



Isotopic signals in an agricultural watershed suggest denitrification is locally intensive in riparian areas but extensive in upland soils

W. A. Sigler[✉] · S. A. Ewing[✉] ·
S. D. Wankel[✉] · C. A. Jones[✉] · S. Leuthold ·
E. N. J. Brookshire[✉] · R. A. Payn[✉]

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Abstract Nitrogen loss from cultivated soils threatens the economic and environmental sustainability of agriculture. Nitrate (NO_3^-) derived from nitrification of nitrogen fertilizer and ammonified soil organic nitrogen may be lost from soils via denitrification, producing dinitrogen gas (N_2) or the greenhouse gas nitrous oxide (N_2O). Nitrate that accumulates in soils is also subject to leaching loss, which can degrade water quality and make NO_3^- available

for downstream denitrification. Here we use patterns in the isotopic composition of NO_3^- observed from 2012 to 2017 to characterize N loss to denitrification within soils, groundwater, and stream riparian corridors of a non-irrigated agroecosystem in the northern Great Plains (Judith River Watershed, Montana, USA). We find evidence for denitrification across these domains, expressed as a positive linear relationship between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- , as well as increasing $\delta^{15}\text{N}$ values with decreasing NO_3^- concentration. In soils, isotopic evidence of denitrification was present during fallow periods (no crop growing), despite net accumulation of NO_3^- from the nitrification of ammonified soil organic nitrogen. We combine previous results for soil NO_3^- mass balance with $\delta^{15}\text{N}$ mass balance to estimate denitrification rates in soil relative to groundwater and streams. Substantial denitrification from soils during fallow periods may be masked by nitrification of ammonified soil organic nitrogen, representing a hidden loss of soil organic nitrogen and an under-quantified flux of N to the atmosphere. Globally, cultivated land spends ca. 50% of time in a fallow condition; denitrification in fallow soils may be an overlooked but globally significant source of agricultural N_2O emissions, which must be reduced along-side other emissions to meet Paris Agreement goals for slowing global temperature increase.

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W. A. Sigler (✉) · S. A. Ewing · C. A. Jones ·
S. Leuthold · E. N. J. Brookshire · R. A. Payn
Land Resources and Environmental Sciences, Montana
State University Bozeman, Leon Johnson Hall Room 334,
Bozeman, MT 59717, USA
e-mail: asigler@montana.edu

W. A. Sigler · C. A. Jones
Montana State University Extension, Montana State
University, Bozeman, MT 59717, USA

S. D. Wankel
Department of Marine Chemistry and Geochemistry,
Woods Hole Oceanographic Institution, Woods Hole,
MA 02540, USA

S. Leuthold
Soil and Crop Sciences Department, Colorado State
University, Fort Collins, CO 80524, USA

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Introduction

Over the last ca. 150 years, anthropogenic fixation of dinitrogen (N_2) gas into reactive N (N_r) has increased by an order of magnitude (annual total mass estimates of 15 Tg N in 1860 to 165 Tg N in 2000; Galloway et al. 2003). Approximately 85% of N_r fixed by humans is used to produce fertilizer for crop production. However, global-scale fertilization has also resulted in a cascade of disruptive side effects on planetary systems (Galloway et al. 2003; Erisman et al. 2008; Rockstrom et al. 2009). Nitrogen fertilizer is typically applied to agricultural soils in a reduced form such as ammonium or urea, which is subject to biogeochemical transformations and loss from soil that compromise the goal of N_r delivery to plants. The generally aerobic conditions common in cultivated soils favor oxidation of reduced N compounds to nitrate (NO_3^-), which is susceptible to export via leaching due to its high solubility and limited potential to sorb to soils (Sparks 2003). Nitrate often dominates the N transported through groundwater and surface water flows and is a primary agent of water quality degradation in aquifers, river networks, and estuaries (Vitousek et al. 1997; Caraco and Cole 1999; Goolsby et al. 1999; Smith 2003; Puckett et al. 2011; Tesoriero et al. 2013). While the need to reduce NO_3^- losses is well recognized, human activity in many systems has resulted in large surplus N storage in soils (Sebilo, et al. 2013; Van Meter et al. 2016), vadose zones (Ascott et al. 2017), and groundwater (Vautier et al. 2021), suggesting water quality response will likely lag behind any management to reduce N inputs (Ehrhardt et al. 2019).

Microbial denitrification is the primary means by which N_r is returned to the non-reactive atmospheric N_2 pool, but this process can also produce the greenhouse gas N_2O (ratio for major river basins in France = 0.015 ± 0.05 ; Billen et al. 2020). Soils and freshwater environments contribute about equally to the 40% of global denitrification that is non-oceanic (groundwater, lakes, rivers; Seitzinger et al. 2006). Excluding surface water, soils have been estimated to host ca. 70% of total terrestrial denitrification (96 Tg N/y), underscoring the importance of their role in global denitrification (Bouwman et al. 2013). Perhaps less understood is the role soils play in the fraction of terrestrial denitrification hosted by groundwater (25%) and riparian areas (5%), due to leaching losses

from soils that deliver NO_3^- to those downstream domains (Goolsby et al. 1999; Bouwman et al. 2013). The growing importance of this central role of soils is evident from a 70% increase in the global soil N budget surplus (inputs minus withdrawal by plants) over the last century (118–202 Tg/y from 1900 to 2000), with parallel increases in terrestrial denitrification (52–96 Tg/y) equating to ca. 45% of the surplus (Bouwman et al. 2013).

Though the general controls on denitrification in soils are well understood (NO_3^- supply, anoxia and organic carbon availability; Del Grosso et al. 2000), specific predictions of denitrification rates across space and time are hampered by a poor understanding of the influence of heterogeneity within the soil environment (Firestone and Davidson 1989; Schlüter et al. 2019). Soils commonly host nitrifying conditions adjacent in space and/or time to denitrifying conditions, and accordingly can support high denitrification rates by providing an abundant supply of NO_3^- and labile C to denitrifying bacterial communities. An abundance of dissolved oxygen (DO) as a more energetically favorable electron acceptor for bacterial metabolism limits denitrification in soil, and DO concentrations are generally lower in soils with higher water content (Smith et al. 1997), though oxygen limited zones may occur within structural units even in well drained soils (Ewing et al. 2006). When not suppressed by toxic conditions, the availability of electron donors and NO_3^- also limit rates of denitrification (Firestone and Davidson 1989). The abundance of organic carbon is the most common limitation on electron donor availability, though the abundance of reduced Fe and S chemical species may be important in systems or zones depleted of labile organic matter (Kolbe et al. 2019; Bochet et al. 2020). High spatial and temporal variability in DO, organic carbon, and NO_3^- hinder direct quantification of denitrification rates, along with difficulty in measuring N_2 production due to the high background concentration of N_2 in the environment (Groffman et al. 2006).

Overcoming these methodological difficulties is perhaps most pressing for the world's croplands, which generate the vast majority of anthropogenic N_2O emissions (Tian et al. 2019). Cropland management to augment N_r (via fertilization) and water (via irrigation and/or crop rotation) availability for crops, can have the unintended consequence of increased leaching and denitrification. Numerous studies have

examined denitrification in irrigated agricultural soils, where anthropogenic controls on water-mediated rates of denitrification are directly evident (Rolston et al. 1982; DeKlein and VanLogtestijn 1996; Scheer et al. 2008; Liu et al. 2011). Studies of the controls on denitrification in non-irrigated systems are much less common, despite the fact that non-irrigated agriculture represents about 80% of global cultivated land area (Siebert et al. 2005; Foley et al. 2011) and has equal or greater challenges with N_r use efficiency. Furthermore, research in the context of non-irrigated agriculture has primarily been conducted in relatively wet climates (>0.5 m annual precipitation; Becker et al. 2007; Sander et al. 2014; Wells et al. 2014; Vazquez et al. 2019), with semi-arid landscapes receiving less attention (Barton et al. 2013), despite 50% of global cultivated land occurring in semi-arid regions (Safriel and Adeel 2005).

