

SOIL AND STREAM CORRIDOR BIOGEOCHEMISTRY OF NITRATE AND SULFATE
AND THE INFLUENCE OF HYDROLOGIC CONNECTIVITY IN AN AGRICULTURAL
SYSTEM, JUDITH RIVER WATERSHED, MONTANA

by

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DEDICATION

I dedicate this work to those curious enough to take chances, to accomplish challenging things in the face of much unknowing, may you always find strength and grounding in the power of the land and the magic of the water.

“If there is magic on this planet, it is contained in water.”

– Loren Eiseley, *The Immense Journey*, 1959.

“The soil is the great connector of our lives, the source and destination of all.”

– Wendell Berry, *The Unsettling of America*, 1977.

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ABSTRACT

Human activities across landscapes alter physical and chemical properties of soil, thereby influencing the movement and chemical composition of soil water. Soil hydrologic and biogeochemical processes thus mediate how land management influences the quality of water that passes through soil in route to groundwater aquifers and streams. Riparian areas are particularly important in mitigating the consequences of land use for the quality of water exported from watersheds. Soils, sediments, and shallow aquifers within riparian areas of stream corridors provide low oxygen environments favoring microbial transformation of solutes for energy and carbon. Despite the limited areal extent compared to the rest of the landscape, this unique biogeochemical character is disproportionately important in determining inorganic solute export, particularly in agricultural systems. For this dissertation, I investigated sources and fate of soil water in an area managed primarily for production of cattle and non-irrigated wheat within the semi-arid Northern Great Plains of North America. I explored patterns in solute concentrations and isotopic compositions across stream corridors draining cultivated soils to infer dominant hydrologic transport and biogeochemical pathways influencing solute loading to ground and surface waters. I investigated the influence of agricultural practices and soil weathering on biogeochemical processes influencing solutes, to answer the overarching research question: *How do upland soils and stream corridors influence water and solute loading from upland aquifers to stream channels in a semi-arid landscape managed for agricultural production?*

Results show that soils are important mixing reservoirs for seasonally variable sources of precipitation, and that water movement through soil transports nitrate and sulfate from cultivated soils. Stream corridors receiving these inorganic solutes from upland groundwaters facilitate biogeochemical pathways of production, transformation, and irreversible loss. Changes in the isotopic composition of these solutes relative to changes in their mass abundance inform gross production and loss in stream corridors at the catchment scale, revealing both internal production of sulfate and/or nitrate and more substantial nitrate loss than indicated by net changes between uplands and streams. Geomorphic constraints on hydrologic connectivity and the arrangement of riparian soils and sediments determine how stream corridors mitigate the consequences of land use on downstream water quality.

CHAPTER ONE

INTRODUCTION

Soil ecosystems are inextricably linked to water quality. Hydrologic and solute transport processes reflect soil structure, sediment stratigraphy, and chemical composition of substrate (Benettin et al., 2015; Schaetzl & Thompson, 2015; Wen et al., 2022). Soils altered by human activity undergo shifts in hydrologic and solute transport patterns (Scanlon et al., 2005), and associated biogeochemical cycling (Böhlke et al., 2002), influencing export rates to ground and surface waters. Diverse soils facilitate varied hydrologic connectivity and biogeochemical function, further confounded by diverse land uses, and are thus a primary control on the quality of water exported from watersheds.

Biogeochemical processes facilitated by riparian systems make stream corridor soils and sediments disproportionately important to mitigating inorganic solute export from watersheds (Hill, 1996; Ledesma et al., 2016; Naiman & Décamps, 1997; Ranalli & Macalady, 2010; Tesoriero & Puckett, 2011). Stream corridor soils and sediments (i.e., substrate) host diverse above and below ground ecosystems that are typically more adapted to shallow groundwater conditions than the surrounding landscape (Chapin et al., 2011; Hill, 2000; Naiman & Décamps, 1997; Silverman et al., 2019). The resulting hydrologic and biogeochemical functions of stream corridors allow for more resilience to ecosystem disturbances like drought or nutrient loading, relative to other areas of the landscape (Cirimo & McDonnell, 1997; Jencso et al., 2010; McGlynn & McDonnell, 2003a; Ranalli & Macalady, 2010). Multiple biogeochemical production and consumption pathways in stream corridors likely contribute to overall net loss or

gain of solutes from upland to stream ecosystems (Burgin et al., 2011; Burgin & Hamilton, 2007).

Human perturbations such as cultivation and mining can impair the quality of ground and surface water that support rural communities. For example, rural communities tend to use private wells to access groundwater as a drinking water source (Johnson et al., 2019). These private drinking water sources are susceptible to human perturbation yet unregulated in terms of human health standards (Backer & Tosta, 2011; DeSimone et al., 2009; Doyle et al., 2018). Agricultural production and mining tend to occur where more arable land or valued ore are available and accessible, often near low density population areas, with the risk of subjecting nearby communities to impaired drinking water sources. A national investigation by the U.S. Geological Survey (USGS) found that over 20% of 1,389 domestic wells tested contained at least one chemical concentration above the maximum contaminant level determined for human health (DeSimone et al., 2009). Nitrate concentrations are particularly high in groundwaters underlying landscapes managed for crop production, posing health exposure risk to agricultural communities (Burow et al., 2010; Ward et al., 2018). While supporting local economies (Goetz et al., 2018; C. Martin et al., 2021), both mining and crop production can be characterized as “resource extraction” that marginalizes communities by increasing environmental health risks (Eggers, 2014; Eggers et al., 2015; Lewis et al., 2017), enhancing socioeconomic disparities (Flora, 2009; Gansauer et al., 2023), and impairing human relationships with the environment (Howard et al., 2020; Josewski et al., 2023; C. Martin et al., 2021). Communities in areas susceptible to these threats to human wellbeing often have the compounding problem of limited access to health care services (Jacquez et al., 2016; Smylie & Firestone, 2015). Investigating the influence of soil

processes on water quality can inform sustainable land management and potentially reduce adverse health exposure risks for vulnerable communities.

Over the past centuries, humans have greatly altered water, nitrogen (N), sulfur (S), and carbon (C) cycling through land use changes for food production and mining (Galloway et al., 2008; Ranalli & Macalady, 2010; Vitousek et al., 1997). Direct and indirect effects of these physical human perturbations to the landscape can increase rates of bedrock and soil weathering, enhancing solute transport and transformation (Holloway & Dahlgren, 1999; Ross et al., 2018; Scanlon et al., 2007; Sullivan et al., 2022; Welch et al., 2021). Soil and bedrock weathering contributes N and S to environmental waters (Holloway et al., 1998; Houlton et al., 2018; Morrison et al., 2012; Wan et al., 2021) and, in combination with pedogenic self-organization, creates variation in soil texture and structure that alters hydrologic residence times (Maher & Chamberlain, 2014; Schaetzl & Thompson, 2015; Vidon & Hill, 2004b). Hydrologic processes further promote both physical and chemical soil and bedrock weathering, dissolve solutes such as nitrate and sulfate, and transport these solutes through terrestrial and aquatic ecosystems. Nitrate and sulfate are highly oxidized, soluble inorganic anions of N and S that are readily transported with water as it moves through soils into groundwaters and surface waters. The contributions of nitrate and sulfate to the landscape from human perturbation have thus become a primary global concern (Foley et al., 2011; Welch et al., 2021) for sustainable water management.

Food production has been revolutionized by the development of synthetic N fertilizer, along with other amendments containing essential elements such as S, phosphorus (P), and potassium (K). However, fertilization practices have tended to contribute solutes in excess of plant uptake that can leach to ground and surface waters. Cumulative effects of agricultural

amendments over the past century have dramatically increased nitrate concentrations in ground and surface waters (Burow et al., 2010; Foley et al., 2011). Both N and S are common agricultural amendments, though S is less likely to be limiting and not as commonly applied. Compared to N and P, less is known about the influence of fertilizer on S loading to ground and surface water and the subsequent effects on the quality of that water (Burow et al., 2010; Hosono et al., 2007; Spruill, 2000). Sources of nutrients like N and S can include mineralization of organic matter in soils (Jørgensen, 1982; Taylor & Townsend, 2010), along with atmospheric deposition (Driscoll et al., 2001; Neff et al., 2002). Managing the balance of improved crop yields with the environmental costs of nutrient additions remains a problem for water quality and human health in agricultural landscapes.

The semi-arid landscapes of the Northern Great Plains (NGP) ecoregion of North America undergo extensive cultivation for non-irrigated cereal crop production and grazing from cattle production. In arid and semi-arid landscapes, changes in the seasonality and form of precipitation due to climate change present challenges for sustainable ecosystem and agricultural management, including mitigation of water quality issues (Hoell et al., 2020; Lee et al., 2008; Qin et al., 2020). To date, these challenges are not well characterized due to limited understanding of agroecosystem function in these landscapes, hindering our ability to develop appropriate solutions and foster sustainable management practices.

My dissertation research explores variation in the biogeochemical function of riparian and upland soils in agricultural regions of the Judith River Watershed (JRW), a tributary of the Missouri River in the NGP. I focus on stream corridors incised into the Moccasin terrace, a well-studied strath terrace landform with a relatively simplified progression of reactive solute storage

and transport from cultivated soils to ground and stream waters. The mouth of the Judith River was likely dammed by the Laurentide ice sheet during the late Illinoian stage (127–190 ka) to form Glacial Lake Winifred (Davis et al., 2006; Zimmerman, 1966a). Recession of the Laurentide ice sheet in the late Pleistocene Epoch (between 20,000 and 11,500 years ago; Dyke et al., 2002; Gowan, 2013) released the ice dam impounding Lake Winifred, rapidly lowering the base level of the Judith River. The resulting stream and river incision into underlying Cretaceous-age marine sandstones and shales (Vuke et al., 2002) likely produced the younger terraces throughout the lower elevation areas of the JRW, including the Moccasin terrace. The incision of mountain-front streams around the upgradient end of the Moccasin terrace isolated the shallow terrace aquifer from any recharge sources originating in the Little Belt mountains, and the impermeability of the shale units likely limits connectivity of the shallow aquifer with deeper aquifers (Sigler et al., 2018; Vuke et al., 2002). Water stored in the shallow terrace aquifer exhibits pervasive high nitrate concentrations (from 15 to 30 mg L⁻¹ nitrate-N; John et al., 2017; Schmidt & Mulder, 2010), due to recharge from infiltration of local precipitation through predominantly cultivated soils (Sigler et al., 2018). Moccasin terrace groundwater is ultimately exported through stream corridors fed by hillslope spring or diffuse subsurface flows from upland aquifers.

The Moccasin terrace stratigraphy and hydrologic isolation from the mountain front provides a simplified hydrologic flow system for studying how water and solutes from upland soils are accumulated in groundwater and processed by stream corridors before export. This simplified flow system and the abundance of solute inputs present an ideal site to investigate hydrologic and biogeochemical processes across upland soils, shallow aquifers, and stream

corridors. Few studies have assessed the ecosystem functions of stream corridors draining cultivated landscapes in semi-arid regions (Hill, 2019), and their distinct capacity to mitigate or augment solute loads.

This dissertation investigates hydrologic and chemical transport and transformation through soils, shallow aquifers, and streams to understand how stream corridor ecosystems mitigate solute loads from non-irrigated agricultural land management. Specifically, this work aims to address the outstanding knowledge gaps in the complex hydrological and biogeochemical mechanisms by which stream corridors influence N and S cycling, including how precipitation source waters and evaporated waters are partitioned across the landscape to drive anoxic conditions, and how riparian substrate influences N and S production and loss processes. My research approach connects land use and geomorphic context to hydrologic and biogeochemical processes for a holistic understanding of agroecosystem controls on water quality. I focus on nitrate and sulfate as the dominant mobile forms of N and S of concern, both of which are influenced by agricultural management practices and shale-derived soils. My research addresses the overarching question: *How do upland soils and stream corridors influence water and solute loading from upland aquifers to stream channels in a semi-arid landscape managed for agricultural production?* I address this broad question through three specific research elements parsing hydrologic and biogeochemical processes. First, I use the isotopic composition of water to investigate the role of cold season precipitation (e.g., snowmelt) in the storage and movement of environmental waters through upland soils, shallow aquifers, and stream corridors. I aim to assess the relative contributions of warm- and cold-season precipitation sources to semi-arid agricultural landscapes for crop production and solute processing. Second, I

use spatiotemporal surveys of water chemistry to investigate reach-scale nitrate and sulfate processing by stream corridors with differing surface versus subsurface hydrologic connectivity between upland aquifers and streams. I assess nitrate and sulfate concentrations and their net change between upland groundwater inflows and stream channel outflows to infer riparian biogeochemical processing pathways. Third, I use patterns in the abundances and isotopic compositions of nitrate and sulfate in terrace groundwater, riparian groundwater, and stream water to assess the gross production and loss pathways associated with solute processing by stream corridors. This research element uses chemical and isotopic compositions of water and solutes to infer the dominant soil and stream corridor processes that influence water quality.

Synthesis of these three research elements demonstrates how patterns in geochemical and isotopic compositions of stream corridor ground and surface waters inform the extent to which riparian substrate influences export of N and S. Through integrating the hydrologic, geochemical, and isotopic components of this work, we gain improved understanding of soil and sediment function in ecosystem processes across stream corridors. The potential of land use practices to exacerbate water quality problems via alteration of soil biogeochemical and hydrologic processes necessitates thoughtful consideration of the feedbacks between management decisions and soil function within and around stream corridors.

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CHAPTER TWO

WATER ISOTOPIC COMPOSITION TRACES SOURCE AND
DYNAMICS OF WATER SUPPLY IN A SEMI-ARID
AGRICULTURAL LANDSCAPE

Contribution of Authors and Co-Authors

Manuscript in Chapter 2

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Contributions: Contributed to experimental design, conducted field sampling, processed samples and results, analyzed and interpreted results, wrote the manuscript.

Co-Author: Stephanie A. Ewing

Contributions: Lead PI on project, contributed to experimental design, guided framing of manuscript, provided extensive feedback on the manuscript.

Co-Author: W. Adam Sigler

Contributions: Contributed to aspects of experimental design and sample collection, edited the manuscript.

Co-Author: Kelsey G. Jencso

Contributions: Established and maintained Montana Climate Office Mesonet station providing soil and atmospheric climate data, edited the manuscript.

Co-Author: Robert A. Payn

Contributions: PI on project, provided extensive guidance on analysis and extensive feedback on the manuscript.

Manuscript Information

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Abstract

Changes in seasonality and form of precipitation alter the structure and function of grassland and steppe ecosystems and pose challenges for land management and crop production in regions like the Northern Great Plains, North America. This research uses isotopic composition of water ($\delta^{18}\text{O}$ and $\delta^2\text{H}$) to explore the sources and fate of soil water in lower-elevation agricultural areas of the Judith River watershed, in the headwaters of the Missouri River, USA. Extensive non-irrigated cereal crop production in this area occurs on well-drained soils and depends on careful water management. Our observations indicate that colder precipitation contributes isotopically distinct water to cultivated terrace soils relative to downgradient groundwaters and streams. Riparian waters also exhibit a higher fraction of contributions from colder precipitation relative to terrace groundwaters and streams. Apparent contributions from colder precipitation in terrace and riparian soil waters suggest that snowmelt is a key component of water supply to these systems. Riparian waters also show evidence of evaporation suggesting that water spends sufficient time in some ponds and open channels in the riparian corridor to reflect fractionation by evaporation. The evolution of water isotopic composition from soils to shallow aquifers to stream corridors indicates source water partitioning as precipitation moves through this semi-arid agricultural landscape. The apparent mixing processes evident in this evolution reveal source water dynamics that are necessary to understand plant transpiration, solute processing, and contaminant leaching processes.

Introduction

In the semi-arid landscapes of the Northern Great Plains (NGP), trajectories of the seasonality and form of precipitation due to climate change present existential challenges for sustainable management of non-irrigated crop production and grassland ecosystems (Hoell et al., 2020; Lee et al., 2008; Qin et al., 2020). Climate analyses in the NGP and similar ecoregions suggest that the area is experiencing warmer winters, wetter springs, drier summers, and shifts in the composition of annual precipitation from snow to rain (Cross et al., 2017; Xu et al., 2013). These changes in the NGP climate appear to propagate shifts in grassland plant communities and regional greening (Berdugo et al., 2020; Brookshire et al., 2020; Currey et al., 2022). The NGP supports one of the largest areas of intact temperate grasslands (ca. 55% of NGP land cover), which are highly vulnerable to economic pressures for conversion to cropland (currently ca. 28% of NGP land cover; Auch et al., 2011; Currey et al., 2022; Drummond, 2007; Lark et al., 2015). Land use changes are shifting patterns in the partitioning of precipitation to evapotranspiration, hydrologic storage, or runoff across the NGP landscape (Liu et al., 2019; Miller et al., 1981; Sigler et al., 2020). Understanding the consequences of the trajectories of land use and climatic changes in the NGP will require detailed understanding of how soil water storage, groundwater recharge, and stream flow generation respond to spatial and temporal dynamics of the precipitation regime.

Snow accumulation and melt drive seasonal and spatial patterns in hydrologic and thermal connectivity that determine the behavior of water and solutes across northern landscapes (Costa et al., 2020; Jasechko et al., 2014; Jencso & McGlynn, 2011; Lundberg et al., 2016; J. Martin et al., 2018; Pellerin et al., 2012). However, the partitioning of melt from ephemeral snow

cover to evapotranspiration, hydrologic storage, or runoff has not been studied as extensively at lower elevations as the flushing effect of melt from higher elevation snow accumulations (Baulch et al., 2019; Boyer et al., 1997; Jencso et al., 2010; Pacific et al., 2010; Pomeroy & Li, 2000). A lack of understanding of snowmelt partitioning limits our ability to predict the trajectories of solute processing and transport at lower elevations. Lower elevations receive higher proportions of precipitation as rainfall compared to higher elevations that receive higher proportions of precipitation as snow. Snowmelt or rainfall that occurs during colder temperatures when evapotranspiration is limited (Wever et al., 2002) contributes to soil water storage and is particularly important in non-irrigated and annually cultivated agricultural systems. The timing of this increase in water availability stimulates crop productivity and drives solute production and leaching (Kort, 1988; Sigler et al., 2022; Simão et al., 2021; Kim J. Van Meter et al., 2020). Identifying the contribution of cold versus warm precipitation to agricultural soils at low elevations in the NGP can reveal precipitation partitioning relevant to seasonal drivers of water availability and biogeochemical processes.

Stable isotopic composition of oxygen and hydrogen in water (i.e., $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values) is initially imparted by the source of precipitation and subsequently altered by evaporation and mixing. Evaporation occurs in water reservoirs exposed to radiative forcing, such as open waters (Bowen et al., 2018, 2019; Brooks et al., 2014; Jasechko et al., 2013; Jinzhao Liu et al., 2022) and shallow soil depths (ca. < 30 cm; (Liu et al., 2021; Martin et al., 2018; Oerter & Bowen, 2019; Sprenger et al., 2016, 2017). Hydrologic mixing occurs in convergent topographic areas and storage areas with sufficient residence times and volumes to integrate source water contributions (e.g., lakes and soils) (Beria et al., 2018; J. Martin et al., 2018; McDonnell et al.,

1991; Sprenger, Stumpp, et al., 2019; Tetzlaff et al., 2014) . Thus, exploration of spatial and temporal variation in the isotopic composition of these reservoirs provides information about the dynamics of potential source waters (Jasechko, 2019; Kendall & Coplen, 2001). Isotopic analysis of environmental water provides a useful tool for assessing the history of water found in soils, terrace aquifers, riparian corridors, and stream channels, which are conceptualized as separate process domains (Montgomery, 1999) that vary in hydrologic and biogeochemical function. Precipitation reflects seasonal variation in the isotopic composition of meteoric water with isotopic values typically lower in colder precipitation than warmer precipitation relative to the local climate (Clark & Fritz, 1997; Criss, 1999; Dansgaard, 1964; Rozanski et al., 1993; Sharp, 2017). The relationship of $\delta^2\text{H}$ with $\delta^{18}\text{O}$ values in precipitation is typically linear with a regionally representative slope, known as the local meteoric water line (Bowen & Wilkinson, 2002; Clark & Fritz, 1997; Dansgaard, 1964; Rozanski et al., 1993; Sharp, 2017). When compared to precipitation, patterns in the isotopic compositions of soil water, groundwater, and stream corridor waters illuminate patterns of infiltration and mixing over seasonal or longer timescales (Liu et al., 2021, 2022). Additionally, evaporation fractionates water by preferentially transferring the lighter isotopes of O and H to the atmosphere (Craig, 1961). Because the effect of variation in O isotopes on the molecular mass of water is generally stronger than the effect of variation in H isotopes, the isotopic composition of residual water typically falls below the local meteoric water lines (Gammons et al., 2006; Sprenger et al., 2016). Considering these potential effects, comparisons of water isotopic compositions across process domains improve our understanding of critical transport and storage dynamics among soils, groundwaters, and stream corridors.

The physical properties of soil shape the response of soil water and solute dynamics to changing precipitation regimes (Rabot et al., 2018; Vogel et al., 2006). Soil weathering creates zones of finer texture and structural units within horizons that alter hydrologic and solute residence times as a function of soil development (Ewing et al., 2006; Maher & Chamberlain, 2014; Schaetzl & Thompson, 2015; Vidon & Hill, 2004). Soil development is shaped by landform geomorphic and stratigraphic controls (e.g., bedrock, topography) that in turn dictates overall soil water holding capacity (Sigler et al., 2020; Vidon & Hill, 2004; Schaetzl & Thompson, 2015). Soil texture and vertical structure influence water movement and storage, therefore affecting the isotopic composition of “mobile water” and “bulk water” in soils (Adams et al., 2020; Liu & Guo, 2022; Sprenger & Allen, 2020). In addition, physical transformation of surface horizons by cultivation and replacement of native perennial vegetation with annual crops transforms soil hydrological processes, which influence groundwater recharge and evapotranspiration in irrigated and non-irrigated systems (Scanlon et al., 2005; Sullivan et al., 2022). Cultivation of soils with inherently limited water holding capacity can lead to increased water loss and nutrient mobilization that impairs ground and surface water quality (Ranalli & Macalady, 2010; Sigler et al., 2020). Inherent development of soils in conjunction with transformations due to cultivation establish soil physical properties that dictate soil hydrology. Patterns of water isotopic composition across landscape process domains reflect soil hydrological processes and allow for improved understanding of the feedback between soil development and soil hydrology.

The goal of this research is to understand the contributions of seasonally variable forms of precipitation to soils, groundwaters, and streams across a strath terrace landform managed for

agricultural production. We assess water content in cultivated soils and patterns in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in water samples from precipitation, soils, upland groundwaters, riparian groundwaters, and streams to infer potential causes of variable partitioning of colder precipitation, warmer precipitation, and evaporated waters among these process domains (Figure 1). We define colder precipitation as occurring during lower temperature weather conditions that dictate lower water isotopic values and can occur October through May in northern latitudes and can arrive as either snow or rain. We define warmer precipitation as occurring during warmer temperature weather conditions that can occur April through October and arrives as rain. We hypothesize that water supply, storage, and hydrologic connections among process domains vary across a landscape to dictate spatial and temporal patterns of hydrologic inputs, mixing, and loss to evaporation. We address this hypothesis through three research objectives:

Objective 1: Determine how soil conditions regulate seasonal inputs of precipitation.

Objective 2: Determine how the terrace aquifer mediates contributions of water from soils and delivery of water to riparian corridors.

Objective 3: Determine how the riparian corridor transforms water received from the terrace aquifer.

We investigate these objectives through assessment of precipitation sources and delivery across landscape process domains to understand soil hydrological processes that drive nutrient transport and biogeochemical processing.

Data and Methods

Section 2.1 Study Area

Our study area is located within the Judith River Watershed (JRW) of central Montana, USA. The Judith River is a tributary of the Missouri River on the western edge of the NGP (Figure 2). Depositional terraces and wider floodplains in the lower-elevation areas of the watershed are extensively cultivated primarily for non-irrigated cereal crop production. Narrower stream corridors dissecting the terraces are often used as pasture for cattle production to increase producer diversification (U.S. Department of Agriculture, 2023). Dominant crop types are spring wheat, winter wheat, and barley with increasing incorporation of pulse crops in cropping system rotations to replace fallow (John et al., 2017; U.S. Department of Agriculture, 2023). Producers incorporate the practice of fallow in non-irrigated cropping systems by using herbicide to suppress vegetation in a field through a growing season with the goal to increase soil water storage for the following cash crop rotation.

The climate of the JRW is semi-arid, with lower elevations receiving mean annual precipitation of 39 cm and mean annual temperature of 6.6°C (based on 30-year normal, 1991–2021, PRISM Climate Group). Precipitation occurring in late spring and early summer accounts for nearly half of the annual total (Figure 3, S1, S2). Rain is the dominant form of precipitation in this region with snow comprising approximately 7-25% of the annual precipitation over the period of study (Figure 3, S2). Severe winds and limited vegetation cover create heterogeneous patterns of snow cover, contributing to uncertainty in determining the total snow-derived water and resulting in substantial spatial and episodic variation in infiltration of snowmelt to soil water storage (Pollock et al., 2018).

Crop production in the JRW occurs on alluvial fans and terraces that host well-drained calcareous soils. Soils are classified as Calciustolls and Argiustolls in the US Taxonomy (U.S. Department of Agriculture, 2022). Soils exhibit generally clay loam textures and relatively shallow gravel zones (40-100 cm) overlying subsurface horizons with > 40% coarse gravel content of variable thicknesses extending to between 1.5 m and 10 m depths (Sigler et al., 2018). This soil and subsurface architecture results in substantial nitrate leaching from cultivated soils, with observations of pervasive high nitrate concentrations (ca. 20 mg L⁻¹ nitrate-N) in shallow terrace aquifers (Schmidt & Mulder, 2010; Sigler et al., 2018).

Initial sampling of precipitation and landscape waters occurred more broadly across the JRW starting in 2012, with subsequent sampling focusing on the Moccasin terrace landform through 2022 (Figure 2, Table 1, S1). The Moccasin terrace is an extensively cultivated strath terrace with a shallow aquifer that is hydrologically isolated from streams or other water sources flowing from the Little Belt mountains (Figure 2; Sigler et al., 2018). The shallow aquifer is perched on relatively impermeable Cretaceous-age marine shales (S. M. Vuke et al., 2002). The shale units limit connectivity with deeper groundwater, so water stored in the shallow aquifer is sourced exclusively from local precipitation infiltrating through predominantly cultivated soils and ultimately exported through stream corridors. As a result of this landform structure, water in this shallow aquifer is relatively young, exhibiting apparent water ages of 1-2 years from tritium-helium (³H-³He) relationships in wells and springs, and average residence times on the order of 20 years estimated from total aquifer volume divided by volumetric discharge (see SI; Sigler et al., 2018, 2020). Terrace groundwaters flowing into stream corridors may contribute directly to the stream channel via channelized surface flow or indirectly via subsurface flow paths through

riparian aquifers. Thus, the Moccasin terrace provides a simplified context for studying the movement of water and solutes through terrace soil, into groundwater and ultimately stream corridors (Figure 1).

Section 2.2 Meteorological and Soil Climate Monitoring

Snow water equivalent was recorded every 15 minutes with a snow scale (Sommer SSG-2) installed in February 2020 at the Montana State University (MSU) Central Agricultural Research Center (CARC) located on the Moccasin terrace (Figure 2). Soil volumetric water content and temperature were measured every 15 minutes at depths of 10, 20, 50, and 90-100 cm by Montana Climate Office (2023) and USDA NRCS (see SI; U.S. Department of Agriculture, 2022). Precipitation volume, air temperature, and relative humidity were measured at 1-hour intervals by the U.S. Bureau of Reclamation (2023).

Section 2.3 Sample Collection and Handling

Water was sampled at varying frequencies and analyzed for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from 2012 through 2022. Rain and snow cover were sampled near Stanford, Moccasin, and Moore, MT (Table 1, S1, Figure 2). Precipitation was also sampled at CARC in collaboration with the Montana Precipitation Isotope Network beginning in 2021 (Table 1, S1). Water was sampled from terrace soils using porous cup tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark) at seven locations across a cultivated field near Moore, MT (Table 1, S1, Figure 2). At each sampling location, a single lysimeter was installed in the fine-textured soil horizon just above the contact with the underlying gravel horizon. Depths of each sampling location range from 60-119 cm depending on the thickness of fine-textured soils (see SI and Sigler et al., 2018). All groundwater and surface water were sampled using a peristaltic pump

(Geotech Environmental Equipment; Denver, CO) and pumped through a 0.45- μ m capsule filter (Geotech Environmental Equipment; Denver, CO) into 20 mL glass scintillation vials. Terrace groundwaters were collected from wells and hillslope spring orifices except at two springs, which required sampling from shallow PVC wells 1-2 meters up-gradient from the orifice due to stagnant water at the orifice (Table 1, S1, Figure 2; see detailed sampling methods in Sigler et al., 2018). Riparian waters were collected from screened groundwater wells, surface water ponds, and spring channels throughout the riparian corridor sites distributed across the Moccasin terrace (Table 1, S1, Figure 2). Casings of riparian sampling wells were 2.54-cm internal diameter PVC directly inserted with a drive point to ca. 1 m depth in riparian soils. Slots were cut in the PVC to provide 30 to 50 cm of screening. Terrace and riparian groundwater samples were collected after purging three well volumes. Stream channel and riparian spring channel waters were collected from turbulent locations presumed to be a well-mixed representation of stream flow.

Samples were either filtered on site using a 0.45- μ m capsule filter (Geotech Environmental Equipment; Denver, CO) or filtered in the lab using 0.2- μ m or 0.45- μ m syringe disc filters. Samples were collected in duplicate as water volume allowed. Samples were filtered into 20mL glass or HDPE scintillation vials with conical caps to eliminate headspace, kept on ice during transport, and stored at room temperature in the lab prior to analysis (detailed methods in supplemental information).

Section 2.4 Isotope Analysis

Water samples were analyzed for oxygen and hydrogen isotopic composition using integrated cavity output spectroscopy (Los Gatos Research; Mountain View, CA) at the MSU

Environmental Analytical Laboratory (EAL). The relative isotopic compositions of the hydrogen and oxygen atoms in water were first measured as atomic mass ratios of $^2\text{H}:^1\text{H}$ for deuterium and $^{18}\text{O}:^{16}\text{O}$ for oxygen-18 (Sharp, 2017). Isotopic ratios were then normalized to their corresponding δ value as the fractional deviation (as per mil or ‰) from the global water standard (Vienna Standard Mean Ocean Water, VSMOW; Craig, 1961; Dansgaard, 1964). Analytical uncertainty was constrained using sealed USGS-certified standards 46 ($\delta^{18}\text{O} = -29.80\text{‰}$ and $\delta^2\text{H} = -235.80\text{‰}$), 47 ($\delta^{18}\text{O} = -19.80\text{‰}$ and $\delta^2\text{H} = -150.20\text{‰}$), and 48 ($\delta^{18}\text{O} = -2.22\text{‰}$ and $\delta^2\text{H} = -2.00\text{‰}$). Analytical memory was accounted for in samples analyzed with insufficient injections to minimize memory effects (see SI; Gröning, 2011). Repeated measurements of the EAL working standard, a groundwater sample from the Gallatin River watershed, MT, over the last five years ($n = 80$, EAL unpublished data) had a standard deviation of 0.6‰ for $\delta^{18}\text{O}$ and 0.9‰ for $\delta^2\text{H}$, providing an estimate of total analytical uncertainty in our samples.

Section 2.5 Local Meteoric Water Line Assessment and Uncertainty

We calculated a local meteoric water line (LMWL) from the isotopic composition of precipitation at the study site (equation. 1; Dansgaard, 1964):

Equation 1:
$$\delta^2\text{H} = m \cdot \delta^{18}\text{O} + b$$

where values for m and b are inferred by a linear regression of local precipitation $\delta^2\text{H}$ values against corresponding $\delta^{18}\text{O}$ values. Comparison of the LMWL to the global meteoric water line ($\delta^2\text{H} = 8.20 \cdot \delta^{18}\text{O} + 11.26$, Rozanski et al., 1993) provides a specific regional perspective on predictable differences in the hydrogen and oxygen isotopic compositions in meteoric waters (Sharp, 2017).

To allow assessment of meaningful deviation of environmental waters from the LMWL, the analytical uncertainty estimates of 0.6‰ for $\delta^{18}\text{O}$ and 0.9‰ for $\delta^2\text{H}$ were used in a Monte Carlo propagation of uncertainty to the LMWL, following the approach of Leuthold et al. (2021). The Monte Carlo ensemble consisted of 5000 realizations to propagate analytical uncertainty to the slope and intercept of the LMWL calculated from precipitation sample results. We determined confidence intervals for the linear model using the 2.5% and 97.5% quantiles of the Monte Carlo ensemble of LMWL realizations.

Mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values were determined for precipitation over the study period based on annual volume-weighted mean water values for years 2012-2022. A sinusoidal model was fit to measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in precipitation to allow interpolation of isotopic composition of precipitation throughout the year. We assessed whether the model fit to our precipitation isotopic data was reasonable by comparing it to a sinusoidal model fit to monthly predictions of isotopic values obtained from the Waterisotopes database (Bowen, 2022) for a central location in our study area (see SI 2.3; Figure S3). The Waterisotopes database uses the precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ dataset from the Global Network of Isotopes in Precipitation (GNIP; IAEA/WMO, 2015) along with latitude and altitude to spatially interpolate precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at a resolution of 5' x 5' across the continents (Bowen et al., 2005; Bowen & Revenaugh, 2003; Bowen & Wilkinson, 2002). Latitude and altitude are geographic controls on temperature (Bowen & Wilkinson, 2002) and vapor pressure which drives relative humidity and determines precipitation isotopic composition (Criss, 1999; Dansgaard, 1964).

We used the model fit to our measurements to develop a pair of volume-weighted annual mean precipitation $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for our study period. The 95% confidence interval of the

sinusoidal model fit to our precipitation isotope data encompasses the model fit to Waterisotopes database values (Figure S3). This comparison suggested that the model based on our measurements was reasonable to fill data gaps; therefore, we used it to interpolate isotopic values of precipitation for each day of the year. We multiplied the daily isotopic values by the volume of precipitation for that day to calculate the corresponding precipitation-weighted isotopic value (U.S. Bureau of Reclamation, 2023). The sum of the precipitation-weighted values divided by the total precipitation volume over a given period yields the precipitation-weighted mean isotopic value for that period, which we calculated for each year of the study period. We then averaged these values to determine a single pair of volume-weighted mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values for precipitation over the entire study period.

Water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values influenced by evaporation plot to the right of the LMWL because evaporation increases $\delta^{18}\text{O}$ values more than $\delta^2\text{H}$ values in the residual water (Craig, 1961). We determined the offset of these reservoirs from the meteoric conditions at the study site by calculating the line-conditioned excess (lc-excess), defined as the difference between the measured $\delta^2\text{H}$ value and that predicted by the LMWL regression model for a corresponding measurement of $\delta^{18}\text{O}$ (equation 2; Landwehr & Coplen, 2006).

Equation 2:
$$lc\ excess = \delta^2H - m \cdot \delta^{18}O + b$$

More negative lc-excess values suggest greater influence of evaporative fractionation in a given water volume, relative to the isotopic composition expected in local meteoric waters (Gammons et al., 2006; Sprenger et al., 2016). We calculated lc-excess values for the 2.5% and 97.5% quantiles of the Monte Carlo ensemble for the LMWL (equation 2) to assess meaningful deviations from zero.

Section 2.5 Statistical Analysis Across Process Domains

We used a generalized linear mixed model to assess whether patterns in isotopic data reflect the effect of process domain (i.e., soil water, terrace groundwater, riparian water, and stream water) on measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and calculated lc-excess values while accounting for repeated measures of the same sites over time (R software version 4.2.1 package ‘nlme’ version 3.1-160). We assigned “water-year” as a fixed effect (i.e., independent variable) in the statistical model because $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in environmental waters are a function of water year specific climatic conditions. We assigned sampling campaign within the year as a random effect to account for the increased probability that results from samples collected closer in time were more similar than samples collected further apart in time. The respective assignments of “water-year” and “sample campaign” allowed us to account for autocorrelation in residual errors of the data. We also included individual site as a random effect in the model to account for the increased probability that results from samples collected at the same site were more similar than samples collected from other sites. Accounting for site to site variation greatly improved the Akaike and Bayesian information criteria when compared to the model not accounting for individual site (ANOVA p-value < 0.001; Schwarz, 1978; Wagenmakers & Farrell, 2004). Uncertainty in the model may be underestimated on the extreme ends of our data because the normality of the residuals assumption was not met for process domains with multimodal results (e.g., terrace groundwater, evaporated riparian water). We performed a 95% family-wise controlled Tukey HSD post hoc test to determine which process domains are associated with a significantly different measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ and calculated lc-excess values when compared to the other process domains.

Results

Section 3.1 Terrace Soil Water Content and Temperature

Temperatures and water contents were most variable in the top 20 cm of terrace soils near Moccasin, MT (Figure 3, S1). The effects of evapotranspiration were limited at soil depths near 50 cm, and soil water contents at these depths reach a minimum of ca. $0.25 \text{ m}^3 \text{ m}^{-3}$, consistent with field capacities typical of the clay loam to coarse sandy loam soils present across our study area (Montana Climate Office, 2023; Sigler et al., 2020). Soil water content at 90 cm reached a minimum less than ca. $0.20 \text{ m}^3 \text{ m}^{-3}$, consistent with field capacities of coarser substrate textures at depth (Figure 3). Soils exhibited peak water content values at all depths during May, with the greatest variation occurring at shallower depths (Figure 3). During the spring season, maximum water contents reached ca. $0.40 \text{ m}^3 \text{ m}^{-3}$ at all depths, suggesting a nearly saturated state assuming porosity consistent with clay loam to sandy clay loam textures (U.S. Department of Agriculture, 2022).

Water content in terrace soils began to decline in early June through the growing season (Figure 3). Overall, the growing season soil water content values exhibited few meaningful responses of volumetric water content to rainfall, presumably due to transpiration dominating the influence of precipitation (e.g., July 2021 across all soil depths; Figure 3). Water began to accumulate deeper in the soil in September through October. Water contents of deeper soils either stabilized or continued to increase through the winter months depending on soil temperatures and contributions from snowmelt (Figure 3). An increase in soil volumetric water content was generally observed when soil temperatures exceed 0°C in shallow depths and snow was present or precipitation was falling (Figure 3, S1). Soil temperatures below 0°C interfered

with the detection of liquid water additions, thus confounding soil volumetric water content measurements at subfreezing temperatures (Ochsner & Baker, 2008). Therefore, increases in water content with warming above freezing were evaluated relative to conditions prior to the onset of freezing. Snowpack insulates the soil and thus helps maintain temperatures above 0°C, facilitating water movement. Periods of greatest observed snowpack (>20mm SWE) coincided with an increase in surface soil temperature to above 0°C and a subsequent increase in soil volumetric water content (e.g., early January 2022; Figure 3).

