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Catchment controls of denitrification and nitrous oxide production rates in headwater remediated agricultural streams

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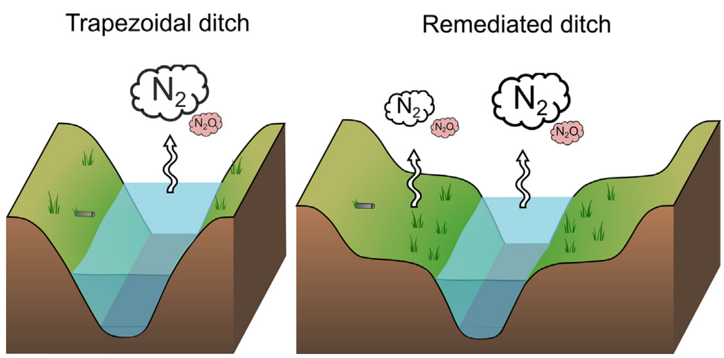
HIGHLIGHTS

- Floodplains increase total system denitrification by 50 %.
- Nitrous oxide production was lower in floodplains than in stream.
- Nitrate-rich catchments promote denitrification and suppress nitrous oxide yields.
- Catchment hydrological processes can override reach-scale nitrate retention.

GRAPHICAL ABSTRACT



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ABSTRACT

Heavily modified headwater streams and open ditches carry high nitrogen loads from agricultural soils that sustain eutrophication and poor water quality in downstream aquatic ecosystems. To remediate agricultural streams and reduce the export of nitrate (NO_3^-), phosphorus and suspended sediments, two-stage ditches with constructed floodplains can be implemented as countermeasures. By extending hydrological connectivity between the stream channel and riparian corridor within constructed floodplains, these remediated ditches enhance the removal of NO_3^- via the microbial denitrification process. Ten remediated ditches were paired with upstream trapezoidal ditches in Sweden across different soils and land uses to measure the capacity for denitrification and nitrous oxide (N_2O) production and yields under denitrifying conditions in stream and floodplain sediments. To examine the controls for denitrification, water quality was monitored monthly and flow discharge continuously along reaches. Floodplain sediments accounted for 33 % of total denitrification capacity of remediated ditches, primarily controlled by inundation and stream NO_3^- concentrations. Despite reductions in flow-weighted NO_3^- concentrations along reaches, NO_3^- removal in remediated ditches via denitrification can be masked by inputs of NO_3^--rich groundwaters, typical of intensively managed agricultural landscapes. Although N_2O production rates were 50 % lower in floodplains compared to the stream, remediated ditches emitted more N_2O than conventional trapezoidal ditches. Higher denitrification rates and reductions of N_2O proportions were predicted by catchments with loamy soils, higher proportions of agricultural land use and lower floodplain elevations. For realizing enhanced NO_3^- removal from floodplains and avoiding increased N_2O emissions, soil type, land use and the design of floodplains need to be considered when implementing remediated streams. Further, we stress the need for assessing the impact of stream remediation in the context of broader catchment processes, to determine the overall potential for improving water quality.

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1. Introduction

Sustained anthropogenic inputs of nitrogen (N) and phosphorous (P) to agricultural soils have fundamentally altered nutrient fluxes to aquatic ecosystems and resulted in water quality deterioration, eutrophication and hypoxia of freshwater and marine environments and higher costs of drinking water production (Andersen et al., 2017; Fowler et al., 2013; Sharpley et al., 2013). Phosphorus mitigation has been the long-standing focus for combating eutrophication (Schindler et al., 2016), but increasing attention is drawn to N as an important co-limiting nutrient in aquatic ecosystems (Conley et al., 2009; Glibert, 2017; Shatwell and Köhler, 2019; Vahtera et al., 2007). Despite raised ambitions in response to extensive policy (e.g. Water Framework Directive and Green Deal; Bieroza et al., 2021) poor water quality status still persists globally. This exposes critical gaps in our understanding of hydrological and biogeochemical functioning of streams and their catchments (Van Meter et al., 2018) and the important role of legacy N in agricultural soils and groundwaters (Basu et al., 2022). Agricultural N sources mainly enter aquatic ecosystems via the interface of headwaters (Abbott et al., 2018; Wollheim et al., 2018), representing ecosystem control points with a complex interplay between hydrological delivery and N removal via denitrification - the microbial reduction of nitrate (NO_3^-) to gaseous N under anoxic conditions (Tank et al., 2021). In these streams, abundant NO_3^- and labile organic carbon (C) sources converge, creating a high potential for denitrification activity. Headwaters in flat and intensively managed agricultural landscapes in temperate regions have been extensively modified into open ditches, characterized by a trapezoidal shape and minimal riparian connectivity, with the overarching purpose of draining excess water from arable land. As a consequence, dissolved NO_3^- bypasses much of the biogeochemically reactive land-water interface of riparian and hyporheic zones and is rapidly moved downstream during high flows, exacerbating eutrophication (Baker et al., 2012; Smith et al., 2008).

Since a large proportion of solutes enter the stream network through headwater agricultural streams and ditches, much focus is now directed towards improving their capacity for biogeochemical nutrient removal; a task that requires comprehensive mitigation strategies and innovative countermeasures (Lintern et al., 2020). To increase denitrification capacity in trapezoidal ditches while maintaining sufficient drainage capacity, two-stage ditches (Powell et al., 2007) have been proposed as cost-efficient stream remediation measures (Roley et al., 2016; Västilä et al., 2021). Two-stage ditches comprise an inset channel flanked by laterally connected floodplains and lower gradient banks with vegetation (Fig. 1a), as an adaptation from natural streams with lateral depositional bars formed by natural fluvial processes (Landwehr and Rhoads, 2003). The larger transect volume of two-stage ditches allows stream water to spread on to floodplains during high flows, relying on riparian connectivity to enhance reach-scale denitrification. Constructed floodplains have been shown to prolong water residence time and remove 2–13 % of stream NO_3^- loads (Mahl et al., 2015; Roley et al., 2012; Speir et al., 2020).

However, denitrification can terminate with nitrous oxide (N_2O) and potentially impose an environmental trade-off between water quality improvements and greenhouse gas emissions from constructed floodplains (Dee and Tank, 2020). Fertilization is a driver of N_2O emissions (Lebender et al., 2014) and elevated NO_3^- concentrations in streams have been linked to higher proportions of sediment denitrification terminating with N_2O (Schade et al., 2016). Previous studies of remediated ditches have focused on the temporal interplay between hydrology and NO_3^- and C substrate limitation of N_2 and N_2O production (Dee and Tank, 2020; Mahl et al., 2015; Roley et al., 2012; Speir et al., 2020). As the implementation of remediated ditches has expanded to a greater diversity of catchments with different dynamics in solute delivery, we need to improve our understanding of N removal capacities and the risk for N_2O emissions across a range of geological settings, soil types, land uses and specific floodplain designs.

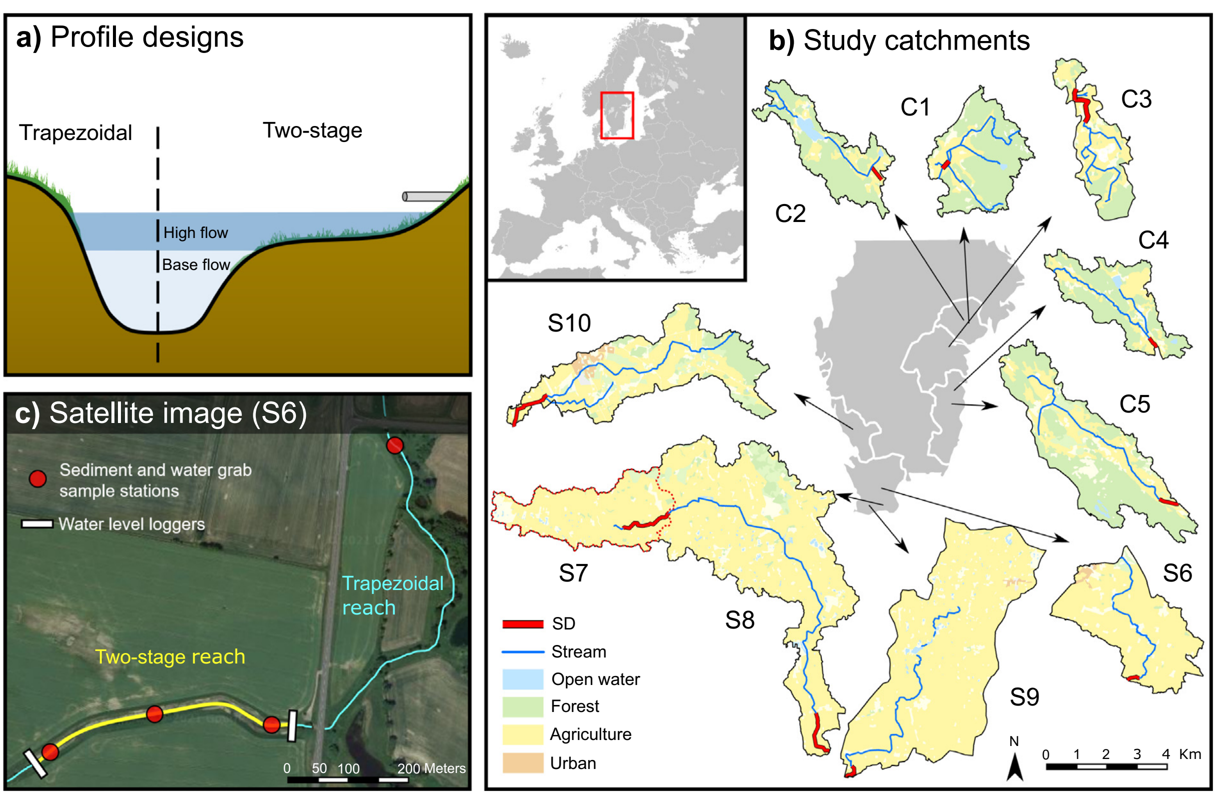

Fig. 1. a) Cross section of trapezoidal (TD) and two-stage (SD) profiles. b) Location of the ten catchments with SD ditches in Central East (C1-C5) and South Sweden (S6-S10). c) Satellite image of one reach in site S6 showing monitoring setup in upstream TD and downstream SD reach (flow direction from North to South). Sediment samples and water grab samples were collected at start of TD reach and at start, middle and end of SD reach, denoted by red circles. Water level loggers were placed at start and end of SD, denoted by white lines.

