DAILY SIGNALS IN NITRATE PROCESSING PROVIDE A HOLISTIC PERSPECTIVE ON STREAM CORRIDOR HYDROLOGIC AND BIOGEOCHEMICAL FUNCTION

by

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ABSTRACT

Understanding interactive pathways of biogeochemical reaction and water movement in stream corridors is critical given the role stream corridors play in mitigating nitrate loading from agricultural watersheds. However, few studies consider the interactive effects of nitrate loading, riparian processing, and stream ecosystem processing, which may limit abilities to predict downstream nitrate delivery. Riparian groundwater inputs and stream ecosystem processing may vary due to daily cycles in evapotranspiration or stream ecosystem primary production. Recent advances in high-frequency monitoring of stream chemistry throughout the day exhibit potential to explore both hydrologic and biogeochemical influences on nitrate attenuation. In this thesis, I explore how diel variations in stream reach nitrate processing can provide holistic perspectives on the attenuation of nitrate along stream corridors within a watershed that is heavily influenced by agricultural land use. Nitrate processing is defined as the evident changes in nitrate concentration in parcels of water as they travel along a given reach of a stream, as measured from nitrate sensors located at the head and base of ca. 0.5 km reaches. To understand controls on diel variation in nitrate processing, we measured diel processing signals in agricultural headwater reaches in Central Montana, USA spanning variable atmospheric and flow conditions from March through August in 2020-2022. Across 168 days with valid data, most signals exhibited little diel variation (n = 106) and this lack of variation occurred most frequently during cooler and shorter days. In contrast, signals with greater variation were common during longer days, warmer temperatures, and lower flows (n = 62). This seasonal shift in patterns suggests that solar radiation and stream flow are primary controls on diel nitrate processing signals in these low-order reaches. In addition to diel variation, less overall nitrate attenuation in the study reach with direct inputs of high-nitrate upland waters suggest that the degree of hydrologic connection to upland aquifers influences apparent reach nitrate processing. This work highlights how understanding the drivers of diel processing signals may lead to a more holistic understanding of how multiple interacting processes in stream corridors influence nitrate delivery to downstream ecosystems.

CHAPTER ONE

MOTIVATION FOR A HOLISTIC APPROACH TO STREAM CORRIDOR RESEARCH

Human activities have doubled the amount of reactive nitrogen on the planet, largely through industrial fertilizer fixation (Schlesinger, 2009). Excessive nutrient concentrations in ground and surface waters leads to impaired water quality relative to regulatory standards, shifts in ecosystem function, and adverse economic impacts (Heisler et al., 2008; Smith et al., 1999). Stream and riparian ecosystems can remove nitrate in transport downstream and understanding the interactive pathways of water movement and biogeochemical reactions influencing this attenuation is critical to predicting nitrate export from agricultural watersheds (McClain et al., 2003; Ranalli & Macalady, 2010). Despite extensive study of many independent mechanisms of nitrate attenuation in specific flow paths within stream corridors, approaches to synthesize the overlapping effects of these multiple pathways of nitrate attenuation are less developed. Due to the potential for riparian and stream processes to vary predictably with the photoperiod, the resulting daily signals in reach nitrate processing may offer perspective on the stream and riparian processes that control whole-corridor behavior.

1.1 The Two Dominant Paradigms of Stream Corridor Nitrate Attenuation Research

A rich history of studies have illuminated the capacity of stream ecosystems to remove and retain nutrients in the stream channel (Ensign & Doyle, 2006; Tank et al., 2008). Removal of nitrate from channel water via denitrification (a form of microbial anaerobic respiration) is a small fraction (ca. 15%) of total nitrate processing in small streams (Mulholland et al., 2008). Additional nitrate processing in stream ecosystems may occur as temporary storage in organic

form due to assimilative uptake associated with algal primary production (Hall et al., 2009). Controls on primary production and associated nutrient uptake in streams include light availability and the stability of stream flow (Bernhardt et al., 2022), nutrient availability (Bernot & Dodds, 2005), and channel size (Peterson et al., 2001).

The biochemical effects of stream ecosystems on reducing nitrate loads are influenced by ambient nitrate concentrations and the internal cycling of nitrogen between mobile and immobile forms. The saturating kinetics of nitrate uptake observed in many stream ecosystems suggest that nitrate removal efficiency may decrease as nitrate availability increases (Hall et al., 2009; Mulholland et al., 2008). This limitation has led some to suggest that many streams with elevated nitrate concentrations are exporting systems, where the magnitude of nutrient export is dominated by hydrologic transport and biological nitrate removal is limited relative to the supply (Tank et al., 2021). Additionally, assimilated nitrogen in algal biomass is not a permanent sink of nitrogen and mineralization can increase stream nitrate concentrations, especially during algal senescence (Hefting et al., 2005; McMillan et al., 2010). Thus, stream ecosystem nitrogen processing may have limited effects on mediating terrestrial nitrate loading if nitrate regeneration and uptake are in balance (Brookshire et al., 2009).

An equally rich, but often conceptually disconnected, thread of literature demonstrates how the distinct anoxic biogeochemistry of riparian aquifers promotes nitrate removal in stream flow generation sourced by lateral contributions from upland waters (Hill, 1996). In contrast to stream ecosystems, denitrification is a primary mechanism of nitrate processing in riparian zones given anoxic conditions, and ample organic carbon and nitrate availability (Ranalli & Macalady, 2010). The hydrologic setting is likely a primary control on the effect of riparian aquifers on

reducing stream nitrate loads because it influences the hydrologic connections between uplands, riparian aquifers, and stream waters that determines the amount of water subject to riparian biogeochemical processing before watershed export. In hydrogeologic settings where high-nitrate waters bypass riparian zones via surface or preferential oxygenated flows, riparian nitrate attenuation is limited as compared to stream corridors where riparian aquifers are recharged by upland waters (Gold et al., 2001; Vidon & Hill, 2004). Studies of the riparian buffering effect are typically based on conceptual models that follow waters traveling to stream channels sourced by lateral contributions from uplands (e.g. Ocampo et al., 2006). However, water in riparian aquifers may also be recharged by the up-valley stream channel, and the influence of waters biogeochemically processed in long-term surface-subsurface exchange flow paths is poorly understood (Ward et al., 2013).

1.2 Using Diel Solute Signals to Synthesize the Dominant Paradigms of Stream Corridor Research

Despite extensive study of independent pathways of sinks and sources of nitrogen within stream corridors, few studies have attempted to address the combined influences of direct upland loading, riparian processing, and stream ecosystem processing on whole-corridor behavior. Such holistic understanding is limited by conventional methods that isolate the biogeochemistry of a narrow definition of hydrologic flow paths. For example, estimates of nitrate processing in stream ecosystems typically exclude the influence of mixing with riparian groundwater inflows by normalizing the longitudinal change in nitrate to that of a nonreactive tracer (Stream Solute Workshop, 1990). While this practice removes potential confounding influences on comparisons of stream ecosystem behavior, it also inherently excludes any nitrate attenuation in the riparian

aquifer from characterization of whole-corridor behavior. Additionally, estimates of riparian nitrate attenuation typically focus on the processing of hillslope inputs in route to the channel, thus neglecting riparian processing of nitrate in longer-residence-time groundwater flow paths recharged by up-valley stream channel waters (e.g. Ocampo et al., 2006). Finally, the integrated influence of riparian aquifers on recharge from uplands combined with recharge from up-valley channel water is much less commonly studied holistically as an aggregated influence of stream corridors (Ward et al., 2013). Breakthroughs in stream corridor science may be better achieved by considering the combined effects of nitrogen processing in stream corridors rather than accentuating the boundaries between individual processes with reductionist approaches.

More holistic and scalable perspectives on nitrate processing in stream corridors may result from attempts to disentangle the effects of riparian buffering and stream ecosystem processes from the aggregated diel processing signals evident along reaches of stream corridors. We define diel processing signals as the within-day variation in the degree to which nitrate concentrations are altered in parcels of water in transport along a stream reach. Our perspective incorporates both groundwater mixing effects on channel nitrate concentrations and stream ecosystem biogeochemical reaction effects on channel nitrate mass. With advances in monitoring technology, diel signals ultimately driven by periodicity in solar radiation are increasingly used to infer rates of related ecosystem and hydrologic processes (Rode et al., 2016). For example, diel signals in nitrate concentrations have been used to assess stream ecosystem nitrogen demand (Heffernan & Cohen, 2010). Diel signals in stream discharge are used to infer the constructive and destructive overlaps of daily cycles in streamflow generation processes such as evapotranspiration (Wondzell et al., 2007). Thus, diel signals in stream nitrate processing may

reflect the influence of the corridor as a whole, incorporating both the influence of the riparian aquifer and the influence of the stream ecosystem on nitrate concentrations.

The limitations introduced by reductionist approaches in stream corridor research are evident in the ambiguity in the causes of diel nitrate signals. For example, diel nitrate signals are well explained by the expected effects of assimilatory uptake in some streams (Heffernan & Cohen, 2010; Roberts & Mulholland, 2007), but biogeochemical drivers of signals in other streams are less clear (Greiwe et al., 2021; Kelly et al., 2021). Additionally, evapotranspiration-influenced groundwater inflows have been suggested to create diel cycles in dissolved organic carbon concentrations (Wilson & Xenopoulos, 2013) and trace metal concentrations (Brick & Moore, 1996). However, controls on the relative effects of groundwater mixing and stream ecosystem uptake on diel nitrate signals are poorly understood.

A conceptual model that integrates multiple hypothesized drivers of diel nitrate signals is a critical step to understanding stream corridor behavior in the context of watersheds. The research contributed here establishes such a model to evaluate controls on diel processing signals and seek a more holistic perspective on the attenuation of nitrate along agricultural stream corridors.

CHAPTER TWO

DIEL PROCESSING SIGNALS PROVIDE HOLISTIC INFORMATION ABOUT THE ATTENUATION OF NITRATE ALONG STREAM CORRIDORS

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Contributions: Developing conceptual models, field data collection, data processing and analysis, original composition of manuscript, manuscript writing and editing, and manuscript administration.

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Abstract

Increasing technological capacities to monitor within-day variation in stream chemistry (i.e. diel solute signals) promise greater understanding of stream corridor biogeochemistry and hydrologic connectivity. However, we lack a theoretical framework for assessing the relative influences of the multiple processes controlling these diel solute signals. Here, we demonstrate the utility of a two-station Lagrangian approach to evaluate diel variation in the processing of nitrate in parcels of stream water (referenced here as diel processing signals) in three agricultural low-order stream reaches in Central Montana, USA. Each reach has high stream ecosystem productivity and varying degrees of hydrologic connection to low-nitrate riparian groundwaters and high-nitrate upland waters. Based on a cluster analysis of 168 days of valid data, diel processing signals with low amplitudes were more common during periods with lower daily solar radiation and diel processing signals with higher amplitudes were more common during periods with higher daily solar radiation and in years with lower stream flows. Many summertime days showed processing signals consistent with evapotranspiration-influenced inflows from low-nitrate riparian groundwater. This inter- and intra- annual shift suggests the influence of diel variation in riparian groundwater inflows is more responsive to meteorological conditions and stream flow than the influence of diel variation in stream ecosystem nitrate uptake in these low-order reaches. Numerical experimentation with Lagrangian transport models demonstrates how stream ecosystem nitrate uptake and evapotranspiration-influenced groundwater inflows may cancel or reinforce each other to produce the typical signals identified by the cluster analysis. Less daily average nitrate attenuation in the study reach with direct inputs of high-nitrate upland waters suggests that the landscape position controlling the degree of

hydrologic connection to upland aquifers influences reach nitrate processing. This work highlights how multiple signal drivers introduced by stream corridors may variably respond to season and streamflow and presents a more holistic and scalable perspective on the relative influences of multiple corridor processes on channel nitrate concentrations.

