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Riparian Processes in Semi-Arid Landscapes: Understanding Controls on Nitrate Loss and Sulfate Production in Agricultural Stream Corridors

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Key Points:

- Complex hydrologic flow paths control the degree to which riparian biogeochemical cycling influences nitrate and sulfate export to streams
- Riparian areas facilitate nitrate loss from agricultural inputs, but inflows from hillslope springs mask riparian influence on streams
- Sulfate production exceeds loss in riparian areas due to weathering of riparian substrate, informing understanding of nitrate dynamics

Supporting Information:

Supporting Information may be found in the online version of this article.

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Abstract

Relative to their limited areal extent, riparian ecosystems are disproportionately important in regulating inorganic solute export from agricultural landscapes. We investigated spatial patterns of solute concentrations in surface and ground waters of stream corridors to infer the dominant hydrologic transport and biogeochemical pathways that influence riparian nitrate and sulfate processing from uplands to streams. We selected three reaches of stream corridors draining an agricultural landscape that vary in hydrologic connection with upland aquifers. Non-irrigated crop production dominates land use in the study area and influences the quality of upland groundwater draining to the stream corridors. We interpret patterns in solute concentrations of riparian groundwater and stream water relative to upland groundwater to infer the influences of biogeochemical processing and hydrologic connectivity. Excess nitrate from cultivated soils is evident in upland groundwater concentrations that consistently exceed the U.S. Environmental Protection Agency public drinking water standard. Nitrate and oxygen concentrations in riparian groundwaters were consistently lower than in terrace groundwater and adjacent stream waters, suggesting rapid consumption of oxygen and influence of anaerobic metabolic reduction processes in subsurface flow. Sulfate concentrations in streams were higher than in terrace groundwater, likely due to weathering of shale-derived substrate in riparian aquifers. The degree of solute mitigation or augmentation by riparian biogeochemical processes depended on the geomorphic context that controlled the fraction of upland water passing through the riparian substrate. Observed net nitrate losses with net sulfate gains from uplands to stream channels reflect flow paths through a complex distribution of redox conditions throughout the riparian areas, emphasizing the importance of considering riparian area heterogeneity in predicting solute export in streams. This research contributes to understanding how stream corridor substrate and geomorphic context controls the biogeochemical and hydrologic processes influencing the quality of water exported from agricultural landscapes.

Plain Language Summary

Riparian (streamside) ecosystems help regulate water quality in agricultural landscapes. This study focused on understanding nitrate and sulfate production and loss pathways in a semi-arid agricultural system in the northern Great Plains. We assessed water samples from upland and riparian groundwater and stream water across three stream corridors that differed in how water flowed through the riparian area. Here, agricultural management practices increase nitrate in upland groundwater, exceeding safe drinking water limits. Soil processes in this shale-dominated system also contribute nitrate and sulfate. Nitrate levels in riparian groundwater and streams were lower than upland groundwater, suggesting microbial processes within riparian areas reduce nitrate levels before reaching streams. However, sulfate levels in riparian groundwater and streams were often higher than upland groundwater, reflecting the influence of shale in this system. Earth surface processes that facilitate sulfate and nitrate production through sediment transport and routing of water are susceptible to land management activities prevalent throughout this agricultural system. Overall, these riparian areas play a vital role in reducing excess nitrate but also contribute to sulfate production, emphasizing the complex mosaic of redox conditions and interacting controls on biogeochemical processes. These findings are important to consider for a more holistic understanding of riparian function for water quality.

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1. Introduction

Despite progress in understanding the fundamental processes influencing riparian area biogeochemical function (e.g., Bernhardt et al., 2017; Hill, 2019; McClain et al., 2003; Naiman & Décamps, 1997), the important and complex interactions of hydrologic and biogeochemical mechanisms by which riparian areas facilitate nitrogen (*N*) and sulfur (*S*) cycling remain unconstrained (Hill, 2019). Riparian areas host shallow and fluctuating saturated conditions in substrate with spatially heterogenous organic matter content, mineral composition, and hydraulic conductivity (Vidon & Hill, 2004b), promoting a dynamic mosaic of solute production, loss, and mixing processes (Chapin et al., 2011; Hill, 2000; Naiman & Décamps, 1997; Silverman et al., 2019). While riparian areas are often disproportionately important for processing inorganic solutes relative to their limited spatial extent (Hill, 1996; Ledesma et al., 2016; Naiman & Décamps, 1997; Ranalli & Macalady, 2010; Tesoriero & Puckett, 2011), a knowledge gap remains of how the interactions of hydrologic processes and biogeochemistry in riparian systems control processing of *N* and *S* loading from uplands before export via the stream.

Direct and indirect effects of land use contributes *N* and *S* loads to stream corridors. through agricultural enhancing chemical mineral weathering and applying fertilizer inputs. In agricultural systems, application of *N* and *S* in crop fertilizers can increase soil water concentrations of oxidized soluble compounds like nitrate and sulfate, when application rates exceed crop demand (Eriksen, 2009; Scanlon et al., 2005; Sebilo et al., 2013; Sigler et al., 2020). The physical effects of agricultural land use on soil and plant community structures alter partitioning of precipitation among evapotranspiration, storage, and runoff (Souza et al., 2023; Sullivan et al., 2022). The transformed soil hydrology facilitates mineralization of soil organic matter, mobilization of solutes, and altered trajectories of chemical weathering. Chemical weathering, particularly of organic-rich sedimentary rocks (Holloway & Dahlgren, 1999; Tuttle et al., 2014), contributes various chemical species to ground and surface waters, including ions of *N* and *S* (Holloway et al., 1998; Houlton et al., 2018; Morrison et al., 2012; Wan et al., 2021). Chemical weathering and fertilizer additions of *N* and *S* increase the probability for transport of pollutant levels of nitrate and sulfate to ground and surface waters (Foley et al., 2011; Holloway et al., 1998; Ross et al., 2018) and need to be considered as interacting controls on solute transport.

Geomorphic controls on the routing of upland water through surface and subsurface flow paths to stream channels influence stream corridor biogeochemical processing of *N* and *S* (Baulch et al., 2019; Hedin et al., 1998; Tesoriero et al., 2013; Van Meter & Basu, 2017). The history of incisional and depositional processes establishing the riparian area influence the extent to which upland waters reach the stream via surface or subsurface flow paths (Ranalli & Macalady, 2010; Vidon & Hill, 2004b; Wymore et al., 2023). Soil horizon development impart vertical and lateral stratigraphic variation in riparian substrate texture (Daniels, 2003; Schaetzl & Thompson, 2015). The stratigraphic organization of riparian substrate determines the nature of water storage and movement, thus creating variation in reduction-oxidation (redox) conditions within the riparian area (Covino, 2017; Devito et al., 2000; Jencso & McGlynn, 2011; Schaetzl & Thompson, 2015; Vidon & Hill, 2004a, 2004b). Over shorter timescales, water supply and seasonal fluctuations in shallow groundwater tables result in variation in the timing of upland inputs to riparian groundwaters and the hydrologic connectivity between riparian substrate and the stream channel (Bergstrom et al., 2016; Jencso et al., 2009), allowing for seasonal variation of riparian influence on stream water chemistry (Burt et al., 1999; Jencso et al., 2010). Variation in riparian substrate that affects hydrologic and solute residence times (Ocampo et al., 2006; Vidon & Hill, 2004a) and variation in hydrologic connectivity among upland aquifers, riparian substrate, and stream channels (Ranalli & Macalady, 2010; Vidon & Hill, 2004b) create a complex mosaic of redox conditions that remain underexplored in their controls on the efficacy of riparian *N* and *S* processing.

Variable redox conditions in riparian aquifers promote a wide variety of microbially-mediated biogeochemical processes based on the local availability of metabolic electron donors (e.g., labile organic carbon) and electron acceptors (e.g., oxygen, nitrate, and sulfate) (Grabs et al., 2012; Harms & Grimm, 2008; Taylor & Townsend, 2010; Ågren et al., 2008). Flow paths through riparian substrate often interact with abundant organic matter (Hedin et al., 1998; Hill et al., 2014; McGlynn & McDonnell, 2003), such that oxygen is quickly exhausted by aerobic heterotrophic demand. In oxygen-limited environments, microbially-mediated *N* and *S* mineralization and reduction become thermodynamically favored (Bernhardt et al., 2017; Burgin et al., 2011; Hedin et al., 1998; Payn et al., 2014; Reinhold et al., 2019; Zarnetske et al., 2012), with nitrate reduction generally providing more energy than sulfate reduction. Thus, spatial and temporal patterns in abundance of electron acceptors with varying energy yields may reflect variation in the redox conditions among subsurface riparian environments, the complexities of which remain underexplored.

We address knowledge gaps in the controls on riparian system biogeochemical function by exploring spatial patterns in ground and surface water chemistry across stream corridors draining an agricultural landscape. This study focuses on an agricultural area hosting a shallow aquifer in the Judith River Watershed (JRW), located in a semi-arid region of the northern Great Plains. We characterize variation in the chemical composition of surface and ground waters within and near three stream corridor reaches that differed in hydrologic connectivity among upland aquifers, riparian aquifers, and stream channels. Two selected reaches had gains in stream flow dominated by subsurface flow through the riparian area, and a third selected reach had gains in stream flow dominated by multiple channelized surface flow paths from hillslope springs.

