Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/scitotenv

A 3D hydrogeochemistry model of nitrate transport and fate in a glacial sediment catchment: A first step toward a numerical model



Hyojin Kim^{a,*}, Peter B.E. Sandersen^a, Rasmus Jakobsen^b, Anders Juhl Kallesøe^a, Niels Claes^c, Gitte Blicher-Mathiesen^d, Nikolaj Foged^c, Jens Aamand^b, Birgitte Hansen^a

a Department of Quaternary and Groundwater Mapping, Geological Survey of Denmark and Greenland (GEUS), C.F. Møllers Allé 8, Building 1110, 8000 Aarhus C, Denmark

^b Department of Geochemistry, Geological Survey of Denmark and Greenland (GEUS), Øster Voldgade 10, DK-1350 Copenhagen K, Denmark

^c HydroGeophysics Group, Department of Geoscience, Aarhus University, C.F. Møllers Allé 4, 8000 Aarhus C, Denmark

^d Department of Bioscience, Aarhus University, Vejlsøvej 25, 8600 Silkeborg, Denmark

HIGHLIGHTS

GRAPHICAL ABSTRACT

- NO₃-behavior was studied using geophysical, hydrogeochemical and geological data.
- The geological structure may determine the denitrification zones in the study site.
- Hydrological connectivity between groundwater and stream may control nitrate load.
- Detailed structural data is essential to upscale point data to catchment level.

ARTICLE INFO

Article history: Received 9 December 2020 Received in revised form 17 February 2021 Accepted 18 February 2021 Available online 25 February 2021

Editor: José Virgílio Cruz

Keywords: Agricultural pollution Hydrogeology Concentration-discharge (C-Q) relationship Groundwater chemistry Subsurface resistivity



ABSTRACT

Diffuse pollution of nitrate from agricultural fields is a critical environmental problem around the world. Sources and sinks of nitrate are heterogeneously distributed over various spatial scales, and the connectivity and transport pathways between them also change at different temporal scales. Therefore, understanding the impact of these variabilities in nitrate transport to the aquatic environment is fundamental for a correct numerical modelling of nitrate transport within a catchment. This study, hence, investigated controls on the spatiotemporal variability of nitrate in a glacial landscape and upscaled it to catchment scale by synthesizing geological, hydrogeochemical, and geophysical information. We found that different parts of the sedimentary succession define the locations of nitrate sinks in this catchment. Denitrification mainly may occur mainly around small patches of postglacial sediments on the outwash plain, which is the youngest formation covering the top layer of the catchment. In contrast, in older geological elements, which constitute the hill and the layers below the outwash plain, oxic, nitrate-containing groundwater was found, probably because of depletion of reduced compounds over the long exposure time. We also found that the boundary between these two formations may govern the seasonal shift of this oxic groundwater's connectivity to the stream consequently nitrate export from the catchment. This conceptual understanding of nitrate transport and sinks then was transformed into a 3D hydrogeochemistry model based on a high-resolution resistivity model of the catchment. We propose that such a basic understanding of how a catchment hydrogeochemically operates should be the first step toward setting up a catchment scale hydrological model with reactive N transport.

© 2021 Elsevier B.V. All rights reserved.

* Corresponding author. *E-mail address:* hk@geus.dk (H. Kim).

https://doi.org/10.1016/j.scitotenv.2021.146041 0048-9697/© 2021 Elsevier B.V. All rights reserved.

1. Introduction

Use of nitrogen (N) fertilizers is essential for food production; however, diffuse N pollution from agricultural fields causes various environmental and public health issues around the world (Galloway et al., 2003; Schullehner et al., 2018; Ward et al., 2018). To improve the cost-effectiveness of agricultural N regulations, countries in Europe, U.S.A and New Zealand explore a spatially targeted approach (e.g., Hashemi et al., 2018; Jha et al., 2010; Sarris et al., 2019; Stenger et al., 2018; Teshager et al., 2017; Uthes et al., 2010). This new approach considers the spatial and temporal variability of leaching, transport, and removal of nitrate at local scale during transport of water and nitrate between the field and the stream; thus, different mitigation strategies will be implemented under different environmental conditions. To design and implement the targeted regulations and to communicate with stakeholders, the effectiveness of various mitigation scenarios needs to be quantified at small scales i.e., field to sub catchment scales. For more precise predictions for the small scale variability, numerical models must adequately represent the local heterogeneity of the hydrogeological and biogeochemical characteristics, which can significantly influence the modelling results (e.g., Jang et al., 2017; Sarris et al., 2019; Yang et al., 2019, 2018). Therefore, solid understandings of how nitrate and water move through a catchment and of the primary controls on nitrate export will be critical for developing the structure of numerical models.

To characterize the spatial and temporal variability of nitrate at catchment scale, field observations are necessary. Streams and rivers provide an integrated response to all hydrological and biogeochemical processes occurring within the catchment. Therefore, stream water chemistry has been extensively investigated to better understand the controls on the spatial and temporal variability of nitrate export at catchment scale. Concentration-discharge (C-Q) relationships are one of the most widely employed approaches (e.g., Bieroza et al., 2018; Godsey et al., 2009; Kim et al., 2017; Moatar et al., 2017; Musolff et al., 2017). Unlike most geogenic elements in pristine conditions, which show "chemostatic behavior" (little to no solute concentration changes over varying discharge; e.g., Godsey et al., 2009; Kim et al., 2017), nitrate and other anthropogenic elements show "chemodynamic behavior" (varying solute concentration with discharge; e.g., Bieroza et al., 2018; Moatar et al., 2017; Musolff et al., 2017). Such dynamic responses are attributed to the balance (or competition) between biogeochemical controls-e.g., the heterogeneous distribution of sinks and sources of nitrate (Blaen et al., 2017; Dupas et al., 2016; Herndon et al., 2015; Musolff et al., 2017, 2016) – and hydrological controls – e.g., temporal variabilities of transport pathways and hydrological connectivity between the source and sink (Blaen et al., 2017; Martin et al., 2004; Molenat et al., 2008; Molénat et al., 2002; Ocampo et al., 2006a, 2006b; Stieglitz et al., 2003; Wriedt et al., 2007). Furthermore, recent studies have proposed to employ the C-Q slope as a tool for water quality and contamination management because it may elucidate the dominant controls on pollutant export (Bieroza et al., 2018; Moatar et al., 2017). Detailed investigations of groundwater chemistry along a profile or a transect provide valuable information about processes that are responsible for nitrate evolution (Böhlke et al., 2002; Böhlke and Denver, 1995; Green et al., 2008; Jessen et al., 2017; Postma et al., 1991; Tesoriero et al., 2000) and quantification of groundwater flow rates and denitrification rates (Böhlke and Denver, 1995; Böhlke and Michel, 2009; Postma et al., 1991; Puckett et al., 2002). Based on these direct observations different redox zones are delineated, including the zone where denitrification may occur.

Though these myriad studies have provided valuable insights into how nitrate evolves in a catchment, transformation of these conceptual, process-based understandings into numerical models has rarely been done. Lack of attempts may be because this knowledge cannot simply be upscaled to the catchment scale without detailed knowledge of the subsurface structure, particularly under geologically heterogeneous settings such as glacial, volcanic, or alluvial environments (e.g., Best et al., 2015; Hansen and Thorling, 2008; Kim et al., 2019; Postma et al., 2012; Rodvang and Simpkins, 2001; Stenger et al., 2018). The subsurface hydrogeological structure, which shapes the network of flow pathways and redox architecture, is highly complicated (Best et al., 2015; Hansen and Thorling, 2008; Kim et al., 2019). In addition, reduced compounds are heterogeneously distributed at various spatial scales due to relatively recent geological events, creating biogeochemical hotspots (Postma et al., 2012; Rodvang and Simpkins, 2001; Stenger et al., 2018).

An increasing number of studies employ various geophysical techniques to map the subsurface structure and to better understand hydrological and biogeochemical processes (Binley et al., 2015; Robinson et al., 2008). For example, the resistivity of the subsurface structure can be interpreted to characterize the hydrostratigraphic structure (e.g., Claes et al., 2020; Vilhelmsen et al., 2019) and the redox architecture (e.g., Hansen et al., 2014, 2021; Kim et al., 2019; Madsen et al., 2020). The towed transient electromagnetic (tTEM) system is a recently developed method to map the near subsurface structure and produces high-resolution 3D resistivity images of the subsurface down to depths of 50-70 m, depending on the lithological properties (Auken et al., 2019). In this study, we investigated how nitrate is mobilized, transported, and removed in the subsurface of a glacial landscape and attempted to upscale the findings to the catchment scale by synthesizing hydrological, geochemical, geological and geophysical information. The primary objectives of this study are 1) characterization of the geological structure of the subsurface by integrating tTEM resistivity results and geological information; 2) identification of controls on the spatial heterogeneity of groundwater chemistry and of dominant processes focusing on nitrate; 3) investigation of nitrate pathways and denitrification zones of the catchment by analyzing the stream's C-Q relationships as well as comparing with soil pore water and groundwater chemistry; and 4) development of a 3D hydrogeochemistry model of nitrate transport and fate at the catchment scale by synthesizing all data. The 3D hydrogeochemistry model will be the basic framework of a numerical representation of denitrification reactions and redox structure of the catchment

2. Material and methods

2.1. Study site

Our study site (Odderbæk catchment; 11 km²) is situated in a glacial landscape in northern Jutland, Denmark (Fig. 1). The catchment is a groundwater dominant system (baseflow index = 0.76; Blicher-Mathiesen et al., 2019). During the last ice age, the catchment was glaciated and the ice advance and retreat events during this period are responsible for the geomorphic features of this catchment (e.g., Larsen et al., 2009). The terrain of the catchment is characterized by two distinctive features: the higher elevation area (33-58 meters above sea level; masl) in the northwestern part of the catchment is an ice-marginal glacial hill, and the lower elevation area (~20 masl) near the stream is an outwash plain from the last ice age (Fig. 1a). The surface soil is predominantly sandy (i.e., meltwater sand); however, the meltwater sand in the outwash plain (orange color in Fig. 1c) is younger than that in the glacial hill (pink color in Fig. 1c). Postglacial freshwater deposits (green colors in Fig. 1c) are distributed on the outwash plain, particularly near the boundary between the glacial hill and the outwash plain. The catchment is intensively used by agriculture as cultivation covers 83% of the catchment, and about 10% of area is drained (1km²; hatched area in Fig. 1c). The crop types vary year to year, but cash crops (mainly cereals, potato, seed grass, oilseed rape) and fodder crops (mainly silage maize and grass in rotation) cover approximately 43% and 46% of the agricultural area, respectively. Permanent grass and set-aside cover approximately 7 and 3% of the area, respectively (Blicher-Mathiesen et al., 2019).