Just as water is applied to augment precipitation in irrigated systems, summer fallow periods (suppression of plant growth with herbicides or tillage throughout a summer growing season) are commonly included in dryland crop rotations to store water for the subsequent crop (Probert et al. 1998; Nielsen et al. 2005). Fallow periods can be limited to an annual non-growing season, can include the summer growing season (summer fallow), or extend for multiple years and collectively represent ca. 50% of a given year across cultivated land area globally (Siebert et al. 2010). There is a growing appreciation for the role of non-growing season fallow periods in overall denitrification losses from cultivated soils (Shang et al. 2020), but relatively few studies address denitrification rates during summer fallow periods (Vazquez et al. 2019). Furthermore, summer fallow periods and associated increases in soil water content have been linked to higher NO_3^- leaching losses (Campbell et al. 2006; John et al. 2017; Sigler et al. 2020), but few studies (Davis et al. 2019) have explored the extent to which these periods of higher soil water content also influence denitrification in soils and downgradient aquifers or riparian corridors.

High leaching and denitrification losses are symptomatic of widespread N_r use inefficiencies in agricultural production (Galloway et al. 2003) but may be particularly severe where and when summer fallowing is practiced (Sigler et al. 2018). These inefficiencies compromise tenets of agroecosystem sustainability, which seek to balance crop production needs

with protection of soil and water resources, while mitigating anthropogenic N loading that leads to N_2O related climate forcing (Committee on Twenty-First Century Systems Agriculture 2010). Minimizing environmental harms resulting from inefficient use of N_r in agricultural production requires detailed knowledge of the interactions between agricultural management practices such as fallowing, and the drivers of denitrification.

The objective of this study is to understand the role of denitrification as a pathway of N_r loss across hydrologically connected soils, groundwater, and stream corridors in non-irrigated agricultural systems. Our strategy to achieve this objective was to explore patterns in dissolved organic carbon (DOC), DO, and NO_3^- concentrations along with isotopic composition of water and NO_3^- within a non-irrigated, semi-arid agroecosystem in central Montana, USA. The isotopic composition of N and O in NO_3^- can help to discern the influence of denitrification, due to the large isotopic fractionation that microbial metabolism imprints on the residual NO_3^- pool (Groffman et al. 2006). We therefore use patterns in $\delta^{15}N$ and $\delta^{18}O$ values in NO_3^- across soil water, groundwater, and stream water to examine rates and environmental drivers of N_r loss to denitrification across these domains. We hypothesize that in soils, DOC supply, consumption of DO, and production of NO_3^- support substantial denitrification during summer fallow periods when higher soil water content is sustained within this semi-arid environment. More broadly, we use patterns in water and NO_3^- isotopes to examine hypotheses (Sigler et al. 2018) that denitrification is minimal in groundwater at this site due to high DO and short residence times (Tesoriero and Puckett 2011) but substantial in riparian corridors (Vidon and Hill 2006) where groundwater travels through saturated, carbon-rich, riparian soils before entering streams.

Methods

Study area

The study area is in central Montana within the Judith River Watershed (HUC 10040103; Fig. 1). The Judith River is a headwater tributary to the Missouri River, and streams and shallow terrace aquifers in the

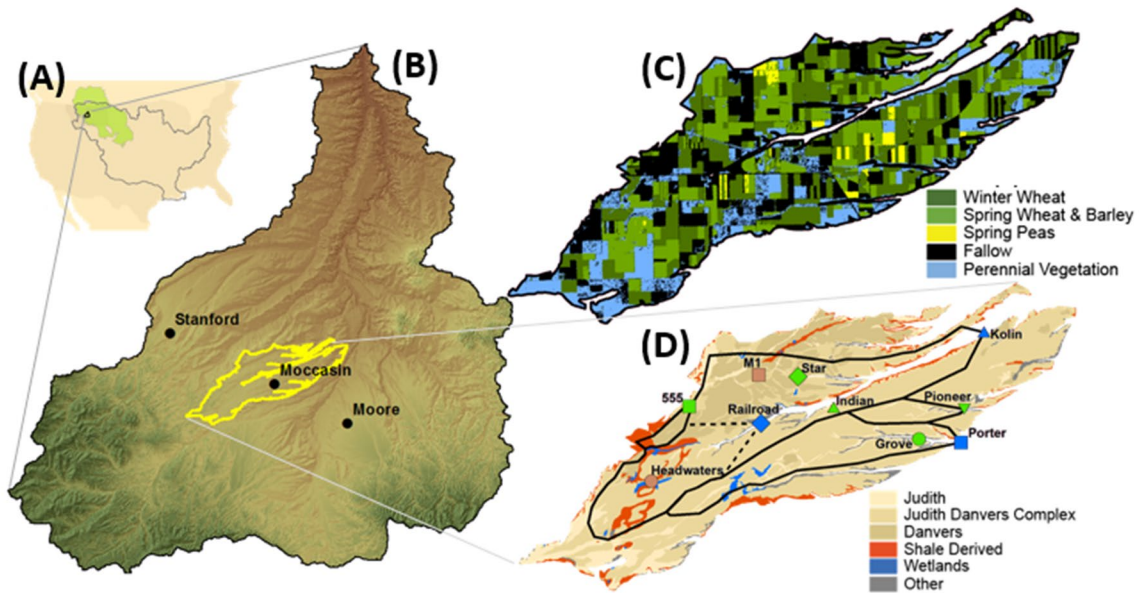


Fig. 1 Study area. Location and character of the Judith River Watershed (JRW) and Moccasin terrace in the context of: **A** the location of the study area within the United States, the northern Great Plains (green shaded area), and the Mississippi Atchafalaya River Basin (gray outline); **B** the locations of the Moccasin terrace and towns nearest to the study fields where lysimeters and rain water samplers were installed; **C**

land use on the Moccasin terrace for the 2014 growing season (USDA 2014); and **D** soil series, catchments (black outlines), and stream sample sites (blue symbols), non-riparian groundwater sample sites (brown symbols), and riparian groundwater sample sites (green symbols) on the Moccasin terrace. Symbol shapes match those of Sigler et al. (2018)

lower elevations of the watershed have chronically elevated NO_3^- concentrations, commonly approaching 20 mg NO_3^- as N/L. Recent research has shown how these NO_3^- concentrations are influenced by variable rainfall, soil characteristics, and agricultural land management practices including chemical summer fallowing (Sigler et al. 2018, 2020). Chemical summer fallowing is the practice of herbicide application to suppress all plant growth over a growing season (total fallow duration of about 21 months given late summer harvest and spring planting), typically for the purpose of increasing stored soil water from precipitation. The study area is in the northern Great Plains region, with a semi-arid climate and mean annual precipitation of 389 mm (1909–2014 period at WRCC Gage # 245761). Cultivated soils in the area are generally well drained, with relatively thin (30–100 cm) zones of clay loam textures overlying horizons dominated by gravel or coarser material. Based on measurements of bulk density of fine textured horizons (1.3 g/cm³; Sigler et al. 2020) and total N in the top 15 cm (1.6 g N/kg; John et al. 2017), we

estimate soil organic nitrogen (SON) is 3,100 kg N/ha in the top 15 cm (Supplemental Information). Unconfined aquifers are perched on shale and generally shallow (1–10 m below ground surface), with a saturated thickness of 2–6 m and mean groundwater residence times ranging from < 1 to 20 years (Sigler et al. 2018). Here we focus on the aquifer within the Moccasin strath terrace (Fig. 1). Topography, stratigraphy, and water chemistry suggest that groundwater recharge on the terrace occurs exclusively via infiltration of precipitation through local soils, and 72% of the terrace area is used for cultivation of annual crops (Sigler et al. 2018). Common crop rotations in the area result in approximately 25% of the terrace being in summer fallow in a year (Sigler et al. 2018) and an overall annual fallow fraction of greater than 0.6 for the annually cultivated portion of the terrace (Sigler et al. 2020). The shallow aquifers and streams emerging from them are well-suited to research on variation in the controls on denitrification because the terrace has well-defined hydrologic boundaries, and soils across the terrace are of varying thicknesses and

textures that dictate a range of water storage and biogeochemical conditions (Sigler et al. 2018, 2020).