We first hypothesize that (a) the geomorphic context of the stream corridor is important to *N* and *S* processing because it influences the extent to which upland water reaches the stream via reactive subsurface riparian flow paths versus relatively nonreactive surface spring channels. We further hypothesize that (b) hydrologic connections among spatially complex riparian substrate influence the net biogeochemical function of stream corridors because it influences transport of solutes among sites of oxidation and reduction. To test these hypothesis we (a) compare solute concentrations in streams that vary in their hydrologic connection with upland aquifers (Figure 1) to assess whether streams with more direct surface connection will demonstrate less net effect of reactivity from riparian groundwater and thus have nitrate and sulfate concentrations more similar to upland groundwater; and (b) compare patterns in the chemical composition of riparian groundwater from sites that differ in substrate texture and hydraulic conductivity to observe variation in nitrate and sulfate concentrations that reflects varying connection between oxidizing and reducing conditions. We compare patterns in chemical composition differences from uplands to streams and the variation in riparian redox conditions to test controls on stream corridor biogeochemical function. Our research advances a more detailed understanding of the influence of stream corridor hydrologic connectivity and geomorphic context on the export of *N* and *S*, particularly from agricultural systems.

2. Materials and Methods

Site selection, methods, and data analysis in this study were primarily aimed at characterizing and interpreting patterns in water chemistry within the riparian area relative to water chemistry in the upland aquifer and stream channel. We conceptualize riparian areas as a separate process domain from upland aquifers or stream channels to acknowledge the natural boundaries created by self-organization of distinct hydrologic and biogeochemical feedbacks within each domain (Montgomery, 1999). We include riparian groundwater flow paths that are recharged from both the hillslope and the stream channel within the riparian process domain due to their shared characteristics of longer residence times and more anaerobic processes relative to the generally faster moving and more oxygenated water in the stream channel (Boulton et al., 1998; Zhao et al., 2021). We define a stream corridor as the combination of the stream channel and the riparian process domains (Fisher et al., 1998) (Figure 1).

2.1. Study Area

The study was conducted in an agricultural area at the lower elevations (1,200–1,300 m. a.s.l.) of the JRW within an area of the Missouri River Basin located in the northern Great Plains ecoregion (Figure 2a). The study area has a semi-arid climate with a 30-year mean annual precipitation of 393 mm and mean annual temperature of 6.6°C (1991–2020, 4-km resolution centered on coordinates: 47.0778, −109.9126; PRISM Group, 2024). Over the 3-year study period (2019–2022), the mean annual precipitation was 300 mm and mean annual temperature was 6.8°C (Figure S1 in Supporting Information S1). Temporal summary statistics were calculated from measurements at 1-hr intervals (U.S. Bureau of Reclamation, 2023).

To minimize confounding influences on hydrologic context, we performed this study on streams draining the Moccasin terrace (Figure 2b), a strath terrace landform with a shallow upland aquifer perched on relatively impermeable shale (Vuke et al., 2002). The incision of mountain-front streams around the upgradient end of the Moccasin terrace has isolated the shallow terrace aquifer from recharge originating from the Little Belt Mountains (Figure 2a), and the impermeability of the shale units comprising the bedrock limits connectivity of the shallow aquifer with deeper aquifers (Sigler et al., 2018; Vuke et al., 2002). Therefore, water stored in the shallow and unconfined Moccasin terrace aquifer is sourced primarily from infiltration of local precipitation through

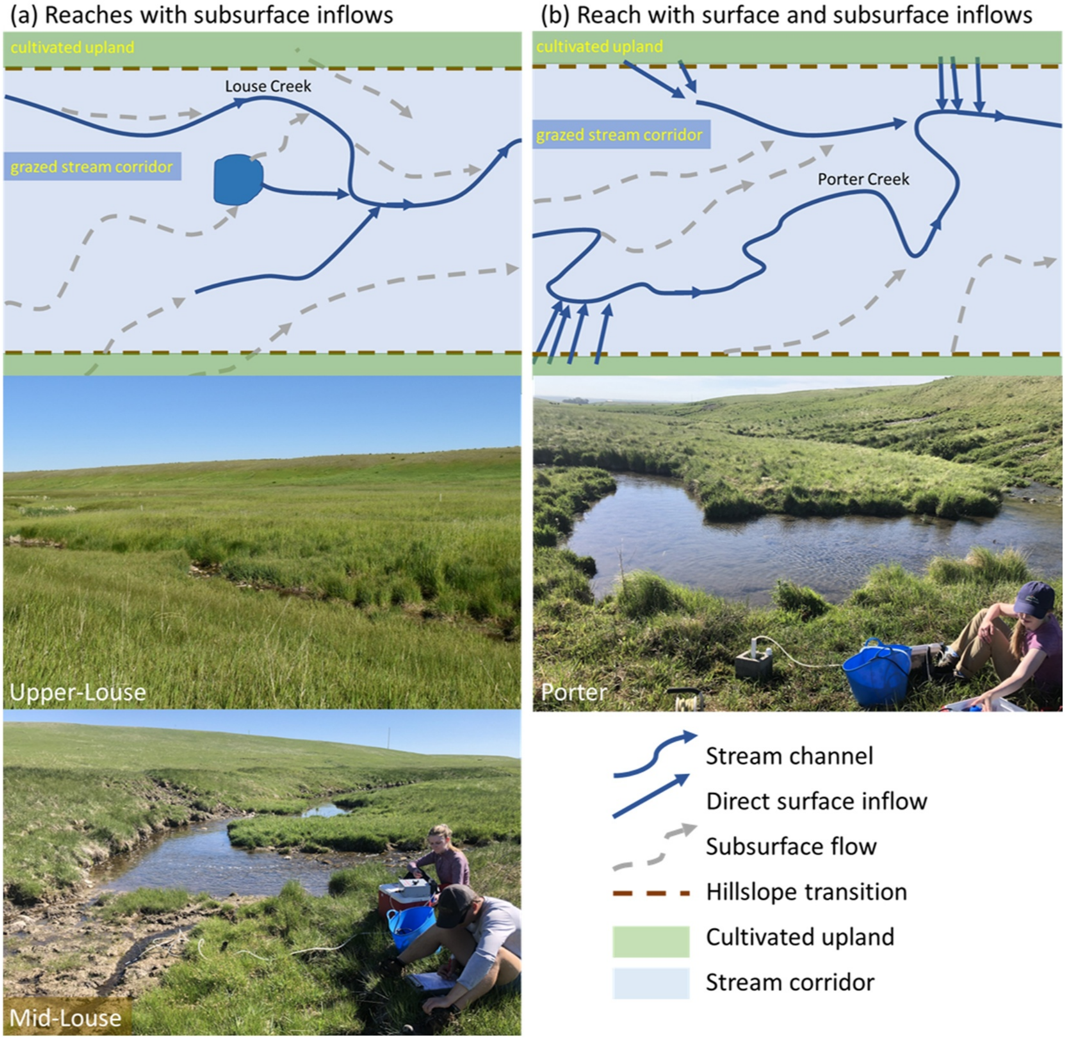

Figure 1. Conceptualizations of hydrologic connectivity among the upland aquifer, riparian aquifer, and stream channel with photos of study reaches. Sites include (a) Louse Creek reaches where subsurface flow paths (dashed gray lines) dominate hydrologic connectivity between the upland aquifer and the stream channel because surface flow paths from the upland aquifer are not apparent. Sites also include (b) a Porter Creek reach where direct surface flow from abundant hillslope springs (straight solid blue lines) dominates hydrologic connectivity between the upland aquifer and the stream channel. Hillslope spring channels are evident on the hillslope in the upper right of the photo. Dashed lines depicting hydrologic connectivity via subsurface flow reflect conjectures in the direction of riparian groundwater flow paths.

cultivated soils and exported through groundwater-fed stream corridors, with perennial channelized flow from hillslope springs draining directly from the upland aquifer into the stream at some locations.

Non-irrigated annual crop production is extensive across the well-drained calcareous soils of the Moccasin terrace, classified as Calciustolls and Argiustolls in the US Taxonomy (U.S. Department of Agriculture, 2022). Soils generally exhibit clay loam textured mineral layers from 40 to 100 cm depths overlying the coarse gravels that host the shallow unconsolidated aquifer, where subsurface horizons with >40% coarse gravel content extend from the bottom of the mineral soil horizons to the ca. 10-m depth of the shale contact (Sigler et al., 2018). Dominant crop types grown in this region are spring wheat, winter wheat, and barley, with increasing incorporation of pulse crops (e.g., lentils) to replace fallow in cropping sequences (U.S. Department of Agriculture, 2023). Typical *N* fertilizer application rates vary from 60 to 100 kg N ha^{-1} year^{-1} for small grains in these cropping systems (John et al., 2017), while *S* fertilizer application rates are more limited due to a lack of information of its positive influence on crop yield and/or protein content (Karamanos et al., 2013; Miller et al., 2024). Minimal use of irrigation on the Moccasin terrace results in crop yields that are typically limited by

