1.2 t m^{-3} (Ellili *et al* 2019), this increase in total N content from 7920 $\pm$ 3132 to 8244 $\pm$ 2772 kg N ha^{-1} represented a mean accumulation of 32.4 kg ha^{-1} yr^{-1} in the first 30 cm of agricultural topsoil.

3.2. Transit time distribution modelling

The GLUE approach yielded 166–1044 behavioral parameter sets among the 16 catchments. Maximum NS efficiencies ranged from 0.71–0.96 among the catchments (figures SI 1 and 2 (available online at https://stacks.iop.org/ERL/15/115011/mmedia)). The modeled N flux behaved similarly to the observed flow-normalized N flux in the long term (figure 3).

The response time (10% transit time) ranged from 1.2–10.8 years, with a median 5%–95% credibility interval of 9.4 years (table 2). The median transit time ranged from 3.8–15.7 years, with a median 5%–95% credibility interval of 7.4 years. The estimated equilibrium time (90% transit time) ranged from 12.7–25.2 years, with a median 5%–95% credibility interval of 20.2 years. The mode (peak) of the TTD ranged from 1.6–13.8 years, with a median 5%–95% credibility interval of 9.8 years. Despite of a variety of TTD shapes (figure 4), response times, median transit

Table 2. Cumulative N surplus (N input), flow-normalized N flux (N output, 1976–2015) and transit time distribution percentiles. Modeled results consist of the Nash–Sutcliffe-weighted median and the 5%–95% credibility interval for generalized likelihood uncertainty estimation (in parentheses).

Catchment	Cumulative surplus (kg N ha^{-1})	Observed cumulative flux (kg N ha^{-1})	Observed retention (%)	Modeled cumulative flux (kg N ha^{-1})	p10 (year)	p50 (year)	p90 (year)	Mode (year)
Arguenon	2645.5	981.4	62.9	918.6 (790.7–1057.5)	7.7 (4.1–13.4)	12.3 (9.2–16.5)	20.0 (12.9–30.1)	10.4 (6.2–15.7)
Aulne	2964.3	1382.0	53.4	1364.2 (1235.1–1497.1)	4.6 (2.2–8.9)	10.1 (7.0–13.4)	22.2 (14.6–33.5)	6.9 (2.9–11.4)
Blavet	2244.9	1140.8	49.2	1102.1 (964.4–1245.0)	7.8 (3.9–14.0)	12.9 (9.7–17.2)	21.7 (13.4–32.9)	10.9 (5.8–16.4)
Couesnon	4424.1	920.0	79.2	902.6 (789.8–1023.7)	3.0 (0.8–7.2)	6.7 (4.0–10.6)	16.0 (8.7–31.1)	4.3 (0.8–9.2)
Don	2787.0	411.8	85.2	379.8 (352.9–406.9)	3.1 (1.7–5.9)	6.9 (5.0–9.6)	15.4 (12.1–20.5)	4.6 (2.4–8.2)
Elle	2096.2	992.6	52.6	972.6 (861.4–1094.1)	8.6 (4.4–16.3)	14.3 (11.1–19.3)	24.0 (15.5–36.2)	11.8 (6.6–18.5)
Elorn	3317.7	1820.1	45.1	1771.4 (1562.2–2029.2)	7.1 (3.3–12.8)	12.8 (9.2–17.0)	23.7 (14.1–36.2)	10.1 (4.8–15.9)
Hyeres	2864.2	1289.3	55.0	1245.2 (1084.0–1397.3)	10.1 (5.5–17.0)	14.2 (11.3–19.8)	21.7 (13.8–31.6)	12.6 (8.3–19.1)
Loch	1872.9	1008.7	46.1	1001.3 (858.4–1132.8)	10.4 (5.8–16.2)	15.7 (12.5–20.9)	25.2 (16.3–40.4)	13.8 (8.7–19.7)
Meu	3402.0	397.9	88.3	377.7 (318.6–444.5)	8.4 (4.1–15.2)	13.0 (9.4–18.2)	21.3 (11.9–33.2)	11.0 (6.1–17.2)
Oust	2341.3	935.1	60.1	888.6 (776.4–1011.6)	6.7 (3.2–13.0)	11.0 (8.1–15.5)	19.4 (11.7–30.1)	9.2 (4.7–14.6)
Scorff	1987.3	917.7	53.8	901.2 (769.0–1007.0)	10.8 (6.3–17.0)	15.2 (12.0–21.1)	22.0 (14.2–36.0)	13.4 (9.4–19.8)
Seiche	4106.0	676.8	83.5	666.1 (581.6–758.7)	3.8 (1.5–8.5)	8.3 (5.8–11.8)	18.8 (10.5–32.7)	5.6 (1.8–10.5)
Vilaine Guipry	3624.5	592.4	83.7	577.5 (521.0–644.5)	2.6 (1.1–6.2)	6.9 (4.8–9.8)	18.4 (11.4–29.8)	3.9 (1.2–8.4)
Vilaine Rieux	2906.6	517.2	82.2	497.5 (439.3–562.6)	4.4 (1.7–9.2)	8.7 (5.9–12.2)	18.2 (10.5–30.3)	6.5 (2.2–11.2)
Vilaine Vitre	3778.7	587.5	84.5	569.1 (513.2–641.7)	1.2 (0.2–4.8)	3.8 (1.8–7.3)	12.7 (5.6–26.2)	1.6 (0.1–6.1)

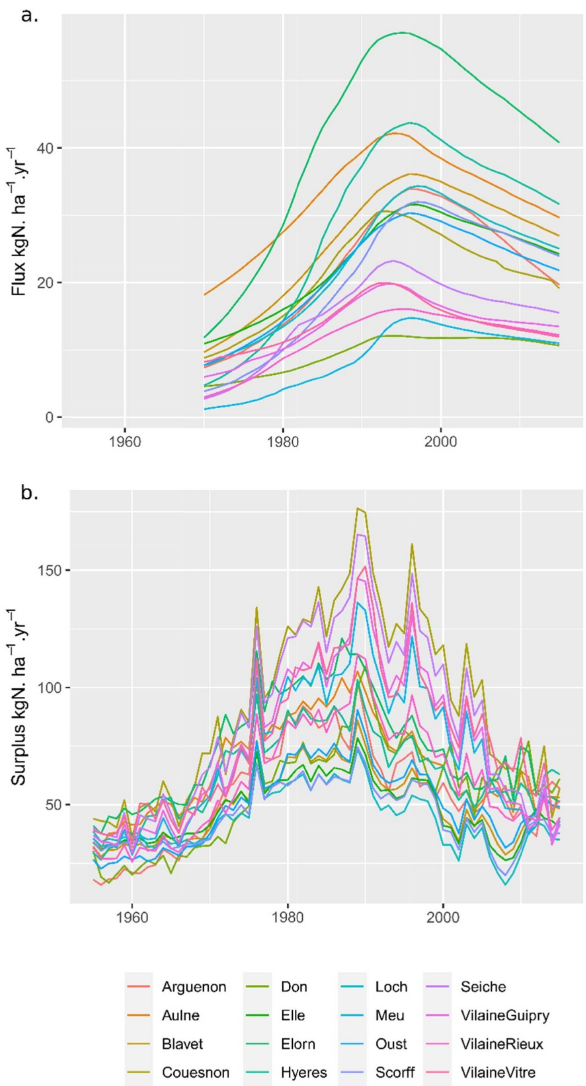

Figure 2. (a) Flow-normalized N flux (1976–2015) and (b) N surplus (1955–2015) in 16 catchments in Brittany.

times, mode and equilibrium time were strongly correlated ($r = 0.83–0.99$, $p < 0.05$, figure SI 3).

3.3. Relation to geographic variables and short-term concentration metrics

The long-term (1976–2015) retention rate was negatively correlated with long-term mean runoff ($r = -0.88$, $p < 0.05$), meaning that higher retention was observed in catchments with lower mean runoff (figure 5(a)). The mode of the TTD was not significantly correlated with long-term runoff. Granite and mixed-lithology catchments generally had longer transit times than schist catchments (figure 5). However, schist catchments had high variability in the TTD mode, and the mixed-lithology catchment Couesnon clustered with its schist-dominated neighbors despite having a substantial percentage (46%) of granite. This suggests that our classification of lithology into three simplified categories explained only some of the variability in the TTD mode. Neither long-term retention nor the TTD mode were significantly correlated with catchment area (figure SI 4).

4. Discussion

4.1. Fate of the missing nitrogen

The range of long-term retention estimated in 16 Brittany catchments (45%–88%) is similar to several

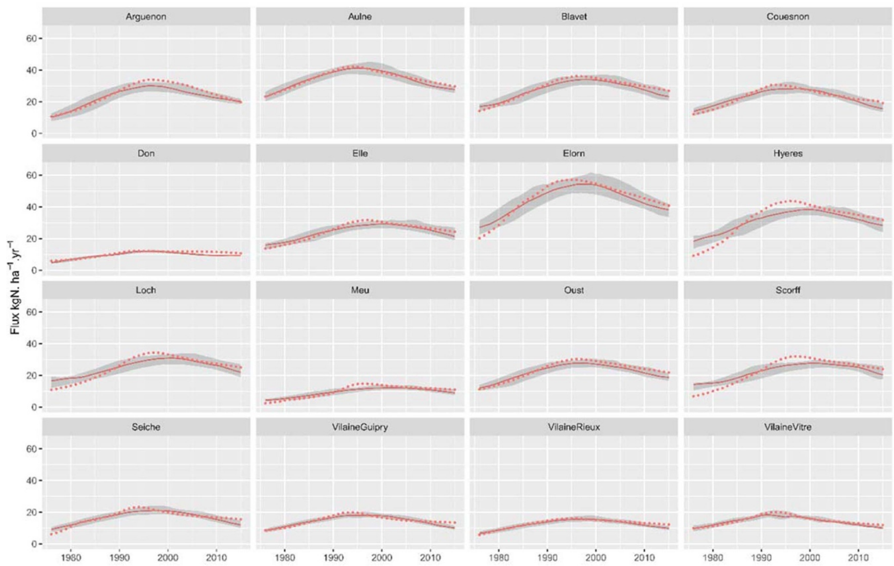

Figure 3. Modeled (solid lines) and observed flow-normalized (dotted lines) N flux in 16 catchments in the Brittany region from 1976–2015. Modeled N flux is the Nash–Sutcliffe-weighted median simulation. Gray bands represent the 5%–95% uncertainty interval.

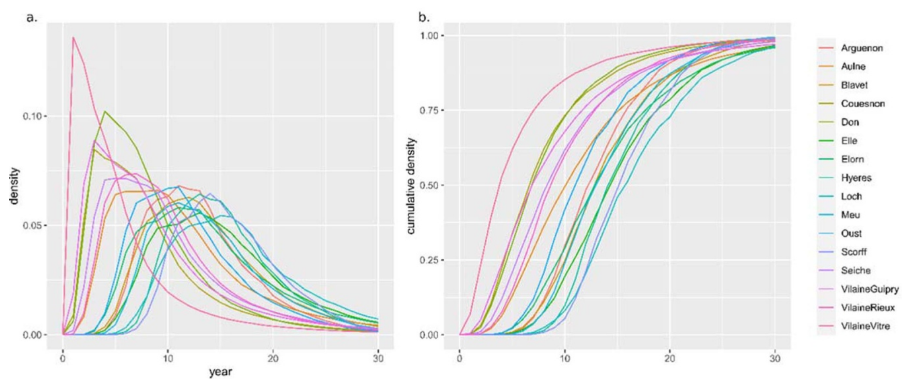

Figure 4. Modeled (a) annual and (b) cumulative nitrate transit time distribution in 16 catchments in the Brittany region from 1976–2015. Curves represent the Nash–Sutcliffe-weighted median of behavioral models according to generalized likelihood uncertainty estimation.

previous estimates in temperate regions. Billen *et al* (2011) estimated that N retention from European catchments that discharge into the Baltic, North, Mediterranean and Black Seas, and the Atlantic Ocean, averaged 78% of the net anthropogenic input. Estimates of retention in the northeastern United States also range from 70%–80% (Howarth *et al* 1996, Boyer *et al* 2002, Howarth *et al* 2006). Studies at more local scales found N retentions of 92% in a Mediterranean catchment (Lassaletta *et al* 2012), 88% in a temperate continental catchment (Ehrhardt *et al* 2019) and 53 ± 24% in 160 French catchments using short-term data from 2005–2009 (Dupas *et al* 2015). We note, however, that these studies use different N input data sources, which explains part of the differences together with differences in catchment properties.

This long-term estimate of N retention is more reliable than the previous estimate from a 5-year period in France, because estimates from short-term studies have a higher risk of being influenced by transient states than long-term studies (Dupas *et al* 2015). This long-term estimate is still subject to several sources of uncertainty, however, including estimation

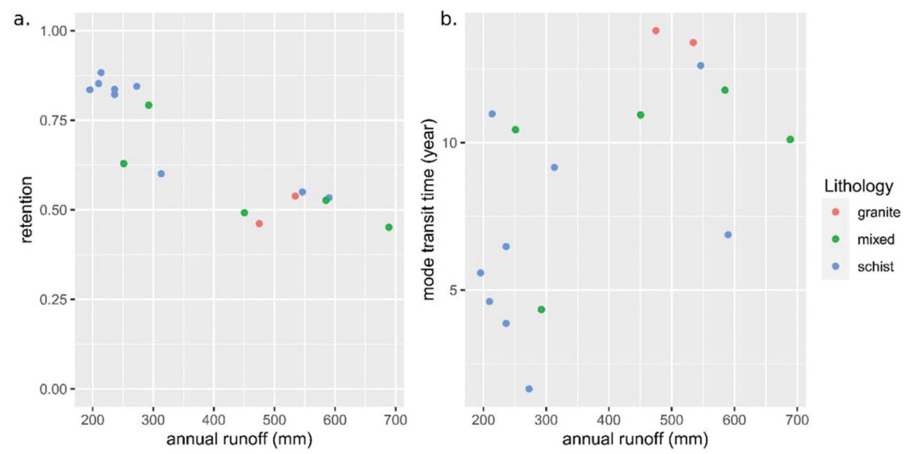

Figure 5. Relations between long-term annual runoff (1976–2015) and (a) long-term retention and (b) the mode of the estimated transit time distribution as a function of the dominant lithology.

of the N surplus, estimation of N load and no consideration of point sources. By construction, estimating the N surplus is uncertain because it is calculated as a difference: in Brittany from 1976–2015, the mean of all diffuse inputs (fertilizers, atmospheric deposition, biological fixation) was 144 kg N ha^{-1} yr^{-1}, and the mean of all agricultural exports (harvest) was 76 kg N ha^{-1} yr^{-1}, resulting in an estimated N surplus of 68 kg N ha^{-1} yr^{-1} (Poisvert *et al* 2017). Because of the calculation by difference, uncertainty of 10% in the input term would cause uncertainty of 21% in the estimate of N surplus. This effect should encourage researchers to focus more on relative differences in retention among catchments rather than their absolute values. A previous study estimated that nitrate represented 88% of total N load and point sources represented a mean of 2% of N load on average in 38 catchments in Brittany from 2005–2009 (Dupas *et al* 2015). Because the data on non-nitrate N and point source inputs were not available for our long-term study period, we decided not to correct our N load estimate and not include point-source inputs, assuming that doing so would have as little effect from 1976–2015 as from 2005–2009.