Sampling and analysis

We infer fate and transport of N_r through components of the agroecosystem from the chemical and isotopic composition of soil water, groundwater, and stream water sampled across space and time between 2012 and 2017. Soil solution chemistry was characterized in samples from tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark) installed in two non-irrigated fields operated by cooperating farmers (Field B near Moccasin, and Field C near Moore, Fig. 1). Lysimeters were installed near the bottom of the fine textured soil horizons, with nine in soils with relatively thin fine-textured zones (40–80 cm; shallow) and nine in soils with relatively thick fine-textured zones (80–120 cm; deep). Lysimeters were visited approximately every two weeks during periods with sufficient soil water to produce samples between 2013 and 2016. Groundwater and surface water sampling between 2012 and 2017 included two wells, five springs, and three stream sites distributed across the Moccasin terrace (Fig. 1; Sigler et al. 2018). The terrace aquifer, which is isolated from riparian influence due to stream incision, was assessed using upland wells. Springs are located both adjacent to and within riparian areas and represent a range of influence from the riparian environment, determined by geomorphic context at the spring orifice. Dissolved oxygen was measured in-situ with a multiparameter water quality meter using a pump and a flow-through cell (YSI 556; YSI Incorporated; Yellow Springs, Ohio, USA). Dissolved organic carbon was determined using a V-TOC CSH Total Carbon Auto-Analyzer (Shimadzu Corporation). Nitrate concentrations were analyzed by ion chromatography (Dionex, ICS-2100, AS18 column) and/or by cadmium reduction and colorimetry (Lachat, QuickChem 8,500; Seal, QuAAtro). Major ions in soil water, groundwater, and stream samples for the four-year sample period (2013–2016) were characterized previously (Sigler et al. 2018). Isotopic composition of NO_3^- ($\delta^{15}N$, $\delta^{18}O$) was analyzed in groundwater and stream samples, with a minimum of four samples for each site selected to represent a range of seasonal and flow conditions. Isotopic

composition of NO_3^- was analyzed in samples from six of the 18 lysimeters, selected to provide equal representation of shallow and deep soil conditions in a field with summer fallow land use in the crop rotation.

Nitrate isotope analyses were conducted at Woods Hole Oceanographic Institution, using the denitrifier method (Sigman et al. 2001; Casciotti et al. 2002). Nitrate N and O isotopic values were corrected for drift and linearity, and δ values were calculated relative to N_2 in air ($\delta^{15}N = [(^{15}N/^{14}N)_{\text{sample}} / (^{15}N/^{14}N)_{\text{air}} - 1] \times 1000$) and to O in Vienna standard mean ocean water (VSMOW; $\delta^{18}O = [(^{18}O/^{16}O)_{\text{sample}} / (^{18}O/^{16}O)_{\text{VSMOW}} - 1] \times 1000$) using reference materials USGS 32, USGS 34 and USGS 35. Analytical uncertainty of NO_3^- isotopic values was calculated from replicate analyses of samples or reference materials with standard deviations (SD) from the means of 0.2‰ for $\delta^{15}N$ and 0.5‰ for $\delta^{18}O$. When summarizing the range of NO_3^- isotope values, the 5% and 95% quantiles are presented as a Q_{5-95} range.

Precipitation has potential to influence NO_3^- isotopic composition via the isotopic ratio of oxygen in water molecules and NO_3^- dissolved in precipitation waters. More than 85% of precipitation in the study area occurs in the rain dominated months between April and November (Sigler et al. 2020). Precipitation samples were collected between 2013 and 2016 during these rain-dominated months at three study fields (Fig. 1), using receptacles containing mineral oil to avoid evaporation. A composite sample of snow was collected from the snowpack near Field B and near Field C on 30 March 2014. Water isotope composition of precipitation was characterized to provide context for interpreting NO_3^- values, with the assumption that it is the primary input of $\delta^{18}O$ for nitrification after accounting for effects of evaporation (Benettin et al. 2018). Rain and snow samples were analyzed for hydrogen (δ^2H) and oxygen ($\delta^{18}O$) isotopic composition in water relative to VSMOW, using off-axis integrated cavity output spectroscopy (Los Gatos Research, Mountain View, CA; Baer et al. 2002). Water isotope analysis was conducted in the Montana State University Environmental Analytical Laboratory, based on reference materials USGS 46, USGS 48, LGR #2C, and LGR #3C. A working local groundwater standard included after every fourth sample across eight runs had a standard deviation from the mean of 0.4‰ for $\delta^{18}O$ and 0.6‰ for δ^2H .

Precipitation derived inputs of NO_3^- (1.6 kg N/ha/yr) were determined to be negligible relative to other inputs (John et al. 2017) and are not addressed further here.

Isotopic signals of denitrification

The N isotopic composition of nitrogenous compounds is subject to fractionation during transformations within the N cycle (Kendall et al. 2007; Denk et al. 2017). In this work, we focus on fractionation during ammonification, nitrification, and denitrification as the primary processes influencing isotopic composition of dissolved NO_3^- in our study waters. Within the Moccasin terrace, cultivated soils are the dominant source of NO_3^- to underlying groundwater and the emergent streams (Sigler et al. 2018). Values for $\delta^{15}\text{N}$ of NO_3^- ($\delta^{15}\text{N}_{\text{NO}_3}$) in soil are influenced by isotopic fractionation during nitrification of N sourced from fertilizer and SON as well as by denitrification that increases $\delta^{15}\text{N}_{\text{NO}_3}$ values in residual NO_3^- (Granger et al. 2008). The $\delta^{18}\text{O}$ in NO_3^- ($\delta^{18}\text{O}_{\text{NO}_3}$) is influenced by nitrification that imparts the isotopic composition of water and O_2 as source oxygen atoms (and associated isotopic effects of incorporation) to the product NO_3^- , along with an isotopic fractionation by denitrification that increases $\delta^{18}\text{O}_{\text{NO}_3}$ values in residual NO_3^- (Granger et al. 2008; Buchwald and Casciotti 2010; Casciotti et al. 2010; Boshers et al. 2019). The expression of $\delta^{18}\text{O}_{\text{NO}_3}$ fractionation via denitrification is also influenced by the $\delta^{18}\text{O}$ value of ambient water due to isotopic exchange with NO_2^- (Granger and Wankel 2016). We characterize N_r losses to denitrification using observed isotopic values and the NO_3^- mass balance, applying isotopic effects (ϵ) based on literature and observed isotopic values (Table S1; Sigler et al. 2021).