2.1 Introduction

Human activities have profoundly altered the nitrogen cycle and doubled the amount of reactive nitrogen in the biosphere (Schlesinger, 2009), yet only a small fraction of nitrogen applied on land reaches the coastal oceans (Galloway et al., 2004). Stream and riparian ecosystems host a predictable sequence of biogeochemical redox reactions that can ultimately reorganize the export of stream solute concentrations delivered by upland terrestrial ecosystems (Hedin et al., 1998). However, most studies of nitrate processing in stream corridors focus on biogeochemical reactions either due to riparian buffering (Hill, 2019) or stream ecosystem metabolism (Ensign & Doyle, 2006; Tank et al., 2008). A more holistic perspective on the watershed-scale influence of nitrate attenuation in stream corridors will require a synthesis of conventional approaches to stream corridor biogeochemistry and hydrology.

Multiple pathways of hydrological connections and biogeochemical reactions in stream corridors may modify or transmit temporal variation in stream nitrate concentrations (i.e. nitrate signals) imparted by watersheds. First, stream corridors may have little capacity to process nitrate loading from upland soils if upland groundwater contributions bypass carbon rich soils in denitrifying riparian aquifers during transport to the channel (e.g. direct upland loading, Figure 1 flow path A) (Ocampo, Sivapalan, et al., 2006). In contrast, longer or slower riparian groundwater flow paths recharged by upland groundwaters may facilitate substantial nitrate

removal given an ample organic carbon supply driving anoxic conditions (e.g. upland-recharged riparian processing, Figure 1 flow path B) (McClain et al., 2003; Vidon & Hill, 2004). Longer or slower riparian groundwater flow paths that are not observable as hyporheic residence time by conventional in-stream tracer experiments may also be recharged by upstream channel waters (e.g. stream-recharged riparian processing, Figure 1 flow paths C) (Payn et al. 2009, Covino et al. 2011). This longer-term hyporheic flow is thus evident as gross gain from groundwater inflow in tracer tests, but represents stream corridor processing of upstream channel water rather than buffering of upland groundwater (i.e. a component of stream water "turnover", Covino and McGlynn 2007). Stream-recharged riparian processing due to stream water turnover and upland-recharged riparian processing may ultimately have indistinguishable mixing effects as groundwater contributions to channel waters (Figure 1 BC) when the subsurface residence times of both are long compared to the characteristic reaction times of anaerobic metabolism (Gooseff et al., 2003; Zarnetske et al., 2011). Nitrate removal in shorter or faster hyporheic flow paths that returns to the channel at similar time scales as advective transport will be within the "window of detection" of conventional stream channel tracer experiments (Ward et al., 2013) and thus be included in nitrate mass removal estimates for stream ecosystems (e.g. stream ecosystem hyporheic processing, Figure 1 flow paths D). Finally, nitrate removal from water flowing within the channel may be dominated by assimilative uptake associated with primary production in typically oxic conditions with more light availability (e.g. stream ecosystem channel processing, Figure 1 flow path E) (Hall et al., 2009). While the collective effects of direct upland loading, riparian processing, and stream ecosystem processing on reach nitrate processing are well

documented (Jarvie et al., 2018; Wollheim et al., 2017), the relative roles of these processes on patterns in nitrate concentrations along stream corridors are poorly understood.

Many stream corridor hydrologic and biogeochemical processes can vary throughout the day and the resulting 24-hour cycles in solute concentrations and groundwater inflows may help deconvolve stream corridor processes. When primary producers in stream ecosystems are not limited by nitrogen, they assimilate more nitrogen during the day when photosynthesis is active (Appling & Heffernan, 2014; Chamberlin et al., 2019). This process drives diel nitrate signals with minima in the afternoon during the peak of stream ecosystem assimilatory nitrate uptake (Heffernan & Cohen, 2010). Additionally, daytime evapotranspiration in riparian ecosystems may lower water tables in the riparian aquifer and thus decrease riparian groundwater inflows to the channel (Wondzell et al., 2010). Diel variation (or lack thereof) in stream discharge due to this effect of evapotranspiration allows inferring daily signals in streamflow generation processes (Wondzell et al., 2007). Diel variation in low-nitrate groundwater inputs to streams may create daily cycles with daytime maxima, though such groundwater mixing effects have been less studied than the controls on stream ecosystem processing (Aubert & Breuer, 2016; Oviedo-Vargas et al., 2022; Wilson & Xenopoulos, 2013). Cumulative effects of the daily variation in stream ecosystem metabolism and groundwater mixing along the stream corridor together determine the aggregate diel solute concentration signals observed at a given point along a stream channel.

Temporal shifts in the amplitude or phase of diel nitrate signals are commonly observed but not always explainable by a single driver. Stream ecosystems with high nitrate demand relative to concentrations often exhibit clear correlations among signal strength (e.g. amplitudes

of diel variation), daily solar radiation, and gross primary production. This correlation suggests light availability controls assimilatory nitrate uptake (Lupon et al., 2016; Roberts & Mulholland, 2007). However, in other streams, inter- and intra-annual variation in the phase and amplitude of diel nitrate signals cannot clearly be explained by a single driver such as solar radiation (Aubert & Breuer, 2016; Greiwe et al., 2021) or gross primary production (Kelly et al., 2021; Oviedo-Vargas et al., 2022). These patterns in diel signals may be better explained by considering the additive effects of multiple signal drivers such as groundwater mixing effects and stream ecosystem uptake (Oviedo-Vargas et al., 2022). Furthermore, diel nitrate signals measured at a single location are commonly used to evaluate local biogeochemistry, despite the potential for upgradient processes to confound conclusions about local effects of the stream corridor (Hensley & Cohen, 2016). This confounding effect may be especially evident where nitrate concentrations are high relative to demand (Bray, 2020). Extracting information about the relative importance of multiple synchronous signal drivers from an observed aggregate signal requires removing confounding influences from cumulative upstream signals and an understanding of how signal drivers may constructively or destructively overlap (*sensu* Seybold et al., 2021).

We suggest that a more holistic understanding of the influence of stream corridor processes on diel nitrate signals will come from Lagrangian characterizations of nitrate signal processing along stream reaches. Due to all the nitrate signal drivers listed above (and many other potential signal drivers not yet mentioned), the processing of nitrate concentrations in parcels of channel water in transport along a reach of the corridor is likely to vary through the day. We thus explore the potential to infer the relative influence of stream corridor processes from nitrate processing signals, which we define as the diel variation in the change in nitrate

concentration in Lagrangian parcels with respect to their time of arrival at the bottom of the reach. This perspective emphasizes understanding the local effects of a corridor on channel water chemistry and minimizes the potential for confounded interpretations due to solute signals that are likely to exhibit a long memory for past processing.

Nitrate processing signal drivers may particularly discernible in agricultural landscapes where the chemistries of riparian and upland groundwaters may strongly differ. For example, upland nitrate loading due to crop fertilization and riparian nitrate removal due to denitrification exaggerate the differences in nitrate concentrations between streams and upland and riparian groundwaters in the terrace landforms of our study area in central Montana (Schmidt & Mulder, 2010; Sigler et al., 2018). Nitrate concentrations in the generally oxic upland aquifers commonly exceed 20 mg NO_3^--N L^{-1} and nitrate concentrations in riparian groundwaters are often near or below detection limits. As a result, meaningful diel variation in inflow of low-nitrate riparian groundwater is likely to be strongly reflected in diel variation in the mixing effect on channel water concentrations (Figure 1 BC). Any direct input of upland waters to the stream is readily observable as nitrate enrichment (Figure 1 A). Finally, the generally unshaded streams are highly productive, likely driving substantial stream ecosystem nitrogen demand by primary producers (Figure 1 DE).

We explore patterns in diel nitrate processing signals in streams draining an agricultural landscape to provide a more holistic perspective on the collection of corridor processes that have potential to mediate nitrogen exports. We hypothesized that the signal drivers associated with stream ecosystem nitrate uptake, evapotranspiration-influenced groundwater inflows from low-nitrate riparian groundwater, and nitrate loading from high-nitrate upland groundwater are the

dominant controls on diel processing signals in this landscape. We focus on interpretation of Lagrangian nitrate processing signals, where more negative changes in nitrate indicate more attenuation of nitrate concentration in parcels of water as they travel a study reach. We start with a simple assumption that the diel variation in the effects of riparian evapotranspiration (Figure 1 BC) and stream ecosystem nitrate uptake (Figure 1 DE) are synchronous with solar radiation. However, we expect these processes to have opposite phases in their effects on the diel processing signal due to the maximum effect of evapotranspiration occurring at night and the maximum effect of ecosystem uptake occurring during the day. We also expect that any direct loading to the channel from upland groundwaters will shift the mean of the nitrate processing signal upward due to the augmenting effects of higher-concentration upland water mixing with the lower-concentration channel water (Figure 1 A).

We explore the viability of these hypotheses by assessing patterns in diel processing signals among three unshaded reaches of agricultural stream corridors, chosen based on their apparent variation in hydrologic connectivity among the channel, riparian, and upland waters. Our approach was to first objectively categorize the typical processing signals observed in our study streams, and then assess how patterns in the day-by-day occurrence of those signals are organized by the variation in hydrologic connectivity among reaches and changes in hydrologic conditions over time. We support this approach with process-based modeling exercises to illustrate the combinations of multiple signal drivers necessary to generate the types of common processing signals observed in these reaches.

2.2 Methods

2.2.1 Site Description and Reach Selection:

The study area is located on a strath terrace in the intermountain basin region of the Judith River Watershed in central Montana, USA (Figure 2a and b). This intermountain basin is on the edge of the Northern Great Plains (Figure 2a) and is extensively cultivated for non-irrigated cereal production, primarily winter wheat. Reaches were selected along two stream corridors incised into the Moccasin Terrace, which is centrally located within the basin (Figure 2b). The basin has a semi-arid climate with an average annual precipitation of 389 mm (1909-2016 period of record), 40% of which falls between March and June (Western Region Climate Center). Soils and shallow unconfined aquifers of the terrace are underlain by relatively impermeable shale units and the floors of stream corridors draining the terrace are generally incised below the top of the shales (Vuke et al., 2002). Incision of the main stem of the Judith River and its tributaries at the southwestern mountain front edge of the Moccasin Terrace limits recharge of the shallow terrace aquifer from mountain-derived waters. Thus, the groundwater overlying the shale is recharged solely by any local precipitation that can infiltrate through the relatively thin agricultural soils to reach the water table.

Local agricultural production and generally anoxic riparian aquifers create distinct water chemistries across riparian aquifers, streams, and upland aquifers on the Moccasin Terrace. Previous mass balance analyses of nitrate movement through the terrace demonstrate high concentrations in the upland aquifer that commonly exceed 20 mg NO_3^--N L^{-1} (Sigler et al., 2018). Riparian groundwaters are often anoxic and have ample dissolved organic carbon conducive for denitrification, resulting in low nitrate concentrations (ca. 0-5 mg NO_3^--N L^{-1}

(Sigler et al., 2018, 2022, Mayerik et al. in prep.)). Stream nitrate concentrations represent an apparent variable mixture of these values in the range of 2-16 mg NO_3^--N L^{-1}. Nitrate is the dominant form of inorganic nitrogen in the stream channels and ammonium concentrations are generally below 0.1 mg NO_3^--N L^{-1} across water sampling sites (Mayernik et al. in prep.).