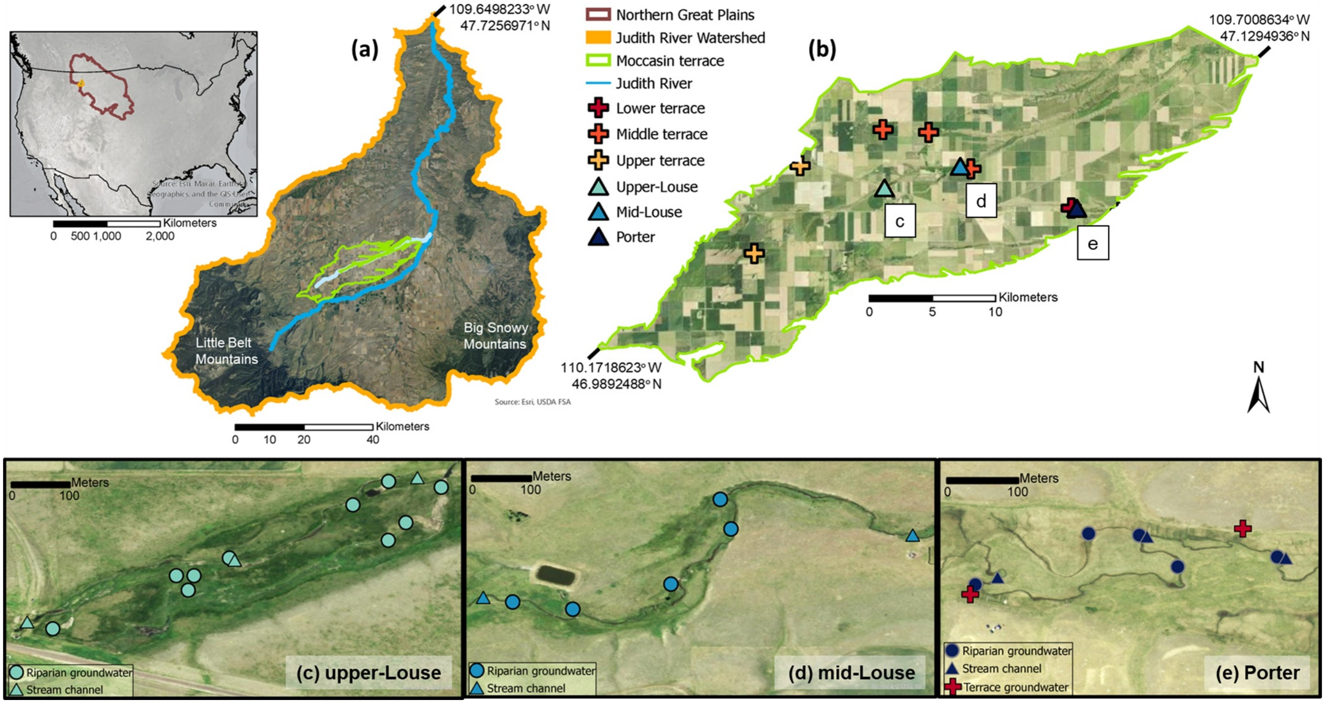

Figure 2. Maps and aerial imagery of the study area and sampling locations (Table S1 in Supporting Information S1). (a) Map of the Judith River Watershed (orange outline), Montana, USA in the northern Great Plains ecoregion (maroon outline, inset). The focal area for this study is a terrace landform outlined in green. (b) Expanded map of the terrace with upland groundwater sampling locations (crosses) and study reach locations (triangles) (c–e) Aerial imagery of each ca. 0.7 km stream reach shows sample site locations for riparian groundwater (circles) and stream water (triangles) along (c) upper- and (d) mid-Louse Creek and (e) Porter Creek. Data sources for the maps include: ESRI, USDA, USGS, FSA; NGP boundary obtained from World Wildlife Fund.

the timing and magnitude of precipitation and soil water storage capacity. Soil architecture combined with cultivation practices that aim to promote soil water storage allow for substantial solute leaching to the shallow upland aquifer, which supplies drinking water to private well owners in the region (Schmidt & Mulder, 2010; Sigler et al., 2018).

We selected study reaches from the first-order streams draining the Moccasin terrace, based on geomorphic context and access permissions. Selected study reaches are structurally typical of stream corridors incised into the shale bedrock, with corridor widths ranging from 150 to 350 m. Riparian groundwater tables are shallow, with depths ranging from 0 to 90 cm below the ground surface and isolated areas of aquifer confinement with heads above the ground surface (Table S1 in Supporting Information S1). The stream corridors are used in middle to late summer as pasture for cattle production (U.S. Department of Agriculture, 2023) and are subject to varying degrees of bioturbation from burrowing of Richardson's ground squirrels.

We selected three ca. 0.7-km reaches of stream corridors on the Moccasin terrace (Figure 2) to compare hydrological and biogeochemical processes in riparian areas with different modes of hydrologic connectivity between upland aquifers and stream channels (Figure 1). Channelized surface flow from hillslope springs dominated gains in stream flow along the reach selected on Porter Creek (Figure 2e). Groundwater flow paths dominated contributions to gains in stream flow along the two reaches selected on Louse Creek (upper-Louse and mid-Louse; Figures 2c and 2d), with no apparent surface flow from uplands to stream channels. Perennial flow from a small artificial pond in the riparian area at the mid-Louse reach suggested it might recharge via more transmissive flow paths from the upland aquifer than the surrounding riparian area, though confirming this was beyond the scope of this study. Reach selection was also motivated by previous work showing that Louse Creek had lower nitrate concentrations than Porter Creek (Sigler et al., 2018). The mid-Louse reach is approximately 4 km downstream of the upper-Louse reach (Figure 2b), allowing for comparison of corridors with differing stream flows and differing proximity to the origin of perennial flow. Stream water up-gradient of the upper-Louse reach was seasonally diverted to the only known pivot irrigation system on the terrace, which heavily influenced stream flows in July 2020 and June 2021 (Foster, 2023). The study reach on Porter Creek was located at a lower elevation on the southeast edge of the terrace, relative to the reaches on Louse Creek that were more centrally located on the terrace (Figure 2b).

2.2. Sample Collection

We collected water samples from soils, terrace aquifers, riparian aquifers, and stream channels. Soil water was sampled from cultivated terrace soils using porous cup tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark) from 2013 to 2016 (Sigler et al., 2018, unpublished data). At each sampling location ($n = 13$; Table S1 in Supporting Information S1) a single lysimeter was installed in the fine-textured soil horizon just above the contact with the underlying gravel horizon, depths from 50 to 120 cm (Text S1.2 in Supporting Information S1 and Sigler et al., 2018). Terrace groundwater was sampled from hillslope springs from 2020 to 2022 ($n = 32$) and hillslope springs and wells from 2013 to 2014 ($n = 39$, Sigler et al., 2018, unpublished data). To assess general patterns in variation with landscape position, we categorized terrace groundwater sampling sites based on their proximity to the study reaches following the general elevation gradient (Figure 2b; Text S1.2 in Supporting Information S1). In 2021 and 2022, we collected a total of 131 groundwater samples from twenty screened wells installed ca. 100 cm deep at select locations in the riparian aquifers of the three study reaches (Figure 2; Text S1.2 in Supporting Information S1). Most well locations were selected from within 2 m of the stream channel to capture groundwater chemistry exchanging with the stream. Some well locations were selected from remnant channels further from the main stream channel to assess groundwater chemistry in areas with less exchange with the stream. Well locations spanned the length of each study reach. From 2020 to 2022, we collected a total of 177 samples from stream channel water at upstream, mid-reach, and downstream locations along each reach (Figures 2c–2e). Data from a total of 17 samples collected from 2013 through 2014 are included for the upstream site at the upper-Louse reach (Table S1 in Supporting Information S1) (Sigler et al., 2018, unpublished data). Water was sampled from turbulent locations in the channel presumed to be a well-mixed representation of stream flow. When streams had measurable flow, we used an acoustic Doppler flow meter (SonTek FlowTracker, Xylem Environmental Solutions, San Diego, California) to measure discharge (velocity-area gauging using the U. S. Geological Survey mid-section method) at the upstream and downstream ends of each study reach at least once during each sampling campaign in 2021 and 2022.

We sampled at times selected to represent seasonal or interannual variation in hydrologic connectivity among terrace aquifers, riparian aquifers, and stream channels, resulting in variable frequencies of sampling (Table S1 in Supporting Information S1). Typically, we collected samples from the same site at similar times of day, limited to one sample collected per site per day, with time of day varying across sites. We observed within-day variation in riparian groundwater levels (Figure S7 in Supporting Information S1) and stream flow rates, and a parallel study observed within-day variation in nitrate concentrations of stream water across these reaches (Foster, 2023). However, the diel change in nitrate concentration at a given location was small relative to patterns observed across space or seasonal to annual time frames. Therefore, for interpretations in this study, we assumed that within-day variation of solute concentrations was negligible relative to variation across seasons, sites, and process domains.

Ground and surface water samples were collected using a peristaltic pump (Geotech Environmental Equipment, Denver, Colorado), through a 0.45-μm capsule filter pre-rinsed with water from the respective sampling location (Geotech Environmental Equipment, Denver, Colorado). At the time of sampling, we measured dissolved oxygen (DO), temperature, specific conductance, and pH using a Professional Plus Quatro multiparameter probe, requiring a flow cell for riparian groundwater samples (YSI Incorporated, Yellow Springs, Ohio; Table S2 in Supporting Information S1). We calibrated each sensor for each sampling campaign per user manual specifications (Text S1.2 in Supporting Information S1). When possible, water was purged from well casings and allowed to recover three times before sample collection. For higher production wells that could not be pumped dry ($n = 10$ of 20; Table S1 in Supporting Information S1), we monitored DO concentrations continuously while pumping the well and collected samples and DO measurements when DO stabilized. For all other wells, DO was not reported because measurements representative of in situ groundwater DO concentrations were not possible.

Combusted 24-mL glass vials capped without headspace were used for samples analyzed for carbon (C) species, and 60-mL HDPE vials capped with headspace were used for samples analyzed for all other solutes. All vials were rinsed three times with filtered sample water before filling. Backup duplicates were collected as water volume allowed. Samples were kept on ice during transport to the lab and stored between 2°C and 4°C prior to analysis.

