Nitrogen-Loads to Streams: Importance of Bypass Flow and Nitrate Removal Processes

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Abstract N-loads from subsurface, drains, and groundwater-fed surface (bypass) flows via two riparian zones (crop field and wetland) to a second order stream were investigated by sampling of shallow and deep groundwater on both sides and monthly measurements of bypass flows from springs, drains, and stream including water quality (nitrate). A push-pull test in the crop field gave a first-order denitrification rate (0.23 day−1). Reactive transport modeling evaluated observations of water chemistry and denitrification processes in the groundwater below the crop field showing that nitrate was completely removed by denitrification with pyrite in the aquifer (model rates of 0.6–2.5 mmol NO3 L−1 yr−1). A drain in the crop field routed ~10% (bypass) of the regional groundwater inflow to the stream. Buffer efficiency was high at 90%. The wetland on the other side of the stream hosts several locations of nitrate-rich bypass flow from springs, predominantly through a non-maintained drainage system of drainpipes and ditches with bypass flow accounting for 59% of the regional flow input. Nitrate was completely removed in groundwater by denitrification with dissolved organic matter in shallow groundwater. The regional inflow and N load to the wetland is amongst the highest recorded and data shows that the N load to the stream is very high. The buffer efficiency ranged from 45% to 83% depending on if all bypass flows contributed to the stream or only the two with visible outflow. A conceptual model for nitrate removal efficiency as a function of Damköhler number and percent bypass flow is proposed.

Plain Language Summary Riparian zones connect agricultural catchments to streams and are important for intercepting and removing nitrate. The effects of bypass flow due to overland flow from natural springs, seeps or through drainpipes are often overlooked. We developed a generic conceptual model for riparian buffer efficiency (ratio of how much nitrate is removed relative to the input) based on detailed field investigations in two contrasting riparian zones (crop field and wetland). One would think that the crop field would be the main source of nitrate to the stream, but it is not. Input of water and nitrate to the stream was much higher on the wetland side, where nitrate-containing groundwater was funneled through the small wetland. The inflow of water was so high that numerous small natural springs and seeps were present and, historically, a network of ditches and drainage pipes were installed to keep the wetland relatively dry. Bypass flow is high (59%) and data shows some of the highest recorded nitrate loads to a stream. Complete removal of nitrate in groundwater flowing through both riparian zones was observed. Buffer efficiency is high with 90% on the crop side and 45%–83% on the wetland side.

1. Introduction

Nutrients applied in connection with agriculture may enter the groundwater and ultimately end up in streams. Riparian lowlands have shown to hold the potential to significantly decrease nitrate (NO3−) concentrations in groundwater flowing from uplands to streams (Hill, 2018, 2019; Peterjohn & Correll, 1984; Sabater et al., 2003; Vidon & Hill, 2005). Restoration of wetlands can therefore be an important mitigation method for increasing NO3 removal (Audet et al., 2020). Denitrification has been demonstrated to be the main removal process of NO3 in riparian aquifers (Hill, 2018, 2019), although additional processes such as plant uptake can be more important than denitrification (Lutz et al., 2020). Denitrification can occur with organic matter as an electron donor (heterotrophic denitrification), but can also occur with inorganic sources via the oxidation of ferrous iron (Fe2+) and reduced sulfur (S; autotrophic denitrification) (Korom, 1992).
Hydrological flow paths and nitrate transport through the riparian lowland are controlled by the inherent heterogeneity, which to a large degree also controls the N-removal efficiency and the occurrence of so called “hot spots” (McClain et al., 2003) for denitrification (e.g., Devito et al., 2000). Typologies and conceptual classification systems for upland hydrological connectivity and deep, shallow or bypassing flow paths have been proposed based on field studies to characterize groundwater-stream interaction and potential N-removal in riparian lowlands (Dahl et al., 2007; Hill, 1996; Jencso et al., 2009; Noij et al., 2012; Vidon & Hill, 2004).

Hydrologic connectivity (e.g., subsurface flow, groundwater-fed surface flow, drainage) across the riparian lowland influences not only the N-transporting flow paths, but also the soil moisture conditions and redox potentials within N-removal zones of the lowland, which in turn may affect the NO$_3$ buffering efficiency of riparian lowlands (Burt, Pinay, et al., 2002; Puckett & Hughes, 2005). In this study, we focus on gaining streams and not streams or rivers that infiltrate to groundwater (see e.g., Lutz, 2020). The magnitude and variance of the upland groundwater- and solute fluxes fed to riparian lowlands are controlled by size- and transmissivity of upland aquifers (Vidon & Hill, 2004). Large and thick regional aquifers provide riparian lowlands with a relatively steady input of groundwater (Hill, 1996). The groundwater loading to a lowland is sometimes referred to as the hydraulic loading by which the riparian zone-to-catchment area ratio becomes important (Audet et al., 2020; Petersen et al., 2020). With deeper aquifers, studies have shown that observed decreases in NO$_3$ concentrations across riparian zones may be due to dilution, instead of removal by denitrification, as mixing of young, shallow nitrate-rich groundwater with older, deeper nitrate-free groundwater can occur (Hefting et al., 2006; Puckett, 2004; Puckett & Cowdery, 2002).

Bypass flow is here defined as the fraction of regional flow reaching a stream via groundwater-fed-surface or drain flow. This is opposite to the definition in for example, Flewelling et al. (2012), where bypass flow is the direct seepage of groundwater and nitrate through the streambed. Likewise, riparian lowland hydrogeology may allow bypassing of nitrate-rich groundwater rather than diffuse flow through the riparian aquifer, which in turn affects nitrate removal efficiency (Burt, Matchett, et al., 1999; Puckett, 2004). Generally, a thick and permeable riparian aquifer (high transmissivity) allows the flow of regional groundwater of varying ages to flow below the nitrate reducing zones near organic-rich top layers (Devito et al., 2000; Hill, 1996; Puckett & Hughes, 2005). In shallow riparian aquifers, the fraction of diffuse subsurface flow may decrease depending on how much bypass flow is generated. This is also observed for low-permeable riparian aquifers, which favor the creation of seeps, springs, and outflow through macropores at the break in slope generating surface flow. As a result rivulets may be formed, discharging directly to the stream as bypass flow or re-infiltrate to the riparian aquifer (Böhlke, O’Connell, & Prestegaard, 2007; Brüschr & Nilsson, 1993; Shabaga & Hill, 2010).

Artificial drainage of riparian lowlands to make them usable for agricultural production is common in agricultural lowland catchments and can potentially increase bypassing of nitrate-rich groundwater (Fenelon & Moore, 1998; Puckett, 2004). Ditches and subsurface drains provide conduits for water to move rapidly through the riparian system, minimizing the riparian lowlands potential nutrient attenuation. Hence, manipulation of the hydrologic flow regimes alters the physical character of riparian systems by routing water directly from the hillslope to the stream, bypassing the denitrifying zones within the entire riparian lowland, and this accordingly becomes manifested in the water quality of adjacent streams.

Few studies have evaluated the combined influence of natural groundwater seeps, springs, macropores, and drainage on how N-loads in riparian lowlands partitions between direct groundwater discharge and bypass flow to the stream. For example, Audet et al. (2020) surveyed more than 20 restored wetlands in Denmark, but only measured surface inlets and outlets, and not groundwater. Petersen et al. (2020) measured and/or estimated all flow paths (subsurface, drains, surface) in riparian lowlands of clayey till catchments. Not surprisingly for this type of geological environment, groundwater fluxes to and from the lowlands were much smaller than drain fluxes. Fenelon and Moore (1998) found in a similar environmental setting that all nitrate essentially was contributed by drain outflow, as groundwater was essentially devoid of nitrate. Böhlke, O’Connell, and Prestegaard (2007) measured discharge from 27 macropores and found these to contribute with ca. a third of total stream discharge and more than half of the loading of nitrate to the stream during high base flow. Shabaga and Hill (2010) demonstrated how upwell groundwater was transported hundreds of meters along rivulet-pipe networks in the upslope parts of their field sites, with
little nitrate removal, converging into diffusive flow and increased nitrate removal in the downslope parts. The rivulet-pipe networks are shallow natural macropore systems that provided conduits for water and solutes across the riparian zones acting similar to a drain system. Clausen et al. (1993) measured nitrate fluxes in precipitation, overland flow, soil solution, groundwater and stream flow in a riparian area and found that the majority of the N flux took place via groundwater, but with little retention by for example denitrification. The importance of groundwater-fed surface flow bypassing (by natural or anthropogenic causes) riparian N removal zones on the delivery of nitrate to streams is therefore still not fully understood.