All three stream reaches selected for this study exhibited net increases in flow of 10-20% over approximately 0.6-0.8 km of channel length and were chosen due to their varying positions in the landscape and varying degrees of direct contributions from the high-nitrate upland aquifer. We chose one reach along Porter Creek, which drains the southeastern part of the Moccasin Terrace (Figure 2b). Multiple springs emerging from the upland aquifer along both sides of the Porter Creek corridor deliver high-nitrate waters (ca. 18 mg NO_3^--N L^{-1}) directly to the stream channel (ca. 16 mg NO_3^--N L^{-1}) via surface flow (Figure 2d). In contrast, no springs are visible at the two study reaches on Louse Creek (Upper and Lower Louse Creek, Figure 2c), with the exception of a dammed and likely spring-fed off-channel stock pond with an overflow that drains to the channel at Lower Louse. Groundwater-fed riparian wetlands and ponds (unclear if natural or excavated) are more common along the Upper Louse and Porter Creek reaches and less common along the Lower Louse reach. Louse Creek drains the center of the terrace and net increases in flow at Upper and Lower Louse are likely predominantly sourced from low-nitrate riparian-processed groundwaters recharged by some combination of upstream channel waters and upland groundwaters. This assumption is supported by lower nitrate concentrations in channel waters at Louse Creek (ca. 2-8 mg NO_3^--N L^{-1}) than Porter Creek (ca. 16 mg NO_3^--N L^{-1}), which was further motivation for our site selection in exploring solute signal behavior. Flows increase between the Upper and Lower Louse study reaches due to the increase in watershed area

with distance downstream, but channel nitrate concentrations tend to decrease with distance downstream between the reaches. The stream channels of all three reaches are unshaded and exhibit high autotrophic algal production in the summer, presumably resulting in high inorganic nitrogen demand. As is common for stream corridors throughout the agricultural study area, all three reaches are fenced for pasture to take advantage of higher forage productivity due to wetter soils in the riparian zones through late summer.

Small stock ponds created by low head dams on Porter Creek and Upper Louse Creek are located upstream of our study reaches. At Upper Louse, the pond is pumped to supply center-pivot irrigation application during the growing season, and stream flow is substantially reduced at both reaches on Louse Creek during those withdrawals.

We conducted field campaigns over three years (2020, 2021, and 2022), capturing a range of stream flow and meteorological conditions over spring and summertime seasons. Field campaigns of one to two weeks were conducted twice in 2020 and once in 2022. In 2021, a longer field campaign spanned a progression of conditions, including an earlier springtime period of snow and soil thaw in March, a cooler late-springtime period of limited evapotranspiration and lower stream productivity in cooler April and May, and a warmer summertime period of higher evapotranspiration and higher stream productivity in warmer June through August. An intensifying hydrologic drought extending from late 2020 through 2022 resulted in decreasing stream flow in all three reaches, to the degree that stream flows were too low in the late summer of 2022 to continue viable data collection.

2.2.2 Data Collection and Processing:

We placed sensor arrays at the upstream and downstream ends of each reach in thalweg locations selected to maximize representation of well-mixed channel water and minimize localized influences on water chemistry. Nitrate concentrations were measured at 15-minute increments using Submersible Ultraviolet Nitrate Analyzers (SUNA V2, Sea-Bird Scientific, Danaher Corporation). Dissolved oxygen (DO) concentrations and water temperatures were measured at 5- or 15-minute increments using compact optical sensors (miniDOT, Precision Measurement Engineering Incorporated). We excluded measurements taken when precipitation events were likely to influence reach hydrologic connectivity to preserve focus on signals synchronized with diel cycles in solar radiation. Criteria for exclusion were defined by at least 0.7 mm of precipitation in the previous 4 hours, as measured at the Central Agricultural Research Center (CARC) Agrimet Weather Station. We excluded measurements taken when nitrate data demonstrated unreasonable values or excessive levels of noise, both of which were likely due to biological or sediment interference with the in-line ultraviolet absorbance detector.

We post-processed data based on co-deployment calibrations to maximize precision between instruments and thus maximize accuracy in evaluating the changes in nitrate concentrations between upstream and downstream sensors. Every two to six weeks, we placed sensors at the same reach in the same location for 12 to 36 hours. Data from this codeployment period were used to develop linear calibration correction models for each instrument by regressing the mean nitrate concentration across co-deployed instruments against the corresponding concentrations from individual instruments. Calibration correction models were checked for excessive extrapolation by ensuring that the range of concentrations used to derive the model was similar to the range of concentrations over which the model was applied. We also

periodically switched the upstream and downstream sensors to ensure that concentration differences between the ends of the reach were not biased by the calibration procedures. This calibration scheme prioritizes on maximizing precision among sensors over absolute accuracy of measurement, but the calibration-corrected nitrate concentrations for individual sensors were still within 10-15% of grab sample measurements analyzed in the lab. This level of accuracy is consistent with the manufacturer's reported uncertainties.

Supporting hydrological and meteorological data collected at each site included travel times for Lagrangian processing, photosynthetically active radiation, stream channel geometry, and point measurements of stream discharge. We used travel times derived from the peak of breakthrough curves from instantaneous-release salt (NaCl) tracer experiments to characterize the time required for a parcel of water to travel the reach (i.e. the modal transport time). During the longer 2021 field campaign, salt tracer experiments were typically conducted every 4 to 6 weeks at each reach and we found that nature of diel processing signals was not strongly influenced by uncertainty in travel times used for Lagrangian transformation. Photosynthetically active radiation (PAR) data were derived from in-field sensors (Li-192, LICOR) and estimated values of clear sky radiation for the study reaches. Average stream channel widths and depths were estimated from transects at 10 to 20 locations along each reach and channel lengths were estimated using Google Earth spatially rectified imagery. During each campaign, we frequently measured stream discharge via velocity-area gauging at the upstream and downstream ends of each reach. Establishment of reliable rating curves for open channel gauges in these highly productive streams would be challenging and establishment of weirs or flumes for gauging stations was outside the scope of this study.

We estimated reach-scale gross primary production using diel processing signals of DO concentrations (i.e. the "two-station" metabolism method (Marzolf et al., 1994; Odum, 1956)) on the days analyzed in modeling exercises detailed in Section 2.2.4. We expect substantial diffuse groundwater inflows in each reach that may contain much different DO concentrations than the stream channel. We accounted for the effect of groundwater inflows in metabolism models following Hall and Tank (2005). To account for uncertainties in field measurements of groundwater inflows, we used the median gross primary production estimate across multiple model estimates with reasonable ranges of both average groundwater inputs and diel variation in groundwater inputs.

2.2.3 Characterization of Typical Diel Signals:

Lagrangian processing signals were calculated using the difference in upstream and downstream signals, with the phase of the upstream signal shifted earlier by the reach travel time to consider concentration changes in parcels of water in transport. The diel processing signals for each 24-hour period of valid data were delineated by time periods starting and ending at 00:00.

Diel processing signals observed during the study were objectively categorized by applying a k-means cluster analysis to hourly average Lagrangian changes in nitrate concentration for every day of valid data across sites (Aubert & Breuer, 2016; Greiwe et al., 2021). Our goal was to categorize days with similar phase and amplitude in diel processing signals, but to ignore any influence of more general trends in nitrate processing across sites and throughout longer time scales. Multi-day trends were quantified by two passes over the nitrate processing signal with a 24-hour sliding-window average (Smith, 1998), the first to remove within-day variation and the second to remove any remaining within-day variation from the first

pass created by consecutive days that were in phase. The nitrate processing signals were then detrended before the cluster analysis by subtracting the multi-day trends. We used the k-means algorithm developed by Hartigan and Wong (1979) via the "stats" package in R (R Core Team, 2020) to partition detrended diel signals from each combination of site and day into a predefined number of groups, with the goal of minimizing within-group variation across all times of day. Minimizing the within-group variation across all times of day using a cluster analysis effectively sorts diel processing signals into categories of common patterns in the daily cycles that occur in midnight to midnight periods.

Choosing an appropriate number of clusters used to categorize the diel processing signals the dataset involves some subjectivity. We evaluated the additional explanatory benefit of various numbers of groups ranging from 1 to 10 by assessing how much each successively added group lowered the overall within-group variation. A threshold for choosing between three or four categories was not obvious, but more than four categories was clearly not necessary to identify the most distinct repeated patterns. We chose the categorization with four groups for interpretation because the additional category demonstrated a distinct amplitude relative to the analysis with only three groups.

2.2.4 Modeling the Overlapping Mechanisms Driving Typical Diel Signals

We developed a Lagrangian reactive transport model for nitrate to explore how multiple processes synchronous with 24-hour daylight cycles may combine to generate the typical nitrate processing signals represented by each group from the cluster analysis. The most exemplary diel processing signal from each group was selected based on the detrended data best predicted by the mean processing signal of that group (according to the coefficient of determination). Only days

with available data for metabolism analysis and little to no acyclic 24-hour trend in nitrate processing were considered.

Lagrangian nitrate processing was simulated based on the mixing effects of groundwater inflows and stream ecosystem processing,

$$\frac{dN}{dt} = \alpha_g\left(N_g - N_s\right) + I - U \quad (1)$$

where $\frac{dN}{dt}$ is the change in nitrate concentration with time in a parcel of water in transport along the channel [M L^{-3} T^{-1}], *U* is stream ecosystem nitrate uptake expressed as a rate of change in concentration (e.g. assimilatory uptake, denitrification, [M L^{-3} T^{-1}]), and *I* is input from nitrate-generating stream ecosystem metabolic processes (e.g. mineralization, nitrification, [M L^{-3} T^{-1}]). The volumetric inflow of groundwater normalized to stream channel volume (α_g, [T^{-1}]) and the difference between groundwater and stream water nitrate concentrations ($N_g - N_s$, [M L^{-3}]) are used to simulate the mixing effect of groundwater inflow on the change in concentration in the channel (Stream Solute Workshop, 1990).

Regardless of whether riparian groundwaters are recharged by upland groundwaters or upstream channel waters, previous estimates of riparian nitrate removal on the Moccasin terrace suggests that riparian water will contain little nitrate by the time it enters the stream (Sigler et al., 2018) and ongoing riparian groundwater research at these sites supports this assumption (Mayernik et al. in prep). Thus, we used 0 mg NO_3^--N L^{-1} for the concentration in groundwater inflows for the models of Louse Creek reaches where there is no evidence of direct upland groundwater inputs. At the Porter reach, nitrate concentrations of inflows vary across mixtures of riparian and direct upland groundwater inputs. We used nighttime changes in concentration along Porter Creek along with the net increase in discharge to estimate a net effective

groundwater concentration of 16 mg NO_3^--N L^{-1} in lateral inflows. This net effective concentration accounts for a weighted average effect of direct upland contributions and riparian processed waters, suggesting that the contributions of riparian processed waters are ca. 10% of inflows if direct inflow of upland groundwaters are assumed to have a concentration of 18 mg NO_3^--N L^{-1} and riparian processed groundwaters are assumed to have a concentration of 0 mg NO_3^--N L^{-1}.