2.3. Chemical Analyses

Samples were analyzed at the Montana State University Environmental Analytical Laboratory (EAL), Bozeman, Montana. Within one week of sample collection, we analyzed nitrate (NO_3^-) using flow injection spectrophotometry (Lachat QuickChem 8,500; Table S2 in Supporting Information S1) and dissolved organic carbon (DOC) and dissolved inorganic carbon (DIC) using combustion catalytic oxidation (Shimadzu TOC VCSN or TOC-L). Within one year of sampling, we analyzed sulfate ($SO_4^{2\text{-}}$) and chloride (Cl^-) using ion chromatography (Dionex Thermo Scientific ICS-2100), and total *S*, major cations (Ca^{2+}, Na^+, Mg^{2+}, K^+), and ferrous iron (Fe^{2+}) using inductively coupled plasma optical emission spectroscopy (ICP-OES, SPECTROBLUE EOP TI). Repeated measurements of a working standard through each instrument run were used to estimate analytical uncertainty for all solutes (EAL unpublished data). We assessed charge balance in all samples using the most abundant cations (Ca^{2+}, Na^+, Mg^{2+}) and anions (HCO_3^-, $SO_4^{2\text{-}}$, Cl^-), assuming DIC concentrations were dominated by bicarbonate (HCO_3^-) given the circumneutral pH of samples (Figure S2 in Supporting Information S1). Charge balance for samples with complete analyses was generally within 10% difference between positive and negative charge ($n = 356$), with some ranging up to 20% difference ($n = 34$). We omitted cation results for samples with a charge balance exceeding 20% difference ($n = 17$) from final reporting (Mayernik et al., 2025) as they reflected problematic analysis by ICP based on comparison to analytical results for other samples collected at the same site (Text S1.3 in Supporting Information S1). Samples with omitted cation results were not included in comparisons of major ion composition.

2.4. Statistical Analyses

We performed a principal component analysis (PCA) of major ion composition to summarize which analytes were most important in describing the variation in chemical composition across process domains and reaches. Major ion components for the PCA included NO_3^-, $SO_4^{2\text{-}}$, DIC, Cl^-, Ca^{2+}, Na^+, and Mg^{2+}. To minimize the influence of dilution on analysis, we based the PCA on molar abundance calculated as the ratio of molar concentration of each ion relative to the total molar concentration of major ions in solution for a sample. The number of samples with complete results and adequate charge balance for these ions varied by process domain (terrace groundwater, $n = 69$; riparian groundwater, $n = 112$; stream water, $n = 187$). Analyses were conducted using *R* statistical software (version 4.2.2; R Core Team, 2023) and custom *R* code (Mayernik et al., 2025).

We fit mixed effects models to assess the potential influence of differences in process domain on differences in nitrate, sulfate, and DIC concentrations (“Concentration”). The associated generalized linear model included the process domain categorical variable (“processDomain”) as the fixed effect of primary interest. The model included the water year of the sampling (“waterYear”) and the week of the year the sampling campaign occurred (“campaign”) as random effects to account for variation attributable to the sampling time rather than process domain. We also assigned the individual sample site location (‘site’) as a random effect to account for correlation in repeated measurements at the same site over time.

$$\text{Concentration} = \beta \cdot \text{processDomain} + u_1 \cdot \text{waterYear} + u_2 \cdot \text{campaign} + u_3 \cdot \text{site} + \varepsilon \tag{1}$$

We fit mixed effects models to assess the potential for differences in the study reaches (i.e., upper-Louse, mid-Louse, or Porter) and terrace groundwater regions (i.e., “upper”, “middle”, or “lower”) to influence differences in nitrate, sulfate, and DIC concentrations. The associated model included the stream reach (“reach”) as a categorical fixed effect, with water year, campaign, and sampling site as random effects.

$$\text{Concentration} = \beta \cdot \text{reach} + u_1 \cdot \text{waterYear} + u_2 \cdot \text{campaign} + u_3 \cdot \text{site} + \varepsilon \tag{2}$$

Mixed effect models were fit using *R* statistical software and package lme4 (version 1.1–35.1; Bates et al., 2015) and custom *R* code (Mayernik et al., 2025). The addition of site location as a random effect improved each model fit without over-parameterizing the model, based on information criteria analysis of variance (i.e., Akaike and Bayesian, *p*-value <0.001; Bolker et al., 2009; Schwarz, 1978; Wagenmakers & Farrell, 2004). The best-fit mixed effects models minimized any bias due to repeated measures. Models may underestimate uncertainty around the extreme values of analyzed data where multimodal distributions did not meet the assumption of normality of residuals. We performed a post hoc 95% family-wise controlled Tukey honest significant difference test to assess confidence in statistical differences ($\alpha = 0.05$) of the best-fit mixed effects models.

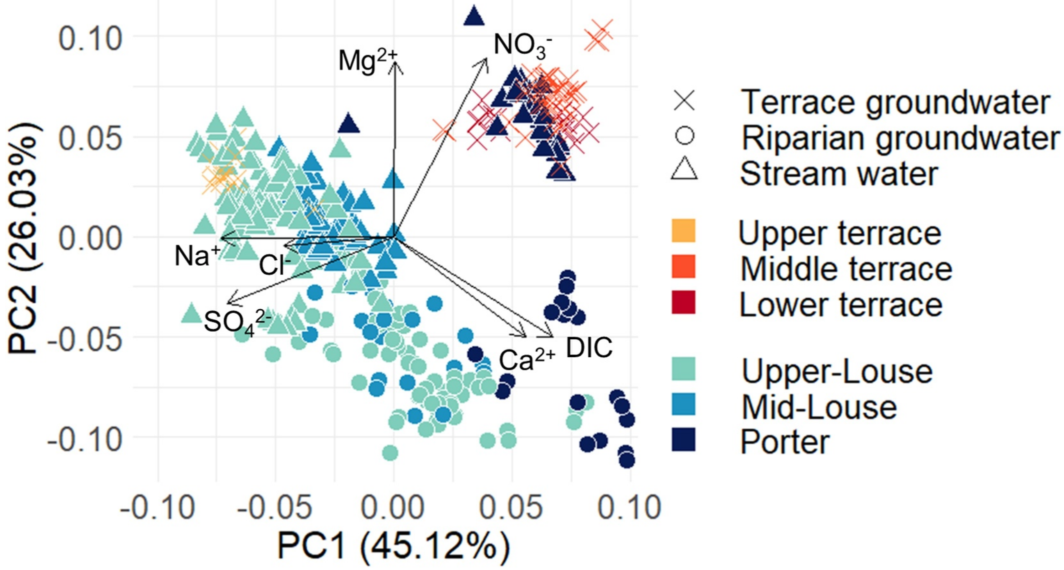

Figure 3. Principal component analysis of nitrate, sulfate, dissolved inorganic carbon, chloride, sodium, magnesium, and calcium molar ratios in terrace groundwater (crosses, *n* = 69), riparian groundwater (circles, *n* = 112), and stream water (triangles, *n* = 187). Color scales indicate position on the terrace including upper, middle, and lower terrace aquifer sites (red scale) and study reaches at upper-Louse, mid-Louse, and Porter creeks (blue scale). Riparian groundwater and stream water were sampled within each study reach.

For each study reach, we performed linear regressions of sulfate versus chloride concentrations from stream water and the nearest terrace groundwater sites (see Section 2.2) to represent the net behavior of the riparian area on the processing of these solutes between upland sources and exported stream waters. We assumed that chloride is produced from shale weathering and undergoes no further chemical transformations across process domains. We also assumed that meaningful transformations of sulfate were unlikely to occur in the terrace aquifer or stream channel process domains, yet further processing were possible in the riparian aquifer. In particular, we assumed limited sorption of sulfate to stream sediments based on observed pH values (Figure S2 in Supporting Information S1) (Kamprath et al., 1956). We regressed sulfate versus chloride concentrations from upper terrace groundwater (Figure 2b) (Sigler et al., 2018, unpublished data) to assess ion contributions from shale weathering to the terrace aquifer. We forced this regression through the origin assuming a positive correlation of sulfate and chloride production from shale weathering and that sulfate would not be produced without chloride and vice versa. We also regressed sulfate versus chloride concentrations from terrace soil water (Sigler et al., 2018, unpublished data) to assess ion contributions from cultivated soil leachate. Comparison of sulfate and chloride concentrations from riparian groundwater relative to these regression lines allowed for interpretation of potential relative contributions of weathering of shale-derived soils, leaching from cultivated soils, and sulfate reactivity in the generally anoxic riparian area.

3. Results

3.1. Biogeochemical Composition of Ground and Surface Waters

PCA results suggest that variation in relative molar abundances of NO_3^-, DIC, and Ca^{2+} were important in differentiating the chemistry of samples among process domains and between Louse and Porter Creeks (Figure 3). Porter Creek stream water was more likely to have a similar relative chemical composition as the middle and lower terrace groundwaters due to higher relative abundance of nitrate and lower relative abundance of sulfate compared to the other stream water in Louse Creek and riparian groundwaters from all three reaches. Louse Creek stream water (particularly at the upper reach) was more likely to have a similar composition as the upper terrace groundwater due to higher relative abundance of sulfate, sodium, and chloride. Riparian groundwaters at all three reaches were also more likely to have higher relative abundances of DIC and Ca^{2+} than the corresponding stream water or terrace groundwater.

Variation in relative abundances of Na^+, SO_4^{2-}, and Cl^- appeared to differentiate samples along the general west to east elevation gradient of the terrace. Stream water progressed from higher to lower relative abundances of these ions from the upper-Louse reach to the mid-Louse reach to the Porter reach (Figure 3). Relative abundance of these ions shifted from higher values in the upper terrace groundwater to lower values in the middle and lower terrace groundwater. Finally, riparian groundwater in the Louse reaches tended to have a higher relative abundance of Na^+, SO_4^{2-}, Cl^- compared to the riparian groundwater in the Porter reach.