Section 3.2 Isotopic Composition of Atmospheric Waters

Variation in precipitation isotopic composition in the study area produced a LMWL with a slope of 7.14 and intercept of -10.4‰ (equation 1; Figure S4). Isotopic values of precipitation oscillated seasonally, where values for snow and rain under colder conditions during the autumnal through vernal periods were generally lower than values for rain under warmer conditions in the vernal through summer periods (Table 2, Figure 4). The Monte Carlo sensitivity analysis of the LMWL is expressed as a 95% confidence interval around the LMWL (Figure S4;) and encompasses the global meteoric water line. Precipitation values and the modelled volume-weighted annual mean) provide a reference against which we evaluated water sample results from soils, aquifers, and streams (Figure 4).

Section 3.3 Isotopic Composition of Landscape Waters

Combining the data across all years of the study and all sample locations, the variability in terrace soil water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values generally decreased from winter through summer (Figure 4a). Lower isotope values for terrace soil waters were observed in January, March, and April (there were no samples collected in February; Figure 4a). These terrace soil water values

were lower than those of all other landscape process domains, except for eight terrace groundwater samples (Table 2; see below for terrace groundwater details). Based on the mixed-model multi-comparison analysis, the population of isotopic values for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in terrace soils was statistically different from that of each of the other landscape process domains (p -value = 0.001 for $\delta^{18}\text{O}$ and p -value < 0.0014 for $\delta^2\text{H}$; denoted by the lower-case letters in Figure 5a). The distribution of residual errors relative to the model predictions for terrace soil waters passed tests for normality.

Soil water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results from sampling depths ca. 100 cm and greater exhibited limited variation over a season despite occasional increases in sample volume (e.g., Figure 7b red and black points) and soil water content (Figure S2). The highest soil water $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value was observed in the shallowest sampling depth where values also appeared to decrease within a season (e.g., 66 cm depth in Figure 7b tan points). Terrace groundwater exhibited higher mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values than soil water, with the exception of eight very low values from a well with head that is highly responsive to major recharge events (M-1 well) during a spring melt period in 2014, when substantial flooding of snowmelt waters occurred (Figure 4a, 8b). Terrace groundwater isotopic compositions otherwise remained relatively consistent across the sample locations, over the course of the year, and throughout the study period (Figure 4a, 6b).

Mean $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values observed across riparian waters were lower than those of the terrace groundwater, though a Tukey HSD multiple comparison of means test did not indicate high confidence in a statistical difference (Table 2, Figure 5a). Riparian surface water samples resulted in some of the highest values observed within this domain and across other process domains (Figure S4). The mean isotope values in stream waters were higher than all other

process domains, yet confidence was low in statistical differences with terrace groundwater or riparian water (Table 2, Figure 5a). Stream water isotope values exhibited limited variation for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Table 2, Figure 5a, 6d).

We interpreted a meaningful influence of evaporation where paired $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of a sample fall below the 95% confidence interval of the LMWL (Figure 5a, 6) and where a negative lc-excess value falls below the 95% confidence interval propagated from uncertainty in the LMWL (equation 2; Figure 5b). While no process domains had a mean lc-excess value that fell below the 95% confidence interval, terrace soil water lc-excess values exhibited the least negative mean lc-excess value, with a population of lc-excess values that were statistically different from all other landscape process domains (p -value = 0.023; Table 3, Figure 5b). Riparian waters resulted in more negative values outside the 95% LMWL confidence intervals than other process domains, but the mean lc-excess value of this process domain showed little statistical difference from the terrace groundwater and stream water (Figure 5b, 6, Table 3).

Discussion

The isotopic composition of terrace soil and riparian waters reflects more distinct contributions from colder precipitation compared to the terrace aquifers and stream channels. Therefore, infiltration of colder precipitation to soil storage may be important to plant productivity and soil biogeochemical processes such as nitrate production and consumption. While the isotopic composition of terrace soil water does not appear to be immediately responsive to individual precipitation events, it is highly variable over space and time and exhibits the most influence from colder precipitation. Terrace aquifers integrate heterogeneities evident in the overlying soils, while stream channels appear to integrate terrace groundwater and

riparian water sources. Areas of the riparian corridor exhibit the influence of evaporation, suggesting retention of water for sufficient time and exposure to the atmosphere for this local processing to take place. This analysis illuminates the relative importance of warmer and colder precipitation source waters and their distribution as hydrologic drivers of soil water availability and landscape processes in low-elevation, semi-arid agricultural systems.

Section 4.1 Soil Conditions Control Seasonal Variation in Infiltration of Precipitation

Annual cycles in the volumetric water content, temperature, and isotopic composition of terrace soil water suggest influence from multiple potential water delivery and storage pathways. Soil waters sampled at the bottom of the fine-textured soil horizons just above the gravel layer (60-119 cm depths) generally exhibited a mixture of colder and warmer precipitation waters with limited evaporative influence (Figure 4, 5; Table 2, 3). Soil conditions conducive to water infiltration were likely variable throughout the winter when soil temperatures in the top 20 cm oscillated between ca. -6 and +3°C (2019-2022; Figure 3, S1; see SI). Snowmelt infiltrated into soils during periods with the largest observed snowpack (>20mm SWE) (e.g., early January 2022; Figure 3). While infiltration into frozen soils is possible and water content measurements of frozen soils are dubious (Gray et al., 2001; Lundberg et al., 2016), increases in apparent soil water content took place after soil temperatures increased above freezing at our monitoring sites. At soil depths below 20 cm, soil temperatures generally remained just above freezing throughout the year (Figure 3), which likely allows for continuous soil water mixing in deeper soil horizons. Rain that falls on snow can deliver a mixture of rain- and snowmelt-derived water into terrace soils. Relative to shallower samples, the more limited variation in isotopic composition of waters extracted from the deeper soils (> 115 cm, Figure 7) suggests integrative mixing effects of

longer-term storage (Carrer et al., 2016; Sprenger et al., 2017) or limited potential for warmer precipitation to reach greater soil depths when evapotranspiration is higher. Evidence of both colder and warmer precipitation sources in these soil water samples, along with field-level spatial and annual temporal variation across sampling locations, indicates mixing processes that result from distinct patterns of water transport through soils.

Soil water contents and isotopic compositions exhibited limited sensitivity to individual precipitation or snowmelt events, indicating effective source water mixing over timescales exceeding the time between weather events, and across spatial scales captured by tension lysimeters (Figure 4, 7). Waters influenced by colder precipitation are stored in soils and can persist throughout the growing season (Figure 4a). Preservation of the colder precipitation signal in soils suggests that warmer precipitation, delivered when soil water contents are reaching saturation (Figure 3e-f), may be more readily available for root uptake or preferentially exported to groundwater. Contributions of colder precipitation to the shallower soil (i.e., 66 cm) are evident in the steady decrease in isotope values in response to a period of consecutive low intensity storms (e.g., April-May 2014 Figure 7b). In the subsequent season, the shallower soil also exhibited incorporation of colder precipitation, yet at higher volumes in response to higher intensity, shorter duration storms that occurred from the end of May into June (April-June Figure 7c). The initially high isotopic values of the shallower soil at the onset of each growing season suggests influence of antecedent precipitation stored from the previous fall following plant senescence and harvest (Figure 7b, c). Limited soil water holding capacity at shallow depths and possible freezing in surface soils can restrict additional accumulation of precipitation received in the intervening colder months, allowing a warmer precipitation isotopic signal to persist over

winter. Our data illustrate how antecedent soil moisture and weather conditions are important determinants of soil water isotopic composition at the onset of a growing season, which is particularly important to managing water content in soils with limited storage capacity. Our findings also indicate that contributions of colder precipitation are important to longer-term soil water storage in these non-irrigated, cultivated systems.

Several lines of evidence speak to the heterogeneity of infiltration processes in these soils. Isotopic composition and volume sampled from individual lysimeters differed across sites and across years (Figure 7). Generally, isotopic compositions of soil water exhibit inconsistent trends across sites in the same cropped field and for an individual site across years (Figure 7). Even soils sampled at similar depths exhibited different patterns in both water content and isotopic composition (e.g., depths 117 cm and 119 cm in Figure 7b, c). One of the deepest soil sampling locations (119 cm) exhibited substantial accumulation of warmer precipitation from 2013 to 2014 and then remained more consistent from 2014 to 2015 (Figure 7a-c). In contrast, the soil water isotopic composition observed at another site with similar depth (117 cm) remained consistent from 2013 to 2014 yet exhibited a colder precipitation signal early in 2015, then showed active accumulation of warmer precipitation (Figure 7a-c). Assuming an equal capacity to buffer isotopic composition in these deeper soils, potential drivers of observed year-to-year changes are differences in duration and intensity of storms, changes in crop rotation, variation in snow accumulation, or atypical drying due to meteorological drought (Kleine et al., 2020; Oerter & Bowen, 2019; Sprenger et al., 2018). The variation in isotopic composition observed at similar soil depths across multiple sites within the same field may be explained by spatial variation in snow accumulation and melt or soil physical properties at the profile scale.

Variation observed in soil water isotopic compositions during the growing season (June and July) suggests that the isotopic composition of water taken up by plants varies year to year according to precipitation delivery and storage patterns in soil. An important consideration for interpreting these data is that a given point of observation captured by a lysimeter within a soil profile reflects effects of physical soil properties that vary within the soil profile (i.e., soil structure) and dictate how mixing processes and potential preferential flow patterns manifest. Recent work demonstrates the occurrence of isotopically distinct preferential flow from soil water stored in smaller pore spaces through direct observation or modelled inference (Allen et al., 2019; Oerter & Bowen, 2017; Sprenger et al., 2015; Stumpp & Maloszewski, 2010). Here, our observations of different isotopic and volumetric patterns at similar depths may be an expression of soil profile heterogeneities (Wanzenek et al., 2018). Additionally, our data capture spatial and temporal variability within and among different soil depths that reflect a range of mixing conditions due to heterogeneities in soil at the field scale. As a result, the range of isotopic values observed in soil water exhibits increased variation and more influence of colder precipitation than the range observed in the terrace groundwater (Figure 5a).

Section 4.2 Mixing Processes Dominate in an Unconfined Terrace Aquifer

Terrace groundwater exhibits a mixture of recharge waters from spatially variable soils that appears less influenced by colder precipitation and more influenced by evaporation than observed pore waters of overlying soils. Soil preferential flow paths facilitate transport of isotopically different source water mixtures from surface soils to the terrace aquifer (Brooks et al., 2010; Sprenger et al., 2016). Decreased spatial and temporal variability in terrace groundwater relative to terrace soil water indicates integration of water received from

heterogeneous terrace soils by a highly conductive aquifer (Figure 4, 5; Table 2; Bowen et al., 2019; Sprenger et al., 2016, 2019). The integrated terrace groundwater signal incorporates spatially variable processes that occur within soil profiles and across soils on the landform (Figure 4, 7). Consistency in terrace groundwater isotopic composition over time exhibited minimal apparent influence from seasonality of precipitation, evaporation, or variation in the timing of water movement through soils (Figure 4, 5; Jasechko et al., 2014). Groundwater recharge occurred when soils are near saturation, which is likely to correspond with periods of high precipitation delivery to soils and, in non-irrigated agricultural systems, periods following a fallow rotation when crops are not grown for an entire season to conserve water (John et al., 2017; Sigler et al., 2020). The similarity of the terrace groundwater isotopic composition to the volume-weighted mean precipitation (Figure 5a, 6) suggests that groundwater recharge incorporates water that varies in isotopic composition at volumes proportional to what is delivered in precipitation. Alternately, this isotopic similarity can indicate that groundwater primarily incorporates water of a similar isotopic composition to that of precipitation delivered during the wettest times of year. Periods when the observed precipitation isotopic compositions aligned with the volume-weighted mean value (Figure 4a) occurred in late spring-early summer and in the fall corresponding with when approximately 50% of annual precipitation is delivered (Figure 3, S2a). The observed terrace groundwater isotopic composition suggests that deep percolation is primarily driven by large precipitation events (in intensity or duration) typically received during the vernal and autumnal seasons when precipitation most closely resembles the volume-weighted mean value, soils may be near saturation, and transpiration is low.

The integrated isotopic signal in terrace groundwater suggests that while precipitation moving through soils may be isotopically variable, soil water transport and groundwater mixing was effective enough to result in groundwater isotopic values similar to the volume weighted mean precipitation value. Assuming steady state turnover of a well-mixed volume, the estimated 20-year groundwater residence time (Sigler et al., 2018) suggests that annual recharge received from deep percolation of soil water is a relatively small fraction (ca. 5%) of the total aquifer volume. While recharge to the terrace aquifer through preferential flow paths likely occurred following wetter antecedent conditions, the limited temporal variability and minimal evaporation effects in terrace groundwater isotopic composition suggest that variation in the isotopic composition of these contributions was masked by relatively rapid mixing with the aquifer volume (Figure 4, 6; Sprenger et al., 2019; Sprenger & Allen, 2020; Stumpp & Maloszewski, 2010). We note that our sampling method using tension lysimeters may bias our assessment of terrace soil water to water from larger pores or preferential pathways in the soil matrix (Orlowski et al., 2016; Sprenger et al., 2015). However, sampling with tension lysimeters does not exclusively sample the most mobile water due to the episodic availability of that water in macropores. Smaller volume lysimeter samples caused by drier soils likely reflect less mobile soil water and larger volume lysimeter samples from wetter soils likely included more mobile soil water (Figure 7). At some sites, periodically increased sample volumes corresponded with seasonally higher precipitation and increased soil water contents (e.g., 66 cm and 117 cm depths in Figure 7). More mobile soil water likely drives recharge of the terrace aquifer during specific seasonal weather and antecedent soil conditions (Figure 7, Table S1; Jasechko et al., 2014). The consistent isotopic composition observed in the terrace groundwater despite the isotopically

variable recharge events suggests relatively rapid mixing of relatively small volumes of deep percolation into a relatively large aquifer volume (Figure 5a, 7).

Section 4.3 Local Processing and Inherited Signals Define Riparian Corridors

The influence of colder precipitation on the isotopic composition of riparian water relative to terrace groundwater (Figure 4a, 5a) suggests this process domain received recharge from local colder precipitation in addition to process domains up-gradient on the landscape. Limited isotopic variation in riparian waters and the general similarity of riparian waters to terrace groundwater suggest efficient integration of source waters by the riparian corridor (Table 2; Figure 4a, 5a). However, some riparian groundwaters reflected increased accumulation of colder precipitation relative to riparian surface water, terrace groundwater, and stream water (Figure 5a, S5, e.g., April and May 2021 in Figure S6). Previous studies found that lack of evapotranspiration in winter months promotes a shallower groundwater table that buffers riparian soil temperatures (Burt et al., 2002; Smerdon & Mendoza, 2010). Increased probability of non-frozen soils in addition to increased snow catch allow colder precipitation to accumulate in riparian soil and groundwaters. Although we did not evaluate riparian soil temperature and water content data during the period of this study, we anticipate similar trends to observations in terrace soils where water accumulates in winter and spring (Figure 3). These infiltration dynamics allow for increased contributions of colder precipitation to riparian groundwater.

Riparian waters undergo local processing in addition to inherited signals. Riparian water isotopic compositions that deviated from the majority and the LMWL (ca. 10% of riparian samples) provide evidence of local processes that promote evaporation (Figure 5b, 6c, S5; Gammons et al., 2006; Sharp, 2017). Increased fractionation in riparian water was especially

evident in riparian surface water where reduced velocity and increased exposure to the atmosphere facilitate evaporation (Figure S5). Riparian corridors encompass flow paths with strong variation in transit and residence times, where longer flow paths promote biogeochemical processes that can decrease nitrate concentrations in water leaving the system and can contribute to N₂O emissions (Chapin et al., 2011; Cheng et al., 2020; Harms & Grimm, 2008; Hedin et al., 1998; Hill, 2019; Hill et al., 2014; Sigler et al., 2022). Areas of more pronounced evaporation within the riparian corridor may reflect increased water residence times and hence exert control on biogeochemical function, reflect the spatial heterogeneity of these ecosystems, and indicate the influence of riparian structure on hydrologic processes.

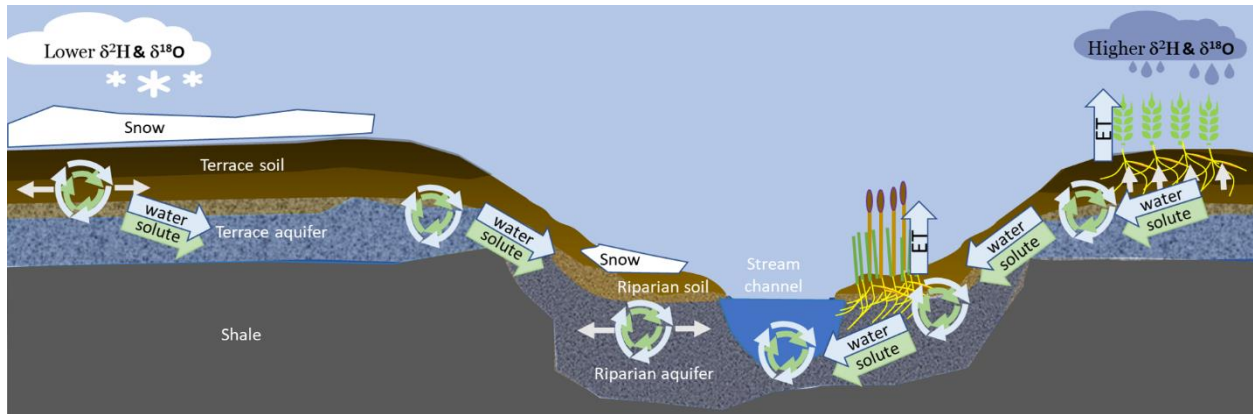
Stream water isotopic compositions indicate a mixture of up-gradient channel water, terrace groundwater, and riparian water. The stream water reflects a relatively consistent mixture of inherited components, with limited evidence of local processes (Figure 5, 6). Instances of increased isotopic signals in the stream water relative to riparian groundwater suggest that colder precipitation (e.g., snowmelt) delivered to the riparian may flush warmer season water into the stream channel (Table 2, Figure 5, 6d). Local evaporative effects on stream water may also result in isotopic signals distinct from up-gradient domains. The stream water exhibited the most consistent isotopic signal and mixture of source waters observed across the process domains, which supports our conceptualization of this terrace-riparian-stream continuum as a gaining system where down-gradient domains integrate the effects of up-gradient processes by way of hydrologic connection (Hill, 2019; Vidon & Hill, 2004).

Conclusions

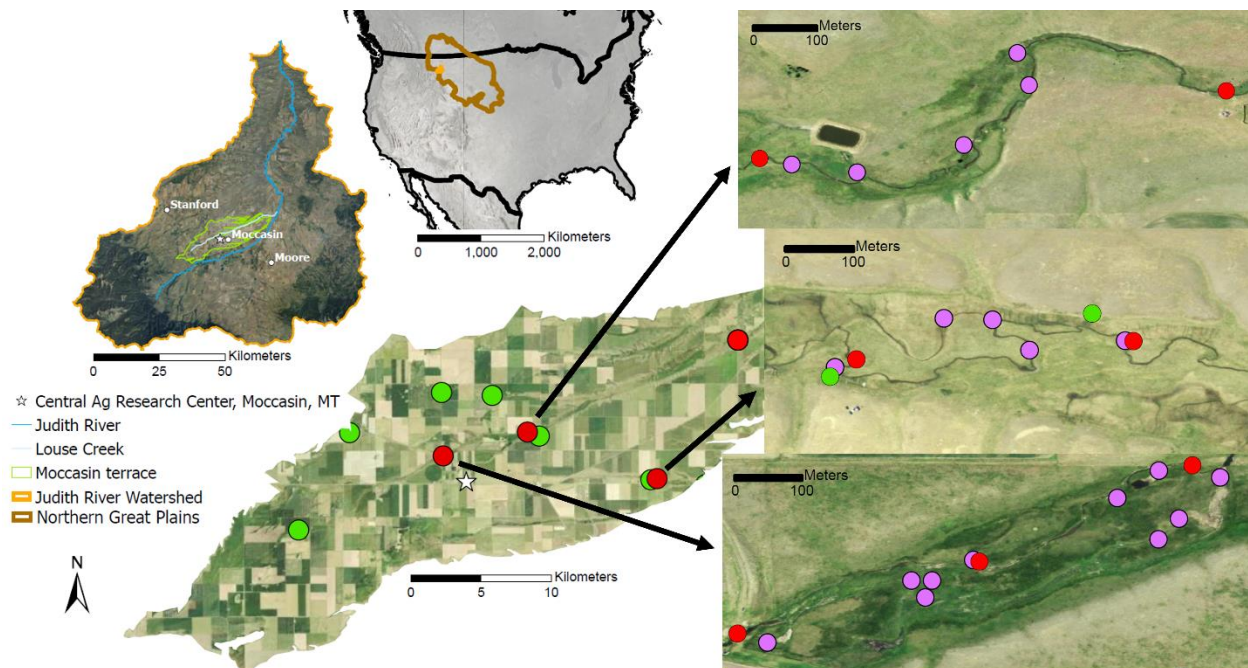
Our data provide a novel analysis of water isotopic compositions across a non-irrigated agricultural setting. Observed $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values in environmental waters across process domains show that soils play an integral role in mixing seasonal precipitation and exhibit spatial variation of mixing and throughflow processes within and across soil profiles. Our results highlight the role of soils in processing water that enters the landscape and indicate that colder precipitation influences water stored in soils across seasonal to annual and longer timescales. The persistence of colder precipitation in soils suggests these source waters contribute to crop production and nutrient processing. We found that shallow riparian aquifers likely receive local contributions from colder precipitation and act as efficient integrators of source waters. Areas within the riparian corridor where increased water retention coupled with exposure to atmospheric forces impart localized signatures of riparian isotopic compositions. Our data show that stream channel waters reflect a mixture of riparian water and terrace groundwater, which suggests influence of direct inflows of terrace groundwater that undergo minimal riparian processing. Streams exhibiting limited riparian influence reflect corridors that are less effective at mitigating export of nutrient loads from agricultural systems. Additional efforts to quantify how soil water storage heterogeneities mediate variable precipitation patterns will further inform the potential consequences of warmer winters with more rain and less snow across both non-irrigated agricultural production and grassland ecosystems.

Acknowledgements

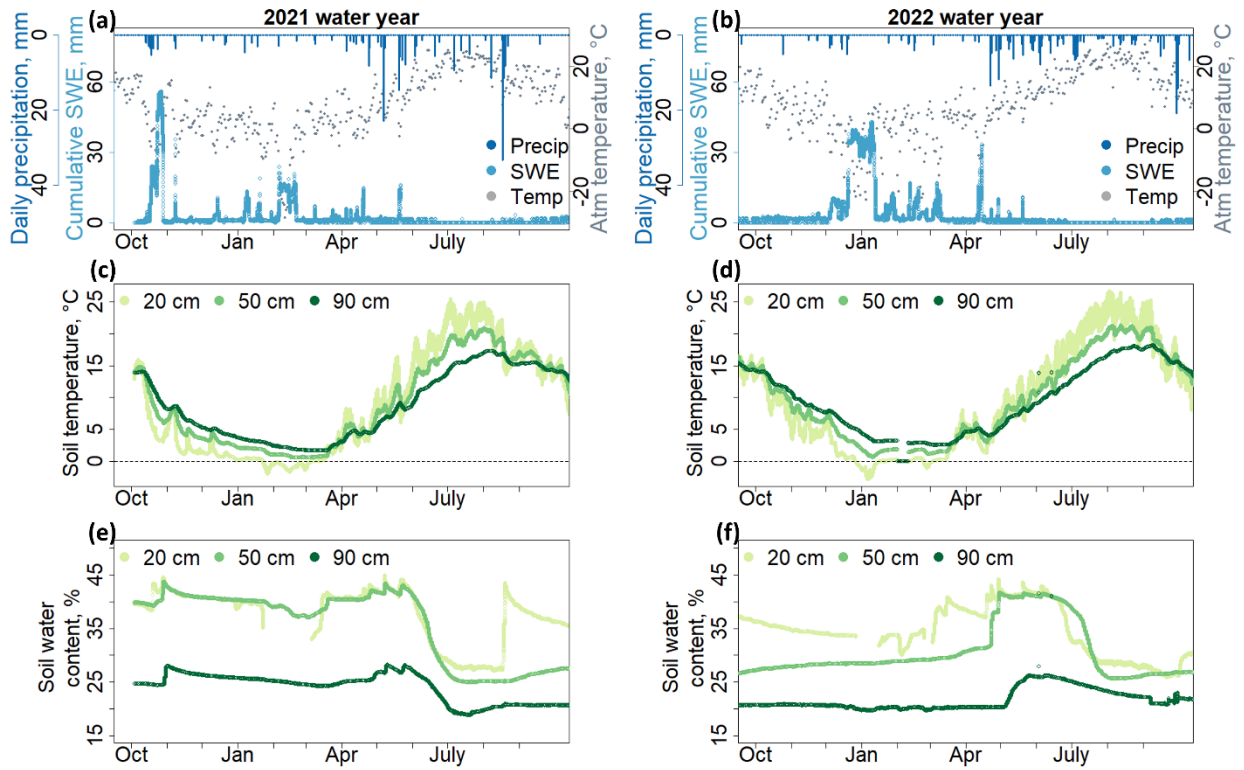
We thank the Consortium for Research on Environmental Water Systems (NSF EPSCoR Cooperative Agreement OIA-1757351), the MSU Nielsen Pedology Graduate Research Fellowship (2021), and the Montana Agricultural Experiment Station partially funded by USDA-NIFA (MAES project numbers MONB00364 and MONB00349) for funding this work. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation or U.S. Department of Agriculture. We appreciate the support and data from the Montana Climate Office, the US Department of Agriculture Natural Resources Conservation Service, the U.S. Bureau of Reclamation, and the Montana Department of Agriculture. A special thank you to Dr. Ann Marie Reinhold for her help with building the conceptual framework. We thank Dr. Toby Koffman, Kevin Hyde, Sam Leuthold, Simon Fordyce, and Skye Keeshin for help with data collection, analysis, and technical assistance. We sincerely thank two anonymous reviewers for their time and constructive feedback.

Figures

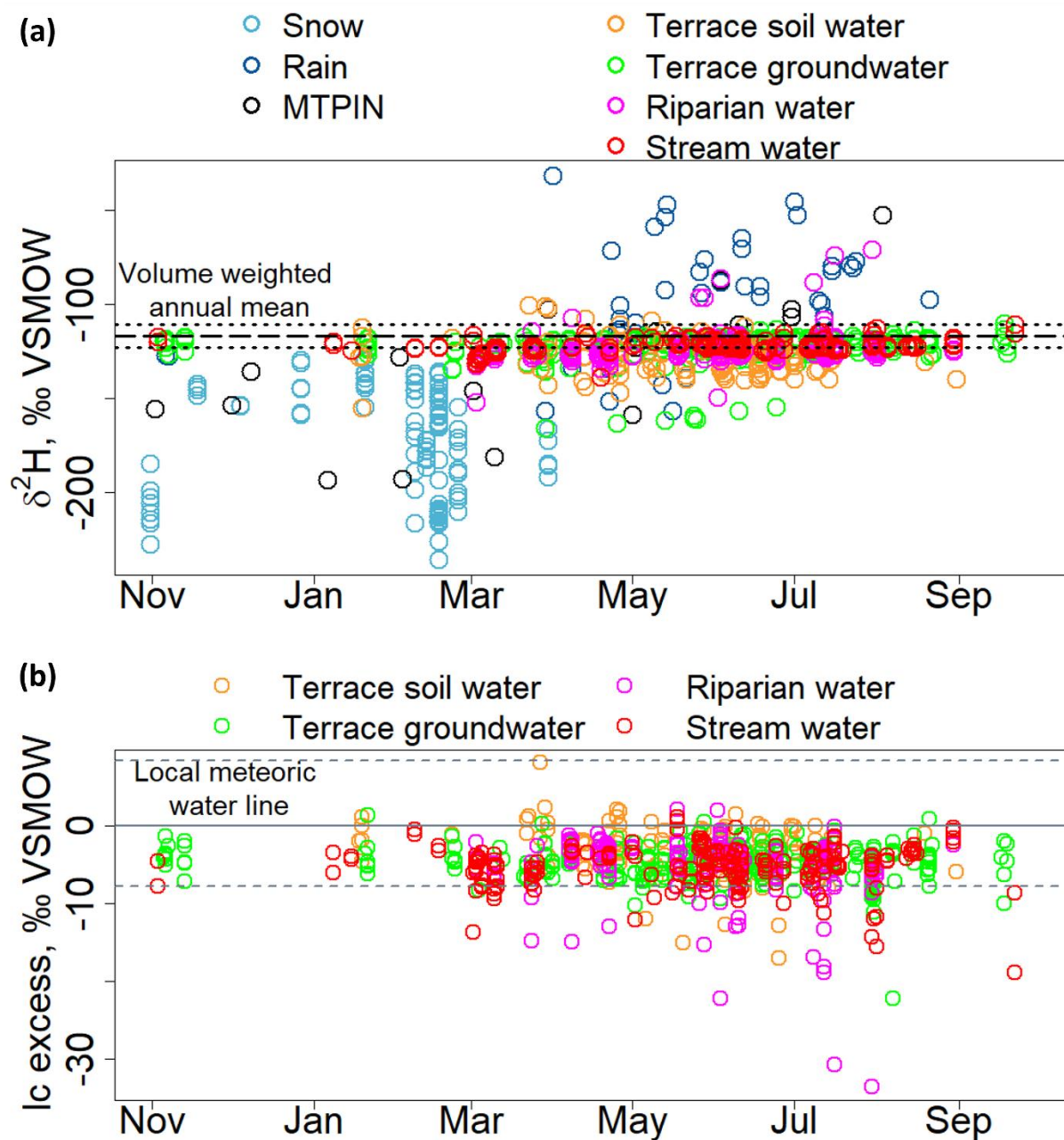
Ch2-Figure 1. The terrace-riparian-stream continuum on the Moccasin terrace. Conceptual diagram of anticipated precipitation infiltration, mixing, and evapotranspiration processes and subsequent solute processing and transport along a hydrologic gradient such as that of the Moccasin terrace. In this landform, nitrate concentrations are generally 20 mg N L^{-1} in the terrace groundwater, near 0 mg N L^{-1} in the riparian groundwater, and 10 mg N L^{-1} in the stream.



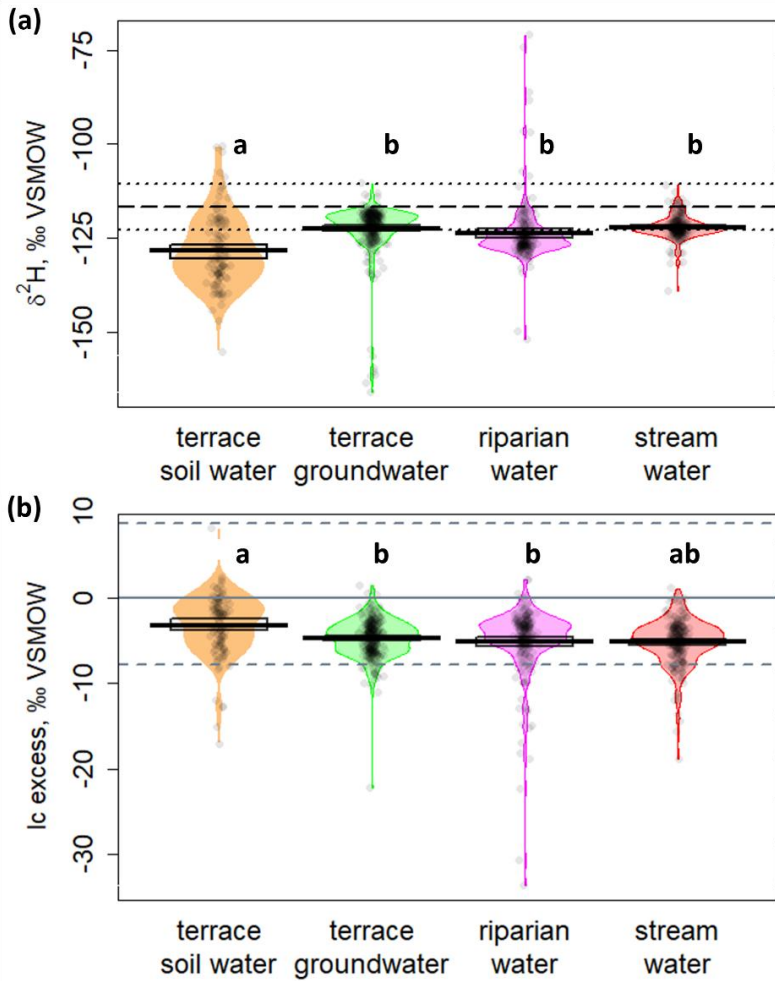
Ch2-Figure 2. Study area and general site locations. The Moccasin terrace is located within the Judith River Watershed (inset, top left) and the Northern Great Plains (inset, top right). The terrace is geographically isolated from mountain water recharge. Areas surrounding the towns of Moore and Stanford host similar soils and shallow aquifers to the Moccasin terrace but are more connected to mountain water recharge. See specific site locations in Table S1. GIS sources: ESRI, USDA, USGS, FSA, NGP boundary obtained from World Wildlife Fund



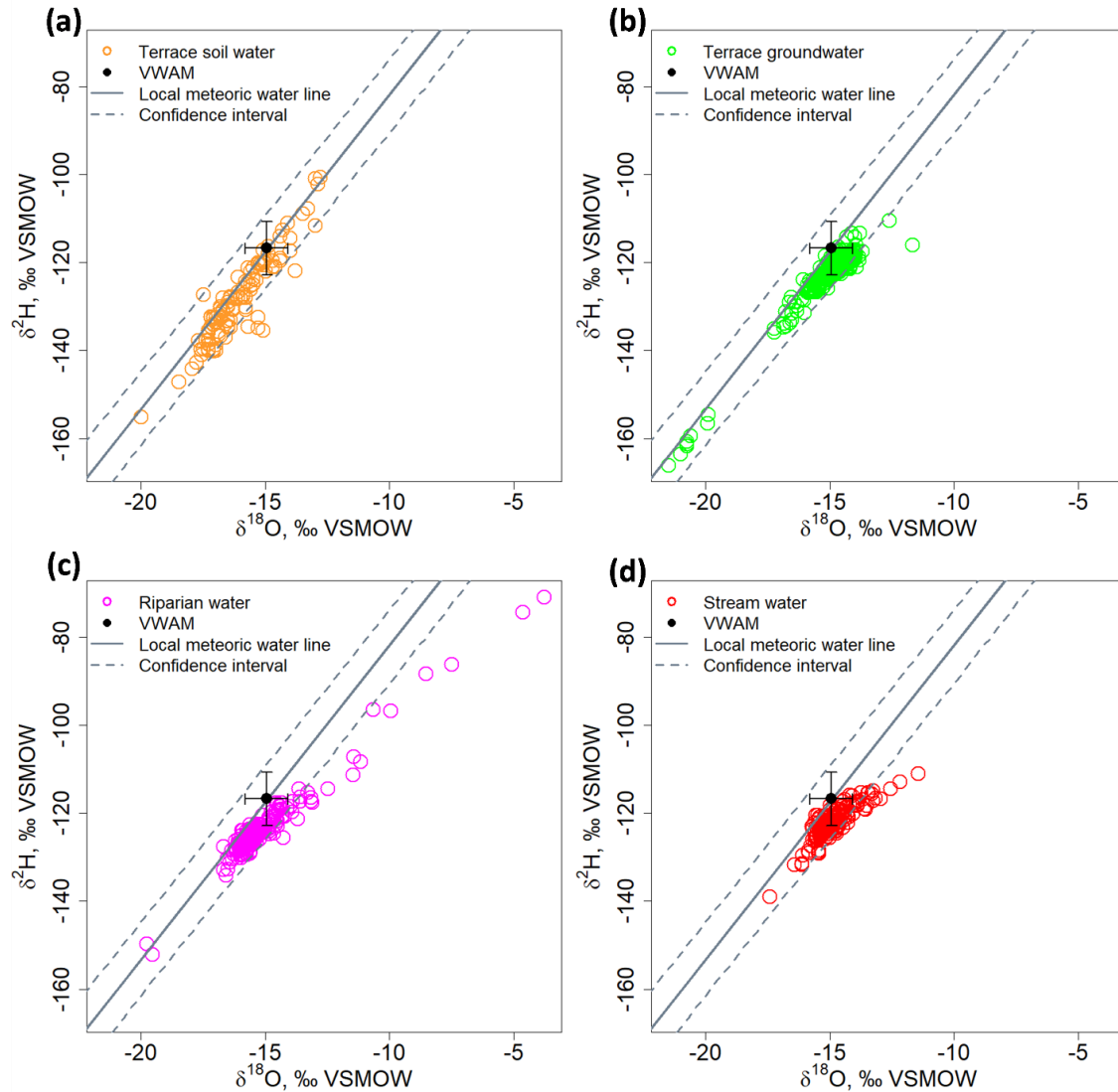
Ch2-Figure 3. Precipitation and soil climate data by 2021 and 2022 water years at the Central Agricultural Research Center, Moccasin, MT. Data include (a, b) daily precipitation, snow water equivalent (SWE), and atmospheric temperature, (c, d) soil temperature at 20 cm, 50 cm, and 90 cm depths, and (e, f) percent soil water content at 20 cm, 50 cm, and 90 cm depths (U.S. Bureau of Reclamation, 2023; Montana Climate Office, 2023). Soil volumetric water content is invalid at soil temperatures below 0°C due to changes in geophysical properties caused by state change from water to ice.