We lack data to uniquely estimate I and to parse the mechanisms of U, so we apply the simplification that net generation of nitrate mass by the stream ecosystem ($I - U$) reflects a steady-state system except for the diel variation in mass consumed during the day by assimilatory nitrate uptake. We estimate daily assimilatory nitrate uptake ($\overline{U}_{NO_3^-,NPP}$, [M L^{-3} T^{-1}]) from daily estimates of gross primary production ($\bar{P}_{GPP}$, [L^{-3} T^{-1}]) using the atomic mass of nitrogen (M_N, [M]) and stoichiometric relationships that assume: carbon fixation follows GPP oxygen generation with a molar ratio of 1:1, net autotrophic production of carbon in biomass is half of gross carbon fixation (Hall & Beaulieu, 2013), and the molar ratio of C fixation to N assimilation is 10.5 (Chamberlin et al., 2019).

$$\overline{U}_{NO_3^-,NPP} = \frac{\bar{P}_{GPP}\ 0.5\ M_N}{10.5} \quad (2)$$

Similar to conventional two-station metabolism models, a Crank-Nicolson finite difference approximation was used to solve Equation 1 in a Lagrangian context, where Δt is the travel time of parcels of water traversing the reach.

$$N_{t+\Delta t} = \frac{N_t - U_{NO_3^-,NPP}\Delta t + \alpha_g N_g \Delta t - \frac{\alpha_g N_t \Delta t}{2}}{1 - \frac{\alpha_g N_t \Delta t}{2}} \quad (3)$$

Net stream ecosystem uptake and groundwater inflow rates were simulated to vary throughout the day in response to the influence of photosynthetically active radiation (PAR) on stream ecosystem GPP and riparian vegetation. To estimate a representative value of PAR experienced by a parcel of water over the transport time ($PAR_{transport}$), we calculated the average PAR integrated over each timestep. Net stream ecosystem uptake was simulated with a linear relationship to $PAR_{transport}$, and α_g was simulated with an inverse linear relationship to $PAR_{transport}$ rescaled between the minimum and maximum values ($\alpha_{g,min}$, $\alpha_{g,max}$).

$$U_{NO_3^-,NPP} = \frac{PAR_{transport}}{PAR_{tot}} \overline{U}_{NO_3^-,NPP} \quad (4)$$

$$\alpha_g = \alpha_{g,max} - \frac{PAR_{transport}}{PAR_{max}} \left(\alpha_{g,max} - \alpha_{g,min}\right) \quad (5)$$

We applied Bayesian inverse modeling approaches with this model (Equation 3) to infer the rate of groundwater inflow during the days considered typical of each cluster. Over a 26-hour period (23:00 to 01:00) associated with each analyzed day, Markov Chain Monte Carlo (MCMC) algorithms were used to sample posterior probability distributions of $\alpha_{g,max}$ and $\alpha_{g,min}$ using the R package rstan (Stan Development Team, 2022). The sampler was configured to use four chains. Each chain contained 2000 iterations for burn in to locate the region of parameter space with the best fit, and 2000 iterations for characterizing the posterior distribution. Convergence was confirmed by inspecting the traces for apparent stability and verifying that the convergence metric $\hat{R} < 1.05$, indicating reasonable convergence based on sufficient mixture across the chains. The prior probability distributions were minimally informed, but distributions were constrained to values considered reasonable based on the ranges of field measurements of net differences in discharge and stream channel geometry (reach length, average depth, and average

width). At Louse Creek, prior probability of $\alpha_{g,max}$was $\alpha_{g,max} \sim \Gamma\ (\alpha = 2, \beta = 2)$ and $\alpha_{g,min}$ was $\alpha_{g,min} \sim \Gamma\ (\alpha = 2, \beta = 2)$. At Porter Creek, prior probability of $\alpha_{g,max}$ was $\alpha_{g,max} \sim \Gamma\ (\alpha = 13, \beta = 2)$ and $\alpha_{g,min}$ was $\alpha_{g,min} \sim \Gamma\ (\alpha = 13, \beta = 2)$. Posterior probability distributions of $\alpha_{g,max}$ and $\alpha_{g,min}$ were used to simulate α_g throughout the day.

Volumetric groundwater inflow to the reach (Q_g, [$L^3\ T^{-1}$]) was estimated using inferred values of α_g and an estimate of the volume of channel water in the reach based on field measurements of reach length (L, [L]), average depth (z, [L]), and average width (w, [L]).

$$Q_g = \alpha_g L z w \quad (6)$$

We estimated the general coefficient of determination (or the Nash-Sutcliffe efficiency, R^2) to characterize the performance of the model in producing predicted values (p_i) that match the observed values (o_i).

$$R^2 = 1 - \frac{\sum_i (p_i - o_i)^2}{\sum_i (\bar{o} - o_i)^2} \quad (7)$$

We report the highest value of the R^2 across the ensemble of 8000 samples from the MCMC to represent the best fit.

2.3 Results

After accounting for travel along the stream channel, diel processing signals showed consistent cyclic behavior not evident in signals at either the upstream or downstream sites. In the late springtime example provided from Upper Louse, the concentrations at the ends of the reach showed little obvious synchrony with the daily photoperiod but showed strong correlation between the upstream and downstream locations (Figure 3a). In contrast, the differential

Lagrangian nitrate processing signals from the same data provide an example of the consistent synchrony with the daily photoperiod (Figure 3b) that was often observed during warmer months.

The occurrence of the four different categories of diel processing signals vary across space and time and reveal clear patterns with respect to landscape position among sites and seasonal variation within a site. Numerical simulations of hypothesized signal drivers reveal how they may or may not be combined to generate the types of processing signals we observed in this study.

2.3.1 Variation in Diel Nitrate Processing Signals Across Space and Time

We refer to the four diel processing signal types as low-amplitude, morning peak, midday peak, and afternoon trough diel processing signals (Figure 4). *Low-amplitude* diel processing signals were most common (106 d) and show little to no diel variation in nitrate processing. *Morning peak* signals were next most common (27 d) and show minimum attenuation shortly after sunrise with subsequently increasing attenuation until early nighttime hours. *Midday peak* signals were the third most common (25 d) and show a decrease in attenuation from around sunrise until a minimum attenuation at solar noon. After solar noon, attenuation increased through the late afternoon to a maximum attenuation with minimal variation at night. *Afternoon trough* signals were least common (10 d) and show an increase in nitrate attenuation beginning in the mid-morning followed by an afternoon decrease in attenuation. Despite clustering together, days with the afternoon trough processing signal demonstrated some of the highest variation in amplitude, where some days had narrow and deep troughs and others with much wider and shallower troughs.

The occurrence of each of the four types of processing signals varied seasonally (Figure 5). At both the Upper and Lower Louse reaches, afternoon trough processing signals were common when the last of the accumulated snow was melting in early March of 2021. Low-amplitude signals then dominated in these reaches through early springtime in 2021 (April through mid-May), except for a springtime snow-storm and subsequent melt in late May (Figures 5b and c). Starting in late May of each year, the higher-amplitude morning and midday peak signals were much more likely to occur. In the summer, the only period with more than a couple consecutive days with low-amplitude processing signals occurred at Porter Creek during the drought-free higher flows in July 2020 (Figure 5d).

Patterns in the occurrence of nitrate processing signals exhibited a clear relationship with stream flow, especially in association with the reduction of flow due to irrigation withdrawals (Figure 5). At Upper Louse, the midday peak signal was common during the lower flow conditions of 2020, including late springtime (ca. 60 L s^{-1}) and after irrigation withdrawals started (ca. 40 L s^{-1} after 10 July). In contrast, the midday peak signal was not evident at higher flows in July before irrigation withdrawal (ca. 75 L s^{-1}), although only a couple of days provided valid data. In late May and early June of both 2020 and 2021, midday and morning peak signals were common at Upper Louse, but Lower Louse showed no evidence of these signals during this time of year in 2021 until after flow was strongly altered by irrigation withdrawals that eliminated continuous flow at Upper Louse and reduced flow by about half at Lower Louse. Additionally, daily average nitrate concentrations in the stream channel generally decreased with decreasing flow associated with inter-annual drought, especially at the Louse Creek reaches (Figure 6).

The same type of signal frequently occurred on the same day across multiple sites where data were available for comparison. Upper Louse and Lower Louse had the same pattern 31 of 34 days with co-occurring data in 2021, and Lower Louse and Porter had the same pattern on 6 out of 10 days with co-occurring data in the summers of 2021 and 2022 (Figures 5c and d). We lack the ability to compare the same days between Upper Louse and Porter, but they generally had different patterns during pre-drought conditions. In the summer of 2020, Upper Louse had no afternoon troughs and generally had midday peaks while Porter generally had morning peak and afternoon trough signals (Figures 5b and d).

Regardless of the type of diel processing signal observed, the magnitude of nitrate attenuation was generally lower in Porter Creek than Louse Creek (Figure 4b), sometimes to the degree that nitrate concentrations were being augmented rather than attenuated. The summertime afternoon trough signals in Porter were an exception, where the diel processing signals had shallower and wider troughs than those occurring during snowmelt at Louse Creek. While nighttime attenuation was generally greater at Louse than Porter on days with this signal type, daytime attenuation was more similar among the study reaches, especially from midday through early evening hours. Additionally, the magnitude of nitrate attenuation across the two streams more frequently overlapped in the midday peak category.

2.3.2 Process-based Characterization of Overlapping Signals

The relative influences of inferred signal drivers varied strongly across exemplary days in each of the four typical diel processing signals (Figure 7). Predicting the phase and amplitude of the overall diel processing signal typically required modeling the constructive or destructive

interference among multiple underlying processes, with varying degrees of success considering the assumption of signal drivers correlating with PAR.

Analysis of a typical low-amplitude processing signal from early in the spring (27 April 2021) at Lower Louse provides an example of a relatively flat aggregated signal emerging simply from relatively flat signal drivers. The weak influence of estimated stream ecosystem uptake and corresponding weak influence of diel variation in riparian groundwater input destructively combine to yield weak variation in nitrate processing signal through the day that demonstrates no correlation with PAR (Figure 7 a-d, $R^2 = 0.97$). The maximum estimated uptake for the day was 0.04 mg NO_3^--N L^{-1} and the median of the ensemble for diel variation in groundwater inflows was also low with range from 1.2 L s^{-1} to 1.4 L s^{-1}.

Analysis of a day typical of the morning peak processing signal (8 June 2022) at Lower Louse shows how simulated signal drivers correlated with PAR fail to predict the timing of a peak occurring before solar noon (Figure 7 e-h, $R^2 = 0.87$). Nitrate concentrations in groundwater were below upstream nitrate concentrations in these simulations (0 vs 3 mg NO_3^--N L^{-1}, respectively) such that diel variation in stream ecosystem uptake and riparian groundwater inflow combine destructively. While both the modeled and observed signal generally decrease in attenuation in the morning hours, the observed signal reaches a minimum of attenuation approximately 3 hours before the modeled signal and nitrate attenuation is underestimated in the evening (after 18:00). Estimated stream ecosystem uptake has a maximum attenuation of 0.18 mg NO_3^--N L^{-1} and median estimated groundwater discharge ranges from 1.2 to 3.4 L s^{-1} over the day.

Analysis of a day typical of the midday peak processing signal (30 May 2020) at Upper Louse illustrates destructive interference between the influence of stream ecosystem uptake and riparian evapotranspiration. The combination of these signal drivers was able to predict a peak correlated with the peak in PAR (Figure 7 i-l, $R^2 = 0.95$). To produce a minimum of attenuation at midday, the medians of the Bayesian posterior distributions suggests riparian inflow ranging from 1.2 L s^{-1} to 4.5 L s^{-1} was required to offset the influence of stream ecosystem uptake (daily max = 0.14 mg NO_3^--N L^{-1}). While this model describes the general character of the observed diel nitrate processing signal, the simulated signal demonstrates clear structural error in comparison to observations at night, where nitrate attenuation was overestimated before sunrise and underestimated in the evening through early nighttime hours.