3.2. Ionic Compositions Across Process Domains

Mean nitrate concentrations differed across process domains, with confidence in these differences supported by multiple comparison tests of mixed effects models ($p < 0.05$ Equation 1; Figure 4a). Mean nitrate concentration was highest in terrace groundwater samples (21.7 mg N L^{-1}), lowest in riparian groundwater samples (1.65 N mg L^{-1}), and intermediate in stream water samples (8.54 N mg L^{-1}).

Sulfate concentrations differed less than nitrate concentrations across process domains, resulting in less statistical confidence that mean sulfate concentration differed among process domains ($p > 0.05$). However, the mean sulfate concentration in terrace groundwater (23.2 mg S L^{-1}) was less than half that of riparian groundwater (64.8 mg S L^{-1}) or stream water (60.7 S mg L^{-1}; Table 1). While less variation in mean sulfate concentrations occurred overall, the interquartile range (IQR) of riparian groundwater sulfate concentrations spanned from 36.9 to 82.5 mg S L^{-1} (Table 1; Figure 4b), while the IQR of terrace groundwater spanned from 9.96 to 21.9 mg S L^{-1} and the IQR of stream water spanned from 49.6 to 80.9 mg S L^{-1}.

Riparian groundwater DIC concentrations were higher than those of the other process domains, with confidence in these differences indicated by multiple comparison tests of means ($p < 0.05$; Figure 4c). Riparian groundwater samples had a higher mean DIC concentration (110 mg C L^{-1}) than samples of terrace groundwater (57.0 mg C L^{-1}) or stream water (66.8 mg C L^{-1}).

3.3. Ionic Compositions Across Study Reaches and Landscape Position on the Terrace

Groundwater sampled at the upper terrace sites had the highest mean concentrations of nitrate (28.3 mg N L^{-1}), sulfate (57.7 mg S L^{-1}), and DIC (81.4 mg C L^{-1}). These sites are up-gradient of all study reaches (Figures 4 and 5a,5d and 5g; Table 1) and are associated with shale weathering in well-drained upland soils (Figure 6a) (Sigler et al., 2018). Samples from the upper terrace groundwater sites had lower mass ratios of NO_3^--N to SO_4^{2-}-S (<0.5) relative to those of terrace soil water (between 2 and 7) sampled at lower elevations (Sigler et al., 2018). Multiple comparison tests indicated confidence ($p < 0.05$) that mean concentrations of sulfate and DIC were higher in the upper terrace groundwater than the middle or lower terrace groundwater. Multiple comparison tests did not show confidence in the difference among mean nitrate concentrations in terrace groundwater due to a few upper terrace groundwater samples with lower nitrate concentrations that could have been diluted following a major precipitation event. However, most upper terrace groundwater samples have higher nitrate concentrations than the middle and lower terrace sites (Figure 5a; Table 1).

Mean nitrate concentrations in riparian groundwater varied among the study reaches, with multiple comparison tests indicating higher confidence in differences between the Louse reaches and the Porter reach. We observed mean nitrate concentrations of 1.05 mg N L^{-1} in riparian groundwater at upper-Louse, 0.01 mg N L^{-1} (less than the analytical limit of detection) at mid-Louse, and 4.59 mg N L^{-1} at Porter (Figure 5b). In more productive wells where in situ DO measurements were valid (Table S1 in Supporting Information S1), we observed DO concentrations that were far below saturation (mean = 0.83 mg L^{-1}; Figure S3 in Supporting Information S1). We observed the highest nitrate concentrations in riparian groundwater from two wells in the Porter reach that we could not pump continuously, so we could not measure DO concentrations representative of in situ conditions for these wells. Due to the higher nitrate concentrations in samples from these two wells, Porter riparian groundwater had the greatest range of nitrate concentrations from below the limit of detection to 14.4 mg N L^{-1} (IQR from 0.01 to 10.2 mg N L^{-1}, Table 1). Multiple comparison tests suggested confidence ($p < 0.05$) that mean nitrate concentrations in the Porter reach stream water (17.0 mg N L^{-1}) were higher than mean nitrate concentrations in the stream water in upper-Louse (7.3 mg N L^{-1}) and mid-Louse (5.9 mg N L^{-1}) reaches (Figure 5c; Table 1).

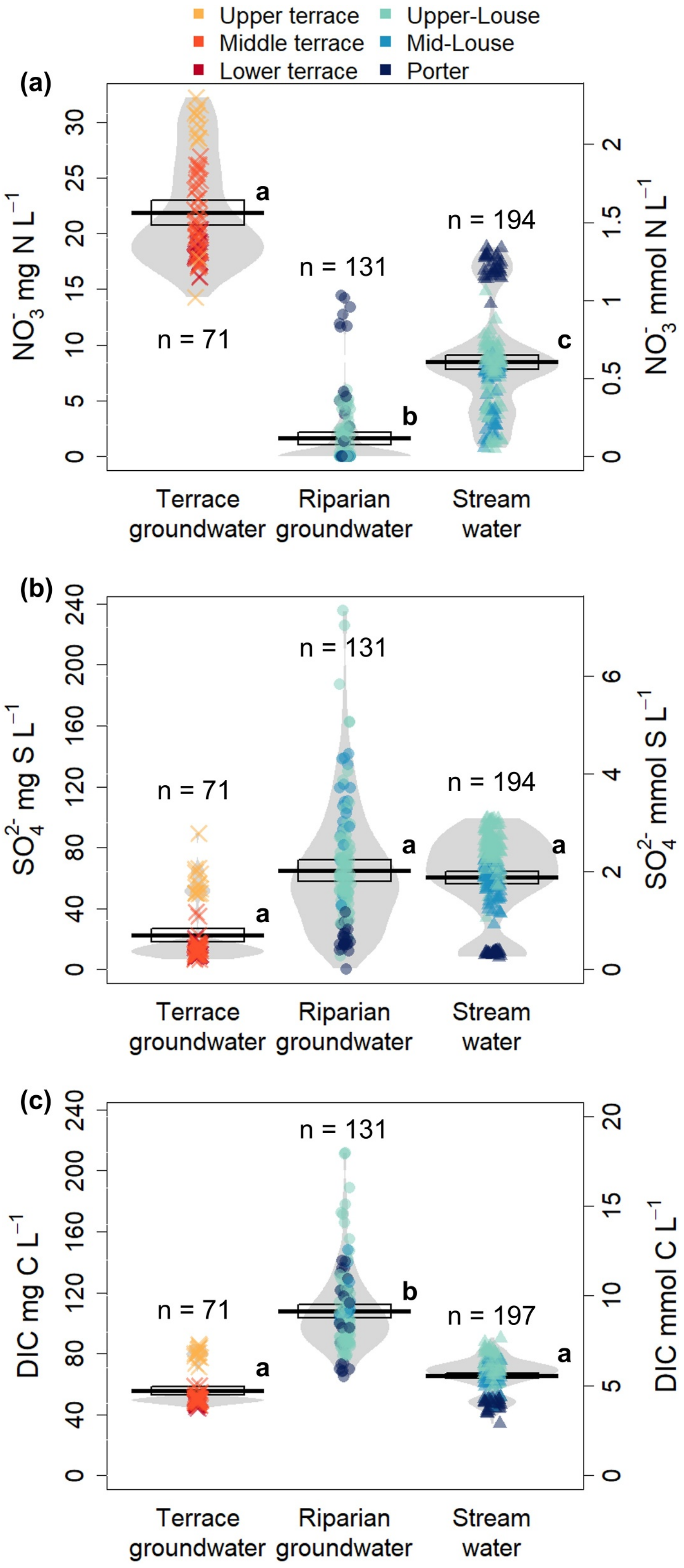
Upper terrace
Middle terrace
Lower terrace
Upper-Louse
Mid-Louse
Porter
(a)
NO_3^- mg N L^{-1}
NO_3^- mmol N L^{-1}
n = 71
n = 131
n = 194
a
b
c
Terrace groundwater
Riparian groundwater
Stream water
(b)
SO_4^{2-} mg S L^{-1}
SO_4^{2-} mmol S L^{-1}
n = 71
n = 131
n = 194
a
a
a
(c)
DIC mg C L^{-1}
DIC mmol C L^{-1}
n = 71
n = 131
n = 197
a
b
a

Figure 4.

Table 1

Summary Statistics for Nitrate (mg N L^{-1}), Sulfate (mg S L^{-1}), and Dissolved Inorganic Carbon (mg C L^{-1}) Results in Terrace Groundwater, Riparian Groundwater, and Stream Water by Reach

		Nitrate–N						Sulfate–S						Dissolved inorganic carbon					
Sample type	Period of record	n	1st Qu.	3rd Qu.	Median	Mean	SD	n	1st Qu.	3rd Qu.	Median	Mean	SD	n	1st Qu.	3rd Qu.	Median	Mean	SD
Terrace groundwater		74	18.3	25.7	20.1	22.1	4.78	74	9.96	21.9	14.3	23.0	19.5	76	49.3	55.4	51.1	57.2	13.2
Upper	2013–2016	16	28.6	30.7	30.0	28.3	4.96	16	50.3	62.9	54.4	57.7	10.4	16	79.4	84.4	81.6	81.4	3.95
Middle	2013–2022	42	18.5	23.7	20.2	20.6	3.98	42	9.94	15.6	12.9	14.5	7.4	42	49.1	52.1	50.5	51.0	3.24
Lower	2013–2022	18	17.9	18.8	18.2	18.4	0.99	18	9.31	15.9	12.1	12.8	3.88	18	47.6	51.1	49.9	49.4	2.12
Riparian groundwater		131	0.0	2.17	0.04	1.65	3.12	131	36.9	82.5	57.9	64.8	41.6	131	92.4	121	105	110	26.8
Upper- Louse	2021–2022	83	0.0	2.03	0.07	1.14	1.64	83	50.3	76.5	61.3	70.1	38.9	83	91.3	120	100	111	29.6
Mid-Louse	2021–2022	22	0.0	0.0	0.0	0.0	0.05	22	83.1	119	104	97.4	32.1	22	107	116	109	114	12.7
Porter	2021–2022	26	0.01	10.2	2.46	4.68	5.40	26	16.2	25.6	18.2	20.3	7.77	26	77.9	124	104	105	26.1
Stream water		199	5.62	9.80	8.18	8.54	4.64	199	49.6	80.9	65.6	60.7	26.6	202	62.1	73.6	69.0	66.8	11.1
Upper- Louse	2012–2022	111	5.62	9.02	7.98	7.32	2.91	112	67.5	88.0	78.3	77.8	13.3	113	67.6	76.3	72.4	72.5	6.86
Mid-Louse	2020–2022	55	3.40	7.98	7.37	5.9	2.59	55	47.6	61.6	55.2	55.3	10.2	56	63.4	71.2	67.6	66.6	6.94
Porter	2020–2022	33	16.5	17.9	16.9	17.1	1.04	32	10.1	11.3	10.6	10.6	0.97	33	45.2	49.7	48.4	47.3	3.85