We assessed signals of denitrification by examining relationships between N and O isotopic composition and concentration of NO_3^- (primary evidence), as well as relationships between $\delta^{15}\text{N}_{\text{NO}_3}$ and the concentration of DO and DOC (corroborating evidence). Evidence for denitrification was assessed using the slope, coefficient of determination (R^2), and probability of falsely identifying a trend (p value) derived from linear regressions of $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\delta^{15}\text{N}_{\text{NO}_3}$ ($\delta^{18}\text{O}:\delta^{15}\text{N}$) and $\delta^{15}\text{N}_{\text{NO}_3}$ versus the natural log of NO_3^- concentration ($\delta^{15}\text{N}:\ln[\text{NO}_3^-]$). We interpreted a positive $\delta^{18}\text{O}:\delta^{15}\text{N}$ slope (Granger and

Wankel 2016) and a negative $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$ slope as a primary evidence of denitrification assuming fractionation associated with first order kinetics (Kendall and McDonnell 1998). The expected influence of oxygen and DOC concentrations on denitrification were explored as corroborating lines of evidence. A negative slope in the $\delta^{15}\text{N}_{\text{NO}_3}$ versus natural log of DO relationship ($\delta^{15}\text{N}:\ln[\text{DO}]$) was interpreted as corroborating evidence that denitrification was suppressed by oxygen and a positive slope in the $\delta^{15}\text{N}_{\text{NO}_3}$ versus DOC relationship ($\delta^{15}\text{N}:\text{DOC}$) was interpreted as corroborating evidence that denitrification was energy limited. Although a measurement of low DO indicates conditions immediately upgradient from the sample site were conducive for denitrification, high DO at a sample site does not preclude the possibility that low DO conditions facilitated denitrification further upgradient, followed by reoxygenation. Similarly, while high DOC at a sample site indicates electron donors may have been present for denitrification locally or immediately upgradient, low DOC does not preclude the possibility that DOC was available upgradient and was removed by respiration and denitrification. Hence, we interpret the DO and DOC relationships independently as separate lines of evidence for denitrification but do not distinguish relative control between these two drivers. Collectively, these regression statistics provide simple metrics for assessing confidence in interpretation of an observed isotopic effect consistent with denitrification.

Estimating fallow soil denitrification rates

Summer fallow land use provides periods of minimal plant uptake that allow a unique opportunity to assess the net effects of nitrification and denitrification on N_r in soil. We use a stochastic Monte Carlo approach to explore the ranges in magnitude of soil denitrification during fallow periods that may be expected to balance the effects of nitrification. For each realization of the Monte Carlo ensemble, a value representing observed soil $\delta^{15}\text{N}_{\text{NO}_3}$ was combined with a random selection of fractionation effects from distributions that span reasonable values observed or implied in the literature (see Table S1 in Supplemental Information; Houlton et al. 2006; Hall et al. 2016; Denk et al. 2017). For the net isotopic effect of ammonification and nitrification of SON, we selected from a uniform

distribution of values ranging from -3 to -20% , with negative values favoring the light isotope in the resulting NO_3^- . For the isotopic effects of denitrification, we selected from a uniform distribution of isotopic effect values ranging from -10 to -35% , favoring loss of the light isotope and retention of the heavy isotope in the residual NO_3^- . To represent the range of soil $\delta^{15}\text{N}_{\text{NO}_3}$ values arising from influence of both denitrification and nitrification, we selected from a normal distribution fit to observed lysimeter $\delta^{15}\text{N}_{\text{NO}_3}$ values during fallow periods. We assumed an SON pool with steady-state isotopic composition such that the NO_3^- derived from SON also has a constant isotopic composition, which is a reasonable assumption given relatively large inventories of SON (3,100 kg N/ha in the top 15 cm of soil; see Supplemental Information).

Total denitrification ($N_{\text{den},T}$) over the period of interest is a function (Eq. 1) of change in NO_3^- pool size over the period of interest (ΔN_T) and the ratio of denitrification to nitrification ($r_{\text{den}} = \frac{N_{\text{den}}}{N_{\text{nit}}}$). The initial size of the soil NO_3^- pool is 10 kg/ha, the approximate mean observed in 14 soil pits at the start of the fallow period. The final size of the pool is 45 kg N/ha based on observations in 13 soil pits at the end of a one-year fallow cycle, representing an ΔN_T value of 35 kg/ha/yr (Sigler et al. 2020). We only included realizations where r_{den} was less than 1 ($N_{\text{den}} < N_{\text{nit}}$) in the Monte Carlo ensemble because an accumulation of NO_3^- was observed in the soil during the fallow period.

$$N_{\text{den},T} = \frac{\Delta N_T}{\left(\frac{1}{r_{\text{den}}} - 1\right)} \quad (1)$$

The $\delta^{15}\text{N}_{\text{NO}_3}$ value is a function of r_{den} , the $\delta^{15}\text{N}$ isotopic effects associated with combined ammonification and nitrification ($\epsilon_{\text{amm+nit}}$) and denitrification (ϵ_{den}), and the $\delta^{15}\text{N}$ value for SON ($\delta^{15}\text{N}_{\text{SON}} = +5\%$; see Table S1 in Supplemental Information; Mariotti et al. 1981; Houlton et al. 2006; Denk et al. 2017; Ewing et al. 2022). The $\delta^{15}\text{N}$ value of newly nitrified NO_3^- entering the soil pool ($\delta^{15}\text{N}_{\text{NO}_3,\text{nit}}$), produced from SON, is a function of $\delta^{15}\text{N}_{\text{SON}}$ and $\epsilon_{\text{amm+nit}}$ ($\delta^{15}\text{N}_{\text{NO}_3,\text{nit}} = \delta^{15}\text{N}_{\text{SON}} + \epsilon_{\text{amm+nit}}$). Equation 2 describes the net isotopic effect of nitrification and denitrification:

$$r_{\text{den}} \approx \left(\frac{\delta^{15}\text{N}_{\text{NO}_3,\text{nit}} - \delta^{15}\text{N}_{\text{NO}_3}}{\epsilon_{\text{den}}} \right) \quad (2)$$

The steady state approximated by Eq. 2 is parallel to Eq. 14 in Denk et al. (2017; $r_{\text{den}} = 1 - f$; $\delta^{15}\text{N}_{\text{NO}_3,\text{nit}} = \delta_{\text{s},0}$; $\delta^{15}\text{N}_{\text{NO}_3} = \delta_{\text{s}}$; $\epsilon_{\text{den}} = \epsilon$) for an open system as described by Fry (2006) and is similar to the steady-state approach in Houlton et al. (2006). The steady state results from the assumption that inputs occur at a constant rate with a constant isotopic value (infinite source pool here is SON), and the assumption that the isotopic fractionation effects of nitrification (more specifically, ammonification plus nitrification) and denitrification are constant. As observations of isotopic composition of NO_3^- used in the model are the integration of N cycling signals transported to lysimeters by the downward flux of soil solution, these rate estimates are attributed to the soil depths of 40–120 cm that overlie lysimeters. This estimate for the fallow condition provides insight about the possible magnitude of denitrification loss during fallow periods, and the relative magnitude of nitrification and denitrification fluxes.

Results and Discussion

We observed evidence of denitrification in soils, groundwater, and streams within agricultural regions of the Judith River Watershed, based on positive $\delta^{18}\text{O}:\delta^{15}\text{N}$ linear relationships and negative $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$ linear relationships (Fig. 2, Table 1). Variation in the strength of these relationships across domains provides evidence of competing processes influencing net isotopic dynamics. Generally, we observed patterns consistent with denitrification suppression by oxic conditions (negative $\delta^{15}\text{N}:\ln[\text{DO}]$ linear relationships) and facilitation by energy availability (positive $\delta^{15}\text{N}:\text{DOC}$ linear relationships; Fig. 3, Table 1). In streams, the presence of a denitrification signal and oxic conditions suggests inmixture of denitrified riparian waters to a domain readily reoxygenated by the atmosphere (Figs. 2, 3).