Here, potential denitrification rates and the fraction ending as N_2O, i.e. N_2O yield, were compared between stream and floodplain sediments of remediated ditches with two-stage design and conventional trapezoidal ditches in ten different catchments, with a focus on understanding catchment controls and the role of floodplain designs (Fig. 1b). Our overarching assumption was that high NO_3^- inputs increases both potential denitrification and N_2O rates. To determine the limiting factors and capacity for reach-scale N removal and N_2O production, we measured sediment and water chemistry, hydrology and catchment characteristics and hypothesized that:

1. Floodplains contribute to reductions in NO_3^- concentrations compared to trapezoidal ditches by increasing reach-scale denitrification activity.
2. Floodplains with lower elevations in relation to the stream channel bed and higher vegetation cover yield higher denitrification rates and suppress N_2O emissions due to prevailing anoxic conditions.

2. Materials and methods

2.1. Site description

Ten agricultural streams and ditches that had been modified into two-stage ditches (Fig. 1a), hereafter referred to as remediated ditches, were selected in Central East (C1–5) and South Sweden (S6–10). Each remediated ditch was paired with an upstream, trapezoidal ditch, equivalent in length (Fig. 1c). The S7 and S8 ditches share the same stream network, as S7 drains an upstream subcatchment nested within the S8 catchment. Study sites are located in tile drained agricultural headwater catchments, ranging between 8 and 42 km^2 in size and dominated by cultivation of both winter and spring sown cereal crops and ley (Fig. 1b). The geology of C1-C5 and S10 catchments is characterized by crystalline bedrock, and in S6-S9 catchments by limestone bedrock. Bedrock is overlaid by quaternary sediments with depths between 10 and 50 m. All studied ditches are of the 1st Strahler order, except C4 which is a 2nd order stream. The lengths of the remediated ditches range between 0.3 and 1.7 km, with floodplains constructed either on one side (C4, S6–7 and S9–10) or two sides (C1–3, C5 and S8) of the inset channel at elevations ranging from 0.25 to 0.94 m in relation to the stream bed. The ratio of floodplain width in relation to channel width ranges from 0.3 to 2.3. The remediated ditches were constructed between 2013 and 2019 by landowners and other stakeholders, aiming to reduce flooding of the nearby fields and improve water quality (Brink et al., 2012; Wiström and Lindberg, 2016; Hedin and Kivivuori, 2015).

Sampling was carried out in 2020–2021, which showed a higher annual precipitation in comparison with five year precipitation averages (SMHI, 2021; Table 1), although S7–9 in South were notably drier. The sites differ in precipitation, soil texture, agricultural land use and floodplain designs (Table 1). Catchments in Central East (C1–5) have lower annual precipitation as well as a lower percentage of agricultural land use and higher clay content in soils compared with catchments in South (S6–10). Floodplain inundation, the overflowing of stream water on floodplains, occurred predominantly in winter and spring at sites with lower floodplains (C4, S6–8). Along each remediated ditch, sampling was carried out in three locations: upstream (UP), mid (MD) and downstream (DN; Fig. 1c) and as paired reference, we sampled upstream of trapezoidal ditches (TD).

For each location along the floodplains in remediated ditches (UP, MD and DN), three 1 m^2 (1 × 1 m) plots were used to visually estimate vegetation cover and classify macrophytes into four functional groups: Reeds (genus *Phragmites* and *Typha*), Grasses, Herbs and Bryophytes. Vegetation observations occurred in May and June 2021. Stream benthic cover was further assessed for all sediment sampling locations in June 2021 by walking 50 m in a zig-zag pattern parallel to the stream and visually determining the stream bed material every 5 m, following the Wolman pebble count method (Wolman, 1954).

2.2. Sediment and water sampling

Stream bed and floodplain sediments were collected at different flow conditions, with and without floodplain inundation from all sites on four occasions (September 2020, November 2020, March 2021 and May 2021; Fig. 2) as well as monthly water grab samples between April 2020–June 2021 to determine potential denitrification and N_2O production rates as well as water and sediment chemistry. Additionally, stream sediments in remediated ditches were collected from CE2 and CE3 at four occasions in 2019 (June, July, August and September) for the same purpose. Stream and floodplain sediments and water samples were collected at the four locations TD, UP, MD and DN. Reference ditch for site S7 was excluded since the ditch originates from a wetland. During November 2020, no samples were collected from sites S7–9 due to logistical constraints. In total, 279 sediment samples were collected between 2019 and 2021. Sediments were sampled down to 3 cm depth with a trowel as 3 cm^3 cubes. For each location, three pseudo-replicates were sampled within 1 m^2 and pooled into one sample. Sediments were placed in airtight plastic bags and stored in coolers during field transportation and at 4 °C back at laboratory.

2.3. Denitrification assays on sediments

Potential denitrification rates, hereafter referred to as denitrification, were measured in 268 sediment samples (11 samples were excluded due to measurement errors) under anoxic conditions with the acetylene inhibition technique, without chloramphenicol (Hellman et al., 2019). To determine potential N_2O production rates, 133 sediment samples were incubated without acetylene (C_2H_2) in parallel with C_2H_2-amended samples, in September 2020 and March 2021. The denitrification and N_2O production rates were determined 1–7 days after sediment sampling and there was no effect of storage time on denitrification rates (ANOVA, $F_{1,\ 245} = 0.5342, p = 0.47$). Microcosms were established with 10 g of homogenized fresh sediments and 20 ml distilled water in 125 ml flasks sealed with septum caps. The microcosms were flushed and purged with 1 atm N_2 5 times before adding 10 ml C_2H_2. We equilibrated the microcosms on a shaker at 170 rpm for 30 min before adding 1 ml substrate to reach final concentrations of 6 mg NO_3^--N L^{-1} (KNO_3) and 7 mg C L^{-1} (as a mixture of glucose, acetate and succinate). The microcosms were incubated in 25 °C with agitation (170 rpm) and gas samples were taken at 30, 75, 120, 150 and 180 min. The N_2O concentrations in gas samples were quantified using a gas chromatograph (Clarus-500, Elite-Q PLOT phase capillary column, PerkinElmer, U.S.) with a ^{63}Ni electron-capture detector. The mass of N_2O was corrected for temperature, partial pressure and the exchange of dissolved N_2O gas with the liquid phase, using the Bunsen coefficient 0.545 for N_2O, calculated according to Breitbarth et al. (2004). Denitrification and N_2O production rates were determined by linear or quadratic regression of N_2O mass over time (3–5 time points) and scaled to μg N g^{-1} DM h^{-1} and μg N g^{-1}C h^{-1}. The N_2O yield (%) was determined by dividing N_2O rates from incubations without acetylene with N_2O rates from incubations with C_2H_2.

2.4. Sediment and water chemistry analyses

Fresh weights of sediment subsamples were measured and dry weights were re-measured after oven drying (105 °C) to determine sediment dry matter (DM). Sediments were analyzed for C and N by dry combustion on a Leco CN analyzer (Leco, TruMac, India).

Bottled water samples were analyzed for NO_3^--N (ISO 15923-1:2013), ammonium-nitrogen (NH_4^+-N; ISO 15923-1:2013), dissolved organic carbon (DOC; SS-EN 1484) and suspended sediments (SS; SS-EN 872:2005). Dissolved oxygen (DO), pH and specific conductivity (SPC) were measured in situ, monthly to bimonthly, using optical and electrode-based sensors mounted to a handheld device (ProDSS, YSI, U.S.).

Dissolved organic matter (DOM) properties in collected water grab samples were determined optically in the laboratory to calculate fluorescence

Table 1
Characteristics of catchment, hydrology, floodplain properties and inundation pattern of remediated ditches. Sites are ordered from North to South. Flow discharge and floodplain inundation were recorded in April 2020–June 2021. Discharge in C3 was recorded in 2018–2021, interrupted between December–March each year. Ditch and floodplains dimensions were measured in March and April 2021 with a GPS levelling device (E600 GNSS Receiver, E-survey, China).

Site	County	Catchment properties					Discharge					Ditch dimensions					Floodplain inundation		
		Area (km^2)	Mean temperature (°C)*	Precipitation (mm)*	Soil texture	Agricultural land use (%)	Q50 (m^3 s^{-1})	Baseflow Index (BFI)	Flashiness Index (RBI)	Runoff (mm yr^{-1})	Year of construction	Ditch length (m)	Floodplain Height (m)	Floodplain width (m)	Channel width (m)	Floodplain design	Frequency (day yr^{-1})	Mean Duration (day)	Max Duration (day)
Central East																			
C1	Södermanland	9.73	8.9 ± 7.5	594	Silty clay	16	0.026	0.875	0.269	206	2012	340	0.60	3.1	2.9	Two-sided	72	8	44
C2	Södermanland	7.91	8.9 ± 7.5	594	Silty clay loam	27	0.032	0.942	0.094	206	2012	730	0.94	3.5	2.8	Two-sided	31	7	16
C3	Östergötland	6.63	8.4 ± 7.6	551	Clay loam	70	0.013	0.807	0.330	114	2014	1500	0.53	3.2	2.3	Two-sided	27	6	20
C4	Kalmar	8.12	8.4 ± 7.2	627	Clay loam	35	0.486	0.944	0.070	1790	2019	320	0.51	1.7	5.4	One-sided	199	56	155
C5	Kalmar	16.32	8.4 ± 7.2	627	Clay loam	38	0.023	0.828	0.302	150	2012	780	0.53	1.4	2.6	One − /Two-sided	100	13	51
South																			
S6	Skåne	13.09	8.8 ± 6.9	707	Loam	84	0.086	0.856	0.303	575	2016	400	0.4	5.7	2.7	One − /Two-sided	149	41	126
S7	Skåne	10.84	9.2 ± 6.6	569	Loam	81	0.022	0.799	0.323	179	2013	1960	0.55/0.25	4.0	2.2	One-sided	124	20	129
S8	Skåne	42.41	9.2 ± 6.6	569	Loam	81	0.117	0.798	0.355	272	2013	1770	0.49	6.8	4.6	One − /Two-sided	98	31	76
S9	Skåne	31.02	9.2 ± 6.6	569	Loam	86	0.075	0.868	0.064	91	2019	630	0.85	–	–	One-sided	0	0	0
S10	Halland	16.38	9.7 ± 7.2	823	Sandy loam	58	0.121	0.720	0.580	723	2014	1760	0.34	2.8	7.4	One-sided	–	–	–