Nitrate concentrations observed in stream water generally decreased over the 3-year study period corresponding with decreases in stream flow across all reaches. Decreases in nitrate and sulfate concentrations over the summer dry seasons were more evident in the Louse reaches than the Porter reach with the Louse reaches also having greater decreases in stream flow than Porter (Figures S5a and S5b in Supporting Information S1). Stream water in the Louse reaches showed the most change in nitrate and sulfate concentrations within a year, coinciding with greater decreases in stream flow due to diversion of stream water for irrigation immediately upstream of the upper-Louse reach (Figure S5a in Supporting Information S1) (Foster, 2023).

Multiple comparison tests suggested confidence ($p < 0.05$) that the mean sulfate concentration in riparian groundwater at upper-Louse (70.1 mg S L^{-1}) and mid-Louse (97.4 mg S L^{-1}) were higher than that at Porter (20.3 mg S L^{-1}) (Table 1; Figure 5e). Riparian groundwater in both Louse reaches demonstrated more variation in sulfate concentrations than riparian groundwater at the Porter reach (Figure 5e), with the highest variation observed at the upper-Louse reach (IQR from 8.74 to 235 mg S L^{-1}; Table 1). Sulfate concentrations in stream water were progressively lower from upper-Louse to mid-Louse to Porter (Figure 5f). Higher sulfate concentrations in riparian groundwaters for the mid-Louse reach do not follow the same pattern along the elevational gradient as exhibited by decreasing concentrations in stream water. Sulfate concentrations in upper- and mid-Louse riparian groundwater were more variable than in those of surface water or terrace groundwater, and the distribution of concentrations spanned values much higher than the middle terrace groundwater sites (Figures 4b and 5d–5f).

Mean DIC concentrations in riparian groundwater were relatively consistent among the study reaches, with multiple comparison tests demonstrating less confidence in differences ($p > 0.05$; Figure 5h; Table 1). Despite a few samples with high DIC in the upper-Louse reach, riparian groundwater in the Porter reach had the highest variation in DIC concentrations based on the IQR from 91.3 to 120 mg C L^{-1}. In general, high nitrate

Figure 4. Distributions of concentrations of (a) nitrate, (b) sulfate, and (c) dissolved inorganic carbon (DIC) for samples collected over space and time for each process domain. Colors indicate position on the terrace for terrace groundwater sites (red scale) and study reach sites (blue scale), with lighter colors representing locations at higher elevations on the terrace (Figure 2). The black line and surrounding box indicate the mean value and 95% confidence interval in the mean, respectively. Width of the shaded area for each distribution indicates the density of concentration values observed. Lower-case letters indicate whether the post hoc Tukey HSD test ($\alpha = 0.05$) identified statistical differences in mean nitrate, sulfate, and DIC concentrations among process domains, after using a mixed effects model to account for the effects of water year, campaign within year, and repeated measures at an individual site.

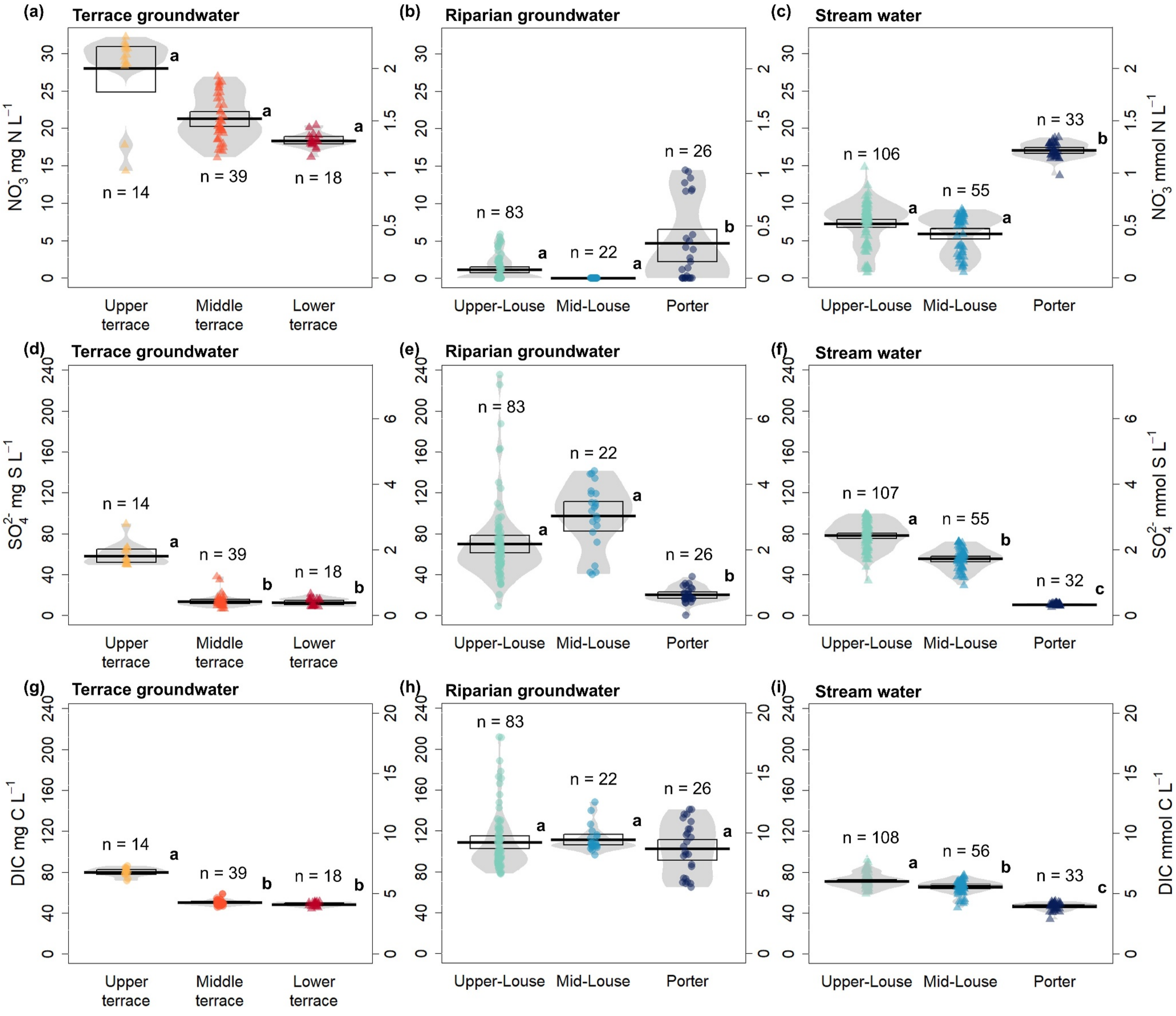

Figure 5. Concentrations of (a–c) nitrate, (d–f) sulfate, and (g–i) dissolved inorganic carbon (DIC) for (a, d, g) terrace groundwater (crosses), (b, e, h) riparian groundwater (circles) and (c, f, i) stream water (triangles). Colors indicate position on the terrace for terrace groundwater sites (red scale) and the study reaches (blue scale), with lighter colors representing locations at higher elevation on the terrace (Figure 2). The black line and surrounding box indicate the mean value and 95% confidence interval in the mean, respectively. Width of the shaded area for each distribution indicates the density of concentration values observed. Lower-case letters indicate whether the post hoc Tukey HSD test ($\alpha = 0.05$) identified statistical differences in nitrate, sulfate, or DIC concentrations across locations within each process domain (i.e., elevation for terrace groundwater or study reaches for riparian groundwater and stream water), after using mixed effects models to account for the effects of water year, campaign within year, and repeated measures at an individual site.

concentrations corresponded with low DIC concentrations, and low nitrate concentrations corresponded with more variation in DIC (Figure S6 in Supporting Information S1). Mean DIC concentrations in stream water decreased across reaches from up-gradient to down-gradient on the terrace (Figure 5i; Table 1).