Like previous studies in France (Dupas *et al* 2015) and North America (Howarth *et al* 2006), we found that runoff predicted N retention well (r = −0.88). Howarth *et al* (2006) hypothesized that high runoff could decrease water residence times in riparian wetlands and low-order streams, thus decreasing denitrification. Dupas *et al* (2015) also pointed out that, due to the short study period in their own study and that of Howarth *et al* (2006), this observation could also be due to catchments being in a transient state, with wetter catchments responding faster to decreasing N inputs than drier catchments. The fact that we observed the same relation with runoff over a 40-year period strengthens the hypothesis of Howarth *et al* (2006) that wet areas are less favorable to permanent N removal via denitrification or long-term accumulation in soils. The lack of correlation between N retention and catchment area results from the secondary role played by riverine processes on N retention compared to hillslope processes in the Brittany region (Casquin *et al* 2020).

The mean annual topsoil N accumulation observed over a 10-year period in Brittany (32 kg ha^{-1} yr^{-1}) represented 64% of the estimated annual retention observed over a 40-year period (51 kg ha^{-1} yr^{-1}). Biogeochemical legacy could therefore account for much of the apparent retention, as also hypothesized by Worrall *et al* (2015) and observed by Van Meter *et al* (2016). Both Van Meter *et al* (2016) and Worrall *et al* (2015) nonetheless concluded that N accumulated primarily in subsoils, suggesting that our estimate of legacy soil N in the topsoil may even underestimate the actual biogeochemical legacy. Besides the lack of data on subsoils, several factors make our estimate uncertain: potential inability of a 10-year period to represent long-term N accumulation, possible bias in the location of soils sampled from 2000–2004 and 2010–2014, and lack of data on non-agricultural soil. Gaining access the spatial location of soil samples in the confidential data for research purposes would allow us to correct potential bias in sampling location and test whether areas with higher observed N retention also accumulate more N in the soil.

Despite these uncertainties, the conclusion that N accumulation exceeds N removal agrees with two independent studies in the 5 km^2 Kervidy-Naizin research catchment in Brittany, where denitrification was estimated to represent only 17% of retention (Durand *et al* 2015) and <10% of N export (Benettin et al2020). This legacy soil N is a potential threat to aquatic ecosystems but also a potential resource for crops that could allow farmers to reduce fertilizer applications. Because much of the N retained is likely to remain in the rooting zone, opportunities exist to recycle it in agrosystems by favoring uptake of the mineralized N by crops. Accumulation of organic N in soils also provides opportunities to sequester organic carbon and contribute to climate change mitigation (Bertrand *et al* 2019).

4.2. Nitrate transit time distribution

Many studies throughout the world have documented a lag time of several years to decades between decrease in N net inputs and improvement in water quality (see Chen *et al* (2018) for a review), although few have related this 'delay' to TTD percentiles. Our estimated mode and median of nitrate TTD of ca. 10 years is similar to those of previous studies on water TTD using chemical tracers and physical-based models in Brittany (Molenat *et al* 2002, Martin *et al* 2004, Ayraud *et al* 2008, Aquilina *et al* 2012, Fovet *et al* 2015). Ehrhardt *et al* (2019) also found modes of 19 and 12 years in two nested temperate catchments, using a similar method with agricultural N surplus as an input and assuming a lognormal transfer function.

As Van Meter and Basu (2015) noted, '[the existence of] biogeochemical nutrient legacies increases time lags beyond those due to hydrologic legacy alone'. Our estimated N TTD matched those previously estimated for water TTD because we assumed that the missing N was permanently retained or removed from the catchment, although the N that accumulated in soil could also be considered to be in transit (Howden *et al* 2011, Sebilo *et al* 2013, Worrall *et al* 2015). As a result, the actual tail of N TTD in Brittany is probably be thicker than our estimate suggests, which explains our focus on the TTD mode rather than on the equilibrium time. With more detailed information about the variation in N storage in soils and the vadose zone during the study period, and more accurate estimates of mineralization and denitrification rates, it would be possible to decrease the risk of equifinality in models such as ELEMeNT, which explicitly decomposes soil legacy, hydrological legacy and denitrification (Van Meter *et al* 2017, 2018, Ballard *et al* 2019).

Comparison of the catchments showed that granite and mixed-lithology catchments generally had longer transit times than schist catchments, although the latter had high variability in transit times. Previous groundwater dating studies have observed the same trend of older water in granite catchments than in schist catchments (Martin *et al* 2006, Ayraud *et al* 2008).

5. Conclusion

This study used long-term time series of N surplus and nitrate-N loads to estimate N retention and TTD in 16 catchments in Brittany, France. Estimated N retention ranged from 45%–88%, and the TTD mode ranged from 2–14 years, which agrees with previous studies in similar contexts. We used a two-step approach, first estimating N retention and then convoluting the remaining, exported N with a lognormal distribution. It provided a long-term mean retention rate and TTD that were useful for capturing the average behavior of catchments during the 40-year study period. We acknowledge the variable nature of both retention and TTD over time and emphasize that our modeling approach should not be used to predict future N loads in Brittany, because the soil N accumulation documented in this study may reach saturation in a not too distant future. Apparent retention was controlled primarily by average runoff, and the TTD mode was controlled in part by lithology. Furthermore, observed variations in soil N storage suggests that the biogeochemical legacy of soils accounted for ca. two-thirds of the catchment-scale N retention. From a methodological perspective, the uncertain fate of this biogeochemical legacy, whether in transit through the catchment, denitrified or taken up by crops, influences the estimated TTD. From a management perspective, this biogeochemical legacy is both a potential threat to aquatic ecosystems and a potential resource that could be recycled in agroecosystems.

Acknowledgments

RD and SE designed the study and carried out the analysis. RD wrote the paper. All authors discussed and interpreted the results and contributed to the text. We would like to thank Dr Robert D Sabo and two anonymous reviewers for their valuable and constructive comments.

Data availability statement

The data that support the findings of this study are openly available at the following URL/DOI: http://osur.eau-loire-bretagne.fr/; http://hydro.eaufrance.fr/ and https://geosciences.univ-tours.fr/cassis/login.

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References

Abbott B W *et al* 2018 Unexpected spatial stability of water chemistry in headwater stream networks *Ecol. Lett.* **21** 296–308

Agreste Bretagne 2019 Synthèse la Bretagne agricole et alimentaire 2019 N° 1

Alexander R B, Johnes P J, Boyer E W and Smith R A 2002 A comparison of models for estimating the riverine export of nitrogen from large watersheds *Biogeochemistry* **57** 295–339

Andersen J H *et al* 2017 Long-term temporal and spatial trends in eutrophication status of the Baltic Sea *Biol. Rev.* **92** 135–149

Aquilina L, Vergnaud-Ayraud V, Labasque T, Bour O, Molénat J, Ruiz L, de Montety V, De Ridder J, Roques C and Longuevergne L 2012 Nitrate dynamics in agricultural catchments deduced from groundwater dating and long-term nitrate monitoring in surface- and groundwaters *Sci. Total Environ.* **435** 167–78

Ayraud V *et al* 2008 Compartmentalization of physical and chemical properties in hard-rock aquifers deduced from chemical and groundwater age analyses *Appl. Geochem.* **23** 2686–707

Ballard T C, Michalak A M, Mcisaac G F, Rabalais N N and Turner R E 2019 Comment on 'Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico' *Science* **365**

Benettin P, Fovet O and Li L 2020 Nitrate removal and young stream water fractions at the catchment scale *Hydrol. Process.* **34** 2725–38

Bertrand I, Viaud V, Daufresne T, Pellerin S and Recous S 2019 Stoichiometry constraints challenge the potential of agroecological practices for the soil C storage *A Rev. Agronomy Sustain. Dev.* **39** 54

Beven K and Freer J 2001 Equifinality, data assimilation, and uncertainty estimation in mechanistic modelling of complex environmental systems using the GLUE methodology *J. Hydrol.* **249** 11–29

Billen G *et al* 2011 *Nitrogen Flows from European Watersheds to Coastal Marine Waters. The European Nitrogen Assessment* (Cambridge: Cambridge University Press) pp 271–97

Boyer E W, Goodale C L, Jaworsk N A and Howarth R W 2002 Anthropogenic nitrogen sources and relationships to riverine nitrogen export in the northeastern USA *Biogeochemistry* **57** 137–69

Casquin A, Gu S, Dupas R, Petitjean P, Gruau G and Durand P 2020 River network alteration of C-N-P dynamics in a mesoscale agricultural catchment *Sci. Total Environ.* **749** 141551

Chen D J *et al* 2018 Legacy nutrient dynamics at the watershed scale: principles, modeling, and implications *Advances in Agronomy*, Vol. 149, ed D L Sparks (San Diego: Elsevier Academic Press Inc) pp 237–313

Core Team R 2019 *R: A Language and Environment for Statistical Computing* (Vienna, Austria: R Foundation for Statistical Computing)

de Lavenne A and Cudennec C 2019 Assessment of freshwater discharge into a coastal bay through multi-basin ensemble hydrological modelling *Sci. Total Environ.* **669** 812–20

De Vries W, Leip A and Winiwarter W 2011 Geographical variation in terrestrial nitrogen budgets across Europe ed M A Sutton, C M Howard and J E Erisman *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives* (Cambridge: Cambridge University Press)

Dupas R, Delmas M, Dorioz J-M, Garnier J, Moatar F and Gascuel-Odoux C 2015 Assessing the impact of agricultural pressures on N and P loads and eutrophication risk *Ecol. Indic.* **48** 396–407

Dupas R, Minaudo C, Gruau G, Ruiz L and Gascuel-Odoux C 2018 Multidecadal trajectory of riverine nitrogen and phosphorus dynamics in rural catchments *Water Resour. Res.* **54** 5327–40

Durand P, Moreau P, Salmon-monviola J, Ruiz L, Vertes F and Gascuel-odoux C 2015 Modelling the interplay between nitrogen cycling processes and mitigation options in farming catchments *J. Agric. Sci.* **153** 959–74

Ehrhardt S, Kumar R, Fleckenstein J H, Attinger S and Musolff A 2019 Trajectories of nitrate input and output in three nested catchments along a land use gradient *Hydrol. Earth Syst. Sci.* **23** 3503–24

Ellili Y, Walter C, Michot D, Pichelin P and Lemercier B 2019 Mapping soil organic carbon stock change by soil monitoring and digital soil mapping at the landscape scale *Geoderma* **351** 1–8

Fovet O, Ruiz L, Faucheux M, Molénat J, Sekhar M, Vertès F, Aquilina L, Gascuel-Odoux C and Durand P 2015 Using long time series of agricultural-derived nitrates for estimating catchment transit times *J. Hydrol.* **522** 603–17

Frei R J *et al* 2020 Predicting nutrient incontinence in the anthropocene at watershed scales *Front. Environ. Sci.* **7** 200

Galloway J N, Aber J D, Erisman J W, Seitzinger S P, Howarth R W, Cowling E B and Cosby B J 2003 The nitrogen cascade *Bioscience* **53** 341–56

Gascuel-Odoux C, Aurousseau P, Durand P, Ruiz L and Molenat J 2010 The role of climate on inter-annual variation in stream nitrate fluxes and concentrations *Sci. Total Environ.* **408** 5657–66

Hirsch R M and Decicco L A 2019 EGRET: exploration and graphics for RivEr trends R package version 3.0.2

Hirsch R M, Moyer D L and Archfield S A 2010 Weighted regressions on time, discharge, and season (WRTDS), with an application to chesapeake bay river inputs *J. Am. Water Resour. Assoc.* **46** 857–80

Howarth R W *et al* 1996 Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: natural and human influences *Biogeochemistry* **35** 75–139

Howarth R W *et al* 2006 The influence of climate on average nitrogen export from large watersheds in the Northeastern United States *Biogeochemistry* **79** 163–86

Howarth R W and Marino R 2006 Nitrogen as the limiting nutrient for eutrophication in coastal marine ecosystems: evolving views over three decades *Limnol. Oceanogr.* **51** 364–76

Howden N J K, Burt T P, Mathias S A, Worrall F and Whelan M J 2011 Modelling long-term diffuse nitrate pollution at the catchment-scale: data, parameter and epistemic uncertainty *J. Hydrol.* **403** 337–51

Howden N J K, Burt T P, Worrall F, Whelan M J and Bieroza M 2010 Nitrate concentrations and fluxes in the River Thames over 140 years (1868-2008): are increases irreversible? Hydrol *Process* **24** 2657–62

Hrachowitz M *et al* 2016 Transit times the link between hydrology and water quality at the catchment scale Wiley Interdisciplinary Reviews-Water **3** 629–657

Kirchner J W, Feng X H and Neal C 2000 Fractal stream chemistry and its implications for contaminant transport in catchments *Nature* **403** 524–7

Kolbe T *et al* 2019 Stratification of reactivity determines nitrate removal in groundwater *Proc. Natl Acad. Sci. USA* **116** 2494–9

Lassaletta L, Romero E, Billen G, Garnier J, García-Gómez H and Rovira J V 2012 Spatialized N budgets in a large agricultural Mediterranean watershed: high loading and low transfer *Biogeosciences* **9** 57–70

Le Moal M *et al* 2019 Eutrophication: a new wine in an old bottle *Sci. Total Environ.* **651** 1–11

Li W C, Liu H, Zhai L, Yen H, Hu W, Lei Q, Stewart R J, Guo S and Ren T 2019 Evaluation of concentration-discharge dynamics and nitrogen export on anthropogenic inputs and stormflow across alternative time-scales *Ecol. Indic.* **98** 879–87