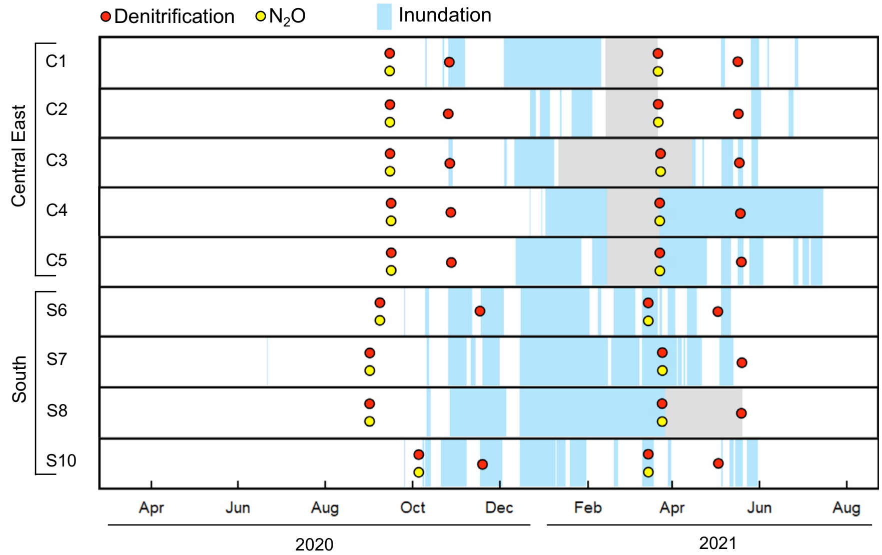

Fig. 2. Inundation of floodplains occurred predominantly in winter and spring across all sites. Blue color denotes recorded inundation events where water stage exceeded floodplain elevation in relation to stream bed from April 2020 to August 2021. Gray color denotes periods of missing water stage data and red and yellow circles show sampling dates for denitrification and N_2O production/N_2O yield, respectively. The figure shows either upstream or downstream inundation in remediated ditches for each site. The location with longest inundation periods chosen to show the onset of inundation in the ditches.

index (FI; McKnight et al., 2001), biological freshness index (BIX; Huguet et al., 2009), humification index (HIX; Ohno, 2002), specific absorbance at 254 nm, normalized for DOC ($SUVA_{254}$; Edzwald et al., 1985), ratio of specific absorbance at 250 nm and 365 nm (E2:E3; Peuravuori and Pihlaja, 1997) and absorbance spectral ratio of slopes between 275 and 295 and 350–400 nm (S_R; Helms et al., 2008), using Matlab (R2020a). These indices are well-established proxies for fingerprinting DOM origin and quality. Water samples were analyzed with a spectrophotometer (Aqualog, Horiba, Japan) equipped with a 150 W Xenon arc lamp, using a high precision quartz cuvette with 1 cm light path. Scans were acquired using excitation-emission matrices (EEM) at excitation and absorbance wavelengths between 240 and 600 nm and emission wavelengths between 212 and 620 nm, at 1 s integration time and 2 nm scan width. Distilled water blanks were scanned each day prior to analysis and the blank signal was subtracted from sample EEM scans to correct for Raman scattering. Raman peak intensities in blank samples were also recorded daily to normalize sample EEM scans and account for the variation in Raman intensities over time. The sample EEM scans were further corrected for inner-filter effect (McKnight et al., 2001) and signal intensities of first and second order Rayleigh scatter lines were removed by applying a Rayleigh masking filter. Instrument bias associated to optical components was automatically corrected in the Aqualog software after each spectral scan. All preprocessing corrections were performed in the Aqualog software.

2.5. Hydrology and geometry surveys

Pressure sensors (HOBO, Onset Computer Corporation, U.S.) were installed to log water stage every 10 min at UP and DN for all ditches. At the same locations, flow discharge was measured with the mid-section method using an acoustic doppler velocimeter (Flowtracker 2, SonTek, U.S.) at 4–8 occasions during different flow conditions in 2020 and 2021. Continuous flow discharge was derived by correlating discharge and corresponding stage data (Fig. S1), using:

$$Q = K(h + a)^p \tag{1}$$

where Q is discharge ($m^3\ s^{-1}$), h *is* stage (m), a is stage at zero flow (m) and K and p are constants (Rantz, 1982).

To determine the effect of floodplain inundation on denitrification, the geometry of selected cross-sections were measured every 50–100 m along all remediated ditches except S9. For this purpose a global GPS device (E600 GNSS Receiver, E-survey, China) with 2 mm accuracy were used, operating in real-time kinematic mode together with a mapping interface (SurPad 4.0, Geoelectron, China). Profile dimensions were surveyed in spring 2021 by walking across chosen cross-sections with the GPS instrument, to obtain length, width and elevation of channels and floodplains. Water stage data from UP and DN were combined with the derived floodplain elevations to calculate the frequency and duration of inundation. Water stage in UP locations was applied to the mean floodplain elevation of the upstream half of the remediated reach and stage data from DN to the downstream half. When water stage exceeded the mean of floodplain elevation it was recorded as an inundation event. The accuracy of recorded events was further cross-validated with field observations of inundation events.

2.6. Statistical analyses

All statistical analyses were performed in R version 1.2 (RStudio Team, 2019). The packages hydrostats and leppott/ContDataQC were used to analyze the hydrological regimes. Analysis of variance (ANOVA) and Pearson correlations were permuted 10,000 times using permuco and RVAideMemoire packages, and the resampling approach was chosen to account for non-normal distributions in the dataset. Base flow index (Gustard et al., 1992) and median flow discharge (Q_{50}) were calculated using *baseflows* and flashiness index (Baker et al., 2004) using *RBIcalc*. Differences in base flow index, flashiness index and Q_{50} between upstream and downstream of remediated ditches were tested using one-way ANOVA (*aovperm*). To test the differences in denitrification rates and N_2O yields in sediments between locations (TD, UP, MD and DN) and profiles (stream and floodplain), two-way ANOVA was used. Differences in denitrification rates and N_2O yield between regions were tested with one-way ANOVA.

To determine the effects of predictor variables (stream and sediment chemistry as well as catchment and ditch properties) on denitrification and N_2O yield, Pearson correlation coefficients were calculated (*perm.cor.test*). The sample distribution of predictor variables was analyzed by scaled principal component analysis (PCA; *rda*) on 4 separate matrices (denitrification and N_2O yield respectively from stream and floodplains respectively) using the Vegan package. Vectors of denitrification rates or N_2O yield were fitted to the PCAs using *envfit* with 10,000 permutations and vectors that were significantly correlated to principal component axes ($p < 0.05$) were included in ordination plots. Grouping of samples were tested statistically between regions (Central East and South), sites and stream vs. floodplains with permutational multivariate analysis of variance (PERMANOVA) using *adonis*.

To analyze changes in stream water quality (NO_3^--N, NH_4^+-N, DOC, DO and DOM indices) in trapezoidal and remediated ditches, two-way ANOVA was used with location and either site or region as factors. Water samples with NO_3^--N and NH_4^+-N concentrations below detection limit (< 2 % of observations) were assigned to detection limit concentrations divided by 2 (Hornung and Reed, 1990). Flow-weighted concentrations of NO_3^--N were calculated by dividing absolute concentrations (mg L^{-1}) with flow (m^3 s^{-1}) to determine the influence of hydrology on concentrations between UP and DN.

Reach-scale retention of NO_3^--N and NH_4^+-N concentrations in % was calculated as $C_{Ret} = (C_{Upstream-} - C_{Downstream}) / C_{Upstream}$ for trapezoidal and remediated ditches, where $C_{Upstream}$ denotes the upstream concentration in mg L^{-1}, and $C_{Downstream}$ the downstream concentration in mg L^{-1}. The samples were further classified into three flow regimes: $Q_{0–25}$, Q_{25}-Inundation and Inundation. The differences in concentration retention % were tested between trapezoidal and remediated under different flow regimes using two-way ANOVA.

3. Results

3.1. Hydrology and floodplain inundation frequency

Median discharge (Q_{50}) at catchment outlets was overall higher in South compared to Central East (Table 1). All remediated ditches were predominantly base flow driven and received inputs from groundwater and subsurface tile drains, with base flow indices ranging between 0.72 and 0.94 and no differences between upstream and downstream (Table S1). However, flashiness index indicated that discharge peaks were reduced along remediated ditches in Central East but enhanced in South.

Floodplain inundation ranged from 31 to 199 days yr^{-1} with a mean duration of 6–56 days per event (Table 1). Floodplain elevation was the main controlling factor for inundation as lower floodplains promoted higher inundation frequency ($r = -0.56$, $p < 0.05$) and longer duration ($r = -0.25$, $p < 0.05$). In South, the onset of floodplain inundation started in September to October and receded in May to June, while in Central East, inundation patterns were less uniform and started from October to December and receded in May to July (Fig. 2).

3.2. Denitrification rates in sediments

Denitrification rates in stream sediments were not statistically different between remediated ditches and trapezoidal ditches (ANOVA, $F_{1,157} = 1.24$, $p = 0.27$; Fig. 1a). In remediated ditches, denitrification in floodplain sediments averaged 3.01 ± 3.78 μg N g^{-1} DM h^{-1}, which was significantly lower compared to denitrification in stream sediments (Fig. 3a), averaging 5.85 ± 7.09 μg N g^{-1} DM h^{-1}. Denitrification rates in floodplain sediments were significantly higher in the South sites than the Central East sites, with stream sediments following the same trend, although non-significant (Fig. 3b). There were no longitudinal differences in denitrification rates for either stream or floodplain sediments (Fig. 3a). Over the course of September 2020 to May 2021, denitrification in floodplain sediments varied significantly between the tested months (ANOVA, $F_{4,104} = 2.91$, $p = 0.03$; Fig. S2). The lowest denitrification rates were measured in September (1.81 ± 2.08 μg N g^{-1} DM h^{-1}) followed by an increase in March (4.87 ± 6.12 μg N g^{-1} DM h^{-1}). By contrast, denitrification rates in stream sediments did not show any seasonal trends (ANOVA, $F_{8,120} = 1.32$, $p = 0.24$; Fig. S2). The floodplain age had a positive effect on denitrification, which increased with year since construction (ANOVA, $F_{4,104} = 6.94$, $p < 0.01$; Fig. S3). Rates in floodplains constructed in 2013 were >3 times higher than in floodplains constructed in 2019, apart from C2 constructed in 2012, which had the lowest denitrification rates. For stream sediments, there were no effects of construction age on denitrification (Fig. S3).