The aim of the present study is; (1) to examine how bypass flow and direct groundwater discharge affect nitrate delivery to a second-order channelized stream located in western Denmark and (2) to develop a simple model for nitrate removal efficiency as a function of two important parameters; the Damköhler number and the percent bypass flow. The Damköhler number expresses the ratio of transport to reaction time scales. Percent bypass flow is the sum of all water not diffusively flowing through the riparian aquifer to the stream, that is, flow in drains and all groundwater-fed surface flows (rivulets, diffuse surface flow). It is a comparative study examining flow and water quality of two riparian zones on opposite sides of the stream. On the northeast side, the riparian zone comprises a crop field flanked by a buffer zone and with a small watershed. On the southwest side, the riparian zone is a wetland receiving groundwater inflow from a much larger watershed resulting in many seeps and which has a poorly functioning drainage system. Nitrate loadings from different flow paths to the stream and their impact on stream water quality are examined. Further, mechanisms responsible for removal of nutrients are studied using water quality data, a push-pull test, and geochemical modeling. We believe the field site to be characteristic to many other lowland riparian valleys and that the results therefore are applicable to many other areas.

2. Study Site

The study was conducted in a riparian lowland situated in the upper part of Holtum catchment in the central part of Jutland, Denmark (Steiness et al., 2019). Holtum stream is characterized as a perennial second-order stream flowing from east to west. The surficial aquifer mainly consists of late Weichselian sandy outwash deposits and clayey tills, underlain by Miocene deposits of clay and sand. The shallow aquifer is partially unconfined/confined. Land use is dominantly agriculture (54%), forest (32%), and urban (14%) areas (Karan et al., 2013). Danish national soil maps classifies the lowland area hosting the field site as pyrite containing, and as containing 6%–>12% org. carbon. The mean annual precipitation and actual evapotranspiration in the catchment were estimated to 984 and 510 mm/yr, respectively (Sebok et al., 2016).

The 3-m wide stream at the field site was channelized likely prior to the 1850s. The average discharge at the field site in 2017 was ∼26,000 m$^3$/day (Steiness et al., 2019). On the northeastern side (the crop side), the riparian lowland comprises a 35-m-wide grass buffer zone between the stream bank and a 145-m-wide agricultural crop field (Figures 1a and 1b). The area is ∼2.3 ha. A drainage-pipe (DR) discharges shallow groundwater from a small surface depression in the agricultural field directly into the stream. Average drain pipe discharge in 2017 was ∼28 m$^3$/day (∼20 L/min, Steiness et al., 2019).

The southwestern side (the wetland side) is an 80-m-wide wetland functioning as a cow pasture. In the wetland (∼1.3 ha), six overland discharge systems are located; two springs (S1 and S2), an overflowing drainage well (DW), an overflow pipe from a pond (PO), a ditch (DI) and a small rivulet (RI). Figure 1b (from now on collectively termed bypass flow). The DI and RI discharge directly to the stream. A submerged drain in the stream is also located at the bend of the stream to the southeast (Figure 1b). Several ditches (D1–D3) also drain the wetland downstream of the study site, Figure 1a. Most of the surface water systems were likely installed to drain the wetland. However, whether S1 and S2 are man-made installations (e.g., broken drain pipes that generate overland flow) or natural sources of bypass flow is not clear. Artesian conditions generating a natural diffuse seepage in the hill slope area above the pond were observed. Steiness et al. (2019) found that the average bypass flow was 233 m$^3$/day. Direct groundwater discharge through the streambed was 13 times less.

The riparian lowland comprises a sandy aquifer with interbedded gravel lenses. The aquifer is unconfined on the crop side of the stream, whereas the aquifer under the wetland is partially confined by a peat layer. The hydraulic conductivity of the riparian sandy aquifer ranges from 0.1 to 50 m day$^{-1}$ with an average of
Groundwater is flowing to the stream from both the crop and wetland sides (Figure 1c). The immediate upland northeast of the crop site is covered by a coniferous forest extending to the topographical border of the catchment. The topographical catchment area is \( \sim 5 \text{ ha} \) (based on a GIS analysis). The upland to the south and southwest of the wetland site is comprised mainly of arable land, with minor forested areas primarily on the hillslopes. The topographical catchment area of \( \sim 25 \text{ ha} \) (based on

**Figure 1.** Field site in Holtum catchment in the central part of Jutland, Denmark (UTM zone 32, N 520513 m E, 6204065 m). (a) Northeast of the stream, a 35-m wide grass-buffer separates the stream and the crop field. Southwest of the stream, a wetland extends to the hillslope. Several ditches are connected to the stream downstream of the field site (D1, D2, and D3). (b) In the riparian wetland six "springs" are located (DI, DW, PO, RI, S1, and S2) representing bypass flow paths. A submerged drain is located in the bend of the stream. In addition, a drain (DR) is located under the crop field. (c) Cross-section showing the geology of the riparian aquifer and groundwater flow directions. Groundwater flows diffusively through the aquifer toward the stream (Steiness et al., 2019). However, notice the small water mound at well TH1. A national monitoring well (DGU 96.1981) is shown with average nitrate concentrations (1990–2018) at two screens (see also Appendix A).

14 m day\(^{-1}\) (Steiness et al., 2019). Groundwater is flowing to the stream from both the crop and wetland sides (Figure 1c).

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a GIS analysis) is 5 times larger than north of the stream. The crop field/wetland to upland area ratios are therefore 47% and 5%, respectively. The wetland receives groundwater from a glaciofluvial sand aquifer, monitored by annual sampling of national monitoring well DGU 96.1981 positioned 2 km upgradient the wetland (Figure 1c). The well has two screens and average concentrations since 1990 are 66 µM DO (2.1 mg O\(_2\)/L), 0.79 mM nitrate (49 mg/L), 0.51 mM sulfate (48.6 mg SO\(_4\)/L), 88 µM dissolved organic carbon (1.05 mg DOC/L) and has an alkalinity of 1.2 meq/L.

3. Materials and Methods

Instrumentation includes 23 piezometers (Figures 1a and 1b) screened at different depths, installed at different times from 2015 to early 2017 (Poulsen et al., 2015; Steiness et al., 2019). All piezometers are equipped with a 9 cm screen near the bottom. Eight piezometers shown in Figure 1 are nested, consisting of a shallow (piezometer name followed by an s) and a deep (piezometer name followed by a d) piezometer screen. These are TH1, TH2, TH3, TH4, TH7, TH9, C10, and C20. In water and solute mass balances, we assume that observations done in the instrumented transect (A-AA in Figure 1a) are representative for the neighboring area along the stream within the crop field.

3.1. Water Sampling and Analysis

Monthly water sampling was carried out between January 2017 and January 2018 from the bypass flows in the wetland, Holtum stream, and the drain (see Figures 1a and 1b; no samples were collected in July 2017). Piezometers were sampled on multiple occasions in the period from November 2015 up until October 2017. In addition, a campaign was conducted in June 2017 to sample the shallow groundwater underneath the peat layer in the wetland. Nineteen point-samples were collected using “mini” piezometers (Figure 1b) (Steiness et al., 2019). The mini-piezometers had an inner diameter of 0.5 cm and were equipped with a 5 cm long screen. They were hammered to the desired depth just below the peat layer. Sampling followed the same procedure as described below for the regular piezometers.

Samples from D1, D2, and D3 were collected in June 2017. The submerged drain was sampled at two separate occasions; in May 2017 and in January 2018. Several piezometers were sampled at multiple depths during installation: TH1d, TH2d, TH3, TH4, TH7d, and TH9d.

Water samples for major an- and cations (Cl, SO\(_4\), F, Br, NO\(_3\), NO\(_2\), PO\(_4\), NH\(_4\), Na, K, Ca, and Mg), sulfide (H\(_2\)S), reduced iron (Fe\(^2+\)), and alkalinity were collected from piezometers (groundwater), bypass flows, surface water (D1, D2, D3, and Holtum stream), the submerged drain, and from the drain on the crop side (DR).