Fig. 1. Digital terrain model (a), orthophotography (b), and soil map (c) of the study site. The locations of monitoring stations of the LOOP and GRUMO programs are shown in (a). (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

2.2. tTEM survey and data processing

In March 2019, the resistivity of the shallow subsurface was mapped using the tTEM system in the study catchment. The tTEM system consists of a 2×4 m² transmitter frame and a receiver coil at a 9 m offset that is towed by an all-terrain vehicle (Auken et al., 2019). The spacing between the survey lines was about 20–30 m and the vertical resolution goes from approximately 2 to 5 m with increasing depth. The depth of the investigation varies between 40 and 70 m, depending on the sediment types and resistivity sequence. The tTEM survey consists of ~32,000 single resistivity models covering approximately 73% of the catchment area. Coupled and heavily noise-influenced data were filtered out before inverting the data. The data were inverted using the Aarhus Workbench software package, which uses the AarhusInv inversion code (Auken et al., 2015; Kirkegaard et al., 2015).

2.3. Water chemistry data

In the study catchment, the chemistry of soil pore water, groundwater, and surface water has been monitored regularly since the 1990s as part of two subprograms of the Nationwide Monitoring and Assessment Program for the Aquatic and Terrestrial Environments of Denmark (NOVANA), which are operated by the Danish Environmental Protection Agency: 1) The National Groundwater Monitoring Program (GRUMO) and 2) Landovervågningen (the Agricultural Monitoring Program; LOOP; Fig. 1a). The GRUMO program monitors the quantity and quality of groundwater, and a full suite of water chemistry parameters including inorganic, organic, and pollutants are monitored at around 1000 boreholes across the nation. In the GRUMO program, groundwater chemistry is measured every 1–6 years.

The LOOP program focuses on assessing and monitoring the impact of agriculture on the aquatic environments (Kronvang et al., 1993). The primary concern is nitrogen and phosphorus (P). LOOP, therefore, monitors the evolution of water chemistry of the near surface environment, i.e., from the root zone to the upper groundwater (<5 m) and further to the surface waters. There are six LOOP catchments, and in five LOOP catchments 1) the soil pore water chemistry is measured weekly in the period of percolation; 2) stream water chemistry is measured biweekly; 3) the upper groundwater chemistry is monitored up to 6 times per year; and 4) stream discharge is measured every day (Supplementary Table 1).

The Odderbæk catchment is one of the LOOP catchments (LOOP2), and in the glacial hill there are 24 GRUMO boreholes (Fig. 1a). All sampling of water is performed by the National Environmental Protection Agency, and the samples are analyzed by certified laboratories in Denmark. The groundwater chemistry and groundwater level data were extracted from the National Borehole Database (JUPITER; www. geus.dk), which is a public database managed by Geological Survey of Denmark and Greenland (GEUS). The soil pore water, stream chemistry and stream discharge data are managed by Aarhus University, and the data are stored in a national database for soil and surface water, Overfladevanddatabasen (ODA). This study focused on major cations $(Ca^{2+}, Mg^{2+}, Na^+ and K^+)$, anions $(HCO_3^-, Cl^-, NO_3^- and SO_4^{2-})$, conductivity and pH of groundwater and NO₃⁻ and conductivity of stream and soil pore water in order to investigate different denitrification processes (Supplementary Table 1). In this study, mmol/L (mM) was used for major cations and anions except nitrate where mg/L was used.

Through the LOOP program, nitrate of soil pore water and the stream has been monitored regularly since 1989 while conductivity monitoring at the stream was discontinued in 2007, and that of soil pore water has been carried out at a lower frequency in this catchment. In general, nitrate concentration decreases from soil pore water to groundwater to the stream. For example, over the entire monitoring period, the means of the monthly averaged concentrations of nitrate in soil pore water, nitrate-containing groundwater in the LOOP wells (>1 mg/L), and the stream are 90 mg/L (min.-max.: 0-312 mg/L), 77 mg/L (11-165 mg/L) and 20 mg/L (8-54 mg/L), respectively (Supplementary Fig. 1b). Conductivity of stream and shallow groundwater is stable around 40-60 mS/m (Supplementary Fig. 1c). Compared to stream and shallow groundwater, conductivity of soil pore water varies in a wider range (23-75 mS/m) and often is more dilute than the other two waters (Supplementary Fig. 1c).

2.4. Geological interpretation of the subsurface structure

The geological structure of the subsurface was interpreted by combining geological and geophysical data. The geological data are 1) Borehole information from JUPITER; 2) Surface geology (Jakobsen et al., 2020; Pedersen et al., 2011); 3) Previous research, including landscape analyses (e.g., Smed, 1981) and results from the national buried valleys mapping project (Sandersen and Jørgensen, 2017); and 4) Digital Elevation Model (DEM). In addition to the tTEM data collected in this study, three types of geophysical data that were collected in previous research were integrated in the geological interpretation: 1) Electromagnetic data (Transient ElectroMagnetic (TEM) soundings); 2) Schlumberger soundings; and 3) Pulled Array Continuous Electrical Soundings (PACES; Sørensen, 1996). The relevant geophysical data were derived from the Danish national GERDA database (www.geus.dk). Geological interpretations of the data were performed using the GeoScene3D software (www.i-gis.dk).

2.5. C-Q analysis

The slopes of the C-Q of nitrate and conductivity were analyzed as follows (Godsey et al., 2009):

 $[C] = aQ^b$

where concentration is C, *a* is a coefficient, Q is discharge, and *b* is an exponent. This equation is log transformed:

 $\log([C]) = b \log Q + a$

and *b* becomes the slope of the C-Q relationship and *a* is the y-intercept, assuming a linear correlation between logC and logQ. In this study, $b \le -0.1$ is negative chemodynamic, -0.1 < b < 0.1 is chemostatic, and $b \ge 0.1$ is positive chemodynamic. The C-Q of nitrate and conductivity showed slightly different patterns from year to year and for low versus high flow regimes. Such variabilities have been reported in previous studies for instance Meybeck and Moatar (2012) and Moatar et al. (2017). The authors proposed to estimate the slopes for above (b_{a50}) and below (b_{b50}) median discharge separately. Therefore, in this study, the slopes were calculated as proposed (median discharge: 66 L/s) for each year if the number of observations was more than five.

2.6. Cluster analysis

The groundwater chemistry was analyzed using the K-means cluster analysis with R. The K-means cluster method is a statistical method to divide data (or observations) without supervision into clusters to minimize the variances within the cluster while maximizing the variance between clusters (MacQueen, 1967). The cluster analysis has been commonly used to interpret the spatial patterns of different groundwater types (e.g., Javadi et al., 2017). In this study, we employed the cluster analysis to group groundwater showing distinctive chemical signatures to analyze the spatial distribution and to identify the governing processes of each cluster. For the cluster analysis, measured data of major cations (Ca²⁺, Mg²⁺, Na⁺, K⁺), anions (HCO₃⁻, Cl⁻, NO₃⁻, SO₄²⁻), conductivity and pH were used as input data. Nitrate was log transformed because it varied over 3 orders of magnitude. In addition, we

hypothesized that 1) nitrate reduction coupled with organic carbon oxidation; 2) carbonate weathering via CO₂; and 3) nitrate reduction coupled with pyrite oxidation were dominant processes, and these reactions will display unique stoichiometric ratios of $HCO_3^-/(Ca^{2+} + Mg^{2+})$ and $SO_4^{2-}/(Ca^{2+} + Mg^{2+})$ (Table 1). Therefore, these ratios were included in the cluster analysis. The input data for the cluster analysis are summarized in Supplementary Table 2.

3. Results

3.1. Geological structure of the Odderbæk catchment

The subsurface geological structure of the study site is characterized by four geological elements: chronologically, 1) Paleogene clay (PC in Fig. 2); 2) Quaternary sediments of clay and sand (QCS in Fig. 2); 3) Quaternary sediments of the glacial hills (GH in Fig. 2); and 4) Sediments of the outwash plain (OP in Fig. 2). The low resistive (<10 Ω m) of the Paleogene clay (PC) constitutes the bottom of the interpreted sedimentary succession. The PC is effectively impermeable; therefore, this layer demarcates a no-flow boundary. The tTEM resistivity model reveals deeply eroded buried valleys in the PC.