Martin C, Aquilina L, Gascuel-Odoux C, Molénat J, Faucheux M and Ruiz L 2004 Seasonal and interannual variations of nitrate and chloride in stream waters related to spatial and temporal patterns of groundwater concentrations in agricultural catchments *Hydrol. Process.* **18** 1237–54

Martin C, Molénat J, Gascuel-Odoux C, Vouillamoz J-M, Robain H, Ruiz L, Faucheux M and Aquilina L 2006

Modelling the effect of physical and chemical characteristics of shallow aquifers on water and nitrate transport in small agricultural catchments *J. Hydrol.* **326** 25–42
Mellander P-E, Jordan P, Bechmann M, Fovet O, Shore M M, Mcdonald N T and Gascuel-Odoux C 2018 Integrated climate-chemical indicators of diffuse pollution from land to water *Sci. Rep.* **8** 944
Molenat J, Durand P, Gascuel-Odoux C, Davy P and Gruau G 2002 Mechanisms of nitrate transfer from soil to stream in an agricultural watershed of French Brittany *Water Air Soil Pollut.* **133** 161–83
Montreuil O, Merot P and Marmonier P 2010 Estimation of nitrate removal by riparian wetlands and streams in agricultural catchments: effect of discharge and stream order *Freshw. Biol.* **55** 2305–18
Oehler F, Bordenave P and Durand P 2007 Variations of denitritication in a farming catchment area *Agric. Ecosyst. Environ.* **120** 313–24
Oenema O, Kros H and de Vries W 2003 Approaches and uncertainties in nutrient budgets: implications for nutrient management and environmental policies *Eur. J. Agronomy* **20** 3–16
Pinay G *et al* 2017 Eutrophication: manifestations, causes, consequences and predictability Joint Scientific Appraisal, report, CNRS - Ifremer - INRA - Irstea (France): 136 pages
Pinay G, Peiffer S, De Dreuzy J-R, Krause S, Hannah D M, Fleckenstein J H, Sebilo M, Bishop K and Hubert-Moy L 2015 Upscaling nitrogen removal capacity from local hotspots to low stream orders' drainage basins *Ecosystems* **18** 1101–20
Poisvert C, Curie F and Moatar F 2017 Annual agricultural N surplus in France over a 70-year period *Nutrient Cycling in Agroecosystems* **107** 63–78
Saby N *et al* 2014 Le programme Base de Données des Analyses de Terre (BDAT): bilan de 20 ans de collecte de résultats d'analyses Etude et Gestion des Sols **21** 141–50
Sebilo M, Mayer B, Nicolardot B, Pinay G and Mariotti A 2013 Long-term fate of nitrate fertilizer in agricultural soils *Proc. Natl Acad. Sci. USA* **110** 18185–9
Seitzinger S, Harrison J A, Böhlke J K, Bouwman A F, Lowrance R, Peterson B, Tobias C and Drecht G V 2006 Denitrification across landscapes and waterscapes: a synthesis *Ecological Appl.* **16** 2064–90
Smetacek V and Zingone A 2013 Green and golden seaweed tides on the rise *Nature* **504** 84–88
Turner R E, Rabalais N N and Justic D 2008 Gulf of Mexico hypoxia: alternate states and a legacy *Environ. Sci. Technol.* **42** 2323–7
Van Breemen N *et al* 2002 Where did all the nitrogen go? Fate of nitrogen inputs to large watersheds in the northeastern USA *Biogeochemistry* **57** 267–93
Van Meter K J and Basu N B 2015 Catchment legacies and time lags: a parsimonious watershed model to predict the effects of legacy storage on nitrogen export *Plos One* **10** 5
Van Meter K J and Basu N B 2017 Time lags in watershed-scale nutrient transport: an exploration of dominant controls *Environ. Res. Lett.* **12** 084017
Van Meter K J, Basu N B and Van Cappellen P 2017 Two centuries of nitrogen dynamics: legacy sources and sinks in the Mississippi and Susquehanna River Basins *Global Biogeochem. Cycles* **31** 2–23
Van Meter K J, Basu N B, Veenstra J J and Burras C L 2016 The nitrogen legacy: emerging evidence of nitrogen accumulation in anthropogenic landscapes *Environ. Res. Lett.* **11** 3
Van Meter K J, Van Cappellen P and Basu N B 2018 Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico *Science* **360** 6387
Vero S E *et al* 2017 Review: the environmental status and implications of the nitrate time lag in Europe and North America *Hydrogeol J.* **26** 7–22
Wang H J, Dai M, Liu J, Kao S-J, Zhang C, Cai W-J, Wang G, Qian W, Zhao M and Sun Z 2016 Eutrophication-driven hypoxia in the East China sea off the Changjiang Estuary *Environ. Sci. Technol.* **50** 2255–63
Worrall F, Howden N J K and Burt T P 2015 Time series analysis of the world's longest fluvial nitrate record: evidence for changing states of catchment saturation *Hydrol. Process.* **29** 434–44
Zhang Q and Hirsch R M 2019 River water-quality concentration and flux estimation can be improved by accounting for serial correlation through an autoregressive model *Water Resour. Res.* **55** 9705–9723

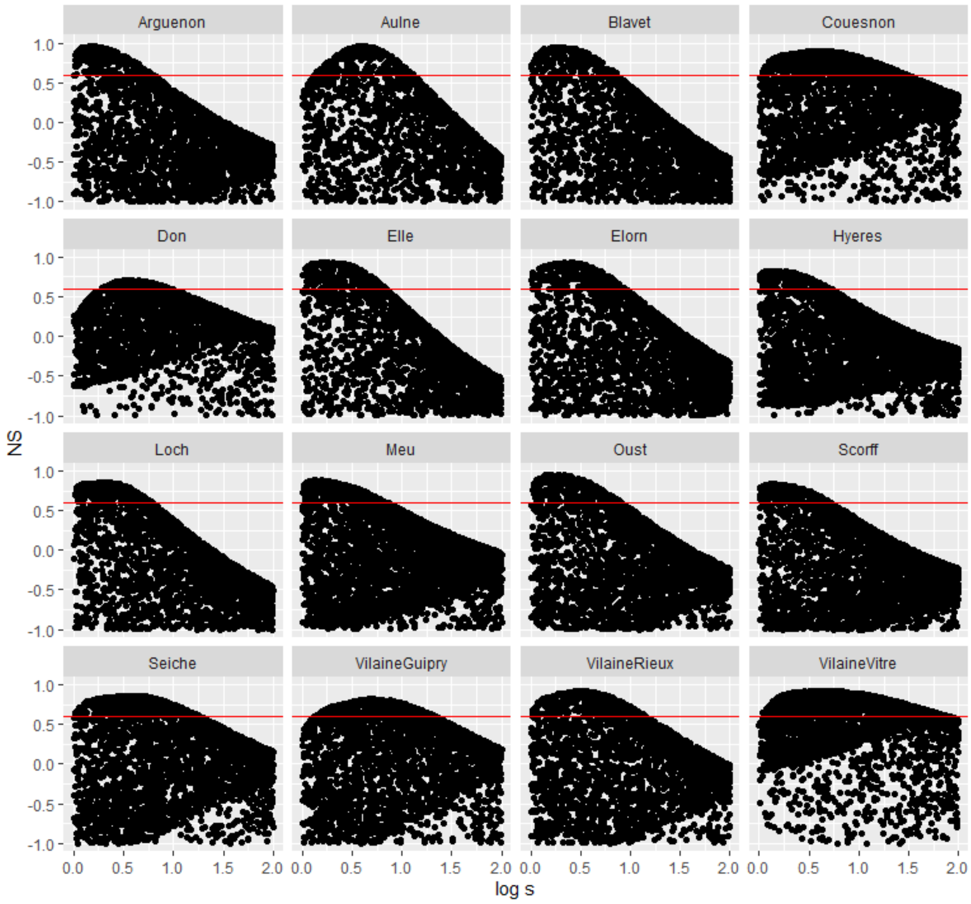

Figure S2: Nash-Sutcliffe (NS) efficiency coefficient for 5000 simulations, parameter σ.

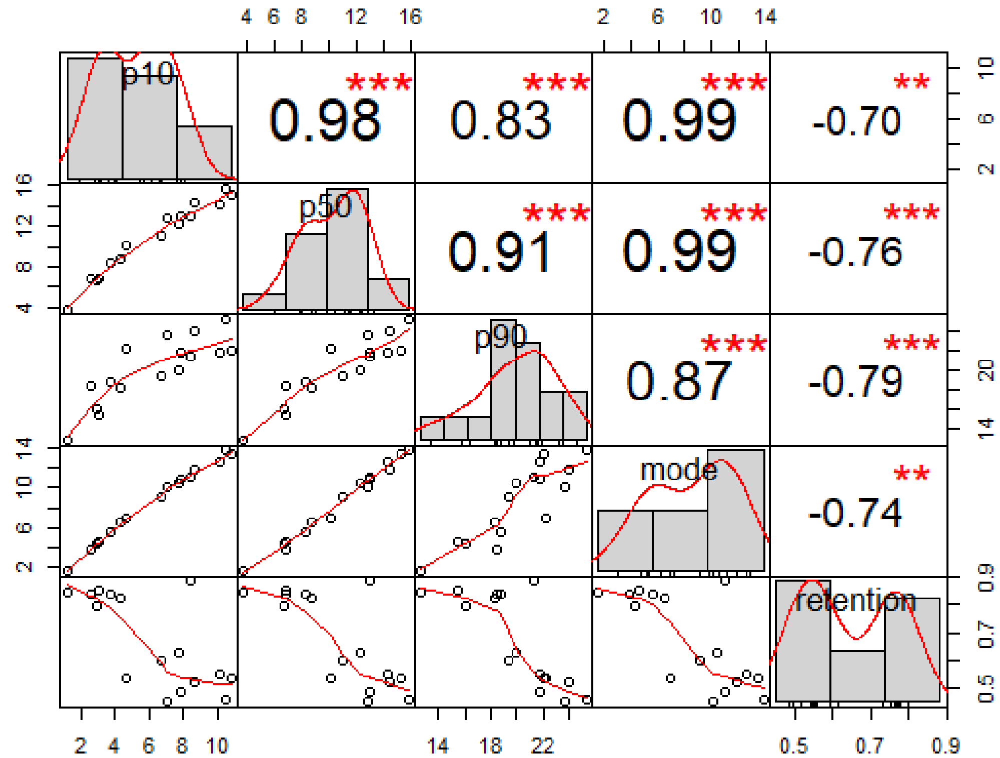

Figure S3. Pearson correlations among transit time distribution percentiles 10% (p10), 50% (p50), 90% (p90), mode and long-term N retention.

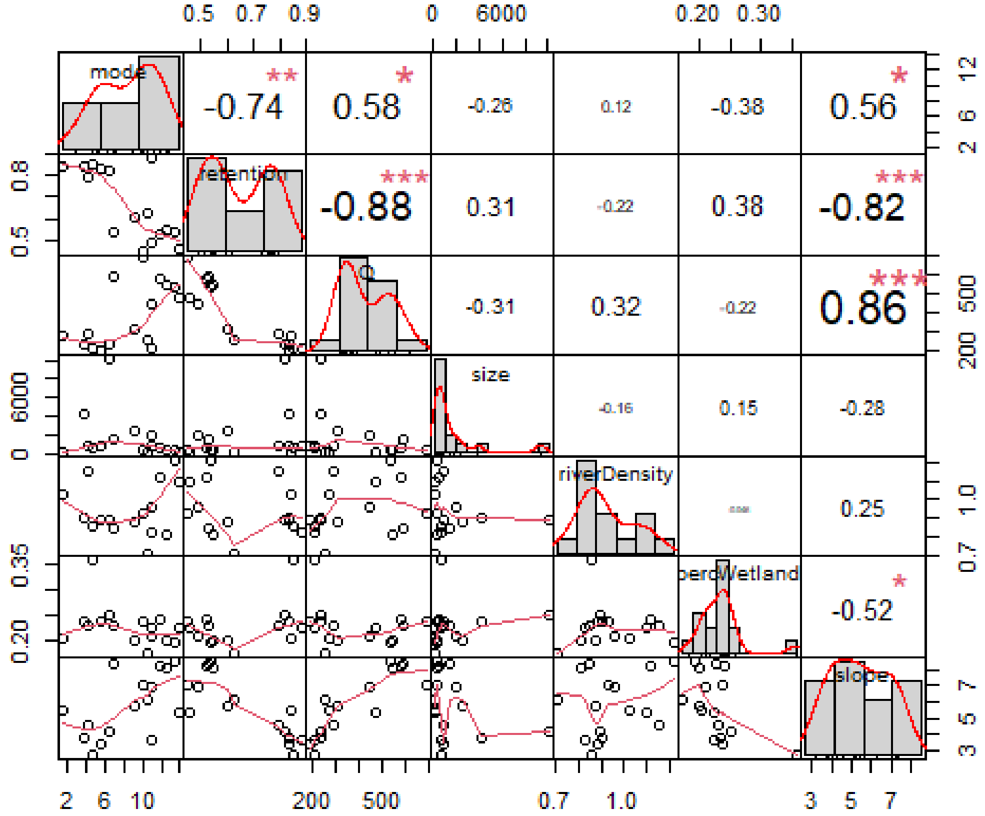

Figure S4. Pearson correlations among transit time distribution mode, long-term N retention and geographic variables.

Study 3: Nitrate transport and retention in western European catchments are shaped by hydroclimate and subsurface properties

Status: Under review in Water Resources Research
DOI: 10.1002/essoar.10505117.1
Authors: Sophie Ehrhardt, Pia Ebeling, Rémi Dupas, Jan H. Fleckenstein, Rohini Kumar, Andreas Musolff

SE, PE, RD and RK provided the data for which SE carried out the analysis, interpreted the data and wrote the paper. All authors helped finalize the paper.

Own contribution:

- Study concept and design: 90 %
- Data analysis: 70 %
- Preparation of figures and tables: 100 %
- Interpretation of the results: 90 %
- Preparation of the manuscript: 90 %

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RESEARCH ARTICLE
10.1029/2020WR029469

Key Points:
- Time lags of nitrogen transport in Western European catchments were 5 years on average and varied in space with hydroclimatic conditions
- Large parts of the diffuse N input was retained in the catchments with differences explained by subsurface properties and specific discharge
- Biogeochemical legacy likely exceeded hydrologic legacy in most of the 238 analyzed catchments

Supporting Information:
Supporting Information may be found in the online version of this article.