Nitrate isotopic composition and linkage across domains

The tight cluster of NO_3^- isotope values for high DO (>0.18 mM) groundwater provides a key reference point for understanding N_r dynamics in upgradient cultivated soils and downgradient riparian areas and is

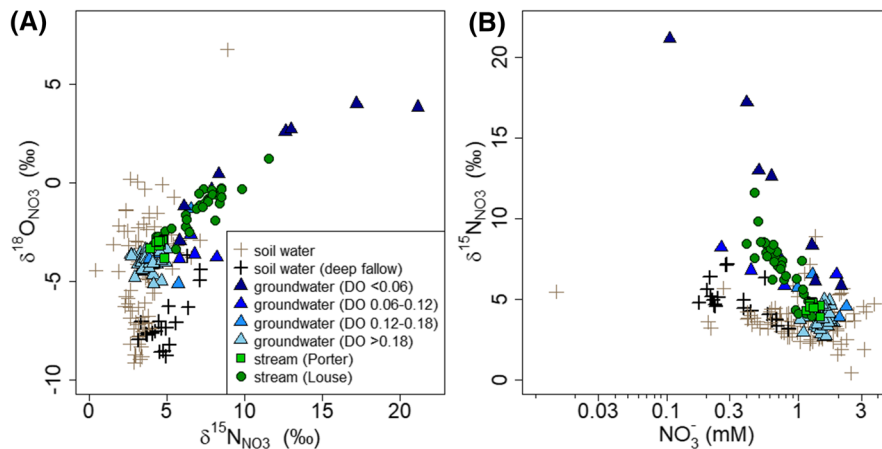


Fig. 2 Nitrate stable isotope results. Comparisons of patterns in isotopic composition and concentration of NO_3^- dissolved in soil water, groundwater, and stream water across the JRW. Data from groundwater samples are differentiated by DO concentration (shades of blue as denoted in the legend with units

of mM). High DO groundwater samples (light blue) represent the terrace aquifer while the lowest DO groundwater samples (dark blue) represent riparian influenced groundwater. **A** $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ in NO_3^- . **B** $\delta^{15}\text{N}$ in NO_3^- versus NO_3^- concentration, note x axis is log scaled

Table 1 Summary of denitrification signals in soil water (**A**), groundwater (**B**), streams (**C**), and notable groups of sites (**D**). Kolin and Railroad are both on Louse Creek. Grove spring is a major source of flow to Porter Creek. Statistics and slopes

based on linear relationships. Highlighted cells (gray) are interpreted as “clear” signals where slope (S) has the expected sign and statistical values exceed an arbitrarily designated threshold ($R^2 \geq 0.5$ and p value < 0.05)

Sites and Sample Groups	Primary Signals						Corroborating Signals					
	$\delta^{18}\text{O}:\delta^{15}\text{N}_{\text{NO}_3}$			$\delta^{15}\text{N}:\ln[\text{NO}_3^-]$			$\delta^{15}\text{N}:\ln[\text{DO}]$			$\delta^{15}\text{N}:\text{DOC}$		
	R^2	p	S	R^2	p	S	R^2	p	S	R^2	p	S
A	All	0.04	0.03	0.4	0.13	<0.05	-0.6	NM	NM	NM	NM	NM
	Fallow	0.09	0.06		0.57	<0.05	-1.4	NM	NM	NM	NM	NM
	Fallow Deep	0.5	<0.05	0.8	0.32	0.01	-1.3	NM	NM	NM	NM	NM
B	All	0.82	<0.05	0.5	0.68	<0.05	-5.2	0.75	<0.05	-2.5	0.01	0.53
	Pioneer	0.88	<0.05	0.4	0.9	<0.05	-6.2	0.55	0.02	-3.1	0.65	0.01
	M1	0.01	0.72		0.72	<0.05	-2.5	0.7	<0.05	-2.4	0.01	0.79
	Headwaters	1	<0.05	0.5	0.24	0.51		0.47	0.32		0.82	0.10
	Indian	0.02	0.66		0.03	0.65		0.03	0.61		0.01	0.78
	Star	0	0.96		0.35	0.41		0.14	0.63		0.78	0.12
	Grove	0.23	0.16		0.02	0.68		0.17	0.31		0.01	0.83
	Spr555	0.85 ¹	0.08		0.91 ¹	0.05 ¹	1.6 ¹	0.32	0.43		0.15	0.62
C	Porter	0	0.94		0.1	0.365		0.02 ²	0.71 ²		0.23	0.16
	Kolin	0.73	<0.05	0.7	0.66	<0.05	-3	0.21 ²	0.09 ²		0.74	<0.05
	Railroad	0.89	<0.05	0.5	0.82	<0.05	-5.7	0.13 ²	0.20 ²		0.36	0.07
D	Kolin & Railroad	0.84	<0.05	0.6	0.74	<0.05	-4.7	0.15 ²	<0.05 ²		0.49	<0.05
	Porter & Grove	0.45	<0.05	0.6	0.73	<0.05	-2.6	0.06 ²	0.35 ²		0.68	<0.05

¹ relationship value exceeds threshold but slope is in the opposite direction as predicted for denitrification

² stream water column DO not expected to be correlated to denitrification

NM indicates “not measured”

Slope values only reported where significantly different from zero (p value < 0.05)

^aRelationship value exceeds threshold but slope is in the opposite direction as predicted for denitrification

^bStream water column DO not expected to be correlated to denitrification

NM indicates “not measured”; Slope values only reported where significantly different from zero (p value < 0.05)

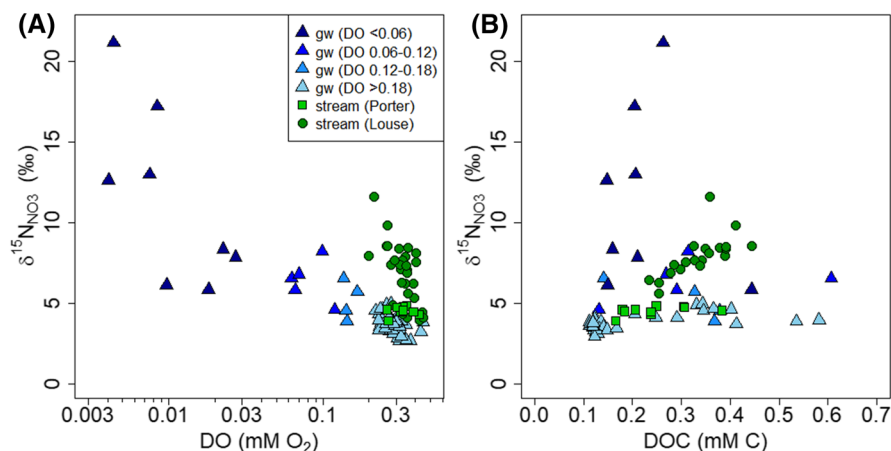


Fig. 3 Nitrate $\delta^{15}\text{N}$ with dissolved oxygen (DO) and dissolved organic carbon (DOC). Comparisons of patterns in $\delta^{15}\text{N}$ in NO_3^- versus DO and DOC dissolved in groundwater and stream water across the JRW. Data from groundwater samples are differentiated by DO concentration (shades of blue as

denoted in the legend with units of mM). High DO groundwater samples (light blue) represent the terrace aquifer while the lowest DO groundwater samples (dark blue) represent riparian influenced groundwater. **A** $\delta^{15}\text{N}$ in NO_3^- versus DO, note x axis is log scaled **B** $\delta^{15}\text{N}$ in NO_3^- versus DOC