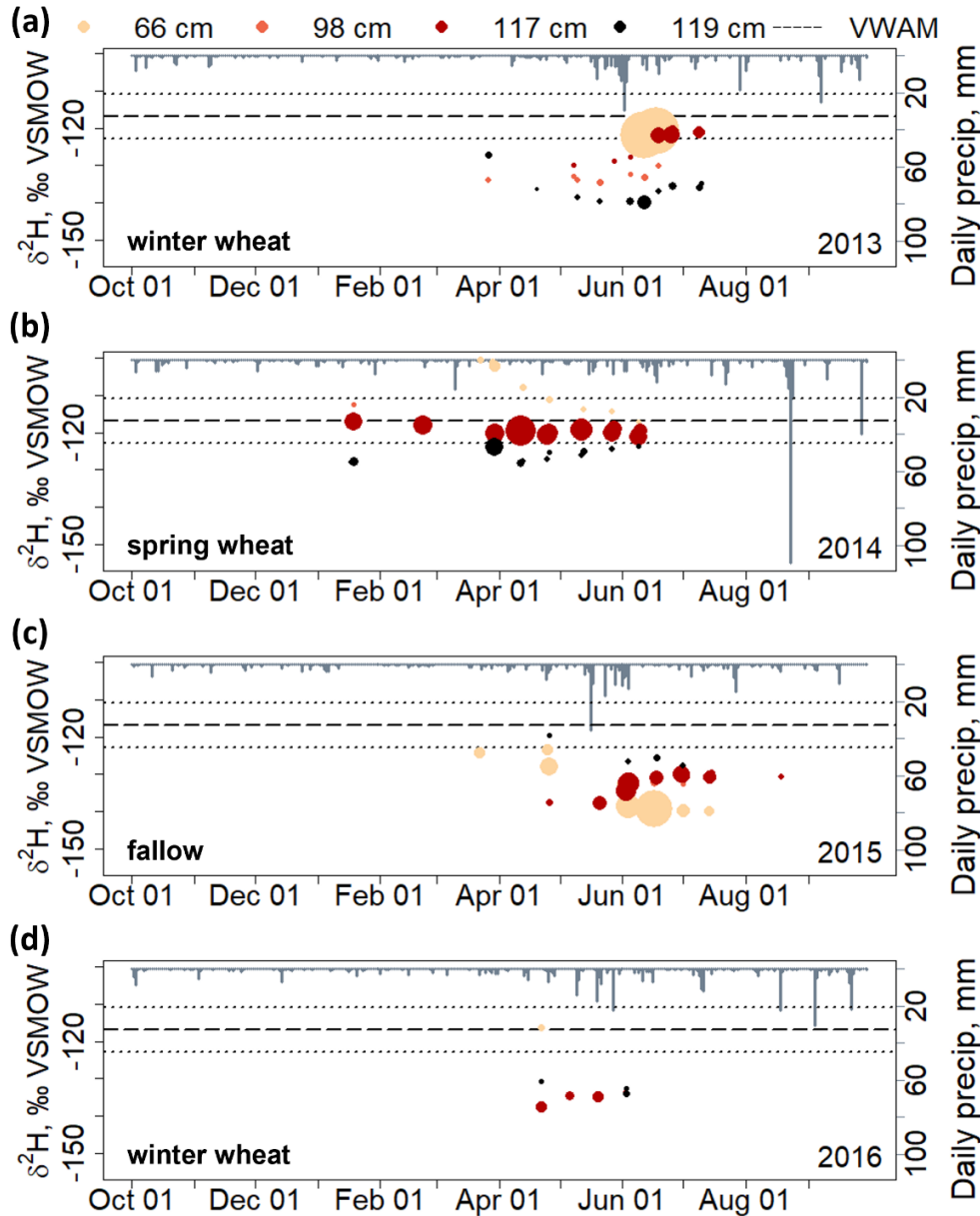
Ch2-Figure 4. Water isotope values by day of water year. Values of $\delta^{18}\text{O}$ (a) and $\delta^2\text{H}$ (b) in precipitation (rain, snow, and monthly composite for the Montana Precipitation Isotope Network, MTPIN), terrace soil water, and terrace groundwater with multiple years (2013-2022) represented. The dashed line indicates the multi-year volume weighted mean precipitation value, with uncertainty (dotted lines) reflecting variability in annual precipitation over the AgriMet record for 2012-2022 (U.S. Bureau of Reclamation, 2023).



Ch2-Figure 5. Values of $\delta^2\text{H}$ and line-conditioned excess by process domain. Distribution of $\delta^2\text{H}$ (a) and lc-excess (b) values in four process domains across the terrace including terrace soils (orange), terrace groundwater (green), riparian surface and groundwater (magenta), and stream water (red). Mean values and 95% frequentist confidence intervals are indicated by black bars for each process domain. Lower-case letters indicate significant difference determined by Tukey HSD post hoc test of the impact of landscape process domain on $\delta^2\text{H}$ and lc-excess after accounting for water year, campaign within year, and individual site. The dashed line on (a) indicates the multi-year volume weighted mean precipitation value, with uncertainty (dotted lines) reflecting variance in annual precipitation over the AgriMet record for 2012-2022 (U.S. Bureau of Reclamation, 2023). The cluster of more negative values in terrace groundwater reflect results from the Montana Department of Agriculture M-1 monitoring well during a rapid snowmelt runoff episode in 2014. The solid-grey, zero-line (b) expresses the local meteoric water line (Figure S4). The 95% confidence intervals (dashed grey) are derived from the Monte Carlo uncertainty analysis (Figure S4, see methods). Values below the lower bound of the confidence interval indicate an evaporative loss signal either from within that domain or via inmixing from up-gradient.



Ch2-Figure 6. Water isotope values in four process domains. Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ from (a) terrace soil water (2014-2016); (b) terrace groundwater sampled from wells (2013-2017) and springs (2013-2022); (c) riparian water sampled from spring channels, ponds, and shallow groundwater (2020-2022); and (d) stream water from two channels (2012-2022) relative to the modeled volume weighted annual mean value (black point with error bars based on variability in annual precipitation over the AgriMet record for 2012-2022 (U.S. Bureau of Reclamation, 2023)). The local meteoric water line (LMWL) and 95% confidence interval are derived from precipitation results (Figure S4; see methods). Points falling outside the confidence interval indicate transformation processes and mixing of inherited transformed waters.



Ch2-Figure 7. Precipitation amounts and terrace soil water $\delta^2\text{H}$ values across years. Daily precipitation (mm) from USBR AgriMet station: MWSM is in grey bars along the top of each panel for water years 2013 (a), 2014 (b), 2015 (c), and 2016 (d). Soil water collected via tension lysimeter across four sampling sites (denoted by color, legend above panel a) representing a range of depths of fine soil material across the study area. Point size is proportional to the volume of the sample collected which ranges from 1.5 mL to 181 mL. The dashed line indicates the multi-year volume weighted mean precipitation value, with uncertainty (dotted lines) reflecting variance in annual precipitation over the AgriMet record for 2012-2022 (U.S. Bureau of Reclamation, 2023). Only sites with four or more samples collected in each of two or more years are included in this figure.

Tables

Ch2-Table 1. Sample Type, Period of Sample Collection, and Total Count

Water sample type	Time period	n	Location description
Rain	2013-2016	51	Privately owned fields near Stanford, Moccasin, and Moore, MT
Snow cover	2014	6	Moore, MT
	2019-2022	114	Moccasin, MT
Montana Precipitation Isotope Network (MTPIN) monthly composite	2021-2022	20	Central Agricultural Research Center, Moccasin, MT
Terrace soil	2013-2016	115	Privately owned field near Moore, MT
Terrace groundwater	2013-2022	214	Wells and terrace springs on the Moccasin terrace
Riparian groundwater, spring channels, and ponds	2020-2022	201	Three stream corridors on the Moccasin terrace
Stream channel water	2012-2022	283	Ten locations across two streams on the Moccasin terrace

Ch2-Table 2. Summary statistics for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ results in precipitation source waters and each process domain

Sample type	Period of record	n	$\delta^{18}\text{O}$					$\delta^2\text{H}$				
			Min	Max	Median	Mean	SD	Min	Max	Median	Mean	SD
Rain	2013-2016	51	-21.5	-3.34	-12.6	-12.6	4.45	-156.7	-31.7	-99.6	-100.7	30.1
Snow	2014, 2019-2022	120	-30.6	-15.0	-22.1	-22.5	3.64	-235.4	-129.2	-165.8	-171.3	27.7
MTPIN monthly composite	2021-2022	20	-25.3	-7.39	-16.5	-16.5	5.02	-193.1	-52.97	-122.9	-127.8	37.7
Terrace soil pore water	2013-2016	115	-20.0	-12.8	-16.3	-16.1	1.27	-155.1	-100.6	-130.0	-128.4	9.54
Terrace groundwater	2013-2022	301	-21.5	-11.7	-14.8	-15.0	1.30	-166.0	-110.4	-120.8	-122.5	7.32
Riparian water	2020-2022	210	-19.8	-3.77	-15.5	-15.1	1.68	-152.0	-70.9	-125.1	-123.7	8.23
Stream channel water	2012-2022	218	-17.4	-11.4	-15.1	-14.9	0.68	-138.9	-111.0	-122.5	-122.2	3.23

Ch2-Table 3. Summary statistics for line-conditioned excess results in each process domain.

Sample type	Period of record	n	lc-excess				
			Min	Max	Median	Mean	SD
Terrace soil pore water	2013-2016	115	-17.0	8.12	-2.29	-3.22	3.60
Terrace groundwater	2013-2022	301	-22.2	1.42	-4.53	-4.72	2.23
Riparian water	2020-2022	210	-33.6	2.06	-4.40	-5.10	4.32
Stream channel water	2012-2022	218	-18.9	1.11	-4.84	-5.16	2.73

Supporting Materials

Section 2. Methods

Study Area. Soils in our study area are susceptible to water loss and nitrate leaching due to relatively thin zones of fine textured material (40-100 cm) overlying subsurface horizons with > 40% coarse gravel content. Approximately 50% of the soils in the field where we sampled soil water are thinner than 60 cm (see figure 5c in Sigler et al., 2020). The shallow terrace aquifer accumulates nitrate leached from overlying soils, resulting in groundwater nitrate concentrations commonly twice the EPA drinking water standard of 10 mg N L⁻¹.

Hydrometeorological and Soil Monitoring. We installed a sonic snow depth sensor (Sommer USH-9) along with the snow scale in February 2020 that recorded observations every 15 minutes. These data are not used in this study. Precipitation volume, air temperature, relative humidity, wind speed, and wind direction are recorded by the MCO and NRCS stations in addition to the sensors operated by the USBR at 15-minute intervals. These data are not used in this study. (MCO, 2023, USDA NRCS 2022; USBR 2023).

Sample Collection and Handling. Rainwater was collected in years 2013-2016 at three locations near Stanford, Moccasin, and Moore, Montana (Figure 1, Table S1). The rain collectors used to accumulate a sample (Product Alternatives, Inc.; Fergus Falls, MN) consisted of a 255mL internal chamber with approximately 5mL of mineral oil suspended on top of the water to minimize evaporative fractionation effects (Sigler et al., 2022). Each time the collector was sampled, the sample volume in the collector was recorded, and the sample was extracted from the internal chamber using a syringe and discharged into a 20mL scintillation vial. The collector was then emptied the mineral oil was replaced to allow accumulation of the next sample.

Snow samples from accumulated snow cover were collected at select locations near Moore (2014) and Moccasin (2019-2020; Table S1). Snow cover was also sampled in 2021 and 2022 from undisturbed snow at 3- to 10-m intervals along established transects near the Central Agricultural Research Center, Moccasin, MT (Table S1). Transects across the perennially vegetated riparian corridor were perpendicular to the stream channel. Transects across the terrace upland traversed cultivated fields with variable crop residue. Samples were collected using a 10 cm-diameter metal core inserted vertically in the snowpack to sample the entire snow column. Snow samples collected in this manner were sealed in Ziploc bags, weighed, and allowed to melt. Once melted, samples were stored in a refrigerator before thoroughly mixing and decanting into collection vials. Snow depth was measured at all locations sampled from 2020 to 2022.

In 2021-2022, additional precipitation samples of accumulated rain and snow were collected as ca. monthly aggregates using a Montana Precipitation Isotope Network sampler (Palmex RS1B) installed at the Central Agricultural Research Center, Moccasin, MT (Figure 1, Table S1; Carstarphen, 2021). During the colder season, the sampler was equipped with a black metal snow tube to increase snow catch and promote snowmelt through siphon into the collection bottle. During the warmer season the sampler was equipped with a weighted delivery tube into the collection bottle. Samples were transferred into vials and filtered in the lab using 0.2µm syringe disc filters before analysis.

Privately owned and managed fields were accessed with permission and advising from cooperating farmers with the goal to capture the influence of cropping system strategies (Table S1; Sigler et al., 2018). At each sampling location, a lysimeter cup was installed in undisturbed fine textured calcareous soil material just above the gravel horizon (50 to 120 cm depth). Terrace soils were sampled one to three times per month during periods of high soil volumetric water

content and once a month otherwise. To extract soil pore water, an internal tension of approximately -15 psi was applied with a hand pump, and a sample was collected after allowing ca. 24 hours of accumulation in the lysimeter reservoir.

At productive riparian groundwater well locations, where continuous pumping was feasible, parameters (i.e., pH, temperature, dissolved oxygen, and conductivity) were monitored using a multimeter (YSI Incorporated; Yellow Springs, OH) and flow-through cell to confirm stable readings before sample collection. At low production riparian groundwater wells, continuous pumping was not possible and insufficient water volumes inhibited accurate multimeter readings. Low production wells were purged three well volumes and sufficient recovery time was allocated between each purge and before sample collection.

All groundwater and surface waters were collected in duplicate (if water volume was sufficient). Samples were stored in a cooler immediately upon collection, transferred to a cooler with ice within two hours, and then to a refrigerator within eight hours. Samples were transferred from the field to the lab in a cooler with ice and stored in the lab at room temperature until analysis.

Isotope Analysis. A memory correction was applied to the 134 precipitation samples and 426 landscape process domain samples collected from 2019 to 2022 (Gröning, 2011), resulting in adjustments of up to 0.1‰ for $\delta^{18}\text{O}$ and 0.5‰ for $\delta^2\text{H}$. To account for memory in samples collected and analyzed with only six injections from 2012 to 2014, analytical uncertainty for $\delta^2\text{H}$ values increased to 2‰ in samples run immediately following USGS standards 46 and 48 (n = 67). For all other samples collected and analyzed with only six injections in this timeframe, analytical uncertainty for $\delta^2\text{H}$ was increased to 1‰ (n = 177). Samples analyzed from 2015 to

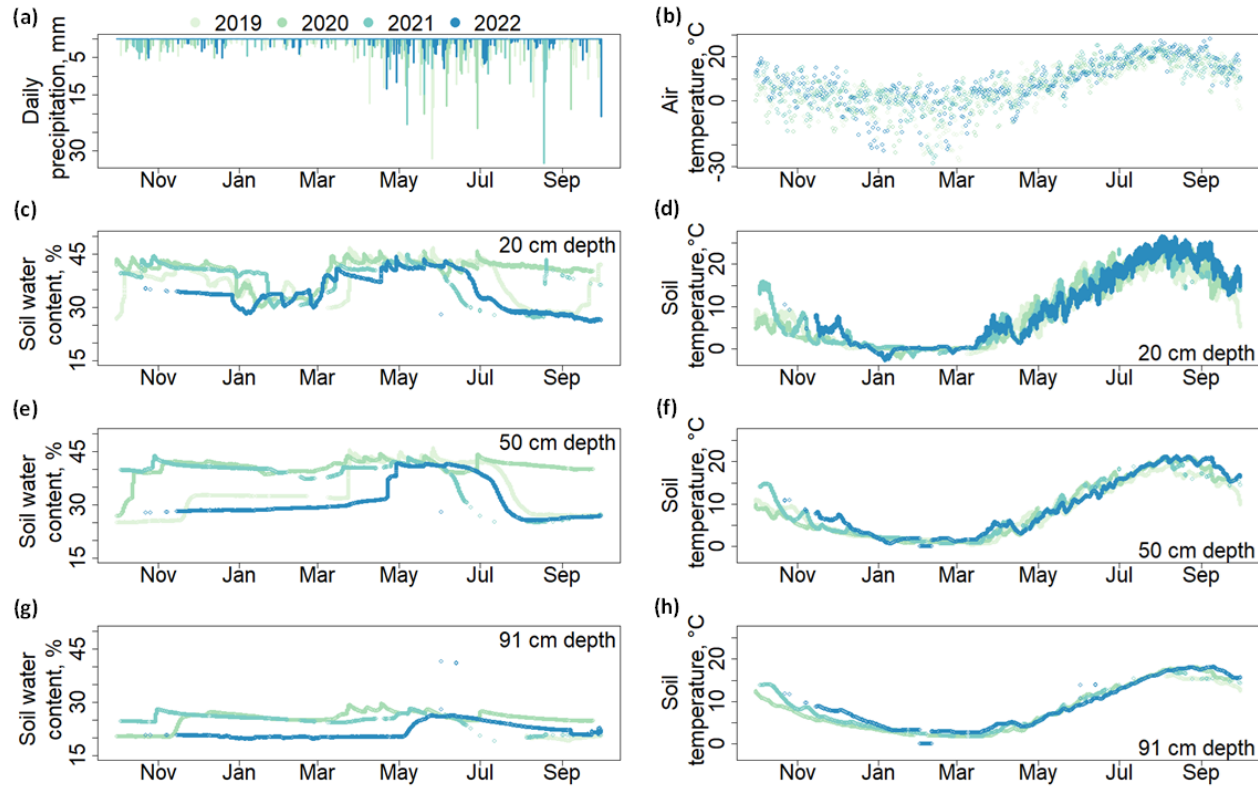
2018 (n = 245, including 31 lysimeter samples collected in 2013) were analyzed with sufficient injections to minimize the influence of analytical memory and no corrections were made.

We compared how well our data and model aligned with a sinusoidal model fit to monthly predictions obtained from the Waterisotopes database (Bowen, 2022; IAEA/WMO, 2015) for a central location in our study area (latitude: 47.067342°N, longitude: 109.966514°W, elevation: 1294.8m). The resolution of Global Network of Isotopes in Precipitation (GNIP) empirical database is coarse around our study site with the closest GNIP data station ca. 500 kilometers away (IAEA/WMO, 2015). We determined that the sinusoidal model fit to our precipitation isotopic data was reasonable given uncertainties in our model fit, the GNIP interpolation, and the incorporation of altitude and latitude in the Waterisotopes interpolation (Figure S1; Bowen, 2022; Bowen et al., 2005; Bowen & Revenaugh, 2003; Bowen & Wilkinson, 2002). Thus, we used the model fit to our precipitation isotopic data to estimate the isotopic composition of a mixture of the total annual precipitation. First, isotopic values for precipitation were estimated for each day of the year using the sinusoidal model. We then calculated the precipitation-weighted isotopic value for a single day using the product of the predicted daily isotopic value and the measured daily precipitation (https://www.usbr.gov/gp/agrimet/station_MWSM.html). We determined the annual volume-weighted mean for each year by summing the weighted values for all days of the year and dividing by the total annual precipitation. We then averaged the annual volume-weighted mean values to produce a single reference $\delta^{18}\text{O}$ and $\delta^2\text{H}$ value for precipitation over the entire study period.

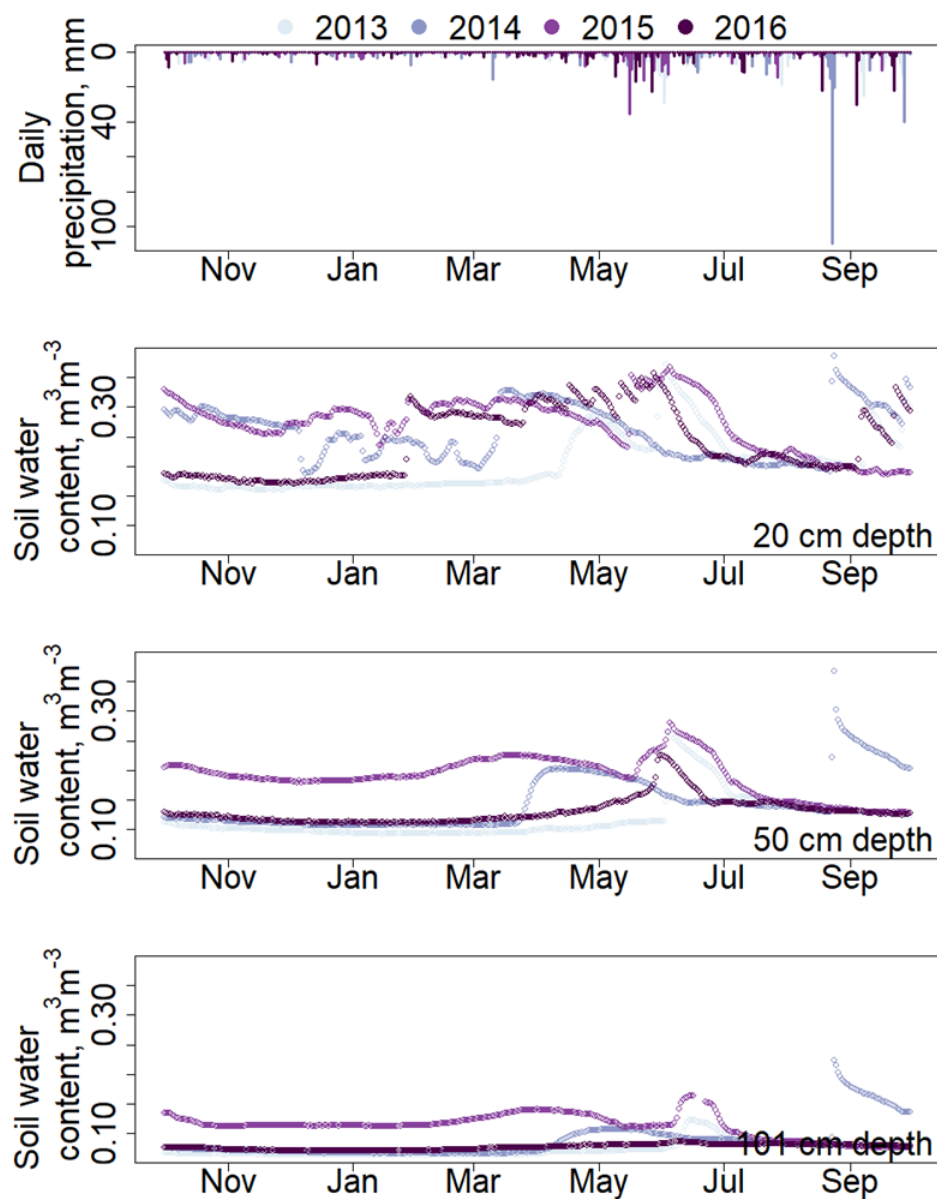
Section 3. Discussion

Soil Physical Properties Control Infiltration of Precipitation. Soil conditions (i.e., soil water content and temperature) and water storage capacity dictate the fate of water delivered to soils providing water for crop production and aquifer recharge. During the fall, winter, and spring seasons, colder precipitation (e.g., snowmelt) most likely enters terrace soil when soil temperatures exceed 0°C to sufficient depths with available pore space (Figure 2 e.g., mid-January 2022). Based on texture alone, these well-drained clay loam soils have estimated ranges in porosity: 0.44 - 0.51 m³ m⁻³, field capacity: 0.22 - 0.38 m³ m⁻³, and wilting point: 0.12 - 0.17 m³ m⁻³, which are consistent with soil conditions measured near our study area (Dingman, 2015, *Physical Hydrology* 3rd edition; Montana Climate Office, 2023; U.S. Department of Agriculture, 2022). Based on these estimates, the mineral soil thicknesses of 60 to 120 cm across our study area are likely to retain 18 to 33 cm of water at average field capacity. Measured volumetric water content values at soil depths of ca. 90 cm plateau around 0.25 - 0.30 m³ m⁻³, reflecting field capacities that decrease with depth due to coarser textured subsurface horizons in our study area (Figure 2; Sigler et al., 2020). We infer that when soil temperature is greater than 0°C and soil volumetric water content exceeds field capacity, additional precipitation entering the soil results in the movement of water through the soil profile and leads to both in-mixing of warmer season precipitation and mobilization of stored waters. This occurs mainly in spring and fall when periods of limited transpiration coincide with expected increases in rainfall and snowmelt.

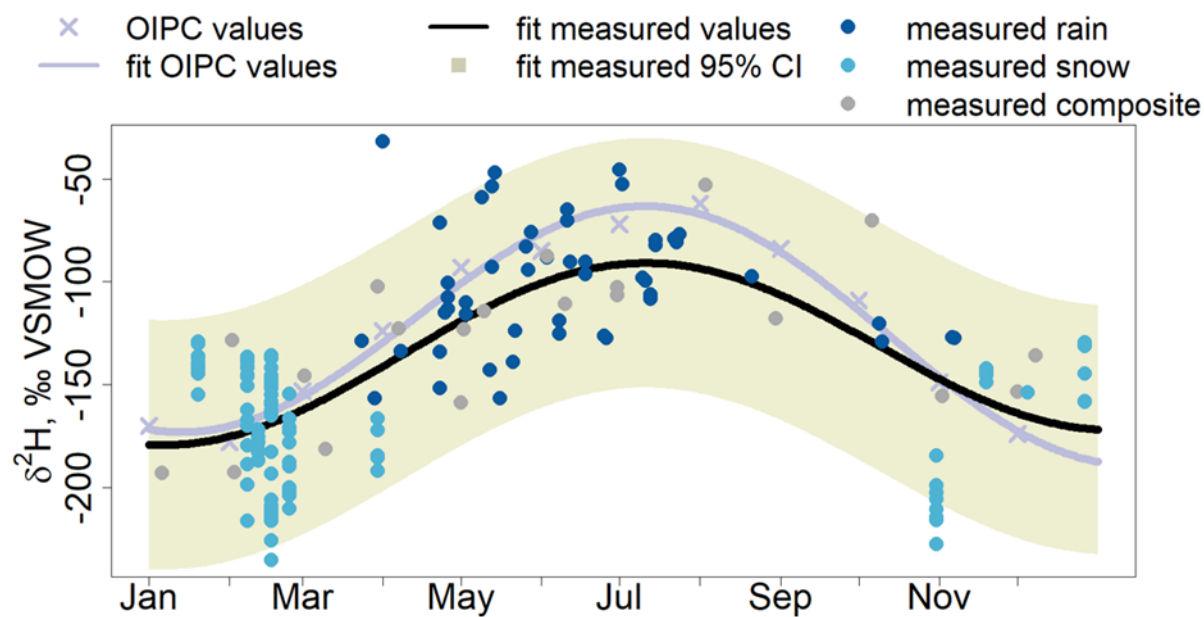
Supporting Figures



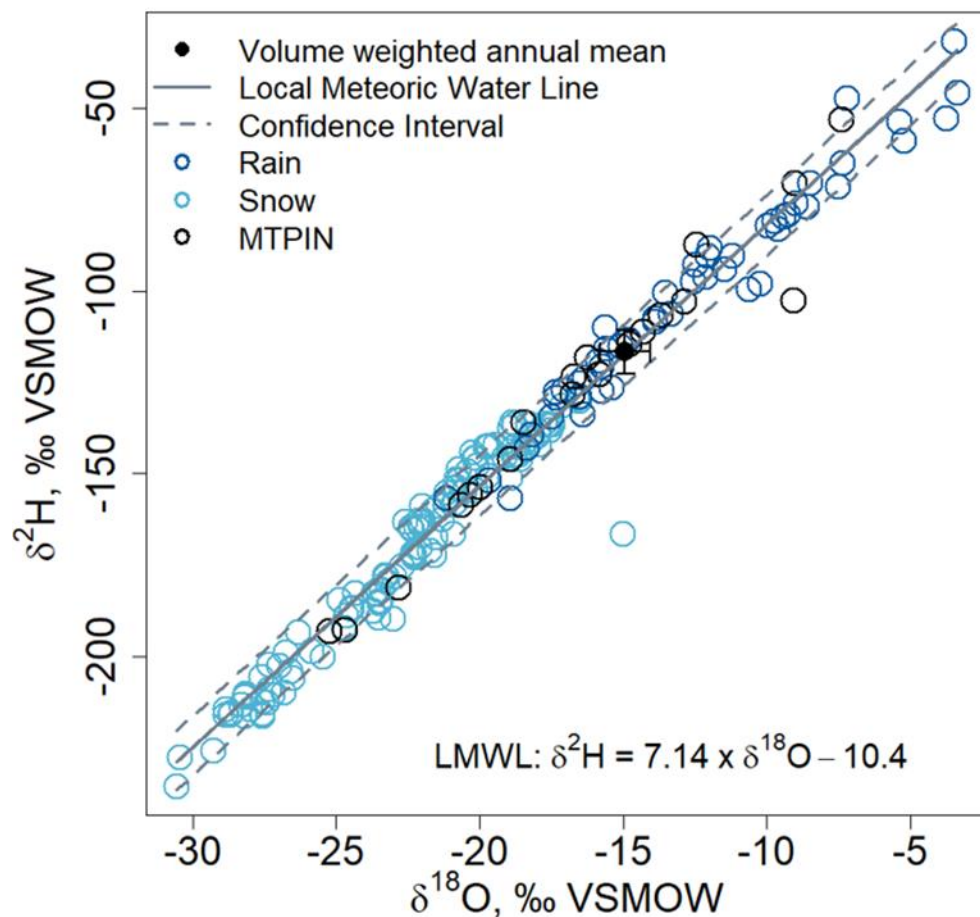
Ch2-Figure S1. Hydrometeorological and soil climate data on the Moccasin terrace over four water years (2019-2022). Data include (a) precipitation (mm) and (b) atmospheric temperature ($^{\circ}\text{C}$); soil water content (m^3m^{-3}) at soil depths of (c) 20 cm, (e) 50cm, and (g) 91 cm; soil temperature ($^{\circ}\text{C}$) at soil depths of (d) 20 cm, (f) 50cm, and (h) 91 cm. Data from USBR AgriMet Station: MWSM and the MCO Moccasin Mesonet station, both located at the Central Agricultural Research Center (U.S. Bureau of Reclamation, 2023; Montana Climate Office, 2023). Soil volumetric water content is invalid at soil temperatures below 0°C due to changes in geophysical properties caused by state change from water to ice.



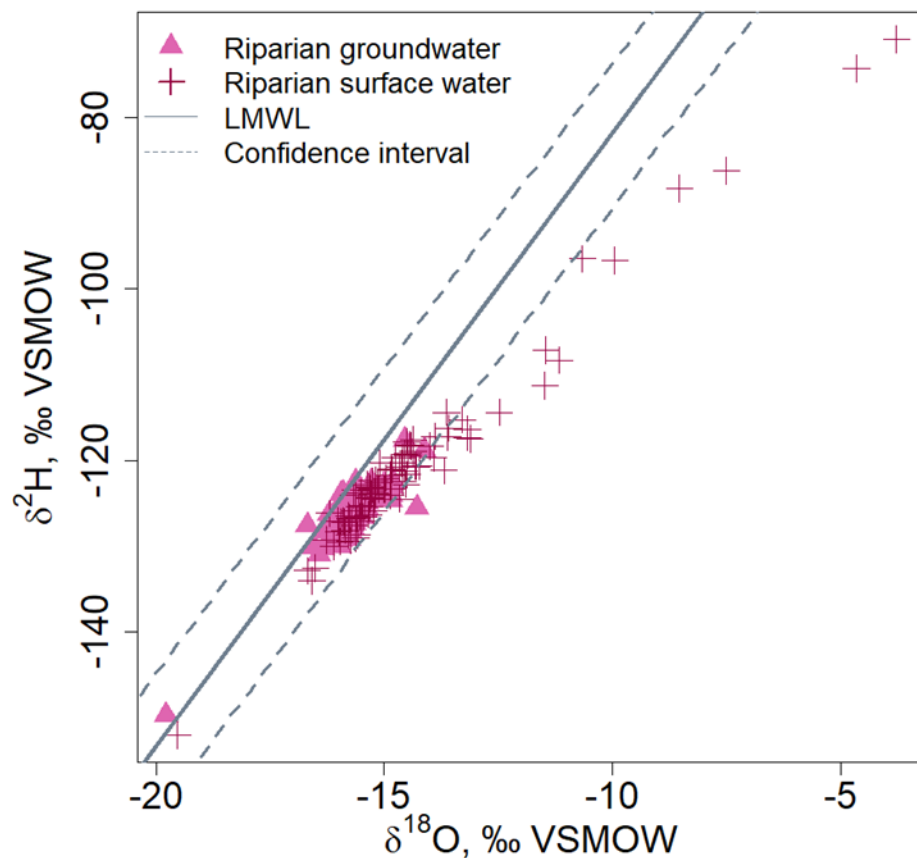
Ch2-Figure S2. Hydrometeorological and soil climate data on the Moccasin terrace over the four water years soil water samples were collected (2013-2016). Data from USBR AgriMet station: MWSM and the NRCS SCAN station: 2119, both located at the Central Agricultural Research Center (U.S. Bureau of Reclamation, 2023; U.S. Department of Agriculture, 2022).



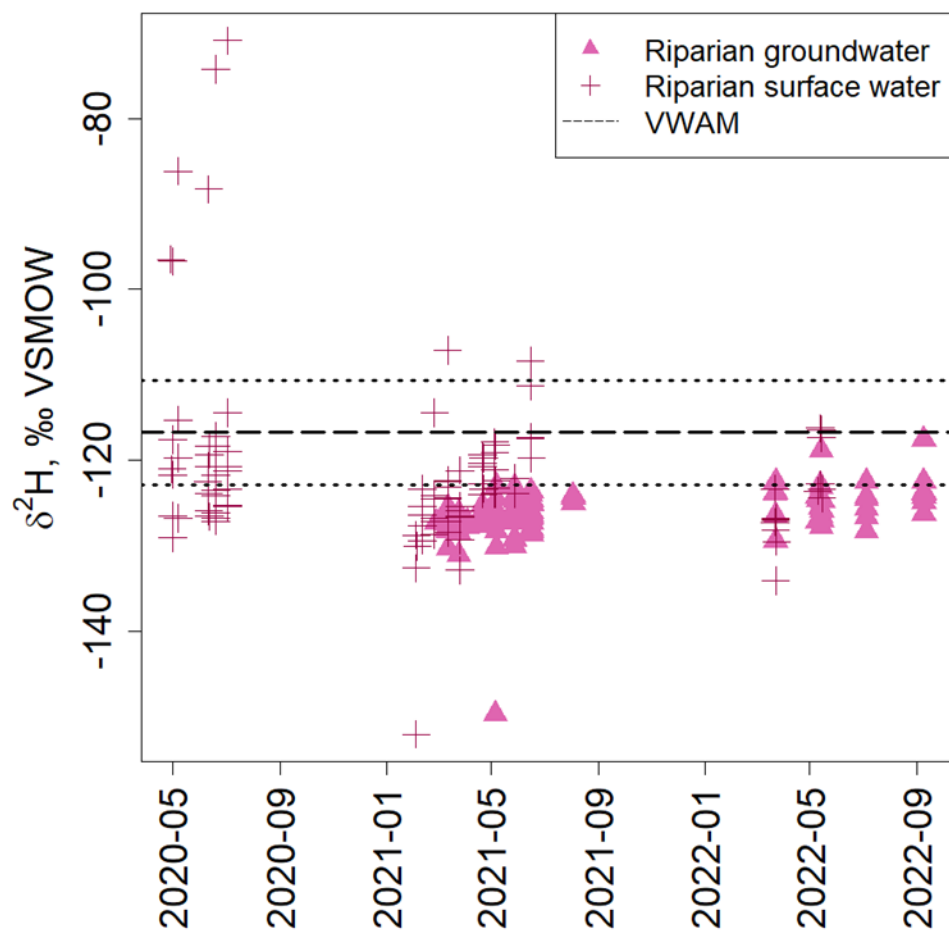
Ch2-Figure S3. Sinusoidal fit and 95% confidence interval for precipitation $\delta^2\text{H}$ results over time relative to a sinusoidal model fit to a sinusoidal model fit to spatially interpolated predicted monthly values for our study site location (latitude: 47.0673°N, longitude: -109.9665°W, elevation: 1295m; Bowen, 2022). Spatially interpolated monthly predictions were obtained using the Online Isotopes in Precipitation Calculator (Bowen, 2022). Measured values represent multiple years from 2013 to 2022 and include direct samples of rain (2013-2016), snow (2014 and 2019-2022), and monthly composites (2021-2022).



Ch2-Figure S4. Water isotopes in snow and rain. Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for precipitation with calculated local meteoric water line (LMWL) and 95% confidence intervals derived from the Monte Carlo sensitivity analysis (see methods) relative to a modeled volume weighted annual mean value (black point) derived from Bowen, G. J. (2022; see SI methods) The Online Isotopes in Precipitation Calculator, version 3.1. <http://www.waterisotopes.org>. Sample values represent multiple years from 2013 to 2022 and include direct samples of rain (2013-2016), snow (2014 and 2019-2022), and monthly composites (2021-2022). Samples were collected near the Central Agricultural Research Center in Moccasin, Montana and at cooperator sites near Moore and Stanford, Montana.



Ch2-Figure S5. Surface and groundwater isotope values in the riparian process domain. Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in riparian groundwater (light purple triangles, 2021-2022) and surface water (dark purple crosses, 2020-2022), all other process domain values (grey). Local meteoric water line (LMWL) and 95% confidence intervals are derived from precipitation results (Figure 4; see methods). Points falling outside the confidence interval indicate transformation processes and mixing of inherited transformed waters.



Ch2-Figure S6. Riparian surface and groundwater $\delta^2\text{H}$ values for sample years 2020-2022. Values of $\delta^2\text{H}$ in riparian groundwater (light purple triangles, 2021-2022) and surface water including riparian spring channels and ponds (dark purple crosses, 2020-2022). The dashed line indicates the multi-year volume weighted mean precipitation value, with uncertainty (dotted lines) reflecting variability in annual precipitation over the AgriMet record for 2012-2022 (U.S. Bureau of Reclamation, 2023).

Supporting Tables

Ch.2-Table S1: Detailed site description, geographic location, and sample collection frequency for water isotopic composition analyses.