A complex succession of the Quaternary sediment with clay and sand (QCS) overlies the PC layer. The QCS covers the entire catchment and is the largest volume among the four geological elements. The infill of the buried valley to the north is predominantly clay till with a few layers of meltwater sand and clay and pre-Quaternary slabs (Fig. 2e; left side valley). The buried valley to the southeast, in contrast, has high-resistivity infill presumably dominated by meltwater sand and gravel (Fig. 2c; right side valley). Above the buried valleys, the QCS is a succession of meltwater sand, clay till and meltwater clay. The tTEM resistivity model shows signs of deformation of the QCS (Profile a in Fig. 2) probably by glaciotectonic or neotectonic processes.

The top layers in the northwestern part of the catchment are the sediments of the glacial hills (GH) with meltwater sand and gravel with patches of sandy tills. The sediments of the GH also show signs of some degree of deformation. The GH represents an old succession of glacial sediments, which might have covered the entire catchment area before the last glaciation. The southeastern part of the GH might have been eroded during a later glaciation. The current GH, therefore, could be a hilly remnant of this layer. The upper part of the GH sediments is described as brownish yellow and non-calcareous in boreholes while the lower part is often described as calcareous and olive brown.

The uppermost layer of the low-lying area in the southeastern part of the catchment constitutes the sediments of the outwash plain (OP), which is the youngest geological element. The southeastern corner of the catchment is mainly yellowish-brown meltwater sand. To the north, near the boundary to the GH, postglacial freshwater sediments and peats are found up to 5 m below the land surface. This organic rich area stands out in the topography as slightly depressed (1–2 m) compared to the surrounding area. Organic-rich freshwater sediments or lake sediments have accumulated in this depression during the postglacial period, resulting in the gyttja and peat found in the area (Fig. 1c).

3.2. C-Q relationships of NO_3^- and conductivity of the stream

The overall C-Q relationships of nitrate and conductivity of the stream showed different patterns below and above the median discharge (66 L/s; Fig. 3a and b). Below the median discharge, the nitrate concentrations were relatively invariant or increased slightly with increasing discharge while above the median discharge, it increased more strongly with increasing discharge (Fig. 3a). In addition, the nitrate C-Q relationships varied from year to year (Supplementary Fig. 2). For example, b_{b50} and b_{a50} of the C-Q ranged between -0.05-1.30 and 0.08-1.05, respectively (Fig. 3c). On average, the nitrate C-Q of the Odderbæk catchment was positively chemodynamic

Table 1

Possible biogeochemical reactions of C and N and stoichiometric ratios of $\frac{HO_3^-}{Ga^{2+}+Me^{2+}}$ and $\frac{SO_4^{2-}}{Ga^{2+}+Me^{2+}}$ of the reactions (Appelo and Postma, 2005).

			1100-	2
Reaction	Equation		$\frac{HCO_3}{Ca^{2+}+Mg^{2+}}$	$\frac{SO_4^{2-}}{Ca^{2+}+Mg^{2+}}$
Nitrate reduction by organic matter	$5CH_2O + 4NO_3^- = 2 N_2 + 4HCO_3^- + H_2CO_3 + 2H_2O$	(1)	HCO_3^- in without changing Mg^{2+} , ar combina Eq. (2) I minor in $(HCO_3^-)(($ $+ Mg^{2+})$	creases directly $g Ca^{2+}$, $hd SO_4^{2-}$. A tion with eads to a crease in Ca^{2+}))
Carbonate dissolution with CO ₂	$Ca_xMg_{(1-x)}CO_3 + CO_2 + H_2O = xCa^{2+} + (1-x)Mg^{2+}$ + 2HCO ⁻	(2)	2	-
Ammonium oxidation-carbonate dissolution	$NH_{4}^{+} + 2O_{2} = NO_{3}^{-} + 2H^{+} + H_{2}O_{2}$ $C_{2}Mm_{2} = CO_{2} + H^{+} = xC_{2}^{2+} + (1 - x)Mm_{2}^{2+} + HCO_{2}^{-}$	(3)	1	-
Pyrite oxidation with oxygen and carbonate dissolution (Eq. (4)) Complete pyrite oxidation-nitrate reduction and carbonate dissolution (Eq.	$\begin{aligned} & \operatorname{FeS}_2 + 15/4 \operatorname{O}_2 + 7/2 \operatorname{H}_2 \operatorname{O} = \operatorname{Fe}(\operatorname{OH})_3 + 2\operatorname{SO}_4^{2-} + 4\operatorname{H}^+ \\ & \operatorname{FeS}_2 + 15 \operatorname{NO}_3^- + 5\operatorname{H}_2 \operatorname{O} = 0.5 \operatorname{N}_2 + 5\operatorname{FeOOH} + 10\operatorname{SO}_4^{2-} + 5\operatorname{H}^+ \end{aligned}$	(4) (5) (6)	1 1	0.5 2

(continued on next page)

for the entire flow regime (averages of $b_{b50} = 0.49$ and $b_{a50} = 0.57$; Fig. 3c).

The C-Q of conductivity also showed a different pattern above and below the median discharge and annual variability (Fig. 3b and c). b_{b50} and b_{a50} of the conductivity C-Q varied between -0.02-0.40 and -0.26-0.04, respectively (Fig. 3c and Supplementary Fig. 3). At high flow regime, the negative chemodynamic pattern was seen in five hydrological years out of 18 years of the observation period, and only three of them were statistically significant (Supplementary Fig. 3). On average, conductivity of the study catchment was positively chemodynamic for the below median discharge (average of $b_{b50} = 0.19$; Fig. 3c) while chemostatic for above the median discharge (average of $b_{a50} = -0.05$; Fig. 3c).

3.3. Cluster analysis of groundwater chemistry

The groundwater chemistry of the Odderbæk catchment was grouped in four clusters (Fig. 4). Cluster 1 (green circles in Fig. 4) was located at shallow depths (<5 m) in the peat area in the OP and at intakes deeper than 100 m below the land surface in the QCS. Cluster 2 (yellow circles in Fig. 4) represented the largest volume and was found in the GH and QCS in a depth range of 5–52 m. Cluster 3 (purple circles in Fig. 4) was located near the outlet in the OP at shallow depths (<3 m). Cluster 4 (red colors in Fig. 4) was found mainly in the OP around the stream at shallow depths (<5 m), except at two locations (40 and 43 m).

Each cluster showed distinctive water chemistry signatures (Fig. 4a– p). Cluster 1 groundwater showed increase of HCO_3^- without increasing $Ca^{2+} + Mg^{2+}$ (Fig. 4a). The Cl⁻ and Na⁺ concentrations were far off from the sea salt line (Na⁺:Cl⁻ = 0.84:1; Fig. 4e). The Cl⁻ concentrations were less than 2 mM while the Na⁺ concentrations increased up to 4.5 mM (Fig. 4e). The SO_4^{2-} concentrations did not change although the $Ca^{2+} + Mg^{2+}$ concentrations varied between 0.1 and 3 mM (Fig. 4i). Nitrate of Cluster 1 was less than 10 mg/L and averaged 3.8 mg/L (Fig. 4 and Supplementary Table 3).

The HCO₃ /Ca²⁺ + Mg²⁺ ratio of the Cluster 2 groundwater was approximately ~1.5, with high nitrate values showing a ~1:1 ratio and low nitrate concentrations showing a ~1:2 ratio (Fig. 4b). The Ca²⁺ + Mg²⁺ concentrations of Cluster 2 increased without increasing SO₄²⁻ (Fig. 4j). Na⁺ and Cl⁻ of this cluster were plotted slightly off the sea salt line (Fig. 4f). The nitrate concentrations of Cluster 2 were high (average: 91 mg/L; Fig. 4 and Supplementary Table 3).

Cluster 3 groundwater was relatively dilute compared to the other clusters. The HCO_3^- concentrations were extremely low, and pH was also notably lower compared to that of the other clusters (Fig. 4o). The $Ca^{2+} + Mg^{2+}$ concentrations increased without increasing HCO_3^- or

 SO_4^{2-} (Fig. 4c and k). Na⁺ and Cl⁻ of the Cluster 3 groundwater were scattered around the sea salt line (Fig. 4g).

Cluster 4 groundwater showed a scattered $Ca^{2+} + Mg^{2+}$ vs. HCO_3^- relationship between 1:2 and 1:1 and the overall $HCO_3^-/Ca^{2+} + Mg^{2+}$ ratio was approximately 0.9 (Fig. 4d). It also showed a SO_4^{2-}/Ca^2 $^+ + Mg^2$ ratio of roughly 0.5 although it was offset by 1–2.5 mM (Fig. 4l). Na⁺ and Cl⁻ of this cluster were scattered around the sea salt line (Fig. 4h). The nitrate concentrations of Cluster 4 were below 10 mg/L and often below 1 mg/L (Fig. 4) with an average of 3.9 mg/L (Supplementary Table 3).