described here as a foundation for discussion of those dynamics in subsequent sections (Fig. 2, Table S2). Values for $\delta^{15}\text{N}_{\text{NO}_3^-}$, $\delta^{18}\text{O}_{\text{NO}_3^-}$, and NO_3^- concentration in high DO groundwater, sampled in terrace aquifer wells and spring outlets isolated from riparian vegetation, cluster tightly near the center of values for soil, reinforcing findings by Sigler et al. (2018) that chemical composition of the Moccasin terrace aquifer is primarily determined by the chemistry of overlying cultivated soils. The isotopic composition of NO_3^- apparently carried from soil to groundwater is likely transferred relatively quickly (0–6 years based on tritium–helium analysis) to stream corridors, due to thin (<6 m) and transmissive terrace aquifers (Sigler et al. 2018). We hypothesize that the shallow, relatively fast-moving groundwater in this terrace system explains why groundwater samples from terrace aquifer wells and spring outlets isolated from riparian vegetation have consistently high DO (Figs. 2 and 3) and that it is riparian sourced DOC that facilitates DO drawdown in the few instances of low DO observed in groundwater sampled at springs. Eight groundwater samples had DO concentrations less than 0.06 mM, seven of which came from a single site (Pioneer), where water emerges from an extensive riparian area. The large riparian area upgradient of the Pioneer site stands in contrast to the two well sites and two of the spring sites (Indian and Grove) where water emerges

directly from the terrace aquifer with no riparian area upgradient. The remaining two spring sites (Star and Spr555) have only a few meters of riparian area upgradient, which does not appear to be sufficient to support notable denitrification (Table 1). Abundant DO in shallow terrace aquifers limiting denitrification outside of riparian corridors stands in contrast to systems with deeper aquifers with longer residence times that facilitate variable subsurface electron donor depletion of DO and complicate prediction of aquifer NO_3^- lag times (Kolbe et al. 2019; Vautier et al. 2021). When sampled upgradient of riparian influence, the consistent $\delta^{15}\text{N}_{\text{NO}_3^-}$, $\delta^{18}\text{O}_{\text{NO}_3^-}$, and NO_3^- concentration of Moccasin terrace groundwater provides a chemical starting point to which stream chemistry can be compared to infer denitrification process within the riparian corridor.

Isotopic signals of denitrification

Both the clearest presence and the clearest absence of denitrification signals were observed in groundwater, with differentiation apparently related to abundance of DO and DOC (Fig. 2; Table 1). Four of the seven groundwater sites exhibited no primary signals of denitrification (Table 1; Indian, Star, Grove, Spr555). Isotopic influence of denitrification in the two non-riparian wells (M1 and Headwaters) was not evident,

with mixed signals from $\delta^{18}\text{O}:\delta^{15}\text{N}$, $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$, $\delta^{15}\text{N}:\ln[\text{DO}]$, and $\delta^{15}\text{N}:\text{DOC}$ relationships (Table 1; Fig. S3). Across all groundwaters, DO explains 73% of the observed variation in $\delta^{15}\text{N}_{\text{NO}_3}$ ($R^2=0.73$, linear regression of $\delta^{15}\text{N}_{\text{NO}_3}$ vs $\ln[\text{DO}]$), consistent with the idea that regardless of DOC abundance, DO needs to be low before substantial denitrification is likely to occur (Fig. 3). The only riparian groundwater site where DO concentrations were consistently low (Pioneer), displayed clear $\delta^{18}\text{O}:\delta^{15}\text{N}$ and $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$ signals of denitrification along with a $\delta^{15}\text{N}:\text{DOC}$ corroborating signal. This clear signal of denitrification at one riparian groundwater site, representing a “hotspot,” juxtaposed to four riparian groundwater sites lacking any evidence of denitrification, underscores the high variability in riparian denitrification rates and extent, similar to findings in other studies (Hedin et al. 1998; McClain et al. 2003; Vidon and Hill 2006). To be clear, this distinction reflects our site selection process, which targeted inclusion of springs draining the terrace aquifer at the base of steep embankments without upgradient riparian vegetation, in order to distinguish denitrification in the terrace aquifer versus riparian groundwater.

Patterns in stream water chemistry and isotopic composition reveal a stronger signal of denitrification in the riparian corridor of Louse Creek than in that for Porter Creek. Unlike fallow soil waters and groundwaters, the strong denitrification signals for Louse Creek (Table 1) could be confounded by algal uptake in the water column, which may also favor the light isotope (Denk et al. 2017). However, the persistence of higher $\delta^{15}\text{N}_{\text{NO}_3}$ values in Louse Creek relative to groundwater through the winter of 2013–2014 when algal growth was likely minimal, supports the hypothesis that denitrification is an important driver of riparian corridor and instream NO_3^- loss. The lack of correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and DO measured in the water column may reflect that stream channel denitrification occurs under anoxic conditions found in the hyporheic zone, benthic sediment, and/or suspended sediment (Harvey et al. 2013; Gomez-Velez et al. 2015; Reisinger et al. 2016; Wells et al. 2019). In general, both the lack of correlation between $\delta^{15}\text{N}_{\text{NO}_3}$ and DO measured in the water column and the persistent $\delta^{15}\text{N}:\text{DOC}$ relationship may simply indicate that riparian denitrification precedes inflows to Louse Creek, where reoxygenation occurs (Table 1, Fig. 3). Porter Creek water indicates no isotopic

evidence of denitrification, when assessed independently. However, leveraging the consistent chemical signature of high DO groundwater in the terrace aquifer, when results from a spring flowing into Porter Creek (Grove Spring) are grouped with those from Porter Creek, stronger $\delta^{18}\text{O}:\delta^{15}\text{N}$, $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$, and $\delta^{15}\text{N}:\text{DOC}$ denitrification signals emerge (Table 1). This pattern from groundwater to stream water supports the inference from mass balance analysis (Sigler et al. 2018), that riparian corridor NO_3^- losses for both Louse (50%) and Porter (15%) creeks are at least partially attributable to riparian denitrification.

Denitrification signals across the full set of lysimeter-sampled soil waters are weak ($\delta^{15}\text{N}:\ln[\text{NO}_3^-]$ $R^2=0.04$, $\delta^{15}\text{N}:\ln[\text{NO}_3^-]$ $R^2=0.13$), but evidence of denitrification is stronger ($R^2=0.50$, 0.32) in deep soils during fallow periods (Table 1). In simplest terms, evidence of denitrification in soil during fallow periods is consistent with findings by Sigler et al. (2020) that soil moisture is higher during fallow periods than in cropped years. Higher water content in the presence of soil organic matter increases the chances of regions with low DO, which would facilitate denitrification (DeKlein and VanLogtestijn 1996; Smith et al. 1997). The concomitant increases in soil NO_3^- concentrations during the fallow year, observed both in lysimeter samples (Sigler et al. 2018) and soil profile inventories (John et al. 2017; Sigler et al. 2020), indicate that ammonification of SON and subsequent nitrification is out-pacing denitrification and leaching losses during this period. Nitrate with the highest $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values occurs early (March–April) in the fallow year when NO_3^- concentrations are low, and isotopic values decrease over the fallow year. These patterns are consistent with denitrification favored by anoxic conditions in more saturated soils associated with snowmelt early in the season, followed by nitrification favored by more oxic conditions and moderate soil water content during the warmer and drier season. Decreases in $\delta^{15}\text{N}_{\text{NO}_3}$ values with increases in NO_3^- concentration during summer suggest nitrification following ammonification of SON, supplying NO_3^- with a $\delta^{15}\text{N}_{\text{NO}_3}$ value of $\sim +5\%$. Decreases in $\delta^{18}\text{O}_{\text{NO}_3}$ values with nitrification may reflect incorporation of oxygen from water having relatively low $\delta^{18}\text{O}$ values, consistent with water stored in soil from snowmelt (Fig. S1) and incorporated by nitrification through the summer fallow period.