Groundwater samples were collected using a peristaltic pump and a flow-cell (WTW Oxi 3310 IDS and HACH HQ30). Water sampling commenced, when flow-cell values of dissolved oxygen, temperature, pH, and electrical conductivity were stable. For sampling of bypass flows, surface, and drain water, the electrodes were immersed directly into the running water. Water samples were in all cases taken with 60 mL polyethylene syringes and immediately filtered in the field through a 0.20 µm cellulose acetate syringe filter (Sartorius Minisart®). To avoid oxygenation of Fe\(^2+\) during filtration (and consequent loss of PO\(_4\) and other ions adsorbing to Fe oxides) the syringe filter was vacuumized to remove oxygen. A vacuum was applied immediately prior to sample filtration using a combination of a dry 60 mL syringe and two three-way valves. Samples for cations were acidified with 1 vol% 1 M HNO\(_3\) and stored in a refrigerator. Anion samples were stored frozen. Anions and cations were analyzed by ion chromatography (Metrohm 820-IC Separation Center with 819-IC Detector). Samples for Fe\(^2+\) and H\(_2\)S analysis were collected in separate 3 mL vials prefilled with, respectively, 0.1 mL of ferrozine solution or 0.3 mL 10 wt% Zn acetate. The Fe\(^2+\) and H\(_2\)S concentrations were measured spectrophotometrically in the laboratory following the procedures by Stookey (1970) and Cline (1969), respectively. Samples for alkalinity (also filtered) were collected in 100 mL acid-washed amber glass bottles and analyzed using endpoint titration on a Metrohm autotitrator. Samples with an ionic imbalance greater than ±6% were excluded from the data analysis.
3.2. Pyrite Measurements

In September 2016, cores were extracted from under the crop field near piezometers TH32 and TH3.3, Figure 1b. Intact cores were collected from 0 to 1 and 1 to 2 m below surface (mbs) using percussion drilling combined with a 1 m liner sampler. The core ends were sealed with caps and additional tape and stored at −18°C to minimize oxidation until analysis.

Five subsamples of sediment with a sample spacing of 0.1 m from depths 1.6–2 mbs were freeze-dried, homogenized (ring-mill grounded) and analyzed. The chromium reducible sulfur (CRS) method was used to measure reduced inorganic sulfur compounds of the material sample following Canfield et al. (1986). The chromium reducible sulfur in this study is mainly presumed to stem from pyrite. From each subsample, 2 g of the dry and homogenized sediment was added to a mixed solution of chromium(II) and concentrated hydrochloric acid (6 M HCl) in an inert N₂ atmosphere. Throughout a 60 min boil, the liberated H₂S from the reduction process was precipitated as Ag₂S in a trap containing 0.5 mL 1 M AgNO₃. Precipitated Ag₂S was then isolated by filtration, washed, dried and weighed. Determination of the pyrite (FeS₂) content of the respective samples was calculated by converting the weight of the precipitate (Ag₂S) to moles sulfur.

3.3. Push-Pull Test: Denitrification Rate

The in situ first order rate constant k of NO₃ reduction underneath the crop field was measured using the single-well push-pull test method as described by Haggerty et al. (1998) and extended by Yang et al. (2007). The principle is to derive the rate constant from the change over time in the concentration of a reactive solute relative to a conservative solute tracer. Using a peristaltic pump, ∼15 L of groundwater from well TH32 was collected directly into a gas-tight aluminum bag, pre-flushed in the field by N₂-gas to remove oxygen. 60 mL of an anoxic NaNO₃ and NaBr stock solution was injected into the bag when half full (at ∼7.5 L) using a syringe. When full, the bag was carefully agitated to mix the solution inside it. The EC of the resulting mixed solution was measured to ∼700 µS/cm (twice the background EC of ∼350 µS/cm) and a sample was withdrawn to acquire the initial NO₃ and Br concentrations of 0.64 and 0.52 mM, respectively, before the peristaltic pump was reversed to inject the solution back into 3 m depth. Recovery was conducted 28 h later, during which EC was monitored; a total of 40 L water was withdrawn. During recovery, 10 water samples were collected covering a range of EC values, implying a range of initial NO₃ concentrations. This enabled multi-point determination of the rate constant after the 28 h reaction time and of its dependency on the initial NO₃ concentration.

The first-order rate constant k (positive for degradation) can be derived from (Haggerty et al., 1998; Yang et al., 2007; after rearrangement):

$$kt = \ln \left( \frac{C^r(t)}{C^r_{inj}(t)} \right) + \ln \left( \frac{1 - e^{-k t_{inj}}}{k t_{inj}} \right)$$

(1)

where t is the time elapsed since injection ended and t_{inj} is the duration of the injection itself. C^r_{inj}(t) and C^r(t) are the relative concentrations of, respectively, the tracer (k = 0) and the reactive solute (k ≠ 0), corrected for the respective background concentration (Yang et al., 2007):

$$C^r_{inj}(t) = C^r_{inj}(t) - C^b_{inj}$$

and

$$C^r(t) = C^r(t) - C^b$$

(2)

where C^b_{inj} and C^b are the injected (i.e., initial), and C^b and C^b the background, tracer and reactive solute concentrations, and C_r(t) and C_t(t) are the tracer and reactive solute concentrations of the samples taken during the test’s “pull” phase. The use of relative concentrations enables rate determinations that do not depend on the fraction of injected-to-recovered amounts. In Equation 1, the second term on the right-hand side corrects for the in situ reaction occurring during the test’s injection (“push”) phase. In our case the duration of the injection was short (t_{inj}<1 h) relative to the t = 28 h reaction time, which makes the right hand term in Equation 1 insignificant (cf., Haggerty et al., 1998). Equation 1 then becomes:
A first order rate constant $k$ (h^{-1}) for each of the 10 samples was calculated by applying Equation 3 with nitrate and bromide as the reactive and tracer solute, respectively; the average value is reported here. The reaction timescale ($\tau_{\text{react}}$) was subsequently calculated as (Ocampo et al., 2006):

$$\tau_{\text{react}} = \frac{1}{k}$$

The reaction timescale is comparable to the first-order reaction half-time $t_{1/2}$, as the two quantities are separated only by a factor of ln(2):

$$t_{1/2} = \ln(2)\tau_{\text{react}} = 0.693\tau_{\text{react}}$$

### 3.4. Reactive Transport Modeling

The hydrochemical modeling software PHREEQC (Parkhurst & Appelo, 2013) was used to simulate the loss of nitrate with depth, observed in the shallow part of the aquifer under the crop field. A one-dimensional (1D) reactive transport model with 10 cells with a 1 m cell length was defined (total 10 m depth). Assuming a vertical Darcy velocity of 0.5 m yr^{-1} (i.e., a 500 mm yr^{-1} recharge rate, Sebok et al., 2016) and a porosity of 0.3, the residence time of water in one cell (i.e., the time step) was set to 0.6 yr (1.9 × 10^7 sec). A dispersivity of 0.1 m and an effective diffusion coefficient of 0.3 × 10^{-9} m^2 sec^{-1} were applied. For all cells (i.e., all depths), equilibrium with goethite and gibbsite was defined, and pyrite and siderite were allowed to precipitate without being present from the start. The database phreeqc.dat was used. The model was run for 50 shifts, corresponding to five flushes of the complete 10-cell model, which ensured stationarity.

The model was calibrated by trial-and-error against observations from the multilevel profiles of TH3, that is, including its sister-piezometers TH32 and TH33. During calibration, the nitrate, oxygen and Fe^{2+} concentrations of the recharging solution were adjusted, and amounts of organic carbon (CH_2O) and pyrite were added to cells 1 to 5, individually, and allowed to react. Also, the goethite stability (i.e., its equilibrium constant) was adjusted (same value used for all 10 cells). For the infiltrating solution, representative values of sulfate (0.2 mM), pH (5.7), and alkalinity (0.6 meq/L) were fixed.

Reacted amounts (of organic carbon or pyrite) ascribed to each cell of 1 m during fitting were entered in units of mM and subsequently recalculated into rates in units of mM yr^{-1} by dividing by the 0.6 yr residence time in the cell.