4. Discussion

4.1. Dominant biogeochemical processes of the groundwater clusters

The groundwater chemistry of each cluster shows distinctive stoichiometric ratios (Fig. 4), and these ratios are good indicators for identifying the dominant biogeochemical processes (Table 1). For example, Cluster 1 shows increasing HCO_3^- without increasing $Ca^{2+} + Mg^{2+}$ (Fig. 4a), indicating that inorganic carbon is not from dissolution of carbonate. Furthermore, the lack of correlation between $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} and its low SO_4^{2-} concentrations indicate that carbonate dissolution is not driven by pyrite oxidation (Fig. 4i). The low nitrate concentrations indicate that nitrate reduction does occur in the Cluster 1 groundwater. The chemical signature of Cluster 1 implies that nitrate in this groundwater may be reduced via organic carbon oxidation (Eq. (1) in Table 1). High Na^+ compared to Cl^- also may be related the abundance of organic matter as well: Na⁺ that is bound onto organic matter might be exchanged with Ca²⁺ or NH₄⁺, resulting in increase of Na⁺ in solution without increasing Cl⁻. Consistent with this, Cluster 1 was found near the peat area in the OP, where both organic carbon concentrations and microbial activities are expected to be high (Fig. 4).

Cluster 2 shows signs of carbonate dissolution. The overall molar ratio of $HCO_3^-/Ca^{2+} + Mg^{2+}$ was 1.55 (Fig. 4b), which is lower than the theoretical stoichiometric ratio of carbonate dissolution with CO_2 , which is 2 (Eq. (2) in Table 1). The lower ratio may be because of weathering of minerals other than carbonate. However, carbonate minerals are more reactive than other primary and secondary minerals; therefore, Ca^{2+} and Mg^{2+} concentrations are likely to be controlled by carbonate dissolution if these minerals are present. Therefore, carbonate dissolution via other acids such as nitric acid produced by ammonium oxidation cannot be ruled out, which will result in a molar ratio of $HCO_3^-/Ca^{2+} + Mg^{2+}$ being 1 (Eqs. (3) and (4) in Table 1). In catchments underlain by carbonate rocks and impacted by acidification due to nitrification of N fertilizers, the streams' $HCO_3^-/Ca^{2+} + Mg^{2+}$ ratio was approximately 1.4, (e.g., Perrin et al., 2008), which is similar to that of



Fig. 2. Transects of the tTEM resistivity model with boreholes and geological elements of the study area. The colors of the boreholes show the lithology. The projection distance for the tTEM resistivity model and borehole data is 25 m. The dashed black lines show the boundaries between geological elements. The blue triangles show the position of the groundwater table and the black boxes next to the boreholes show the sampled/screened interval. The geological elements are, from the bottom up, Paleogene clay (PC), Quaternary sequence of clay and sand (QCS), Glacial hill (GH), and Outwash plain (OP).

Cluster 2. Therefore, we conclude that either nitric acid leached from the soil layer or in-situ nitrification in groundwater may be responsible for the low $HCO_3^-/Ca^{2+} + Mg^{2+}$ ratio of Cluster 2.

The nitrate concentrations of Cluster 2 were highest compared to those of other clusters: the average concentration of nitrate of this cluster was 90.9 mg/L (standard deviation (sd): 33.4; Supplementary Table 3). While the SO_4^{2-} concentrations of Cluster 2 were low (average: 0.4 mM; sd: 0.15; Supplementary Table 3) and showed no correlation with $Ca^{2+} + Mg^{2+}$. Altogether, the Cluster 2 chemistry indicates no nitrate reduction. Cluster 2 is mainly located in the GH and QCS units, which are the older formations in this catchment. We hypothesize that due to relatively long exposure time for weathering including oxidation, reduced compounds such as pyrite, which is highly reactive and is usually present in a trace amount, have been oxidized and are depleted while carbonates may still exist. More oxidized and welldrained conditions in the upslope area compared to the lowland area have been documented in many catchments (e.g., McAleer et al., 2017; Molenat et al., 2008). Therefore, nitrate reduction may not occur due to lack of reduced compounds, and weathering including dissolution of carbonate minerals with CO₂ and probably with acid generated by nitrification may be the dominant processes for Cluster 2.

Cluster 3 was the most dilute groundwater among the four clusters, and its pH was much lower than that of other clusters (Fig. 4). Its low HCO_3^- and SO_4^{2-} concentrations indicate that neither carbon dioxide nor sulfuric acid is the source of protons. Instead, nitric acid produced by oxidation of ammonia may supply protons and induce weathering reactions (Eq. (3) in Table 1). Indeed, soil acidification and increase of solute fluxes in agricultural watersheds due to nitric acid from N-fertilizers have been well documented (e.g., Kim et al., 2020; Perrin et al., 2008). Cluster 3 was found at shallow depths (3–5 m deep) mainly around the catchment outlet (Fig. 4). Thus, it is likely that carbonates have been leached out of this layer over time by natural (CO_2) and/or anthropogenic acids (nitric or sulfuric acids). The combination of shallow depths of Cluster 3 groundwater and lack of reactive carbonates implies that its chemistry does not evolve much further from the rainwater composition, resulting in low solute concentrations and low pH.



Fig. 3. Concentration-discharge (C-Q) relationships and the C-Q slopes of nitrate and conductivity at the outlet of the Odderbæk catchment. The C-Q relationships of nitrate and conductivity are shown in (a) and (b), respectively. The dot colors represent the sampling year. The vertical black line is the median discharge. Nitrate has been monitored for the entire monitoring period (1989 to current) while conductivity was measured between 1989 and 2007. (c) Each year's slopes for below and above the median discharge were shown in the yellow and light green columns, respectively. The statistically significant and insignificant slopes are shown in closed and open circles, respectively. The red squares indicate the mean value of the slopes.

The solute concentrations of Cluster 4 were similar to those of Cluster 2 except nitrate and sulfate (Fig. 4 and Supplementary Table 3). Its low nitrate concentrations (average: 3.9 mg/L) indicate that denitrification is occurring. The overall molar ratio of $SO_4^{2-}/Ca^{2+} + Mg^{2+}$ of Cluster 4 was 0.57, but those of individual wells ranged between 0.2 and 1.78. This variability may indicate that pyrite is oxidized via different reactions. Pyrite oxidation coupled with oxygen reduction (Eq. (5) in Table 1) followed by dissolution of carbonate with protons (Eq. (4) in Table 1) will result in $SO_4^{2-}/Ca^{2+} + Mg^{2+} = 0.5$ (Appelo and Postma, 2005). When pyrite is present, nitrate can be reduced via pyrite oxidation as well, and this coupled reaction may or may not produce protons, which will cause dissolution of carbonates if they are present (Appelo and Postma, 2005). When pyrite oxidation is coupled with complete nitrate reduction (Eq. (6) in Table 1) followed by carbonate dissolution with protons (Eq. (4) in Table 1), these reactions will yield the $SO_4^{2-}/$ $Ca^{2+} + Mg^{2+}$ ratio = 2 (Appelo and Postma, 2005). However, incomplete pyrite oxidation-nitrate reduction will not dissolve carbonate because protons are consumed during the reaction (Eq. (7) in Table 1; Appelo and Postma, 2005). There are, however, no reports of groundwater where none of the Fe(II) is oxidized. These ratios may indicate that in Cluster 4, pyrite oxidation may be coupled with all three reactions mentioned above but mainly with oxygen reduction.

4.2. Controls on the C-Q of the Odderbæk catchment

In the Odderbæk catchment, the C-Q of nitrate was positive chemodynamic regardless of flow regime while that of conductivity was positive chemodynamic below the median discharge and chemostatic above the median discharge. These C-Q relationships are rather atypical. For example, Moatar et al. (2017) analyzed the b_{b50} and b_{a50} of C-Q relationships of major solutes including NO₃⁻⁻ and conductivity of nearly 300 catchments across France using 40-year long monitoring data. Among their study catchments, the Odderbæk's nitrate and conductivity C-Q were observed in about 6% (the up-up type in the supporting information of Moatar et al., 2017) and less than 1% of the catchments (the up-flat type in the supporting information of Moatar et al., 2017), respectively, and only one catchment matched both nitrate and conductivity C-Q of our study site. The authors hypothesized that the positive chemodynamic pattern at low flow is due to either a transport limited condition (i.e., remobilization or reconnection of $NO_3^$ sources to the stream) or dominance shift from biogeochemical to hydrological controls (i.e., shorter reaction time for denitrification in and near stream zones; Moatar et al., 2017). The authors further concluded that the second hypothesis may be more plausible based on the negative chemodynamic pattern of Cl⁻:NO₃⁻ and positive correlations of b_{b50} with both summer temperature and chlorophyll concentrations. However, our catchment is much smaller (11 km²) than their study watersheds (50–110,000 km²); thus, the role of instream/near stream processes may be minor in displaying stream chemistry in our catchment. Furthermore, the decrease of reaction time cannot explain the positive chemodynamic pattern of conductivity at low discharge of our catchment.