Comparing changes in sulfate relative to changes in chloride provides perspective on the general effect of these stream corridors on upland waters before export in stream channels. Sulfate varied more with chloride in upper terrace groundwaters than in cultivated terrace soil waters (Figure 6a). Regressions of sulfate versus chloride for terrace groundwater and stream water samples show that the Louse reaches had much more variation in sulfate with respect to chloride than the Porter reach (Figure 6b). Some riparian groundwater wells at the upper- and mid-Louse reaches had a higher sulfate concentration than would be expected from the chloride concentration when compared to the general transformation observed from terrace groundwater to stream water for the associated

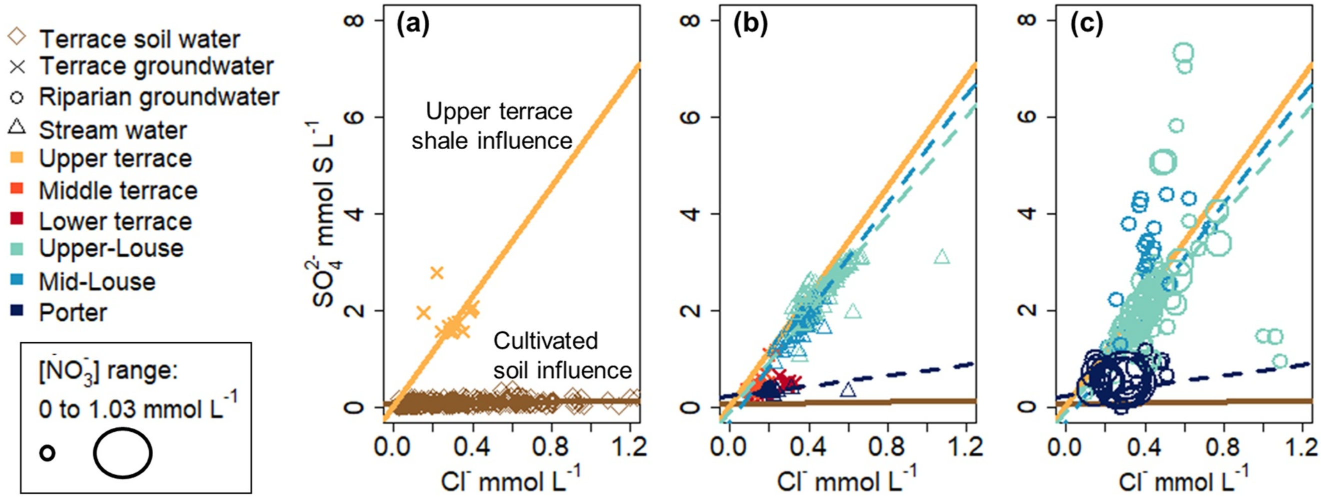

Figure 6. Sulfate versus chloride concentrations in (a) terrace soil water and upper terrace groundwater, (b) middle and lower terrace groundwater (red scale crosses) and stream water (blue scale triangles), and (c) riparian groundwater (blue scale circles). In (a), a regression of sulfate on chloride concentrations derived from upper terrace groundwater indicates influence of weathered shale (yellow) and a regression of terrace soil water indicates influence of cultivated soil (brown line). In (b), a regression of sulfate on chloride concentrations for stream water samples and the nearest terrace groundwater sites (Louse Creek and middle terrace; Porter Creek and lower terrace) characterize a linear sulfate to chloride relationship for each study reach (dashed lines). In (c), all regressions provide a reference for the proportional net generation of chloride and sulfate by the riparian ecosystem inferred from riparian groundwater. Riparian groundwater point size is scaled to the corresponding nitrate concentration (mmol N L^{-1}) for that sample.

reach (Figure 6c). One riparian groundwater well at upper-Louse had multiple instances of lower sulfate concentration relative to chloride when compared to the calculated regression. The distinct results from this site occurred consistently in 2021 with samples collected in 2022 having a similar ratio to the regression slope. Many of the riparian groundwater samples with higher or lower sulfate than expected appeared to have lower nitrate concentrations relative to the variation observed in the respective reach (Figure 6c).

4. Discussion

Differences among the study reaches in the apparent processing of upland groundwaters by the riparian process domain suggest that geomorphic setting of stream corridors is a primary influence on hydrologic behavior and soil weathering products associated with biogeochemical function. Hydrologic connectivity of the stream corridor with the upland aquifer and across redox sites within the stream corridor combine with different chemical composition of the source upland groundwater to constrain the magnitude of nitrate and sulfate loss or gain unique to each stream corridor. This combination of factors regulates the varying quality of water down-gradient.

4.1. Solute Inputs to the Stream Corridor Depend on Corridor Location Across the Terrace

Interpreting controls on stream corridor biogeochemistry begins with understanding the controls on chemical inputs from upland soil and groundwater process domains. With the general decrease in elevation from the southwest to northeast areas of the terrace (Figure 2b), observed patterns in nitrate, sulfate, and other weathering products in upland groundwater suggest a decrease in relative contributions of solutes from weathering of shale-derived materials and an increase in the relative contributions of solutes from cultivated soils. More exposure of shale to aerobic conditions at higher elevations on the terrace enhance weathering rates, contributing to the upper terrace groundwater sites having high concentrations of nitrate and sulfate (Figures 5a and 5d) and strong influence of other shale-derived solutes (Figure 3), consistent with interpretation by Sigler et al. (2018). High magnitudes of nitrate concentration observed across all terrace groundwater sites despite a relative decrease in nitrate concentration from upper to lower terrace sites suggests a decrease in influence from shale weathering coinciding with uniform influence of cultivation practices, including substantial *N* fertilizer additions. The similarly low sulfate concentrations observed in data from samples of cultivated terrace soil water (Figure 6a) and lower terrace groundwater (Figure 6b) suggest that lower terrace groundwaters readily influenced by cultivated soil water inputs. Using these relationships along with isolation of the aquifer from other inputs (Vuke et al., 2002), we infer that variation in groundwater chemistry across the terrace primarily reflects solutes derived from overlying soils.

Decreases in sulfate concentration from upper terrace groundwater (60 mg S L^{-1}) to lower terrace groundwater (10 mg S L^{-1}; Figures 5a and 5d) were disproportionate to the decreases in nitrate concentration (from 30 to 20 mg N L^{-1}) (Figures 3 and 5a and 5d), suggesting that contributions of sulfate directly reflect weathering of upland soils while contributions of nitrate reflect shale weathering yet are enhanced by land use practices (e.g., fertilizer application, enhanced mineralization of organic matter). In addition, lower sulfate concentrations relative to chloride concentrations in lower terrace soil and ground waters compared to upper terrace groundwater (Figures 6a and 6b) may reflect increasing influence of crop uptake of *S* that limits sulfate concentrations in cultivated soil leachate, diluting sulfate in terrace groundwater. Low sulfate concentrations observed in both the lower terrace soil water and groundwater also support the increasing influence of cultivated soils on groundwater across the terrace. While mineralization of soil organic matter is well known to contribute to concentrations of sulfate (Eriksen, 2009) along with nitrate (John et al., 2017; Sigler et al., 2020), the contribution from this process to sulfate in groundwater remain poorly understood relative to *N* and phosphorus dynamics (Burow et al., 2010; Hosono et al., 2007; Spruill, 2000). However, increasing observations of *S* leaching from soils, particularly in agricultural systems (Apostolakis et al., 2022; Eriksen, 2009), combined with potentially increasing *S* fertilization (Aula et al., 2019; Miller et al., 2024) emphasize the importance of understanding the solute mass balance between upland soils and riparian biogeochemical processing of *S* in addition to *N*.

4.2. Stream Corridor Biogeochemical Efficacy Depends on the Fraction of Upland Groundwater Routed Through Reactive Subsurface Riparian Flow Paths

Differences in how the chemistry of Porter and Louse stream waters compare to adjacent upland waters illustrate that the relative amount of terrace groundwaters routed across the riparian surface rather than through the riparian substrate is important to predicting solute exports in stream channels. Thus, the geomorphic setting of the stream corridor that determines the presence or absence of hillslope springs strongly influences the extent to which riparian biogeochemistry can transform upland water quality. Despite clear evidence of nitrate loss and sulfate production in riparian groundwater at the Porter reach (Figures 5b and 5e), solute concentrations observed in the stream water more closely resembled those of lower terrace groundwater than riparian groundwater (Figures 3 and 5) and were relatively consistent over time. Therefore, hillslope spring contributions to the stream with limited subsurface interaction may mask any influence of riparian groundwater inflows, supporting the importance of physical controls on the efficacy of riparian biogeochemical function for downstream water quality (Covino, 2017; Devito et al., 2000; Grabs et al., 2012; Ranalli & Macalady, 2010; Vidon & Hill, 2004a, 2004b). In contrast, solute concentrations in stream water at the Louse reaches reflect more influence from riparian biogeochemical processing through subsurface flow paths, resulting in lower nitrate concentrations and higher sulfate concentrations relative to the surrounding terrace groundwater and the Porter stream water (Figures 3 and 5). Routing of upland groundwater and up-gradient stream water (i.e., hyporheic flow) through the riparian aquifer increases the probability of weathering or metabolic reactions prior to export to the stream channel (Bernhardt et al., 2017; Boulton et al., 1998; Ranalli & Macalady, 2010). Stream solute concentrations also tended to be low during low flow conditions at the Louse reaches (Figure S5 in Supporting Information S1), suggesting that during lower flow conditions the fraction of water routed through the riparian substrate before export in the channel may be higher (Foster, 2023; Warren et al., 2022) or the residence times in the riparian substrates are longer, allowing for more complete reactions (Briggs et al., 2014).

4.3. Subsurface Flow Paths Deliver Nitrate and Sulfate to and From Sites With Variable Redox Conditions

Because all three study reaches were managed as pasture, seasonal cattle grazing potentially contributes to nitrate and sulfate processing in the riparian areas (Prado et al., 2022). However, contributions from seasonal cattle grazing to solute cycling are likely insubstantial relative to continuous inputs from upland groundwater and weathering of shale-derived substrate. Therefore, we interpret observed variation of nitrate and sulfate concentrations in riparian groundwater as being driven primarily by variable redox conditions facilitated by riparian substrate heterogeneity which we acknowledge is influenced by land use practices (e.g., artificial stock ponds, road construction, erosional deposition from upland cultivation).