The overlap of diel variation in stream ecosystem uptake and the combined influence of riparian groundwater and direct contribution from upslope groundwater in Porter Creek creates a more complex logical pathway to predicting a typical afternoon trough diel processing signal (31 July 2021, Figure 7 m-o, $R^2 = 0.92$). Groundwater inflow was higher than that of the Louse Creek reaches (ranging from 9.0 to 10.2 L s^{-1}), but daytime reductions in groundwater discharge had the opposite effect on the variation in nitrate processing than the Louse Creek study reaches due to variable concentration differences between stream and groundwater. Upstream concentrations during the day (16.5 mg NO_3^--N L^{-1}) were higher than the flow-weighted groundwater concentration (16.0 mg NO_3^--N L^{-1}) but upstream concentrations at night (15.9 mg NO_3^--N L^{-1}) were lower than this concentration. The resulting variation in mixing effects through the day induced greater attenuation of nitrate concentrations during the day, such that the influence of groundwater inflow was constructive with stream ecosystem uptake. The stream

ecosystem signal driver had a maximum of 0.15 mg NO_3^--N L^{-1} in attenuation of nitrate concentrations.

2.4 Discussion

The four typical diel nitrate processing signals identified by the cluster analysis likely reflected common additive outcomes of synchronous processes in these headwater stream corridors draining an agricultural landscape. The model results provide a process-based context for interpreting why diel processing signals may vary throughout seasons, among flow states, and across sites. Patterns of nitrate processing signals observable in this agricultural setting with strongly differing upland and riparian chemistries provide an opportunity to understand the processes underlying stream corridor nitrate removal that may be less apparent in the nitrate processing signals of other settings.

2.4.1 The Synchronous Processes Underlying Diel Processing Signals

Reasonable combinations of diel variations in stream ecosystem uptake and evapotranspiration-influenced groundwater inflows described the timing of signal minima and maxima in three of the four typical diel processing signals (Figure 7). However, the simplifications or assumptions we have made in modeling process synchrony with solar radiation should be acknowledged before suggesting that "good" model fits specifically support the hypothetical processes, or perhaps more importantly, before attempting to define alternative hypotheses that explain the structure of residual error in "poor" model fits. First, the assumption that assimilatory nitrate uptake is in phase with PAR is not valid if the sources of nitrogen for assimilation varies or if the synthesis of proteins is not a consistent fraction of overall GPP.

Second, the assumption that the response of riparian evapotranspiration to solar radiation immediately translates into reduced groundwater discharge is not consistent with the lags in evapotranspiration effects observed at watershed outlets (Kirchner et al., 2020), though it could be more appropriate for the local effects emphasized by our Lagrangian processing signal approach. The potential for a viscosity effect on hydraulic conductivity in the riparian aquifer may also require consideration if solar radiation results in meaningful diel swings in riparian groundwater temperatures (Oviedo-Vargas et al., 2022; Schwab et al., 2016). Finally, characterization of the potential for diel variation in denitrification and nitrification driven by oxygen dynamics in variably saturated riparian soil (Duncan et al., 2015) or stream ecosystem denitrification or nitrate production (Hensley & Cohen, 2020) may be necessary to explain stream corridor processing signals measured in the channel. Even the best-fitting inferred models derived here are undoubtedly flawed representations of reality, but the potential for confounding processes should not limit initial numerical experiments that explore the dominant mechanisms driving diel processing signals and facilitate development of alternative hypotheses that may explain patterns in residual error.

While research has suggested that evapotranspiration-influenced groundwater inflows can influence diel solute signals via a mixing effect on stream concentrations (Hem, 1948; Wilson & Xenopoulos, 2013), we are unaware of other studies that constrain the conditions in which evapotranspiration can have a meaningful effect on diel nitrate processing signals. Model results for Louse Creek suggest that small variations in riparian groundwater discharge can destructively mask the signal driven by stream ecosystem uptake when riparian groundwater concentrations are substantially lower than those of the stream. While our simplified model should probably not

be interpreted as explicit representations of reality, the groundwater discharge estimates of 1 to 4 L s^{-1} were reasonable in that they were in the same order of magnitude as the net gains of 5-10 L s^{-1} estimated in Upper Louse by manual flow measurements. In contrast, diel variation in the difference between the groundwater inflow and stream channel concentrations may drive the processing signal more than the diel variation in groundwater inflow for streams like Porter Creek, where groundwater inflow concentrations were more similar to channel concentrations. The interactive effects of differences in concentration and variation in flow on the groundwater mixing signal aligns with previous work demonstrating that trace metals with large concentration differences across the stream and groundwaters could produce stream signals characteristic of evapotranspiration without resulting in detectable changes in stream discharge (Brick & Moore, 1996). These results highlight the need to understand concentration dynamics in addition to groundwater inflows to assess the combined influence of stream ecosystem uptake and evapotranspiration-influenced groundwater inflows on diel processing signals.

Signal drivers not correlated with PAR are necessary to explain the timing of minimum attenuation in the morning peak processing signal (Figure 7 e-h). Considering just these two signal drivers also tends to underestimate nitrate attenuation in the evening of all the higher-amplitude signals. Explaining these components of typical diel signals in nitrate processing clearly requires independent verification that our assumptions about the phase of stream ecosystem uptake and riparian evapotranspiration are correct or hypotheses regarding alternative processes.

At least part of the increase in nitrate attenuation through the afternoon and evening may be explained by diel variation in stream ecosystem denitrification. Given ample nitrate

availability, afternoon decreases in stream channel DO concentrations can cause increases in stream ecosystem denitrification (Christensen et al., 1990). This variation in denitrification may be amplified by afternoon exudation of labile organic carbon by primary producers (Heffernan & Cohen, 2010), and afternoon increases in temperature (Zheng & Bayani Cardenas, 2018). These effects are likely strongest when hyporheic flows have a higher potential to influence the chemistry of channel waters at low flows and when gross primary production drives substantial variation in DO and dissolved organic carbon. The role of denitrification may explain why the morning peak signal primarily occurs when flows were low and algal production was high. The potential for denitrification to explain the residual errors left by our models adds to a growing body of research suggesting the need to understand the role of stream ecosystem denitrification in diel nitrate signals and overall stream corridor nitrate processing (Hensley & Cohen, 2020; Kelly et al., 2021).

This study demonstrates a Lagrangian approach useful for exploring how multiple hydrologic and biogeochemical drivers in stream corridors combine to produce diel processing signals. Mechanisms underlying diel variation in stream nitrate are frequently assessed for the influence of dominant drivers on the variation observed at individual monitoring single stations rather than exploring multiple concurrent influences on Lagrangian signal processing along stream corridors (Aubert & Breuer, 2016; Greiwe et al., 2021; Lupon et al., 2016). In contrast, analyses of diel cycles in stream stage more commonly consider how multiple processes may constructively or destructively determine daytime hydrologic signals (Kirchner et al., 2020; Wondzell et al., 2010). We use similar principles applied in a Lagrangian perspective to assess how constructive and destructive signal driver interactions mediate common additive outcomes

represented in diel processing signals. This Lagrangian approach may be necessary to isolate within-reach processes from upgradient effects when nitrate concentrations are high relative to biological demand (Bray, 2020; Hensley & Cohen, 2016). We join Seybold et al. (2021) in suggesting that developing frameworks to describe the nature of synchrony among individual drivers is key to understanding overlapping ecosystem processes, such as those that drive diel nitrate processing signals.

2.4.2 Variation in Diel Nitrate Processing Signals Across Space and Time

Patterns in the occurrence of the four categories of diel processing signals were likely driven by differences in the relative importance of multiple corridor signal drivers over space in time, as illustrated in the modeling exercise. Landscape position likely influenced the relative importance of signal drivers through upstream-downstream differences in channel flow and differences in hydrologic connectivity among the channel, riparian groundwater, and upland groundwater. Season and drought likely influenced the relative importance of signal drivers through plant or algal life cycles, meteorological conditions, and channel flows

Regardless of the cause, channel flows should be considered a master variable in determining the amplitude of signals because they influence the potential influences of both mixing and benthic or hyporheic biogeochemical processes on channel water chemistry. The potential for signal development to be accentuated at lower flows is relevant to the variation in diel processing signals created either by landscape position or meteorological conditions.

The influence of landscape position via hydrologic connectivity was most evident in the generally less attenuation in nitrate processing signals of Porter Creek reach relative to those of either of the Louse Creek reaches (Figure 4b). Porter Creek clearly demonstrated a smaller

fraction of upland water processed by riparian groundwaters (Ocampo, Sivapalan, et al., 2006; Vidon & Hill, 2004) as would be expected considering the number of springs contributing upland waters directly to the channel. Model results also suggest that stream ecosystem uptake occurs simultaneously and can influence diel nitrate processing signals riding atop higher background nitrate concentrations (Figure 7). Diel nitrate processing signals, therefore, have potential to reveal the relative contributions of riparian groundwater inflows, direct upland groundwater inflows, and stream ecosystem nitrate uptake on channel nitrate dynamics.

The common occurrence of higher-amplitude nitrate processing signals in both Porter Creek and Louse Creek reaches during the late springtime and summertime of 2021 and 2022 suggests the relative influences of riparian inflow and stream ecosystem nitrate uptake were similar at each site. The more common occurrence of low-amplitude processing signals in Porter during the summertime of 2020 may be related to reduced diel variation in riparian-stream hydrologic connectivity in higher-flow conditions or a reduced effect of the same variation in hydrologic connectivity when mixing with higher stream flows. The hydrologic context of baseline groundwater levels created by landscape position and longer-term meteorological conditions are likely to influence how much riparian evapotranspiration can influence processing signals in the channel.

The prevalence of high-amplitude signals late in the summer or late in the drought suggests that the inextricable links between flow, irrigation extraction, and season in an agricultural landscape are primary controls on diel nitrate processing signals in these reaches (Figure 5). The dominance of diel processing signals characteristic of riparian evapotranspiration or potentially denitrification in the summer periods aligns with the effect of increased PAR and

temperature inputs on the relative variation in signal drivers such as stream ecosystem nitrate uptake (Lupon et al., 2016) and evapotranspiration-influenced groundwater inflows (Lundquist & Cayan, 2002). In these reaches, increased PAR and temperature were correlated with reduced flows, which will inherently magnify the effect of signal drivers that introduce the same amount of low-nitrate groundwater or decrease the mass of nitrate in channel transport by the same amount. Thus, the seasonal transitions in diel processing signals may reflect a combination of enhanced signal drivers and the sensitivity to the effect of signal drivers to flow.

Despite potential covariance in the influences of season and stream flow, we find some evidence of stream flow as an independent control on diel processing signals and reach nitrate processing. Enhanced effects of hydrologic turnover on stream chemistry at lower flows (Mallard et al., 2014) may explain why signals influenced by groundwater mixing were generally more common at sites with similar seasonal conditions yet lower flows. Additionally, the direct relationship between flow and concentration in Louse Creek reaches adds another, more general line of evidence that riparian nitrate processing has a greater influence on channel nitrate dynamics at low flows (Figure 6b). Declining concentrations with the progressive hydrologic drought may be the result of a greater proportion of stream channel or upland waters being processed by the riparian aquifer (Warren et al., 2022) or decreasing nitrate supply from upland soils (Loecke et al., 2017). In either scenario, low flows are expected to exaggerate the mixing effects of lower-nitrate groundwater contributions if the absolute gains in groundwater are similar across flow states.