Here we propose that the C-Q of nitrate and conductivity in the Odderbæk catchment is controlled by hydrological connectivity between different sources of water and nitrate. Fig. 5 shows conductivity and nitrate concentrations of stream water and the median values of these constituents of the groundwater clusters and soil pore water with 1st and 3rd quartiles. As discharge increases to the median discharge (dark pink to light pink colors of the stream markers), conductivity and nitrate of stream water evolve toward Cluster 2 (oxic groundwater in the GH and QCS), implying a higher contribution of Cluster 2 in this flow regime. At above the median discharge (light pink to green colors of the stream marker), the stream's conductivity and nitrate are placed between those of Cluster 2 and Cluster 3 (oxic in the OP) groundwaters. At the highest discharge (dark green color), the stream chemistry becomes similar to that of Cluster 3 and soil

Science of the Total Environment 776 (2021) 146041



Fig. 4. Cluster analysis results of the groundwater chemistry. The spatial distribution of groundwater clusters is shown in the map and the numbers in the markers indicate the sampling depth. The hashed areas show the drained fields. The concentrations (mM) of $Ca^{2+} + Mg^{2+}$, HCO_3^- , Na^+ , CI^- and SO_4^{2-} , pH and conductivity of each cluster are shown in (a) to (p). The nitrate concentrations of the respective cluster (columns) are shown in colors (mg/L) and those of the other clusters are shown in gray.

pore water, implying high contribution of shallow subsurface flow or drain flow (Fig. 5). Increases of the contribution of Cluster 3 that is found at shallow depths (<5 m depth) and soil pore water at high flow rates are anticipated. However, the higher contribution of Cluster 2 groundwater is counter intuitive because it is found in the upslope in the GH area and at depth deeper than 5 m below the land surface in the OP.

A higher contribution of upslope groundwater to the stream discharge during the wet season has been reported in other catchments (Martin et al., 2004; Molenat et al., 2008; Molénat et al., 2002; Ocampo et al., 2006a, 2006b; Stieglitz et al., 2003; Wriedt et al., 2007). The studies found that during the dry season, hydrologically discrete groundwater units are disconnected, thus the stream discharge is mainly dominated by near stream units such as riparian zone groundwater which typically shows low nitrate concentrations. As the catchment wets up the disconnected hydrological units become reconnected as the groundwater table rises and becomes more transmissive (Molenat et al., 2008; Wriedt et al., 2007), as perched groundwater is transiently developed (Ocampo et al., 2006a, 2006b) or as the stream channels are reconnected (Wriedt et al., 2007). In these sites, although the responses are relatively damped and delayed compared to those in the lowland or riparian zone, the upland groundwater table fluctuates seasonally by a few meters in response to the variations in recharge. However, in our study site, neither such a quick response of the groundwater table nor perched groundwater has been observed in the upslope area of the GH.

Instead, we hypothesize that either the higher contribution of the Cluster 2 groundwater in the OP or a seasonal shift in the flow direction of groundwater around the edge of the GH is responsible for the C-Q of

nitrate and conductivity of our study catchment. As the catchment wets up, the groundwater table of Cluster 2 in the OP might rise and consequently its contribution to the stream discharge might increase as well. In this case, the nitrate concentrations of the overlying Cluster 1 and/or Cluster 4 groundwater (low nitrate) in the OP will fluctuate seasonally with the Cluster 2 groundwater table changes (high nitrate). However, such patterns have not been observed in those wells (Supplementary Fig. 4). The first hypothesis cannot be completely ruled out because of the structural heterogeneity of the catchment; however, we conclude that the Cluster 2 groundwater in the OP may play a minor role in the positive chemodynamic pattern of nitrate and conductivity.

The second explanation may be more probable. The lower boundary of the GH is defined by an irregular clayey layer (blue to green colors) which is deformed likely due to glaciotectonic processes (Fig. 2 profile d). This clay layer is locally discontinued; thus, groundwater recharges into the QCS. The boundary between the GH and OP is demarcated by a small ridge of the PC, which is impermeable (Fig. 2 profile d). When the groundwater table is below this boundary, the groundwater in the GH and QCS flows more or less parallel to the stream along the buried valley. When the groundwater table rises above the boundary, the groundwater around the edge of the GH runs over the boundary and flows to the stream. The cluster analysis showed that denitrification (Cluster 1 and 4) occurs in the lowland area at the boundary between the GH and OP at shallow depth (Fig. 4). However, these areas are drained. Therefore, we further postulate that the over-spilled groundwater runs mainly through drains, bypassing the denitrification layer, delivering high nitrate groundwater to the stream.

Fig. 6 shows the groundwater table of two wells located at the boundary between the GH and OP (profile c and profile d in Fig. 2) of



Fig. 5. Conductivity vs. nitrate of stream water (circle), the groundwater clusters (square) and soil pore water (triangle). The colors of the dots represent stream discharge. For the stream, the measured values are shown while for the groundwater clusters and soil pore water, the median values with 1st and 3rd quartiles are shown.

hydrological year (June 1st to May 30th) of 1996 and 2014. The C-O of nitrate and conductivity of the stream of these years are also shown in the figure. The hydrological year 1996 (June 1st 1995–May 30th 1996) was extremely dry (Supplementary Fig. 1a). During this year, the groundwater head of DGU 40. 964 (profile c in Fig. 2) stayed at about 1.5 m below the land surface except two points with a groundwater table of approximately 0.9 m (Fig. 6c). In this year, nitrate and conductivity were chemostatic while the discharge fluctuated by a factor of ~3 (Fig. 6a and b). In contrast, in the hydrological year 2014 (June 1st 2013–May 30th 2014), which was a normal year, the groundwater table of the two wells and nitrate concentrations of the stream showed a similar response pattern to discharge (Fig. 6e, g and h). The nitrate concentrations of the stream increased when the groundwater table of these two wells rose during the winter. These observations confirm a threshold-like response of the Cluster 2 groundwater in the GH, which is controlled by the geological structure.

In summary, we conclude that the geological structure forms discrete groundwater units with distinctive groundwater chemistry and plays a critical role on controlling the hydrological connectivity among these units thus governs nitrate export from the catchment. This concept is similar to the catchment storage hypothesis that explains the non-linearity of rainfall-runoff generation responses (e.g., McGuire and McDonnell, 2010; Mcnamara et al., 2011; Spence, 2010): A storage in discrete hydrological units, for instance soil moisture (Detty and McGuire, 2010) or groundwater in bedrock depressions (e.g., Freer et al., 2002; Tromp-van Meerveld and McDonnell, 2006a; Tromp-van Meerveld and McDonnell, 2006b) acts as a threshold to generate significant runoff and solute export (e.g., Birkel et al., 2017). In our catchment, the glacio-tectonically deformed clay layers may define the groundwater storages. The spatial heterogeneity of the groundwater units and temporal variability of their connectivity further emphasize the importance of the detailed information of the subsurface structure to better understand water and solute transport at the catchment scale.

4.3. A 3D hydrogeochemistry model of nitrate transport and fate of the Odderbæk catchment

A conceptual model to explain nitrate export from our catchment is shown in Fig. 7. At low flow in the dry season (i.e., summer), groundwater near the stream may be the dominant source of the stream discharge. This groundwater is mainly in the OP at relatively shallow depth (Fig. 7a) where denitrification occurs; therefore, it shows low nitrate. Oxic, high-nitrate groundwater along the QCS below the OP layer may also contribute to the stream discharge; however, it might play a minor role. During the dry season, the groundwater in the uplands i.e., the GH and QCS may flow parallel to the stream because the groundwater storage in these geological units is below the threshold needed to activate the nitrate pathways toward the stream (Fig. 7a).

At the onset of the wet season (i.e., winter), the groundwater storage in the GH and QCS fills up. Once the groundwater storage is full, the water and nitrate pathway to the stream is activated (Fig. 7b). The oxic, highnitrate groundwater runs over the boundary between the GH and OP and is rapidly transported via drains to the stream. As a result, the nitrate concentrations and conductivity of the stream increase. At the highest discharge events, near surface flow may be activated, which is responsible for the negative chemodynamic pattern of conductivity in wet years.

Here, we further projected the knowledge of water and nitrate transport into the catchment subsurface in 3D using the tTEM resistivity model of this catchment (Fig. 7c). First, the resistivity models together with lithological information from boreholes were used to generate hydrostratigraphic units (Fig. 7d) based on the clay fraction concept (Foged et al., 2014) using the K-means clustering on the clay fraction and resistivity values (Vilhelmsen et al., 2019). The tTEM resistivity models and hydrostratigraphic units were afterwards projected on a regular grid, covering the area with a 25 m horizontal and 2 m vertical discretization (Fig. 7c and d). These hydrostratigraphic units in Fig. 7d can also represent the sediment texture (i.e., most clavey vs. least clayey). The two most clayey units were considered as no flow zones. The two least clayey units in here were interpreted as sand where water and nitrate dominantly flow through. Then, the hydrogeochemistry model was produced by integrating the hydrostratigraphic unit structure, geological structure, soil map and groundwater cluster results. In this catchment, denitrification mainly occurs in the Cluster 1 (nitrate reduction-organic carbon oxidation) and Cluster 4 (nitrate reduction-pyrite oxidation) groundwater which are mostly found in the postglacial sediment area (gyttja and peat in Fig. 1c) in the OP at depth shallower than 5 m; thus, the nitrate denitrification zones (Fig. 7e) were delineated based on the groundwater chemistry and the soil map. Sand in the OP shallower than 5 m was Cluster 3 (Fig. 4), where no nitrate reduction occurs and nitric acid produced by nitrification mediates weathering reactions (Fig. 7e). This layer is underlain by Cluster 2. Sand in the GH and QCS is Cluster 2, where carbonate dissolution is the dominant process and nitrate reduction might be negligible or extremely low (Fig. 7e).