Denitrification rates were also expressed as per C content in the sediment, but this did not alter the denitrification patterns for stream and floodplain, seasonality or longitudinal reach effects as observed with rates expressed per dry matter (Fig. S4). In stream sediments, N % increased significantly from trapezoidal to remediated ditches (ANOVA, $F_{3,126} = 2.88$, $p = 0.04$; Fig. S5) and C % followed the same trend (ANOVA, $F_{3,126} = 2.43$, $p = 0.07$), indicating that remediated stream beds promote higher organic matter accumulation. This was further corroborated by increases in the cover of fine benthic organic material from trapezoidal to remediated ditches (Fig. S5).

3.3. Predictors of denitrification

The combined composition of water and sediment chemistry as well as catchment and ditch properties were significantly different between sites in Central East and South, both for stream and floodplains (PERMANOVA, $p < 0.05$; Fig. 4a, b). Higher land use % and sand content in combination with higher NO_3^--N concentrations characterized South sites compared to Central East sites (Fig. 4). C and N content in sediments were the strongest predictors for denitrification in stream sediments (C $r = 0.51$, $p < 0.05$ and N $r = 0.49$, $p < 0.05$; Fig. 4a), indicating that OM is limiting denitrification in stream sediments. Denitrification in floodplain sediments also correlated with C ($r = 0.26$, $p < 0.05$) and N content ($r = 0.26$, $p < 0.05$) but this relationship was weaker compared to stream sediments (Fig. 4b). Water chemistry showed contrasting responses for denitrification. Stream denitrification was not correlated with NO_3^--N, DOC, DO and pH, SS (Fig. 4a; Fig. S6), whereas floodplain denitrification increased with higher NO_3^--N and lower DOC concentrations (Fig. 4a) as well as higher DO concentrations and pH (Fig. S6). There were no correlations between denitrification and sediment C:N or stream DOC:NO_3^--N with either linear (Fig. S6) or non-linear regression (not shown).

Floodplain elevation relative to the stream bed influenced denitrification, with lower floodplains promoting higher denitrification rates ($r = -0.21$, $p < 0.05$) and peaking at elevations between 0.25 and 0.55 m. The PCA indicated that denitrification also increased with higher inundation frequencies (Fig. 4c). However, when testing directly for the effect of hydrology on denitrification, there were no significant correlations with denitrification and floodplain inundation frequency, duration or flow discharge (Fig. S6). Total vegetation cover was also positively correlated with denitrification (Fig. 4b; Fig. S6). Reed and grass species cover were identified as opposing correlates with denitrification (Fig. 4b; Fig. S6a), but both variables were more strongly predicted by inundation frequency on floodplains (Reed: $r = 0.67$, $p < 0.05$; Grass: $r = -0.49$, $p < 0.05$).

3.4. N_2O production rates and yields and its predictors in sediments

There were no difference in N_2O production rates (ANOVA, $F_{1,73} = 2.81$, $p = 0.08$; Fig. 3c) or N_2O yields (ANOVA, $F_{1,73} = 0.47$, $p = 0.50$; Fig. 3e) in stream sediments between trapezoidal and remediated ditches. Production rates of N_2O were lower in floodplain sediments compared to stream sediments (Fig. 3c). However, N_2O yields were higher in floodplain sediments (mean 0.38 ± 0.36), compared to stream sediments (mean 0.28 ± 0.25; Fig. 3c). Notably, regional characteristics influenced both N_2O rates and yields in the opposite direction as for denitrification rates, where the lowest N_2O rates and yields were observed in the South sites for both stream and floodplain sediments (Fig. 3d, f). Sites C1–2 and C4 showed a distinct shift towards N_2O as end-product of denitrification in floodplains. Older remediated ditches significantly suppressed N_2O yields in both stream (ANOVA, $F_{4,54} = 3.06$, $p = 0.03$) and floodplain sediments (ANOVA, $F_{4,53} = 3.00$, $p = 0.03$), with elevated N_2O yields in the youngest remediated ditches (C4 and S9; Fig. S3). As observed for denitrification, the C2, being the oldest remediated ditch, was the exception with high N_2O yields (Fig. S3).

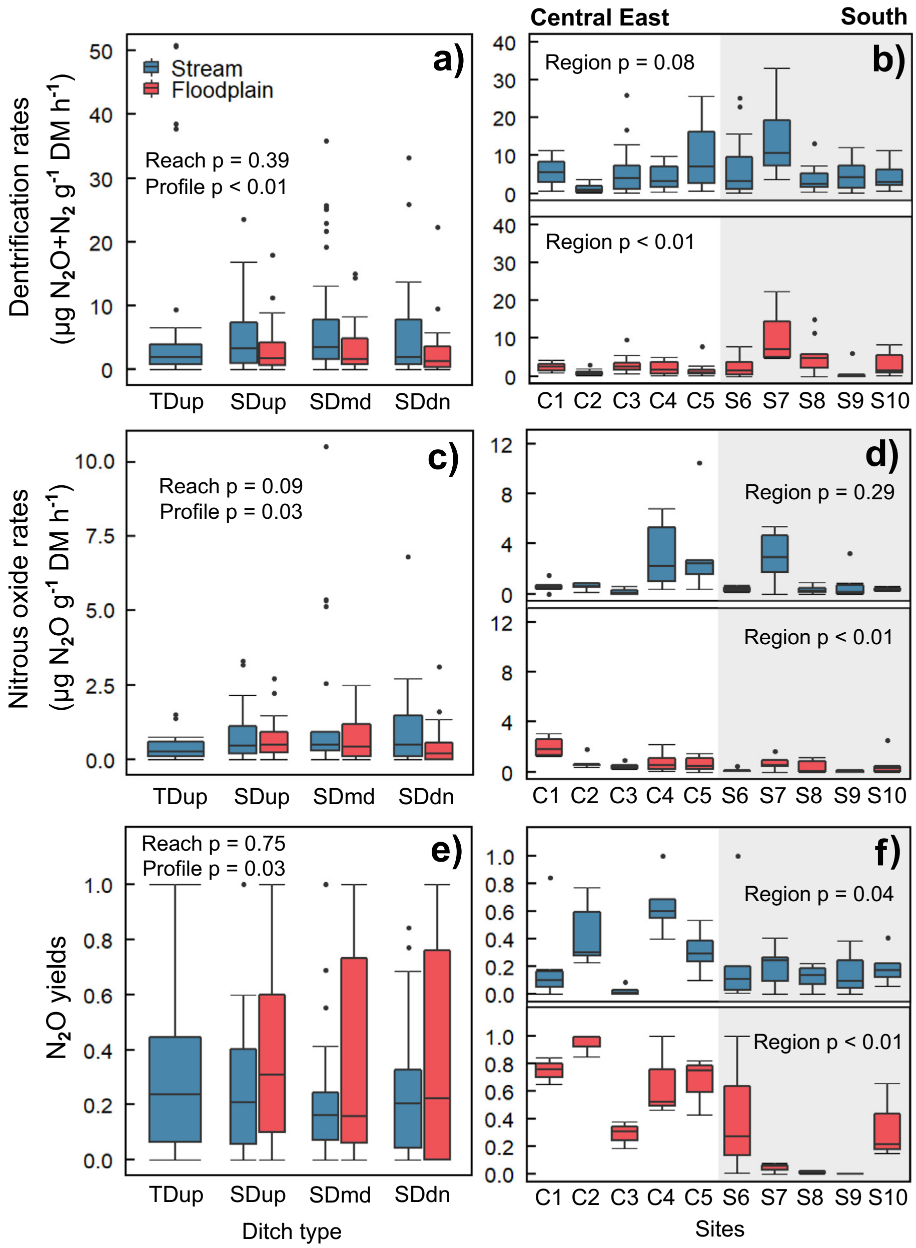

Fig. 3. Potential denitrification (PD) rates, potential N_2O rates and N_2O yields (N_2O:denitrification ratios) from sediments sampled between September 2020 and May 2021. PD rates are shown a) longitudinally in trapezoidal ditch (TDup) and upstream (SDup), middle (SDmd) and downstream (SDdn) of remediated ditches and for b) sites in Central East (C1-C5) and South regions (C6-S10). N_2O rates are shown c) longitudinally and for d) sites in Central East and South regions and N_2O yields are shown e) longitudinally and for f) sites in Central East and South regions. Box colors denote stream and floodplain sediments and *p*-values of two-way or one-way ANOVAs are shown within each panel.

The N_2O rates in stream sediments correlated with C and N content in sediments, but were not predicted by stream chemistry, similarly to denitrification (Fig. 4c; Fig. S6). The proportion of N_2O as an end-product was explained by smaller DOM particle-sizes in stream water (Fig. S6), and was not correlated with the composition of predictor variables (Fig. 4c). In floodplains, N_2O rates also correlated with high C and N content in sediments, and that higher total vegetation and grass cover suppressed N_2O rates (Fig. 4d; Fig. S6). Nitrous oxide yields were predicted by changes in stream chemistry, especially low NO_3^--N and high DOC concentrations as well as high clay content and low proportions of agricultural land use (Fig. 4d; Fig. S6). Although floodplain elevation did not affect N_2O rates, the N_2O yields increased with higher floodplain elevations, in direct contrast to the effects on denitrification (Fig. S6). Despite the positive correlation between N_2O yields and floodplain elevation, there was no significant effect from inundation frequency (Fig. S6). Allochthonous C (FI), pH and DO also predicted higher N_2O yields in floodplain sediments, suggesting that C availability and redox states play an important role for regulating N_2O yields.