### 4. Results

#### 4.1. Hydrology

Details about the riparian zone hydrogeology and hydrology can be found in Steiness et al. (2019). Precipitation was 928 mm in 2017%, 11% higher than recorded precipitation at a nearby station (833 mm, 2012–2014, Müller et al., 2017). The wetland is composed of an ~1 m thick peat layer on top of a sandy 15–30 m riparian aquifer (Figure 1c). A 20–30 m sandy unit was also found below the crop field (Figure 1c). An analytical model was used to investigate the connection between the regional groundwater input of 1955 L m^{-1} day^{-1} (using the average K of 14 m/day) and the wetland hydrology (Appendix A). If K was 5 or 30 m/day, the input decreased or increased by 22% and 38%, respectively. Steiness et al. (2019) reported a stream flow gain of 2,130 L m^{-1} day^{-1} in 2017 as a result of the mean total water flux from the wetland. Stream flow gain was measured on a monthly basis and time series of discharge would have given a more accurate estimate of stream flow gain. There is a reasonable agreement (within 9%) of the two water fluxes. Hill (2019) reported values of subsurface water fluxes to riparian buffers from several studies. For sloping landscapes with sandy sediments, water fluxes ranged up to 1,200 L m^{-1} day^{-1}. The calculated water flux (1,955 L m^{-1} day^{-1}), and even the flux with a lower K value, is very high explaining why it is a wetland, the need for drainage, and still...
with the occurrence of many natural bypass flows. The high input of water from the upland damped seasonal changes in hydraulic heads in most piezometers on the wetland side (seasonal change of 0.16–0.18 m). Bypass flow via direct run-off to the stream was significant contributing with 59% to stream flow gain (Steiness et al., 2019). Discharge varied amongst the different bypass flows, but were all relatively stable in 2017 (see also Figure 5b). Direct discharge through the streambed and northeastern and southeastern stream banks were 4% and 17% (base flow) of stream flow gain, respectively. The free drain from the crop field contributed with 7% of stream flow. The residual (13%) could be unmeasured bypass flow and unknown flow from the submerged drain in the wetland. Bypass flows could thus account for roughly 60%–70% of the water budget. The high bypass flow fraction is reflected in the water stable isotope composition of stream water (Table 1). Groundwater sampled by the piezometer network gave an average δ^18O of −7.79‰ close to the medians of precipitation, bypass flow and stream flow (Table 1). If only base flow, typically old groundwater, contributed to stream flow, then the seasonality of δ^18O in precipitation (σ = 1.4) would be nearly muted in stream water (σ ~ 0). This is not the case, stream water δ^18O still displays a seasonality (σ = 0.24), because bypass flow from the wetland (and upstream locations) discharges young water with a memory of precipitation and a seasonality of σ = 0.19. The source of this younger water can be recent infiltrated rainwater just upstream the hillslope and direct rainfall on the wetland. The δ^18O signal in shallow groundwater indicated that there were zones of re-infiltration of bypass flow. Geological heterogeneity (e.g., variable thickness and permeability of the peat layer) can affect the distribution of flow paths. Base flow with older groundwater accounted for ~21%, but hydraulic head data from the piezometer network is not detailed enough to indicate if there are preferential flow paths in the subsurface. In summary, the hydrology of the site is therefore very stable due to the high input of regional groundwater (Hill, 1996).

4.2. Water Chemistry
Table 2 and Figures 2–4 give a summary of the main results of the major water chemistry in deep and shallow groundwater, bypass flows, and the stream. EC in groundwater is on average higher on the wetland side. The bypass flows also had a higher EC than in drainage from the crop field. Groundwater was anoxic (DO < 0.5 mg/L) except for shallow groundwater in the crop field (<2 mbs) and wetland, and frequently contained micromolar concentrations of sulphide (median 1.7 µM), indicating sulfate reduction. A plume of DO extended roughly halfway into the wetland (Figures 2a and 3a). For example, groundwater from TH10 had DO concentrations 1.4–2.12 mg/L. Reduced iron (Fe^{2+}) or ferrous conditions were found in the area between the DO plume and the stream (Figure 2a). At the crop side, nitrate was found to depths of 6 mbs with maximum concentration of 1.25 mM (78 mg/L) near wells TH3, TH32, and TH33 (Figure 2b). Only traces of nitrate were found in deeper samples in wells TH1 (at the border to the buffer zone) and TH2 (in the buffer zone). On the wetland side, nitrate concentrations in groundwater were lower with the highest concentrations in shallow groundwater near the hillslope (Figure 2b). A small plume of nitrate extended ~50 m into the wetland (Figure 3c). Groundwater at piezometer ST1 (screened 1.5 m below the streambed just upstream of the ditch, Figure 1b), TH6 and TH8 (located ~1 and 1.5 m from the stream banks, respectively) contained no nitrate.

Concentrations of SO4 were higher in groundwater at the crop side indicating that nitrate could be reduced by, for example, pyrite. TH1 and TH2 located in the buffer zone indicated the presence of a SO4 plume moving toward the stream (Figure 2b). On the other hand, alkalinity was higher on the wetland side indicating organic matter oxidation, e.g., denitrification and/or sulfate reduction (Figure 3b). All waters were subsaturated for calcite. A negative correlation between sulfate and sulfide (R^2 = 0.23) was observed across all samples collected on the wetland side, indicating quantitatively important sulfate reduction beneath the peat. Alongside, elevated ferrous iron concentrations persisted beneath the peat suggesting reductive iron release.

The bypass flows showed relatively stable high nitrate concentrations with a slight seasonality (Figure 4). Concentrations were higher in bypass flows than groundwater and it appears that these are tapping zones of shallow groundwater with higher concentrations. Drainage from the crop field and the submerged drain (only two samples) on the wetland side had on average a nitrate concentration of 0.25 and 0.52 mM, respectively.
4.3. Nitrate Loads to Stream

Monthly NO\textsubscript{3} loads to the stream from bypass flows (Figure 5a) were calculated from the measured bypass flow concentrations (Figure 4) and measured flow rates (Figure 5b). Overall, the bypass flows sustain a constant high N-input to the wetland surface and possibly to the stream. The highest nitrate loadings (kg N day\textsuperscript{−1}) were from S1 and RI mainly because the highest discharges were measured here (averaging 81 m\textsuperscript{3}day\textsuperscript{−1} and 58 m\textsuperscript{3}day\textsuperscript{−1}, respectively). Despite the similar nitrate concentrations at S2, S1, and RI, the lowest nitrate loading was from S2, due to a low discharge (average of 10 m\textsuperscript{3}day\textsuperscript{−1}).

The combined average N-load from all bypass flows was 708 kg N yr\textsuperscript{−1}. From DI and RI, both visibly discharging directly into the stream, the N-load was 219 kg N yr\textsuperscript{−1}. On the crop side of the stream an annual N-load to the stream from the drain, discharging directly into the stream, was 16.8 kg N yr\textsuperscript{−1}. The N-load from bypass flows was around 13 to 42 times higher than the N-load from the drain in the crop field.

| Table 1  | Statistics of δ\textsuperscript{18}O in Precipitation, Bypass Flow, and Stream |
|----------|--------------------------------------------------------------------------------|
| Precipitation | Median $\sigma$  |
|           | $-7.69$  | $1.4$  |
| All bypass flows | $-7.71$  | $0.19$  |
| Stream   | $-7.94$  | $0.24$  |

Note. Precipitation data is from a nearby climate station (Voulund 2012–2014, UTM-E: 510000, UTM-N: 621000, Table 1 in Müller et al., 2017). Median values in ‰. $\sigma$ is standard deviation.

| Table 2  | Summary of Water Chemistry With Mean (Top), Minimum (Middle), and Maximum (Bottom) Concentrations |
|----------|------------------------------------------------------------------------------------------------|
|          | EC (\mu S/cm) | $O_2$ (mg/L) | NO\textsubscript{3} (mM) | SO\textsubscript{4} (mM) | Fe$^{2+}$ (10\textsuperscript{−2} mM) | Alk. (meq/L) |
| Crop field |                                                                 |
| Deep GW\textsuperscript{1} | Mean 288 | 0.21 | 0.08 | 0.44 | 6.2 | 1.11 |
|            | Min. 179 | 0.03 | 0 | 0 | 0.7 | 0.1 |
|            | Max. 400 | 0.7 | 1.25 | 1.25 | 10.1 | 2.4 |
| Free drain | Mean 317 | 8.7 | 0.11 | 0.22 | 1.8 | 1.21 |
|            | Min. 253 | 7.5 | 0.06 | 0.12 | 0 | 0.99 |
|            | Max. 361 | 10.1 | 0.2 | 0.38 | 9.3 | 1.4 |
| Wetland   |                                                                 |
| Deep GW\textsuperscript{2} | Mean 355 | 0.33 | 0.02 | 0.02 | 9.4 | 1.57 |
|            | Min. 205 | 0.02 | 0 | 0 | 0.1 | 0.4 |
|            | Max. 583 | 2.12 | 0.35 | 0.35 | 32.6 | 3.3 |
| Shallow GW\textsuperscript{3} | Mean 411 | 1.02 | 0.1 | 0.26 | 6.0 | 1.23 |
|            | Min. 157 | 0.11 | 0 | 0 | 0 | 0.36 |
|            | Max. 696 | 6.4 | 0.93 | 0.75 | 16 | 2.22 |
| Springs   | Mean 439 | 8.3 | 0.60 | 0.25 | 0.17 | 1.01 |
|            | Min. 331 | 5.6 | 0.14 | 0.1 | 0 | 0.38 |
|            | Max. 575 | 12.5 | 0.97 | 0.34 | 2.5 | 2.24 |
| Submerged drain | Mean 509 | 7.35 | 0.52 | 0.43 | 0.8 | 2.61 |
|            | Min. 498 | 6.52 | 0.51 | 0.42 | 0.8 | 2.55 |
|            | Max. 520 | 8.18 | 0.52 | 0.44 | 0.9 | 2.66 |
| Stream    | Mean 300 | 8.7 | 0.10 | 0.28 | 0.36 | 1.30 |
|            | Min. 262 | 7.7 | 0.05 | 0.14 | 0.02 | 1.07 |
|            | Max. 338 | 9.8 | 0.18 | 0.36 | 0.36 | 1.44 |

Note. Springs, stream and free drain from crop field were measured on a monthly basis from January 2017 to January 2018 (except July 2017, $n = 12$). The submerged drain on the wetland side was measured May 2017 and January 2018. Deep groundwater (GW) was sampled November 2015 up until October 2017. Shallow groundwater on the wetland side was measured once (June 2017, $n = 19$). All data are accessible from the Harvard dataverse via https://doi.org/10.7910/DVN/FJUXOV.
Samples collected in June 2017 from three ditches (D1, D2, and D3; Figure 1) downstream of the field site also showed high NO\textsubscript{3} concentrations. D1, D2, and D3 had 0.86, 0.99, and 0.38 mM of NO\textsubscript{3} respectively.