2.5 Conclusions

A holistic and scalable model of stream corridor behavior is rooted in a conceptual model that aggregates the influences of direct upland contribution, riparian groundwater contribution, and stream ecosystem processing on nitrate signals in channel waters. Particularly in our agricultural setting with high-nitrate upland waters and denitrifying riparian aquifers, accentuated Lagrangian diel processing signals may offer distinct information about the collection of independent signal drivers that ultimately determine whole-corridor effects on nitrate processing. Low-nitrate riparian inflows due to the combination of upland-recharged and stream-recharged nitrate processing likely influence diel cycles in riparian groundwater inputs. The resulting evapotranspiration-influenced diel signals observed in this study highlight the need to better understand the influences of riparian solute processing on both upland waters and long-term hyporheic flow (Payn et al., 2009; Ward et al., 2013). Furthermore, we find that direct upland loading influences the magnitude of nitrate attenuation and stream ecosystem nitrate uptake may simultaneously attenuate nitrate. While the locally recharged aquifers in this setting exaggerate the effects of crop fertilization on upland groundwater nitrate concentrations, these general processes are common in other agricultural landscapes, especially those with transmissive upland aquifers due to artificial drainage (Kelley et al., 2017; Tank et al., 2021).

The solute processing signal approach may be extended to additional environmental tracers of water movement or metabolic activity to help provide additional information about stream corridor signal drivers, especially in corridors where the variation in nitrate concentrations between upland and riparian groundwaters is less distinct. Multiple tracers with contrasting characteristics may be necessary to evaluate both hydrologic and biogeochemical

influences on solute signals (Abbott et al., 2016). Coupled analyses of conservative and non-conservative solutes (e.g. nitrate and chloride in Lupon et al. (2016)) may illuminate similar signal drivers in other landscapes. As an alternative to nitrate signals, dissolved organic carbon signals can also be influenced by both diel variation in groundwater mixing effects and stream ecosystem processing (Oviedo-Vargas et al., 2022; Wilson & Xenopoulos, 2013). As diel signals are increasingly measured in a wider range of solutes and streams, theoretical frameworks for characterizing how overlapping processes shape signals are critical to extracting information about biogeochemical and hydrologic behavior from solute processing signals.

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Figures

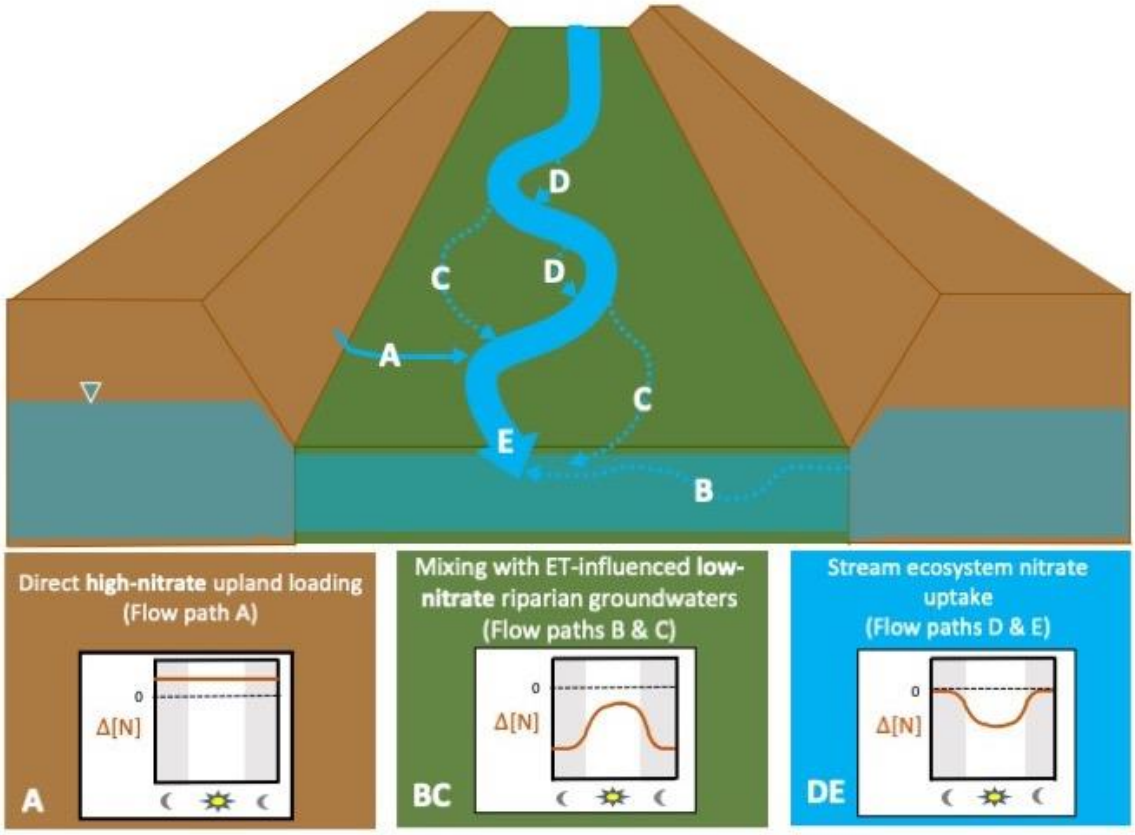


Figure 1
Conceptual model relating the independent effects of direct upland loading, stream ecosystem processing, and riparian processing on diel variation in stream reach nitrate processing, where Δ[N] refers to the change in nitrate concentration as water travels along the stream channel.

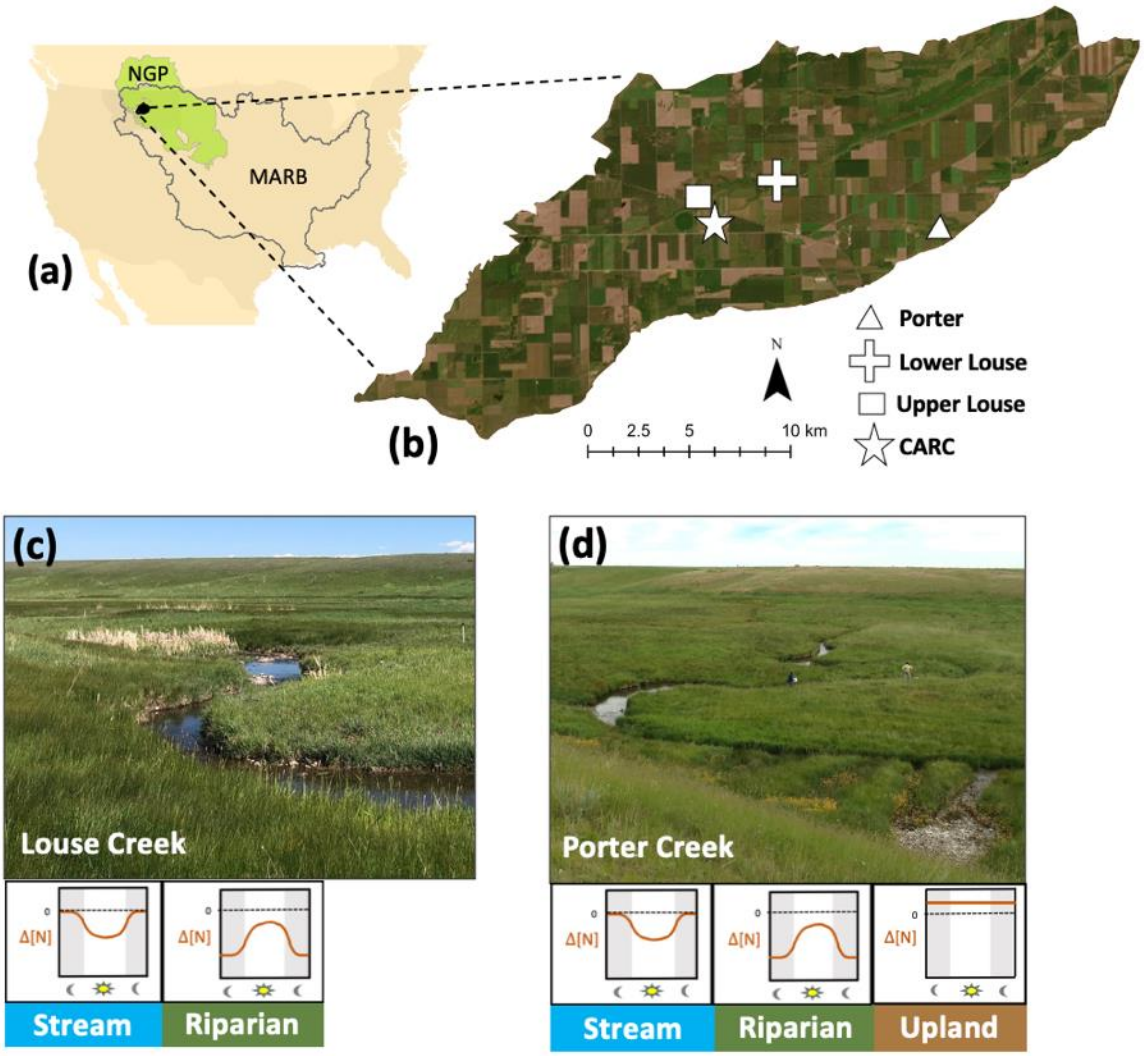


Figure 2
(a) Location of Moccasin Terrace within the Mississippi Atchafalaya River Basin (MARB) and Northern Great Plains (NGP), (b) the Moccasin Terrace (a strath terrace) including symbols showing locations of study reaches, and (c and d) and photos of the reaches with processes thought to be important to diel processing signals in each reach (Louse in c and Porter in d). Note the gravel-bed springs visible in bottom right of (d) at Porter.

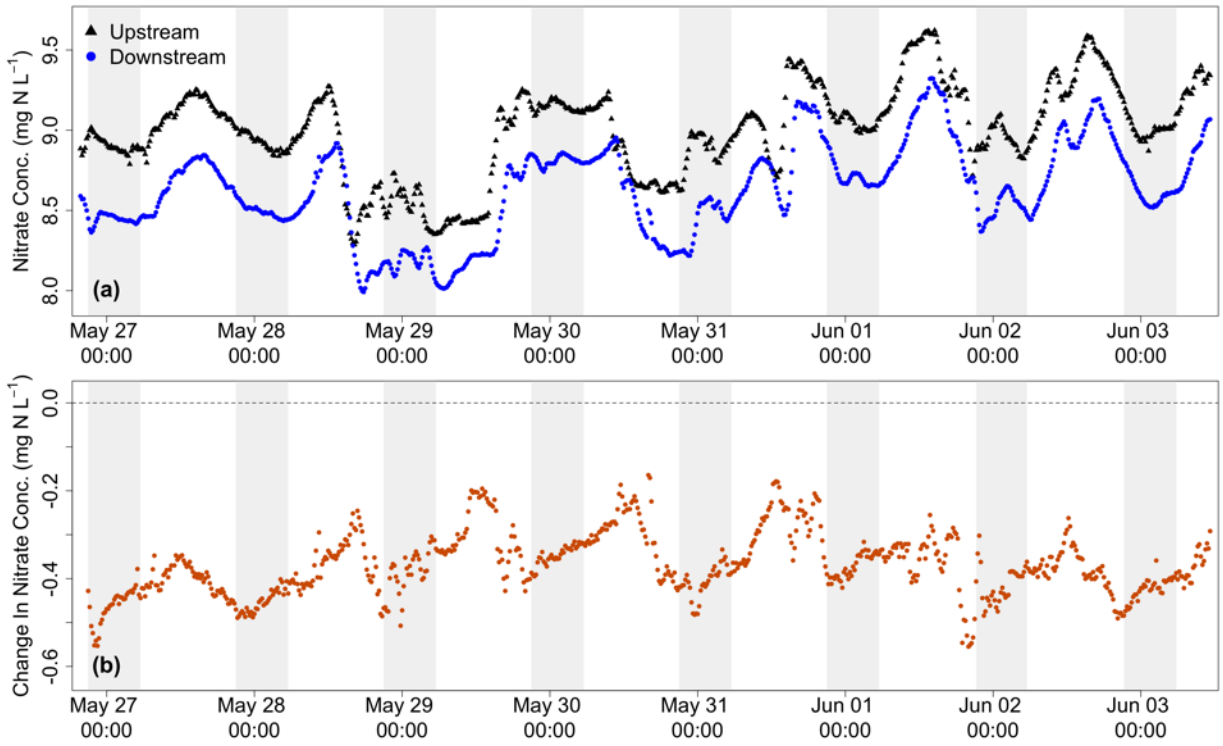


Figure 3
Nitrate monitoring results from a selected week at Upper Louse, 2020. Top panel (a) shows nitrate concentrations at upstream and downstream sites, while bottom panel (b) shows the difference between downstream and upstream concentrations as parcels of water traverse the reach (after the Lagrangian transformation was applied).