3.5. Potential impact of denitrification on water quality

Flow-weighted NO_3^--N concentrations were reduced from upstream to downstream of remediated ditches (ANOVA, $F_{1,220} = 4.84$, $p = 0.03$), indicating that denitrification can contribute to N removal. The reduction was significant both for all estimated flows and lower flows within the range of measured discharge and stage (Fig. S7). The pattern of increasing Q_{50} from up- to downstream also confirmed that additional drainage water entered along remediated reaches (Table. S1). However, there were no

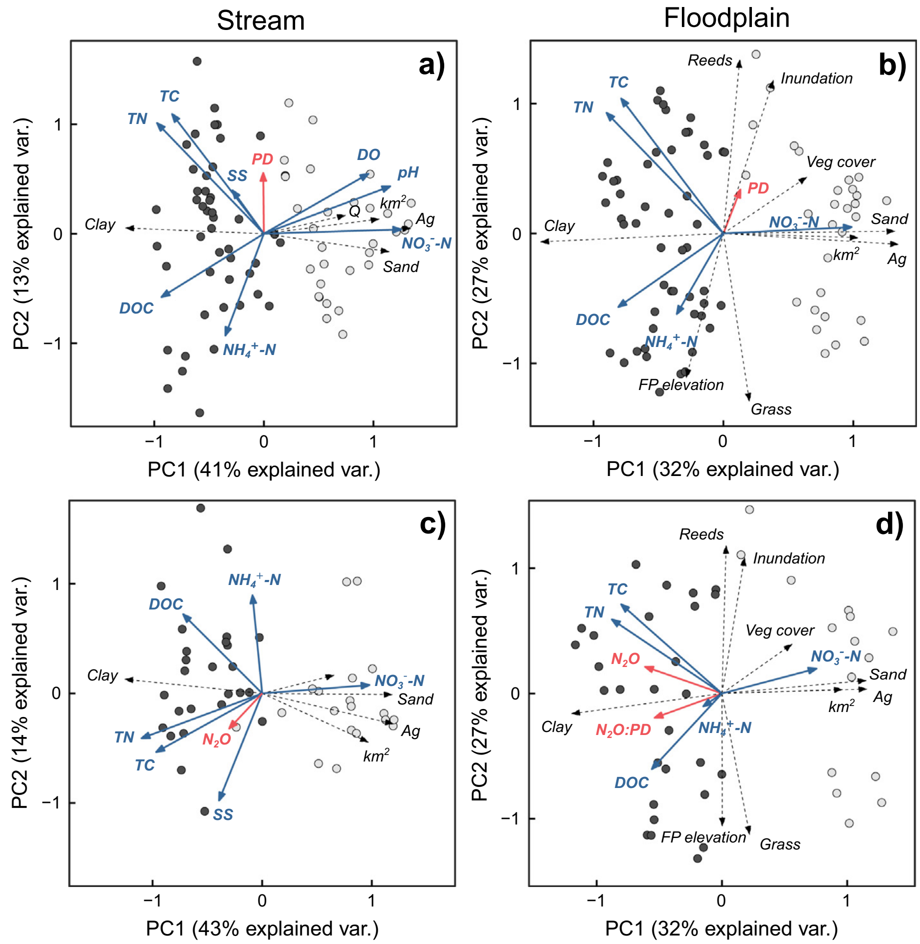

Fig. 4. Principal component analysis (PCA) of predictor variables (water and sediment chemistry, catchment and ditch properties) in stream (a, c) and floodplain sediments (b, d). Correlation with denitrification rates (PD) in a) stream sediments and b) floodplain sediments. Correlation with N_2O rates and N_2O yields (N_2O:PD) in c) stream sediments and d) floodplain sediments. The influence of predictor variables on sample distributions are indicated by blue (water, sediment) and dashed (catchments properties) vectors. PD, N_2O and N_2O:PD that are significantly correlated ($p < 0.05$) with the ordinations are shown as red vectors, with length proportional to the strength of the correlation. Circle color denote samples from Central East (black circles) and South (white circles). Sample sites with missing variables were removed from the analyses and descriptor variables were standardized to equal standard deviations. TC = total carbon, TN = total nitrogen, SS = suspended sediments, DOC = dissolved organic carbon, DO = dissolved oxygen, FP elevation = floodplain elevation, Ag = agricultural land use %, km^2 = Catchment area.

differences in absolute concentrations (Fig. 5a, c) and retention % (Fig. 5b, d) of NO_3^--N and NH_4^+-N in stream water, indicating that additional NO_3^--rich inputs along remediated ditches can mask the effect from denitrification.

Despite higher variation in retention of NO_3^--N and NH_4^+-N concentrations during low flow ($Q_{0–25}$) and base flow (Q_{25}-Inundation), there were no significant differences between trapezoidal and remediated ditches for any of the three flow regimes between April 2020 and June 2021 (Fig. 5b, d). The only site with significantly higher retention along remediated ditches compared to trapezoidal ditches was site S9 (ANOVA, $F_{1,23} = 9.02$, $p < 0.05$).

4. Discussion

4.1. Regional differences in catchment controls of denitrification

The higher capacity for denitrification in South confirmed that catchments with the highest NO_3^--inputs had the largest NO_3^- removal. This pattern can be attributed to the combination of high agricultural land use proportions and naturally well-drained soils (loam and sandy loam) in South, compared to the mixed land use and clay dominated soils in Central East. These soil related differences expand on previous studies, studying effects of denitrification, which have focused on catchments with loamy soils (Mahl et al., 2015; Roley et al., 2012; Speir et al., 2020; Powell and Bouchard, 2010). Although N_2O production rates followed denitrification in both stream and floodplain sediments, the relative production of N_2O did not increase under higher stream NO_3^- concentrations, observed particularly in the South. Contrasting responses in N_2O yields to high NO_3^- concentrations have been reported previously, with either no influence (Beaulieu et al., 2011) or positive effects on N_2O yields (Schade et al., 2016). The measured potential N_2O yields were higher than previous in situ and potential estimates (Beaulieu et al., 2011; Dee and Tank, 2020; Weigelhofer et al., 2013). This could be due to methodological differences in incubation period and substrate concentrations. For example, shorter incubation times can prematurely terminate N_2O reduction, resulting in overestimated N_2O rates (Weier et al., 1993). Further, potential denitrification rates overestimate in situ production rates in sediments (Mahl et al., 2015; Roley et al., 2012), which thereby restricts accurate scaling of these rates to ecosystem level. Nevertheless, substrate amended incubations provide a comparable basis for delineating the influence of sediment and water chemistry on N removal. Regardless of the differences in relation to in situ rates, our potential rates demonstrate a consistent differentiation between stream and floodplains as well as regions, driven by catchment-specific controls.

There was a complex interplay between denitrification and NO_3^-, C availability and redox states, where low NO_3^- concentrations coincided

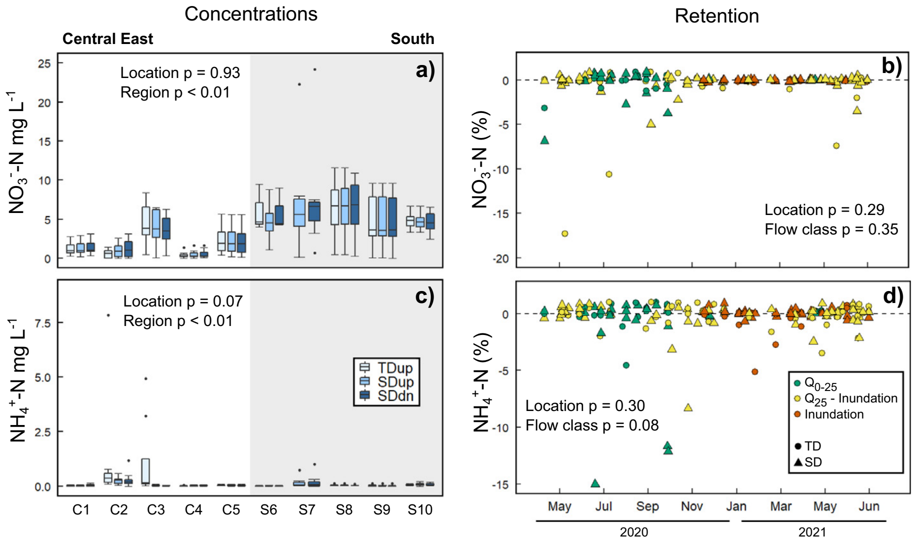

Fig. 5. Water concentrations of nitrogen species and nitrogen removal from April 2020 to June 2021. a) NO_3^--N and b) NH_4^+-N concentrations of all sites at upstream the trapezoidal ditches (TDup), and upstream (SDup) and downstream (SDdn) remediated ditches. Seasonal retention of concentrations of c) NO_3^--N and d) NH_4^+-N concentrations along trapezoidal ditches (TD) and remediated ditches (SD). Retention of concentrations of nitrogen species was calculated as $C_{Ret} = (C_{Upstream-} - C_{Downstream}) / C_{Upstream}$ and was divided into the three flow regimes, Q_{0-25}, Q_{25}-Inundation and Inundation. *P*-values of two-way ANOVAs are shown within each panel.

with recalcitrant DOM compounds, low pH and oxic conditions in floodplains of Central East that concomitantly suppressed denitrification and increased N_2O rates and yields. The negative correlation between N_2O yields and FI in floodplain sediments, together with higher ratios of humified (HIX) and allochthonous (FI) DOM in Central East ditches, indicated that a shift from labile DOM towards recalcitrant DOM increased N_2O yields. This builds on previous findings that labile DOM fractions control denitrification activity (Barnes et al., 2012), and suggests that labile DOM do not only limit denitrifiers but also increase incomplete denitrification. Similar controls were found for N_2O rates, although non-significant, which suggests that N_2O yields are not only a product of denitrification efficiency, but are also regulated by the capacity for N_2O production. This is consistent with recent work showing that the production rate of N_2O increased in an estuary when the ratio of allochthonous DOM and NO_3^- were higher (Aalto et al., 2021). Also differences in the composition of microbial communities could explain differences in N_2O yield or N_2O production rates (Jones et al., 2022; Philippot et al., 2011), but this was not considered in the present study. Although the effect of land use and soil type covaried, we conclude that the catchment characteristics are important controls for both of NO_3^- and labile C availability, which ultimately promote higher N removal in remediated ditches without the expense of higher N_2O production.

4.2. Stream denitrification

The small temporal variation in denitrification rates in stream sediments were mainly limited by C and N content in the sediments and decoupled from hydrology and water chemistry. Although in situ denitrification rates in agricultural stream sediments are commonly limited by stream NO_3^- (Mahl et al., 2015; Mulholland et al., 2009; Roley et al., 2012), our results suggests that the enzymatic activity of denitrifiers is instead controlled by the organic matter content and its delivery of C compounds, similar to what has been observed in an estuary (Aalto et al., 2021). A dependency on the mineralization of organic matter and thereby release of electron donors could also explain the small temporal variation observed in denitrifications rates in these sediments. The increase in organic matter quantity and FBOM substrates along remediated stream beds suggests that the true effect size of denitrification is in fact higher in remediated ditches compared to trapezoidal ditches, as C consistently limited denitrification in the stream sediments. The C accumulation in remediated ditches can be explained by reduced water velocities in remediated ditches that promote primary production and increased sedimentation of senescing vegetation. The trend of decreasing flashiness from upstream to downstream of remediated ditches further indicates a higher potential for sediment deposition in lower parts of the reaches. Although this may result in higher stream sediment denitrification, instream deposition of fine sediments is expected to negatively affect drainage capacity (Landwehr and Rhoads, 2003) and benthic fauna (Piggott et al., 2015). These findings imply that the inset channels of the remediated ditches have not reached fluvial equilibrium, as observed in other remediated ditches (Krider et al., 2017; Mahl et al., 2015), and may require occasional channel dredging to maintain drainage function.