Site	SiteType	YearSampled	AnnualCounts	Latitude	Longitude	Comments
FieldA	Precip-Rain	2013, 2014	1, 5	47.2141	-110.1593	Rain gauge site at Field A near grain bins; manual gage and tipping bucket
FieldB	Precip-Rain	2013, 2014, 2015, 2016	2, 6, 5, 4	47.0556	-109.8391	Rain gauge site at Field B in corner of Grove yard; manual gage and tipping bucket
FieldC	Precip-Rain	2013, 2014, 2015, 2016	1, 7, 5, 4	46.9974	-109.6134	Rain gauge site at Field C near fence on North end near Well 3; manual gage and tipping bucket
Rain_Breanna	Precip-Rain	2015	11	46.9830	-109.6191	Rain gage at Brandon's house that Breanna was collecting samples from
FieldB	Precip-Snow	2014	3	47.0553	-109.8594	Field B snow sample location (coordinates only accurate to field scale)
FieldC	Precip-Snow	2014	3	46.9970	-109.6115	Field C snow sample location (coordinates only accurate to field scale)
MTPIN collector	Precip	2021, 2022	10, 10	47.0584	-109.9535	Collects monthly composite precipitation sample
CAS	Precip-Snow	2019, 2020, 2021	14, 20, 38	47.0584	-109.9535	Central Agricultural Research Center field snow sample locations (coordinates only accurate to

RR	Precip-Snow	2022	42	47.0681	-109.9639	field scale; multiple locations sampled within field) Upper Louse Creek riparian corridor snow sample location (coordinates only accurate to field scale; multiple locations sampled within field)
C2E.01	Soil	2013, 2015	2, 1	46.9962	-109.6129	Judith project soil lysimeter location
C2E.07	Soil	2013, 2014, 2015, 2016	7, 12, 10, 4	46.9929	-109.6130	Judith project soil lysimeter location
C2E.08	Soil	2013, 2014, 2015, 2016	11, 11, 4, 3	46.9924	-109.6130	Judith project soil lysimeter location
C2E.10	Soil	2013, 2014, 2015, 2016	3, 8, 9, 1	46.9913	-109.6130	Judith project soil lysimeter location
C2W.04	Soil	2013, 2014, 2015	7, 1, 5	46.9946	-109.6145	Judith project soil lysimeter location
C2W.06	Soil	2013, 2014	1, 2, 9	46.9935	-109.6145	Judith project soil lysimeter location
C3W.01	Soil	2014	4	46.9962	-109.6126	Judith project soil lysimeter location
PS01	Spr	2013, 2014, 2015, 2016, 2017, 2020, 2021	11, 8, 3, 6, 3, 3, 4	47.0570	-109.8336	Terrace spring; Also identified as Grove Spring
PS02	Spr	2020, 2021, 2022	3, 4, 1	47.0578	-109.8301	Terrace spring
IS01	Spr	2013, 2014, 2015, 2016, 2017, 2020, 2021, 2022	11, 24, 5, 6, 3, 3, 8, 2	47.0758	-109.9048	Terrace spring; also identified as Indian

Star	Spr	2013, 2014	13, 3	47.0937	-109.9351	Terrace spring at Star Road
Spr555	Spr	2013, 2014	13, 8	47.0775	-110.0265	Terrace spring trib 555 near Benchland, MT
Headwaters	Terrace Well	2013, 2014	10, 7	47.0350	-110.0591	Louse Creek Headwaters Well at Mudsprings Road; at diesel shop
M1	Terrace Well	2013, 2014, 2015, 2016, 2017	15, 10, 4, 7, 2	47.0950	-109.9676	MDA M1 Monitoring Well
RR11	Riparian pond	2020, 2021	6, 5	47.0674	-109.9659	
RR14	Riparian pond	2020, 2021, 2022	7, 6, 1	47.0693	-109.9610	
RR12	Riparian side channel	2020, 2021	5, 7	47.0682	-109.9640	Spring channel emerges in riparian floodplain
RR22	Riparian seep	2020	1	47.0682	-109.9640	Seep emerges in riparian floodplain
RR34	Riparian side channel	2020, 2021	5, 8	47.0693	-109.9599	Spring channel emerges in riparian floodplain; includes RR24 and RR44 due to very close proximity
RR54	Riparian side channel	2021, 2022	5, 1	47.0695	-109.9608	Spring channel emerges in riparian floodplain
LL11	Riparian side channel	2020, 2021, 2022	3, 8, 1	47.0775	-109.9110	Spring channel emerges in riparian floodplain
LL12	Riparian side channel	2020, 2021, 2022	3, 6, 1	47.0792	-109.9089	Spring channel emerges in riparian floodplain
LL22	Riparian seep	2020, 2021	2, 1	47.0793	-109.9089	Seep emerges in riparian floodplain
PC11	Riparian side channel	2020, 2021, 2022	2, 4, 1	47.0578	-109.8314	Channel outlet of spring-fed stock pond in riparian floodplain

PC12	Riparian side channel	2020, 2021, 2022	3, 3, 1	47.0576	-109.8303	Spring channel emerges in riparian floodplain
RW01	Riparian groundwater	2021, 2022	6, 4	47.0672	-109.9661	Groundwater sampled from shallow well within riparian floodplain
RW02	Riparian groundwater	2021, 2022	5, 1	47.0681	-109.9642	Groundwater sampled from shallow well within riparian floodplain
RW03	Riparian groundwater	2021	4	47.0678	-109.9640	Groundwater sampled from shallow well within riparian floodplain
RW04	Riparian groundwater	2021, 2022	8, 5	47.0689	-109.9606	Groundwater sampled from shallow well within riparian floodplain
RW05	Riparian groundwater	2021, 2022	4, 1	47.0694	-109.9600	Groundwater sampled from shallow well within riparian floodplain
RW06	Riparian groundwater	2021, 2022	5, 1	47.0683	-109.9633	Groundwater sampled from shallow well within riparian floodplain
RW07	Riparian groundwater	2021, 2022	5, 1	47.0692	-109.9614	Groundwater sampled from shallow well within riparian floodplain
RW08	Riparian groundwater	2021, 2022	9, 4	47.0681	-109.9639	Groundwater sampled from shallow well within riparian floodplain
RW09	Riparian groundwater	2021, 2022	5, 1	47.0695	-109.9608	Groundwater sampled from shallow well within riparian floodplain
RW10	Riparian groundwater	2021, 2022	5, 1	47.0686	-109.9608	Groundwater sampled from shallow well within riparian floodplain

LW01	Riparian groundwater	2022	1	47.0777	-109.9120	Groundwater sampled from shallow well within riparian floodplain
LW03	Riparian groundwater	2021, 2022	2, 2	47.0779	-109.9096	Groundwater sampled from shallow well within riparian floodplain
LW04	Riparian groundwater	2021, 2022	1, 2	47.0792	-109.9089	Groundwater sampled from shallow well within riparian floodplain
LW05	Riparian groundwater	2021, 2022	1, 3	47.0788	-109.9087	Groundwater sampled from shallow well within riparian floodplain
PW01	Riparian groundwater	2021, 2022	2, 3	47.0571	-109.8335	Groundwater sampled from shallow well within riparian floodplain
PW02	Riparian groundwater	2021, 2022	2, 1	47.0578	-109.8321	Groundwater sampled from shallow well within riparian floodplain
PW03	Riparian groundwater	2021, 2022	2, 3	47.0577	-109.8314	Groundwater sampled from shallow well within riparian floodplain
PW04	Riparian groundwater	2022	1	47.0573	-109.8309	Groundwater sampled from shallow well within riparian floodplain
PW05	Riparian groundwater	2021, 2022	2, 1	47.0575	-109.8297	Groundwater sampled from shallow well within riparian floodplain
Kolin	Stream channel	2012, 2013, 2014, 2015, 2016, 2017	14, 14, 24, 6, 5, 3	47.1178	-109.7778	Louse Creek at Kolin Road
Porter	Stream channel	2015, 2016, 2017	6, 6, 3	47.0548	-109.7985	Porter Creek at County Road 311

RR01	Stream channel	2012, 2013, 2014, 2019, 2020, 2021, 2022	15, 11, 24, 14, 21, 19, 2	47.0673	-109.9665	also identified as UpperLouse1
RR02	Stream channel	2019, 2022	4, 9	47.0683	-109.9633	includes RR05 and RR07 due to very close proximity
RR04	Stream channel	2019, 2020, 2021, 2022	5, 15, 15, 12	47.0696	-109.9604	includes RR03 due to very close proximity
LL01	Stream channel	2020, 2021, 2022	5, 11, 1	47.0778	-109.9126	includes LL04 due to very close proximity
LL02	Stream channel	2020, 2021, 2022	8, 16, 12	47.0787	-109.9059	
PC01	Stream channel	2020, 2021, 2022	6, 5, 2	47.0572	-109.8333	also identified as PorterCk1
PC02	Stream channel	2020, 2021	5, 5	47.0575	-109.8296	also identified as PorterCk2

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CHAPTER THREE

RIPARIAN PROCESSES IN SEMI-ARID LANDSCAPES: BALANCING NITRATE MITIGATION AND SULFATE AUGMENTATION IN AGRICULTURAL SYSTEMS

Contribution of Authors and Co-Authors

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Manuscript Information

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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 and temporal patterns in stream corridor solute concentrations to infer dominant hydrologic transport and biogeochemical pathways influencing nitrate and sulfate concentrations. We selected three reaches of stream corridor with varying hydrologic connectivity with upland groundwaters within a semi-arid northern Great Plains agricultural landscape. We inferred the influence of biogeochemical processing and hydrologic connectivity on water quality from solute concentration patterns in riparian groundwater and stream water relative to upland groundwater. Excess nitrate from cultivated soils is evident in upland groundwater concentrations that consistently exceed the U.S. Environmental Protection Agency public drinking water standard. Weathering of the organic-rich marine shale underlying shallow aquifers also contributes nitrate and sulfate to ground and surface waters. Nitrate concentrations in riparian groundwaters were consistently lower than those in terrace groundwater and adjacent stream waters, indicating likely influence of metabolic reduction processes like denitrification. Generally, sulfate concentrations in streams were higher than those in terrace groundwater, reflecting products from local weathering of shale-derived substrate that would also produce nitrate and contribute to accumulation of fine soil material. Results indicate consistent loading to terrace aquifers from upland soil water influenced by agricultural management practices, with riparian processes contributing to persistent net nitrate losses and net sulfate gains in stream water. This research provides a catchment-scale perspective on the biogeochemical and hydrological function of stream corridors that control the quality of water of non-irrigated agricultural landscapes.

Introduction

The complex interaction of processes influencing biogeochemical cycling in stream riparian areas remain poorly understood (Bernhardt et al., 2017; Hill, 2019), inhibiting our ability to interpret catchment-scale controls on stream corridor biogeochemistry. Riparian areas host vegetation adapted to soils with typically higher water content and a shallow and fluctuating groundwater table (Chapin et al., 2011; Hill, 2000; Naiman & Décamps, 1997; Silverman et al., 2019). Fluctuating water availability through spatially heterogeneous organic matter and mineral substrate (Vidon & Hill, 2004b) facilitate temporally and spatially diverse biogeochemical processes in subsurface waters that can strongly differ from those in upland soils and aquifers. Thus, riparian areas are often disproportionately important for altering inorganic solute export from the landscape relative to their limited spatial extent (Hill, 1996; Ledesma et al., 2016; Naiman & Décamps, 1997; Ranalli & Macalady, 2010; Tesoriero & Puckett, 2011). Here, we conceptualize riparian areas of stream corridors as a separate physical and biogeochemical process domains from upland aquifers or stream channels, expanding on the geomorphological concept (Montgomery, 1999) to acknowledge the boundaries created by self-organization of hydrologic and biogeochemical feedbacks within domains. We include riparian flow paths that are both recharged by and discharged to the stream (often termed hyporheic zones) within the riparian process domain due to more consistency of the biogeochemical activity in these flow paths with anoxic riparian aquifers (Boulton et al., 1998; Zhao et al., 2021) than stream channels. Comparisons of solute concentrations across process domains and assessment of spatial and temporal patterns within process domains provide clues about the sources of solutes and the dominant biogeochemical reactions influencing solute concentrations. This research explores

patterns of solute concentrations in environmental waters across an agricultural landscape to investigate how riparian ecosystems transform nitrate and sulfate loads from upland groundwaters prior to export into stream channels.

Bedrock weathering contributes various chemical species to ground and surface waters, including ions of sulfur (S), sodium, and chloride (Holloway et al., 1998; Houlton et al., 2018; Morrison et al., 2012; Wan et al., 2021). Weathering of organic-rich sedimentary rocks, such as shale and sandstone, releases more dissolved solids than weathering of other types of bedrock (Holloway & Dahlgren, 1999; Houlton et al., 2018; Morrison et al., 2012; Tuttle et al., 2014). Direct and indirect effects of physical anthropogenic alterations of the landscape (e.g., cultivation or mining) can increase contributions of solutes by promoting bedrock and soil weathering. Human transformations of bedrock, soil, and plant community structure tend to expose more reactive surfaces and alter partitioning of precipitation among evapotranspiration, storage, and runoff, increasing the probability for transport of inorganic N and S to ground and surface waters (Holloway & Dahlgren, 1999; Ross et al., 2018; Scanlon et al., 2007; Welch et al., 2021).

Human perturbations from food production often provide additional solute loading through soil amendments, mobilizing dissolved chemical species that commonly impair water quality (Foley et al., 2011; Miller et al., 1981; Tilman & Clark, 2015). In particular, N and S in fertilizers can increase soil water concentrations of oxidized soluble compounds like nitrate and sulfate when applied to agricultural landscapes above crop demand or where soils are vulnerable to leaching (Eriksen, 2009; Sebilo et al., 2013; Sigler et al., 2020). Dissolved inorganic compounds are readily transported through cultivated soils into shallow groundwater and streams when soil water exceeds water holding capacity (Beven & Germann, 2013; Scanlon et al., 2005).

Export of these compounds from agricultural systems indicates loss of soil nutrients that would otherwise be available for soil microbe and plant uptake. Inefficiencies in nutrient management, particularly for N, are pervasive across agricultural systems, leading to high solute concentrations in ground and surface waters (Burow et al., 2010; Kelley et al., 2017; Sabo et al., 2019; Schuh et al., 1997). Loss of sulfate from cultivated soils is of increasing concern, as S deficiencies in crops become more apparent with reduction in atmospheric S deposition from pollution control measures, leading to increased application of S fertilizer (Apostolakis et al., 2022; Aula et al., 2019; Eriksen, 2009; Sharma et al., 2024). Thus, nitrate and sulfate loading from agricultural landscapes continues to threaten agriculture sustainability and water quality (Driscoll et al., 2001; Galloway et al., 2008; Kopáček et al., 2017; Wang & Zhang, 2019).

Because agricultural landscapes are connected to stream channels via stream corridors, geomorphic and substrate controls on biogeochemical cycling in riparian areas can influence N and S export from these systems (Baulch et al., 2019; Hedin et al., 1998; Tesoriero et al., 2013; K. J. Van Meter & Basu, 2017). In addition, the spatial and stratigraphic organization of riparian substrate determines the nature of water storage, pathways of water movement, and locations of reducing conditions within the riparian area (Covino, 2017; Devito et al., 2000; Jencso & McGlynn, 2011; Vidon & Hill, 2004b, 2004a). Riparian substrate includes the texture and stratigraphy imparted by soil horizon development and the reorganization of sediment inputs from erosional or depositional processes. Stream corridor sediment deposits include layers of finer and coarser textures dictating discontinuous spatial variation in pore structure and permeability (Schaetzl & Thompson, 2015). Substrate derived from shale is particularly high in clay, having moderate porosity and low permeability, thus promoting water retention that is more

likely to facilitate anoxic conditions (Hasenmueller et al., 2017; Schaetzl & Thompson, 2015; Wald et al., 2013). Riparian areas host intermittently saturated conditions that result in development of organic soil horizons and redoximorphic features indicative of reducing conditions (Daniels, 2003; Ranalli & Macalady, 2010; Schaetzl & Thompson, 2015).

Additionally, seasonal fluctuations in riparian groundwater tables can result in varied hydrologic connectivity between the riparian aquifer and stream channel (Bergstrom et al., 2016; Jencso et al., 2009), allowing for seasonal variation of riparian groundwater influence on the chemistry of stream water (Burt et al., 1999; Jencso et al., 2010). Therefore, primary controls on the influence of riparian area processes on exported water quality include variation in hydrologic connectivity among the upland, riparian, and stream channel process domains (Ranalli & Macalady, 2010; Vidon & Hill, 2004b) and variation in riparian substrate influencing hydrologic and solute residence times (Ocampo et al., 2006; Vidon & Hill, 2004a).

The availability of electron donors like labile organic carbon and electron acceptors like oxygen, nitrate, and sulfate determines the potential for microbially-mediated riparian biogeochemical processes (Ågren et al., 2008; Grabs et al., 2012; Harms & Grimm, 2008; Taylor & Townsend, 2010). Because shallow groundwater flow paths often interact with abundant organic matter in riparian areas, oxygen is quickly exhausted by aerobic heterotrophic demand. In these oxygen-limited environments, the thermodynamic favorability of various anaerobic metabolic pathways influences the potential for microbially-mediated N and S mineralization and reduction (Bernhardt et al., 2017; Burgin et al., 2011; Hedin et al., 1998; Payn et al., 2014; Reinhold et al., 2019). For example, nitrate reduction is more energetically favorable than sulfate reduction in anaerobic respiration of similar organic matter (Hedin et al., 1998), and comparisons

of nitrate and sulfate concentrations with less reactive solutes may reflect variation in the reducing conditions among subsurface riparian environments (Payn et al., 2014). By limiting oxygen availability in frequently saturated environments (Hefting et al., 2004; Miele et al., 2023; Tesoriero & Puckett, 2011) and providing labile organic carbon in excess of that consumed by aerobic respiration (Hedin et al., 1998; Hill et al., 2014; McGlynn & McDonnell, 2003b), riparian areas facilitate strongly reducing conditions that act as biogeochemical reactors between hillslopes and streams. These reactors may promote resilience of exported water quality to ecosystem perturbation within the watershed (Cirimo & McDonnell, 1997; Hill, 2000; Jencso et al., 2010; McGlynn & McDonnell, 2003a; Naiman & Décamps, 1997; Ranalli & Macalady, 2010), yet few studies have assessed how riparian areas mitigate or augment solute concentrations, specifically nitrate and sulfate, in stream corridors of cultivated landscapes within semi-arid regions (Hill, 2019).

Despite a fundamental understanding of processes influencing riparian area biogeochemical function, the complex interactions of hydrologic and biogeochemical mechanisms by which stream corridors influence N and S cycling remains underexplored, particularly in semi-arid, cultivated landscapes. To address this knowledge gap, we studied an agricultural landscape in the Judith River Watershed (JRW), a semi-arid region of the northern Great Plains. In this system, a stark contrast in water chemistry between upland and riparian groundwater, provide a useful lens into riparian function and biogeochemical processes. We first differentiated the geochemical compositions of upland groundwater, riparian groundwater, and stream water across stream corridors with differing hydrologic connectivity among these process domains. We hypothesized that the nature of hydrologic connectivity between upland aquifers

and streams is a primary control on the net effects of stream corridor biogeochemical processing on nitrate and sulfate export downstream. We further hypothesized that variation in riparian substrate within stream corridors controls corresponding variation in nitrate and sulfate reduction, thus regulating the effects of cultivation practices on water quality (Figure 1). We tested these hypotheses with two specific research objectives in comparisons of stream reaches with differing hydrologic connectivity among upland aquifers, riparian aquifers, and stream channels: (1) Infer biogeochemical processing influencing N and S cycling in stream corridors from patterns in solute concentrations of upland groundwater, riparian groundwater, and stream water; and (2) Determine controls on the net change in nitrate and sulfate concentrations between upland groundwater inflows and stream channel outflows in an agricultural system. In addressing these objectives, this research advances a more detailed understanding of stream corridor biogeochemical function on solute processing and export from agricultural systems.

Methods

Section 2.1 Study Area

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

Our study is focused on 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 any recharge sources originating in the Little Belt Mountains (Figure 2a), and the impermeability of the shale units limits connectivity of the shallow aquifer with deeper aquifers (Sigler et al., 2018; Vuke et al., 2002). Therefore, water stored in the shallow Moccasin terrace aquifer is sourced primarily from infiltration of local precipitation through cultivated soils and exported through groundwater-fed stream corridors, with perennial flow directly from the upland aquifer at hillslope springs to the channel at some locations.

Non-irrigated annual crop production occurs on well-drained calcareous soils of the Moccasin terrace. Soils are classified as Calciustolls and Argiustolls in the US Taxonomy (U.S. Department of Agriculture, 2022). Soils generally exhibit clay loam textures and relatively shallow gravel zones (40-100 cm) resulting in subsurface horizons with > 40% coarse gravel content extending to between 1.5 m and 10 m depths (Sigler et al., 2018). Dominant crop types cultivated from these soils are spring wheat, winter wheat, and barley, with increasing incorporation of pulse crops to replace fallow in cropping sequences (U.S. Department of Agriculture, 2023). The cultivated soil and subsurface architecture allows for substantial solute leaching to the shallow aquifer that supplies drinking water to private well owners in the region (Schmidt & Mulder, 2010; Sigler et al., 2018).

This study focuses on corridors of first-order streams draining the Moccasin terrace. The selected study reaches are typical of the structure of stream corridors incised into the shale

bedrock, with widths of the riparian areas ranging from 150 to 350 m. Riparian groundwater tables in these corridors are shallow, with depths ranging from 0 cm to 90 cm below the ground surface and isolated areas of apparent aquifer confinement with heads above the ground surface (Table S1). These corridors are typically managed for cattle production (Figure 2; U.S. Department of Agriculture, 2023) due to water and forage availability during drier periods of the year.

We selected three ca. 0.7-km reaches of stream corridors on the Moccasin terrace (Figure 2), to compare hydrological and biogeochemical behavior of stream corridors with different modes of riparian hydrologic connectivity between upland aquifers and stream channels. We selected two reaches on Louse Creek (upper-Louse and mid-Louse; Figure 2c, d), where the gains in stream flow were dominated by diffuse subsurface flow via riparian groundwater flow paths along the reaches. We selected a third reach on Porter Creek (Figure 2e) where the gains in stream flow along the reach were dominated by multiple channelized direct surface inflows from hillslope springs. Reach selection was also motivated by previous observations of Louse Creek having lower nitrate concentrations than Porter Creek and the terrace groundwater (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 diverted for irrigation by a single pivot. The diversion 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 edge of the terrace compared to the more centrally located reaches on Louse

Creek. The stream corridors of all three reaches in this study were subject to periodic cattle grazing and varying degrees of bioturbation from burrowing of Richardson's ground squirrels.

Section 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), 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 (SI section 1.2 and Sigler et al., 2018). Terrace groundwater was sampled from hillslope springs from 2020 to 2022 ($n = 32$) and hillslope springs and wells in 2013 and 2014 ($n = 39$, Sigler et al., 2018, unpublished data). To assess general patterns in variation with landscape position, we categorized sampling sites based on their proximity to our study reaches following the general elevation gradient (Figure 2b; SI section 1.2). We sampled riparian groundwater from 20 wells installed ca. 100 cm deep in the riparian areas of the three stream reaches from 2021 to 2022 ($n = 131$) (Figure 2; SI section 1.2). Most well locations were selected from within a 2-m distance of the stream channel to capture groundwater chemistry exchanging with the stream. Some well locations were selected from remnant channels further from the stream to assess groundwater chemistry with less exchange with the stream. Locations spanned the length of each study reach. We sampled stream channel water at upstream, mid-reach, and downstream locations along the study reaches (Figure 2c-e) from 2020 to 2022 ($n = 177$) and included data from the upstream site at upper-Louse reach (Table S1) sampled in 2013 and 2014 ($n = 17$; 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 meaningful flow, we measured discharge (SonTek FlowTracker Handheld ADV, Xylem Environmental Solutions, San Diego, California) at the upstream and downstream ends of each study reach at least once during each sampling campaign in 2021 and 2022 via velocity-area gauging (U.S. Geological Survey mid-section method).

We sampled at times selected to represent seasonal or interannual variation in hydrologic connectivity among terrace aquifers, riparian aquifers, and stream channels. At the time of sampling, we measured DO, temperature, specific conductance, and pH using a Professional Plus Quatro multiparameter probe (YSI Incorporated, Yellow Springs, Ohio; Table S2). We calibrated each sensor for each sampling campaign per user manual specifications (SI section 1.2)

Ground and surface water samples were collected using a peristaltic pump (Geotech Environmental Equipment, Denver, Colorado), through a pre-rinsed 0.45- μm capsule filter (Geotech Environmental Equipment, Denver, Colorado). When possible, water was purged from groundwater well casings and allowed to recover three times before sample collection. If faster recovery wells could not be purged ($n = 10$ of 20), we monitored dissolved oxygen (DO) concentrations continuously while pumping and collected samples when DO stabilized. For slow recovery wells, DO was not reported because measurements were not representative of in situ groundwater DO concentrations due to limited pumping time for readings to stabilize.

Samples were collected into combusted 24-mL glass vials capped without headspace for carbon (C) species and into 60-mL HDPE vials capped with headspace for other solutes. All vials were rinsed three times with filtered sample water before filling. Duplicates were collected as

water volume allowed. Samples were kept on ice during transport to the lab and stored in a refrigerator between 2°C and 4°C prior to analysis.

Section 2.3 Chemical Analysis

Samples were analyzed at the Montana State University Environmental Analytical Laboratory (EAL), Bozeman, Montana. We analyzed nitrate (NO_3^-) (Lachat QuickChem 8500), dissolved organic carbon (DOC), and dissolved inorganic carbon (DIC) within one week of sample collection using a liquid combustion analyzer (Shimadzu TOC VSH; Table S2). Within one year of sampling, we analyzed sulfate (SO_4^{2-}) and chloride (Cl^-) using an ion chromatograph (Dionex Thermo Scientific ICS-2100), and total S, major cations (Ca^{2+} , Na^+ , Mg^{2+} , K^+), and ferrous iron (Fe^{2+}) using ICP-OES (SPECTROBLUE EOP TI). Repeated measurements of an environmental groundwater working standard through each instrument run provided estimates of 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-} , Cl^-), assuming DIC concentrations were dominated by bicarbonate (HCO_3^-) given circumneutral pH values (Figure S2). 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 ($n = 34$). Samples with a charge balance exceeding 20% difference ($n = 17$) reflected problematic cation analysis by ICP based on comparison to other analytical results for same site (SI section 1.3), were omitted from final reporting, and not included in comparisons of the full ion suite.

Section 2.4 Statistical Analysis

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 all sample locations and times. Major ion components for the PCA included NO_3^- , SO_4^{2-} , DIC, Cl^- , Ca^{2+} , Na^+ , and Mg^{2+} . The number of samples with complete results for these ions varied by process domain (terrace groundwater, $n = 69$; riparian groundwater, $n = 112$; stream water, $n = 187$).

We fit mixed effects models to our data to assess the differences in measured nitrate, sulfate, and DIC concentrations ('Conc') among the terrace groundwater, riparian groundwater, and stream water process domains (Objective 1). The associated generalized linear model defined process domain ('processDomain') as the independent variable (i.e., fixed effect) and water year ('waterYear') and sampling campaign within the year ('campaign') as random effects to account for variation attributable to the sampling time. Sampling campaign within the year was defined as the week of the year the campaign occurred. We assigned individual sample site location ('site') as a random effect to account for correlation in repeated measurements at the same site over time.

$$(1) \quad \text{Conc} = \beta \cdot \text{processDomain} + u_1 \cdot \text{waterYear} + u_2 \cdot \text{campaign} + u_3 \cdot \text{site} + \varepsilon$$

We also used mixed effects models to assess the differences in measured nitrate, sulfate, and DIC concentrations among the three study reaches (i.e., upper-Louse, mid-Louse, or Porter) and terrace groundwater site positions (i.e., 'upper', 'middle', or 'lower') (Objective 2). The model for this analysis included the stream reach ('reach') as the independent variable, with water year, sampling campaign within the year, and sample site location as random effects.

$$(2) \quad \text{Conc} = \beta \cdot \text{reach} + u_1 \cdot \text{waterYear} + u_2 \cdot \text{campaign} + u_3 \cdot \text{site} + \varepsilon$$

Mixed effect models were fit using R statistical software (version 4.2.2) and package lme4 (version 1.1-35.1).

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 models may underestimate uncertainty around the extreme ends of our 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 ($\alpha = 0.05$) among process domains in nitrate, sulfate, and DIC concentrations, after accounting for the effects of water year, campaign within year, and repeated measures at an individual site. This post hoc multiple comparison test was based on the best-fit mixed effects model, such that any bias due to repeated measures (i.e., pseudoreplication) and temporal autocorrelation in error is minimized. We performed the same post hoc test to assess confidence in statistical differences ($\alpha = 0.05$) among study reaches.

We performed linear regressions of sulfate versus chloride concentrations using data from stream water and proximal terrace groundwater (see section 2.2) to represent the net behavior of each reach's riparian area in the relative transformations of these ion concentrations. We assumed that relative transformations of sulfate or chloride were unlikely to be associated with reactions occurring in the terrace aquifer or stream channel process domains. We also assumed limited sorption of sulfate to stream sediments based on observed pH values (Figure S2) (Kamprath et al., 1956). To assess ion contributions from shale weathering in the terrace aquifer, we regressed sulfate versus chloride concentrations using data from the two well locations categorized as

upper terrace groundwater (Figure 2b) (Sigler et al., 2018, unpublished data). To assess the relative contributions of cultivated soil leachate, we regressed sulfate versus chloride concentrations from terrace soil water (Sigler et al., 2018, unpublished data). We compared riparian groundwater sulfate and chloride concentrations with these regression lines to assess relative contributions of weathering, leaching from agricultural soils, and sulfate reactivity in the generally anoxic riparian groundwaters.

Results

Section 3.1 Geochemical Composition of Ground and Surface Waters

PCA results suggest that variation in nitrate, DIC, and Ca^{2+} concentrations were important in differentiating samples from different process domains (Figure 3). Nitrate concentrations tended to be inversely related to DIC and Ca^{2+} concentrations across process domains. Particularly, riparian groundwater showed lower nitrate concentrations associated with higher DIC and Ca^{2+} concentrations, distinguishing this process domain from the higher nitrate concentrations in terrace groundwaters and stream waters.

Variation in Na^+ , SO_4^{2-} , Mg^{2+} , and Cl^- concentrations were important for differentiating samples from the three study reaches, with stream water demonstrating a progression from higher to lower concentrations from upper-Louse to mid-Louse to Porter reaches (Figure 3). These ions also strongly differentiated middle and lower terrace groundwaters from upper terrace groundwaters. The upper terrace groundwater had higher nitrate concentrations than the middle and lower terrace groundwater. The chemical composition of Porter stream water tended to group

closely with the lower terrace groundwater, while the stream water chemistry in the upper- and mid-Louse reaches was distinct from any of the terrace groundwater chemistry.

Section 3.2 Ionic Compositions Across Process Domains

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

Sulfate concentrations differed less than nitrate concentrations across the process domains. Multiple comparison tests indicated less confidence ($p > 0.05$) that samples from different process domains had different mean sulfate concentrations, likely due to the wide distribution of values in riparian groundwater samples (Figure 4b). However, the mean sulfate concentration in terrace groundwater (23.2 mg L^{-1}) was less than half that of riparian groundwater (64.8 mg L^{-1}) or stream water (60.7 mg L^{-1} ; Table 1). The interquartile range (IQR) of riparian groundwater sulfate concentrations was 36.9 to 82.5 mg S L^{-1} (Table 1; Figure 4b) and was greater than that of terrace groundwater (IQR 9.96 to 21.9 mg S L^{-1}) or stream water (IQR 49.6 to 80.9 mg S L^{-1}).

Riparian groundwater DIC concentrations were higher than those of other process domains, based on confidence indicated by multiple comparison tests using the best fit mixed effects models ($p < 0.05$; Figure 4c). Riparian groundwater had a higher mean DIC concentration (110 mg C L^{-1}) than that of samples from either the terrace groundwater (57.0 mg C L^{-1}) or stream water (66.8 mg C L^{-1}) process domains.

Section 3.3 Ionic Compositions across Study Reaches and Landscape Position on the Terrace

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}) in terrace groundwater were observed at the upper terrace sites, which are up-gradient of all study reaches (Figure 4 and 5a,d,g; Table 1) and are associated with shale weathering in well-drained upland soils (Figure 6a) (Sigler et al., 2018). Nitrate, sulfate, and DIC concentrations in terrace groundwater tended to decrease from these values across the terrace. Multiple comparison tests (*eq. 2*) indicated some confidence ($p < 0.05$) that mean concentrations of SO_4^{2-} and DIC were higher in the upper terrace groundwater than the middle or lower terrace groundwaters. The nitrate concentrations in the upper terrace groundwater were generally higher than those elsewhere on the terrace, though statistical tests did not provide high confidence in a difference in means (Figure 5a; Table 1).

Mean nitrate concentration 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. Upper-Louse riparian groundwater had a mean nitrate concentration of 1.05 mg N L^{-1} , mid-Louse riparian groundwater had a mean concentration less than the analytical limit of detection of 0.01 mg N L^{-1} , and Porter riparian groundwater had a mean concentration of 4.59 mg N L^{-1} (Figure 5b). In faster recovery wells, where DO could be measured, we observed generally low DO concentrations (mean = 0.83 mg L^{-1} ; Figure S3) across all reaches. Higher mean concentrations in the Porter reach riparian groundwater were influenced by two sites that had slow recovery rates (and hence no DO results) but had consistently higher nitrate than all other riparian groundwater sampling sites across all reaches. These sites with higher nitrate concentrations resulted in Porter riparian groundwater exhibiting the greatest range of nitrate

concentrations from undetectable to 14.4 mg L^{-1} (IQR from 0.01 to 10.2 mg N L^{-1} , Table 1). Mean nitrate concentrations in the stream channel of the Porter reach (17.0 mg N L^{-1}) were higher than mean nitrate concentrations in the upper-Louse (7.3 mg N L^{-1}) and mid-Louse (5.9 mg N L^{-1}) reaches (Figure 5c; Table 1). Nitrate concentrations in the Porter reach stream water were also more similar to those in terrace groundwater than riparian groundwater. Stream water at the Porter reach showed little seasonal variation in nitrate concentration compared to the upper- and mid-Louse reaches that showed decreases in nitrate concentrations over the spring and summer (Figure S5).

Multiple comparison tests suggested confidence that the mean sulfate concentration in riparian groundwater at upper-Louse (70.1 mg S L^{-1}) was lower than that at mid-Louse (97.4 mg S L^{-1}) and higher than that at Porter (20.3 mg S L^{-1}) (Table 1; Figure 5e). Sulfate concentrations in upper-Louse riparian groundwater had the greatest variation (IQR from 8.74 to 235 mg S L^{-1} ; Table 1). Riparian groundwater in both Louse reaches demonstrated more variation in sulfate concentrations than riparian groundwater at the Porter reach (Figure 5e, Table 1). Sulfate concentrations in stream water decreased from upper-Louse to mid-Louse to Porter reaches (Figure 5f). The variation in the mean sulfate concentrations in riparian groundwaters among the study reaches did not follow the same spatial pattern across the terrace as terrace groundwaters or stream waters, due to the mid-Louse reach having higher concentrations than the upper-Louse reach. Sulfate concentrations in upper- and mid-Louse riparian groundwater were more variable than in surface water or terrace groundwater, and the distribution of concentrations spanned values both higher and lower than proximal terrace groundwater samples (Figure 4b and 5d-f).

Upper terrace groundwater had the smallest differences in chloride with respect to differences in sulfate, while cultivated terrace soil water had the greatest differences in chloride with respect to differences in sulfate (Figure 6a). Some riparian groundwater at the upper- and mid-Louse reaches showed a greater difference in sulfate concentration relative to chloride than the general transformation observed from terrace groundwater to stream water (Figure 6c). A few riparian groundwater samples from upper-Louse showed a greater difference in sulfate concentration relative to chloride than the general relationship between terrace groundwater and stream water. Many of the sulfate to chloride relationships deviating from the regressions for the terrace groundwater and the stream water appeared to be associated with lower nitrate concentrations (Figure 6c). Stream water in the Louse reaches generally had a higher proportion of sulfate to chloride concentration compared to the Porter reach (Figure 6b).

Mean DIC concentrations in riparian groundwater were relatively consistent among the study reaches, with multiple comparison tests demonstrating lower confidence in differences (Figure 5h). Mean DIC values of 111 mg L^{-1} for upper-Louse, 114 mg L^{-1} for mid-Louse, and 105 mg L^{-1} for Porter were within each other's standard errors for DIC (Table 1). The Porter Creek reach demonstrated the highest variation in riparian groundwater DIC concentrations (IQR from 91.3 to 120 mg L^{-1}). In general, high nitrate concentrations corresponded with low DIC concentrations, and low nitrate concentrations corresponded with the greatest ranges of DIC (Figure S6). Mean DIC concentrations in stream water decreased across reaches with landscape position on the terrace (Figure 5i; Table 1).

Section 3.4 Hydrologic Conditions across Study Reaches

Seasonal and interannual decreases in flow associated with diversion for upland irrigation and drought were more evident in the Louse reaches than the Porter reach (Figure S5a). The upper- and mid- Louse reaches had higher average flows in 2020 (69 and 98.7 L s⁻¹, respectively) than in 2022 (too low to measure and 14.1 L s⁻¹). Stream flows at the Porter reach were higher in 2020 (40.9 L s⁻¹) than in 2022 (19.6 L s⁻¹) but showed less variation in total magnitude than the Louse reaches. The Louse Creek reaches showed the most change in flow within a year coinciding with the seasonal initiation of diversion for upland irrigation (Figure S5a) (Foster, 2023), particularly in 2021 when upper-Louse had 32.5 L s⁻¹ in March and no measurable flow by June and mid-Louse had 50.8 L s⁻¹ in May and 11.8 L s⁻¹ in June. Decreases in flow through the spring and summer and across years corresponded with decreases in nitrate concentrations (Figure S5a,b). Over this time period, sulfate concentrations in the Louse Creek stream water generally increased through May, then decreased through August, then occasionally increased again, while remaining relatively constant in Porter Creek stream water (Figure S5c).

Discussion

Solute concentration patterns across process domains suggest that the geologic setting influences hydrology and soil weathering products, contributing to stream corridor biogeochemical functions that regulate water quality. Solutes in upland groundwater vary spatially across the landform, reflecting influence of agricultural management on inputs to stream corridors. Concentration patterns across process domains show nitrate loss and sulfate gain from stream corridors. Patterns within reaches show how hydrogeologic factors combined

with relative source water contributions constrain the magnitude of nitrate and sulfate loss or gain unique to each stream corridor.

Section 4.1 Variation in Upland Groundwater Inputs to the Stream Corridor across the Terrace

The patterns we observed in terrace groundwater (Figure 5a and d) reflect the cumulative effects of hydrologic flow through soils across the Moccasin terrace, with higher elevation, shale-derived soils contributing higher nitrate and sulfate concentrations compared to lower elevation, alluvium-derived soils (Sigler et al. , 2018). Along with decreasing nitrate and sulfate concentrations, other solutes in terrace groundwater confirm a shift in the relative influence of solutes delivered to stream corridors (Figure 3). More exposure of shale to weathering at higher elevations on the terrace likely contributed to relatively higher concentrations of multiple weathering products observed in the upper terrace groundwater sites, consistent with interpretation by Sigler et al. (2018). The observed patterns in nitrate, sulfate, and other weathering products suggest a decrease in the relative contribution of solutes from weathering of shale-derived materials, and an increase in the relative contribution of solutes from cultivated soils with distance down-gradient on the terrace.