4.4. Pyrite Extraction

The core from 1.6 to 2.9 mbs was used for analysis of FeS\textsubscript{2}. The sediment consisted of well-sorted sand with few pebbles. In the shallowest sample at 1.6 mbs, pyrite was not detected. Samples from 1.7, 1.8, 1.9, and 2.0 mbs contained, respectively, 1.5, 1.8, 2.0, and 1.9 mmol pyrite kg\textsuperscript{-1} dry sediment. The depth interval from 2.1 to 2.9 mbs was represented by a single mixed sediment sample; this sample had a pyrite content of 3.0 mmol kg\textsuperscript{-1} dry sediment.

4.5. Nitrate Retention Under the Agricultural Field

A push-pull test was conducted on September 13–14, 2016 at 3 m depth, within the anoxic zone, in well TH32. During installation of the well, the day before the push-pull test, the NO\textsubscript{3} concentration decreased...
with depth from 0.8 mM at 1.6 m depth to 0.08 mM at the 3 m test depth (i.e., background nitrate concentration), implying denitrification at the 3 m test depth; the background Br concentration at 3 m depth was 5.3 µM. The multilevel profile of TH33 was obtained on September 14, 2016 and showed NO$_3^-$ concentrations of 0.88, 0.55, 0.51, and 0.04 mM in 1.5, 2, 3, and 4 mbs, respectively. In February 2016, a few meters from TH32, the NO$_3^-$ concentration likewise decreased from 1.2 mM at 1.9 m depth to 0.6 mM at 3.2 m depth, and was below the detection limit at 4.2 m depth. Application of Equation 3 returned first-order rate constants ($k$) for nitrate reduction ranging from 1.5 $\times$ $10^{-2}$ to 0.68 day$^{-1}$ (average 0.23 day$^{-1}$), corresponding to reaction timescales ($\tau_{\text{react}}$) of ca. 1–66 days with a mean of 4 days. At the slowest of these rate estimates ($k = 1.5 \times 10^{-2}$ day$^{-1}$) just $\sim$1% of an initial concentration would be present after about 300 days.

### 4.6. Reactive Transport Modeling

Figure 6 shows the results of the reactive transport model (solid lines) and the observed chemical components from piezometers TH3, TH32, and TH33 (scatter points) located at the crop field. The observations showed that the most shallow samples of TH3, $\sim$1.5–2 mbs or $\sim$0.5–1 m below the groundwater table, contained up to 1.25 mM nitrate, but was anoxic (<0.25 mg O$_2$ L$^{-1}$) and ferrous (>0.4 mg Fe$^{2+}$ L$^{-1}$). Just an additional 0.5–1 m deeper in the profile nitrate concentrations generally declined to below detection limit (Figure 6b). This suggests ongoing denitrification, which necessitated an even higher nitrate concentration in the recharge at the groundwater table. Accordingly, for the infiltrating solution in the model, a higher
A nitrate concentration of 2 mM was applied, together with an O\textsubscript{2} concentration of 0.3 mM (corresponding to saturation), and an Fe\textsuperscript{2+} concentration of zero.

Overall, the fit of the model results with the observed was satisfactory (Figure 6). The water table at TH3 (i.e., in Figure 6) was at 1 mbs. In the model, oxygen is depleted within the first 0.5 m below the water table (i.e., above 1.5 mbs) by reaction with organic carbon. This corresponds to an organic carbon reduction rate of 1.2 mmol C L\textsuperscript{−1} yr\textsuperscript{−1} in the most surficial part of the aquifer, where pyrite was not detected (cf., above). Deeper, where pyrite was detected, the model suggests NO\textsubscript{3} reduction exclusively by pyrite, with average nitrate reduction rates of 2.5 mmol NO\textsubscript{3} L\textsuperscript{−1} yr\textsuperscript{−1} between 1.5 and 2.5 mbs, decreasing to 0.6 mmol NO\textsubscript{3} L\textsuperscript{−1} yr\textsuperscript{−1} between 2.5 and 3.5 mbs, where nitrate becomes depleted. The corresponding rates of pyrite oxidation are 0.9 and 0.2 mmol FeS\textsubscript{2} L\textsuperscript{−1} yr\textsuperscript{−1}, respectively. Between 1.5 and 2.5 mbs, the reaction is a complete oxidation of pyrite followed by goethite precipitation:

\[
5\text{FeS}_2 + 15\text{NO}_3^- + 5\text{H}_2\text{O} \rightarrow 5\text{FeOOH} + 10\text{SO}_4^{2-} + \frac{15}{2}\text{N}_2 + 5\text{H}^+ \\
\text{(R1)}
\]

Consistent with this reaction, concentrations of SO\textsubscript{4} increased and decreases in pH and alkalinity were observed, while, generally no or little concurrent release of ferrous iron occurred (Figures 6c–6f). Between 2.5 and 3.5 mbs the modeled denitrification occurred by incomplete pyrite oxidation:

\[
5\text{FeS}_2 + 14\text{NO}_3^- + 4\text{H}^+ \rightarrow 5\text{Fe}^{2+} + 10\text{SO}_4^{2-} + 7\text{N}_2 + 2\text{H}_2\text{O} \\
\text{(R2)}
\]

Contrary to Reaction 1, Reaction 2 releases Fe\textsuperscript{2+} and consumes protons, which is consistent with observed increases in ferrous iron and pH over this depth interval.

Below 3.5 mbs, the model results suggested concurrent reduction of sulfate and iron oxides by organic carbon oxidation followed by precipitation of pyrite (not shown in Figure 6). Here, the ferrous iron removed from solution by pyrite precipitation is replaced by iron released by iron oxide reduction, according to the overall reaction:

- Figure 4. Nitrate concentration measured on a monthly basis from bypass flows (drain is at the crop field) and stream.
Figure 5. (a) Nitrate loads calculated from concentrations and discharges measured on a monthly basis from (b) bypass flows and flow from the drain (DR).

Figure 6. Measured (points) and modeled (lines) water chemistry in the aquifer below the crop field. The water table is at 1 mbs. Reactive transport modeling was conducted using PHREEQC-3.
15CH₂O + 8SO₄²⁻ + 4FeOOH + H⁺ → 4FeS₂ + 15HCO₃⁻ + 10H₂O  \hspace{2cm} (R3)

This reaction is consistent with the observed removal of SO₄ from solution, increased alkalinity and pH and invariable ferrous iron concentration below 3.5 mbs (Figures 6c–6f). Concurrent sulfate and iron oxide reduction (i.e., Reaction 3) is feasible for iron oxides that are slightly less stable than goethite (Appelo & Postma, 2005). In line with this, the fitted saturation index of −0.4 for goethite in the model was slightly negative. The simulated rate of organic carbon oxidation between 3.5 and 4.5 mbs was 4.8 mmol C L⁻¹ yr⁻¹, dropping to 0.3 mmol C L⁻¹ yr⁻¹ from 4.5 to 5.5 mbs. In summary, the reactive transport modeling substantiated that water chemistry observations underneath the crop field are quantitatively consistent with, predominantly, denitrification by pyrite. The observations from TH3, TH32, and TH33 included in Figure 6 represent the deepest occurrences of nitrate found underneath the crop field; all other piezometers indicate denitrification at shallower depths. Sulfate appears to penetrate to greater depths elsewhere under the crop field (cf., Figure 2b), indicating some spatial heterogeneity in the riparian aquifer’s redox conditions, although all observations support persistent anoxic and ferrous conditions below a few meters depth, and hence the thermodynamic feasibility of denitrification.