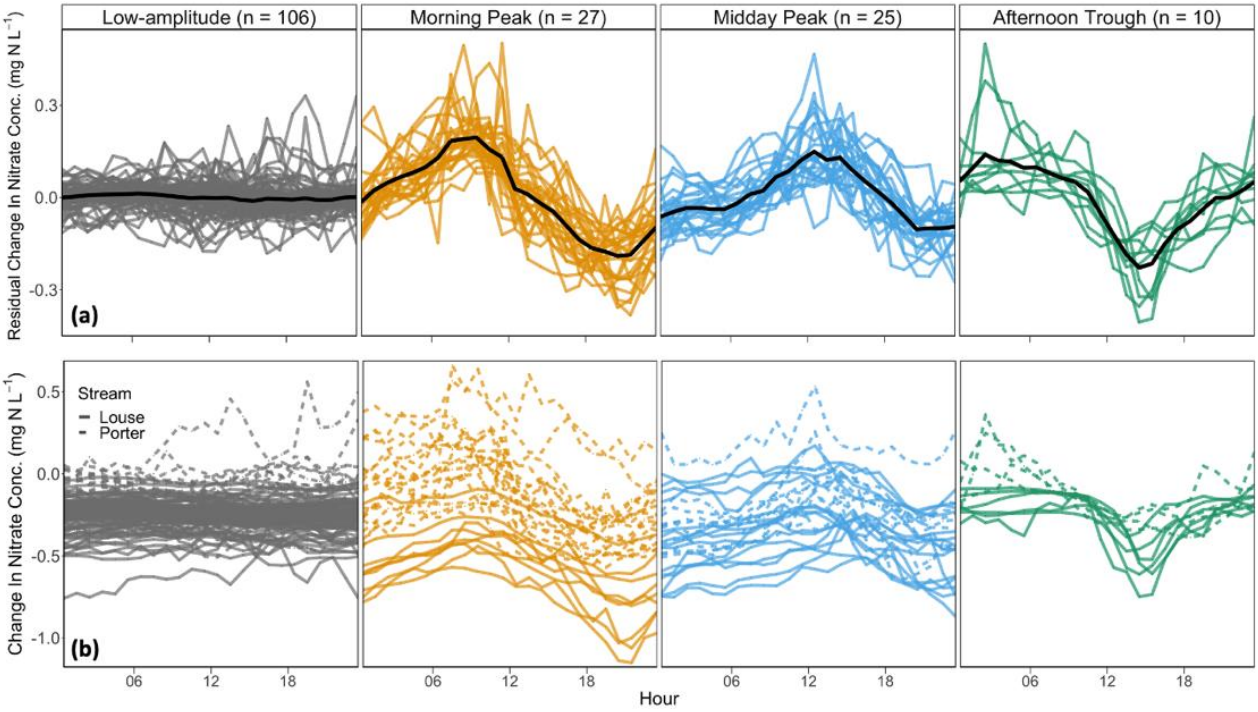


Figure 4
Categories of diel nitrate processing signals, where top panel (a) shows data centered around a double-passed 24-hour sliding window mean and bottom panel (b) shows raw changes in concentration. The thick black line in (a) is the mean of each cluster.

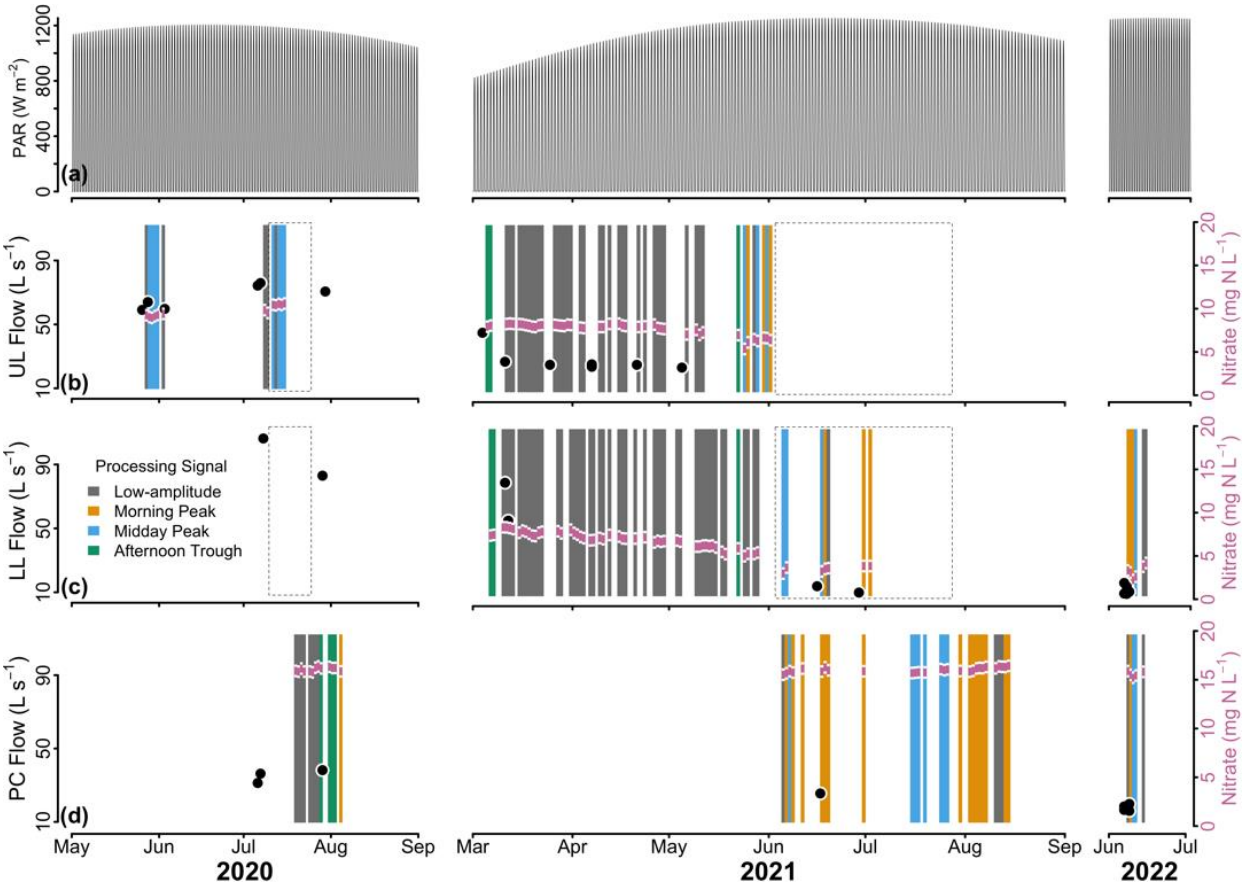


Figure 5

Diel patterns across sites and throughout time. Clear sky solar radiation is shown in (a). Diel patterns, flow, and nitrate concentrations are shown for each reach in (b – Upper Louse), (c – Lower Louse), and (d – Porter Creek). Upstream flow is shown in black points at each site corresponding to the left y-axis and daily mean upstream nitrate concentrations are shown in pink corresponding to the right y-axis. The black dashed boxes denote approximate time periods when upstream irrigation withdrawals directly from Louse Creek reduced stream flow by approximately half at Upper Louse and Lower Louse.

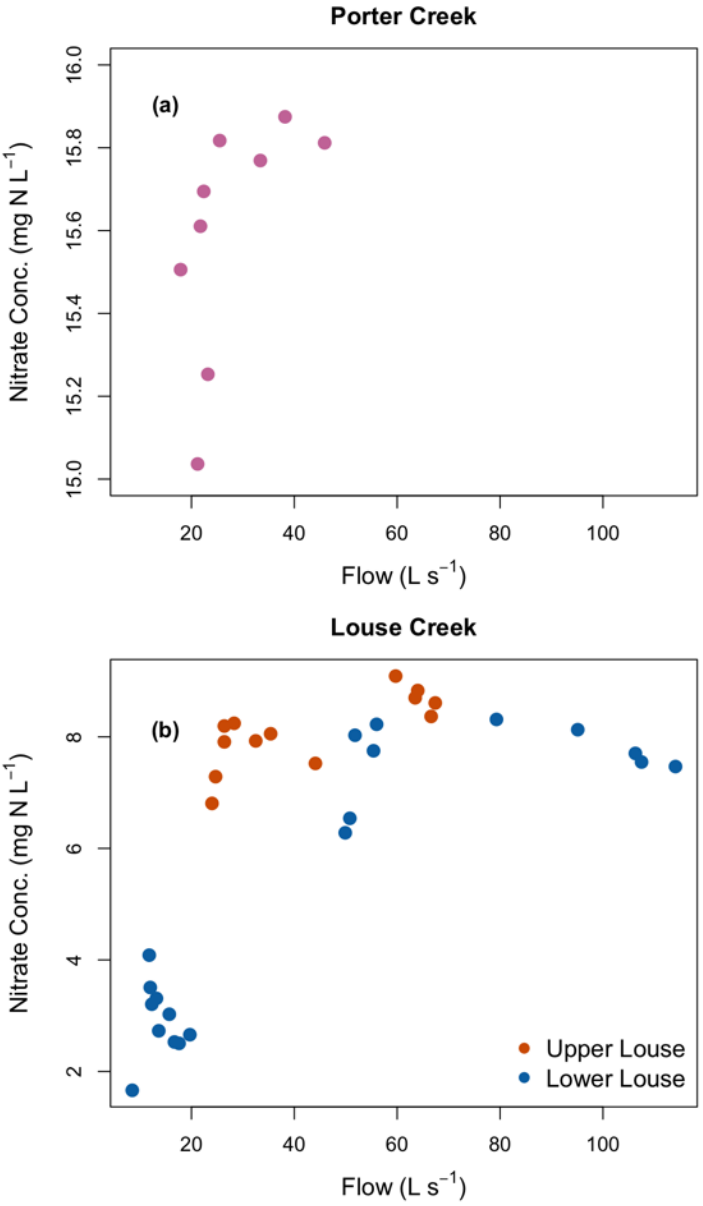


Figure 6
Daily mean flow versus daily mean nitrate concentrations at upstream and downstream sites of each reach. Note difference in scale on y-axis between (a) Porter Creek and (b) Louse Creek.