Decreases in nitrate concentration (from 30 to 20 mg L⁻¹) were proportionally less than those of sulfate (from 60 to 10 mg L⁻¹; Figure 5a, d) across the terrace, suggesting that application of fertilizer and soil organic matter mineralization were more influential sources of N compared to S. The shale-influenced upper terrace groundwaters have lower nitrate-N: sulfate-S mass ratios (< 0.5) relative to soil water sampled from locations lower in elevation on the terrace. Higher nitrate-N: sulfate-S mass ratios (from 2 to 7) reflect the influence of N fertilizer additions and mineralization of soil organic N on soil water nitrate concentrations (Sigler et al. 2018), as a

function of management practices on soils with limited water holding capacity (Sigler et al., 2020). Relative to N, less common fertilizer S amendments (Franzen, 2018) and more limited sulfate-S from mineralization of soil organic S (Eriksen, 2009) contribute lower sulfate-S concentrations and higher nitrate-N/sulfate-S mass ratios to soil water that then recharges groundwater. Thus, substantial N fertilization and potentially increasing S fertilization that enhance crop production in the NGP (Lawrence et al., 2018; Miller et al., 2019, 2024) also contribute nitrate and increasingly sulfate to soil leachate that recharges groundwater

Higher sulfate concentrations relative to chloride concentrations in terrace groundwater compared to soil waters (Figure 6a and b) reflect contributions of low sulfate concentrations from soil water influenced by agricultural practices and crop uptake to expected shale-derived sources. Despite broadly observed S leaching from soils in agricultural systems (Apostolakis et al., 2022; Eriksen, 2009), less is known about the influence of S from fertilizer and crop use efficiency on water quality compared to N and phosphorus (Burow et al., 2010; Hosono et al., 2007; Spruill, 2000) likely due to the limited role of S in eutrophication. While mineralization of soil organic matter is well known to contribute to concentrations of nitrate (John et al., 2017; Sigler et al., 2020) and sulfate (Eriksen, 2009) in cultivated soil waters, the contribution of this process to groundwater sulfate is poorly understood in non-irrigated agricultural systems of semi-arid regions like the one studied here. Our observations of terrace soil water and the cumulative influence on groundwater chemistry suggest that sulfate contributions from non-irrigated cultivated soils are occurring, and are distinct and limited relative to geogenic sources, and will likely increase over time with increased fertilization. This emphasizes the importance of

understanding riparian biogeochemical processing of S which is less energetically favorable than N.

Section 4.2 Stream Corridor Processes Result in Net Nitrate Losses

We observed consistent nitrate losses between the terrace and riparian aquifers that contributed to lower concentrations in the stream channel (Figures 4 and 5). In riparian groundwater, low observed nitrate and DO concentrations (Figure 4a and S3) suggest that anaerobic riparian biogeochemical processes had a strong influence on the nitrate delivered from the terrace aquifer. Higher DOC concentrations in riparian groundwater compared to terrace groundwater (Figure S4) suggests C availability for heterotrophic nitrate reduction (i.e., respiratory denitrification) in the riparian area, which may be a primary biogeochemical reduction pathway in our stream corridors (Taylor & Townsend, 2010; Tesoriero & Puckett, 2011). Additionally, the inverse relationship of nitrate with riparian groundwater DIC generally followed the expected stoichiometric relationship of denitrification (Figure S6; Table S3, eq. 1 & 2) (Burow et al., 2010; Hedin et al., 1998; Stumm & Morgan, 1996). While denitrification is likely an important metabolic pathway influencing observed riparian groundwater, identification of specific nitrate reduction pathways, including non-heterotrophic pathways (e.g., fermentation or chemoautotrophy), cannot be based solely on concentrations of N, O and C phases (Burgin & Hamilton, 2007; Donald E. Canfield et al., 2010). We suspect co-occurrence of multiple processes occurs in our observed stream corridors due to the heterogeneity in riparian substrate that likely promotes variable redox conditions and metabolite availability.

The detailed patterns of net nitrate loss from terrace groundwater to riparian and stream water (Figure 3 and 5) show that nitrate loss in riparian substrate far exceeds aerobic nitrate

production from soil weathering or organic matter mineralization. Pervasive low DO concentrations suggest limitations to nitrification in the riparian aquifer. However, nitrate production by shale weathering (Wan et al., 2021) or mineralization of soil organic matter likely occur in riparian substrate where oxygen is more available. Produced nitrate may be transported periodically or episodically (e.g., by fluctuating groundwater levels, Figure S7) to oxygen-limited sites (Burt et al., 2002; Duncan et al., 2015; Tesoriero et al., 2013). The likely production of nitrate within oxic areas of riparian substrate suggests production of sulfate and other solutes may also result.

Section 4.3 Sulfate Production Outweighs Sulfate Losses in Stream Corridors

We observed sulfate gains between the terrace and riparian aquifers that contributed to higher concentrations in stream water from Louse Creek, but not Porter Creek (Figures 4 and 5; Table 1). Areas where riparian groundwater sulfate concentrations were higher than those of terrace groundwater (Figure 4b and 5d,e) indicate locations of sulfate production likely by oxidation of sulfide in shale, mineralization of organic S in shale or soil, or re-oxidation of sulfide precipitated with reduced iron (Table S3 eq. 6, 7) (Morrison et al., 2012; Tuttle et al., 2014). Contact with shale-derived material due to stream incision and mobilization of shale alluvium from side channels suggests that the generation of sulfate in riparian substrate masks the ability to detect sulfate reduction processes using concentration measurements alone. Energetically favored nitrate reduction is likely more prevalent than sulfate reduction and may include coupling with sulfide oxidation (e.g., Table S3 eq. 5) (De Gussemme et al., 2009; Hosono et al., 2014; Reinhold et al., 2019; Severe et al., 2023), particularly at sites where labile C becomes limited and sulfide is abundant (Burgin & Hamilton, 2007; Cardoso et al., 2006;

Tesoriero & Puckett, 2011). These sites also tended to have sulfate concentrations relative to chloride (Figure 6c) that were consistent with the upper terrace shale influence (Figure 6a), despite influence of cultivated soil waters likely diluting the shale weathering signal in the upper terrace groundwater. Sulfate concentrations in the Porter riparian groundwater were higher than those of the terrace groundwater contributing to this lower elevation reach (Figure 2b) but were much lower than those at upper- and mid-Louse (Figure 5d,e). This suggests that any local production in the Porter riparian area was subject to dilution by terrace groundwater with more contributing area of cultivated soil.

Variation in the proportion of sulfate production relative to chloride production evident at individual riparian groundwater wells (Figure 6c) suggests localized variation in production and loss processes influencing sulfate in distinct ways within a stream corridor, since chloride is likely to be relatively conservative after production by weathering. Higher sulfate production than expected based on observed chloride indicates spatially variable production and loss processes within the stream corridor. These areas may reflect some combination of weathering of shale with a relatively higher ionic composition of sulfate compared to terrace groundwater, mineralization of soil organic matter, or independent production of additional sulfate from metabolic processes such as chemoautotrophic sulfide oxidation (Burgin & Hamilton, 2007; Severe et al., 2023). Production of sulfate and chloride in the riparian area likely contributes to the proportional increase in sulfate and chloride concentrations observed in the stream water of the Louse reaches relative to terrace groundwater (Figure 6b). These findings reveal that stream corridors are a potential source of sulfate, a riparian ecosystem function that, to our knowledge, has had limited acknowledgment and exploration (Hill et al., 2000; Schoepfer et al., 2014).

Riparian groundwater with sulfate and chloride concentrations comparable to those of stream water (Figure 6c) suggests areas with preferential flow paths where contributing water moved relatively rapidly in the subsurface or where more hydrologic exchange occurred with the stream channel. Each reach had higher production wells suggesting the presence of higher hydraulically conductive lenses that, if connected, could promote preferential flow paths (Burt et al., 1999; Devito et al., 2000). Preferential flow paths in the stream corridor likely convey water to and from sites within the riparian area where biogeochemical reactions occur (Bernhardt et al., 2017; Dwivedi et al., 2018; Ranalli & Macalady, 2010; Vidon & Hill, 2004a). These findings suggest that S cycling is important to consider in shale-dominated systems, particularly when geomorphic processes facilitate weathering via sediment transport or routing of water (Morrison et al., 2012).

We observed evidence that localized sulfate losses occurred within stream corridors that were net sources of sulfate, indicating that gross sulfate production outweighed gross sulfate loss processes and masked dilution effects of low sulfate concentrations leaching from cultivated upland soils. Riparian groundwaters with lower sulfate concentrations relative to chloride than expected suggest localized areas of sulfate loss (Figure 6c versus 6b). Sites with strongest evidence of sulfate removal also showed low nitrate concentrations (Figure 6c), suggesting promotion of sulfate reduction due to the depletion of nitrate as the more energetically favorable electron acceptor (Hedin et al. 1998). Sites within the riparian area that promote sulfate loss will become more important to understand as S loading in soil leachate shifts with S fertilizer management practices responding to increasing crop S deficiencies (Gerson & Hinckley, 2023). Anaerobic respiration of DOC via sulfate reduction could contribute to observed DIC

concentrations in riparian groundwater (Table S3 eq. 3) (Miao et al., 2012), though limited evidence of ubiquitous sulfate reduction across our study area suggests that energetically favored solutes such as nitrate and iron were likely more important for microbial respiration. The complexity of spatial patterns in chemistry and redox conditions evident at our riparian sites is consistent with previous findings in riparian areas of forested systems (Jencso et al., 2010; Ranalli & Macalady, 2010; Vidon & Hill, 2004a) and suggests influence of complex hydrologic flow paths.

Section 4.4 Variation in the Influence of Riparian Biogeochemistry on Stream Water Is a Function of Complex Hydrologic Flow Paths

Stream water solute concentrations can reflect the influence of riparian biogeochemical pathways through complex hydrologic flow paths connecting the riparian aquifer to the stream. The relative influence of subsurface flow to the stream channel depends on the mode of hydrologic connection. Solute concentrations observed in the Porter Creek stream water more closely resembled those of lower terrace groundwater than riparian groundwater (Figure 3 and 5) (Zimmerman, 1966a) and was relatively consistent over time, despite clear evidence of nitrate loss and sulfate production in riparian groundwater (Figure 5b and e). This suggests that riparian groundwater contributions were less evident in the Porter reach, where direct contributions from hillslope springs to the stream masked the influence of riparian groundwater inflows (Covino, 2017; Devito et al., 2000; Grabs et al., 2012; Ranalli & Macalady, 2010; Vidon & Hill, 2004b, 2004a). In contrast, the upper- and mid- Louse stream waters had lower nitrate concentrations and higher sulfate concentrations relative to middle terrace groundwater (Figure 3 and 5), suggesting more influence from biogeochemical processing of terrace groundwater that occurs

within the riparian ecosystem either before reaching the stream channel (Ranalli & Macalady, 2010) or through interaction of stream water with adjacent riparian substrate (Boulton et al., 1998). Limited expected sorption of sulfate to stream sediments (Kamprath et al., 1956) supports riparian ecosystem processes as the primary loss pathways in these corridors. Fluctuations of in-stream solute concentrations at the Louse reaches also co-varied with in-stream flow (Figure S5), suggesting decreases in flow may correspond to increased riparian processing of source waters prior to contributing to stream flow generation (Foster, 2023; Warren et al., 2022). These findings support that increased influence of biogeochemical pathways on stream water chemistry occurs when more upland water flows through, rather than across, riparian substrate.

Variation in riparian solute concentrations can reflect the influence of substrate heterogeneities on reducing conditions. Lower nitrate concentrations observed concomitant with generally higher sulfate concentrations in riparian groundwater at the mid-Louse reach (Figure 3, 5, and 6) compared to other reaches may reflect more extensive areas of finer shale-derived material (Josh et al., 2012; Morrison et al., 2012). Heterogeneities in riparian substrate texture create variation in solute mobilization and redox conditions, promoting multiple biogeochemical processes within the same process domain (Bishop et al., 2011; Landon et al., 2000; Tetzlaff et al., 2009; Vidon et al., 2010). Evidence of clay-rich, shale-derived materials suggest areas that facilitate anoxic conditions and likely contribute to production or retention of shale-derived solutes during oxic periods.

Conclusions

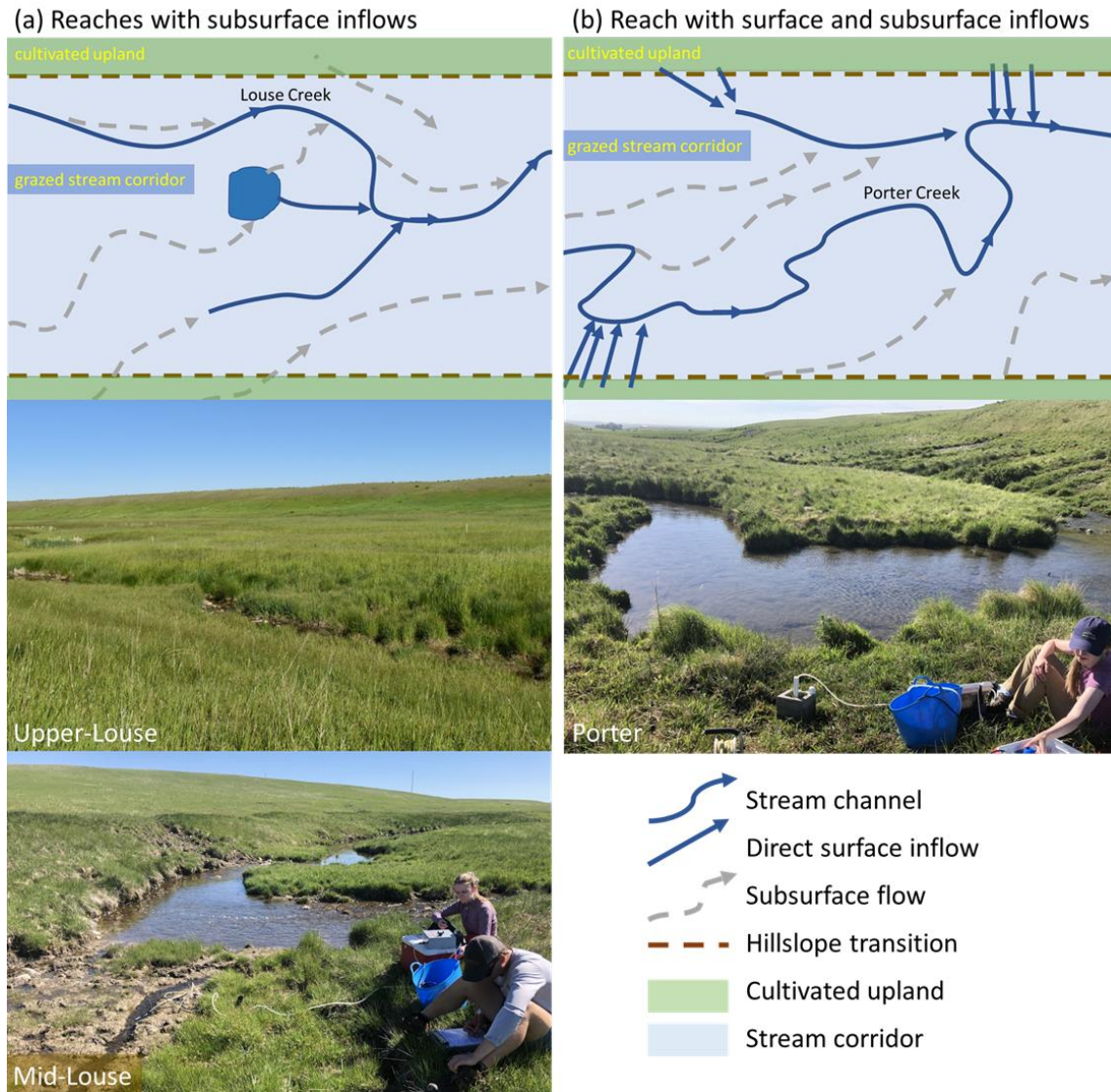
Variation in solute composition among riparian groundwater sites within the same study reach demonstrates the complexity of redox conditions and hydrologic connection in the riparian

domain that determines the net biogeochemical processing before export to streams. Comparison of reaches with contrasting hydrologic connectivity and examination of solute concentrations within these reaches illustrate how stream corridor geomorphic structure and riparian substrate mitigate or augment solute exports from agricultural landscapes. Assessment of sulfate concentrations in conjunction with nitrate concentrations lends insight into the production of solutes from shale-derived soils and the presence and extent of reducing conditions and hydrologic connectivity influenced by riparian substrate/soil stratigraphy. Nitrate and sulfate concentrations also suggest that solute leaching from cultivated upland soils masks the influence of shale weathering on upland groundwater quality. Variation in riparian groundwater solute concentrations that did not necessarily depend on C supply and oxygen limitation suggests mixing along complex flow paths and alternate reduction pathways. Riparian geomorphology and subsurface stratigraphy reflect a complex geologic history of stream incision, sediment transport, and land use, which influences riparian area function at the catchment-scale that influences downstream water quality.

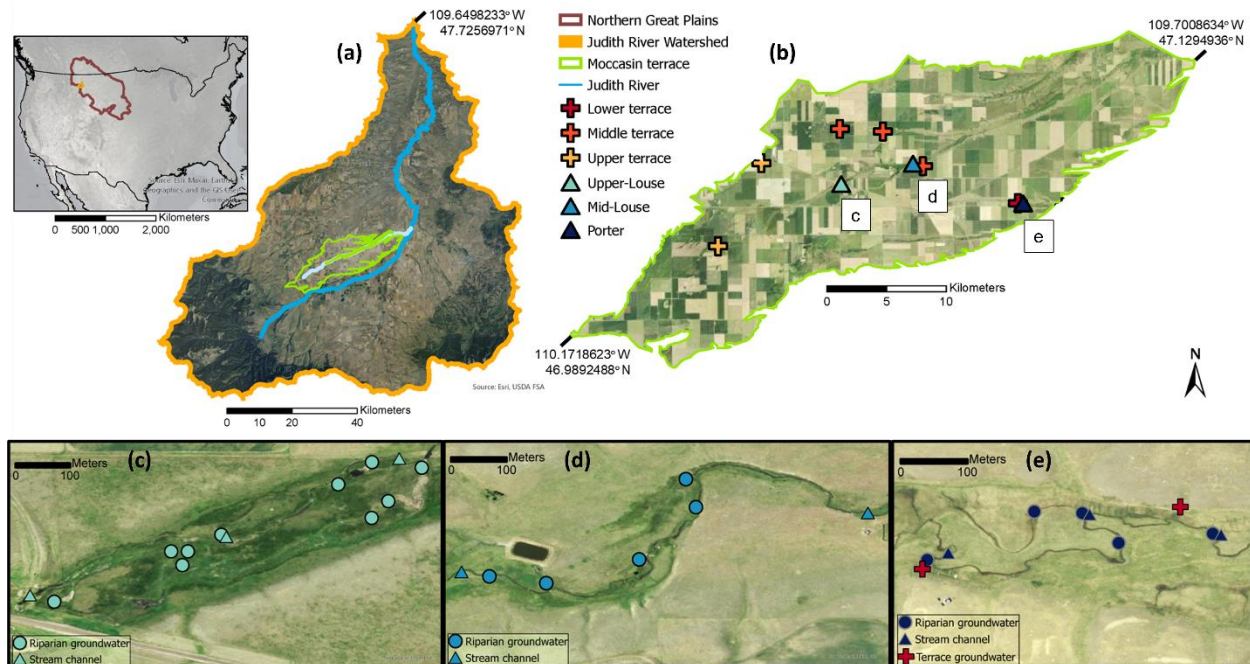
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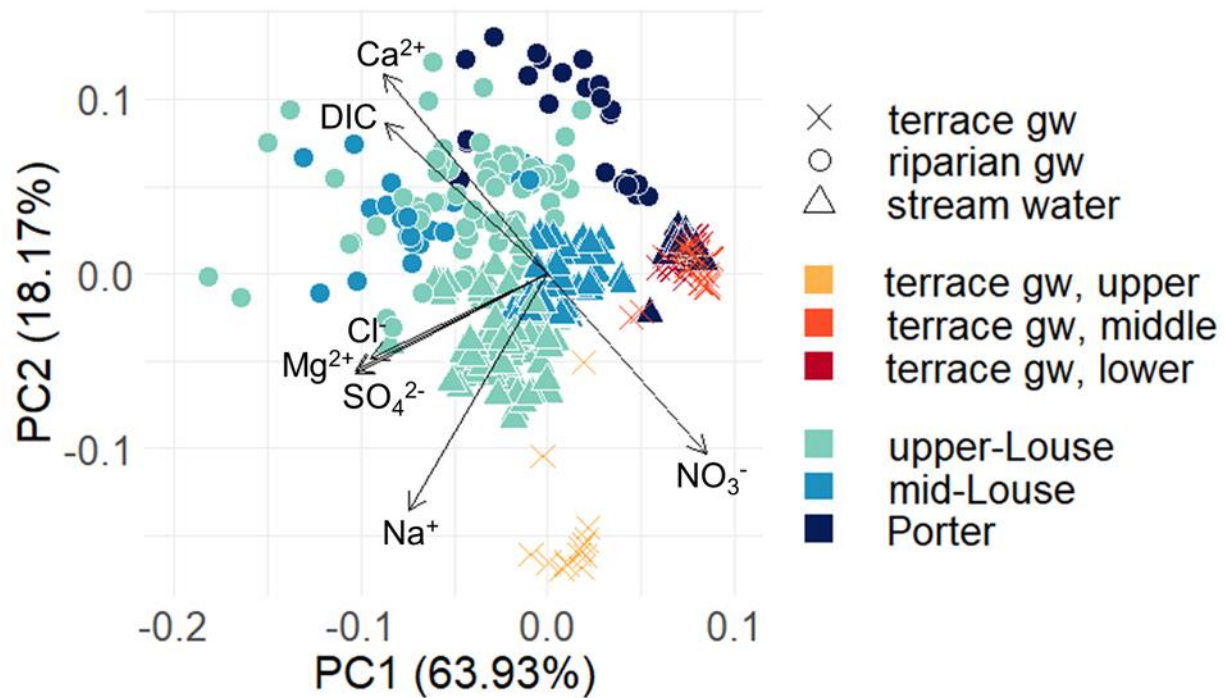
Science Foundation or U.S. Department of Agriculture. We appreciate the use of data from Dr. Adam Sigler and the U.S. Bureau of Reclamation and the Montana Department of Agriculture. We thank Skye Keeshin, Zoe Durkin, Sean Williams, Madisynn Weber, Rachel Anderson, and Claire Wells for help with data collection, analysis, and technical assistance. We thank Dr. Kelsey Jencso for feedback on research approach and ideas. We thank anonymous reviewers for their time and constructive feedback.

Figures

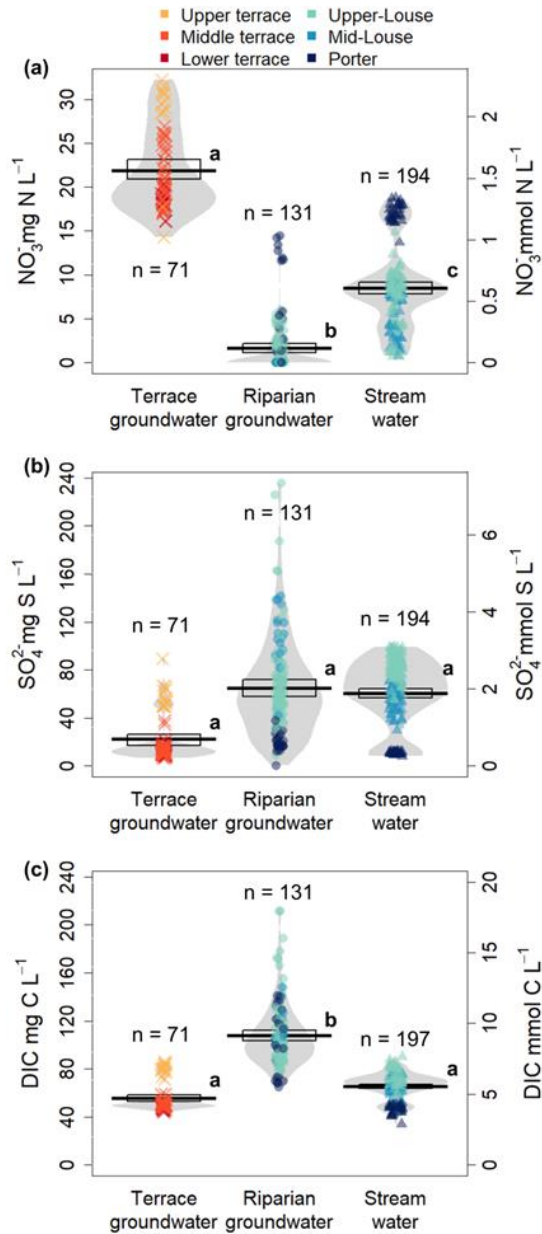
Ch.3-Figure 1. Photos of study reaches and conceptualizations of connectivity among the upland aquifer, riparian aquifer, and stream channel. Sites include (a) Louse Creek reaches where surface connectivity between uplands and the channel is not apparent and (b) a Porter Creek reach where direct surface flow from abundant hillslope springs connects the upland aquifer and the channel. Solid lines depict surface flow. Dashed lines depict subsurface flow, with grey color indicating conjecture in the direction of riparian groundwater flow paths.



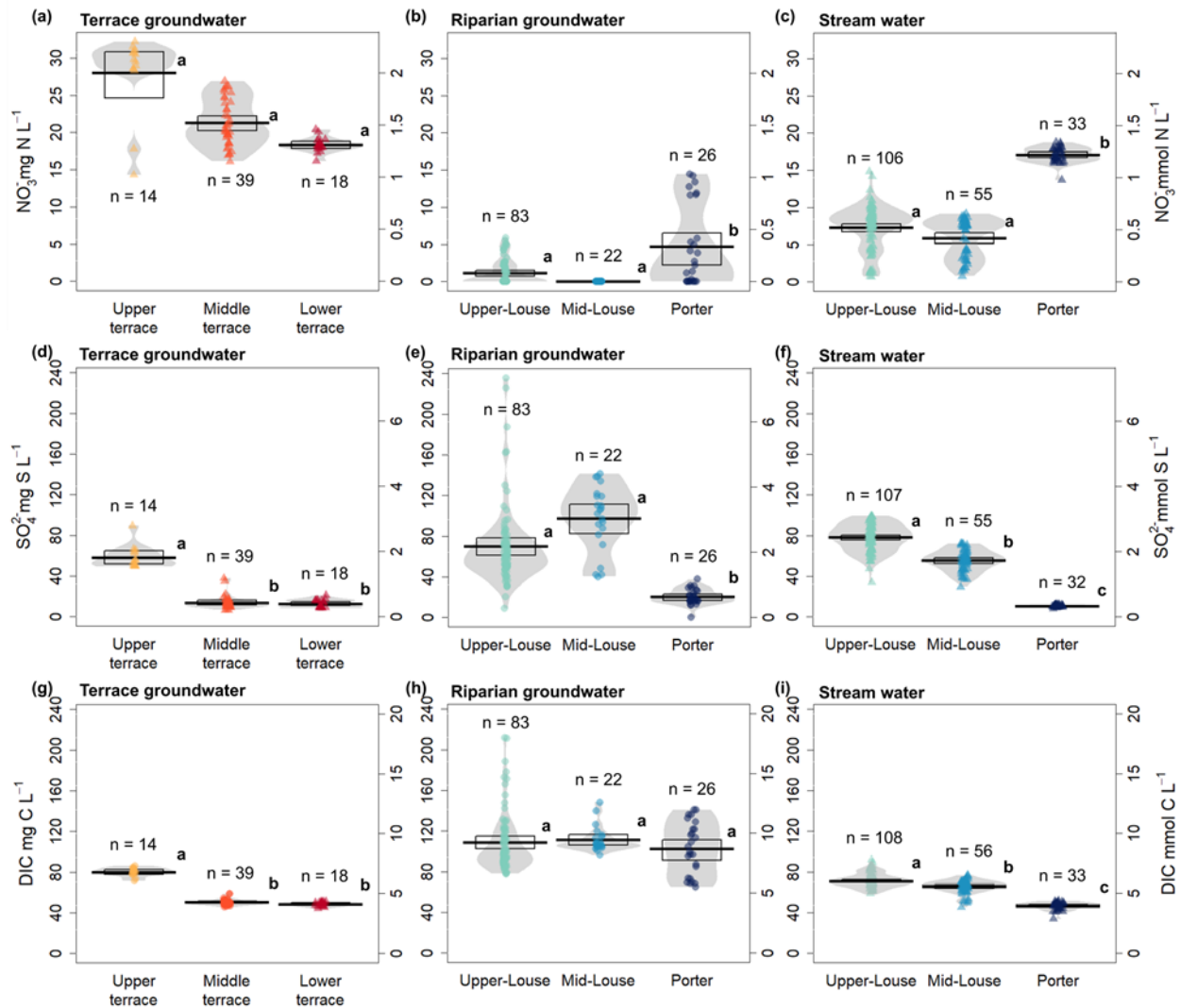
Ch.3-Figure 2. Maps and aerial imagery of the study area and sampling locations. (a) Map of the Judith River Watershed (JRW; orange outline), Montana, USA in the northern Great Plains ecoregion (NGP; maroon outline, inset). The focal area for this study is a terrace landform outlined in green. (b) Expanded 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 show 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.



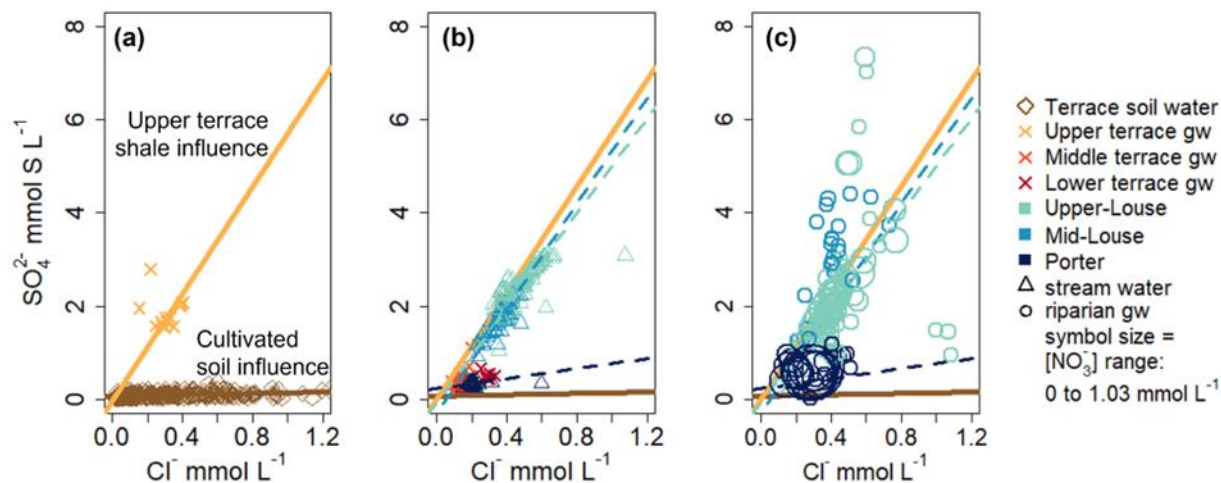
Ch.3-Figure 3. Principal component analysis of nitrate, sulfate, dissolved inorganic carbon (DIC), chloride, sodium, magnesium, and calcium concentrations in terrace groundwater (crosses, $n = 69$), riparian groundwater (circles, $n = 112$), and stream water (triangles, $n = 187$). Color scales indicate 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



Ch.3-Figure 4. Distributions of concentrations of (a) nitrate, (b) sulfate, and (c) 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.



Ch.3-Figure 5. Concentrations of (a-c) nitrate, (d-f) sulfate, and (g-i) 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 within 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.



Ch.3-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 weathered shale influence (yellow) and a regression of terrace soil water indicates cultivated soil influence (brown line). In (b), a regression of sulfate on chloride concentrations for proximal terrace groundwater and stream channel water samples characterizes a linear sulfate to chloride relationship for each study reach (dashed lines). Middle terrace groundwater is considered proximal to upper- and mid- Louse reaches, and lower terrace groundwater is considered proximal to Porter reach. 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.

Tables

Ch.3-Table 1. Summary statistics for nitrate, sulfate, and DIC in terrace groundwater, riparian groundwater, and stream water by reach.

Sample type	Period of record	Nitrate - N						Sulfate - S						Dissolved Inorganic Carbon					
		n	1 st Qu.	3 rd Qu.	Median	Mean	SD	n	1 st Qu.	3 rd Qu.	Median	Mean	SD	n	1 st Qu.	3 rd 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

Supporting Materials

Introduction

The supporting information included provides additional description of materials and methods, detailed site description of sample locations (Table S1), data included in the analyses for this study (Data Set S1 to S3), additional data visualizations (Figures S1 to S8), and examples of plausible biogeochemical reactions that include nitrate and sulfate (Table S2). Data files include geochemical results and field parameters for samples collected from 2020-2022 (Data Set S1) and geochemical results for samples collected from 2013 to 2016 (Data sets S2 and S3). Known imperfections in the data are indicated by a flag included in the data set (Data set S1). Data from 2013 to 2016 only include analytical results with flags determined “ok”.

Text S1. Extended Description of Materials and Methods

Text S1.1. Extended Description of Study Area

Geomorphic Context. Age and provenance of upper terrace gravels and the associated landforms in the JRW are poorly constrained, but the Moccasin and surrounding upper terraces are generally regarded as Quaternary pediment remnants (e.g., Lindsey, 1982; Vuke et al., 2002) with terrace gravels transported and deposited by braided rivers during the Pleistocene (Porter et al., 1996; Vine, 1956; Zimmerman, 1966b). Terraces became stranded by incision of the Judith River and its tributaries associated with Pleistocene glacial meltwater pulses of varying magnitude (Smith et al., 2020). The mouth of the Judith River was likely dammed by the Laurentide ice sheet during the late Illinoian stage (127–190 ka) to form Glacial Lake Winifred (Davis et al., 2006; Zimmerman, 1966a). Recession of the Laurentide ice sheet in the late Pleistocene (between 20,000 and 11,500 years ago; Dyke et al., 2002; Gowan, 2013) released the

ice dam impounding Lake Winifred, rapidly lowering the base level of the Judith River. The resulting stream and river erosion into underlying Cretaceous-age marine sandstones and shales (Vuke et al., 2002) likely produced the broad inset floodplains observed on the Moccasin terrace and the younger terraces throughout the lower elevations of the JRW (Alden, 1932).

Agricultural Context. Crop production in the JRW includes summer fallow where producers control undesired vegetation with herbicides to promote soil water storage for the subsequent crop. Soil water stored during fallow promotes N mineralization from organic matter and subsequent nitrification of ammonium into nitrate (Sigler et al., 2022). Application of N fertilizers supplements soil nitrate and ensures sufficient N for crop production and protein content. High nitrate-N concentrations (from 15 to 30 mg N L⁻¹) in upland groundwater that supply drinking water to private well owners in the region (Schmidt & Mulder, 2010; Sigler et al., 2018) exceed U.S. Environmental Protection Agency drinking water standards. These concentrations reflect leaching losses relative to limited but spatially extensive nitrate transformation in cultivated soils (Sigler et al., 2022). Sulfur fertilization and sulfate leaching likely also occur, albeit at lower levels due to lower demand. Based on previous observations of sulfate in soils and groundwater (Sigler et al. 2018), a similar set of processes likely occurs for S, albeit in response to lower rates of S fertilization due to lower crop demand (Aula et al., 2019; Eriksen, 2009; Sharma et al., 2024).

Text S1.2. Extended Description of Sample Collection and Handling

Terrace Soil Water. Samples were collected from four locations within a field near the Porter reach and eleven locations across a field southeast of the Moccasin terrace (Table S1; Sigler et al., 2018). Depths of each sampling location ranged from 50 to 120 cm, depending on

the thickness of fine-textured soils. Privately owned and managed fields were accessed with permission and advising from cooperating farmers with the goal to capture the influence of cropping system strategies. At each sampling location, a lysimeter cup was installed in undisturbed fine textured calcareous soil material just above the gravel horizon (50 to 120 cm depth). Terrace soils were sampled one to three times per month during periods of high soil volumetric water content and once a month otherwise. To extract soil pore water, an internal tension of approximately -15 psi was applied with a hand pump, and a sample was collected after allowing ca. 24 hours of accumulation in the lysimeter reservoir.

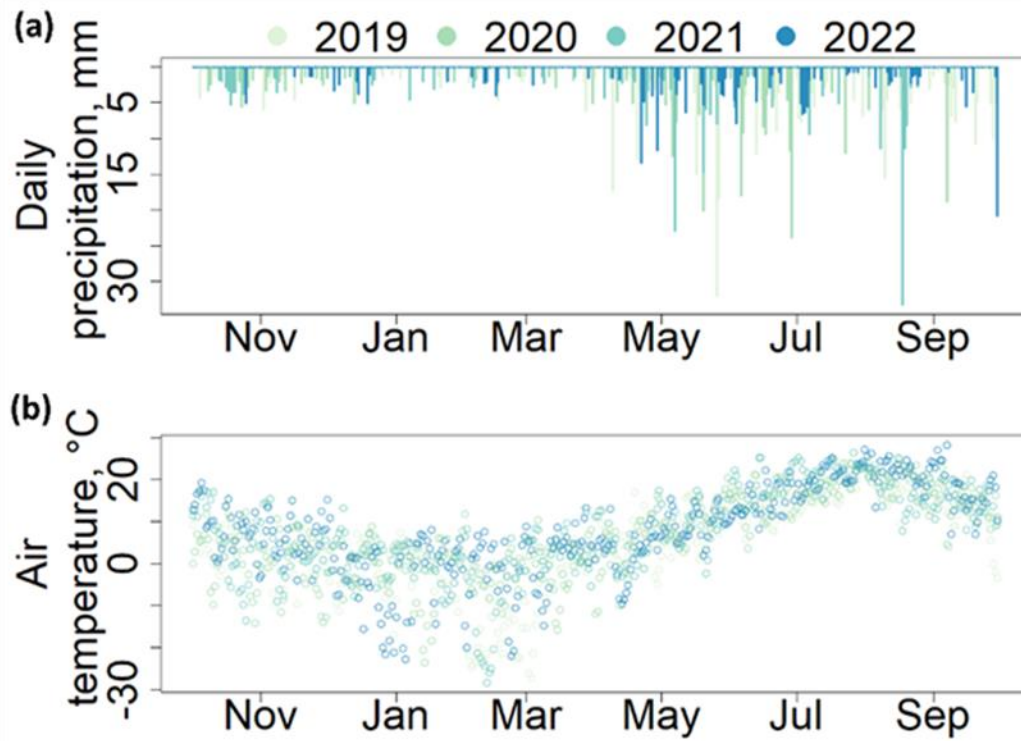
Terrace Groundwater. Sites in the lower terrace category were at lower elevations and considered representative of groundwater contributing to the Porter Creek reach. Middle terrace sites were at intermediate elevations and considered representative groundwater contributing to the Louse Creek reaches. Upper terrace sites were at higher elevations and considered representative of groundwaters farther from stream drainages. We included samples collected from the Montana Department of Agriculture at groundwater monitoring well M-1 (site identification # 133047 and name MOS-1 in MBMG, 2024). Two hillslope springs sampled from 2013 to 2014 required sampling from shallow PVC wells installed 1-2 meters up-gradient from the orifice due to stagnant water at the spring orifice (Sigler et al., 2018).