5. Discussion

5.1. Nitrate Distribution and Removal Processes in Shallow Groundwater

Nitrate infiltrating to groundwater underneath the crop field was effectively removed before reaching the stream. Reactive transport modeling suggests that denitrification of 2 mM nitrate occurred by autotrophic denitrification with pyrite (which was found to be present; Section 4.4) in the top 2 m below the groundwater table (Figure 6), corresponding to a simulated 1.2 year travel time. The in situ rate measurement (push-pull) and the reactive transport model thus agree in suggesting complete reduction of a few mM nitrate within about a year. Production of SO₄ results in a plume of elevated SO₄ concentrations at 3–8 mbs in the aquifer under the crop field (Figure 2b), as a legacy of denitrification by pyrite (Jessen et al., 2017). At a field site 50 km north of the Holtum field site, Postma et al. (1991) reported average sediment FeS₂ concentrations of 3.6 mmol kg⁻¹, that is, similar to the concentrations of 1.5–3.0 mmol kg⁻¹ at our site. In addition, Postma et al. (1991) found FeS₂ to be the main electron donor for O₂ and NO₃ reduction in the aquifer. Böhlke, Wanty, et al. (2002) also reported denitrification coupled with reduced ferrous and sulfur compounds, including FeS₂. Both studies were conducted within sandy outwash aquifers similar to our site. Such sediment FeS₂ concentrations are likely sufficient for sustaining denitrification for many decades (cf., Jessen et al., 2017). Nitrate discharge to the stream via groundwater from the crop side could therefore continue to be low for many years. Recall, however, that a drain on the crop side gives a load of 16.8 kg N yr⁻¹ to the stream (Figure 5). The reactive transport model (Figure 6) suggests that denitrification is followed by pyrite precipitation in some places (e.g., the location of TH3), as SO₄ and iron oxides react with organic matter. Buried organic carbon in the stream valley can originate from, e.g., an old stream meander (Devito et al., 2000).

Sulfidic and ferrous groundwaters underneath the wetland are strongly indicative of reducing conditions, under which denitrification is thermodynamically feasible. Because the groundwater entering from the regional aquifer south-west of the field site is oxic and not sulfidic, and has a low DOC content, the driver for the reducing conditions at the wetland is most likely sedimentary organic carbon within the riparian aquifer (i.e., sulfate reduction requires an electron donor). Water-logged conditions at the wetland prevent pyrite oxidation by gaseous oxygen as a plausible source of sulfate. Rather, sulfate in the wetland groundwater could be a legacy of denitrification with reduced inorganic sulfur compounds in the hinterland, or the sulfate could originate from oxidation by groundwater-borne (residual) oxygen or nitrate of pyrite within or underneath the wetland’s peat. Another potential electron donor for denitrification is the organic carbon or DOC derived from peat degradation.

Jensen et al. (2017) found that DOC leaching from a surface peat layer caused denitrification 1–2 m below the peat layer. Conditions for a similar process at our site appears plausible. No nitrate was found near the stream in ST1 1.5 m below the streambed and TH6 and TH8 1 and 1.5 m from the stream banks, respectively, indicating effective denitrification (by pyrite ad/or sedimentary dissolved organic carbon) along subsurface

...
flow paths to the stream. However, even if nitrate reached the streambed, denitrification could effectively remove nitrate (Flewelling et al., 2012). At an even more downstream site, Karan et al. (2013) found high nitrate concentrations below a peat layer and within the top five meters of a sandy aquifer across an entire riparian wetland. The wetland was less dominated by bypass flows and most of the regional flow input to the wetland and the stream was via the conductive sandy aquifer with persistent aerobic conditions and, hence, limited nitrate reduction potential.

Table 3 lists first-order denitrification rates (starting with maximum rate) at other locations for different types of electron acceptors (pyrite, organic matter, or unknown). The rates were estimated based on in situ or laboratory experiments (centimeter to meter-scale, e.g., Böhlke, Wanty, et al., 2002; Pauwels et al., 1998), concentration gradients and travel times (centimeter to kilometer scale, e.g., Flewelling et al., 2012; Tesoriero & Puckett, 2011), and 1D-3D models fitting a rate to observations (meter to kilometer scale, e.g., Ocampo et al., 2006; Frind et al., 1990) With pyrite as electron acceptor, the highest rates are for meter-scale in situ experiments (Boisson et al., 2013; Pauwels et al., 1998). An exemption is the study by Jessen et al. (2017), who used an equilibrium-based reaction between nitrate and pyrite to model 2D kilometer-scale nitrate removal. From the push-pull test we estimated a $k$ of 0.23 day$^{-1}$ on the crop side based on denitrification with pyrite, which compares well with rates from Boisson et al. (2013) and Pauwels et al. (1998).

On the wetland side, denitrification is most likely related to a reaction with dissolved organic matter. We have no information of local denitrification rates with organic matter. Observations from a similar site just downstream, gave a maximum rate just below the peat layer of 0.25 day$^{-1}$ (Ribas et al., 2017), that is, very similar to the rate with pyrite denitrification. This rate also compare well with literature-based estimates (Table 3).

The rates in Table 3 decrease with increasing scale, which in part may be explained by the methods used to calculate or simulate rates. For example, for in situ tests, like the push-pull tests, decrease in NO$_3$ concentrations were monitored relative to decrease in concentration of a conservative tracer. Small-scale mixing is thus accounted for. At the hillslope-wetland scale (up to kilometer scale), the denitrification rate is most often calculated based on 1D advective transport not taking into account dispersion. An exemption is if the travel time is based on age-tracers, which are known to be affected by dispersion (Tesoriero & Puckett, 2011). At the regional scale, models may include unknown dispersion (both physical and numerical), which will dilute nitrate in the aquifer with less need for denitrification.

Nitrate removal in water arriving as groundwater to the stream at our site was found to be substantial and near 100%. Our results can be compared with the compilation of field data in Ocampo et al. (2006), who evaluated nitrate removal efficiency (0%–100%) from nine field studies and compared these with a calculated Damköhler number ($D$), defined as:

$$D = \frac{\tau_{\text{trans}}}{\tau_{\text{react}}}$$

(6)

where $\tau_{\text{trans}}$ was computed as travel length divided by pore water velocity and $\tau_{\text{react}}$ is as defined above. From Steiness et al. (2019) we obtain a hydraulic gradient of 0.01 and 0.02 toward the stream from the hillslope north and south of the stream, respectively. With a mean hydraulic conductivity of 14 m/day (Steiness et al., 2019) and a porosity of 0.3, $\tau_{\text{trans}}$ is estimated to 75 and 310 days from the start of the buffer zone and northern hillslope to the stream, respectively. On the wetland side, $\tau_{\text{trans}}$ is 86 days from the southern hillslope to the stream. This gives $D \sim 0.17–71$ and 21 on the crop and wetland sides, respectively. From Figure 10 in Ocampo et al. (2006) it is clear that ~100% NO$_3$ removal occurs at $D > 8–10$.

### 5.2. Nitrate Loading From Bypass Flows and Buffer Efficiency

Bypass flows are therefore the main source of N-loading to the stream. The upland to the crop field consists of coniferous forest so the main input of nitrate to groundwater is the crop field. Hansen et al. (2012) estimated the regional annual agricultural N surplus in Western Jutland in 2007 to 143 kg N ha$^{-1}$ yr$^{-1}$, NO$_3$ leaching from the root zone have been reported by Dalgaard et al. (2011) to amount to ~60% of the N-surplus for Danish conditions. The crop field represents ~2 ha giving potentially 172 kg N yr$^{-1}$ leaching from
crop field due to application of N-fertilizers. Of this only 16 kg N yr\(^{-1}\) reaches the stream through the drain. The crop side of the riparian lowland therefore has an N-removal efficiency of 90%. Consistently, based on drain discharge measurements from Steiness et al. (2019) one can estimate that the bypass flow to the stream from the drainpipe is ~10% of the total flow.
In the wetland, several bypass flow contribute up to 59% of the stream flow gain (Steiness et al., 2019). The high nitrate concentrations in bypass flows (Figure 4) result in a high N input to the wetland surface and eventually the stream (Figure 5). If all bypass flows contribute independently, the N-load to the stream is 708 kg yr$^{-1}$, which must be considered a maximum. If the contributions from bypass flows are not independent, so that the same nitrate was measured multiple times and, effectively, only the ditch (DI) and the rivulet (RI) that visibly connect to the stream deliver nitrate to the stream, the resulting load of 218 kg N yr$^{-1}$ by bypass flow is still significant.

The upland southwest of the field site mainly consists of intensively farmed arable lands. Borehole 96.1981 from the national well database shows elevated nitrate concentrations to at least 20–30 mbs or 12–20 m below the water table (Figure 1c). This suggests that there is little to no reduction capacity (e.g., pyrite) at or above this depth in the aquifer similar to the conceptual model by Böhlke, Wanty, et al. (2002). The regional groundwater inflow to the wetland thus can have high nitrate concentrations, as confirmed by nitrate data from TH10, the mini-piezometers, and bypass flows.