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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 limited 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 transport times with an average riverine concentration peak arriving 5 years after application. Longer transport times were evident in catchments with high potential evapotranspiration and low precipitation seasonality. On average the catchments retained 72% (Interquartile Range: 18%) 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 by fostering denitrifying conditions or soil N recycling 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. We assessed long-term data covering nitrogen in- and output for Western-European catchments to quantify (a) the needed transport time until reappearance in the river and (b) the quantity of reappeared nitrate. The excess N transport through the Western European catchments had an average time lag of 5 years; and the variation in this transport time was mainly controlled by hydrological parameters with high seasonality in precipitation favoring faster transports. Furthermore large parts of the nitrate was retained in the catchments, with differences explained by subsurface characteristics such that 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 being leached down 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 wastewater. High N inputs especially in economically developed countries have led to increased riverine nitrogen 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 & Grizzetti, 2011; Dupas et al., 2013).

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Several regulations at federal, national or international levels have been implemented, for example, 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. While these measures have proven successful in selected areas (e.g., Kronvang et al., 2008), many catchments have seen no or only little improvement in water quality (Bouraoui & Grizzetti, 2011; Meals et al., 2010; Vero et al., 2017). The mismatch between implemented measures such as reductions in the nutrient inputs and the observed water quality in streams can be related to transport processes and retention within the catchments. 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 a persistent 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, that is, 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, long travel times and a resulting temporary storage of reactive N in the soil, unsaturated zone and in groundwater (Ascott et al., 2017; Ehrhardt et al., 2019; Kumar et al., 2020), 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 approaches that jointly characterize N transport timescales and retention under different land-use and management practices can help better understanding the N trajectories for reactive N dynamics at a catchment scale (e.g., Ehrhardt et al., 2019; Van Meter & 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 multi-annual 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. 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), only a few studies have 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, 2018). 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 (a) TT scales and (b) retention. Furthermore, we connect both to catchment characteristics to discuss their (c) main controlling factors. These results 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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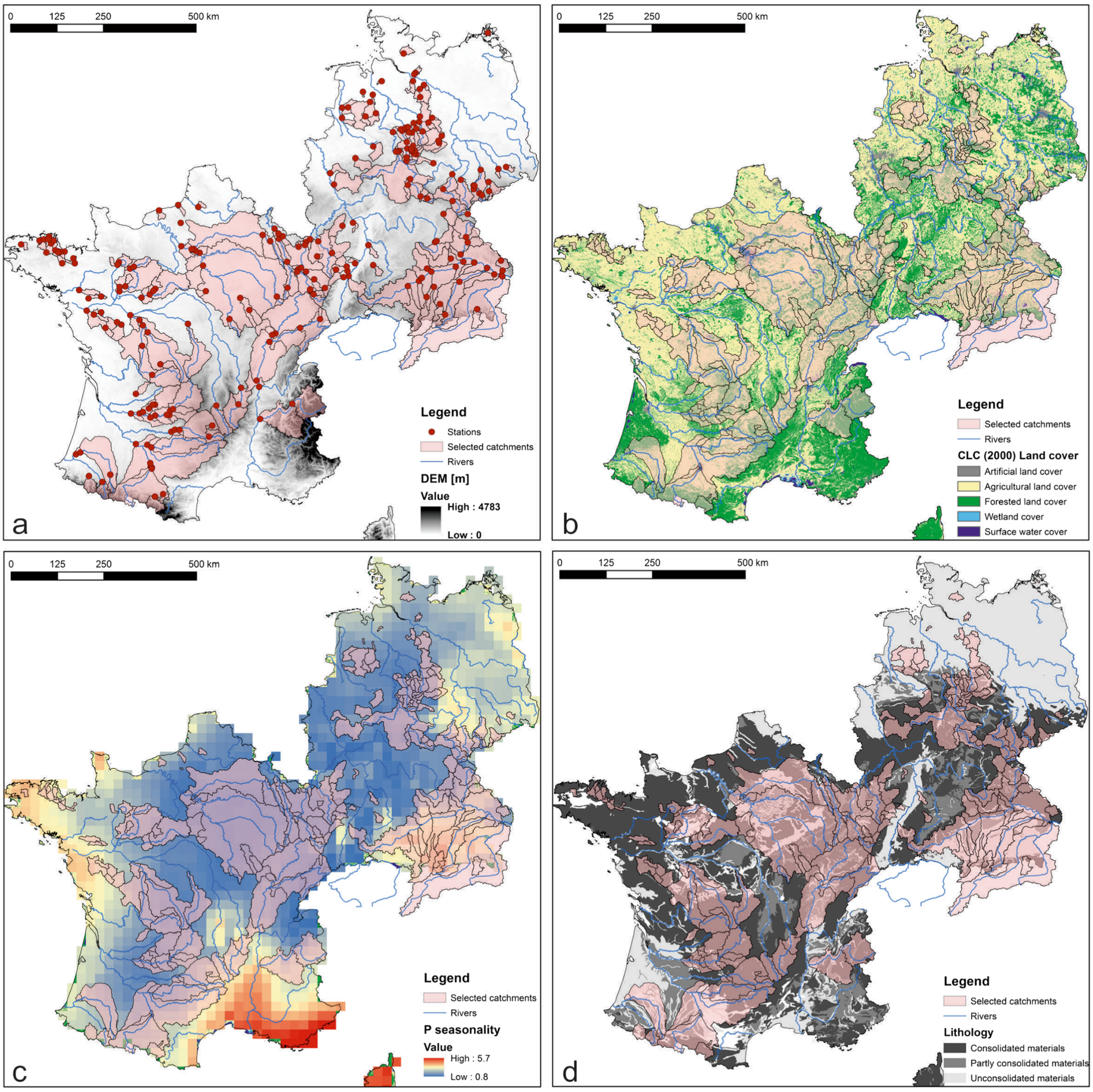

Figure 1. Study catchments (n = 238) based on the quality criteria with selected catchment characteristics: (a) Elevation (EEA, 2013), (b) Land cover (CLC, 2000), (c) Precipitation seasonality, (d) Lithology (BCR & UNESCO, 2014).

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.

By focusing on NO_3-N loads, here we do not account for riverine N export in other mineral (NO_2-N, NH_4-N) or organic N forms. In recent studies by Ebeling et al. (2021) and Dupas et al. (2015) NO_3-N was found to be the dominant form of exported N across the study catchments. Moreover, for the German catchments presented here, 71% of samples did not have information on all N species available. Calculating the loads of

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exported N for samples where full information was available revealed that across the German catchments, a median of 92.4% of mineral N species was obtained as NO_3-N. And compared to total N (mineral and organic species) a median of 81.4% was in form of NO_3-N. Assuming similar conditions for other catchments, we acknowledge that our analysis based on only NO_3-N may miss 18.6% of loads that is exported by other N-species.

Overall the data selection 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 (Tables S1.1 and S1.2 in Supporting Information S1). 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 to 1,848 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 with a median value of the catchment average sand content for the upper 1 m of soil to be around 44.6% (median estimated across all catchments). 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 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 Center-West (MSC-W) of the European Monitoring and Evaluation Program (EMEP) (Bartnicky & Fagerli, 2006; Bartnicky & Benedictow, 2017).

In agricultural areas, biological fixation was already included as an input in the N budgets. The biologically fixed N fluxes to non-agricultural land use types, for example, to green lands (urban and natural) or forests, 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} year^{-1}; Cleveland et al., 1999), for natural and urban grassland (to 2.7 kg N ha^{-1} year^{-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} year^{-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 Section S2 in Supporting Information S1 for further information).

Due to the lack of spatially and temporally reliable long-term data on N input by wastewater, we did not consider this point source. For France, Dupas et al. (2015) estimated the contribution from domestic and

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industrial point sources to total N loads to be 3% during the period 2005–2009, and we hypothesized that the negligible contribution of point sources also held for Germany. However, we acknowledge a high uncertainty of wastewater inflow that may have been higher in the past (Westphal et al., 2020).

2.3. Nitrogen Output as Riverine NO_3-N Concentrations and Loads

Continuous (and regular) time series of discharge and concentrations are needed for adequately calculating the retention parameters based on the N surplus and in-stream NO_3-N loads. Gaps in the discharge time series at 30 runoff stations in Germany were therefore 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 modeled data. These bias-corrected modeled 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 de Cicco (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 adopted 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.

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

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

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 Zambrano-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.

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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. This mass calculation assumes that catchment delineation based on topography approximates subsurface catchments and that no significant amounts of N are bypassing the surface water gauging station. The cumulative flux differences were calculated based on two approaches: (a) using the annual frames of the overlapping years in in- and outflux, while disregarding time shifts; and (b) applying the derived TTs, to compare the convolved inputs with the corresponding annual exported load.

$$\text{Retention} = 1 - \frac{N_{\text{out}}}{N_{\text{in}}} = 1 - \frac{\sum_{i=ts}^{te} NO_3 - N_{\text{flux}\,i}}{\sum_{i=ts}^{te} N_{\text{input}\,i}} \quad (3)$$

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 (TT and retention; 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 annual 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 (Tables S3 and S4 in Supporting Information S1). 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).

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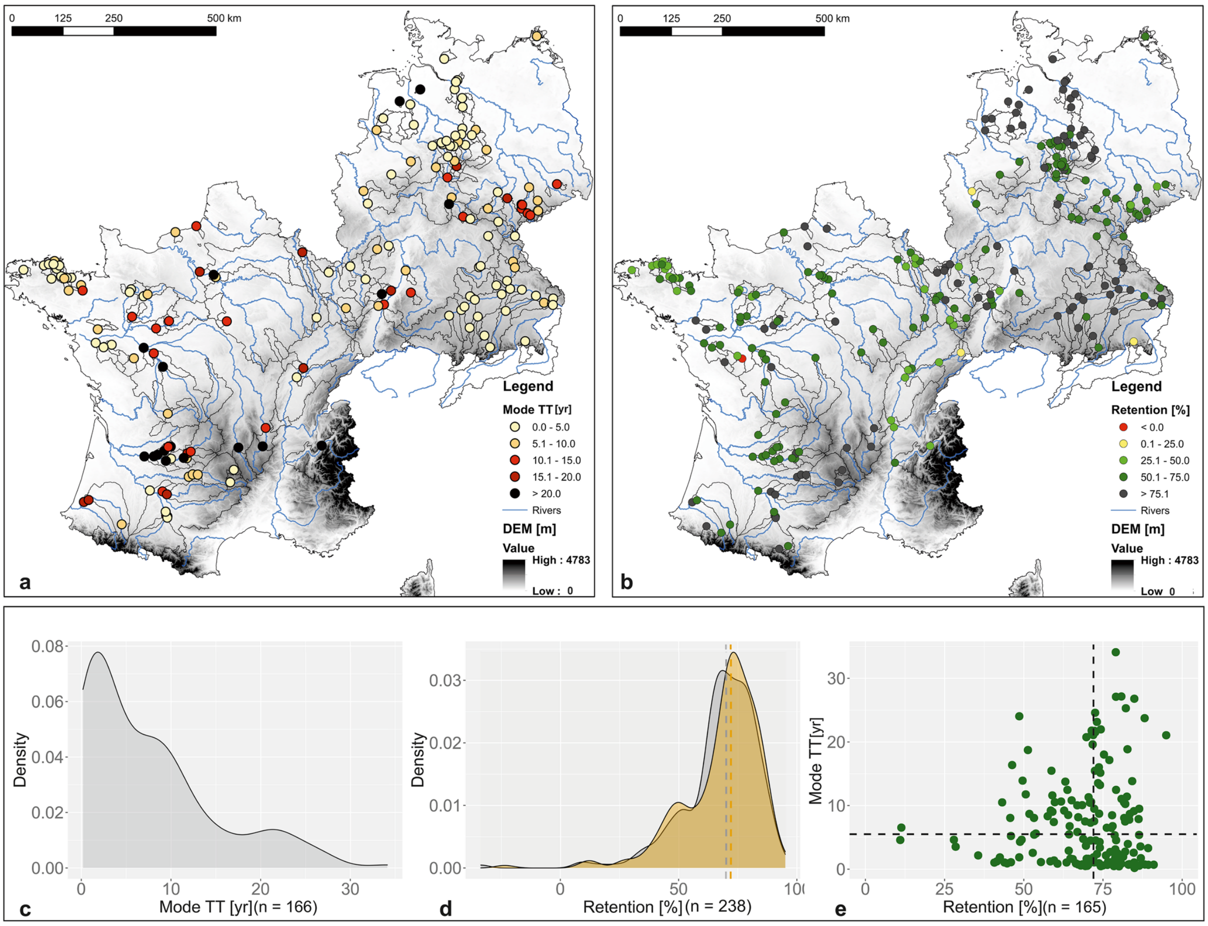

Figure 2. (a) Spatial variation of the TT modes in the 166 catchments with an $R^2 \geq 0.6$. (b) Spatial variation of the overlapping retention in all of the analyzed catchments ($n = 238$). (c) Histogram of the mode TTs. (d) Histogram of the retention for the overlapping time (beige curve) and the convolved retention (gray 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.

3.2. Nitrogen Retention

The median N retention of the selected catchments ($n = 238$) was 72% (sd: 16%; Table S3 in Supporting Information S1; 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 and Text S5 in Supporting Information S1), 48% of the catchments had 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} year^{-1} (Interquartile Range, IQR: 42.0 kg N ha^{-1} year^{-1}), decreasing by around 36%, when assuming the bootstrapped difference in medians of 22.6 kg N ha^{-1} year^{-1} (95% CI: 20.5–25.6 kg N ha^{-1} year^{-1}) in comparison to the 2010s. Diffuse N input in the 2010s was around 38.4 kg N ha^{-1} year^{-1} (IQR: 23.1 kg N ha^{-1} year^{-1}). The median N load in the 1980s was 12.4 kg N ha^{-1} year^{-1} (IQR: 6.1 kg N ha^{-1} year^{-1}) with a bootstrapped difference of medians of 1.2 kg N ha^{-1} year^{-1} (95% CI: 0.8–1.6 kg N ha^{-1} year^{-1}) to the 2010s (median N load: 11.2 kg N ha^{-1} year^{-1}; IQR: 5.7 kg N

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Table 1
Ranked Drivers for Explaining the Variability in Transport Times and N Retention Across the Study Catchments Based on the Partial Least Squares Regression (PLSR) Analysis, Along With the Corresponding Explained Variability (R^2), VIPs and Signs (See Also Section S6 in Supporting Information S1 for Details)

Transport time $R^2 = 0.49$			Retention $R^2 = 0.69$		
Variable	VIP	Sign	Variable	VIP	Sign
Potential evapotranspiration	2.1	+	Depth to bedrock	1.9	+
Precipitation seasonality	2.1	–	Consolidated aquifer material	1.5	–
Coefficient of variation of discharge	1.9	–	Porous aquifer material	1.5	–
Topographic wetness index	1.5	–	Specific discharge	1.5	–
Median winter discharge	1.3	–	Precipitation frequency	1.4	–

Note. The sign indicates the direction of influence.

ha^{-1} year^{-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%.