Riparian Groundwater. Casings for riparian groundwater sampling wells were constructed from 2.54-cm internal diameter PVC installed to ca. 1-m depth in riparian soils and sediments. Thin (< 5 mm) slots were cut into the bottom of the casings to provide 30 to 50 cm of screening. We monitored dissolved oxygen (DO) concentrations continuously while pumping through a flow cell.

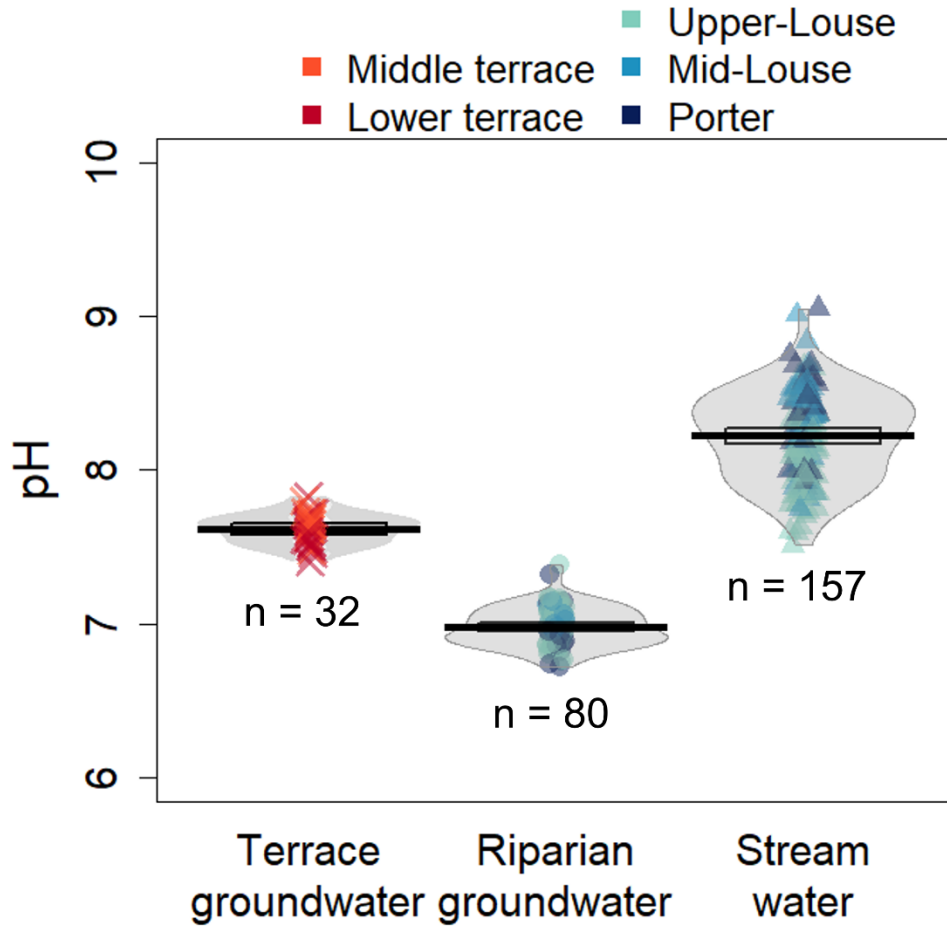
In Situ Sensor Calibration. We calibrated the DO sensor to water saturated air each day prior to collecting samples and measurements. We calibrated specific conductance and pH once prior to the start of each multi-day sampling campaign, within 24 hours of the first measurement. We performed a 3-point calibration of the pH sensor using standards of pH 10, pH 7, and pH 4. Specific electrical conductivity (corrected to a water temperature of 25 °C) was calibrated to a standard of 1412 $\mu\text{S cm}^{-1}$.

Text S1.3. Extended Description of Chemical Analyses Charge Balance: Samples with a charge balance exceeding 20% difference ($n = 17$) were generally dominated by negative charge with a low Ca^{2+} than expected based on other results from the same site. Precipitation of Ca^{2+} in the sample bottle likely occurred prior to analysis for these samples. Few instances of low Mg^{2+} and Na^+ contributed to charge balance dominated by anion concentrations. Two samples from 2020 resulted in a charge balance dominated by positive charge due to high Na^+ concentrations than expected from other results from the same site. Two riparian groundwater samples from 2021 resulted in a charge balance dominated by positive charge due to high Ca^{2+} concentrations than expected from other results from the same site.

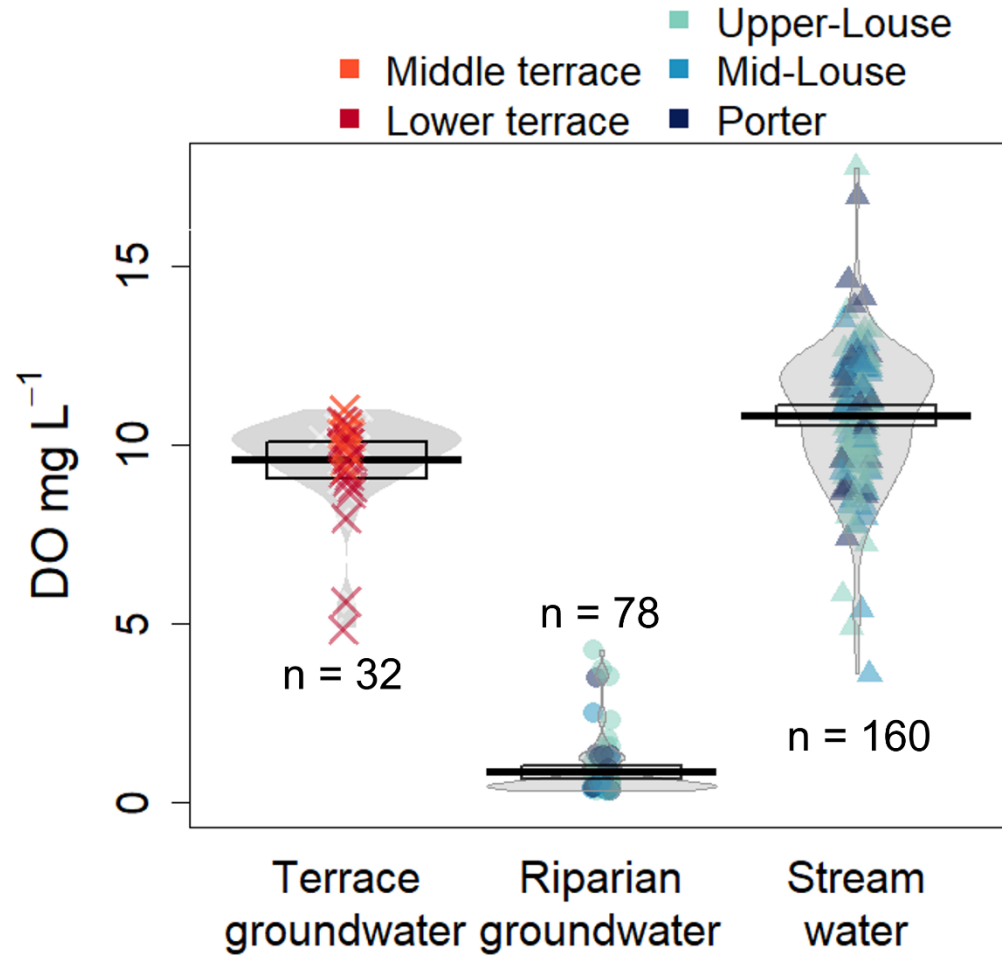
Supporting Figures



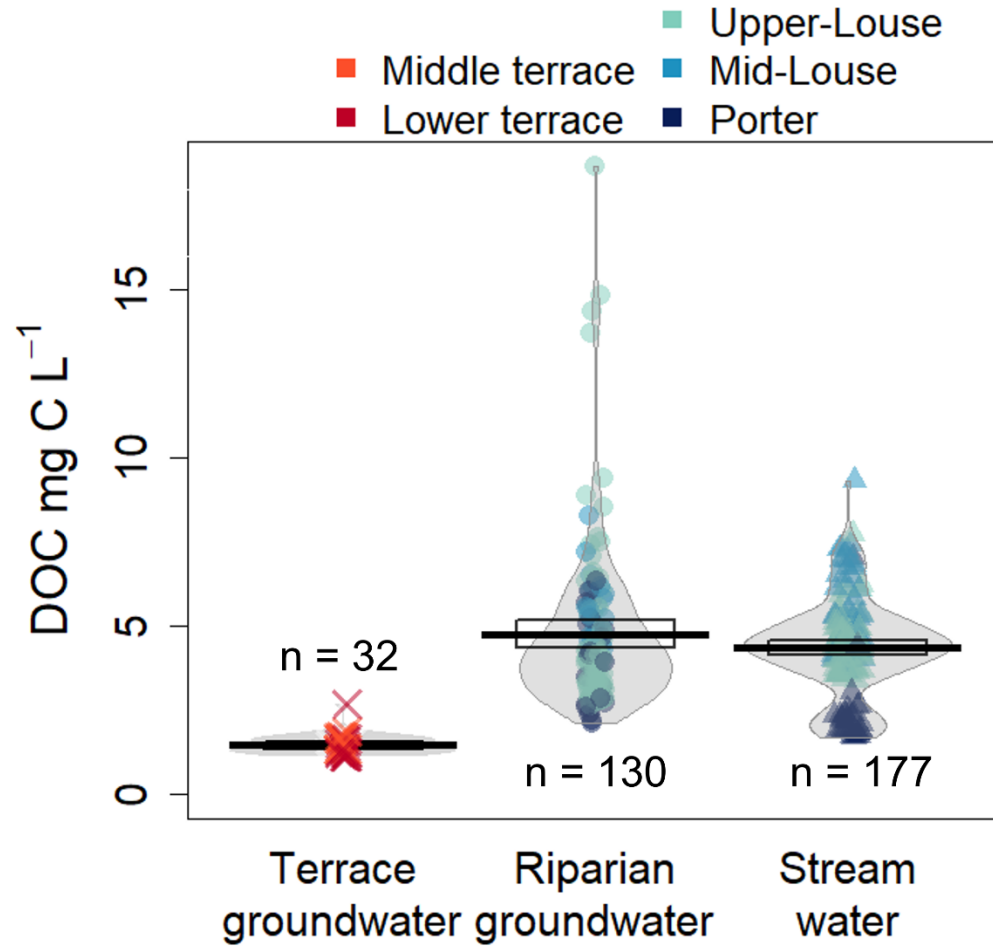
Ch.3-Figure S1. Hydrometeorological data on the Moccasin terrace over four water years (2019-2022). Data include (a) precipitation (mm) and (b) atmospheric temperature (°C). Data from Bureau of Reclamation AgriMet Station: MWSM located at the Central Agricultural Research Center (USBR, 2023).



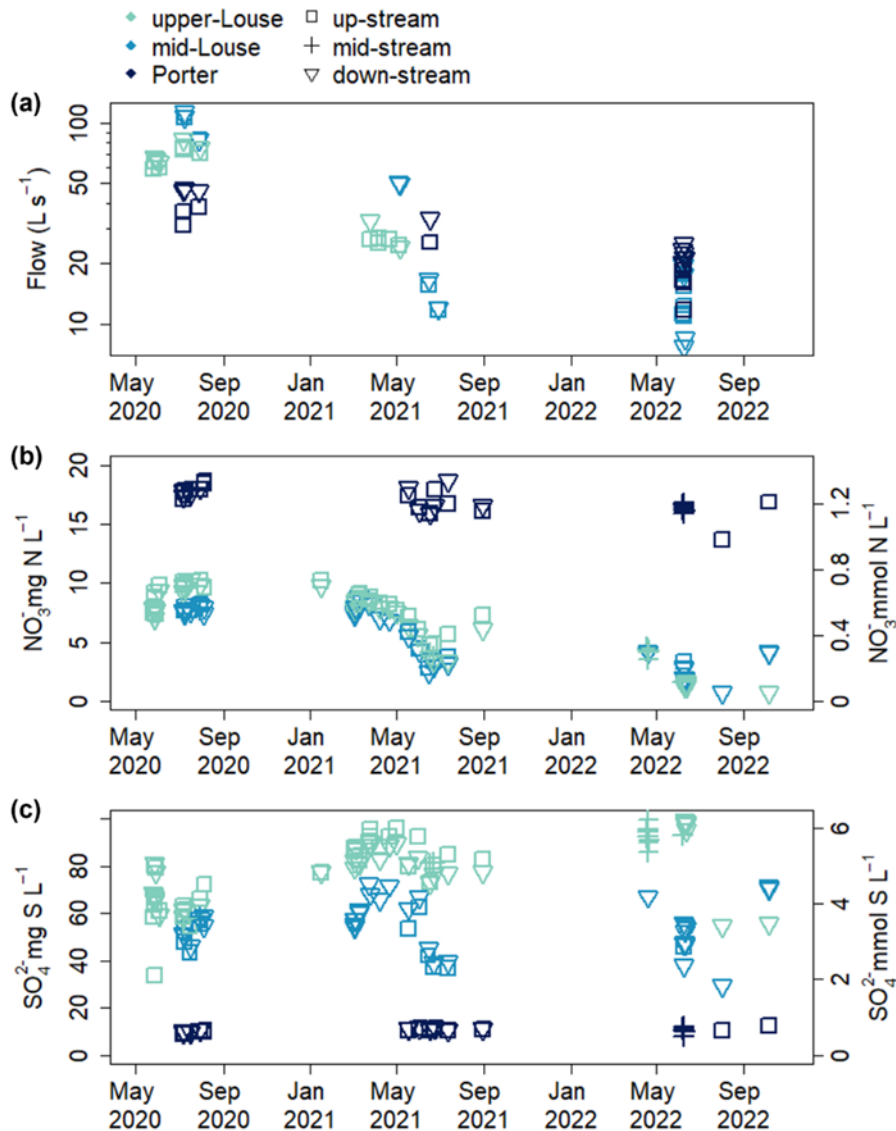
Ch.3-Figure S2. pH across process domains (shape) for two terrace landscape positions and three stream reaches (color; Figure. 2).



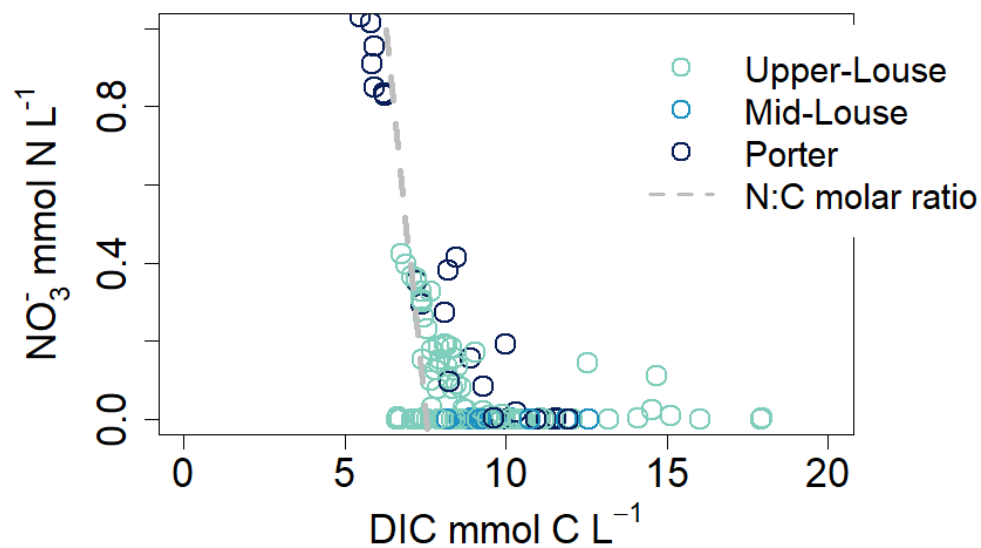
Ch.3-Figure S3. Concentrations of dissolved oxygen (mg L^{-1}) across process domains (shape) two terrace landscape positions and three stream reaches (color; Figure. 2).



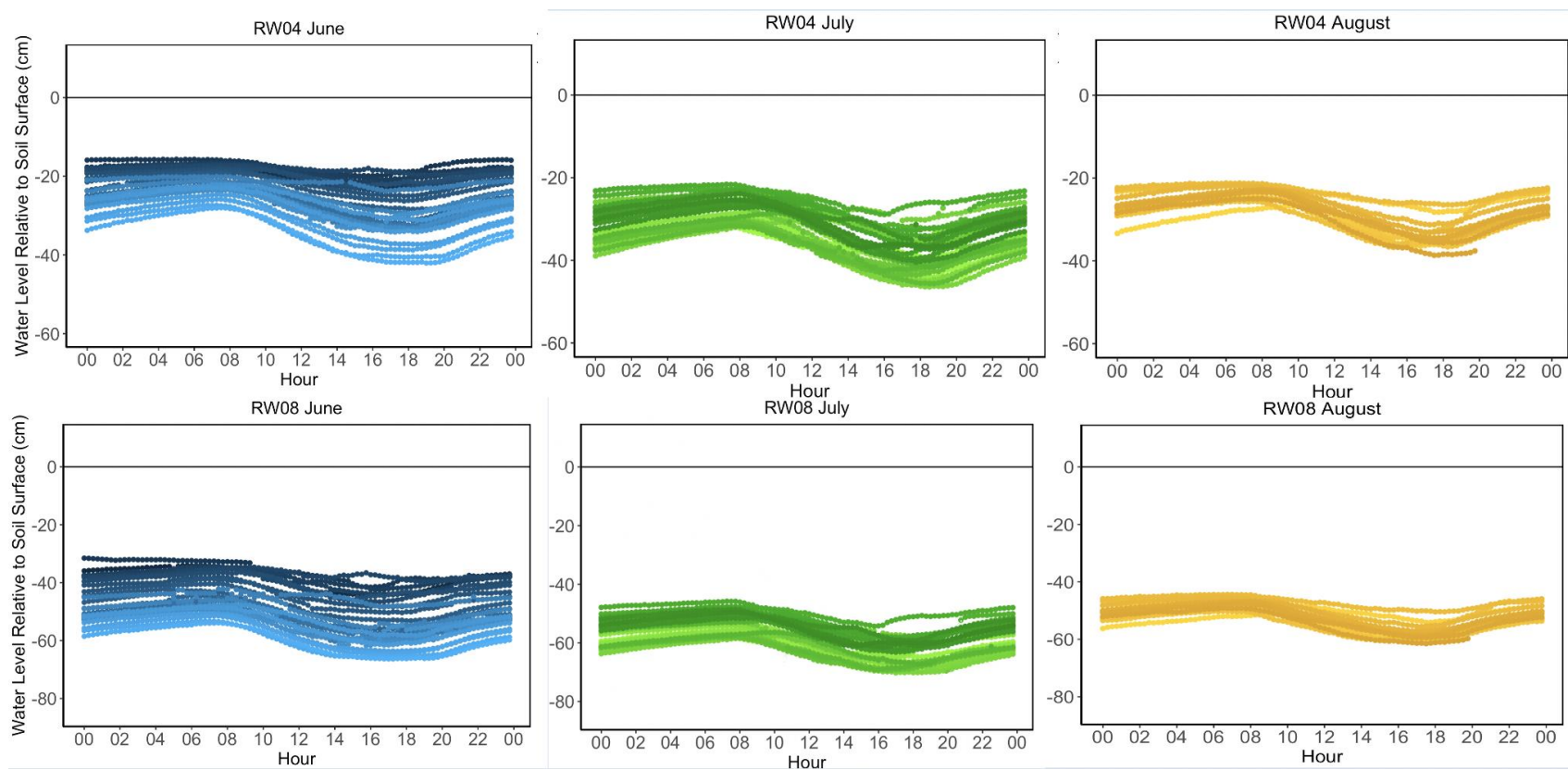
Ch.3-Figure S4. Concentrations of dissolved organic carbon (mg C L⁻¹) across process domains (shape) for three stream corridors (color; Figure. 2).



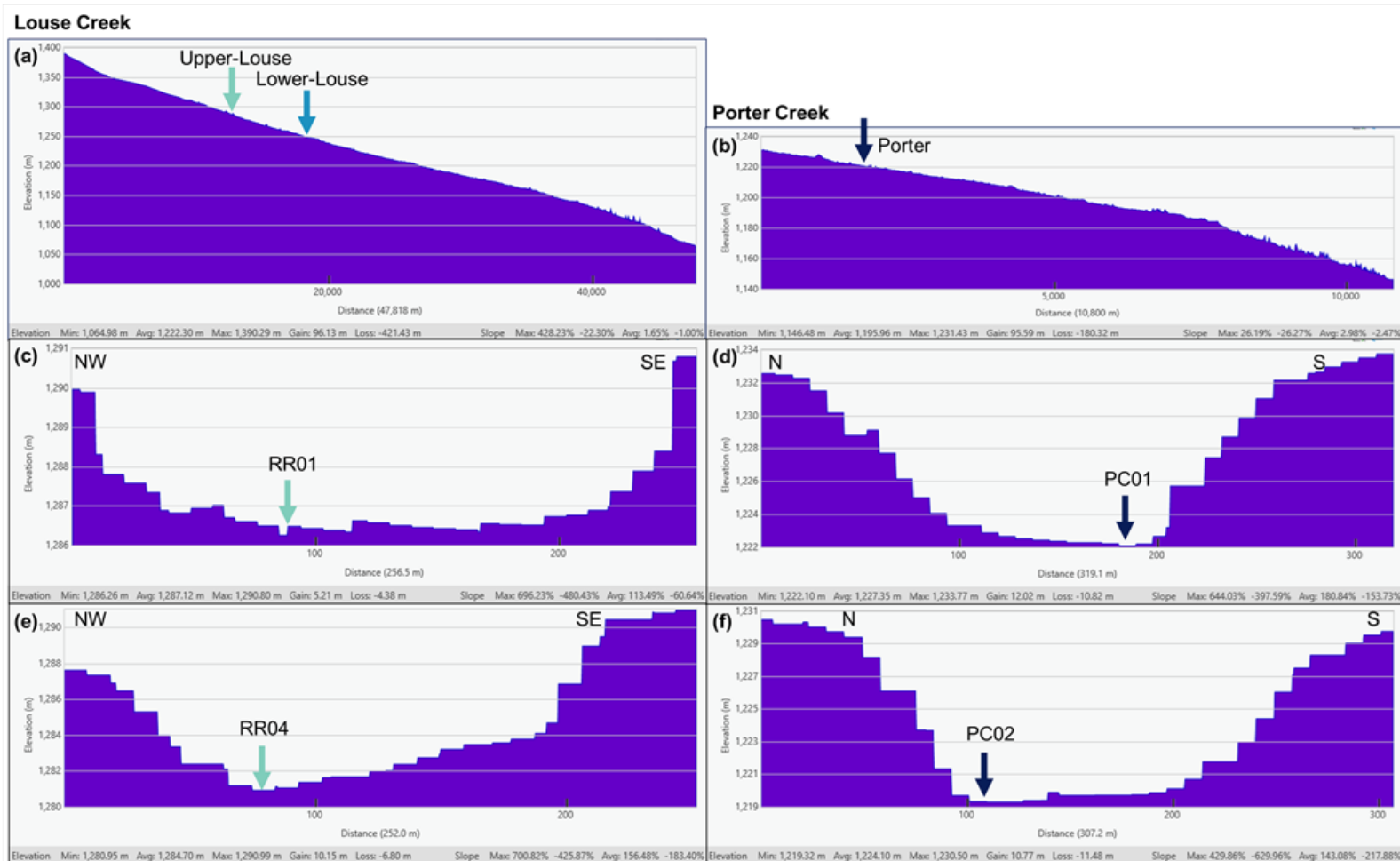
Ch.3-Figure S5. Stream flow (a), nitrate concentration (b), and sulfate concentration (c) over the study period. Concentrations of dissolved organic carbon (mg C L^{-1}) across process domains (shape) for three stream corridors (color; Figure. 2). Upper Louse reach is green, mid-Louse is light blue, and Porter is dark blue. Square symbols indicate the up-stream site within the stream reach, inverse triangle symbols indicate the down-stream site within the stream reach, and crosses indicate a mid-stream site.



Ch.3-Figure S6. Nitrate concentration versus dissolved inorganic carbon concentration for riparian groundwater in the three stream reaches. Concentrations are shown in mmol L^{-1} to relate empirical values to the theoretical stoichiometric relationship between the consumption of nitrate and production of inorganic carbon species (8:10 mols) for the denitrification pathway (dashed grey line with slope = -0.8; Table 4 eq. 1) (Stumm & Morgan, 1996). Bicarbonate (HCO_3^-) is the assumed dominant dissolved inorganic carbon (DIC) species in these waters due to an average observed pH of 7.8 (Figure S3).



Ch.3-Figure S7. Riparian groundwater level over time. Water level was measured using a pressure transducer in wells located within reach 1: RW04 (a-c) and RW08 (d-f) for months June (a and d), July (b and e), and August (c and f). Water level is plotted relative to the soil surface (black line at zero). Water level is plotted against time in hours over the course of a day, with each line corresponding to data from a different day within each month. The color gradient shifts from dark to light as the days progress through the month.



Ch.3-Figure S7. Longitudinal (a-b) and cross-section (c-f) profiles for Louse and Porter creeks. Longitudinal profiles extend from the apparent channel head to the stream confluence with the Judith River. Cross-sections are taken across the upstream and downstream sampling sites at upper-Louse (c, e) and porter (d, f) reaches, with stream sampling sites indicated on the panel.

Supporting Tables

Ch.3-Table S1. Detailed site description, geographic location, and sample collection frequency for geochemical analyses.

Site	SiteType	YearSampled	AnnualCounts	Latitude	Longitude	Comments
PS01	Lower terrace groundwater	2020, 2021, 2022	3, 5, 1	47.0570	-109.8336	Terrace spring
PS02	Lower terrace groundwater	2020, 2021, 2022	3, 5, 1	47.0578	-109.8301	Terrace spring
IS01	Middle terrace groundwater	2013, 2014, 2020, 2021, 2022	10, 3, 3, 9, 2	47.0758	-109.9048	Terrace spring; also identified as Indian
M1	Middle terrace groundwater	2013	2	47.0950	-109.9676	MDA M1 Monitoring Well #133047
Star	Middle terrace groundwater	2013, 2014	10, 1	47.0937	-109.9351	Terrace spring at Star Road
Headwaters	Upper terrace groundwater	2013, 2014	12, 2	47.0350	-110.0591	Louse Creek Headwaters Well at Mudsprings Road; at diesel shop
Spr555	Upper terrace groundwater	2013, 2014	1, 1	47.0775	-110.0265	Terrace spring trib 555 near Benchland, MT
RW01	Riparian groundwater	2021, 2022	7, 4	47.0672	-109.9661	Groundwater sampled from shallow well within riparian floodplain

RW02	Riparian groundwater	2021, 2022	6, 1	47.0681	-109.9642	Groundwater sampled from shallow well within riparian floodplain
RW03	Riparian groundwater	2021	6	47.0678	-109.9640	Groundwater sampled from shallow well within riparian floodplain
RW04	Riparian groundwater	2021, 2022	9, 5	47.0689	-109.9606	Groundwater sampled from shallow well within riparian floodplain
RW05	Riparian groundwater	2021, 2022	5, 1	47.0694	-109.9600	Groundwater sampled from shallow well within riparian floodplain
RW06	Riparian groundwater	2021, 2022	7, 1	47.0683	-109.9633	Groundwater sampled from shallow well within riparian floodplain
RW07	Riparian groundwater	2021, 2022	6, 1	47.0692	-109.9614	Groundwater sampled from shallow well within riparian floodplain
RW08	Riparian groundwater	2021, 2022	10, 4	47.0681	-109.9639	Groundwater sampled from shallow well within riparian floodplain
RW09	Riparian groundwater	2021, 2022	6, 1	47.0695	-109.9608	Groundwater sampled from shallow well within riparian floodplain
RW10	Riparian groundwater	2021, 2022	6, 1	47.0686	-109.9608	Groundwater sampled from shallow well within riparian floodplain
LW01	Riparian groundwater	2021, 2022	3, 1	47.0777	-109.9120	Groundwater sampled from shallow well within riparian floodplain
LW03	Riparian groundwater	2021, 2022	4, 2	47.0779	-109.9096	Groundwater sampled from shallow well within riparian floodplain
LW04	Riparian groundwater	2021, 2022	3, 2	47.0792	-109.9089	Groundwater sampled from shallow well within riparian floodplain
LW05	Riparian groundwater	2021, 2022	4, 3	47.0788	-109.9087	Groundwater sampled from shallow well within riparian floodplain

PW01	Riparian groundwater	2021, 2022	5, 3	47.0571	-109.8335	Groundwater sampled from shallow well within riparian floodplain
PW02	Riparian groundwater	2021, 2022	3, 1	47.0578	-109.8321	Groundwater sampled from shallow well within riparian floodplain
PW03	Riparian groundwater	2021, 2022	3, 3	47.0577	-109.8314	Groundwater sampled from shallow well within riparian floodplain
PW04	Riparian groundwater	2021, 2022	3, 1	47.0573	-109.8309	Groundwater sampled from shallow well within riparian floodplain
PW05	Riparian groundwater	2021, 2022	3, 1	47.0575	-109.8297	Groundwater sampled from shallow well within riparian floodplain
RR01	Stream water	2013, 2014, 2019, 2020, 2021	13, 12, 1, 15, 21	47.0673	-109.9665	also identified as ‘Railroad’ in Sigler et al., (2018)
RR02	Stream water	2021, 2022	2, 10	47.0683	-109.9633	includes RR05 and RR07 due to very close proximity
RR04	Stream water	2020, 2021, 2022	13, 17, 11	47.0696	-109.9604	
LL01	Stream water	2020, 2021, 2022	5, 13, 1	47.0778	-109.9126	includes LL03 and LL04 due to very close proximity
LL02	Stream water	2020, 2021, 2022	7, 18, 12	47.0787	-109.9059	
PC01	Stream water	2020, 2021, 2022	7, 6, 2	47.0572	-109.8333	
PC02	Stream water	2020, 2021	4, 6	47.0575	-109.8296	
PC03	Stream water	2022	8	47.0577	-109.8313	

C1E.01	Soil	2013, 2014, 2015	6, 9, 4	46.9963	-109.6147	Judith project soil lysimeter location
C1E.10	Soil	2013, 2015	1, 5	46.9913	-109.6148	Judith project soil lysimeter location
C2E.01	Soil	2013, 2015	2, 1	46.9962	-109.6129	Judith project soil lysimeter location
C2E.07	Soil	2013, 2014, 2015, 2016	4, 13, 12, 7	46.9929	-109.6130	Judith project soil lysimeter location
C2E.08	Soil	2014, 2015, 2016	11, 7, 4	46.9924	-109.6130	Judith project soil lysimeter location
C2E.10	Soil	2013, 2014, 2015, 2016	4, 12, 12, 4	46.9913	-109.6130	Judith project soil lysimeter location
C2W.04	Soil	2013, 2015	2, 5	46.9946	-109.6145	Judith project soil lysimeter location
C2W.06	Soil	2014, 2015	3, 12	46.9935	-109.6145	Judith project soil lysimeter location
C3W.01	Soil	2013, 2014, 2015, 2016	12, 20, 10, 5	46.9962	-109.6126	Judith project soil lysimeter location
C3W.04	Soil	2013	1	46.9946	-109.6126	Judith project soil lysimeter location
C3W.10	Soil	2013, 2014, 2015	3, 10, 5	46.9913	-109.6128	Judith project soil lysimeter location
B3E.03	Soil	2013, 2014, 2015, 2016	9, 6, 3, 13	47.0532	-109.8597	Judith project soil lysimeter location
B3E.04	Soil	2013, 2014, 2015, 2016	11, 2, 2, 3	47.0526	-109.8597	Judith project soil lysimeter location
B4W.04	Soil	2013	5	47.0526	-109.8595	Judith project soil lysimeter location
B4W.07	Soil	2013, 2014, 2015, 2016	2, 10, 2, 7	47.0490	-109.8596	Judith project soil lysimeter location

Ch.3-Table S2. Summary of the measured water quality and chemistry parameters and the methods used to measure them.

Parameter	Sample collection device	Analytical method	Reported unit	Uncertainty	Limit of detection
Dissolved oxygen	Measured in situ	Electrochemical (YSI Incorporated, Yellow Springs, OH)	mg L ⁻¹	± 2mg L ⁻¹	None given
Temperature	Measured in situ	N/A (YSI Incorporated, Yellow Springs, OH)	°C	± 2°C	None given
Specific conductance	Measured in situ	Four electrode cells (YSI Incorporated, Yellow Springs, OH)	µS cm ⁻¹	± 0.5%	None given
pH	Measured in situ	Glass combination electrode (YSI Incorporated, Yellow Springs, OH)	NA	± 0.2	None given
Nitrate, as nitrogen	ashed 24 mL glass, no head space	Colorimetry (Lachat QuickChem 8500)	mg L ⁻¹	± 5%	0.01
Total Carbon	ashed 24 mL glass, no head space	Liquid combustion (Shimadzu, TOC VCSH)	mg L ⁻¹	± 10%	0.2
Dissolved Organic Carbon	ashed 24 mL glass, no head space	Liquid combustion (Shimadzu, TOC VCSH)	mg L ⁻¹	± 10%	0.3
Dissolved Inorganic Carbon	ashed 24 mL glass, no head space	DIC =Total Carbon-DOC	mg L ⁻¹	± 10%	0.2
Sulfate	Acid-washed 60 mL HDPE	Ion chromatography (Dionex, ICS-2100)	mg L ⁻¹	± 10%	0.02
Chloride	Acid-washed 60 mL HDPE	Ion chromatography (Dionex, ICS-2100)	mg L ⁻¹	± 10%	0.01
Calcium, Sodium, Magnesium, Iron (II)	Acid-washed 60 mL HDPE	Inductively coupled plasma optical emission spectroscopy (Perkin Elmer, 5300 DV)	mg L ⁻¹	± 10%	None given

Ch.3-Table S3. Select examples for candidate biogeochemical processes of nitrate and sulfate.

Equation	Candidate biogeochemical processes	Reaction examples
1	Heterotrophic nitrate reduction	$5CH_3COO^- + 8NO_3^- + 13H^+ \rightarrow 10CO_{2(g)} + 14H_2O + 4N_2$
2	Dissolution and dissociation of inorganic carbon species	$CO_{2(g)} + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
3	Heterotrophic sulfate reduction	$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^-$
4	Iron sulfide precipitation	$Fe^{2+} + S^{2-} \rightarrow FeS_{(s)}$
5	Autotrophic denitrification coupled with sulfide oxidation	$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 2H_2O + 5Fe^{2+} + 7N_2 + 10SO_4^{2-}$
6	Additional sulfur oxidation pathway	$2FeS_2 + 7O_{2(aq)} + 2H_2O \rightarrow 2Fe^{2+} + 4H^+ + 4SO_4^{2-}$
7	Additional sulfur oxidation pathway	$2S + 3O_{2(aq)} + 2H_2O \rightarrow 2H_2SO_4 \rightarrow 4H^+ + 2SO_4^{2-}$

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CHAPTER FOUR

NITRATE AND SULFATE ISOTOPES INDICATE DYNAMIC
PRODUCTION AND LOSS PATTERNS OF CONTAMINANTS
IN STREAM CORRIDORS DRAINING AGRICULTURAL
LANDSCAPES

Contribution of Authors and Co-Authors

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Abstract

Stream corridors are disproportionately important to mitigating contaminant export in runoff from landscapes, yet limited understanding about controls on riparian biogeochemical processes challenges effective management of water quality problems. We investigate the biogeochemical transformation of nitrate and sulfate in hydrologically constrained stream corridors draining an extensively cultivated terrace landform. To infer riparian biogeochemical processes, we examined patterns in nitrate and sulfate concentration and isotopic composition in water samples collected from upland groundwater, riparian groundwater, and stream channel water from three ca. 0.7-km reaches. Stream corridors that consistently had net nitrate loss, higher nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values (up to ca. +40‰ and +15‰, respectively) generally corresponded with lower nitrate concentrations ($< 5 \text{ mg L}^{-1}$) relative to terrace groundwater inflows (ca. +20 mg N L^{-1}). Nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values were highest in riparian groundwaters, providing convincing evidence for nitrate loss processes that favor lighter isotopes. Evidence of sulfate produced within these same stream corridors had low sulfate- $\delta^{34}\text{S}$ values and intermediate sulfate- $\delta^{18}\text{O}$ values (ca. -18‰ and +6‰, respectively), suggesting sulfide oxidation from marine shale weathering. We use the difference in isotopic composition between terrace groundwater and stream water and relationships between isotopic compositions and concentrations to constrain the potential magnitude of gross gains and losses influencing observed net sulfate gains and nitrate losses. Our results reveal how a combination of biogeochemical and mixing processes contribute to the irreversible loss of nitrate and overall gains of sulfate in stream corridors that influence water quality.

Keywords

Isotope geochemistry, shale weathering, riparian area, bacterial sulfate reduction, denitrification, northern Great Plains

Introduction

Stream corridors can mitigate excess nitrate and sulfate exported from upland landscapes through transformation of solute loads in riparian ecosystems (Hill, 1996; Ledesma et al., 2016; Naiman & Décamps, 1997; Ranalli & Macalady, 2010; Tesoriero & Puckett, 2011). However, the controls on hydrological and biogeochemical processes in riparian ecosystems remain unresolved (Bernhardt et al., 2017; Covino et al., 2018; Hill, 2019; Jencso et al., 2010). This knowledge gap and the potential adverse effects of nitrate and sulfate on human and animal health (Backer, 2000; DeSimone et al., 2009; Ward et al., 2018) demand investigation of their processing pathways within stream corridors. In agricultural landscapes, nitrate and sulfate cycling are particularly important because fertilizer additions and transformed soil hydrodynamics can alter solute loads (Scanlon et al., 2005; Sullivan et al., 2022). Here, we explore variation in isotopic compositions and concentrations of nitrate and sulfate to investigate how riparian substrate (i.e., alluvium and weathered bedrock) within stream corridors contributes to production and loss of solute loads from groundwater draining cultivated upland soils.