Variation in solute concentrations observed across riparian areas suggest that our sampling captured a complex arrangement of subsurface flow paths and redox zones created by heterogeneous riparian substrate. Low nitrate concentrations concomitant with high but variable sulfate concentrations in riparian groundwaters at the Louse reaches (Figures 3, 5 and 6) may reflect hydrologic flow paths in frequent contact with reducing conditions yet limited in contact duration (Hedin et al., 1998; Zarnetske et al., 2012). These patterns may also reflect contact with oxidizing conditions promoting weathering of shale-derived material (Josh et al., 2012; Morrison et al., 2012). Evidence of solutes from shale weathering suggest potential accumulation of clay weathering products, which lead to development of redox zones with lower hydraulic conductivity, higher organic matter content, and lower oxygen concentrations (Hasenmueller et al., 2017; Schaetzl & Thompson, 2015; Wald et al., 2013) that promote anaerobic loss processes. Riparian wells that could be pumped continuously provide evidence of substrate with higher hydraulic conductivity, which may reflect areas in the riparian that facilitate solute transport and limit solute loss processes. The variation in substrate hydraulic conductivity that is evident in differences in the productivity of the riparian wells (Table S1 in Supporting Information S1) results in variation in solute mobilization and redox conditions, promoting diverse biogeochemical pathways within the same process domain (Bishop et al., 2011; Landon et al., 2000; Tetzlaff et al., 2009; Vidon et al., 2010). While riparian function is often conceptualized as relatively structured flow paths determined by well-organized distribution in head, these results argue for consideration of variable hydrologic and biogeochemical exchanges between localized higher conductivity flow paths and adjacent lower-conductivity substrate in order to adequately understand the net influence of riparian biogeochemical processes on stream water chemistry.

4.4. Stream Corridor Processes Promoting Anoxic Conditions Result in Net Nitrate Losses

While only Louse Creek demonstrated a strong net decrease in nitrate from uplands to streams, the riparian groundwaters of both Louse Creek and Porter Creek demonstrated strong potential for a net loss of nitrate relative to upland groundwaters or stream waters (Figures 4 and 5). In riparian groundwater, relatively low nitrate and DO concentrations (Figure 4a and S3) suggest that riparian biogeochemical processes promoted anaerobic pathways of nitrate loss from the terrace groundwater inputs. High DOC concentrations in riparian groundwater (Figure S4 in Supporting Information S1) suggest *C* availability for heterotrophic nitrate reduction (i.e., respiratory denitrification; Taylor & Townsend, 2010; Tesoriero & Puckett, 2011), which may be a primary biogeochemical reduction pathway in the study reaches. Additionally, the inverse relationship of nitrate abundance with riparian groundwater DIC generally followed the expected stoichiometric relationship of denitrification (Figure S6; Table S3 in Supporting Information S1, Equations 1 and 2) (Burow et al., 2010; Hedin et al., 1998; Stumm & Morgan, 1996). While denitrification is likely an important metabolic pathway in riparian areas, our observations of variation in *N*, *O*, and *C* species do not isolate the specific nitrate reduction pathways contributing to observed *N* loss. We suspect co-occurrence of multiple processes, such as fermentation or chemoautotrophy (Burgin & Hamilton, 2007; Canfield et al., 2010), in the observed riparian areas due to the heterogeneity of riparian substrate that likely promotes variable redox conditions and metabolite availability.

Consistent patterns of net nitrate loss from terrace groundwater to riparian groundwater (Figures 3 and 5) show that nitrate loss in riparian substrate far exceeds any riparian nitrate production from shale weathering or organic matter mineralization. Pervasive low DO concentrations (Figure S3 in Supporting Information S1) suggest limitations to nitrification in saturated regions of the riparian substrate. However, nitrate production by shale weathering (Wan et al., 2021) or mineralization of soil organic matter likely occur in riparian substrate where and when oxygen is more available. Nitrate produced may be transported periodically or episodically (e.g., by fluctuating groundwater levels or infiltration of precipitation, Figure S7 in Supporting Information S1) to the oxygen-limited aquifer (Burt et al., 2002; Duncan et al., 2015; Tesoriero et al., 2013), where the oxygen is quickly consumed and nitrate loss occurs due to anaerobic reduction (Briggs et al., 2014).

4.5. Incision and Deposition of Shale-Derived Material Promote Net Sulfate Gains in Stream Corridors

Net increases in sulfate observed from the upland groundwaters to stream waters of Louse Creek indicate sulfate production processes occurred in excess of sulfate loss in the riparian area, which is important to consider in addition to nitrate dynamics for overall stream corridor biogeochemical function. Concurrent increases in chloride concentrations indicate shale weathering as a dominant source of the observed increase in sulfate. Assuming shale-derived substrates in the stream corridor have similar mineral composition to the shales in the upper terrace, similar proportions of sulfate concentrations relative to chloride concentrations in Louse Creek stream water and riparian groundwaters (Figures 6a and 6c) suggest solute production also occurs from weathering of shale-derived substrate within the riparian area. Stream incision and mobilization of shale alluvium increase contact of shale-derived material with riparian groundwater. These findings reveal that riparian areas can be potential sources of sulfate, a function that, to our knowledge, has had limited acknowledgment and exploration in freshwater systems (Hill et al., 2000; Schoepfer et al., 2014).

The riparian groundwater at the Porter reach had some evidence of sulfate production processes within the riparian area, but to a lesser degree than the Louse reaches (Figures 5d and 5e). Some of the lower-sulfate water from the spring channels flowing from the terrace aquifer may infiltrate into the riparian substrate and dilute riparian groundwater concentrations, contributing to the apparently limited sulfate production. Regardless of the influence of the riparian groundwater on Porter Creek, direct surface contributions from hillslope springs far exceed contributions from subsurface flow paths to the stream channel. The differences in sulfate processing apparent between stream corridors at Porter Creek and Louse Creek emphasize that geomorphic setting and source water chemical composition influence the extent of sulfate exported downstream.

Riparian groundwater sampled from individual wells had sulfate to chloride ratios that varied from what would be expected due to weathering of shale with a consistent mineral composition (Figure 6c), suggesting localized variation in sulfate production and loss processes influencing riparian groundwater. An increase in sulfate production relative to chloride production may result from some combination of mineralization of soil organic *S*, weathering of shale with variable mineral composition, and production of sulfate from oxidation of iron sulfides (Table S3 in Supporting Information S1, Equations S6 and S7) (Morrison et al., 2012; Tuttle et al., 2014). In addition to aerobic chemoautotrophic oxidation of sulfides, anaerobic sulfide oxidation can produce sulfate using nitrate as the electron acceptor (e.g., Table S3 in Supporting Information S1, Equation S5) (Burgin & Hamilton, 2007; De Gusseme et al., 2009; Severe et al., 2023). Coupling of nitrate reduction with sulfide oxidation is more likely to occur at sites where labile *C* becomes limited and sulfide is abundant (Cardoso et al., 2006; Tesoriero & Puckett, 2011). This chemoautotrophic process results in an increase in sulfate and decrease in nitrate, providing another possible mechanism for concentration patterns observed.

While we expect sulfate loss processes in highly anoxic environments like riparian aquifers that have extensive nitrate loss, identifying occurrence of sulfate loss is challenging in the presence of net production without comparison to another more conservative weathering product such as chloride. Riparian groundwaters with lower sulfate to chloride ratios than expected from weathering alone suggest a localized influence of sulfate loss (Figure 6c vs. Figure 6b). Sites with the strongest evidence of sulfate loss also had low nitrate concentrations (Figure 6c), suggesting promotion of sulfate reduction with the depletion of nitrate as the more energetically favored electron acceptor (Hedin et al., 1998). Evidence of localized sulfate reduction in riparian groundwater that demonstrates net sulfate gains suggests that gross sulfate production is greater than gains inferred from concentrations alone. Net sulfate production is likely sustained by phases in sulfate cycling that can re-oxidize to sulfate, such as iron sulfides. While H_2S gas evasion is an irreversible loss mechanism for sulfate, thermodynamic probabilities suggest it occurs less consistently compared to N_2 or N_2O evasion for nitrate, emphasizing the importance of understanding *S* cycling for sulfate processing by stream corridors.

5. Conclusions

Examination of solute concentrations illustrates how geomorphic structure and riparian substrate facilitate net solute exports from uplands to streams. In this study, solute contributions ultimately delivered to stream corridors from upland groundwater vary depending on location on the terrace and the degree of subsurface hydrologic connection with the stream channel. The net effect of riparian biogeochemical processes on stream water chemistry depends first on the fraction of upland water passing through riparian substrate and second on the complexity of flow paths and redox conditions influencing riparian groundwater quality. In line with our first hypothesis, we found that the stream reach with surface spring channel connection to the upland aquifer had the least apparent influence of riparian biogeochemical processing, while the stream reaches with only subsurface riparian flow paths had higher nitrate and sulfate transformation. Predominantly anoxic conditions among riparian groundwater sites facilitated substantial nitrate losses yet consistent patterns of net sulfate production demonstrate the complexity of redox conditions within riparian areas, supporting our second hypothesis. Sulfate production despite nitrate loss emphasizes the need to understand the mosaic of varying redox zones that control solute exchanges to better predict the net biogeochemical processing before export in streams. The combined influence of geomorphic context of and solute exchange across riparian substrates evident in this study is important to consider in other stream corridors for a more holistic understanding of the biogeochemical influence on water quality, particularly in agricultural landscapes where we commonly seek strategies for mitigation of impaired water quality.

Data Availability Statement

The geochemical data sets used in the study are shared in Supporting Information S1. Data and code used for analyses and visualizations in this study are available at HydroShare with CC-0 1.0 Universal (Mayernik et al., 2025).

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