Estimating fallow soil denitrification rates

The Monte Carlo ensemble of realizations of the isotopic composition of NO_3^- produced a median annual denitrification rate of 26 kg N/ha/yr and an interquartile range of 12–56 kg N/ha/yr (Fig. 4C), values well within the range of denitrification estimates across ecosystem types reported for annual timeframes (0 to 239 kg N/ha/yr; Phillips 2008). The mode of the ensemble was 7 kg N/ha/yr, which is approximately half of values summarized for agricultural soils from a global synthesis (14 kg N/ha/yr; Seitzinger et al. 2006) and the mean value from a literature review (13 kg N/ha/yr; Barton et al. 1999). The mode of the ensemble is less than the 25th quartile value (12 kg N/ha/yr), and is reported here as a conservatively low estimate. A denitrification rate of 7 kg N/ha/yr would suggest 17% of the NO_3^- entering the soil pool from SON during the fallow period is lost

to denitrification. We anticipate that overall warm season denitrification rates are higher during summer fallow years when soils are wetter, relative to summers with crops present when soils are drier (DeKlein and VanLogtestijn 1996). Implications for patterns in the N_2O component of denitrification surrounding summer fallow are less clear due to limited research. Nitrous oxide emissions are commonly quantified as a fraction of N fertilizer applied, an approach focused on cropped years, but with recent attention to the role of non-growing season fallow periods (Shang et al. 2020). Some research has found higher N_2O emissions from crop relative to fallow (Verma et al. 2006). Other studies have found N_2O fluxes associated with precipitation events were higher than those associated with fertilizer application (Barton et al. 2008; Wilson et al. 2015). Further work is needed to quantify denitrification rates during summer fallow relative to cropped years, and to illuminate drivers

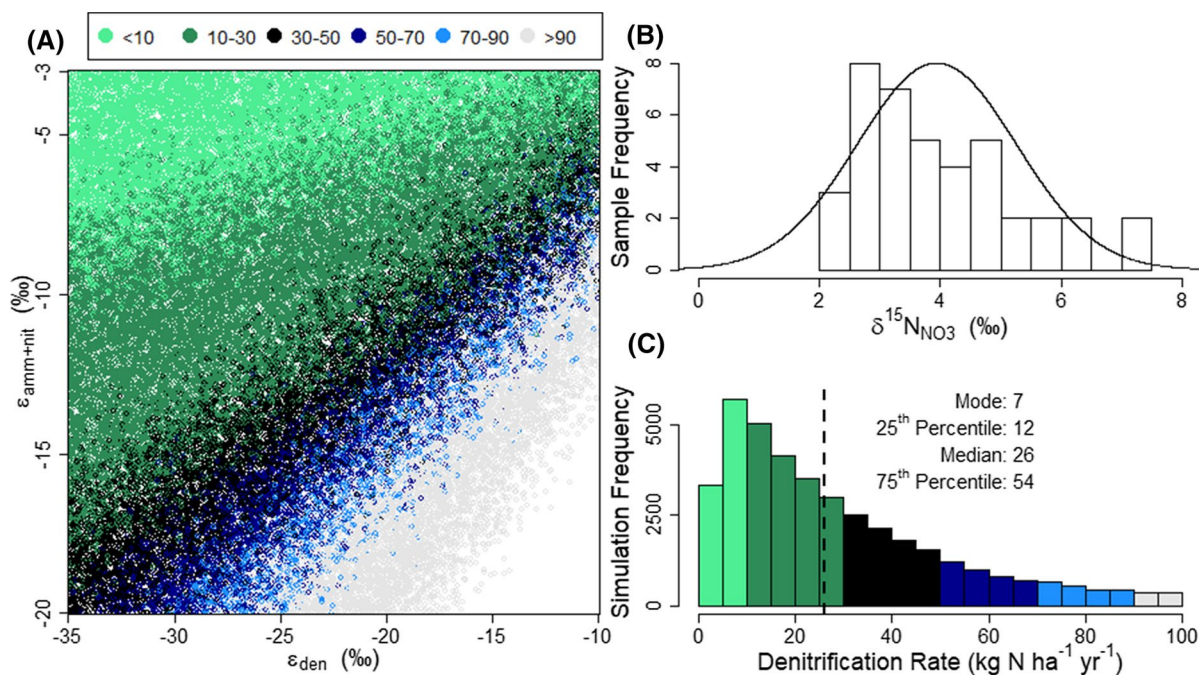


Fig. 4 Simulation based estimates of annual soil denitrification rates during fallow. **A** Monte Carlo simulation (50,000 realizations) results for the annual denitrification rate during the fallow year ($N_{\text{den,T}}$) based on Eqs. 1 and 2 and assumptions described in the methods section. Each point represents results from one realization with annual soil denitrification rate depicted by color according to the legend and isotope effect values for ammonification+nitrification ($\epsilon_{\text{amm+nit}}$) and denitrification (ϵ_{den}) correspond to the Y and X axes. The bottom

right portion of the plot represents parameter space where simulations produced r_{den} values greater than 1, values which are not meaningful according to model assumptions. **B** Frequency of $\delta^{15}\text{N}$ values observed in soil lysimeter samples ($\delta^{15}\text{N}_{\text{NO}_3}$; $n=38$), with a line depicting the normal distribution fit to the data that was used to generate $\delta^{15}\text{N}_{\text{NO}_3}$ values for the Monte Carlo simulation. **C** Frequency of annual denitrification rates simulated with the Monte Carlo analysis (same data in panel A)

of N_2O emissions associated with both denitrification and nitrification under summer fallow conditions to inform mitigation strategies (Barton et al. 2013; Vazquez et al. 2019).

Our upland soil denitrification estimates on the order of 7–26 kg N/ha/yr suggest that large gross losses of NO_3^- to denitrification may occur during summer fallow periods, even when they are masked by net NO_3^- accumulation from mineralization of SON. As a result, these losses may be obscured or interpreted as leaching loss in mass balance approaches where denitrification is not directly quantified (Bouwman et al. 2013; John et al. 2017). A 26 kg N/ha/yr loss of NO_3^- during fallow years might be expected to result in a measurable loss of SON over time. However, given that uncertainty in SON values is approximately 310 kg/ha (10% of 3,100 kg/ha; see Supplemental Information), losses of less than 30 kg N/ha/yr would be difficult to detect without decades of data. Long-term SON trends are not available for our study area, but under a similar climate in Montana, soil organic carbon decreased over time in systems with summer fallow periods in rotation (Engle et al. 2017), a result standing in contrast to increasing SON observed in wetter climates where summer fallowing is not practiced (Sebilo et al. 2013; Van Meter et al. 2016). If the soil denitrification rate is 26 kg N/ha/yr, this loss is 1.5–2.5 times higher than estimated leaching rates (11–18 kg/ha/yr; Sigler et al. 2018) and at least 25% of common fertilizer rates in the watershed (60–100 kg/ha/yr; John et al. 2017). Loss of N_r from soils represents a loss of stored fertility, and SON derived losses will ultimately be offset by increased fertilizer application, likely exacerbating fertilizer N_r use inefficiency, increasing N_2O emissions and further degrading downstream water quality.