Riparian areas within stream corridors act as biogeochemically reactive buffers between upland groundwaters and stream waters (Cirimo & McDonnell, 1997; Jencso et al., 2010; Ranalli & Macalady, 2010; Vidon & Hill, 2004a), allowing for resilience to human perturbations of water quality. Riparian areas host relatively shallow, fluctuating groundwater tables (Hill, 2000; Naiman & Décamps, 1997), where flow paths can intercept a relatively abundant supply of labile organic matter from productive vegetation (Chapin et al., 2011; Silverman et al., 2019; Taylor &

Townsend, 2010). Carbon supply promotes aerobic heterotrophic demand that quickly depletes oxygen and allows for biogeochemical transformation of less energetically favorable solutes (Burgin et al., 2011; Hedin et al., 1998; Hefting et al., 2004; Miele et al., 2023; Payn et al., 2014). The thermodynamic and kinetic favorability of different metabolic pathways influences microbially-mediated nitrogen (N) and sulfur (S) mineralization and reduction. Given a similar carbon source and similar solute availability (Payn et al., 2014), nitrate is metabolically favored over sulfate in anaerobic respiration. Therefore, in low oxygen environments, mass change in nitrate relative to sulfate within a system reflects the supply of carbon, nitrate, and sulfate to reaction sites.

In riparian areas, mass changes in nitrate and sulfate reflect variable subsurface flow paths that can be influenced by human perturbations. Variable riparian substrate likely hosts sites of higher and lower permeability, promoting shorter and longer hydrologic residence times that facilitate solute transport and transformation. Variation in substrate permeability reflects land use management influences on geomorphic processes, such as construction of water impoundments for cattle grazing and erosion and deposition enhanced by upland cultivation. Hydrologic exchange across variable riparian substrate allows for delivery of oxidized solutes to reducing zones (i.e., low permeability) and reduced solutes to oxic zones (i.e., high permeability) (Bernhardt et al., 2017). Prevalence of reducing and oxidizing conditions in riparian areas requires consideration of sulfate as a reactive solute, in contrast to studies of well-mixed, more oxygenated river or groundwater systems (Hosono et al., 2014; Ruff et al., 2023; Saka et al., 2024). Thus, in riparian areas, availability of labile carbon and solute transport through oxidizing

and reducing environments facilitates biogeochemical processes at disproportionate rates relative to their areal extent, compared to the larger extent of upland landscapes.

In addition to effects on riparian areas, human land uses can contribute excess nitrate and sulfate to ground and surface waters (Driscoll et al., 2001; Hosono et al., 2010; Puckett et al., 2011; Vitousek, Mooney, et al., 1997). Dominant sources of nitrate and sulfate in cultivated landscapes are fertilizer application and internal soil processes such as organic matter mineralization and, to a lesser degree, mineral weathering. Fertilizer applications in excess of crop demands make excess inorganic N and S loading to ground and surface water common in agricultural systems (Foley et al., 2011; Sharma et al., 2024; Sigler et al., 2018; Tesoriero et al., 2013). Loss of nitrate and sulfate from cultivated soils can result in nutrient deficiencies in cereal crops (Aula et al., 2019; Eriksen, 2009; Sabo et al., 2019; Sebilo et al., 2013; Sharma et al., 2024). Sulfur limitation on crop yields is an emerging concern in agricultural systems (Aula et al., 2019; Eriksen, 2009; Miller et al., 2024; Sharma et al., 2024), with currently limited understanding of S biogeochemical pathways in soils and shallow aquifers (Chalk et al., 2017; Gerson & Hinckley, 2023). Accumulation of nitrate and sulfate in groundwater underlying cultivated soils and subsequent loading to stream corridors can persist despite changes in land use practices, due to solute legacies in soils and sediments (Basu et al., 2022; Scanlon et al., 2007; K. J. Van Meter et al., 2016; Weitzman et al., 2022).

Land use may enhance bedrock weathering that contributes inorganic forms of both N (Holloway & Dahlgren, 1999; Houlton & Morford, 2015) and S (Bufe et al., 2021; Morrison et al., 2012; Tuttle & Grauch, 2009) to ground and surface waters. Weathering of organic-rich sedimentary rocks, such as shale and sandstone, releases more dissolved solids than weathering

of other types of bedrock (Holloway & Dahlgren, 1999; Houlton et al., 2018; Morrison et al., 2012; Tuttle et al., 2014). Human activities (e.g., cultivation, mining) expose reactive soil and bedrock surfaces and alters subsurface hydrology, promoting production and mobilization of inorganic N and S (Brown et al., 1983; Deonarine et al., 2023; Hayes et al., 2014; Scanlon et al., 2007; Welch et al., 2021). In agricultural systems, altered subsurface hydrology and fertilizer additions compound bedrock N and S contributions, creating high probability for solute transport to ground and surface waters.

For nitrate and sulfate, the relationships between isotopic composition and concentration across a landscape provide information about sources and biogeochemical transformation. Biogeochemical transformations include oxidation and reduction processes that determine the form and mobility of N and S species and are often metabolically driven, resulting in kinetically controlled isotopic fractionation (Seal et al., 2000; Sharp, 2017). Enzyme-mediated metabolic reactions prefer lower mass isotopes, resulting in higher fractionation effects. In processes such as heterotrophic denitrification and bacterial sulfate reduction, strong preferential transformation of ions containing the lower mass and more abundant isotopes (^{14}N , ^{32}S , and ^{16}O) result in a residual pool with lower concentrations, higher $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in nitrate, and higher $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in sulfate (Denk et al., 2017; Fry, 2006; Kendall, 1998; Mariotti et al., 1981; Sharp, 2017). In contrast, precipitation of secondary sulfate salts such as gypsum favors the higher mass isotopes of S and oxygen (O), resulting in a residual pool with lower concentration and lower sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values (Ewing et al., 2008). Discerning these effects of biogeochemical transformation from mixing processes requires careful assessment of solute sources and patterns of isotopic composition and concentrations. Therefore, isotopic change in

nitrate and sulfate reflects the biogeochemical controls on mass change, including substrate variability and solute supply.

Interpreting patterns in the relationships of solute isotopic compositions with concentrations in stream corridors requires careful consideration of environmental constraints on transport and mixing within the system that dictate the isotopic expression of fractionating and non-fractionating mass loss and gain (Fry, 2006; Houlton et al., 2006; Van Stempvoort et al., 2023). Environmental systems can be conceptualized as *open* or *closed*, depending on whether processing within the system includes continuous mixing with inputs during mass loss (open), or if processing within the system is isolated from new inputs during mass loss (closed) (see Rayleigh models in Criss 1999 and Denk 2017). For nitrate, previously observed extensive mass loss at our study site (Mayernik et al., in review; Sigler et al., 2022) requires consideration of both approaches to address isotopic processing at different spatial scales. First, we evaluate stream corridors as open systems approximated as steady-state and well-mixed flow-through reactors (Figure 1) to interpret changes in the observed solute concentrations and isotopic compositions from the upland aquifer inputs to the stream channel outputs. We use an open, steady-state system perspective (Denk et al., 2017; Houlton et al., 2006; Sigler et al., 2022) to integrate the influence of multiple microbial processes and flow paths. Second, we use a closed-system perspective to consider the potential influence of fractionating loss that may occur in parcels of water moving along flow paths within the riparian aquifer (Figure 1 inset). For sulfate, previously observed mass gain at our study site (Mayernik et al., in review) requires consideration of closed system processes juxtaposed with mixing processes. Because the overall system behavior includes multiple pathways of production, loss, and mixing, the overlapping

controls on solute isotopic composition remain challenging to separate. This combined approach allows us to explore complex processes underlying the net isotopic change along stream corridors.

A riparian aquifer likely represents a complex combination of open and closed scenarios (Houlton et al., 2006) given the interactions of biogeochemical activity with spatiotemporal variation in hydrologic flow and storage within riparian substrate (Bernhardt et al., 2017). Many studies using isotopic tracers in environmental systems may inappropriately describe the fractionation effect observed as synonymous with a single heterotrophic reduction pathway (e.g., denitrification; Denk et al., 2017; Hall et al., 2016; André Mariotti et al., 1988; Mulholland et al., 2008; Sigler et al., 2022). With this work, we acknowledge that heterotrophic reduction processes are likely dominant in some cases and argue for the use of *apparent isotopic effect* when describing the system-level isotopic and concentration changes that commonly reflect multiple, co-occurring production and loss pathways. Our work documents how ecosystem level self-organization in stream corridors leads to apparent isotopic effects that can be remarkably consistent, despite system complexity.

The goal of this research is to understand how nitrate and sulfate production and loss within riparian substrate contribute to changes in solute isotopic compositions and concentrations observed between upland groundwaters and streams. Our primary approach to achieving this goal was to analyze spatial patterns in concentrations and isotopic compositions of nitrate (nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and sulfate (sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) across stream corridors in an agricultural system within the northern Great Plains (Figure 2). High nitrate concentrations (ca. 20 mg N L^{-1}) in the upland groundwater of this system directly reflects the combined effects of

upland soil processes and agricultural soil management; this upland groundwater is the primary source of stream flow generation in these stream corridors (Mayernik et al., 2024, in review; Sigler et al. 2018, 2022). Clear distinctions among the chemical and isotopic compositions of upland groundwaters, riparian groundwaters, and stream waters in our study area provides a useful lens into the gross losses and gains of solutes occurring due to mixing of contributions from uplands and fractionation effects from biogeochemical reactivity along these stream corridors.

We hypothesize that transformation processes of riparian substrate (e.g., mineral weathering and mineralization of organic matter) represent a gross contribution of solute mass to riparian groundwater and stream water. We further hypothesize that net losses in nitrate observed in these systems reflect substantial heterotrophic nitrate reduction that outpace the gross gains. Finally, we hypothesize that the observed net increase in sulfate concentrations reflects a lack of microbially-mediated sulfate reduction to balance the gross gains from weathering or mineralization. We test these hypotheses with three specific research objectives through comparisons of stream corridors with differing hydrologic connectivity among upland aquifers, riparian aquifers, and stream channels:

1. Evaluate relative contributions of nitrate and sulfate sources in stream corridors from upland soils and riparian substrate.
2. Constrain estimates of potential combinations of gross losses and gains of nitrate within stream corridors that result in net nitrate loss.
3. Constrain estimates of potential combinations of gross losses and gains of sulfate within stream corridors that result in net sulfate gain.

In addressing these objectives, this research contributes an approach to combining solute isotopic composition and concentration data to parse the relative contributions of loading versus processing facilitated by riparian systems. In the agricultural landscape of our study area, we aim to improve understanding of how stream corridors mitigate water quality issues, to inform management of riparian ecosystems within semi-arid agricultural systems.

Methods

Section 2.1 Study Area

Our study took place within the Judith River Watershed (JRW) of central Montana, USA. The Judith River is a tributary of the Missouri River in the northern Great Plains ecoregion (Figure 2). Our study area was in the lower elevations (1,200-1,300 m. a.s.l.) of the JRW, which have a semi-arid climate with a mean annual precipitation of 393 mm and temperature of 6.6°C (1991–2021, 4-km resolution centered on coordinates: 47.0778, -109.9126; PRISM Climate Group).

Our study focused on stream corridors draining the Moccasin terrace (Figure 2b), a strath terrace landform with a shallow upland aquifer perched on relatively impermeable Cretaceous-age marine shales (Vuke et al., 2002). The incision of mountain-sourced streams around the upgradient end of the Moccasin terrace isolated the shallow terrace aquifer from any recharge sources originating in the Little Belt mountains (Figure 2a), and the impermeability of the shale units limits connectivity of the shallow aquifers with deeper aquifers (Sigler et al., 201; Vuke et al., 2002). Therefore, water stored in the shallow Moccasin terrace aquifer is sourced primarily from infiltration of local precipitation through cultivated soils and exported through the groundwater-fed stream corridors. Thus, the Moccasin terrace provides a simplified hydrologic

context for studying the influence of land use on water quality as solutes move from soils to streams.

The Moccasin terrace uplands host primarily well-drained calcareous soils, classified as Calciustolls and Argiustolls in the US Taxonomy (U.S. Department of Agriculture, 2022). The shallow soil horizons on the terrace are predominantly managed for non-irrigated, no-till cereal crop production. Soils generally exhibit clay loam textures and relatively shallow gravel zones (40-100 cm), resulting in subsurface horizons with > 40% coarse gravel content between 1.5 m and 10 m thick (Sigler et al., 2018). Agricultural management and soil architecture result in substantial nitrate leaching to the shallow aquifer, with pervasive high nitrate concentrations (ca. 20 mg L⁻¹ nitrate-N) observed in shallow terrace aquifers (Mayernik et al., in review; Schmidt & Mulder, 2010; Sigler et al., 2018) that supply drinking water to local residents.

Soils in exposed shale upgradient on the terrace and soils developed from shale-derived substrate within stream corridors include high clay soils classified as Vertisols (Udorthentic Chromusterts) and poorly drained hydric and sub-irrigated soils with strong redoximorphic features classified as Mollisols (Typic Haplaquolls, Aquic Haplustolls, and Cumulic Endoaquolls) (U.S. Department of Agriculture, 2022). Chemical weathering of exposed shale-derived substrate supplies solutes to the system, including sulfate and nitrate (Zimmerman, 1966b, 1966a). Stream corridor soils have intermittent, shallow gravel layers. Depths to the riparian groundwater tables are typically less than 90 cm below the ground surface, resulting in wetter soil conditions in the dry season relative to the upland soils. The stream corridors in this study area experienced varying degrees of perturbation by land management (e.g., cattle grazing and water impoundments) and bioturbation (e.g., Richardson's ground squirrel burrowing).

We selected three 0.7-km study reaches of stream corridors (two on Louse Creek and one on Porter Creek; Figure 2). Reach selection incorporates variation in the mode of hydrologic connectivity between upland aquifers and the stream channel, which allows us to compare riparian processing of nitrate and sulfate from differing hydrologic contexts commonly observed across the terrace. Terrace groundwater flowing into the stream corridors either directly contributes to the stream channel via channelized surface flow from multiple hillslope springs (e.g., dominant in Porter reach; Figure 2e) or indirectly contributes to the channel via diffuse subsurface flow paths through riparian substrate (e.g., dominant at Louse reaches; Figure 2c,d). All study reaches are gaining water from the terrace aquifer, and solute concentrations in the ground and surface waters of the stream corridor reflect the combined effects of hydrologic connectivity with uplands, the riparian system, and biogeochemical processing (Mayernik et al., in review; Sigler et al., 2018).

Section 2.2 Sample Collection

We sampled water from terrace aquifers, riparian aquifers, and stream channels. Terrace groundwater was sampled from hillslope springs in 2021 ($n = 3$) and hillslope springs and wells from 2012 to 2014 ($n = 51$, Sigler et al., 2022). We categorized terrace groundwater sites into ‘upper,’ ‘middle,’ and ‘lower’ areas (Figure 2b) to assess general variation in terrace groundwater character with elevation (SI section 1.2). We sampled riparian groundwater in 2021 from eight wells installed ca. 100 cm deep across the three reaches ($n = 19$; SI section 1.2). Riparian well locations were selected to span variation in biogeochemical potential relative to proximity to surface water features. We sampled stream water from turbulent locations in the channel presumed to be a well-mixed representation of stream flow at upstream and downstream

ends of each study reach in 2021. The mid-Louse reach is approximately 4-km downstream of the upper-Louse reach (Figure 2b), allowing for comparison of corridors with differing proximity to the origin of perennial flow. We also report data from samples collected from 2012 to 2014 at locations along Louse and Porter Creek downstream of the 2021 reach sites ($n = 42$; Sigler et al., 2022b) (Table S1). The Kolin site in Louse Creek was approximately 17-km downstream of the mid-Louse reach (Figure 2b) and the Porter311 site in Porter Creek was approximately 4-km downstream of Porter reach, just off the terrace eastern boundary.

We sampled at times selected to represent seasonal or interannual variation in hydrologic connectivity among terrace aquifers, riparian aquifers, and stream channels. At the time of sampling, we measured dissolved oxygen (DO), temperature, specific conductance, and pH using a Professional Plus Quatro multiparameter probe (YSI Incorporated, Yellow Springs, Ohio; Table S2). We calibrated each sensor for each sampling campaign per user manual specifications (SI section 1.2).

All samples were collected using a peristaltic pump (Geotech Environmental Equipment, Denver, Colorado), through a pre-rinsed 0.45- μm capsule filter (Geotech Environmental Equipment, Denver, Colorado). When possible, water was purged from groundwater well casings and allowed to recover three times before sample collection. If the capacity of the sampling pump was insufficient to purge groundwater in more transmissive aquifers ($n = 5$ of 8), we monitored DO concentrations continuously while pumping and collected samples when DO stabilized. For wells in less transmissive aquifers, a representative *in situ* DO for groundwater was not reported because a stable DO concentration could not be measured before the well casing was pumped dry.

Samples were collected into 60-mL HDPE vials with headspace for nitrate and sulfate concentration and isotopic analyses. All vials were rinsed three times with filtered sample water before filling. Duplicates were collected as water volume allowed. Samples were kept on ice during transport to Montana State University and stored in a refrigerator between 2°C and 4°C or frozen prior to analysis.

Section 2.3 Solute Concentration Analysis

Samples were analyzed for solute concentrations at the Montana State University Environmental Analytical Laboratory (EAL), Bozeman, Montana. We analyzed nitrate (Lachat QuickChem 8500) within two weeks of sample collection. The nitrate analytical method does not distinguish nitrate from combined nitrate and nitrite. Nitrite was assumed negligible based on occasional analyses (Lachat QuickChem 8500), so we report results as nitrate-N. Sulfate (Dionex Thermo Scientific ICS-2100) was analyzed within one year of sampling. Repeated measurements of an environmental groundwater working standard through each instrument run provided estimates of analytical uncertainty for all solutes (EAL unpublished data). Results for analytical working standards inform reported uncertainties in sample results, which were generally < 10% for all analytes (detail on uncertainties and limits of detection in Table S2).

Section 2.4 Isotopic Composition Analysis

Water samples collected in 2021 were analyzed for isotopic compositions of nitrate (nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) and sulfate (sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$) at the Environmental Isotope Laboratory (EIL; University of Waterloo). Prior to analysis, samples were stored in 60 mL HDPE vials and frozen within 48 hours of collection. Water samples collected from 2012 to 2014 were analyzed only for nitrate- $\delta^{15}\text{N}$ and nitrate- $\delta^{18}\text{O}$ at Woods Hole Oceanographic

Institution (data reported previously in Sigler et al., 2022). All samples were analyzed for water $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values (SI section 1.3) (Mayernik et al., 2024; Sigler et al., 2022). Isotopic ratios (e.g., $^{15}\text{N}:^{14}\text{N}$, $^{34}\text{S}:^{32}\text{S}$, $^{18}\text{O}:^{16}\text{O}$) are translated to a δ value, which is the relative deviation of the observed (*obs*) isotopic ratio (*R*) from an accepted standard (*std*) in per mil, ‰ ($\delta = [(R_{obs} - R_{std})/R_{std}] \cdot 1000\text{‰}$).

Isotopes of nitrogen were normalized to the isotope value of the global standard N_2 pool in the atmosphere (AIR), as the most abundant source of N_2 (Sharp, 2017). Isotopes of sulfur were normalized to the isotope value of the global standard of Cañon Diablo Troilite (VCDT), a meteorite found at Meteor Crater, Arizona, USA (Sharp, 2017). The global standard for normalizing isotopes of oxygen is the ocean (Vienna Standard Mean Ocean Water, VSMOW) (Craig, 1961; Dansgaard, 1964).

Both analyses for nitrate- $\delta^{15}\text{N}$ and nitrate- $\delta^{18}\text{O}$ used a cadmium catalyst converted nitrate to nitrite, which was followed by a chemical conversion to nitrous oxide (McIlvin & Altabet, 2005; Spoelstra et al., 2014). Nitrous oxide was analyzed for nitrate- $\delta^{15}\text{N}$ and nitrate- $\delta^{18}\text{O}$ using an Isoprime Trace Gas continuous flow mass spectrometer (GV Instruments Ltd., Manchester, United Kingdom). Two certified United States Geological Survey (USGS) standards (USGS 34 and USGS 35, values shown in Table S3) and one lab working standard (EIL EGC 17) were used as calibration standards for normalization. Reported uncertainties were $\pm 0.5\text{‰}$ for nitrate- $\delta^{15}\text{N}$ and $\pm 1\text{‰}$ for nitrate- $\delta^{18}\text{O}$ (EIL; University of Waterloo).

Sulfate was precipitated from water samples as barium sulfate and combusted for sulfate- $\delta^{34}\text{S}$ analysis using a 4010 Elemental Analyzer (Costech Instruments, Italy) coupled to a precisiON continuous flow isotope ratio mass spectrometer (Elementar Americas, USA). Sulfate

precipitate underwent pyrolysis combustion to gas for sulfate- $\delta^{18}\text{O}$ analysis using an Elementar Vario Pyro Cube elemental analyzer coupled to an Isoprime continuous flow isotope ratio mass spectrometer (GV Instruments Ltd., United Kingdom). Three certified International Atomic Energy Agency (IAEA) standards (IAEA SO-5, IAEA SO-6, and NBS-127; Table S3) were used to correct sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ to BaSO_4 for normalization. Reported uncertainties were $\pm 0.3\text{‰}$ for sulfate- $\delta^{34}\text{S}$ and $\pm 0.3\text{‰}$ for sulfate- $\delta^{18}\text{O}$ (EIL; University of Waterloo).

Section 2.5 Mixing, Production, and Loss Analysis

We developed relatively simple models of mixing and fractionation effects of loss to constrain the potential processes generating the observed patterns in concentrations and isotopic compositions of nitrate and sulfate in stream corridors. These models were designed to account for riparian production, mixing with upland inputs, and fractionating effects of losses in describing the observed differences among upland groundwaters, riparian groundwaters, and stream waters (Figure 1).

2.5.1 Stream Corridor Analysis

We first assumed the stream corridor system acted as an open, well-mixed reservoir that was operating under steady-state flow-through conditions in processing terrace groundwater inputs before export as stream water (Figure 1). We assumed processes affecting gains and losses of solutes within the mixed reservoir were riparian production (local generation due to weathering or mineralization) and biogeochemical losses (microbial metabolism or mineral precipitation). Conservation of mass in the steady-state solute budget for a given period of time balances the mass inputs (M_{in}) defined by contributions from terrace groundwaters (M_t) and

riparian production (M_p) with the mass outputs (M_{out}) defined by the sum of irreversible biogeochemical loss (M_l) and export to the stream (M_s).

$$M_{in} = M_t + M_p = M_{out} = M_l + M_s \quad (1)$$

Derivation of isotopic mixing models were facilitated by considering the mass inputs and outputs as fractions of the total input, where the fraction of the inputs associated with terrace groundwater (f_{terr}) and riparian production (f_p) must sum to one.

$$f_t + f_p = \frac{M_t}{M_{in}} + \frac{M_p}{M_{in}} = 1 \quad (2)$$

Fractional losses are similarly derived based on outputs to biogeochemical loss (f_l) or stream water (f_s), recognizing that these fractions must also sum to one.

$$f_l + f_s = \frac{M_l}{M_{in}} + \frac{M_s}{M_{in}} = 1 \quad (3)$$

The isotopic composition of the mass inputs (δ_{in}) and outputs (δ_{out}) are thus defined by mixing models:

$$\delta_{in} = f_p \cdot \delta_p + f_t \cdot \delta_t \quad (4a)$$

$$\delta_{out} = f_l \cdot \delta_l + f_s \cdot \delta_s \quad (4b)$$

where δ_t is the isotopic composition of the terrace inputs, δ_p is the isotopic composition of riparian production, δ_l is the isotopic composition of the biogeochemical loss, and δ_s is the isotopic composition of the mass remaining in the mixed reservoir and exported to the stream. To conserve mass of individual isotopes in a model assuming steady-state isotopic composition, the isotopic composition of inputs must equal that of outputs.

$$f_p \cdot \delta_p + f_t \cdot \delta_t = f_l \cdot \delta_l + f_s \cdot \delta_s \quad (4c)$$

For sulfate, observations suggest riparian production of shale-derived weathering products distinct from terrace groundwater contributions, with relationships between sulfate concentration and sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ dominated by mixing processes that differed by reach, with limited fractionating effects of loss. Therefore, we applied equation 4a to the stream corridors to evaluate the assumption that δ_l and C_l are negligible and assess the influence of mixing processes on exported stream water. We interpreted the highest sulfate concentration samples as reflecting δ_{in} close to the expected δ_p because their corresponding sulfate- $\delta^{34}\text{S}$ resembled expected values for Cretaceous age marine shale (Claypool et al., 1980; Van Stempvoort et al., 2023). Assuming these samples also contained constant terrace groundwater contributions, we used observed δ_t and C_t to calculate f_p and δ_p . We executed separate mixing models for Porter and Louse creeks because their high sulfate- $\delta^{34}\text{S}$ values had very different concentrations. For Louse Creek we executed two mixing models for high and low sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values to infer potential effects of fractionation from mineral precipitation on the riparian sulfate pool. The resulting mixing relationships were consistent with observed signals, improving our confidence in the accuracy of the mixing model.

For nitrate, observations indicated that fractionating effects of loss were not negligible, so we used the isotopic change between the terrace aquifer and the stream channel to infer riparian losses relative to gains. In the open, mixed reservoir, stream water isotopic value is a function of the apparent isotopic effect (ϵ_a), input composition (δ_{in}), and the mass exported to the stream (f_s) parallel to Denk et al. (2017) equation 14 for an open system under steady-state conditions:

$$\delta_s = \epsilon_a \cdot f_s + (\delta_{in} - \epsilon_a) \quad (5a)$$

We refer to ϵ_a as an apparent isotopic effect because of its inference from observations that likely reflect more than one mechanism of fractionating effects of loss (Houlton et al., 2006).

$$\epsilon_a = \frac{\delta_s - \delta_{in}}{f_l} \quad (5b)$$

To be comparable to our field data, these models of riparian function need to reflect patterns in concentration rather than mass. Based on previous work (Mayernik et al., 2024; Sigler et al., 2018), we assume the effects of evapotranspiration are negligible relative to the flow through the riparian system and the streams are exclusively gaining water from the terrace aquifer. Thus, the volume of water in the stream is approximately equal to the volume of contributions from the terrace. With this assumption, equation 5 can be rewritten in terms of concentration using $f_s = \frac{C_s}{C_{in}}$, where C_s is the solute concentration exported to the stream ($\frac{M_s}{V_s}$) and C_{in} is the solute concentration resulting from the addition of riparian production of mass to terrace groundwater ($\frac{M_t + M_p}{V_t}$).

$$\delta_s = \epsilon_a \frac{C_s}{C_{in}} + (\delta_{in} - \epsilon_a) \quad (6)$$

This derivation suggests that the open mixed volume scenario would generate a linear relationship between δ_s and C_s , where the slope of that relationship would be $\frac{\epsilon_a}{C_{in}}$. With this derivation we can use equation 6 with a given apparent isotopic effect, ϵ_a , to infer C_{in} from an observed linear relationship in field data, where stream samples reflect terrace water that has spent varying amounts of time in the riparian system. Using the inferred C_{in} , we then calculate C_p contributed by riparian production based on field data estimates of terrace inputs, C_t .

To constrain the total input nitrate concentration to the stream corridor, we applied equation 6 to nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values as functions of nitrate concentration and used the 95%

confidence intervals in the estimate of the slope relative to an isotopic effect with a minimum of -40‰ and a maximum of -10‰ (Denk et al., 2017). We only considered values of $C_{in} \geq C_t$ as physically feasible realizations because of the upland source for water in these stream corridors. We used these estimates of C_{in} to derive f_t and f_s using C_t and C_s , assuming constant volume, to be able to solve equation 4c and estimate δ_p , recognizing that $\delta_l = \delta_s + \epsilon_a$. We also determined C_l from equation 4b, C_s , and C_{in} to assess the mass loss relative to mass produced. We generated a Monte Carlo ensemble using the open, mixed reservoir and mixing models to estimate contributions of riparian produced nitrate δ_p and C_p across different plausible combinations of ϵ_a and C_{in} values, and thus different potential stream corridor biogeochemical behaviors.

We executed 35,000 realizations of the Monte Carlo ensemble. Each realization randomly selected an ϵ_a value from a uniform distribution constrained by literature values and the isotopic effect with no contribution of riparian production to total input concentration (i.e., $C_{in} = C_t$ in $\epsilon_a = m \cdot C_{in}$, where m is the empirically observed slope; Table 1). Each realization also selected a stream water nitrate concentration from a uniform distribution between the maximum and minimum observed values in Louse Creek from 2012 to 2021 because of the exclusively diffuse subsurface flow through these riparian systems. We derived the corresponding stream water nitrate- $\delta^{15}\text{N}$ value for each realization using a slope and intercept pair randomly selected from a Monte Carlo ensemble of linear regressions for stream water nitrate- $\delta^{15}\text{N}$ versus nitrate concentration. This Monte Carlo ensemble consisted of 5,000 realizations to propagate standard error of the slope and intercept calculated from the observed linear relationship in field data from the stream. We used a constant terrace groundwater nitrate- $\delta^{15}\text{N}$ value and nitrate concentration

because we expected negligible variation with the aquifer residence time of ca. 20 years (Sigler et al., 2018).

2.5.2 Riparian Flow Path Analysis

Based on observed patterns, we conceptualized the solute concentrations and isotopic compositions from discrete samples of riparian groundwater as reflecting relatively isolated locations along subsurface flow paths (Figure 1 inset). These flow paths are integrated into the open, well-mixed reservoir model for the bulk effect of the riparian aquifer on export to the stream but require application of a closed system model to understand specific flow path dynamics. We therefore used a Rayleigh closed system model to assess plausible riparian groundwater isotopic transformation of nitrate-N and O and sulfate-S and O.

$$\delta_r = \epsilon_R \cdot \ln f_r + \delta_s \quad (7a)$$

$$\delta_r = \epsilon_R \cdot \ln \frac{C_r}{C_s} + \delta_s \quad (7b)$$

Based on observed patterns in riparian samples relative to stream water, and because the stream reflects the mass remaining in the mixed reservoir, we assumed δ_s and C_s as the input to individual riparian flow paths that undergo irreversible fractionating loss (ϵ_R), where δ_r and C_r reflect the mass remaining in the riparian flow path. We therefore interpret riparian groundwater results as demonstrating different degrees of Rayleigh fractionation in the isotopic composition of the residual solute mass within water having traveled various distances along closed flow paths.

We applied equation 7b with $\epsilon_{R,N}$ constrained by literature values from -40‰ to -10‰ (Denk et al., 2017) to infer the effects of microbially-mediated nitrate reduction on riparian nitrate- $\delta^{15}\text{N}$ values. In this application, we used δ_s and C_s values from the maximum and

minimum Louse Creek stream water nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values and corresponding nitrate concentration from 2021 to correspond with when riparian groundwater was sampled. To estimate $\epsilon_{\text{R,O}}$ of nitrate- $\delta^{18}\text{O}$ values corresponding with $\epsilon_{\text{R,N}}$ values, we used C_{in} determined from nitrate- $\delta^{15}\text{N}$ relationships with the slope determined by the linear regression of nitrate- $\delta^{18}\text{O}$ values with nitrate concentration. We assessed the ratio between these paired isotopic effects ($\epsilon_{\text{R,N}} : \epsilon_{\text{R,O}}$) as the slope of the linear relationship between nitrate- $\delta^{15}\text{N}$ and nitrate- $\delta^{18}\text{O}$ to further evaluate the potential for closed system processes to contribute to riparian solute loss.

To explore the plausible fractionation effects of microbially-mediated sulfate reduction, we applied equation 7b with $\epsilon_{\text{R,S}}$ constrained by literature values from -40‰ to -15‰ for sulfate- $\delta^{34}\text{S}$ (Claypool et al., 1980) and with $\epsilon_{\text{R,O}}$ from -10‰ to -4‰ for sulfate- $\delta^{18}\text{O}$ (Holser et al., 1979; Lloyd, 1968). In this application, we used δ_s and C_s values for the minimum observed sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in the upper-Louse stream water from 2021 because these values appear to best explain the limited riparian groundwater samples that suggest fractionation effects of loss.

We applied equation 7b to assess $\epsilon_{\text{R,S}}$ of mineral precipitation (*sensu* Ewing et al., 2008) to infer the potential for gypsum formation along flow paths to influence the isotopic composition of groundwater samples that consistently showed high sulfate concentrations (Mayernik et al., in review). The potential for sulfate mineral precipitation was reinforced by observations of white precipitates in evaporites at the Louse field sites. In this application, we used δ_p and C_p values calculated from mixing relationships above as the input values and riparian groundwater from mid-Louse to define a sequence of δ_r and C_r along a conceptualized precipitation flow path (Figure 1a). We assessed the slope of the linear relationship between

sulfate- $\delta^{34}\text{S}$ and sulfate- $\delta^{18}\text{O}$ as the ratio between the two precipitation fractionation factors ($\epsilon_{\text{R,S}}; \epsilon_{\text{R,O}}$) to further evaluate the possibility that closed system precipitation processes contributed to riparian observations.

Results

Section 3.1 Nitrate Concentration and Isotopic Composition

Across all sites where samples were analyzed for nitrate isotopic composition, terrace groundwater consistently had low nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values with high concentrations. The highest concentration observed across all sites was measured at an upper terrace groundwater site with a value of 32 mg N L^{-1} (Table 2). The lowest concentration observed across terrace groundwater sites (14.3 mg N L^{-1}) was also observed at an upper terrace groundwater site. The nitrate- $\delta^{15}\text{N}$ values for terrace groundwater ranged from $+2.42\text{‰}$ to $+6.53\text{‰}$, and the corresponding nitrate- $\delta^{18}\text{O}$ values ranged from -5.15‰ to -2.63‰ (Figure 3, Table 2). The mean concentration for observed terrace groundwater was 21.9 mg N L^{-1} , with mean values of $+3.76\text{‰}$ for nitrate- $\delta^{15}\text{N}$ and -3.97‰ for nitrate- $\delta^{18}\text{O}$. The isotopic composition of nitrate observed in terrace groundwaters was relatively consistent compared to the variation in nitrate isotopic composition in riparian groundwaters, where sites for riparian groundwater had nitrate- $\delta^{15}\text{N}$ values that ranged from $+6.1\text{‰}$ to $+39.7\text{‰}$ and nitrate- $\delta^{18}\text{O}$ values that ranged from -1.12 to $+14.6\text{‰}$.

Nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in riparian groundwaters were consistently greater than those of terrace groundwater and stream water. Relative to all sites, the riparian wells sampled at Porter had the greatest range of observed nitrate- $\delta^{15}\text{N}$ values ranging from $+6.1\text{‰}$ to $+39.1\text{‰}$

and nitrate- $\delta^{18}\text{O}$ values ranging from -1.12‰ to $+14.6\text{‰}$, with nitrate concentrations ranging from 1.17 to 14.4 mg N L $^{-1}$ (Table 2). Nitrate concentrations measured in upper-Louse riparian groundwaters were consistently less than or equal to 5.0 mg N L $^{-1}$ (Figure 3) and exhibited a range in nitrate- $\delta^{15}\text{N}$ values from $+14.5\text{‰}$ to $+39.7\text{‰}$ and $\delta^{18}\text{O}$ values from $+2.76\text{‰}$ to $+11.8\text{‰}$. Nitrate concentrations measured in mid-Louse riparian groundwaters were too low (< 0.05 mg N L $^{-1}$) for reliable analysis of isotopic composition. Riparian groundwater had consistently low DO concentrations (from 0.4 to 3.5 mg L $^{-1}$) across all sites where it could be reliably measured (Figure S1), which were lower than those observed in terrace groundwater and stream water (ca. 7 to 17 mg L $^{-1}$).

Stream water at the upper- and mid-Louse reaches showed similar nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values. Upper-Louse stream water nitrate- $\delta^{15}\text{N}$ values ranged from $+3.91\text{‰}$ to $+12.3\text{‰}$ and nitrate- $\delta^{18}\text{O}$ values ranged from -3.37‰ to $+1.66\text{‰}$ (Figure 3; Table 2). Mid-Louse stream water nitrate- $\delta^{15}\text{N}$ values ranged from $+6.42\text{‰}$ to $+9.62\text{‰}$ and nitrate- $\delta^{18}\text{O}$ values ranged from -2.08‰ to -1.12‰ . Compared to the stream water of the Louse Creek reaches, stream water at Porter Creek had lower and more consistent nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values, with nitrate- $\delta^{15}\text{N}$ ranging from $+2.76\text{‰}$ to $+4.11\text{‰}$ and nitrate- $\delta^{18}\text{O}$ ranging from -4.65‰ to $+3.16\text{‰}$, similar to terrace groundwater. Nitrate- $\delta^{15}\text{N}$ values in Porter reach stream water and the downstream Porter Creek site remained relatively consistent across seasonal and annual timescales (Figure S3).

The open, mixed reservoir model (eq. 5) fit to the approximately linear relationship of nitrate- $\delta^{15}\text{N}$ and concentration values of stream water had slope of $-0.37 \pm 0.03\text{‰}$, constraining an estimate of the ratio of the apparent isotopic effect ϵ_a to the concentration of total inputs ($m = \frac{\epsilon_a}{C_{in}}$; Figure 3b). Considering a potential range of ϵ_a from -40‰ to -10‰ based on

literature values for nitrogen loss processes, we calculated a range of potential C_{in} (terrace groundwater concentration with added mass from riparian production) from 25.0 to 117 mg N L⁻¹. The minimum C_{in} estimate from this exercise is within the range of concentrations observed directly in terrace groundwater (Table 2). Linear regression of nitrate- $\delta^{18}\text{O}$ and nitrate concentration values resulted in a slope of $-0.22 \pm 0.03\text{‰}$ (Figure 3c). Based on this slope, the potential range of C_{in} values calculated from the nitrate- $\delta^{15}\text{N}$ model suggest potential isotopic effects for nitrate- $\delta^{18}\text{O}$ range from -30‰ to -5‰ ($\epsilon_a = m \cdot C_{in}$).

We assessed potential closed system Rayleigh models of riparian groundwater isotopic composition versus concentration based on the same range of fractionation effects assumed for the open, mixed reservoir model. For δ_s and C_s in this model, we used stream water results from Louse Creek in 2021 (Table S4). We used the minimum nitrate- $\delta^{15}\text{N}$ observed of $+5.26\text{‰}$, with the corresponding nitrate- $\delta^{18}\text{O}$ of -2.77‰ and $C_s = 8.14 \text{ mg N L}^{-1}$; and the maximum nitrate- $\delta^{15}\text{N}$ observed of $+9.62\text{‰}$ with nitrate- $\delta^{18}\text{O} = -1.12\text{‰}$ and $C_s = 3.07 \text{ mg N L}^{-1}$ (Figure 3). The closed system models simulate the general shape of the relationship of isotopic composition to concentration necessary to explain our observations in riparian groundwaters.