4.4. Implications and future research

Integration of qualitative knowledge of a catchment's hydrogeochemical characteristics into the numerical modelling framework is one of the key challenges in hydrological and biogeochemical modelling at the catchment scale (e.g., Fatichi et al., 2016; Sarris et al., 2019). The field observations provide fundamental knowledge of the system and an essential dataset to build, test and validate the modelling structure; however, models often are disconnected from them (Fatichi et al., 2016). The hydrogeochemistry model of this study is a demonstration



Fig. 6. C-Q relationships of nitrate (a and e) and conductivity (b and f) of the stream and depth to the groundwater table (c, g, d and h) of DGU 40. 946 and DU 48. 996 in hydrological year 1996 and 2014. The colors show the sampling month. The locations of these two wells are shown in Fig. 2.

Science of the Total Environment 776 (2021) 146041



Fig. 7. Conceptual model and hydrogeochemical model of water and nitrate transport in the Odderbæk catchment. The dry and wet seasons' water and nitrate pathways are shown in (a) and (b), respectively. The tTEM resistivity grid, the hydrostratigraphic unit and the hydrogeochemistry model are shown in (c), (d) and (e), respectively. The color code of the groundwater cluster is the same as that in Fig. 4, except clay (blue), which represents an impermeable layer. The color scale of resistivity is the same as that in Fig. 2. Surface topography is shown in (c) and (d), and its color scale is the same as that in Fig. 1.

of how the qualitative and conceptual understandings of the catchment at small scale (i.e., point to profile) can be upscaled and generalized to the catchment scale. This model may be the first step toward a numerical representation of the spatial and temporal heterogeneity of denitrification of this catchment.

However, several research questions remain to fully translate conceptual understandings of nitrate fate and transport into numerical simulations. Parameterization of denitrification rates is not trivial. Defining representative denitrification rates for different biogeochemical zones can be difficult because of hotspots and hot moments of denitrification, the rates can vary orders of magnitude on a small spatial scale (e.g., Groffman et al., 2009; Pinay et al., 2015). In addition, denitrification rates may be quantified differently depending on employed methods (Groffman et al., 2006; Seitzinger et al., 1993; Smith et al., 1996). Therefore, the quantification methods and delineation of different rate zones should be carefully designed according to the simulation methods and objectives of modelling. It is also important to evaluate the uncertainty of the subsurface structure and its contribution to hydro-bio-geochemical models. In the areas where data are collected, uncertainty is inherently connected to the collected data and can then be taken into account in the further analysis. However, in areas without data, the uncertainty is caused by the lack of information. Data gaps in the collected geophysical data may be addressed using various geostatistical techniques. Recent studies have attempted to address this issue using multipoint statistics (e.g., Madsen et al., 2020; Vilhelmsen et al., 2019). Through such multi-disciplinary efforts, the conceptual knowledge may be better represented in the modelling structure, and the model performance and predictability may be improved for the right reasons.

5. Conclusions

In this study, we investigated the evolution of nitrate in a glacial landscape by synthesizing hydrological, geological, biogeochemical, and geophysical information. We found that the subsurface hydrogeological structure plays an important role in nitrate removal and transport. The geochemical characteristics of the groundwater was determined by the weathering history of the geological elements, and the groundwater in each geological element was shown to be hydrologically discrete. The geological structure together with the climate probably controls the temporal variability of hydrological connectivity among these groundwaters, and consequently the timing and magnitude of nitrate export from the catchment. Lastly, this conceptual understanding of the nitrate behavior in the system was upscaled to the catchment scale using the highresolution resistivity model. Uncertainties of the structural information and parameterization of denitrification rates still require further research. Here we show how synthesis of long-term aquatic monitoring data together with high-resolution geophysical data can be used to establish a conceptual model of the hydrogeochemical conditions of the subsurface in a catchment. This information is crucial for setting up numerical models of N-transport at the catchment level, which will be important for designing the spatially targeted N-regulation of agriculture.

CRediT authorship contribution statement

Hyojin Kim: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Writing – original draft, Writing – review & editing, Visualization. **Peter B.E. Sandersen:** Investigation, Writing – review & editing. **Rasmus Jakobsen:** Writing – review & editing. **Anders Juhl Kallesøe:** Investigation, Writing – review & editing. **Niels Claes:** Software, Visualization, Writing – review & editing. **Gitte Blicher-Mathiesen:** Data curation, Writing – review & editing. **Nikolaj Foged:** Software, Writing – review & editing. **Writing – review** & editing. **Birgitte Hansen:** Writing – review & editing, Supervision, Project administration, Funding acquisition.

Declaration of competing interest

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

Acknowledgments

We would like to thank two anonymous reviewers for constructive comments. This study was funded by Innovation Fund Denmark under Award number 8855-00025B (MapField: Field-scale mapping for targeted N-regulation and management).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi. org/10.1016/j.scitotenv.2021.146041.

References

- Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, Geochemistry, Groundwater and Pollution. Second edition. CRC Press https://doi.org/10.1201/ 9781439833544.
- Auken, E., Christiansen, A.V., Kirkegaard, C., Fiandaca, G., Schamper, C., Behroozmand, A.A., Binley, A., Nielsen, E., Effersø, F., Christensen, N.B., Sørensen, K., Foged, N., Vignoli, G., 2015. An overview of a highly versatile forward and stable inverse algorithm for airborne, ground-based and borehole electromagnetic and electric data. Explor. Geophys. 46, 223–235. https://doi.org/10.1071/EG13097.
- Auken, E., Foged, N., Larsen, J.J., Lassen, K.V.T., Maurya, P.K., Dath, S.M., Eiskjær, T.T., 2019. tTEM – a towed transient electromagnetic system for detailed 3D imaging of the top 70 m of the subsurface. GEOPHYSICS 84, E13–E22. https://doi.org/10.1190/geo2018-0355.1.
- Best, A., Arnaud, E., Parker, B., Aravena, R., Dunfield, K., 2015. Effects of glacial sediment type and land use on nitrate patterns in groundwater. Groundw. Monit. Remediat. 35, 68–81. https://doi.org/10.1111/gwmr.12100.
- Bieroza, M.Z., Heathwaite, A.L., Bechmann, M., Kyllmar, K., Jordan, P., 2018. The concentration-discharge slope as a tool for water quality management. Sci. Total Environ. 630, 738–749. https://doi.org/10.1016/j.scitotenv.2018.02.256.