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 (Table 1). Variables that are connected to the catchment's hydroclimatological characteristics were found to be most important (see also Figure S6.1 in Supporting Information S1). Potential evapotranspiration (PET) was analyzed as the most important variable 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 the second most influential predictor. 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 (a) higher coefficients of variation of discharge, (b) higher topographic wetness indices (TWI) and (c) higher median winter discharges.

The N retention across the catchments was well predicted by the PLSR ($R^2 = 0.69$, excluding one negative outlier, Table 1). Three of the five most important parameters (see also Figure S6.2 in Supporting Information S1) referred to subsurface characteristics, while two predictors were hydrological descriptors. Depth to bedrock (i.e., distance from ground surface to continuous bedrock) was connected to high retention and was the most important predictor. At the same time, a high share of consolidated and porous aquifer materials were associated with low retention, while vice versa catchments with a high share of unconsolidated aquifers (VIP = 1.4, rank 6) favored higher retention. In context of hydrological parameters: high specific discharge and precipitation frequency, both favoring low retention were ones appear as most informative ones associated with the N retention across the study catchments.

4. Discussion

The results of a comparison of diffuse N input and riverine N output time series from 238 West European catchments revealed the median peak TTs of 5 years and a median retention of 72%. While differences in estimated TTs among the catchments were mainly explained by hydroclimatic properties, differences in the retention were mainly explained by hydrologic and subsurface properties.

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.

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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; Figure S7 in Suppporting Information S1; 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-García & 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 in areas with high groundwater levels (e.g., Grabs et al., 2012): 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). As previous studies that indicated no signs of dilution patterns in a concentration-discharge relationship during high-flow conditions across the majority of the analyzed catchments in either France (Moatar et al., 2017) or Germany (Ebeling et al., 2021), we assume rather a mobilization of N from shallow nitrate sources than a bypass of N, for example, by overland flow.

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.

A 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 generally 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 pronounced changes in evapotranspiration with increasing temperature (Donnelly et al., 2017) will likely counteract this trend by favoring for longer TTs with more drying conditions. Since the climate is expected to manifest differently within Europe, reliable predictions of future N TTs on regional scales 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 (e.g., Goyette et al., 2019; Powers et al., 2015). Furthermore the method, assuming a constant (static) 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; Kumar et al., 2020; 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%). We thus do not capture N that may leave the catchment by other mineral or organic N species (see Section 2); and as well we cannot exclude the possible role of long flow pathways that do not return to the rivers within the observation period. 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.

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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. (2021), 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 sulfide 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 in a recent study, Ebeling et al. (2021) found a very limited evidence for denitrification in these (German) areas. 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). We note that so far there is no clear soil data evidence for a buildup of a soil-legacy in the Alpine foothills comparable to Dupas et al. (2020) findings for the Armorican Massif of to the large scale-evidence presented by Van Meter et al. (2016).

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 (providing electron donors, 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.

One 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; Kumar et al., 2020; 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

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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. The other hydrologic predictor for retention was the precipitation frequency p-lambda. According to Botter et al. (2013), a high frequency of flow-producing rainfall events will increase the likelihood of a more persistent discharge regime. In connection to N transport we argue that catchments with a high frequency of runoff events and a more persistent discharge regime are supposed to more permanently export N from soil sources, counteracting the N retention.

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} $year^{-1}$ (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. Furthermore, increased temperature stress and precipitation variability under future climate is likely to affect plant N uptake and subsequent unintentional NO_3-N leaching (e.g., Hatfield et al., 2011; Jabloun et al., 2015; Wang et al., 2015).

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 across the studied catchments. The observed rather 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. It is worth mentioning here that these numbers may be lower as we refer to the N exported as NO_3-N that though accounts for the majority (81.4% in the German catchments, see Section 2) but not all riverine N loads. 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.

In line with the above 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 a buffer effect, which stems from the accumulated biogeochemical legacy – acting as a secondary source and constituting a system inert to declining N inputs. A similar kind of biogeochemical dominance was also reported in a recent study for northwestern French catchments (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.

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} $year^{-1}$ (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} $year^{-1}$). 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. These observations 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.

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.

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1. 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 this time lag in the response of N concentrations to changing N inputs.
2. Our analyses suggest a minor role of hydrologic legacy to explain the high retention of N in catchments (around three-fourths of incoming N). 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 (i.e., increase plant-availability of soil N, catch-crops, supporting riparian rehabilitation, decreasing land drainage or by increasing levels of bio-available organic carbon; Abbott et al., 2018; Hunter et al., 2006).
3. 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.
4. 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 complement modeling approaches assisting different large scale water quality management activities.

Data Availability Statement

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 and quantity data for French catchments are available at http://www.hydroshare.org/resource/d8c43e1e8a5a4872bc0b75a45f350f7a (Ehrhardt et al., 2021). 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 et al., 2020). Catchment characteristics for Germany and France are available at https://www.hydroshare.org/resource/c7d4df3ba74647f0aa83ae92be2e294b/(Ebeling & Dupas, 2021).

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References

Abbott, B. W., Moatar, F., Gauthier, O., Fovet, O., Antoine, V., & Ragueneau, O. (2018). Trends and seasonality of river nutrients in agricultural catchments: 18 years of weekly citizen science in France. *The Science of the Total Environment*, *624*, 845–858. https://doi.org/10.1016/j.scitotenv.2017.12.176

Ai, L., Shi, Z. H., Yin, W., & Huang, X. (2015). Spatial and seasonal patterns in stream water contamination across mountainous watersheds: Linkage with landscape characteristics. *Journal of Hydrology*, *523*, 398–408. https://doi.org/10.1016/j.jhydrol.2015.01.082

Allain, M. (1951). *France GEOLOGIQUE. Atlas universel Quillet physique, économique, politique. Tome 1: France et union française (1951)*. Retrieved from https://www.mapmania.org/map/76435/geology_of_france__carte_geologique_de_la_france__5038_x_4687

Allred, B. J., Bigham, J. M., & Brown, G. O. (2007). The impact of clay mineralogy on nitrate mobility under unsaturated flow conditions. *Vadose Zone Journal*, *6*(2), 221–232. https://doi.org/10.2136/vzj2006.0064

Ascott, M. J., Gooddy, D. C., Wang, L., Stuart, M. E., Lewis, M. A., Ward, R. S., & Binley, A. M. (2017). Global patterns of nitrate storage in the vadose zone. *Nature Communications*, *8*(1), 1–7. https://doi.org/10.1038/s41467-017-01321-w

Bach, M., & Frede, H. G. (1998). Agricultural nitrogen, phosphorus and potassium balances in Germany-Methodology and trends 1970 to 1995. *Zeitschrift für Pflanzenernährung und Bodenkunde*, *161*, 8. https://doi.org/10.1002/jpln.1998.3581610406

Bain, D. J., Green, M. B., Campbell, J. L., Chamblee, J. F., Chaoka, S., Fraterrigo, J. M., et al. (2012). Legacy effects in material flux: Structural catchment changes predate long-term studies. *BioScience*, *62*(6), 575–584. https://doi.org/10.1525/bio.2012.62.6.8

Bartnicky, J., & Benedictow, A. (2017). *Atmospheric deposition of nitrogen to OSPAR convention waters in the period 1995–2014*.

Bartnicky, J., & Fagerli, H. (2006). *Atmospheric nitrogen in the OSPAR convention area in the period 1990–2004*.

Basu, N. B., Destouni, G., Jawitz, J. W., Thompson, S. E., Loukinova, N. V., Darracq, A., et al. (2010). Nutrient loads exported from managed catchments reveal emergent biogeochemical stationarity. *Geophysical Research Letters*, *37*(23). https://doi.org/10.1029/2010gl045168

Benettin, P., Rinaldo, A., & Botter, G. (2013). Kinematics of age mixing in advection-dispersion models. *Water Resources Research*, *49*(12), 8539–8551. https://doi.org/10.1002/2013wr014708

BGR and CGMW. (2005). *The 1:5 million international geological map of Europe and adjacent areas (IGME 5000)*. Retrieved from https://geoviewer.bgr.de/mapapps4/resources/apps/geoviewer/index.html?cover=geologie_igme5000_ags&tab=geologie&lang=de

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Water Resources Research 10.1029/2020WR029469

BGR and UNESCO. (2014). *International hydrogeological map of Europe 1: 1,500,000 (IHME1500). Digital map data v1.1*. Retrieved from http://www.bgr.bund.de/ihme1500/http://www.bgr.bund.de/ihme1500/

Bingham, A. H., & Cotrufo, M. F. (2016). Organic nitrogen storage in mineral soil: Implications for policy and management. *The Science of the Total Environment*, *551–552*, 116–126. https://doi.org/10.1016/j.scitotenv.2016.02.020

Birkel, C., Soulsby, C., & Tetzlaff, D. (2015). Conceptual modelling to assess how the interplay of hydrological connectivity, catchment storage and tracer dynamics controls nonstationary water age estimates. *Hydrological Processes*, *29*(13), 2956–2969. https://doi.org/10.1002/hyp.10414

Blume, T., & van Meerveld, H. J. (2015). From hillslope to stream: Methods to investigate subsurface connectivity. *Wiley Interdisciplinary Reviews-Water*, *2*(3), 177–198. https://doi.org/10.1002/wat2.1071

BMU, B. f. U., Naturschutz und Reaktorsicherheit. (2003). Hydrologischer Atlas von Deutschland. Grundwasser. Retrieved from http://www.hydrology.uni-freiburg.de/forsch/had/had_bezug.htm

Botter, G., Basso, S., Rodriguez-Iturbe, I., & Rinaldo, A. (2013). Resilience of river flow regimes. *Proceedings of the National Academy of Sciences*, *110*(32), 12925–12930. https://doi.org/10.1073/pnas.1311920110

Botter, G., Bertuzzo, E., & Rinaldo, A. (2011). Catchment residence and travel time distributions: The master equation. *Geophysical Research Letters*, *38*(11), a–n. https://doi.org/10.1029/2011gl047666

Bouraoui, F., & Grizzetti, B. (2011). Long term change of nutrient concentrations of rivers discharging in European seas. *The Science of the Total Environment*, *409*(23), 4899–4916. https://doi.org/10.1016/j.scitotenv.2011.08.015

Bouwman, A. F., Beusen, A. H., Griffioen, J., Van Groenigen, J. W., Hefting, M. M., Oenema, O., et al. (2013). Global trends and uncertainties in terrestrial denitrification and N_2O emissions. *Philosophical Transactions of the Royal Society of London B Biological Sciences*, *368*(1621), 20130112. https://doi.org/10.1098/rstb.2013.0112

Buydko, M. I. (1974). *Climate and life*. Academic Press.

CEC. (1991). Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources. (No L 375/1). Official Journal of the European Communities. Retrieved from https://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX%3A31991L0676

CLC. (2000). CORINE land cover 2000. Retrieved from https://land.copernicus.eu/pan-european/corine-land-cover

Cleveland, C. C., Townsend, A. R., Schimel, D. S., Fisher, H., Howarth, R. W., Hedin, L. O., et al. (1999). Global patterns of terrestrial biological nitrogen (N_2) fixation in natural ecosystems. *Global Biogeochemical Cycles*, *13*(2), 623–645. https://doi.org/10.1029/1999gb900014

de Vries, W., Leip, A., Reinds, G. J., Kros, J., Lesschen, J. P., Bouwman, A. F., et al. (2011). Geographical variation in terrestrial nitrogen budgets across Europe. In M. A. Sutton, C. M. Howard, J. W. Erisman, G. Billen, A. Bleeker, P. Grennfelt, H. van Grinsven, & B. Grizzetti (Eds.), *The European nitrogen assessment. Sources, effects and policy perspectives* (pp. 317–344): Cambridge University Press.

Donnelly, C., Greuell, W., Andersson, J., Gerten, D., Pisacane, G., Roudier, P., & Ludwig, F. (2017). Impacts of climate change on European hydrology at 1.5, 2 and 3 degrees mean global warming above preindustrial level. *Climatic Change*, *143*(1–2), 13–26. https://doi.org/10.1007/s10584-017-1971-7

Dupas, R., Curie, F., Gascuel-Odoux, C., Moatar, F., Delmas, M., Parnaudeau, V., & Durand, P. (2013). Assessing N emissions in surface water at the national level: Comparison of country-wide vs. regionalized models. *The Science of the Total Environment*, *443*, 152–162. https://doi.org/10.1016/j.scitotenv.2012.10.011

Dupas, R., Delmas, M., Dorioz, J. M., Garnier, J., Moatar, F., & Gascuel-Odoux, C. (2015). Assessing the impact of agricultural pressures on N and P loads and eutrophication risk. *Ecological Indicators*, *48*, 396–407. https://doi.org/10.1016/j.ecolind.2014.08.007

Dupas, R., Ehrhardt, S., Musolff, A., Fovet, O., & Durand, P. (2020). Long-term nitrogen retention and transit time distribution in agricultural catchments in western France. *Environmental Research Letters*, *15*(11), 115011. https://doi.org/10.1088/1748-9326/abbe47

Dupas, R., Jomaa, S., Musolff, A., Borchardt, D., & Rode, M. (2016). Disentangling the influence of hydroclimatic patterns and agricultural management on river nitrate dynamics from sub-hourly to decadal time scales. *The Science of the Total Environment*, *571*, 791–800. https://doi.org/10.1016/j.scitotenv.2016.07.053

Ebeling, P., & Dupas, R. (2021). *CCDB—catchment characteristics data base France and Germany*. Retrieved from https://www.hydroshare.org/resource/c7d4df3ba74647f0aa83ae92be2e294b/

Ebeling, P., Kumar, R., Weber, M., Knoll, L., Fleckenstein, J. H., & Musolff, A. (2021). Archetypes and controls of riverine nutrient export across German catchments. *Water Resources Research*, *57*(4). https://doi.org/10.1029/2020wr028134

EC. (2009). *Regions 2020. The climate change challenge for European regions*. Retrieved from http://ec.europa.eu/regional_policy/sources/docoffic/working/regions2020/pdf/regions2020_climat.pdf