Applying a simple analytical model, regional water- and N-fluxes were calculated (Appendix A). The NO$_3^-$ concentrations from borehole 96.1981 were used as a baseline for the concentration of the upland groundwater. This resulted in a water flux of 1955 L m$^{-2}$ day$^{-1}$ and an N-flux of 22–27.2 g N m$^{-2}$ day$^{-1}$. This further gives an annual regional N-load to the riparian wetland of 1,033 kg N yr$^{-1}$ (average 1990–2008) and 1,293 kg N yr$^{-1}$ (year 2007). Hill (2019) reported values of N-fluxes to riparian buffers from several studies. For sloping landscapes with sandy sediments, N-fluxes were up to 26 g N m$^{-2}$ day$^{-1}$. The N-load (22–27.2 g N m$^{-2}$ day$^{-1}$) to the riparian wetland are hence in the high end of reported fluxes.

The mean residence time of regional discharge to the wetland is ∼10, 20, and 6 years with K values of 14, 5, and 30 m/day, respectively (Appendix A). As our data is from 2017, we now base the calculations on the N load using 2007 data from borehole 96.1981 and a mean residence time of 10 years. As no nitrate enters the stream by groundwater, the N removal is 1,293–708 = 585 kg N yr$^{-1}$ or 450 kg N ha$^{-1}$ yr$^{-1}$ (wetland area of 1.3 ha). This is equivalent to a buffer efficiency of 45%. These removal rates compare well with other studies conducted in Danish riparian lowlands, located in Western Jutland, with N-removal capacities of 400 kg NO$_3^-$ N ha$^{-1}$ yr$^{-1}$ (Brüsch & Nilsson, 1993) and 119–340 kg NO$_3^-$ N ha$^{-1}$ yr$^{-1}$ (Hoffmann et al., 2006). A recent study by Audet et al. (2020) on eight restored wetlands in Denmark reported lower removal rates of 42 kg Total Nitrogen ha$^{-1}$ yr$^{-1}$, with similar rates for NO$_3^-$, corresponding to buffer efficiencies between 2%-42%. These lower rates are in line with other studies listing removal rates of 9–70 kg NO$_3^-$ N ha$^{-1}$ yr$^{-1}$ (Pärn et al., 2012) and 35–40 kg NO$_3^-$ N ha$^{-1}$ yr$^{-1}$ (Jensen et al., 2017). Generally, there are little information on which flow paths contribute to the N loading, e.g., like in Böhlke, O’Connell, and Prestegaard (2007) who found that 27 macropores contributed with over half of the nitrate loading to the stream during high base flow.

These calculations were done assuming all bypass flow contribute individually to the N load to the stream. If we instead use the N load of 218 kg N yr$^{-1}$ as measured from only DI and RI (the two with visible outlets to the stream), the N loss is 1,293–218 = 1,075 kg N yr$^{-1}$ (buffer efficiency of 83%). This is equivalent to 827 kg N ha$^{-1}$ yr$^{-1}$, much higher than reported in other studies. If this indeed was the case, re-infiltration of surface water in the wetland would prove to be an important N-removal process. Revsbech et al. (2005) showed that nitrate concentrations in the water column of a flooded meadow decreased exponentially by a $\tau_{react}$ of ∼1 day, and re-infiltration and diffusion could therefore be a substantial sink. Re-infiltration is supported by Steiness et al. (2019), who observed a small downward gradient between TH9s and TH9d and enriched isotope values in shallow groundwater in the center of the wetland. Re-infiltration was also found to be important by Petersen et al. (2020).

In summary, the two sides (crop and wetland) show distinctly different characteristics. At first, one would think that the crop field would be the main source of nitrate to the stream, but this is not the case (except for the drain). This side of the stream is well protected by a redox front (pyrite) just a few meters below the water table, a high crop field to upland area ratio (47%), and no nitrate source in the upland. The regional inflow of groundwater is therefore low and bypass flow (10%) only occurs as drain flow. On the wetland side, the wetland to upland ratio is very low (5%) giving a relatively high inflow of groundwater. This groundwater has high nitrate concentrations, because of the deep position of the redox front (12–20 m below the water
table) in the regional aquifer connecting to the wetland from southwest. Bypass flow is significant (59%) on the wetland side. Böhlke, O’Connell, and Prestegaard (2007) also found that 27 macropores contributed significantly to bypass flow with a third of stream flow. Within the next one-two decades, the N-load via bypass flow on the wetland side will likely decline, as the monitoring wells at the catchment boundary have shown a decline in nitrate concentrations. For example, nitrate concentrations in well 96.1981 were 22%–33% lower in 2018 than in 2007.

The role of bypass flow containing high nitrate levels is not only limited to the field site. Several ditches draining the wetland downstream of the field site were found to have high nitrate concentrations. It appears that bypass flow plays an important role in the delivery of nutrients along this section of Holtum stream. The temporal variability in water stable isotopes in this headwater stream indicate that water in the stream is composed of a large fraction of young water due to bypass flow and less of older base flow (Kirchner, 2016). Along the headwater stream, land use and depth to redox front determine if bypass flow also contribute with nitrate. The extent of bypass flow is due to regional input of water creating natural seeps and springs and management of the wetland, that is, (1) channelization of the stream, (2) installation of a drainage network, and (3) no maintenance of the drainage network resulting in broken drainpipes.

5.3. Implications—Conceptual Model

A conceptual model for buffer efficiency is developed and compared with our results. For this, we define the fraction of water passing a riparian lowland as bypass flow $f_{\text{bypass}}$ and the fraction of diffuse flow through the riparian aquifer $f_{\text{diff}}$ and assume that $f_{\text{bypass}} + f_{\text{diff}} = 1$. In our terminology, bypass flow therefore includes flow via subsurface drains, rivulet-pipe flow (fast flow component, cf., Shabaga & Hill, 2010), and diffuse surface flow (slow flow component), the two latter ones being the result of groundwater-fed surface flow. We further assume that no NO$_3$ degradation occurs along bypass flow paths, and that groundwater is already sub-oxic (oxygen-free) when it meets the riparian aquifer, within which NO$_3$ removal follows the first-order rate law:

$$C_t = C_0 e^{-kt}$$

(7)

where $C_0$ is the (initial, $t = 0$) NO$_3$ concentration of water arriving to the riparian aquifer and $C_t$ is the concentration in water leaving the aquifer, after time $t$. The use of a first-order rate law is a simplification of the geochemical reaction network and rate laws used by Chen and MacQuarrie (2004) and Zhang et al. (2013). Nevertheless, first-order denitrification with either pyrite or organic matter is often assumed (Table 3). Equation 7 allows calculation of the overall NO$_3$ removal efficiency (fraction), i.e., the average concentration of NO$_3$ in all water arriving to a riparian lowland ($C_0$) relative to that of all water leaving the lowland ($C_{\text{out}}$, equal to $f_{\text{bypass}} C_0 + f_{\text{diff}} C_0$), by:

$$\text{Nitrate removal efficiency} = 1 - \frac{C_{\text{out}}}{C_0} = 1 - f_{\text{bypass}} - f_{\text{diff}} e^{-kt}$$

(8)

Combining with the Damköhler number definition (Equation 6), and realizing that time $t$ in Equations 7 and 8 is equivalent to the travel time $\tau_{\text{trans}}$ in Equation 4 yields:

$$1 - \frac{C_{\text{out}}}{C_0} = 1 - f_{\text{bypass}} - f_{\text{diff}} e^{-D \tau_{\text{trans}}}$$

(9)

Equation 9 shows that the NO$_3$ removal efficiency is not a function of time per se, but is instead a function of the time relative to reaction rate, as expressed by the Damköhler number. Further, the removal efficiency depends on $f_{\text{bypass}}$ (and therefore also on $f_{\text{diff}} = 1 - f_{\text{bypass}}$), and is independent from the initial NO$_3$ concentration when first-order kinetics applies. Equation 9 therefore allows us to calculate very generally the NO$_3$ removal efficiency for any denitrifying riparian lowland as a function of bypass fraction and the riparian aquifer’s Damköhler number. Accordingly, Figure 7 applies Equation 9 to illustrate the effect on the NO$_3$ removal efficiency of the occurrence of bypass flow across a riparian zone in combination with the denitrification rates (expressed as reaction timescales, $\tau_{\text{react}}$) and travel times ($\tau_{\text{trans}}$) encountered within the riparian aquifer. In Figure 7, the x-axis indicates the percentage of bypass flow, and the y-axis shows a large range
of Damköhler numbers. As indicated above, flow paths in Figure 7 are assumed to have either an infinitely short travel time, indicating bypass flow with no time for denitrification, or a long travel time, indicating diffuse groundwater flow in the riparian aquifer, which further is assumed to be denitrifying (sub-oxic throughout). The color scale yields bluish colors when more than 80% (i.e., >0.8) of the nitrate loaded to a riparian zone becomes reduced before water exits to the stream.

Our field site’s Damköhler numbers (derived above) for the two sides of the stream are superimposed on Figure 7. On the agricultural side, only 10% of the water arrived to the stream as bypass flow via the drain (fbypass = 0.1), resulting in an overall removal efficiency above 90%. On the wetland side, the high percentage of bypass flow (60%–70%) keeps the overall nitrate removal efficiency at less than ∼40% at any Damköhler number, including, of course, the estimated value. In other words, bypass flow completely controls the overall NO3 removal efficiency.