4.3. The role of floodplains in denitrification

Denitrification and N_2O production were concomitantly limited by organic matter, but lower C:N ratios in stream water decreased the relative proportion of N_2O production. Denitrification in floodplain sediments contributed to on average 33 % of total denitrification in remediated ditches, reflecting the potential when floodplains are activated by anoxic conditions (Dee and Tank, 2020; Speir et al., 2020). Although denitrification in floodplain sediments, as opposed to stream sediments, responded to changes in water chemistry and increased in spring when inundation was more pronounced, the rates did not exceed that of stream sediments even during inundation. The proportion of denitrification in floodplain vs. stream sediments from our study falls within the range of reported ratios between 12 and 60 % (Mahl et al., 2015; Roley et al., 2012; Speir et al., 2020; but see Powell and Bouchard, 2010), which underlines the large variation in N removal capacity of floodplains across seasons and sites. Moreover, the observed increase in denitrification with floodplain age up to eight years supports previous findings that floodplain sediments mature over time via organic matter accumulation and higher C availability (Speir et al., 2020). Yields were consistently higher in floodplains and exceeded that of stream sediments by >50 %, as the relative proportion of N_2O production increased with lower total denitrification activity. This shows that constructed floodplains with fluctuating redox conditions and lower potential for denitrification can favor incomplete denitrification and a higher proportion of harmful N_2O emissions, as previously demonstrated (Dee and Tank, 2020). On the other hand, the production rates of N_2O were lower in floodplain sediments, meaning that they contribute less N_2O to the atmosphere in absolute quantities in relation to stream sediments. Nevertheless, remediated ditches as a system composed of both stream and floodplain sediments emit more N_2O and therefore have a higher impact on climate warming than trapezoidal ditches.

In contrast to comparable studies with substrate limited denitrification assays (Mahl et al., 2015; Roley et al., 2012; Speir et al., 2020), our potential denitrification rates in the floodplain sediments were better predicted by stream NO_3^- than sediment C, suggesting that denitrifier activity was controlled by periodic inundation events that deliver NO_3^- rather than long-term C accumulation in the sediment. However, reed species cover predicted denitrification activity, as in other wetlands (Ruiz-Rueda et al., 2009) where reeds fuel denitrification by providing labile C through rhizodeposition (Hernandez and Mitsch, 2007). The negative correlation between both N_2O rates and yields and vegetation cover further suggests that the presence of labile C, in contrast to more recalcitrant C, promote complete denitrification and suppress N_2O production, especially in combination with higher NO_3^- availability and prevalent anoxic conditions in the sediments. Here, floodplain elevation was a more reliable proxy for anoxic conditions than inundation frequency and discharge. In addition to stream overflow, the water content in floodplain sediments is controlled by the groundwater table and since floodplain elevation indicates the distance to this level, it also indicates the probability of water saturation in the absence of inundation. Nonetheless, continuous inundation is not favorable as sustained anaerobic conditions can shift NO_3^- reduction towards dissimilatory nitrate reduction resulting in recycling instead of removal of N and thereby hindering improvement of water quality (Aalto et al., 2021). Since N removal in floodplains and the relative suppression of N_2O depend on both anoxic conditions and the delivery of NO_3^- and C compounds, we emphasize the importance of floodplain elevations that can accommodate sufficient periodic inundation (between 0.25 and 0.55 m in this study) as a key control to enhance denitrification.

4.4. Implications for water quality management at catchment scale

The additional denitrification activity in remediated ditches from floodplain sediments can lead to reductions in flow-weighted NO_3^- concentrations, but due to the absence of upstream flow data we could not test if this was true also for trapezoidal ditches. No reductions were observed in absolute concentrations which suggests that there was a substantial input of NO_3^--rich groundwaters along remediated ditches. This was corroborated by consistently high base flow indices across all ditches, implying a predominant mode of groundwater-driven hydrology due to increased hydrological connectivity between floodplains and the hyporheic zone. Due to limited flow measurements during higher flows, there were uncertainties in extrapolated discharge-stage rating curves in these ranges. However, all ditch hydrology was dominated by base flows which reduced the sensitivity towards over- or underestimation of high flows. Previously, floodplains have mainly been conceptualized as reservoirs for stream water overflow (Mahl et al., 2015; Speir et al., 2020), but as they extend the riparian corridor, it is important to also acknowledge their function as conduits for groundwater recharge from the hyporheic zone. As NO_3^- concentrations in groundwater often exceed that of stream water due to long-term crop fertilization (Puckett et al., 2011; Schilling and Zhang, 2004), it is likely that NO_3^--rich groundwater inputs masked the effect of NO_3^- removal from sediment denitrification. Due to the high dependency on catchment-governed lag times of NO_3^- delivery (Basu et al., 2022), we emphasize that remediated ditches themselves are not able to remove legacy NO_3^-, and other in-field measures are required to target these sources. In these catchments, the improvements in water quality can take time to be realized. Although the magnitude of drainage and groundwater NO_3^- inputs may greatly exceed that of denitrification removal rates, floodplains still remain relevant as proximal drivers for denitrification in the riparian zone, permanently removing NO_3^- from both the water column and groundwater (Sigler et al., 2022).

Our measured retention of NO_3^- concentrations were consistent with previous reported changes between −5 to 3 % (Davis et al., 2015; Hodaj et al., 2017; Roley et al., 2012). In contrast, reach-scale estimates of N removal based on denitrification rates in remediated ditches ranged between 27 and 70 % (Hanrahan et al., 2018; Speir et al., 2020), which highlights the challenges associated with accurate N flux mass balancing, especially accounting for tile drainage and groundwater inputs and contributions from legacy N stores.

In combination with catchment typology, the floodplain elevations also impacted denitrification and N_2O yield, suggesting an optimal elevation between 0.25 and 0.55 m to ensure sufficient anoxic conditions and thereby enhancing denitrification while suppressing the relative contribution of N_2O. As lower floodplain elevations were mainly designed in South catchments, we argue that there is a synergy between hydrologically connected floodplains together with high concentrations of NO_3^- and labile C that promotes complete denitrification. The higher floodplain elevations in Central East, with lower inundation frequencies, was motivated by a stronger focus on P mitigation and to maintain floodplain stability (Lindmark et al., 2013). Accordingly, Trentman et al. (2020) indicated that floodplain inundation lasting <8 days maintains oxidative conditions in sediments and thereby promotes P adsorption. However, this also reveals a potential trade-off between N and P mitigation with remediated ditches: lower floodplains and prolonged inundation can lead to sustained reducing conditions and an increased risk for the release of chemically adsorbed P (Trentman et al., 2020). As a measure for targeting N removal, it is important to be aware that the implementation of remediated ditches in clay catchments can increase the risk for N_2O emissions.

The role of denitrification as the primary N sink in aquatic ecosystems is debated and has been argued to be of only minor importance, activated mainly in hotspots of low-order streams during base flow and rarely exceeding 10 % of total N retention (Weigelhofer et al., 2013). Yet, others have shown that longer transient storage times can play a crucial role for denitrification to increase N removal and also suppress N_2O emissions (Quick et al., 2016; Zarnetske et al., 2011). Despite the wealth of information about reactivity rates, our knowledge is still limited about how the extended river corridor, e.g., through constructed floodplains, influences hyporheic exchange and transient storage of solutes, needed to determine both water and N residence times. In addition, tracing of isotopic N species (Zarnetske et al., 2011) and high-frequency monitoring of stream metabolism and NO_3^- (Jarvie et al., 2018) could offer an improved mechanistic understanding of the balance between denitrification and autotrophic uptake as well as the role of autotroph mediation of denitrification in floodplains. Modeling studies that account for both NO_3^- and water mass balance could further be used to disentangle catchment background effects, such as travel time for legacy N processes, from mitigation-specific effects (Chang et al., 2021; Ilampooranan et al., 2019).

5. Conclusion

Constructed floodplains of remediated ditches contributed to higher reach-scale NO_3^- removal, but did not reduce absolute NO_3^- concentrations. This was due to confounding catchment processes such as drainage and groundwater inputs along reaches that likely obscured reductions in stream NO_3^- concentrations downstream of remediated ditches. Remediated ditches in high NO_3^--input catchments, associated with loamy soils and high agricultural land use proportions, had the highest potential for both reducing NO_3^- export and N_2O emissions. We further confirmed that lower floodplain elevations and higher vegetation cover enhanced denitrification while suppressing N_2O yields. Overall, floodplains had lower N_2O production rates compared to stream sediments, but the periodic inundation of floodplains imposes a risk for elevated N_2O yields by suppressing total denitrification.

To realize the potential for NO_3^- removal with remediated ditches, it is critical to engineer the dimensions of floodplains for sufficient inundation as well as selecting appropriate placement in high NO_3^--input catchments. In addition, the multiple water quality benefits of remediated ditches, for example, flood prevention, bank stability and P mitigation also need to be considered during implementation to achieve a holistic solution for reducing eutrophication and erosion. Headwater agricultural catchments are under increasing pressures from legacy N stores and more frequent spells of flooding and drought. This leads to accelerating N losses and reduces the efficacy of single mitigation measures, such as remediated ditches. Thus, we further recommend a suite of complementary measures in these landscapes and an evaluation of potential water quality-climate impact tradeoffs before their implementation.

CRediT authorship contribution statement

Lukas Hallberg: Conceptualization, Methodology, Data curation, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Sara Hallin:** Methodology, Formal analysis, Writing – review & editing. **Magdalena Bieroza:** Conceptualization, Methodology, Formal analysis, Writing – review & editing, Funding acquisition.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2022.156513.

References

Aalto, S.L., Asmala, E., Jilbert, T., Hietanen, S., 2021. Autochthonous organic matter promotes DNRA and suppresses N2O production in sediments of the coastal Baltic Sea. Estuar. Coast. Shelf Sci. 255, 107369. https://doi.org/10.1016/j.ecss.2021.107369.