- Binley, A., Hubbard, S.S., Huisman, J.A., Revil, A., Robinson, D.A., Singha, K., Slater, L.D., 2015. The emergence of hydrogeophysics for improved understanding of subsurface processes over multiple scales. Water Resour. Res. 51, 3837–3866. https://doi.org/ 10.1002/2015WR017016.
- Birkel, C., Broder, T., Biester, H., 2017. Nonlinear and threshold-dominated runoff generation controls DOC export in a small peat catchment. J. Geophys. Res. Biogeosci. 122, 498–513. https://doi.org/10.1002/2016JG003621.
- Blaen, P.J., Khamis, K., Lloyd, C., Comer-Warner, S., Ciocca, F., Thomas, R.M., MacKenzie, A.R., Krause, S., 2017. High-frequency monitoring of catchment nutrient exports reveals highly variable storm event responses and dynamic source zone activation. J. Geophys. Res. Biogeosci. 122, 2265–2281. https://doi.org/10.1002/2017JG003904.
- Blicher-Mathiesen, G., Holm, H., Houlborg, T., Rolighed, J., Estrup Andersen, H., Vodder Carstensen, M., Grewy Jensen, P., Wienke, J., Hansen, B., Thorling, L., 2019. Landovervågningsoplande 2018.
- Böhlke, J.K., Denver, J.M., 1995. Combined use of groundwater dating, chemical, and isotopic analyses to resolve the history and fate of nitrate contamination in two agricultural watersheds, Atlantic Coastal Plain, Maryland. Water Resour. Res. 31, 2319–2339. https://doi.org/10.1029/95WR01584.
- Böhlke, J.K., Michel, R.L., 2009. Contrasting residence times and fluxes of water and sulfate in two small forested watersheds in Virginia, USA. Sci. Total Environ. 407, 4363–4377. https://doi.org/10.1016/j.scitotenv.2009.02.007.
- Böhlke, J.K., Wanty, R., Tuttle, M., Delin, G., Landon, M., 2002. Denitrification in the recharge area and discharge area of a transient agricultural nitrate plume in a glacial outwash sand aquifer, Minnesota. Water Resour. Res. 38, 10-1–10-26. https://doi. org/10.1029/2001WR000663.
- Claes, N., Paige, G.B., Grana, D., Parsekian, A.D., 2020. Parameterization of a hydrologic model with geophysical data to simulate observed subsurface return flow paths. Vadose Zo. J. 19, 1–19. https://doi.org/10.1002/vzj2.20024.
- Detty, J.M., McGuire, K.J., 2010. Threshold changes in storm runoff generation at a tillmantled headwater catchment. Water Resour. Res. 46, W07525. https://doi.org/ 10.1029/2009WR008102.
- 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. Sci. Total Environ. 571, 791–800. https:// doi.org/10.1016/j.scitotenv.2016.07.053.
- Fatichi, S., Vivoni, E.R., Ogden, F.L., Ivanov, V.Y., Mirus, B., Gochis, D., Downer, C.W., Camporese, M., Davison, J.H., Ebel, B., Jones, N., Kim, J., Mascaro, G., Niswonger, R., Restrepo, P., Rigon, R., Shen, C., Sulis, M., Tarboton, D., 2016. An overview of current applications, challenges, and future trends in distributed process-based models in hydrology. J. Hydrol. 537, 45–60. https://doi.org/10.1016/j.jhydrol.2016.03.026.
- Foged, N., Marker, P.A., Christansen, A.V., Bauer-Gottwein, P., Jørgensen, F., Høyer, A.-S., Auken, E., 2014. Large-scale 3-D modeling by integration of resistivity models and borehole data through inversion. Hydrol. Earth Syst. Sci. 18, 4349–4362. https://doi. org/10.5194/hess-18-4349-2014.
- Freer, J., McDonnell, J.J., Beven, K.J., Peters, N.E., Burns, D.A., Hooper, R.P., Aulenbach, B., Kendall, C., 2002. The role of bedrock topography on subsurface storm flow. Water Resour. Res. 38, 5-1-5-16. https://doi.org/10.1029/2001wr000872.
- Galloway, J.N., Aber, J.D., Erisman, J.W., Seitzinger, S.P., Howarth, R.W., Cowling, E.B., Cosby, B.J., Galloway, J.N., 2003. The nitrogen cascade. Bioscience 53, 341–356. https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2.
- Godsey, S.E., Kirchner, J.W., Clow, D.W., 2009. Concentration-discharge relationships reflect chemostatic characteristics of US catchments. Hydrol. Process. 23, 1844–1864. https://doi.org/10.1002/hyp.7315.
- Green, C.T., Puckett, L.J., Böhlke, J.K., Bekins, B.A., Phillips, S.P., Kauffman, L.J., Denver, J.M., Johnson, H.M., 2008. Limited occurrence of denitrification in four shallow aquifers in agricultural areas of the United States. J. Environ. Qual. 37, 994–1009. https://doi.org/ 10.2134/jeq2006.0419.
- Groffman, P.M., Altabet, M.A., Böhlke, J.K., Butterbach-bahl, K., Mark, B., Firestone, M.K., Giblin, A.E., Kana, T.M., Nielsen, L.P., Voytek, M.A., Groffman, P.M., Altabet, M.A., Bohlke, J.K., Butterbach-bahl, K., David, M.B., Firestone, M.K., Giblin, A.E., Kana, T.M., Nielsen, L.P., Voytek, M.A., 2006. Methods for measuring denitrification: diverse approaches to a difficult problem. Ecol. Appl. 16, 2091–2122. https://doi.org/10.1890/ 1051-0761(2006)016[2091:mfmdda]2.0.co;2.
- Groffman, P.M., Butterbach-Bahl, K., Fulweiler, R.W., Gold, A.J., Morse, J.L., Stander, E.K., Tague, C., Tonitto, C., Vidon, P., 2009. Challenges to incorporating spatially and temporally explicit phenomena (hotspots and hot moments) in denitrification models. Biogeochemistry 93, 49–77. https://doi.org/10.1007/s10533-008-9277-5.
- Hansen, B., Thorling, L., 2008. Use of geochemistry in groundwater vulnerability mapping in Denmark. Geol. Surv. Denmark Greenl. Bull. 15, 45–48.
- Hansen, A.L., Christensen, B.S.B., Ernstsen, V., He, X., Refsgaard, J.C., 2014. A concept for estimating depth of the redox interface for catchment-scale nitrate modelling in a till area in Denmark. Hydrogeol. J. 22, 1639–1655. https://doi.org/10.1007/s10040-014-1152-y.
- Hansen, B., Voutchkova, D.D., Sandersen, P.B.E., Kallesøe, A., Thorling, L., Møller, I., Madsen, R.B., Jakobsen, R., Aamand, J., Maurya, P., Kim, H., 2021. Assessment of complex subsurface redox structures for sustainable development of agriculture and the environment. Environ. Res. Lett. 16, 025007. https://doi.org/10.1088/1748-9326/abda6d.
- Hashemi, F., Olesen, J.E., Børgesen, C.D., Tornbjerg, H., Thodsen, H., Dalgaard, T., 2018. Potential benefits of farm scale measures versus landscape measures for reducing nitrate loads in a Danish catchment. Sci. Total Environ. 637–638, 318–335. https:// doi.org/10.1016/j.scitotenv.2018.04.390.
- Herndon, E.M., Dere, A.L., Sullivan, P.L., Norris, D., Reynolds, B., Brantley, S.L., 2015. Landscape heterogeneity drives contrasting concentration–discharge relationships in shale headwater catchments. Hydrol. Earth Syst. Sci. 19, 3333–3347. https://doi.org/ 10.5194/hess-19-3333-2015.
- Jakobsen, P.R., Hermansen, B., Tougaard, L., 2020. Danmarks digitale jordartskort (Surface geology map), 1:25000. Version 5.0 Geological Survey of Denmark, Report 2020/18 (29 p).

- Javadi, S., Hashemy, S.M., Mohammadi, K., Howard, K.W.F., Neshat, A., 2017. Classification of aquifer vulnerability using K-means cluster analysis. J. Hydrol. https://doi.org/ 10.1016/j.jhydrol.2017.03.060.
- Jessen, S., Postma, D., Thorling, L., Müller, S., Leskelä, J., Engesgaard, P., 2017. Decadal variations in groundwater quality: a legacy from nitrate leaching and denitrification by pyrite in a sandy aquifer. Water Resour. Res. 53, 184–198. https://doi.org/10.1002/ 2016WR018995.
- Jha, M.K., Schilling, K.E., Gassman, P.W., Wolter, C.F., 2010. Targeting land-use change for nitrate-nitrogen load reductions in an agricultural watershed. J. Soil Water Conserv. 65, 342–352. https://doi.org/10.2489/jswc.65.6.342.
- Kim, H., Dietrich, W.E., Thurnhoffer, B.M., Bishop, J.K.B.B., Fung, I.Y., 2017. Controls on solute concentration-discharge relationships revealed by simultaneous hydrochemistry observations of hillslope runoff and stream flow: the importance of critical zone structure. Water Resour. Res. 53, 5375–5377. https://doi.org/10.1002/2016WR019722.
- Kim, H., Høyer, A.-S., Jakobsen, R., Thorling, L., Aamand, J., Maurya, P.K., Christiansen, A.V., Hansen, B., 2019. 3D characterization of the subsurface redox architecture in complex geological settings. Sci. Total Environ. 693, 133583. https://doi.org/10.1016/j. scitotenv.2019.133583.
- Kim, J.H., Jobbágy, E.G., Richter, D.D., Trumbore, S.E., Jackson, R.B., 2020. Agricultural acceleration of soil carbonate weathering. Glob. Chang. Biol. 1–15. https://doi.org/10.1111/gcb.15207.
- Kirkegaard, C., Andersen, K., Boesen, T., Christiansen, A.V., Auken, E., Fiandaca, G., 2015. Utilizing massively parallel co-processors in the AarhusInv 1D forward and inverse AEM modelling code. ASEG Ext. Abstr. 2015, 1–3. https://doi.org/10.1071/aseg2015ab125.
- Kronvang, B., Aertebjerg, G., Grant, R., Kristensen, P., Hovmand, M., Kirkegaard, J., 1993. Nationwide monitoring of nutrients and their ecological effects: state of the Danish aquatic environment. Ambio 22, 176–187. https://doi.org/10.2307/4314067.
- Larsen, N.K., Knudsen, K.L., Krohn, C.F., Kronborg, C., Murray, A.S., Nielsen, O.B., 2009. Late Quaternary ice sheet, lake and sea history of southwest Scandinavia - a synthesis. Boreas 38, 732–761. https://doi.org/10.1111/j.1502-3885.2009.00101.x.
- MacQueen, J., 1967. Some methods for classification and analysis of multivariate observations. Proceedings of the Fifth Berkeley Symposium on Mathematical Statistics and Probability.
- Madsen, R.B., Kim, H., Kallesøe, A.J., Sandersen, P.B.E., Norvin, T., Hansen, T.M., Christiansen, A.V., Møller, I., Hansen, B., 2020. 3D multiple point geostatistical simulation of joint subsurface redox and geological architectures. Hydrol. Earth Syst. Sci. Discuss. https://doi.org/10.5194/hess-2020-444 in review.
- Martin, C., Aquilina, L., Gascuel-Odoux, C., Molénat, J., Faucheux, M., 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, 1237–1254. https://doi.org/10.1002/hyp.1395.
- McAleer, E.B., Coxon, C.E., Richards, K.G., Jahangir, M.M.R., Grant, J., Mellander, P.E., 2017. Groundwater nitrate reduction versus dissolved gas production: a tale of two catchments. Sci. Total Environ. 586, 372–389. https://doi.org/10.1016/j.scitotenv.2016.11.083.
- McGuire, K.J., McDonnell, J.J., 2010. Hydrological connectivity of hillslopes and streams: characteristic time scales and nonlinearities. Water Resour. Res. 46, 2010WR009341. https://doi.org/10.1029/2010WR009341.
- Mcnamara, J.P., Tetzlaff, D., Bishop, K., Soulsby, C., Seyfried, M., Peters, N.E., Aulenbach, B.T., Hooper, R., 2011. Storage as a metric of catchment comparison. Hydrol. Process. 25, 3364–3371. https://doi.org/10.1002/hyp.8113.
- Meybeck, M., Moatar, F., 2012. Daily variability of river concentrations and fluxes: indicators based on the segmentation of the rating curve. Hydrol. Process. 26, 1188–1207. https://doi.org/10.1002/hyp.8211.
- 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 Resour. Res. 53, 1270–1287. https://doi.org/ 10.1002/2016WR019635.
- Molénat, J., Durand, P., Gascuel-Odoux, C., Davy, P., Gruau, G., 2002. Mechanisms of nitrate transfer from soil to stream in an agricultural watershed of French Brittany. Water Air Soil Pollut. 133, 161–183. https://doi.org/10.1023/A:1012903626192.
- 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). J. Hydrol. 348, 363–378. https://doi.org/10.1016/j.jhydrol.2007.10.005.
- Musolff, A., Schmidt, C., Rode, M., Lischeid, G., Weise, S.M., Fleckenstein, J.H., 2016. Groundwater head controls nitrate export from an agricultural lowland catchment. Adv. Water Resour. 96, 95–107. https://doi.org/10.1016/j.advwatres.2016.07.003.
- Musolff, A., Fleckenstein, J.H., Rao, P.S.C., Jawitz, J.W., 2017. Emergent archetype patterns of coupled hydrologic and biogeochemical responses in catchments. Geophys. Res. Lett. 44, 4143–4151. https://doi.org/10.1002/2017GL072630.
- Ocampo, C.J., Sivapalan, M., Oldham, C., 2006a. Hydrological connectivity of upland-riparian zones in agricultural catchments: implications for runoff generation and nitrate transport. J. Hydrol. 331, 643–658. https://doi.org/10.1016/j.jhydrol.2006.06.010.
- Ocampo, C.J., Sivapalan, M., Oldham, C.E., 2006b. Field exploration of coupled hydrological and biogeochemical catchment responses and a unifying perceptual model. Adv. Water Resour. 29, 161–180. https://doi.org/10.1016/j.advwatres.2005.02.014.
- Pedersen, S.A.S., Hermansen, B., Nathan, C., Toug, 2011. Digitalt kort over Danmarks jordarter 1:200.000 (version 2).
- Perrin, A.-S., Probst, A., Probst, J.-L., 2008. Impact of nitrogenous fertilizers on carbonate dissolution in small agricultural catchments: implications for weathering CO₂ uptake at regional and global scales. Geochim. Cosmochim. Acta 72, 3105–3123. https://doi. org/10.1016/j.gca.2008.04.011.