Finally, we may extend Equation 9 to also include degradation along the bypass flow, which necessitates the definition of separate Damköhler numbers for the two flow paths:

\[
1 - \frac{C_{\text{out}}}{C_0} = 1 - f_{\text{bypass}}e^{-D_{\text{bypass}}} - f_{\text{diff}}e^{-D_{\text{diff}}}
\]

Degradation along the bypass flow paths could result from diffusion of labile organic carbon from low-permeable peat strata into adjacent high-permeable zones of fast flow or into diffuse surface flow path where flow is slower (Shabaga et al., 2010). Yet, for degradation along bypass flow paths to be significant, denitrification rates along these flow paths need to be high as well, because of the low residence times that characterizes bypass flow.

6. Conclusion
This study shows N-removal buffer efficiency of two riparian lowlands situated on opposite sides of a second order stream. Nitrate loading to the stream depended on the nitrate loading to, and redox conditions within, the regional aquifer, and on how groundwater arriving to the riparian aquifer was divided into bypass flow versus diffuse flow, representing different residence times and redox environments.

The riparian lowland with a crop field and a buffer zone situated to the northeast of the stream has a small upland with low water- and N-flux inputs. Despite the ongoing cultivation, only a small amount of nitrate-rich water was allowed rapid transition to the stream through a drainpipe. Nitrate in groundwater was effectively removed by autotrophic denitrification with pyrite in the aquifer under the crop field. Organic matter is believed also to be present (not measured) as reactive transport modeling suggests that SO4 produced from pyrite oxidation is reduced by organic matter (shown by increase in alkalinity). Buffer efficiency was estimated to 90%.

The riparian wetland was connected to a five times larger upland dominated by arable lands and received both a high water- and N-flux. By appearance, the wetland represents a considerable potential for N-removal, but this potential is not fully realized. Bypass flow ensured that nitrate-rich water could move rapidly across the riparian lowland to the stream. Clear signs of water table management, represented by old surface and subsurface drainage systems, are the causes of high fractions of bypass flow. The N-load to the stream is 708 kg N yr\(^{-1}\) if all bypass flows individually contribute to the stream and 218 kg N yr\(^{-1}\) if only the two overland sources that directly discharge to the stream, i.e., a ditch and a rivulet, are accounted for. Compared to a calculated regional input of nitrate in 2007 (1,293 kg N yr\(^{-1}\)) this gives buffer efficiencies of 45% and 83%, respectively. Thus, two conclusions arise; (1) if the total load to the stream is indeed 708 kg N yr\(^{-1}\), then N-load to the stream is very high and buffer efficiency is rather low. (2) If the total load to the
stream is indeed 218 kg N yr\(^{-1}\), then surface re-infiltration to the peat layer and aquifer in the wetland is a significant process in N-removal.

The observation that bypass flow (drains, groundwater-fed surface flow) was important at this site resulted in the development of a conceptual model for nitrate removal efficiency as a function of the Damköhler number and the bypass fraction. The model requires information of a number of parameters such as estimates of the denitrification rates, groundwater velocity and the bypass fraction. The model is simple and assumes subsurface flow is diffuse, that is, it does not account for preferential flow through high-K conduits (\(\tau_{\text{trans}}\)).

Water table management is a common practice conducted in riparian lowlands situated in agricultural lowland catchments. Reasons for the difference in N-removal efficiency can largely be attributed to vastly different external and internal factors. External factors include upland size (wetland-to-catchment area ratio), land use, and redox conditions in the upland aquifer, resulting in vastly different inputs across the upland-riparian interface. These factors are to a large degree magnified by the conditions met in the riparian zone; this is especially true for the riparian wetland, which is altered by anthropogenic changes affecting the subsurface and surface flow components to the streams. An improvement in the N-removal capacity would likely involve a rearrangement (restoration) of the entire stream valley. This would likely restrict the use of the stream valley with consequences for the current land use as productive agricultural land.

Appendix A: Upland-Riparian Groundwater Water- and N-Flux Calculation

Approximately 2,000 m southwest of TH10 borehole 96.1981 is located, screened at two depths. The well is located near the topographic divide of the catchment. Well 96.1981 shows high nitrate concentrations in groundwater at depths 20–35 MBS. This suggests that nitrate reduction in the upland aquifer is poor. The water table and water flux from borehole 96.1981 to piezometer TH10 was calculated using an analytical model. A conceptualization of the simplified unconfined aquifer is presented in Figure A.1.

The unconfined aquifer receives recharge (\(R\)) equal to the mean annual precipitation minus actual evapotranspiration for Holtum catchment reported by Sebok et al. (2016). Borehole 96.1981 is situated at \(x_0\) (0 m) having a hydraulic head \(h_0\) (64.87 m, see Figure A.1b). At the opposite end, piezometer TH10 is located at 2,000 m with a hydraulic head of \(h_L\) (59.39 m). An impermeable bottom is assumed at elevation \(z_b\) (45 m). The saturated thickness is equal to \(h - z_b\). A 1D steady state flow equation for an unconfined aquifer was used to calculate the head distribution \(h(x)\) and flux \(q(x)\) (in units of m\(^3\) day\(^{-1}\) per meter wetland;

\[
h(x) = \sqrt{\left(h_0 - z_b\right)^2 + \frac{R}{K} \left(Lx - x^2\right) + \left(h_L - z_b\right)^2 - \left(h_0 - z_b\right)^2} - x + z_b
\]

(A.1)

\[
q(x) = -\frac{K}{2} \left(\frac{R}{K} - 2x + L\right) + \left(h_L - z_b\right)^2 - \left(h_0 - z_b\right)^2)
\]

(A.2)

The head distribution is shown in the conceptual model, Figure A.1. A water divide is predicted ~450 m from 96.1981. This simple model therefore confirms that the well is located near the topographic divide as seen in Figure A.1a.

The calculated \(q_L = 2000\) m at the entrance to the wetland is 1.96 m\(^3\) day\(^{-1}\) m\(^{-1}\). With a wetland width of 130 m along the hillslope-riparian wetland interface at the field site, this yields an upland to riparian wetland groundwater flux of 252 m\(^3\) day\(^{-1}\) or 2.9 \times 10\(^{-3}\) m\(^3\) sec\(^{-1}\). In comparison, Steiness et al. (2019) measured a mean contribution from the southwest to the stream flow gain of 3.2 \times 10\(^{-3}\) m\(^3\) sec\(^{-1}\). The results are most sensitive to the choice of \(R/K\). Recharge (\(R\)) is relatively well known, so the main uncertainty is related to \(K\). Slug test (Steiness et al., 2019) gave a range of 0.1–50 m/day (mean of 14 m/day). If \(K\) is 5 m/day or 30 m/day, then \(q_L = 2000\) m decreased and increased by 22% and 38%, respectively. The velocity-weighted av-
Average residence time was calculated to \( \sim 10 \) years (20 and 6 years with a \( K \) of 5 and 30 m/day, respectively) from the simulated water divide at 450 m to the entrance to the wetland at 2,000 m (assuming a porosity of 0.3).

Borehole 96.1981 has two filters where nitrate concentrations are measured on a regular basis (yearly) as part of the national groundwater-monitoring program (Figure A.1). The average NO\(_3\) concentrations over the period 1990–2018 were 1.02 and 0.57 mM for the top and bottom filter, respectively. With an average residence time of about 10 years the nitrate input to the wetland could also be estimated from what was measured in 2007 (10 years before the current investigation). The 2007 concentrations were somewhat higher with 1.39 and 0.6 mM in the top and bottom filters, respectively. Three other monitoring wells are also present in the vicinity of well 96.1981. They all have similar concentration ranges.

The N-load from upland to riparian wetland was calculated based on the average (1990–2018) and 2007 nitrate concentrations (\( C \)) from borehole 96.1981 times the groundwater-riparian wetland flux.

\[
N_{\text{load}} = q_{L=2000\text{m}} \cdot C
\]

The regional N-load yields an input of 22–27.2 g N day\(^{-1}\) m\(^{-2}\) giving an annual regional N-flux of 1,033–1,293 kg N yr\(^{-1}\) with a wetland width of 130 m.
Data Availability Statement

The authors would like to thank family Hauge for granting us access to the field site. The authors would also like to thank the people who have participated in field trips and assisted in collecting the data: Francesca Parmanozone, Iris Tobelaim, Joel Tirado-Conde, and Wenjing Qin. This research was part of the TRenDS project and funded by Innovation Fund Denmark (grant no. 4106-00027B). Data are accessible from the Harvard dataverse via https://doi.org/10.7910/DVN/FJUXOV.

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