Abbott, B.W., Gruau, G., Zarnetske, J.P., Moatar, F., Barbe, L., Thomas, Z., Fovet, O., Kolbe, T., Gu, S., Pierson-Wickmann, A., Davy, P., Pinay, G., 2018. Unexpected spatial stability of water chemistry in headwater stream networks. Ecol. Lett. 21 (2), 296–308. https://doi.org/10.1111/ele.12897.

Andersen, J.H., Carstensen, J., Conley, D.J., Dromph, K., Fleming-Lehtinen, V., Gustafsson, B.G., Josefson, A.B., Norkko, A., Villnäs, A., Murray, C., 2017. Long-term temporal and spatial trends in eutrophication status of the Baltic Sea: eutrophication in the Baltic Sea. Biol. Rev. 92 (1), 135–149. https://doi.org/10.1111/brv.12221.

Baker, D.B., Richards, R.P., Loftus, T.T., Kramer, J.W., 2004. A new flashiness index: characteristics and applications to midwestern rivers and streams1. JAWRA J. Am. Water Resour. Assoc. 40 (2), 503–522. https://doi.org/10.1111/j.1752-1688.2004.tb01046.x.

Baker, D.W., Bledsoe, B.P., Price, J.M., 2012. Stream nitrate uptake and transient storage over a gradient of geomorphic complexity, north-Central Colorado, USA. Hydrol. Process. 26 (21), 3241–3252. https://doi.org/10.1002/hyp.8385.

Barnes, R.T., Smith, R.L., Aiken, G.R., 2012. Linkages between denitrification and dissolved organic matter quality, Boulder Creek watershed, Colorado. Journal of Geophysical Research: Biogeosciences 117 (G1). https://doi.org/10.1029/2011JG001749.

Basu, N.B., Van Meter, K.J., Byrnes, D.K., Van Cappellen, P., Brouwer, R., Jacobsen, B.H., Jarsjö, J., Rudolph, D.L., Cunha, M.C., Nelson, N., Bhattacharya, R., Destouni, G., Olsen, S.B., 2022. Managing nitrogen legacies to accelerate water quality improvement. Nat. Geosci. 15 (2), 97–105. https://doi.org/10.1038/s41561-021-00889-9.

Beaulieu, J.J., Tank, J.L., Hamilton, S.K., Wollheim, W.M., Hall, R.O., Mulholland, P.J., Peterson, B.J., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Dodds, W.K., Grimm, N.B., Johnson, S.L., McDowell, W.H., Poole, G.C., Valett, H.M., Arango, C.P., Bernot, M.J., Burgin, A.J., Schlesinger, W.H., 2011. Nitrous oxide emission from denitrification in stream and river networks. Proc. Natl. Acad. Sci. U. S. A. 108 (1), 214–219.

Bieroza, M.Z., Bol, R., Glendell, M., 2021. What is the Deal with the green Deal: will the new strategy help to improve european freshwater quality beyond the water framework Directive? Sci. Total Environ. 791, 148080. https://doi.org/10.1016/j.scitotenv.2021.148080.

Breitbarth, E., Mills, M., Friedrichs, G., Laroche, J., 2004. The bunsen gas solubility coefficient of ethylene as a function of temperature and salinity and its importance for nitrogen fixation assays. Limnol. Oceanogr. Methods 2. https://doi.org/10.4319/lom.2004.2.282.

Brink, K., Juhlin, L., Kuhlau, Å., 2012. Svärtaåprojektet. 2010–2012. Erfarenheter av praktiskt åtgärdsarbete i samarbete med lantbrukare i Svärtaåns avrinningsområde. Rapport 2013: 23. Länsstyrelsen Södermanlands län, pp. 1–44.

Chang, S.Y., Zhang, Q., Byrnes, D.K., Basu, N.B., Meter, K.J.V., 2021. Chesapeake legacies: the importance of legacy nitrogen to improving Chesapeake Bay water quality. Environ. Res. Lett. 16 (8), 085002. https://doi.org/10.1088/1748-9326/ac0d7b.

Conley, D.J., Paerl, H.W., Howarth, R.W., Boesch, D.F., Seitzinger, S.P., Havens, K.E., Lancelot, C., Likens, G.E., 2009. Controlling eutrophication: nitrogen and phosphorus. Science 323 (5917), 1014–1015. https://doi.org/10.1126/science.1167755.

Davis, R.T., Tank, J.L., Mahl, U.H., Winikoff, S.G., Roley, S.S., 2015. The influence of two-stage ditches with constructed floodplains on water column nutrients and sediments in agricultural streams. JAWRA J. Am. Water Resour. Assoc. 51 (4), 941–955. https://doi.org/10.1111/1752-1688.12341.

Dee, M.M., Tank, J.L., 2020. Inundation time mediates denitrification end products and carbon limitation in constructed floodplains of an agricultural stream. Biogeochemistry 149 (2), 141–158. https://doi.org/10.1007/s10533-020-00670-x.

Edzwald, J.K., Becker, W.C., Wattier, K.L., 1985. Surrogate parameters for monitoring organic matter and THM precursors. J. AWWA 77 (4), 122–132. https://doi.org/10.1002/j.1551-8833.1985.tb05521.x.

Fowler, D., Coyle, M., Skiba, U., Sutton, M.A., Cape, J.N., Reis, S., Sheppard, L.J., Jenkins, A., Grizzetti, B., Galloway, J.N., Vitousek, P., Leach, A., Bouwman, A.F., Butterbach-Bahl, K., Dentener, F., Stevenson, D., Amann, M., Voss, M., 2013. The global nitrogen cycle in the twenty-first century. Philos. Trans. R. Soc. B Biol. Sci. 368 (1621), 20130164. https://doi.org/10.1098/rstb.2013.0164.

Glibert, P.M., 2017. Eutrophication, harmful algae and biodiversity - challenging paradigms in a world of complex nutrient changes. Mar. Pollut. Bull. 124 (2), 591–606. https://doi.org/10.1016/j.marpolbul.2017.04.027.

Gustard, A., Bullock, A., Dixon, J.M., 1992. Low flow estimation in the United Kingdom. Institute of Hydrology.

Hanrahan, B.R., Tank, J.L., Dee, M.M., Trentman, M.T., Berg, E.M., McMillan, S.K., 2018. Restored floodplains enhance denitrification compared to naturalized floodplains in agricultural streams. Biogeochemistry 141 (3), 419–437. https://doi.org/10.1007/s10533-018-0431-4.

Hedin, J., Kivivuori, H., 2015. Tullstorpsåprojektet. Utvärdering. Tvåstegsdiken och kantavplaning sträckan Stora Markie-Stävesjö Ålholmens dikningsföretag. Rapport. Naturvårdsingenjörerna AB, pp. 1–22.

Hellman, M., Bonilla-Rosso, G., Widerlund, A., Juhanson, J., Hallin, S., 2019. External carbon addition for enhancing denitrification modifies bacterial community composition and affects CH4 and N2O production in sub-arctic mining pond sediments. Water Res. 158, 22–33. https://doi.org/10.1016/j.watres.2019.04.007.

Helms, J.R., Stubbins, A., Ritchie, J.D., Minor, E.C., Kieber, D.J., Mopper, K., 2008. Absorption spectral slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter. Limnol. Oceanogr. 53 (3), 955–969. https://doi.org/10.4319/lo.2008.53.3.0955.

Hernandez, M.E., Mitsch, W.J., 2007. Denitrification potential and organic matter as affected by vegetation community, wetland age, and plant introduction in created wetlands. J. Environ. Qual. 36 (1), 333–342. https://doi.org/10.2134/jeq2006.0139.

Hodaj, A., Bowling, L.C., Frankenberger, J.R., Chaubey, I., 2017. Impact of a two-stage ditch on channel water quality. Agric. Water Manag. 192, 126–137. https://doi.org/10.1016/j.agwat.2017.07.006.

Hornung, R.W., Reed, L.D., 1990. Estimation of average concentration in the presence of nondetectable values. Appl. Occup. Environ. Hyg. 5 (1), 46–51. https://doi.org/10.1080/1047322X.1990.10389587.

Huguet, A., Vacher, L., Relexans, S., Saubusse, S., Froidefond, J.M., Parlanti, E., 2009. Properties of fluorescent dissolved organic matter in the gironde estuary. Org. Geochem. 40 (6), 706–719. https://doi.org/10.1016/j.orggeochem.2009.03.002.

Ilampooranan, I., Van Meter, K.J., Basu, N.B., 2019. A race against time: modeling time lags in watershed response. Water Resour. Res. 55 (5), 3941–3959. https://doi.org/10.1029/2018WR023815.

Jarvie, H.P., Sharpley, A.N., Kresse, T., Hays, P.D., Williams, R.J., King, S.M., Berry, L.G., 2018. Coupling high-frequency stream metabolism and nutrient monitoring to explore biogeochemical controls on downstream nitrate delivery. Environ. Sci. Technol. 52 (23), 13708–13717. https://doi.org/10.1021/acs.est.8b03074.

Jones, C.M., Putz, M., Tiemann, M., Hallin, S., 2022. Reactive nitrogen restructures and weakens microbial controls of soil N2O emissions. Commun. Biol. 5 (1), 1–12. https://doi.org/10.1038/s42003-022-03211-4.

Krider, L., Magner, J., Hansen, B., Wilson, B., Kramer, G., Peterson, J., Nieber, J., 2017. Improvements in fluvial stability associated with two-stage ditch construction in Mower County, Minnesota. JAWRA J. Am. Water Resour. Assoc. 53 (4), 886–902. https://doi.org/10.1111/1752-1688.12541.

Landwehr, K., Rhoads, B.L., 2003. Depositional response of a headwater stream to channelization, east Central Illinois, USA. River Res. Appl. 19 (1), 77–100. https://doi.org/10.1002/rra.699.

Lebender, U., Senbayram, M., Lammel, J., Kuhlmann, H., 2014. Impact of mineral N fertilizer application rates on N2O emissions from arable soils under winter wheat. Nutr. Cycl. Agroecosyst. 100 (1), 111–120. https://doi.org/10.1007/s10705-014-9630-0.

Lindmark, P., Karlsson, L., Nordlund, J., 2013. Tvåstegsdiken - ett steg i rätt riktning? Rapport 2013:15. Jordbruksverket

Lintern, A., McPhillips, L., Winfrey, B., Duncan, J., Grady, C., 2020. Best management practices for diffuse nutrient pollution: wicked problems across urban and agricultural watersheds. Environ. Sci. Technol. 54 (15), 9159–9174. https://doi.org/10.1021/acs.est.9b07511.