Ehrhardt, S., Ebeling, P., & Dupas, R. (2021). *Exported French water quality and quantity data*. Retrieved from https://www.hydroshare.org/resource/d8c43e1e8a5a4872bc0b75a45f350f7a/

Ehrhardt, S., Kumar, R., Fleckenstein, J. H., Attinger, S., & Musolff, A. (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. https://doi.org/10.5194/hess-23-3503-2019

EPA, U. S. E. P. A. (1972). *Federal water pollution control amendments of 1972. Clean water act. 33 U.S.C. § 1251 et seq*. Retrieved from https://www3.epa.gov/npdes/pubs/cwatxt.txt

European Environment Agency. (2016). *CORINE land cover 2012 v18.5*. Retrieved from https://land.copernicus.eu/pan-european/corine-land-cover

European Environment Agency. (2017). *Waterbase—UWWTD: Urban waste water treatment directive—reported data*. Retrieved from https://www.eea.europa.eu/data-and-maps/data/waterbase-uwwtd-urban-waste-water-treatment-directive-5#tab-european-data

European Environment Agency. (2018). *European waters. Assessment of status and pressure*. Retrieved from https://www.eea.europa.eu/publications/state-of-water

European Environment Agency. (2020). *CORINE land cover 2000 v2020u1. From EEA*. Retrieved from https://land.copernicus.eu/pan-european/corine-land-cover

Fiori, A., Russo, D., & Di Lazzaro, M. (2009). Stochastic analysis of transport in hillslopes: Travel time distribution and source zone dispersion. *Water Resources Research*, *45*(8). https://doi.org/10.1029/2008wr007668

Godsey, S. E., Aas, W., Clair, T. A., Wit, H. A. d., Fernandez, I. J., Kahl, J. S., et al. (2010). Generality of fractal 1/f scaling in catchment tracer time series, and its implications for catchment travel time distributions. *Hydrological Processes*, *24*(12), 1660–1671. https://doi.org/10.1002/hyp.7677

Goyette, J.-O., Bennett, E. M., & Maranger, R. (2018). Differential influence of landscape features and climate on nitrogen and phosphorus transport throughout the watershed. *Biogeochemistry*, *142*(1), 155–174. https://doi.org/10.1007/s10533-018-0526-y

Water Resources Research
10.1029/2020WR029469

Grabs, T., Bishop, K., Laudon, H., Lyon, S. W., & Seibert, J. (2012). Riparian zone hydrology and soil water total organic carbon (TOC): Implications for spatial variability and upscaling of lateral riparian TOC exports. *Biogeosciences*, *9*(10), 3901–3916. https://doi.org/10.5194/bg-9-3901-2012

Griffis, T. J., Chen, Z., Baker, J. M., Wood, J. D., Millet, D. B., Lee, X., et al. (2017). Nitrous oxide emissions are enhanced in a warmer and wetter world. *Proceedings of the National Academy of Sciences of the United States of America*, *114*(45), 12081–12085. https://doi.org/10.1073/pnas.1704552114

Haitjema, H. M. (1995). On the residence time distribution in idealized groundwatersheds. *Journal of Hydrology*, *172*, 20. https://doi.org/10.1016/0022-1694(95)02732-5

Harman, C. J. (2015). Time-variable transit time distributions and transport: Theory and application to storage-dependent transport of chloride in a watershed. *Water Resources Research*, *51*(1), 1–30. https://doi.org/10.1002/2014wr015707

Hatfield, J. L., Boote, K. J., Kimball, B. A., Ziska, L. H., Izaurralde, R. C., Ort, D., et al. (2011). Climate impacts on agriculture: Implications for crop production. *Agronomy Journal*, *103*(2), 351–370. https://doi.org/10.2134/agronj2010.0303

Häußermann, U., Bach, M., Klement, L., & Breuer, L. (2019). *Stickstoff-Flächenbilanzen für Deutschland mit Regionalgliederung Bundesländer und Kreise—Jahre 1995 bis 2017—Methodik, Ergebnisse und Minderungsmaßnahmen*. Retrieved from https://www.umweltbundesamt.de/sites/default/files/medien/1410/publikationen/2019-10-28_texte_131-2019_stickstoffflaechenbilanz.pdf

Heidbüchel, I., Yang, J., Musolff, A., Troch, P., Ferré, T., & Fleckenstein, J. H. (2020). On the shape of forward transit time distributions in low-order catchments. *Hydrology and Earth System Sciences*, *24*(6), 2895–2920. https://doi.org/10.5194/hess-24-2895-2020

Hirsch, R. M., & de Cicco, L. (2019). *EGRET: Exploration and graphics for river trends, R package version.3.0.2*.

Hirsch, R. M., Moyer, D. L., & Archfield, S. A. (2010). Weighted regressions on time, discharge, and season (WRTDS), with an application to Chesapeake Bay river inputs. *Journal of the American Water Resources Association*, *46*(5), 857–880. https://doi.org/10.1111/j.1752-1688.2010.00482.x

Howarth, R. W., Swaney, D. P., Boyer, E. W., Marino, R., Jaworski, N., & Goodale, C. (2006). The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. *Biogeochemistry*, *79*(1–2), 163–186. https://doi.org/10.1007/s10533-006-9010-1

Howden, N. J. K., Burt, T. P., Worrall, F., Mathias, S., & Whelan, M. J. (2011). Nitrate pollution in intensively farmed regions: What are the prospects for sustaining high-quality groundwater? *Water Resources Research*, *47*(6). https://doi.org/10.1029/2011wr010843

Howden, N. J. K., Burt, T. P., Worrall, F., Whelan, M. J., & Bieroza, M. (2010). Nitrate concentrations and fluxes in the River Thames over 140 years (1868-2008): Are increases irreversible? *Hydrological Processes*, *24*(18), 2657–2662. https://doi.org/10.1002/hyp.7835

Hunter, H., Fellows, C., Rassam, D., DeHayr, R., Pagendam, D., Conway, C., et al. (2006). *Managing riparian lands to improve water quality: Optimising nitrate removal via denitrification*. Retrieved from http://www.ozcoasts.gov.au/pdf/CRC/57-riparian_guidelines.pdf

Jabloun, M., Schelde, K., Tao, F., & Olesen, J. E. (2015). Effect of temperature and precipitation on nitrate leaching from organic cereal cropping systems in Denmark. *European Journal of Agronomy*, *62*, 55–64. https://doi.org/10.1016/j.eja.2014.09.007

Jasechko, S., Kirchner, J. W., Welker, J. M., & McDonnell, J. J. (2016). Substantial proportion of global streamflow less than three months old. *Nature Geoscience*, *9*(2), 126–129. https://doi.org/10.1038/ngeo2636

Kirchner, F., Neal, X., & Neal, C. (2000). Fractal stream chemistry and its implications for contaminant transport in catchments. *Nature*, *403*(6769), 524–527. https://doi.org/10.1038/35000537

Knoll, L., Breuer, L., & Bach, M. (2020). Nation-wide estimation of groundwater redox conditions and nitrate concentrations through machine learning. *Environmental Research Letters*, *15*(6), 064004. https://doi.org/10.1088/1748-9326/ab7d5c

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

Kumar, R., Hesse, F., Rao, P. S. C., Musolff, A., Jawitz, J. W., Sarrazin, F., et al. (2020). Strong hydroclimatic controls on vulnerability to subsurface nitrate contamination across Europe. *Nature Communications*, *11*(1), 6302. https://doi.org/10.1038/s41467-020-19955-8

Kumar, R., Samaniego, L., & Attinger, S. (2013). Implications of distributed hydrologic model parameterization on water fluxes at multiple scales and locations. *Water Resources Research*, *49*(1), 360–379. https://doi.org/10.1029/2012wr012195

Kunkel, R., & Wendland, F. (2006). Diffuse Nitrateinträge in die Grund- und Oberflächengewässer von Rhein und Ems- Ist-Zustands- und Maßnahmenanalysen. In F. J. GmbH (Ed.), *Schriften des Forschungszentrums Jülich* (Vol. 62, p. 143). Reihe Umwelt/Environment Jülich.

Marx, A., Kumar, R., Thober, S., Rakovec, O., Wanders, N., Zink, M., et al. (2018). Climate change alters low flows in Europe under global warming of 1.5, 2, and 3 °C. *Hydrology and Earth System Sciences*, *22*(2), 1017–1032. https://doi.org/10.5194/hess-22-1017-2018

McMahon, P. B., Dennehy, K. F., Bruce, B. W., Böhlke, J. K., Michel, R. L., Gurdak, J. J., & Hurlbut, D. B. (2006). Storage and transit time of chemicals in thick unsaturated zones under rangeland and irrigated cropland, High Plains, United States. *Water Resources Research*, *42*(3). https://doi.org/10.1029/2005wr004417

Meals, D. W., Dressing, S. A., & Davenport, T. E. (2010). Lag time in water quality response to best management practices: A review. *Journal of Environmental Quality*, *39*(1), 85–96. https://doi.org/10.2134/jeq2009.0108

Merz, C., Steidl, J., & Dannowski, R. (2009). Parameterization and regionalization of redox based denitrification for GIS-embedded nitrate transport modeling in Pleistocene aquifer systems. *Environmental Geology*, *58*(7). https://doi.org/10.1007/s00254-008-1665-6

Moatar, F., Abbott, B. W., Minaudo, C., Curie, F., & Pinay, G. (2017). Elemental properties, hydrology, and biology interact to shape concentration-discharge curves for carbon, nutrients, sediment, and major ions. *Water Resources Research*, *53*(2), 1270–1287. https://doi.org/10.1002/2016wr019635

Molenat, J., Gascuel-Odoux, C., Ruiz, L., & Gruau, G. (2008). Role of water table dynamics on stream nitrate export and concentration in agricultural headwater catchment (France). *Journal of Hydrology*, *348*(3–4), 363–378. https://doi.org/10.1016/j.jhydrol.2007.10.005

Musolff, A. (2020). *WQQDB—Water quality and quantity data base Germany: Metadata*. HydroShare.

Musolff, A., Fleckenstein, J. H., Rao, P. S. C., & Jawitz, J. W. (2017). Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. *Geophysical Research Letters*, *44*(9), 4143–4151. https://doi.org/10.1002/2017gl072630

Musolff, A., Grau, T., Weber, M., Ebeling, P., Samaniego-Eguiguren, L., & Kumar, R. (2020). *WQQDB: Water quality and quantity data base Germany*. Retrieved from http://www.ufz.de/record/dmp/archive/7754

Nolan, B. T., Hitt, K. J., & Ruddy, B. C. (2002). Probability of nitrate contamination of recently recharged groundwaters in the conterminous United States. *Environmental Science and Technology*, *36*(10), 2138–2145. https://doi.org/10.1021/es0113854

Ocampo, C. J., Sivapalan, M., & Oldham, C. (2006). Hydrological connectivity of upland-riparian zones in agricultural catchments: Implications for runoff generation and nitrate transport. *Journal of Hydrology*, *331*(3–4), 643–658. https://doi.org/10.1016/j.jhydrol.2006.06.010

Water Resources Research 10.1029/2020WR029469

Panagos, P., Borrelli, P., Poesen, J., Ballabio, C., Lugato, E., Meusburger, K., et al. (2015). The new assessment of soil loss by water erosion in Europe. *Environmental Science & Policy*, *54*, 438–447. https://doi.org/10.1016/j.envsci.2015.08.012

Poisvert, C., Curie, F., & Moatar, F. (2017). Annual agricultural N surplus in France over a 70-year period. *Nutrient Cycling in Agroecosystems*, *107*(1), 63–78. https://doi.org/10.1007/s10705-016-9814-x

Powers, S. M., Tank, J. L., & Robertson, D. M. (2015). Control of nitrogen and phosphorus transport by reservoirs in agricultural landscapes. *Biogeochemistry*, *124*(1–3), 417–439. https://doi.org/10.1007/s10533-015-0106-3

Roa-García, M. C., & Weiler, M. (2010). Integrated response and transit time distributions of watersheds by combining hydrograph separation and long-term transit time modeling. *Hydrology and Earth System Sciences*, *14*(8), 1537–1549. https://doi.org/10.5194/hess-14-1537-2010

Samaniego, L., Kumar, R., & Attinger, S. (2010). Multiscale parameter regionalization of a grid-based hydrologic model at the mesoscale. *Water Resources Research*, *46*(5). https://doi.org/10.1029/2008wr007327

Samaniego, L., Thober, S., Kumar, R., Wanders, N., Rakovec, O., Pan, M., et al. (2018). Anthropogenic warming exacerbates European soil moisture droughts. *Nature Climate Change*, *8*(5), 421–426. https://doi.org/10.1038/s41558-018-0138-5

Sebilo, M., Mayer, B., Nicolardot, B., Pinay, G., & Mariotti, A. (2013). Long-term fate of nitrate fertilizer in agricultural soils. *Proceedings of the National Academy of Sciences of the United States of America*, *110*(45), 18185–18189. https://doi.org/10.1073/pnas.1305372110

Shi, Z. H., Ai, L., Li, X., Huang, X. D., Wu, G. L., & Liao, W. (2013). Partial least-squares regression for linking land-cover patterns to soil erosion and sediment yield in watersheds. *Journal of Hydrology*, *498*, 165–176. https://doi.org/10.1016/j.jhydrol.2013.06.031

Stevenson, F. J. (1986). *Cycles of soil: Carbon, nitrogen, phosphorus, sulfur, micronutrients*: Wiley.