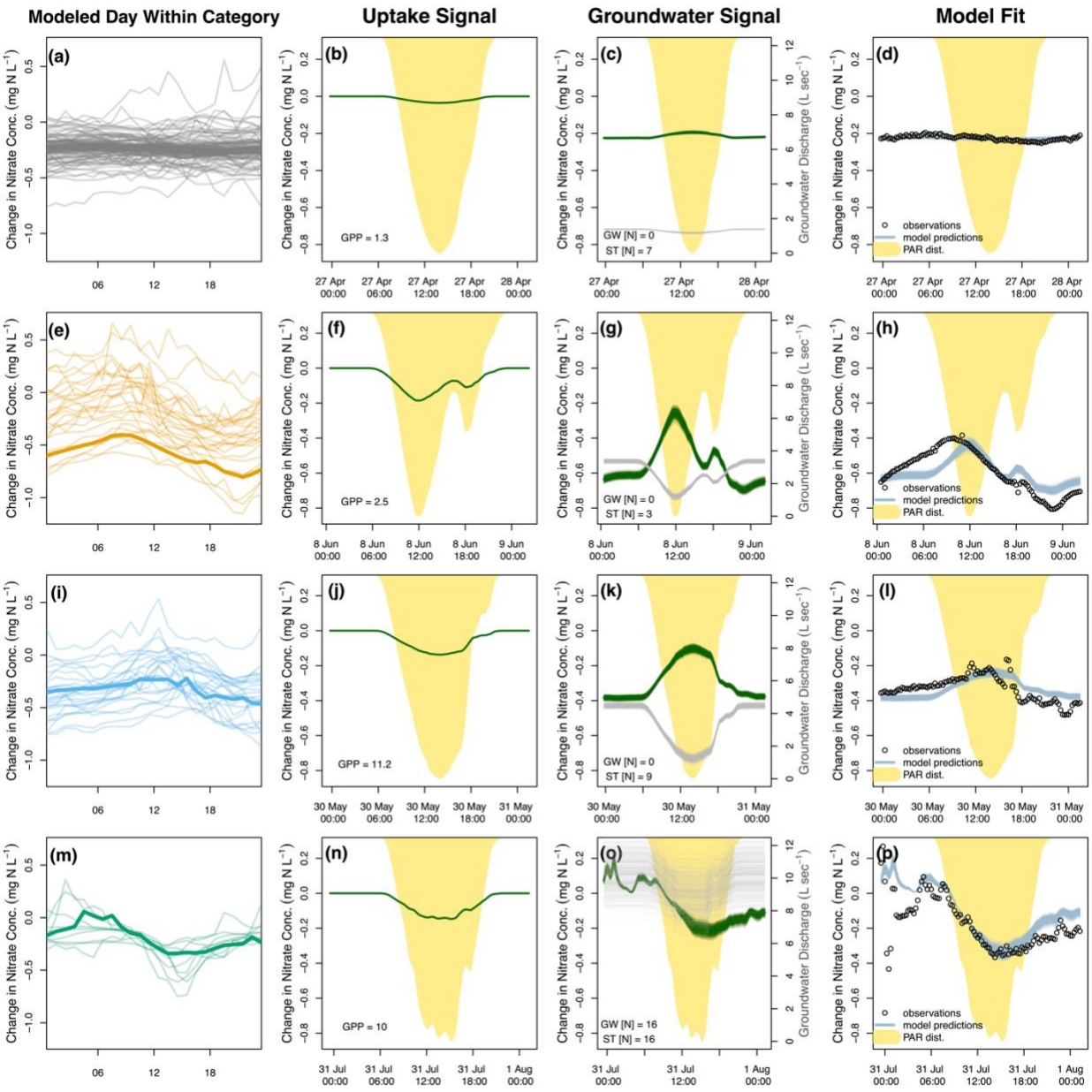


Figure 7
The influence of assimilatory nitrate uptake and estimated groundwater inflows on a single day (bolded) within each cluster (a, e, i, m). Each row shows results from a category of diel processing signals. The second column (b, f, j, n) shows the estimated effect of assimilatory nitrate uptake on the change in nitrate concentration, with daily GPP estimate noted in text (g O_2 $m^{-2}d^{-1}$). The third column (c, g, k, o) demonstrates the estimated influence of groundwater discharge on the change in nitrate concentration in green, where nitrate concentrations in groundwater and average upstream concentrations are noted in mg NO_3^--N L^{-1}. The fourth column (d, h, l, p) shows the model fit, including the combined signals of uptake and groundwater discharge.

Tables

	Minimum Groundwater Discharge (L s^{-1})	Maximum Groundwater Discharge (L s^{-1})
Low-amplitude	1.14-1.20	1.37-1.40
Morning peak	1.00-1.35	3.26-3.50
Midday peak	0.95-1.53	4.32-4.63
Afternoon trough	6.81-11.0	8.23-12.7

Table 1
95% credible intervals for groundwater discharge estimates for the exemplary day from each cluster.

CHAPTER THREE

THE ROLE OF DIEL PROCESSING SIGNALS IN THE FUTURE OF STREAM CORRIDOR RESEARCH

This research synthesizes a history of independent conceptual models for the dominant processes influencing solute concentrations along stream corridors to provide an integrated framework for evaluating whole-corridor effects on channel nitrate concentration processing. We categorize overlapping spatial and temporal scales of water movement and biogeochemical reaction in stream corridors into three primary causal pathways, all of which have distinct influences on nitrate processing signals measured in the channel. These pathways include riparian groundwater processing, stream ecosystem processing, and direct upland loading. Inter- and intra- annual shifts in observed nitrate processing signals support hypothesized drivers of solar radiation and stream flow, which lends credibility to using such signals to assess nitrate attenuation. The results of this research show progress toward a more scalable model of the role of stream corridors in whole-watershed controls on water quality.

More conclusive inference of ecosystem function from this approach requires a more complete understanding of the composite processes that combine to create the overall signal. First, diel nitrate signals alone are unlikely to contain sufficient information to parse out the relative influences of all nitrogen cycling processes in stream ecosystems (Hensley & Cohen, 2020; Kunz et al., 2017). While diel nitrate signals are predominantly driven by assimilatory nitrate uptake in some highly productive streams (Heffernan & Cohen, 2010), stream ecosystem nitrogen cycling is composed of many overlapping processes (Burgin & Hamilton, 2007). To better understand how non-assimilatory nitrogen cycling influences diel nitrate signals, future

research should investigate diel processing signals of additional solutes. For example, comparisons of dissolved oxygen and carbon dioxide signals may reveal the relative influence of anaerobic versus aerobic metabolism and suggest the potential role of stream ecosystem denitrification (e.g. Jarvie et al., 2018). Additionally, signals of alternate nitrogen species (e.g. ammonium, dissolved nitrogen gas, nitrous oxide) could inform the influence of diel variation in non-assimilatory processes. Second, our assumption that the mixing effect of evapotranspiration-influenced groundwater inflows is synchronous with solar radiation would be better supported with field studies of local evapotranspiration effects. Diel cycles in stream discharge commonly suggest the cumulative effects of evapotranspiration over a watershed are lagged behind solar radiation, but the effects of riparian evapotranspiration on local groundwater inflows may be more synchronous with solar radiation (Wondzell et al., 2007). Robust study of diel variation in the groundwater hydraulic gradients in the riparian aquifer would help clarify the timing of riparian groundwater mixing effects.

Understanding controls on the relative effects of riparian nitrate processing, direct upland loading, and stream ecosystem nitrate uptake are critical to using diel variation to infer the broader role of the corridor in changing daily average concentrations and loads. Parsing the distinct information about each process from diel processing signals using the modeling framework presented here could help develop conceptual models of how individual processes in stream corridors aggregate to affect whole-corridor behavior across space and time. In particular, I hypothesize that the hydrologic connection of a reach to upland and riparian aquifers interacts with instream assimilatory nitrate uptake to govern the propensity of a reach to concentrate, dilute, or remove nitrate on a daily basis. To assess the influence of both stream ecosystem

nitrate processing and groundwater mixing effects on channel nitrate dynamics, comparisons of nitrate loads and concentrations may be particularly useful. For example, riparian-processed inflows containing no nitrate will not change the downstream load but will reduce concentrations as water travels along a given reach. To this end, the nutrient processing domains framework (Valett et al., 2022) defined by bivariate comparisons of changes in load vs. changes in concentration along a reach is a promising framework to understand how individual signal drivers influence the capacity of a stream reach to alter both downstream nitrate abundance (loads) and local nitrate availability (concentrations). By applying a similar framework to the average behavior within each of the 168 days in this dataset, we could better understand how the relative influences of signal drivers vary across hydrogeologic settings, through hydrologic drought conditions, and through seasons.

The framework presented in this work could also be used to make predictions about riverine nitrate processing at larger spatial scales. Estimates of nitrate removal along river networks commonly treat rivers as a series of steam reaches by upscaling nitrate removal estimates within the window of detection (e.g. Alexander et al., 2009). This approach assumes that empirical studies at the reach scale capture the predominant hydrologic and biogeochemical processes within a reach and can be upscaled based on predictable physical characteristics (Ward et al., 2022). Yet biogeochemical reactions in the complete population of flow paths in stream corridors are not fully encompassed in river network models due to the complexity of overlapping scales driving hydrologic transport and biogeochemical reaction in stream corridors. For example, the degree to which riparian aquifers are recharged by up-valley stream channel waters versus upland waters is poorly understood (Payn et al., 2009; Ward et al., 2013). Our

work suggests that the population of riparian flow paths influencing stream nitrate dynamics can be simplified into those inside versus outside of the window of detection, if nitrate removal can be assumed to proceed to completion in the longer-term riparian flow paths that are not characterized by stream ecosystem mass removal but partially recharged by upstream channel waters. This approach hinges on identifying unique information about riparian nitrate processing, stream ecosystem nitrate processing, and direct upland nitrate loading in diel nitrate processing signals, which may be less evident in stream corridors with higher flow or smaller differences in concentrations. Thus, we suggest future research should expand upon this approach to evaluate groups of flow paths with similar biogeochemical character across a wider range of settings, perhaps by employing multiple tracers with contrasting characteristics (Abbott et al., 2016). Further application of such a framework could inform more scalable models of the role of the stream corridor in controlling the fate and transport of nitrogen applied to cultivated soils, which is critical to predicting downstream nitrate delivery and local nitrate concentrations.

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APPENDIX

DATA HANDLING AND PRODUCTS

Data associated with this thesis are organized into data products with a common organization designed to enhance data reproducibility and transparency. Each data product reflects a major step in the workflow and a natural breakpoint before further analysis. For example, the SUNA data products are organized into three main components for each combination of site and year of data in this study: 1) the primary data product, where basic quality assurance procedures were applied (e.g. removing measurements when the sensors were out of water) 2) the calibration data product, where calibration procedures are evaluated and applied and 3) the Lagrangian transformation of upstream and downstream data. Within each data product, there are four folders organized such that users can understand what data was used in creating the outcome of the workflow and how it was processed. The input folder contains all data necessary for the workflow. The protocol folder contains R scripts and information necessary to produce the data in proceeding folders. The incremental folder contains derived data and figures not included as part of the final product. The product folder contains the outcome of the workflow, such as final data tables, metadata, figures displaying the final data tables, and a readable summary of the major components of the workflow.

All data products associated with this thesis are located on the project OneDrive. Additionally, data products associated with major analyses (e.g. the cluster analysis and modeling analysis) are located in the repository HydroShare and will be publicly available upon submission of this manuscript. Foster, M. (2022). Foster Diel Signals Manuscript Data, HydroShare, http://www.hydroshare.org/resource/98901099ca1b4c728a9beb9d8a28983a