Our denitrification rate estimates based on $\delta^{15}\text{N}_{\text{NO}_3^-}$ and first order kinetics are sensitive to the magnitude of the assumed isotopic fractionation effects. This source of uncertainty illustrated by the Monte Carlo analysis (Fig. 4) is seldom assessed or reported in work based on the same isotopic principles (Lutz et al. 2020), but may be important to appropriate confidence in research conclusions. More work is needed to better constrain the isotopic effects associated with ammonification plus nitrification and denitrification as well as additional possible loss pathways of intermediate reactants to refine these rate estimates. The

steady state approach to application of nitrification and denitrification isotopic effects (Eq. 2) to determine the net composition of the NO_3^- pool is a simplified approach for estimating the range of possible denitrification rates suggested by observed $\delta^{15}\text{N}_{\text{NO}_3^-}$ values. Future modeling considering more complicated temporal patterns of nitrification and denitrification is necessary to enhance understanding of net denitrification in agricultural soils. Additional enhancement of the soil denitrification model could also be accomplished at this site by incorporating $\delta^{18}\text{O}_{\text{NO}_3^-}$ as a second tracer, a step that would require refined characterization of $\delta^{18}\text{O}$ in rain and snow along with storage and transport dynamics through soil.

Implications for landscape N budgets and future work

The isotopic composition of NO_3^- at these sites suggests that denitrification is occurring in both riparian corridors (which include soils, shallow subsurface flow and side channels, ponds and impoundments) and cultivated soils of our study area, a finding widely supported in the literature (Hedin et al. 1998; Bouwman et al. 2013; Billen et al. 2020). Riparian areas had the strongest isotopic signals of denitrification, with some riparian groundwater hotspots suggesting near complete NO_3^- removal. While riparian denitrification is well documented with observations and modeling because it confers water quality benefits for streams (Zarnetske et al. 2012; Oldham et al. 2013), these N_r losses must be evaluated in a broader landscape context and in light of associated greenhouse gas (N_2O) emissions. Here, when riparian denitrification is normalized to the catchment area (1–5 kg N/ha/yr; Sigler et al. 2018), these losses are small relative to potential direct losses (7–26 kg N/ha/yr) from more spatially extensive cultivated soils (Fig. 5). Further, the NO_3^- undergoing denitrification in riparian corridors is primarily sourced from upgradient cultivated soils, highlighting the central role of cultivated soils in overall N_r budgets for cultivated landscapes. These findings support both calls to bolster strategic management of riparian corridors and wetlands (Cheng et al. 2020) and to allocate more attention to N management in the soils of uplands and headwater catchments (Pinay and Haycock 2019). Loss of N_r from cultivated soils via denitrification and leaching not only limits agricultural productivity but also has

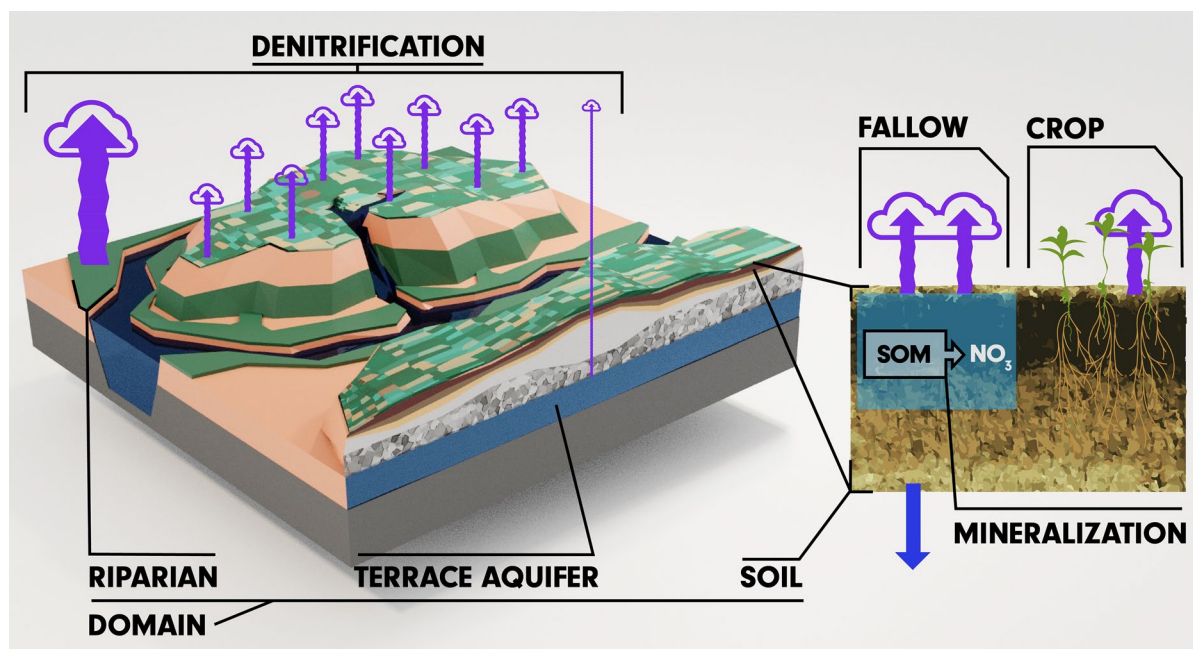


Fig. 5 Landscape denitrification domains. Size of upward facing arrows represent magnitude of denitrification N flux for the different portions of the landscape. Denitrification within oxy-

genated terrace aquifers is minimal. Large magnitude N losses in riparian areas are localized, while lower magnitude losses in upland soils are spatially extensive

contributed to a ten-fold increase in N₂O emissions from croplands since the 1860s (Stevens and Laughlin 1998; Tian et al. 2019; Billen et al. 2020). Results from our work suggest that fallow periods play a disproportionately important role in N_r loss from cropland soils both directly to denitrification, and to leaching (Sigler et al. 2020) of NO₃⁻ that is subject to denitrification down gradient. More generally, this work shows that spatial connection, as well as transport and reactivity dynamics, shape the isotopic patterns that we observe (Abbott et al. 2016). Ultimately our work supports the view that protecting thin riparian buffers is often insufficient to restore water quality and biogeochemical function in managed aquatic ecosystems (Pinay and Hancock 2019).

Evidence of concurrent nitrification and denitrification during fallow periods is consistent with previous work indicating that the two processes can be tightly coupled in space and time in soils (Seitzinger et al. 2006). Decades of work has suggested that nitrification occurs near oxygenated macropores and that oxygen and NO₃⁻ diffuse into adjacent micropores, where microbial respiration uses up oxygen, leading to anoxia and denitrification (Parkin 1987; Parkin

and Berry 1999; Schlüter et al. 2018). Soils in semi-arid regions with crops present are typically dry with only episodic periods of soil water content above field capacity, but summer fallowing dramatically increases the duration and spatial extent of high soil water content (Sigler et al. 2020). For future work, we pose the hypothesis that overall soil water is increased during fallow periods, but that interspersed faster drying zones adjacent to macropores or coarse texture anomalies create complex networks of oxic and anoxic zones in close proximity, with high potential for coupled nitrification and denitrification. The patterns of oxic/anoxic zones are likely controlled by climate, management, parent material, and soil structure (Ewing et al. 2006; Sigler et al. 2020). Based on this hypothesis, we posit that fallow periods may create the perfect storm for high rates of nitrification, which produces NO₃⁻ at high risk of loss to leaching or denitrification in cultivated soil. As global cultivated land spends ca. 50% of time in a fallow condition, additional work is needed to quantify denitrification rates during fallow periods and the extent to which these processes contribute to N₂O emissions from food production systems (Clark et al. 2020), which

are necessary to meet Paris Agreement goals to slow global temperature increase.

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Data availability Data and code available as a resource on Hydroshare (Sigler et al. 2022).

Declarations

Conflict of interest The authors declare that they have no conflicts of interest.

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