Tesoriero, A. J., Gronberg, J. A., Juckem, P. F., Miller, M. P., & Austin, B. P. (2017). Predicting redox-sensitive contaminant concentrations in groundwater using random forest classification. *Water Resources Research*, *53*(8), 7316–7331. https://doi.org/10.1002/2016wr020197

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

Van der Velde, Y., de Rooij, G. H., & Torfs, P. J. J. F. (2009). Catchment-scale non-linear groundwater-surface water interactions in densely drained lowland catchments. *Hydrology and Earth System Sciences*, *13*(10), 1867–1885. https://doi.org/10.5194/hess-13-1867-2009

Van der Velde, Y., Rooij, G. H. d., Rozemeijer, J. C., van Geer, F. C., & Broers, H. P. (2010). Nitrate response of a lowland catchment: On the relation between stream concentration and travel time distribution dynamics. *Water Resources Research*, *46*(11), 1–17. https://doi.org/10.1029/2010wr009105

Van Meter, K. J., & Basu, N. B. (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. https://doi.org/10.1371/journal.pone.0125971

Van Meter, K. J., & Basu, N. B. (2017). Time lags in watershed-scale nutrient transport: An exploration of dominant controls. *Environmental Research Letters*, *12*(8), 084017. https://doi.org/10.1088/1748-9326/aa7bf4

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

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

Van Meter, K. J., Van Cappellen, P., & Basu, N. B. (2018). Legacy nitrogen may prevent achievement of water quality goals in the Gulf of Mexico. *Science*, *360*(6387), 427–430. https://doi.org/10.1126/science.aar4462

Vero, S. E., Basu, N. B., Van Meter, K., Richards, K. G., Mellander, P.-E., Healy, M. G., & Fenton, O. (2017). Review: The environmental status and implications of the nitrate time lag in Europe and North America. *Hydrogeology Journal*, *26*(1), 7–22. https://doi.org/10.1007/s10040-017-1650-9

von Lutzow, M., Kogel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B., & Flessa, H. (2006). Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions—A review. *European Journal of Soil Science*, *57*(4), 426–445. https://doi.org/10.1111/j.1365-2389.2006.00809.x

Wang, L., & Burke, S. P. (2017). A catchment-scale method to simulating the impact of historical nitrate loading from agricultural land on the nitrate-concentration trends in the sandstone aquifers in the Eden Valley, UK. *The Science of the Total Environment*, *579*, 133–148. https://doi.org/10.1016/j.scitotenv.2016.10.235

Wang, Z., Qi, Z., Xue, L., Bukovsky, M., & Helmers, M. J. (2015). Modeling the impacts of climate change on nitrogen losses and crop yield in a subsurface drained field. *Climatic Change*, *129*(1–2), 323–335. https://doi.org/10.1007/s10584-015-1342-1

Wassenaar, L. I. (1995). Evaluation of the origin and fate of nitrate in the Abbotsford Aquifer using the isotopes. *Applied Geochemistry*, *10*, 15–405. https://doi.org/10.1016/0883-2927(95)00013-A

Webster, J. R., Mulholland, P. J., Tank, J. L., Valett, H. M., Dodds, W. K., Peterson, B. J., et al. (2003). Factors affecting ammonium uptake in streams – An inter-biome perspective. *Freshwater Biology*, *48*(8), 1329–1352. https://doi.org/10.1046/j.1365-2427.2003.01094.x

Wendland, F., Blum, A., Coetsiers, M., Gorova, R., Griffioen, J., Grima, J., et al. (2007). European aquifer typology: A practical framework for an overview of major groundwater composition at European scale. *Environmental Geology*, *55*(1), 77–85. https://doi.org/10.1007/s00254-007-0966-5

West, P. C., Gerber, J. S., Engstrom, P. M., Mueller, N. D., Brauman, K. A., Carlson, K. M., et al. (2014). Leverage points for improving global food security and the environment. *Science*, *345*(6194), 325–328. https://doi.org/10.1126/science.1246067

Westphal, K., Musolff, A., Graeber, D., & Borchardt, D. (2020). Controls of point and diffuse sources lowered riverine nutrient concentrations asynchronously, thereby warping molar N:P ratios. *Environmental Research Letters*, *15*(10). https://doi.org/10.1088/1748-9326/ab98b6

Wold, S., Sjostrom, M., & Eriksson, L. (2001). PLS-regression: A basic tool of chemometrics. *Chemometrics and Intelligent Laboratory Systems*, *58*(2), 109–130. Doi. https://doi.org/10.1016/S0169-7439(01)00155-1

Worldometers.info. (2020). *Europe-population*. Retrieved from https://www.worldometers.info/world-population/europe-population/

Wriedt, G., Spindler, J., Neef, T., Meißner, R., & Rode, M. (2007). Groundwater dynamics and channel activity as major controls of in-stream nitrate concentrations in a lowland catchment system? *Journal of Hydrology*, *343*(3–4), 154–168. https://doi.org/10.1016/j.jhydrol.2007.06.010

Wyns, R., Mathieu, F., Vairon, J., Legchenko, A., Lachassagne, P., & Baltassat, J.-M. (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. https://doi.org/10.2113/175.1.21

Yang, J., Heidbüchel, I., Musolff, A., Reinstorf, F., & Fleckenstein, J. H. (2018). Exploring the dynamics of transit times and subsurface mixing in a small agricultural catchment. *Water Resources Research*, *54*(3), 2317–2335. https://doi.org/10.1002/2017wr021896

Water Resources Research
10.1029/2020WR029469

Zambrano-Bigiarini, M., & Rojas, R. (2013). A model-independent particle swarm optimisation software for model calibration. *Environmental Modelling & Software*, *43*, 5–25. https://doi.org/10.1016/j.envsoft.2013.01.004
Zhang, Y.-C., Slomp, C. P., Broers, H. P., Passier, H. F., & Cappellen, P. V. (2009). Denitrification coupled to pyrite oxidation and changes in groundwater quality in a shallow sandy aquifer. *Geochimica et Cosmochimica Acta*, *73*(22), 6716–6726. https://doi.org/10.1016/j.gca.2009.08.026

References From the Supporting Information

Ballabio, C., Lugato, E., Fernandez-Ugalde, O., Orgiazzi, A., Jones, A., Borrelli, P., et al. (2019). Mapping LUCAS topsoil chemical properties at European scale using Gaussian process regression. *Geoderma*, *355*, 113912. https://doi.org/10.1016/j.geoderma.2019.113912
CIESIN, C. f. I. E. S. I. N.-C. U. (2017). *Gridded population of the world, version 4 (GPWv4): Population density, Revision 10*. https://doi.org/10.7927/H4DZ068D
CLC. (2016). CORINE land cover 2012 v18.5. Retrieved from https://land.copernicus.eu/pan-european/corine-land-cover
Cornes, R. C., van der Schrier, G., van den Besselaar, E. J. M., & Jones, P. D. (2018). An ensemble version of the E-OBS temperature and precipitation data sets. *Journal of Geophysical Research: Atmospheres*, *123*(17), 9391–9409. https://doi.org/10.1029/2017jd028200
European Environment Agency. (2013). *DEM over Europe from the GMES RDA project (EU-DEM, resolution 25 m)—Version 1*. Retrieved from https://sdi.eea.europa.eu/catalogue/srv9008075/api/records/66fa7dca-8772-4a5d-9d56-2caba4ecd36a
FAO/IIASA/ISRIC/ISSCAS/JRC. (2012). *Harmonized world soil database*. Retrieved from https://webarchive.iiasa.ac.at/Research/LUC/External-World-soil-database/HTML/
Shangguan, W., Hengl, T., Mendes de Jesus, J., Yuan, H., & Dai, Y. (2017). Mapping the global depth to bedrock for land surface modeling. *Journal of Advances in Modeling Earth Systems*, *9*(1), 65–88. https://doi.org/10.1002/2016ms000686
Vigiak, O., Grizzetti, B., Zanni, M., Aloe, A., Dorati, C., Bouraoui, F., & Pistocchi, A. (2019). *Domestic waste emissions to European freshwaters in the 2010s (v. 1.0)*. Retrieved from https://data.jrc.ec.europa.eu/dataset/0ae64ac2-64da-4c5e-8bab-ce928897c1fb
Vigiak, O., Grizzetti, B., Zanni, M., Aloe, A., Dorati, C., Bouraoui, F., & Pistocchi, A. (2020). Domestic waste emissions to European waters in the 2010s. *Scientific Data*, *7*(1), 33. https://doi.org/10.1038/s41597-020-0367-0

AGU PUBLICATIONS

Water Resources Research

Supporting Information for

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

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Introduction

The Supporting Information provide tables, figures and explanations to better understand the discussed catchment characteristics (S1), to present a comparison of data sets (S2) and to summarize analyses results for TTs and retention (S3) as well as to illustrate the transport time approach (S4). This is followed by a short discussion of a negative outlier in the retention (S5) and the results of the PLSR (S6). Lastly, a correlation matrix of selected hydroclimatic variables visualizes collinearity in the predictors (S5).

S1. Catchment characteristics

Category	Variable	Unit	Description and method	Data source
	Area_km2	km²	Catchment area	
Topography	dem.mean	masl	Mean elevation of catchment, from DEM rescaled from 25 to 100 m resolution using average	EEA (2013)
	dem.median	masl	Median elevation of catchment, from DEM rescaled from 25 to 100 m resolution using average	EEA (2013)
	slo.mean	°	Mean topographic slope of catchment, from DEM	EEA (2013)
	slo.median	°	Median topographic slope of catchment, from DEM	EEA (2013)
	twi.mean	-	Mean topographic wetness index (TWI, Beven & Kirkby, 1979)	EEA (2013)
	twi.med	-	Median topographic wetness index (TWI, Beven & Kirkby, 1979)	EEA (2013)
	twi.90p	-	90^{th} percentile of the TWI as a proxy for riparian wetlands (following Musolff et al., 2018)	EEA (2013)
Land use	f_artif	-	Fraction of artificial land cover (Class 1 Level 1 CORINE)	CLC (2016)
	f_agric	-	Fraction of agricultural land cover (Class 2 Level 1 CORINE)	CLC (2016)
	f_forest	-	Fraction of forested land cover (Class 3 Level 1 CORINE)	CLC (2016)
	f_wetl	-	Fraction of wetland cover (Class 4 Level 1 CORINE)	CLC (2016)
	f_water	-	Fraction of surface water cover (Lass 5 Level 1 CORINE)	CLC (2016)
	pdens	inhabitants km^{-2}	Mean population density	CIESIN (2017)
Nutrient sources	N_T_YKM2	t N km^{-2} yr^{-1}	Mean N input from point sources (from EU-DWE database)	Vigiak et al. (2019); Vigiak et al. (2020)
	BOD_T_YKM2	t N km^{-2} yr^{-1}	Mean biochemical oxygen demand input from point sources (from EU-DWE database)	Vigiak et al. (2019); Vigiak et al. (2020)
	N_T_YEW	t N inh^{-1} y^{-1}	Calculated N input per person (from EU-DWE database) N_T_YKM2 / nEW * Area_km2	Vigiak et al. (2019); Vigiak et al. (2020)
	nEW	-	Calculated number of inhabitants, pdens * Area_km2	*CIESIN (2017)*
	n_UWWTP	-	Number of point sources from European database (UWWTP database)	EEA (2017)
Lithology and soils	f_porous	-	Fraction of porous aquifer (code 1 and 2 of aquifer type)	BGR & UNESCO (eds.) (2014)
	f_fissured	-	Fraction of fissured aquifer (code 3 and 4 of aquifer type)	BGR & UNESCO

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				(eds.) (2014)
	f_hard	-	Fraction of locally aquiferous and non-aquiferous aquifer (code 5 and 6 of aquifer type)	BGR & UNESCO (eds.) (2014)
	f_consol	-	Fraction of consolidated rocks (Lithology Level 5)	BGR & UNESCO (eds.) (2014)
	f_part_consol	-	Fraction of partly consolidated rocks (Lithology Level 5)	BGR & UNESCO (eds.) (2014)
	f_uncons ol	-	Fraction of unconsolidated rocks (Lithology Level 5)	BGR & UNESCO (eds.) (2014)
	dtb.median	cm	Median depth to bedrock in the catchment	Shangguan et al. (2017)
	f_sand f_silt f_clay	-	Mean fraction of sand in soil horizons of the top 100 cm Mean fraction of silt in soil horizons of the top 100 cm Mean fraction of clay in soil horizons of the top 100 cm	FAO/IIASA/ISRIC/ISSCAS/JRC (2012)
	soilN.mean	g kg^{-1}	Mean top soil N in catchment	Ballabio et al. (2019)
	soilCN.mean	-	Mean top soil C/N ratio in catchment	Ballabio et al. (2019)
Hydrology	Q_mean	$m^3 s^{-1}$	Mean discharge (period 1986-2015 used for all hydrologic variables)	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	Q_median	$m^3 s^{-1}$	Median discharge	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	Q_spec	mm	Mean annual specific discharge	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	Q_CVQ	-	Coefficient of variation of time series of daily Q	Musolff (2020); Musolff et al. (2020); HYDRO

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				MEDDE (2019)
	Q_medSum	$m^3 s^{-1}$	Median summer discharge (months May-October)	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	Q_medWin	$m^3 s^{-1}$	Median winter discharge (months November-April)	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	Q_Sum2Win	-	Seasonality index of Q, as ratio between median summer and median winter Q	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	BFI	-	Base flow index calculated according to WMO [2008] with lfstat package (version 0.9.4) in R	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
	flashi	-	Flashiness index of Q as the ratio between 5% percentile and 95% percentile of Q time series	Musolff (2020); Musolff et al. (2020); HYDRO MEDDE (2019)
Climate	P_mm	mm	Mean annual precipitation (period 1986-2015 used for all climatic variables)	Cornes et al. (2018)
	P_SIsw	-	Seasonality of precipitation as the ratio between mean summer (Jun-Aug) and winter (Dec-Feb) precipitation	Cornes et al. (2018)
	P_SI	-	Seasonality index of precipitation as the mean difference between monthly P averages and year average	Cornes et al. (2018)
	P_lambda	-	Mean precipitation frequency λ as used by Botter et al. (2013)	Cornes et al. (2018)
	P_alpha	-	Mean precipitation depth as used by Botter et al. (2013)	Cornes et al. (2018)
	PET_mm	mm	Mean potential evapotranspiration	Cornes et al.

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				(2018)
	AI	-	Aridity index as AI=PET_mm/P_mm	Cornes et al. (2018)
	T_mean	°C	Mean annual temperature	Cornes et al. (2018)

Table S1.1. Selected catchment characteristics with their associated methods and data sources (Ebeling & Dupas, 2020).

Category	Variable	Median	Range
Morphology	Area [km^2]	923.2	19.2 to 62516.5
	Dem.median [m]	305.3	15.3 to 1848.3
	Slope median [°]	2.9	0.4 to 24.9
Hydrology of hydroclimate	P [mm]	815.8	551.1 to 1526.7
	T mean [°C]	9.6	4.3 to 13.3
	BFI (base flow index)	65	29.3 to 97.5
	Aridity index	0.94	0.4 to 1.5
	TWI.median (topogr. wetness index)	8.4	6.6 to 10.3
Soil & Lithology	F_sand [%]	43.5	26.0 to 82.0
	F_silt [%]	32.8	11.0 to 41.1
	F_clay [%]	23.0	7 to 39.6
	F_hard [%]	53.3	0 to 100
	F_fissured [%]	25.9	0 to 100
	F_porous [%]	4.9	0 to 100
Land use	F_agric [%]	56.5	0 to 97.6
	F_forest [%]	36.7	0 to 100
	F_artificial [%]	5.0	0 to 31.3
	Pdens [inhabitants km^{-2}]	91.8	11.2 to 1088.0

Table S1.2. Selected properties of the analyzed catchments.