Mahl, U.H., Tank, J.L., Roley, S.S., Davis, R.T., 2015. Two-stage ditch floodplains enhance N-removal capacity and reduce turbidity and dissolved P in agricultural streams. JAWRA J. Am. Water Resour. Assoc. 51 (4), 923–940. https://doi.org/10.1111/1752-1688.12340.

McKnight, D.M., Boyer, E.W., Westerhoff, P.K., Doran, P.T., Kulbe, T., Andersen, D.T., 2001. Spectrofluorometric characterization of dissolved organic matter for indication of precursor organic material and aromaticity. Limnol. Oceanogr. 46 (1), 38–48. https://doi.org/10.4319/lo.2001.46.1.0038.

Mulholland, P.J., Hall, R.O., Sobota, D.J., Dodds, W.K., Findlay, S.E.G., Grimm, N.B., Hamilton, S.K., McDowell, W.H., O'Brien, J.M., Tank, J.L., Ashkenas, L.R., Cooper, L.W., Dahm, C.N., Gregory, S.V., Johnson, S.L., Meyer, J.L., Peterson, B.J., Poole, G.C., Valett, H.M., Thomasn, S.M., 2009. Nitrate removal in stream ecosystems measured by 15N addition experiments: denitrification. Limnol. Oceanogr. 54 (3), 666–680. https://doi.org/10.4319/lo.2009.54.3.0666.

Ohno, T., 2002. Fluorescence inner-filtering correction for determining the humification index of dissolved organic matter. Environ. Sci. Technol. 36 (4), 742–746. https://doi.org/10.1021/es0155276.

Peuravuori, J., Pihlaja, K., 1997. Molecular size distribution and spectroscopic properties of aquatic humic substances. Anal. Chim. Acta 337 (2), 133–149. https://doi.org/10.1016/S0003-2670(96)00412-6.

Philippot, L., Andert, J., Jones, C.M., Bru, D., Hallin, S., 2011. Importance of denitrifiers lacking the genes encoding the nitrous oxide reductase for N2O emissions from soil. Glob. Chang. Biol. 17 (3), 1497–1504. https://doi.org/10.1111/j.1365-2486.2010.02334.x.

Piggott, J.J., Townsend, C.R., Matthaei, C.D., 2015. Climate warming and agricultural stressors interact to determine stream macroinvertebrate community dynamics. Glob. Chang. Biol. 21 (5), 1887–1906. https://doi.org/10.1111/gcb.12861.

Powell, K.L., Bouchard, V., 2010. Is denitrification enhanced by the development of natural fluvial morphology in agricultural headwater ditches? J. N. Am. Benthol. Soc. 29 (2), 761–772. https://doi.org/10.1899/09-028.1.

Powell, G.E., Ward, A.D., Mecklenburg, D.E., Jayakaran, A.D., 2007. Two-stage channel systems: part 1, a practical approach for sizing agricultural ditches. J. Soil Water Conserv. 62 (4), 277–286.

Puckett, L.J., Tesoriero, A.J., Dubrovsky, N.M., 2011. Nitrogen contamination of surficial aquifers—a growing legacy. Environ. Sci. Technol. 45 (3), 839–844. https://doi.org/10.1021/es1038358.

Quick, A.M., Reeder, W.J., Farrell, T.B., Tonina, D., Feris, K.P., Benner, S.G., 2016. Controls on nitrous oxide emissions from the hyporheic zones of streams. Environ. Sci. Technol. 50 (21), 11491–11500. https://doi.org/10.1021/acs.est.6b02680.

Rantz, S.E., 1982. Measurement and computation of streamflow. Measurement and Computation of Streamflow (USGS Numbered Series No. 2175; Water Supply Paper. 2175. U.S. G.P.O.. https://doi.org/10.3133/wsp2175.

Roley, S.S., Tank, J.L., Stephen, M.L., Johnson, L.T., Beaulieu, J.J., Witter, J.D., 2012. Floodplain restoration enhances denitrification and reach-scale nitrogen removal in an agricultural stream. Ecol. Appl. 22 (1), 281–297. https://doi.org/10.1890/11-0381.1.

Roley, S.S., Tank, J.L., Tyndall, J.C., Witter, J.D., 2016. How cost-effective are cover crops, wetlands, and two-stage ditches for nitrogen removal in the Mississippi River Basin? Water Resour. Econ. 15, 43–56. https://doi.org/10.1016/j.wre.2016.06.003.

RStudio Team, 2019. RStudio: Integrated Development for R. RStudio, Inc., Boston, MA. http://www.rstudio.com/.

Ruiz-Rueda, O., Hallin, S., Bañeras, L., 2009. Structure and function of denitrifying and nitrifying bacterial communities in relation to the plant species in a constructed wetland. FEMS Microbiol. Ecol. 67 (2), 308–319. https://doi.org/10.1111/j.1574-6941.2008.00615.x.

Schade, J.D., Bailio, J., McDowell, W.H., 2016. Greenhouse gas flux from headwater streams in New Hampshire, USA: patterns and drivers. Limnol. Oceanogr. 61 (S1), S165–S174. https://doi.org/10.1002/lno.10337.

Schilling, K., Zhang, Y.-K., 2004. Baseflow contribution to nitrate-nitrogen export from a large, agricultural watershed, USA. J. Hydrol. 295 (1), 305–316. https://doi.org/10.1016/j.jhydrol.2004.03.010.

Schindler, D.W., Carpenter, S.R., Chapra, S.C., Hecky, R.E., Orihel, D.M., 2016. Reducing phosphorus to curb lake eutrophication is a success. Environ. Sci. Technol. 50 (17), 8923–8929. https://doi.org/10.1021/acs.est.6b02204.

Sharpley, A., Jarvie, H.P., Buda, A., May, L., Spears, B., Kleinman, P., 2013. Phosphorus legacy: overcoming the effects of past management practices to mitigate future water quality impairment. J. Environ. Qual. 42 (5), 1308–1326. https://doi.org/10.2134/jeq2013.03.0098.

Shatwell, T., Köhler, J., 2019. Decreased nitrogen loading controls summer cyanobacterial blooms without promoting nitrogen-fixing taxa: long-term response of a shallow lake. Limnol. Oceanogr. 64 (S1), S166–S178. https://doi.org/10.1002/lno.11002.

Sigler, W.A., Ewing, S.A., Wankel, S.D., Jones, C.A., Leuthold, S., Brookshire, E.N.J., Payn, R.A., 2022. Isotopic signals in an agricultural watershed suggest denitrification is locally intensive in riparian areas but extensive in upland soils. Biogeochemistry https://doi.org/10.1007/s10533-022-00898-9.

SMHI, 2021. Ladda ner meteorologiska observationer. Swedish Meteorological and Hydrological Institute. https://www.smhi.se/klimatdata/meteorologi/ladda-ner-meteorologiska-observationer/#param=precipitation24HourSum,stations=all,stationid=85240.

Smith, D.R., Livingston, S.J., Zuercher, B.W., Larose, M., Heathman, G.C., Huang, C., 2008. Nutrient losses from row crop agriculture in Indiana. J. Soil Water Conserv. 63 (6), 396–409. https://doi.org/10.2489/jswc.63.6.396.

Speir, S.L., Tank, J.L., Mahl, U.H., 2020. Quantifying denitrification following floodplain restoration via the two-stage ditch in an agricultural watershed. Ecol. Eng. 155, 105945. https://doi.org/10.1016/j.ecoleng.2020.105945.

Tank, J.L., Speir, S.L., Sethna, L.R., Royer, T.V., 2021. The case for studying highly modified agricultural streams: farming for biogeochemical insights. Limnol. Oceanogr. Bull. 30 (2), 41–47. https://doi.org/10.1002/lob.10436.

Trentman, M.T., Tank, J.L., Jones, S.E., McMillan, S.K., Royer, T.V., 2020. Seasonal evaluation of biotic and abiotic factors suggests phosphorus retention in constructed floodplains in three agricultural streams. Sci. Total Environ. 729, 138744. https://doi.org/10.1016/j.scitotenv.2020.138744.

Vahtera, E., Conley, D.J., Gustafsson, B.G., Kuosa, H., Pitkänen, H., Savchuk, O.P., Tamminen, T., Viitasalo, M., Voss, M., Wasmund, N., Wulff, F., 2007. Internal ecosystem feedbacks enhance nitrogen-fixing cyanobacteria blooms and complicate management in the Baltic Sea. Ambio 36 (2/3), 186–194.

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

Västilä, K., Väisänen, S., Koskiaho, J., Lehtoranta, V., Karttunen, K., Kuussaari, M., Järvelä, J., Koikkalainen, K., 2021. Agricultural water management using two-stage channels: performance and policy recommendations based on northern European experiences. Sustainability 13 (16), 9349. https://doi.org/10.3390/su13169349.

Weier, K.L., Doran, J.W., Power, J.F., Walters, D.T., 1993. Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. Soil Sci. Soc. Am. J. 57 (1), 66–72. https://doi.org/10.2136/sssaj1993.03615995005700010013x.

Weigelhofer, G., Welti, N., Hein, T., 2013. Limitations of stream restoration for nitrogen reduction in agricultural headwater streams. Ecol. Eng. 60, 224–234. https://doi.org/10.1016/j.ecoleng.2013.07.057.

Wiström, D., Lindberg, G., 2016. Havsmiljö Gamlebyviken del 3 Övergödningen som en resurs - Slutrapport. Västerviks kommun, pp. 1–29.

Wollheim, W.M., Bernal, S., Burns, D.A., Czuba, J.A., Driscoll, C.T., Hansen, A.T., Hensley, R.T., Hosen, J.D., Inamdar, S., Kaushal, S.S., Koenig, L.E., Lu, Y.H., Marzadri, A., Raymond, P.A., Scott, D., Stewart, R.J., Vidon, P.G., Wohl, E., 2018. River network saturation concept: factors influencing the balance of biogeochemical supply and demand of river networks. Biogeochemistry 141 (3), 503–521. https://doi.org/10.1007/s10533-018-0488-0.

Wolman, M.G., 1954. A method of sampling coarse river-bed material. Trans. Am. Geophys. Union 35, 951–956. https://doi.org/10.1029/TR035i006p00951.

Zarnetske, J.P., Haggerty, R., Wondzell, S.M., Baker, M.A., 2011. Dynamics of nitrate production and removal as a function of residence time in the hyporheic zone. Journal of geophysical research. Biogeosciences 116 (G1). https://doi.org/10.1029/2010JG001356.