- Pinay, G., Peiffer, S., De Dreuzy, J.R., Krause, S., Hannah, D.M., Fleckenstein, J.H., Sebilo, M., Bishop, K., Hubert-Moy, L., 2015. Upscaling nitrogen removal capacity from local hotspots to low stream orders' drainage basins. Ecosystems 18, 1101–1120. https:// doi.org/10.1007/s10021-015-9878-5.
- Postma, D., Boesen, C., Kristiansen, H., Larsen, F., 1991. Nitrate reduction in an unconfined sandy aquifer: water chemistry, reduction processes, and geochemical modeling. Water Resour. Res. 27, 2027–2045. https://doi.org/10.1029/91WR00989.
- Postma, D., Larsen, F., Thai, N.T., Trang, P.T.K., Jakobsen, R., Nhan, P.Q., Long, T.V., Viet, P.H., Murray, A.S., 2012. Groundwater arsenic concentrations in Vietnam controlled by sediment age. Nat. Geosci. 5, 656–661. https://doi.org/10.1038/ngeo1540.
- Puckett, L.J., Cowdery, T.K., McMahon, P.B., Tornes, L.H., Stoner, J.D., 2002. Using chemical, hydrologic, and age dating analysis to delineate redox processes and flow paths in the riparian zone of a glacial outwash aquifer-stream system. Water Resour. Res. 38, 9-1–9-20. https://doi.org/10.1029/2001WR000396.
- Robinson, D.A., Binley, A., Crook, N., Day-Lewis, F.D., Ferré, T.P.A., Grauch, V.J.S., Knight, R., Knoll, M., Lakshmi, V., Miller, R., Nyquist, J., Pellerin, L., Singha, K., Slater, L., 2008. Advancing process-based watershed hydrological research using near-surface geophysics: a vision for, and review of, electrical and magnetic geophysical methods. Hydrol. Process. 22, 3604–3635. https://doi.org/10.1002/hyp.6963.
- Rodvang, S.J., Simpkins, W.W., 2001. Agricultural contaminants in Quaternary aquitards: a review of occurrence and fate in North America. Hydrogeol. J. 9, 44–59. https://doi. org/10.1007/s100400000114.
- Sandersen, P.B.E., Jørgensen, F., 2017. Buried tunnel valleys in Denmark and their impact on the geological architecture of the subsurface. Geol. Surv. Denmark Greenl. Bull. 38, 13–16.
- Sarris, T.S., Scott, D.M., Close, M.E., Humphries, B., Moore, C., Burbery, L.F., Rajanayaka, C., Barkle, G., Hadfield, J., 2019. The effects of denitrification parameterization and potential benefits of spatially targeted regulation for the reduction of N-discharges from agriculture. J. Environ. Manag. 247, 299–312. https://doi.org/10.1016/j. jenvman.2019.06.074.
- Schullehner, J., Hansen, B., Thygesen, M., Pedersen, C.B., Sigsgaard, T., 2018. Nitrate in drinking water and colorectal cancer risk: a nationwide population-based cohort study. Int. J. Cancer 143, 73–79. https://doi.org/10.1002/ijc.31306.
- Seitzinger, S.P., Nielsen, L.P., Caffrey, J., Bondo, P., Seitzinger, S.P., Nielsen, L.P., Caffrey, J., Christensen, P.B., 1993. Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochemistry 23, 147–167.
- Smed, P., 1981. Landskabskort Midtjylland: Geografforlaget.
- Smith, R.L., Garabedian, S.P., Brooks, M.H., 1996. Comparison of denitrification activity measurements in groundwater using cores and natural-gradient tracer tests. Environ. Sci. Technol. 30, 3448–3456. https://doi.org/10.1021/es960042g.
- Sørensen, K., 1996. Pulled array continuous electrical profiling. First Break https://doi.org/ 10.4133/1.2922124.
- Spence, C., 2010. A paradigm shift in hydrology: storage thresholds across scales influence catchment runoff generation. Geogr. Compass 4, 819–833. https://doi.org/10.1111/ j.1749-8198.2010.00341.x.
- Stenger, R., Clague, J.C., Morgenstern, U., Clough, T.J., 2018. Vertical stratification of redox conditions, denitrification and recharge in shallow groundwater on a volcanic hillslope containing relict organic matter. Sci. Total Environ. 639, 1205–1219. https:// doi.org/10.1016/j.scitotenv.2018.05.122.
- Stieglitz, M., Shaman, J., McNamara, J., Engel, V., Shanley, J., Kling, G.W., 2003. An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Glob. Biogeochem. Cycles 17, 1105. https://doi.org/10.1029/ 2003GB002041.
- Teshager, A.D., Gassman, P.W., Secchi, S., Schoof, J.T., 2017. Simulation of targeted pollutant-mitigation-strategies to reduce nitrate and sediment hotspots in agricultural watershed. Sci. Total Environ. 607–608, 1188–1200. https://doi.org/10.1016/j. scitotenv.2017.07.048.
- Tesoriero, A.J., Liebscher, H., Cox, S.E., 2000. Mechanism and rate of denitrification in an agricultural watershed: electron and mass balance along groundwater flow paths. Water Resour. Res. 36, 1545–1559. https://doi.org/10.1029/2000WR900035.
- Tromp-van Meerveld, H.J., McDonnell, J.J., 2006a. Threshold relations in subsurface stormflow: 2. The fill and spill hypothesis. Water Resour. Res. 42, 1–11. https://doi. org/10.1029/2004WR003800.
- Tromp-van Meerveld, H.J., McDonnell, J.J., 2006b. Threshold relations in subsurface stormflow: 1. A 147-storm analysis of the Panola hillslope. Water Resour. Res. 42. https://doi.org/10.1029/2004WR003778 n/a-n/a.
- Uthes, S., Matzdorf, B., Müller, K., Kaechele, H., 2010. Spatial targeting of agrienvironmental measures: cost-effectiveness and distributional consequences. Environ. Manag. 46, 494–509. https://doi.org/10.1007/s00267-010-9518-y.
- Vilhelmsen, T.N., Auken, E., Christiansen, A.V., Barfod, A.S., Marker, P.A., Bauer-Gottwein, P., 2019. Combining clustering methods with MPS to estimate structural uncertainty for hydrological models. Front. Earth Sci. 7, 1–15. https://doi.org/10.3389/feart.2019.00181.
- Ward, M., Jones, R., Brender, J., de Kok, T., Weyer, P., Nolan, B., Villanueva, C., van Breda, S., 2018. Drinking water nitrate and human health: an updated review. Int. J. Environ. Res. Public Health 15, 1557. https://doi.org/10.3390/ijerph15071557.
- 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? J. Hydrol. 343, 154–168. https://doi.org/10.1016/j. jhydrol.2007.06.010.
- Yang, X., Jomaa, S., Zink, M., Fleckenstein, J.H., Borchardt, D., Rode, M., 2018. 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.
- Yang, X., Jomaa, S., Rode, M., 2019. Sensitivity analysis of fully distributed parameterization reveals insights into heterogeneous catchment responses for water quality modeling. Water Resour. Res. 55, 10935–10953. https://doi.org/10.1029/2019WR025575.