S2. Comparison of data sets for nitrogen input from agricultural sources

Text S2. Comparison of data sets for nitrogen input from agricultural sources.

To estimate systematic differences between both national N surplus time series, we selected the European estimation for croplands [kg] by West et al. (2014) as reference. Because this data set covers only the years around 2000 with a 5 arc minute resolution, we could not take it as a consistent substitute for the national data.
A comparison of the national with the European excess N showed a good fit (23 vs. 19 kg N ha^{-1} yr^{-1}) for the French data (Table S2.), but an underestimation of the national estimations (34 vs. 47 kg N ha^{-1} yr^{-1}) for Germany by 28%. The estimates of retention in Germany may therefore be slightly higher than assumed taking the national N input data. But all in all, the methodological offset between both national data sets can be assumed as acceptable due to the comparison with the reference by West et al. (2014) and under consideration of uncertainties in the national as well as European estimations. Furthermore, a comparison of the national N diffuse input in comparison to the European

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N excess data promised a more consistent estimation for N input per hectare (Figure S2.).

Table S2. Comparison of different N contributions according to the national and European data sets for 1997 to 2003.

Median N contribution [kg N ha^{-1} yr^{-1}]	France	Germany
Surplus	23	34
Surplus European	19	47
Biological fixation	5	5
Atmospheric deposition	7	11

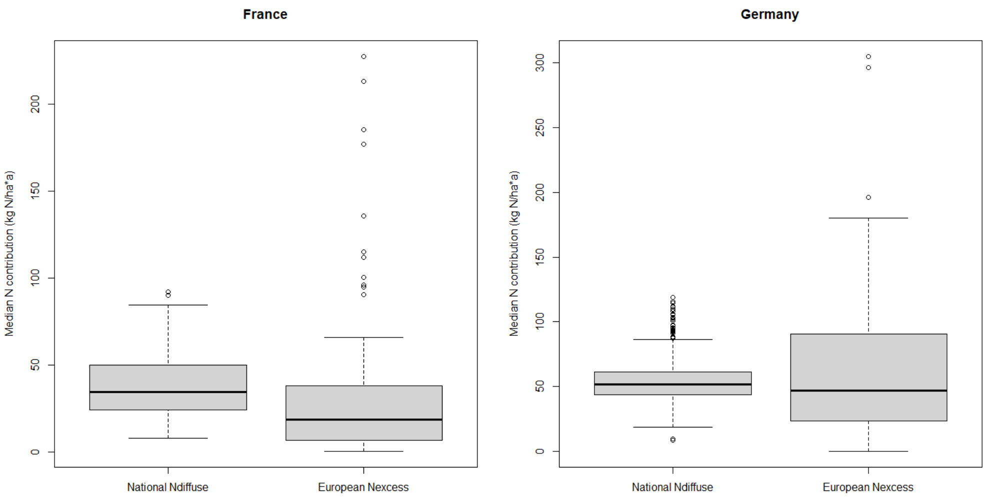

Figure S2. Boxplots showing the national diffuse N inputs versus the European N excess estimation according to West et al. (2014) for France (left) und Germany (right).

S3. Results for estimating mode TTs and retention

Parameter	Median	Range
n	238 (166)	
Mode TT [a]	5.5 (5.4)	0.2 to 34.1 (0.2 to 34.1)
P50 [a] (TTD percentile for 50%)	11.0 (10.5)	1.0 to 34.2 (1.2 to 34.2)
P75 [a] (TTD percentile for 75%)	19.1 (17.4)	1.4 to 38.3 (1.4 to 38.2)
R^2 [%]	0.79 (0.85)	0 to 0.99 (0.6 to 0.99)
n	238	
Retention [%]	71.9	-23.6 to 95.0
Annual N input load (kg ha^{-1})	44.5	8.5 to 113.2
Annual N exported load (kg ha^{-1})	11.6	2.8 to 71.0
Retention with the convolved N input [%]	70.1	-33.6 to 94.5

Table S3. Summary of selected parameters of estimated N TTDs and the N retention.

S4. Convolved N input with the log-normal TTD of five randomly selected catchments

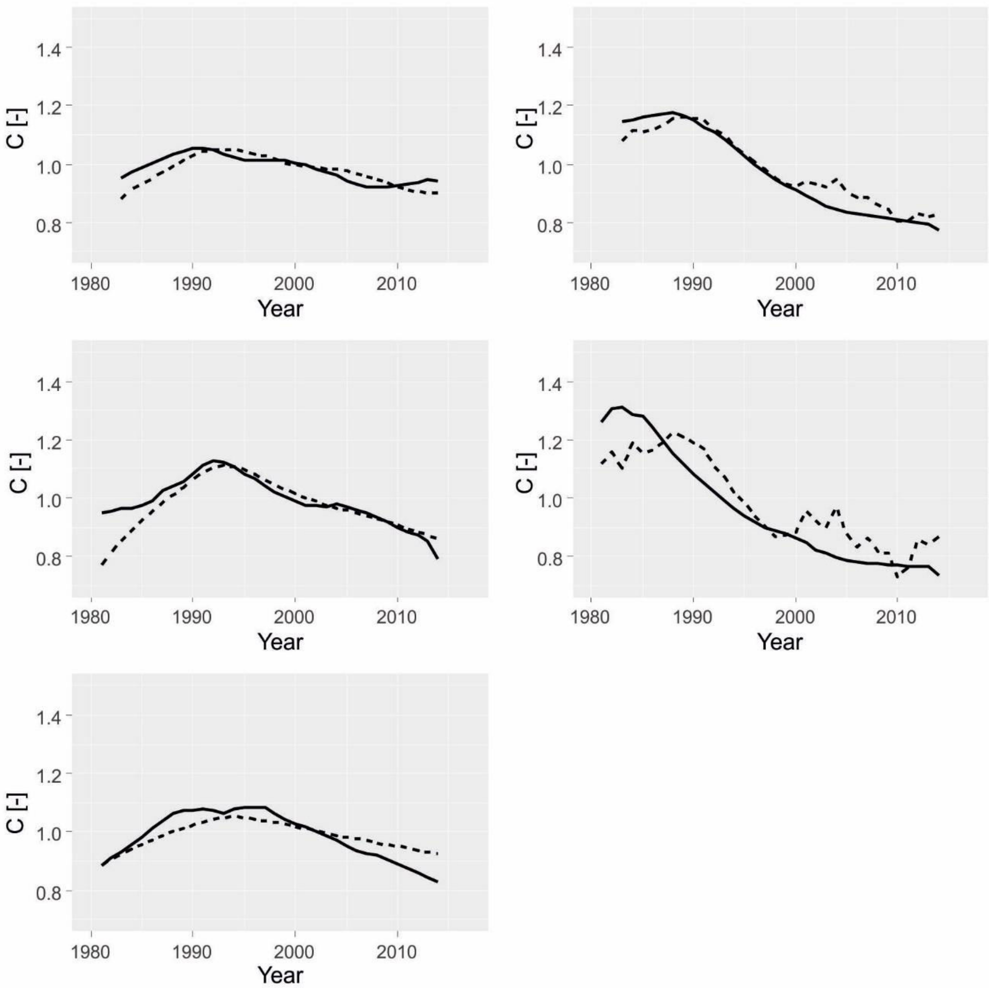

Figure S4. Modelled N output concentrations (scaled to 1, y-axis) derived from the N input convolved with the log-normal travel time distributions (dashed lines) and the scaled observed flow-normalized annual NO_3-N concentrations (solid lines) over time of five randomly selected catchments.

S5. Explaining the negative outlier in the retention estimation

At one station, available in the public French data base, 5% of the time series show extraordinary high discharge values between 1992 and 2017. The database does not provide any labeling or explanation for these irregularities. While the flow-normalized loads calculated by the software package EGRET were affected by these outliers, flow-normalized concentrations were unaffected. Since 95% of the time series showed no anomalies and since unaffected concentrations are used for estimating transport times, we decided to include this catchment in the study to achieve the greatest possible spatial coverage but excluded this catchment for the PLSR.

S6. Plotting the PLSR results for predicting TTs and retention

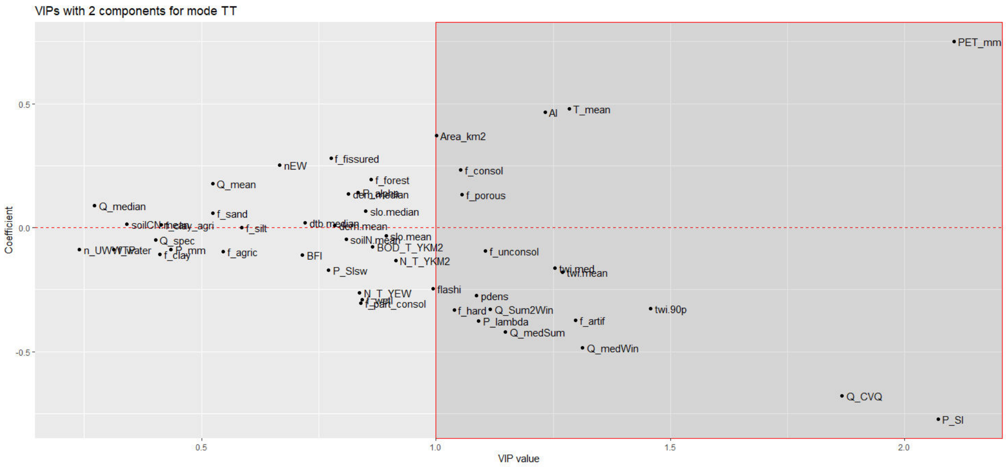

Figure S6.1. Plot of the PLSR results for predicting the mode TTs using 2 components.

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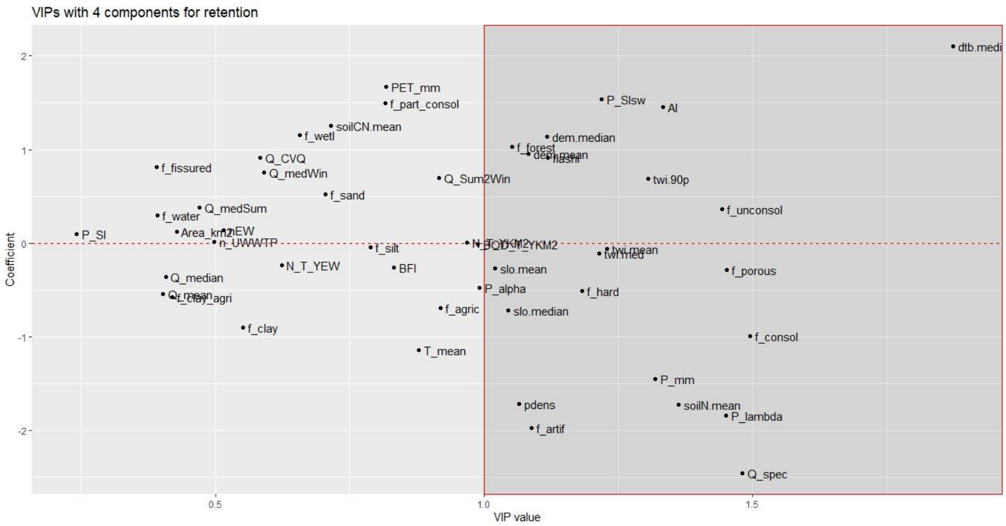

Figure S6.2. Plot of the PLSR results for predicting the retention using 4 components.

S7. Hydroclimatic variables

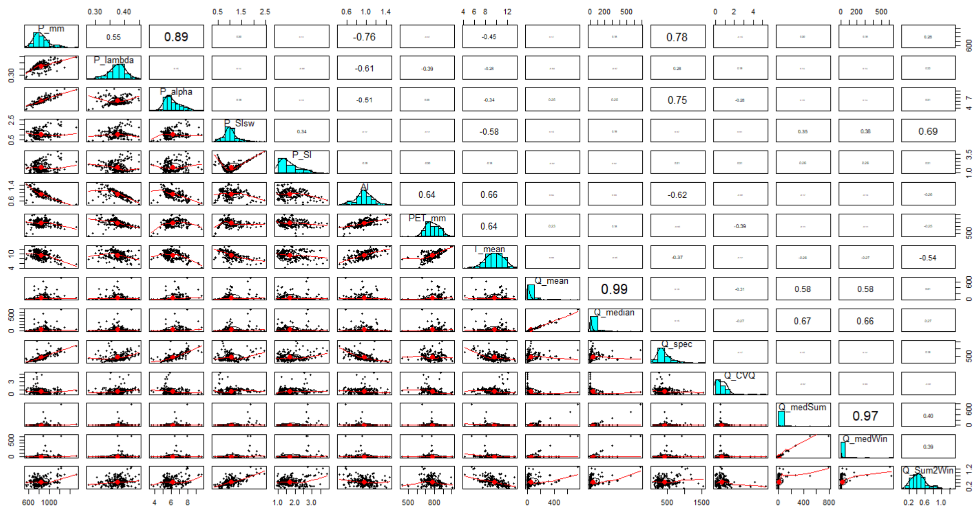

Figure S7. Correlation matrix for selected hydroclimatic variables.

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List of publications

First-author manuscripts in ISI-listed journals

Ehrhardt, S., Kumar, R., Fleckenstein, J. H., Attinger, S. and Musolff, A. (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.

Co-authored manuscripts in ISI-listed journals

Dupas, R., Ehrhardt, S., Musolff, A., Fovet, O. and Durand, P. (2020), 'Long-term ni-trogen retention and transit time distribution in agricultural catchments in western France', *Environmental Research Letters* **15**(11).

Cardenas, P., Lange, C. B., Vernet, M., Esper, O., Srain, B., Vorrath, M. E., Ehrhardt, S.,Müller, J., Kuhn, G., Arz, H. W., Lembke-Jene, L. and Lamy, F. (2019), 'Biogeochemical proxies and diatoms in surface sediments across the drake passage reflect oceanicdomains and frontal systems in the region', *Progress in Oceanography* **174**, 72–88.

Wu, S., Kuhn, G., Diekmann, B., Lembke-Jene, L., Tiedemann, R., Zheng, X., Ehrhardt, S., Arz, H., Lamy, F. (2019), 'Surface sediment characteristics related to provenance and ocean circulation in the Drake Passage sector of the Southern Ocean', *Deep Sea Research Part I: Oceanographic Research Papers* **154**.