Section 3.2 Sulfate Concentration and Isotopic Composition

Terrace groundwater generally had low sulfate concentrations, high sulfate- $\delta^{34}\text{S}$ values, and low sulfate- $\delta^{18}\text{O}$ values distinct from stream corridor results. Across all samples, groundwater at the lower terrace site had the lowest sulfate concentration of 10 mg S L^{-1} , the second highest sulfate- $\delta^{34}\text{S}$ value of -7.37‰ , and the lowest sulfate- $\delta^{18}\text{O}$ value of -2.46‰ (Figure 4). Sulfate composition of the two groundwater samples at the middle terrace site was

slightly increased relative to the lower site, with sulfate- $\delta^{34}\text{S}$ from -12.3‰ to -11.9‰ , sulfate- $\delta^{18}\text{O}$ from -2.08‰ to -1.51‰ , and concentrations from 13.4 to 12.3 mg S L⁻¹.

Riparian groundwater sites at upper-Louse had the greatest range in sulfate- $\delta^{34}\text{S}$ values, from -19.3‰ to -3.15‰ . Riparian groundwater sites at the mid-Louse reach consistently had the lowest sulfate- $\delta^{34}\text{S}$ values (from -23.0‰ to -18.4‰) and had higher sulfate concentrations (from 71.3 to 138 mg S L⁻¹). Sulfate- $\delta^{34}\text{S}$ values in riparian groundwater sites at Porter ranged from -19.2‰ to -11.9‰ . Sulfate- $\delta^{18}\text{O}$ values had the greatest range in riparian groundwater across reaches, ranging from -0.47‰ to $+5.98\text{‰}$ (Figure 4a; Table 2). In riparian groundwater of the upper- and mid-Louse reaches, higher sulfate- $\delta^{34}\text{S}$ values corresponded with higher sulfate- $\delta^{18}\text{O}$ values and sulfate concentrations, while riparian groundwater at the Porter reach had lower sulfate- $\delta^{34}\text{S}$ values with higher sulfate- $\delta^{18}\text{O}$ values (Figure 4a). Upper-Louse was the only reach that showed high sulfate- $\delta^{34}\text{S}$ and high sulfate- $\delta^{18}\text{O}$ with lower concentrations in riparian groundwater (Figure 4b, 4c). Mid-Louse was the only reach that showed higher sulfate- $\delta^{34}\text{S}$ values and higher sulfate- $\delta^{18}\text{O}$ values with higher concentrations in riparian groundwater (Figure 4b, 4c).

Sulfate- $\delta^{34}\text{S}$ values were similar in upper-Louse and mid-Louse stream waters, with consistent values from -16.8‰ to -16.4‰ for upper-Louse and from -17.7‰ to -15.8‰ for mid-Louse (Figure 4; Table 2). Upper-Louse stream water showed consistently higher sulfate concentrations (69.7 to 97.9 mg S L⁻¹) than mid-Louse (36.8 to 65.6 mg S L⁻¹) despite similar isotopic composition (Figure 4b and 4c). Porter stream water had the highest sulfate- $\delta^{34}\text{S}$ values, ranging from -8.59‰ to -7.61‰ , the lowest sulfate- $\delta^{18}\text{O}$ values from -2.34‰ to -1.89‰ with low sulfate concentrations from 10.3 to 11.6 mg S L⁻¹.

We calculated mixing models for mixtures of sulfate from terrace groundwater and to explore the potential for mixing with riparian produced sulfate (Figure 4). For Louse Creek, we performed two models with the middle terrace site and two riparian endmembers with different isotopic composition, reflecting recent weathering of marine shale-derived substrate or cycling through precipitation and dissolution processes. For the mixture weighted towards the high sulfate concentration (138 mg S L^{-1} ; Table S4) observed in mid-Louse riparian groundwater, isotopic values asymptote at sulfate- $\delta^{34}\text{S} = -19.0\text{‰}$ and sulfate- $\delta^{18}\text{O} = +6.78$. For the second mixture weighted towards the lowest sulfate- $\delta^{34}\text{S}$ value (-23‰) observed in mid-Louse riparian groundwater, the isotopic values asymptote at sulfate- $\delta^{34}\text{S} = -24.5\text{‰}$ and sulfate- $\delta^{18}\text{O} = +0.99\text{‰}$. For Porter Creek, we performed one mixing model with the lower terrace site and weighted the mixture towards the riparian groundwater site with the lowest sulfate- $\delta^{34}\text{S}$ value (-19.2‰). The mixture for Porter resulted in isotopic values asymptote at sulfate- $\delta^{34}\text{S} = -24.7\text{‰}$ and sulfate- $\delta^{18}\text{O} = +7.51\text{‰}$.

Closed system models for irreversible sulfate fractionating loss provided the general shape necessary to describe the pattern of isotopic composition versus concentration in riparian groundwater at upper-Louse, with slopes of $\epsilon_{\text{S}}: \epsilon_{\text{O}} = +4$ and $+3.5$; Figure 4a. The linear relationship between sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values from riparian groundwater in mid-Louse resulted in slope of $\epsilon_{\text{S}}: \epsilon_{\text{O}} = 0.85$ (Figure 4a). Additionally, in these samples, the closed system relationship (eq. 7) of sulfate- $\delta^{34}\text{S}$ and sulfate- $\delta^{18}\text{O}$ values with concentration resulted in ϵ_{S} of $+6.48\text{‰}$ (Figure 4b) and ϵ_{O} of $+7.26\text{‰}$ (Figure 4c).

Section 3.3 Simulating Isotopic Change

In order to explain the apparent isotopic effect of net nitrate loss in the Louse reaches, the Monte Carlo exploration of the range of riparian production conditions produced a range of δ_p from -55‰ to -10‰ . Model simulations showed that low magnitude apparent isotopic effects ($\epsilon_a > -10\text{‰}$) from fractionating loss could be associated with a large range of mass loss in the riparian (from 4 to 23 mg N L⁻¹) that corresponded with a lower range of mass produced in the riparian (from 0 to 5 mg N L⁻¹) (Figure 5a). A higher input of mass from riparian production required a higher magnitude apparent isotopic effect of loss ($\epsilon_a < -20\text{‰}$) for more mass loss.

The Monte Carlo ensemble suggested that negligible amounts of nitrate produced in the riparian groundwater allowed for a wide range of isotopic composition in that input to explain the observed differences between terrace and stream waters (Figure 5b). Increases in the N mass produced above ca. 10 mg N L⁻¹ required increasingly more negative isotopic composition of the riparian produced input as well as more negative apparent isotopic effects of loss ($\epsilon_a < -10\text{‰}$) to explain the behavior of the riparian system. The range of total N mass loss in the riparian system co-varied with total mass N produced, which ranged from 5 to ca. 55 mg N L⁻¹ (Figure 5c). The highest nitrate- $\delta^{15}\text{N}$ values ($-10\text{‰} \geq \delta_p \geq -14\text{‰}$) resulted from apparent isotopic effects of loss between ca. -10‰ and -15‰ (Figures 5b and 5c).

Discussion

In our study area, stream corridors promote production, loss, and mixing of nitrate and sulfate that are integrated into consistent changes in mass and isotopic composition despite ecosystem complexity. Stream corridors integrate the accumulated influence of agriculture

management practices, soil organic matter mineralization, and soil mineral weathering on the chemistry of terrace and riparian aquifers. Relatively simple models to assess mixing and isotopic fractionation effects generally explain the various processing pathways of N and S cycling facilitated by these stream corridors, allowing for more comprehensive understanding of complex stream corridor ecosystem functions that contribute to apparent isotopic effects and patterns in water quality.

Section 4.1 Weathering of Shale and Cultivation Practices Influence Supply of Nitrate and Sulfate to Stream Corridors

Observed terrace groundwater nitrate and sulfate likely included some contributions from weathering of shale-derived soils that combines with nitrate and sulfate from cultivated soils, reflecting organic matter mineralization and fertilizer application. For nitrate, influence of shale weathering was most evident in the upper terrace groundwater sites that had nitrate concentrations up to ca. 30 mg N L⁻¹ (Figure 3) (Mayernik et al., in review; Sigler et al., 2018), which was 10 mg N L⁻¹ higher than the average concentration across terrace sites. The range of observed nitrate- $\delta^{15}\text{N}$ values across all terrace sites (+2.4‰ to +6.5‰; Table 2) is comparable to expected values for mineralized N in soils (+3‰ to +5‰; Kendall & McDonnell, 1998; Sharp, 2017; Sigler et al., 2022) and to reported values for rock-water extracts from Cretaceous-age marine shales in Montana (Montross et al., 2013) and other areas of the United States (+2‰ to +8‰; Holloway & Dahlgren, 2002). In cultivated soils in our study area, nitrate from fertilizer application (nitrate- $\delta^{15}\text{N}$ ca. 0 ‰; Houlton & Morford, 2015; Kendall & McDonnell, 1998; Sharp, 2017) mixes with nitrate derived from organic matter mineralization (Sigler et al., 2022). This combination of sources leaches to the shallow terrace aquifers when nitrate supply exceeds

plant uptake and when water percolation outpaces root interception of nitrate. The higher nitrate concentrations in the upper terrace sites relative to the lower terrace and the consistency in nitrate- $\delta^{15}\text{N}$ values along with nitrate- $\delta^{18}\text{O}$ values (-5.1‰ to -2.6‰) across the terrace sites support the inference that contributions from shale-derived nitrate have similar isotopic composition to the combination of mineralized N from soil organic matter and synthetic N from fertilizer in cultivated soils.

Terrace groundwater sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values and concentrations indicate influence of agriculture management practices on cultivated soils with higher sulfate- $\delta^{34}\text{S}$ values and lower sulfate concentrations than expected for sulfate derived from weathering of marine shale. In the JRW, fertilizer applications of S occur at much lower rates and less consistently than those of N (e.g., 20 kg S ha^{-1} ; Miller et al., 2024, versus 110 kg N ha^{-1} ; John et al., 2017). Sulfate can have $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of -5‰ to $+12\text{‰}$ and 0 to $+20\text{‰}$, respectively, in fertilizer and 0 to $+8\text{‰}$ and 0 to $+5\text{‰}$, respectively, for mineralized soil organic matter (Jakóbczyk-Karpierz & Ślósarczyk, 2022; Krouse et al., 2000; Saka et al., 2024; Tuttle et al., 2009). Observed sulfate- $\delta^{34}\text{S}$ values in terrace groundwater (ca. -10‰) could reflect influence of fertilizer S and mineralized S sources that increased the sulfate- $\delta^{34}\text{S}$ values from the Cretaceous age marine shale signature (from -10‰ to -40‰ ; Claypool et al., 1980; Van Stempvoort et al., 2023). The higher observed sulfate- $\delta^{34}\text{S}$ values in terrace groundwater than expected for shale-derived sulfate and relatively low sulfate concentrations could also occur from a slow release of stabilized organic S through mineralization upon cultivation. In minimally disturbed grassland soils that have been relatively stable for thousands of years, the $\delta^{34}\text{S}$ values may have increased over time relative to the value at the onset of shale weathering, analogous to higher nitrate- $\delta^{15}\text{N}$

in soils relative to $\text{N}_2\text{-}\delta^{15}\text{N}$ of 0‰. Oxidation of sulfide is pH dependent, influenced by iron availability, and can be microbially-mediated, leading to variable incorporation of $\text{O}_2\text{-}\delta^{18}\text{O}$ (Van Stempvoort & Krouse, 1993). Assuming atmospheric $\text{O}_2\text{-}\delta^{18}\text{O}$ of +23‰ and high sulfate- $\delta^{18}\text{O}$ from sources discussed, observed sulfate- $\delta^{18}\text{O}$ values in terrace groundwater (ca. -2‰) suggest oxidation of sulfide that incorporated ambient soil water- $\delta^{18}\text{O}$ (Van Stempvoort & Krouse, 1993; Van Stempvoort et al., 2023), which ranged from -20‰ to -12.8‰ at these sites (Mayernik et al., 2024). Our observations likely reflect S cycling through a combination of recent shale weathering, soil organic matter mineralization, and fertilizer additions contributing to stream corridors.

Section 4.2 Influence of Stream Corridor Production and Loss on Nitrate Mitigation

Biogeochemical processes in stream corridors resulted in net loss of nitrate in streams relative to loading from the terrace aquifer (Mayernik et al., in review). Lower nitrate concentrations and higher nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values observed in riparian groundwaters relative to terrace groundwater (Figure 3) reflect reducing conditions in riparian areas (Hill et al., 2014; Naiman & Décamps, 1997; Ranalli & Macalady, 2010) that facilitate persistent fractionating loss. Calculated apparent isotopic effects of nitrate loss processes on nitrate- $\delta^{18}\text{O}$ (from -35‰ to -3.5‰) in the riparian system (Figure 3b and 3c) span the expected ranges for nitrate reduction (Granger et al., 2008), aerobic ammonia oxidation (Casciotti et al., 2010), and nitrification and/or annamox (Buchwald & Casciotti, 2010) that incorporate ambient riparian groundwater- $\delta^{18}\text{O}$ (ca. -20‰ to -14‰; Mayernik et al. 2024) and/or $\text{O}_2\text{-}\delta^{18}\text{O}$ (ca. $+23.5 \pm 1\text{‰}$ for atmospheric O_2). Consistently high nitrate- $\delta^{18}\text{O}$ values in riparian groundwater corresponded

with high nitrate- $\delta^{15}\text{N}$ values and were higher than those in terrace groundwater, providing evidence for consistent, irreversible, isotopic fractionating loss processes as the primary loss pathways (Denk et al., 2017; Granger & Wankel, 2016; Kendall & McDonnell, 1998). The higher nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values and low nitrate concentrations at specific sites in the riparian groundwater suggest varying influence of closed system conditions for parcels of water along subsurface flow paths (Figure 1 inset).

In stream water, the observed linear relationships between nitrate concentration and corresponding nitrate- $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values were consistent across space and time (Figure 3), indicating that physical constraints moderate solute exchange and mixing in the riparian areas to maintain consistent contributions to the stream channel. The consistent relationships do not change with the different modes of hydrologic connection between the stream channel and the terrace aquifer in Louse Creek versus Porter Creek. Rather, hydrologic connection appears to alter the relative magnitude of apparent isotopic effect expressed in the stream channel. Comparisons of Louse and Porter suggest that riparian function is similar between the reaches, but landscape position and geomorphic setting remain a primary control on how much the riparian system can alter water chemistry between uplands and streams.

Generation of Monte Carlo ensembles allowed for exploration of the range of potential nitrate contributions from riparian production and loss pathways to explain the observed changes in isotopic compositions between the terrace and stream waters. Patterns in the ensemble results (Figure 5) suggest that high levels of gross production and loss of nitrate require a higher-magnitude apparent isotopic effect of loss. Net losses composed of higher gross production and loss would also require values of nitrate- $\delta^{15}\text{N}$ from riparian production that are much lower

(< -10‰; Figures 5b and 5c) than would be expected from weathering of shale (+2‰ to +8‰; Holloway & Dahlgren, 2002) or mineralization of organic N (+3‰ to +5‰; Houlton & Morford, 2015; Kendall & McDonnell, 1998; Sharp, 2017; Sigler et al., 2022). The observed discrepancy in ensemble results from expected source values could indicate production of low nitrate- $\delta^{15}\text{N}$ from a process or suite of processes that remain poorly understood. For example, reversible loss processes (e.g., dissimilatory nitrate reduction to ammonium) likely also influence nitrate- $\delta^{15}\text{N}$ in stream corridors (Burgin & Hamilton, 2007), yet we have limited understanding of how these pathways might contribute to the apparent isotopic effect we observed (Denk et al., 2017).

The Monte Carlo ensemble also constrained the potential magnitudes of contributions from riparian production and loss processes, indicating higher gross loss than inferred from net changes in concentrations between the terrace and stream water (Figure 5). Ensemble results indicate a wide range of nitrate mass produced within the riparian systems (Figure 5) may contribute to the terrace groundwater inputs. Potential for riparian production of N implies that irreversible nitrate losses are likely higher than inferred from the net nitrate loss observed across most catchment-scale studies (Dwivedi et al., 2018; Harms & Grimm, 2008; Ranalli & Macalady, 2010; Sigler et al., 2022; Vidon et al., 2010). Diel and seasonal fluctuations of shallow groundwater tables in riparian areas (Burt et al., 2002; Duncan et al., 2015; Hefting et al., 2004) could produce periodic exposure of riparian substrate to oxygen that would promote nitrate production via mineralization and nitrification, increasing gross mass produced. This produced nitrate would then promote reduction processes when anoxic conditions return or are intercepted along flow paths (Bernhardt et al., 2017), increasing gross mass loss. Therefore, ensemble results may support dynamic cycling of N between reduced and oxidized states that

alter the isotopic composition prior to export to the stream channel. Our exploration of the riparian processing scenarios contributing to nitrate observations reinforces the need for continued research on the integration of multiple and connected production and loss processes (Houlton et al., 2006; Perakis et al., 2011) that explain the consistent apparent isotopic effect of net loss within these stream corridors.

Section 4.3 Stream Corridors Augment Sulfate with Weathering of Shale-Derived Alluvium and Limited Irreversible Losses

Evidence of riparian sulfate- $\delta^{34}\text{S}$ values consistent with weathering of marine-derived shale (Figure 4) suggests production of sulfate via sulfide oxidation. Sulfate- $\delta^{34}\text{S}$ produced from sulfide oxidation during shale weathering is thought to undergo limited S isotope fractionation (Claypool et al., 1980; Seal et al., 2000), and therefore should closely resemble the sulfide- $\delta^{34}\text{S}$ value from the geologic source. Sulfide oxidation incorporates surrounding water- $\delta^{18}\text{O}$ values into sulfate- $\delta^{18}\text{O}$ values, typically adhering to a range with a lower boundary of sulfate- $\delta^{18}\text{O}$ = water- $\delta^{18}\text{O}$ and an upper boundary of sulfate- $\delta^{18}\text{O}$ = water- $\delta^{18}\text{O}$ $\times$ 0.62 + 9 due to variable influence of O_2 - $\delta^{18}\text{O}$ of +23‰ (Saka et al., 2024; Van Stempvoort & Krouse, 1993). Therefore, previously observed ambient riparian groundwater- $\delta^{18}\text{O}$ values at these sites from -20‰ to -14‰, with evaporated riparian surface water ranging up to -3.8‰ (Mayernik et al., 2024), suggest an expected range of -20‰ to +6.6‰ for sulfate- $\delta^{18}\text{O}$ values, encompassing our observed values of -2‰ to +6‰, and supporting the contribution of ambient water to sulfide oxidation. The consistently higher sulfate- $\delta^{18}\text{O}$ values in riparian groundwater compared to terrace groundwater (Figure 4a,c) suggest that the circumstances of oxidation in riparian

substrate are distinct from those in terrace soils. Fluctuating shallow groundwater tables in riparian areas allow for incorporation of atmospheric O_2 - $\delta^{18}\text{O}$ of +23‰ in sulfide oxidation. The more frequent fluctuations between oxic and anoxic conditions in riparian areas compared to terrace soil water (Naiman & Décamps, 1997) could yield distinctly higher sulfate- $\delta^{18}\text{O}$ values in riparian groundwater, allowing for more influence of O_2 - $\delta^{18}\text{O}$ with surrounding groundwater- $\delta^{18}\text{O}$ (Van Stempvoort & Krouse, 1993) into the higher concentration of sulfate. Additionally, sulfide oxidation to sulfate may occur in areas where evaporated surface waters are prevalent, after which sulfate is transported along riparian flow paths to more anoxic sites in the riparian aquifer. Thus, sulfate results for riparian groundwater suggest sulfate from oxidation of sulfide with sulfide- $\delta^{34}\text{S}$ values reflecting marine shale and $\delta^{18}\text{O}$ values reflecting hydrologic flow paths through riparian substrate intercepting oxidizing and reducing conditions.

Pathways of exchange with ambient water- $\delta^{18}\text{O}$ during riparian oxidation processes to form sulfate may result in stream sulfate- $\delta^{18}\text{O}$ values lower than implied by mixing riparian with terrace groundwaters (Figure 4). Sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in Porter riparian groundwater, consistent with the influence of marine shale weathering observed in mid-Louse, had a corresponding concentration lower than sulfate with comparable isotopic composition at mid-Louse (Figure 4b and 4c). The Porter site patterns indicate that smaller fractions of water are chemically influenced by shale weathering than those of the Louse reaches, suggesting that abundant inflows from hillslope springs might obscure the relative contribution of sulfate inputs from weathering in this stream corridor.

While the range of sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in riparian groundwater suggests sulfide oxidation from shale weathering with evaporated waters and O_2 , patterns at the mid-Louse reach

suggest sulfate loss consistent with precipitation to gypsum ($\text{CaSO}_4\cdot 2\text{H}_2\text{O}$). The positive linear relationship between sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values at these sites (Figure 4a) and the nonlinear relationships between sulfate concentration and S and O isotopic compositions (Figures 4b and 4c) reflect patterns consistent with precipitation of $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$, which favors the heavier isotopes of S and O (Claypool et al., 1980; Ewing et al., 2008). Precipitation decreases sulfate concentration in solution, acting as a loss process. Field observations of white precipitates in evaporating water close to our sampling sites also supported the potential supersaturation of sulfate minerals. The linear relationship between the observed sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values in mid-Louse riparian groundwater (Figure 4a) had slope of $0.85 \pm 0.12\text{‰}$ which is remarkably similar to laboratory analyses of precipitation to $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ in closed batch reactors ($0.83 \pm 0.2\text{‰}$; Lloyd, 1968; Thode & Monster, 1965), supporting evidence of N processes that may reflect closed system riparian flow paths (Figure 1 inset). However, the closed system fractionation effects based on the relationships between observed sulfate concentration and $\delta^{34}\text{S}$ or $\delta^{18}\text{O}$ values ($+6.48\text{‰}$ and $+7.26\text{‰}$, respectively; Figures 4b and 4c) were much higher than those observed in laboratory settings ($+1.65 \pm 0.16\text{‰}$ and $+1.90 \pm 0.2\text{‰}$, respectively; Lloyd, 1968; Thode & Monster, 1963). These discrepancies may reflect cyclic sulfate precipitation and dissolution (Böttcher et al., 2001; D. E. Canfield et al., 1998).

In these stream corridors, iron monosulfide (FeS) precipitation is a likely intermediary in sulfate formation processes. We observed precipitation of FeS as black coatings adjacent to pooling water in areas where sulfate reduction was evident from the smell of hydrogen sulfide (Duball et al., 2020). Microbially-mediated sulfate reduction to sulfide (Claypool et al., 1980) results in low sulfide- $\delta^{34}\text{S}$ ($\epsilon_{R,Sr} - 40\text{‰}$ to -15‰), which formation of FeS can incorporate. Re-

oxidation of FeS to sulfate would thus contribute low sulfate- $\delta^{34}\text{S}$ without affecting sulfate- $\delta^{18}\text{O}$, providing additional support for observations of lower sulfate- $\delta^{34}\text{S}$ and higher sulfate- $\delta^{18}\text{O}$ in riparian groundwater relative to terrace groundwater, but not explaining the higher concentrations. Additional analyses of sulfide- $\delta^{34}\text{S}$ along with sulfate- $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values and bacterial functional groups could help constrain isotopic effects of intermediate processes contributing to the patterns we observed. Evidence of precipitation processes suggests that sulfide or sulfate can be retained in these corridors, serving as a temporary loss pathway that retains the precipitate while source materials are exported. The mid-Louse mixing scenarios derived from varying degrees of precipitation influence suggest that mineral precipitation and dissolution processes could modify the isotopic composition of sulfate that undergoes mixing processes.

Irreversible sulfate loss through microbially-mediated reduction pathways appeared limited. Some upper-Louse riparian groundwater values aligned with patterns reflecting irreversible fractionating loss (Figure 4) (Claypool et al., 1980; Lloyd, 1968), supporting the presence of closed system riparian flow paths contributing to the stream (Figure 1 inset). Sulfate- $\delta^{34}\text{S}$ values in stream water at upper-Louse deviated from the endmember mixing relationships (Figure 4b), suggesting that irreversible sulfate loss in riparian systems may contribute to stream water in this reach. Sulfate- $\delta^{18}\text{O}$ values at these same sites (Figure 4c) were inconsistent with irreversible fractionating loss and instead support re-oxidation of sulfide with ambient groundwater. The relatively limited irreversible sulfate loss patterns compared to nitrate losses indicate that conditions favoring these processes are spatially limited likely due to lower energetic favorability than microbially-mediated nitrate reduction processes (Hedin et al., 1998)

and S cycling through some combination of sulfate reduction, precipitation, and re-oxidation. Readily produced sulfate from shale weathering could also mask patterns indicating reduction processes. Sulfate isotopic effects reflect mixing of distinct endmembers and reversible fractionating loss from precipitation and dissolution processes unlikely to occur for N. Stream corridors integrate riparian flow paths undergoing multiple production and mostly reversible loss processes for sulfate, resulting in a relatively consistent mixture with net gains of sulfate exported to stream channels.

Section 4.4 Implications for Using Nitrate and Sulfate Isotopic Effects to Infer Stream Corridor Ecosystem Function

Assessment of sulfate in conjunction with nitrate clarifies contributions from bedrock weathering, despite less consistency of management practices for S fertilizer (Eriksen, 2009; Gerson & Hinckley, 2023). Our inferred contributions from riparian sulfate production ranged from 30 to 138 mg S L⁻¹ (Table 2). Based on previously observed estimates of nitrate to sulfate ratios in flow paths through shale-derived substrate (Brown et al., 1983; Miller et al., 1981), we can infer contributions of shale-derived nitrate concentrations ranging from 2 to 10 mg N L⁻¹. Thus, evidence of riparian produced sulfate supports likely contributions of nitrate from shale weathering in the riparian area.

Our work demonstrates how relatively simple mixing and fractionation models can simulate the general patterns of observed nitrate and sulfate isotopic change in complex stream corridors. Model results suggest that fractionating N loss likely masks substantial nitrate production in these stream corridors, and that riparian production likely results from multiple, related N cycling processes resulting in low nitrate- $\delta^{15}\text{N}$ values of produced nitrate (Figures 3

and 5). Observations showed riparian sulfate production was substantial and promoted clear mixing processes influenced by reversible loss through precipitation and dissolution that may influence the apparent riparian produced endmember (Figure 4). The hydrologic setting of our observations resulted in consistent *apparent isotopic effects* in stream corridors, allowing for model parameter constraints that improved our understanding of the multiple organism- and site-specific processes integrated into these observed effects.

Conclusions

These stream corridors facilitate dynamic cycling of solutes, revealed by isotopic compositions of nitrate and sulfate. Results indicate that both nitrate and sulfate are likely produced from weathering of shale-derived substrate within the riparian area. Sources of nitrate and sulfate undergo reversible and irreversible loss and re-oxidation processes. For nitrate, evidence of primarily irreversible loss along subsurface riparian flow paths reflects metabolic favorability in anoxic environments. Exploration of the range of isotopic compositions of riparian produced nitrate suggests that low nitrate- $\delta^{15}\text{N}$ values ($< -10\text{‰}$) result from processes that remain poorly understood. For sulfate, riparian production of sulfate from initial sulfide oxidation with shale weathering and subsequent cycling between aqueous and solid phases resulted in distinct isotopic compositions in riparian groundwater compared to terrace groundwater. Both nitrate and sulfate results suggest that these stream corridors are primed for biogeochemical cycling of N and S, but irreversible loss occurs primarily for nitrate. Variation in both nitrate and sulfate isotopic composition among riparian sites reflects heterogeneities in riparian substrate that promote closed system processing of a parcel of water moving along a flow path through oxic and anoxic conditions. Consistent relationships between solute

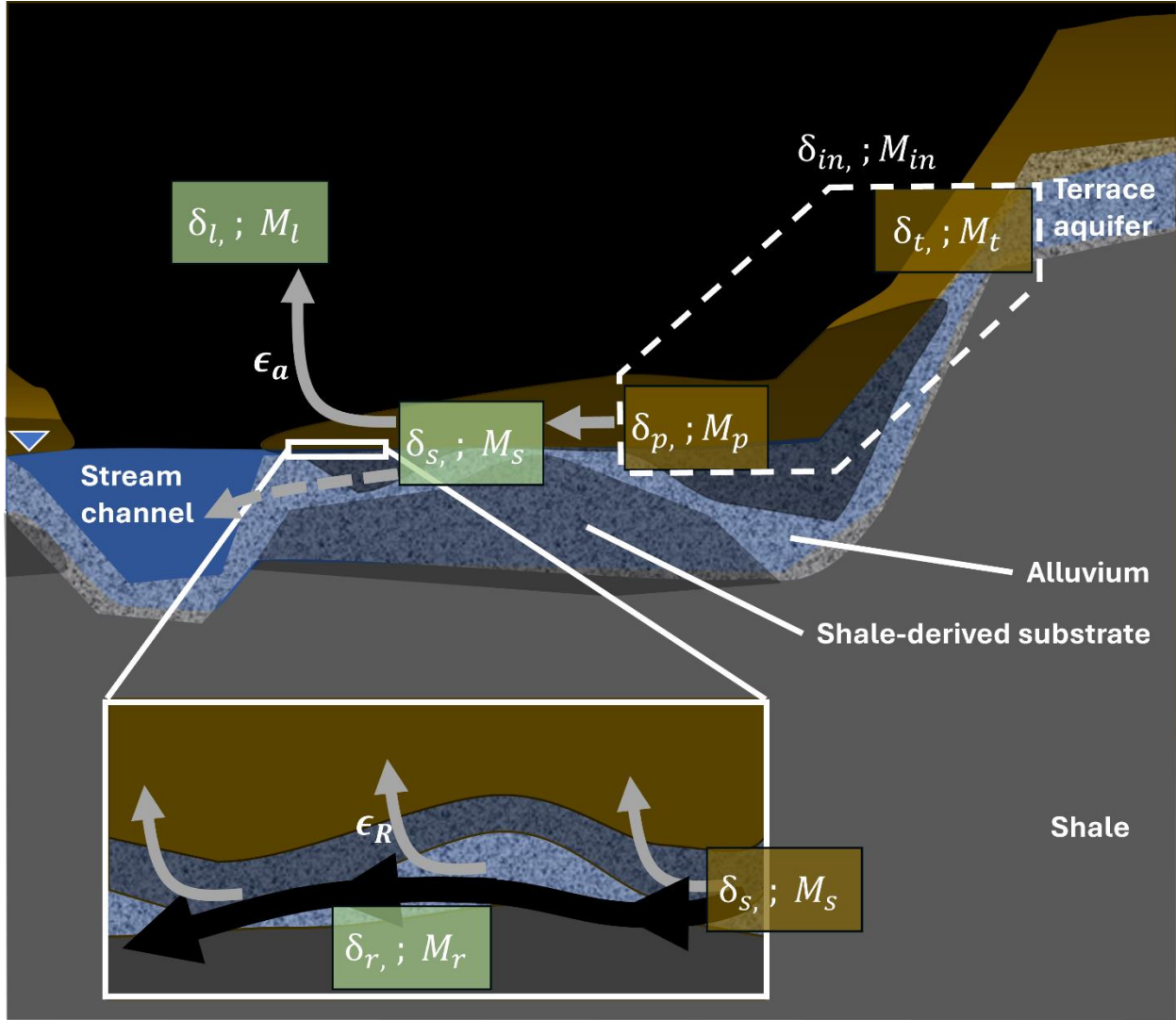
concentrations and isotopic compositions in stream water across time and space, and relative to terrace groundwater, reflect integration of multiple production and loss pathways moderated by hydrologic connection and geomorphic constraints. The systematics across these stream corridors incorporate multiple flow paths with varying degrees of closed and open system effects that produce strikingly consistent stream water geochemical and isotopic composition. This work emphasizes the need to constrain controls on catchment-scale apparent isotopic effects by evaluating additional processing pathways that likely contribute to patterns observed across stream corridor ecosystems.

Acknowledgements

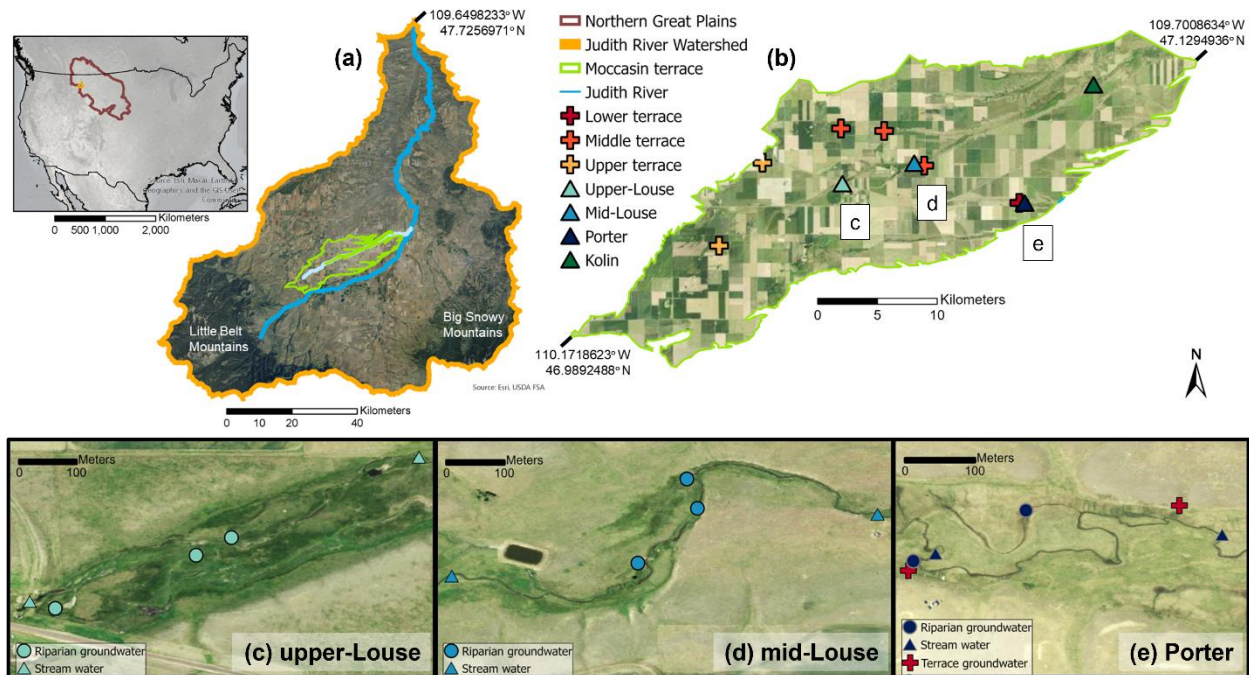
We thank Adam Sigler, Tobias Koffman, Zoe Durkin, Skye Keeshin, Madison Foster, Sean Williams, Madisynn Weber, Rachel Anderson, and Simon Fordyce for help with data collection, analysis, and technical assistance. We appreciate the use of data from the U.S. Bureau of Reclamation and the Montana Department of Agriculture. We thank anonymous reviewers for their time and constructive feedback. We are grateful for the funding that supported this work: USDA-ARS, Sustainable Soils for Healthy Communities and Climate Resilience in the Semi-Arid West (agreement # 58-3032-3-005); NSF EPSCoR, Consortium for Research on Environmental Water Systems (Cooperative Agreement OIA-1757351), Montana State University Grad School PhD Completion Grant (2024), the Montana State University Nielsen Pedology Graduate Research Fellowship (2021), the Montana Water Center Water Resource Fellowship (2023) and base funding (USGS 104b #G21AP10628-02), and the Montana Agricultural Experiment Station (project numbers MONB00364 and MONB00349) partially funded by USDA-NIFA. Any opinions, findings, and conclusions or recommendations expressed

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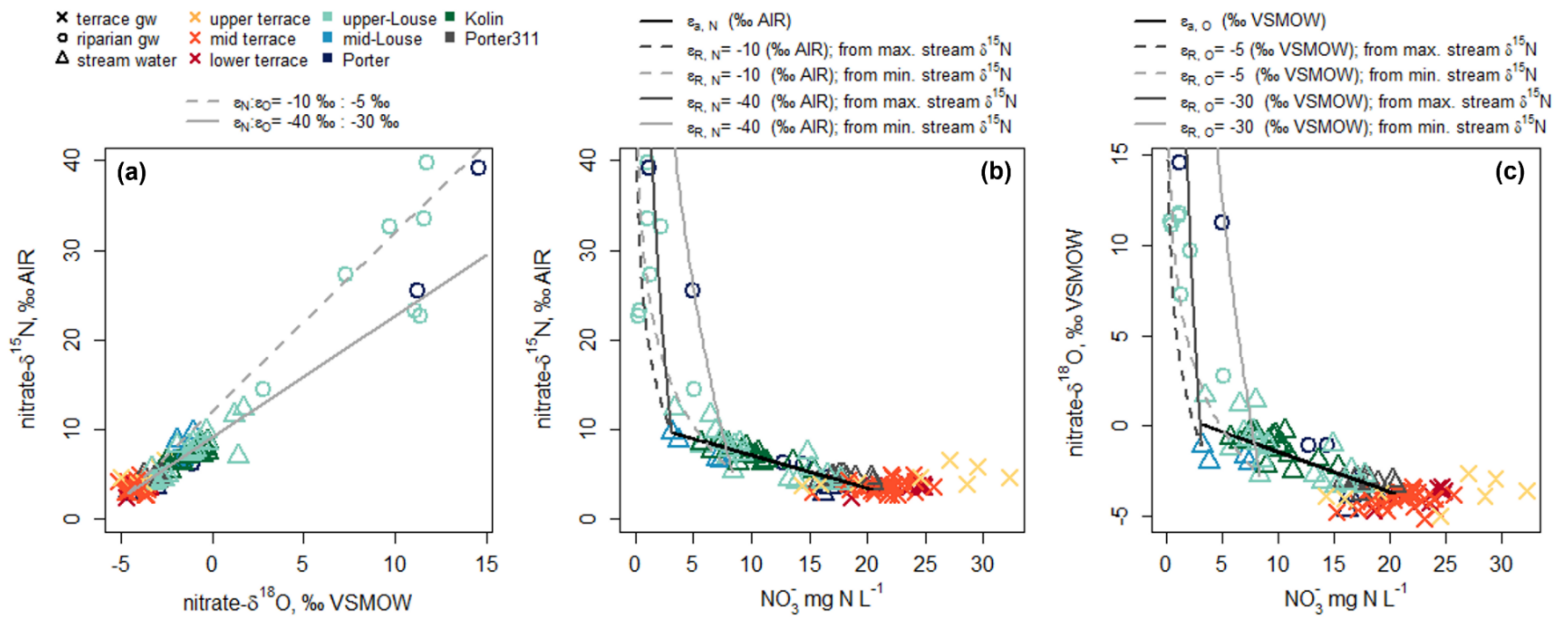
Figures



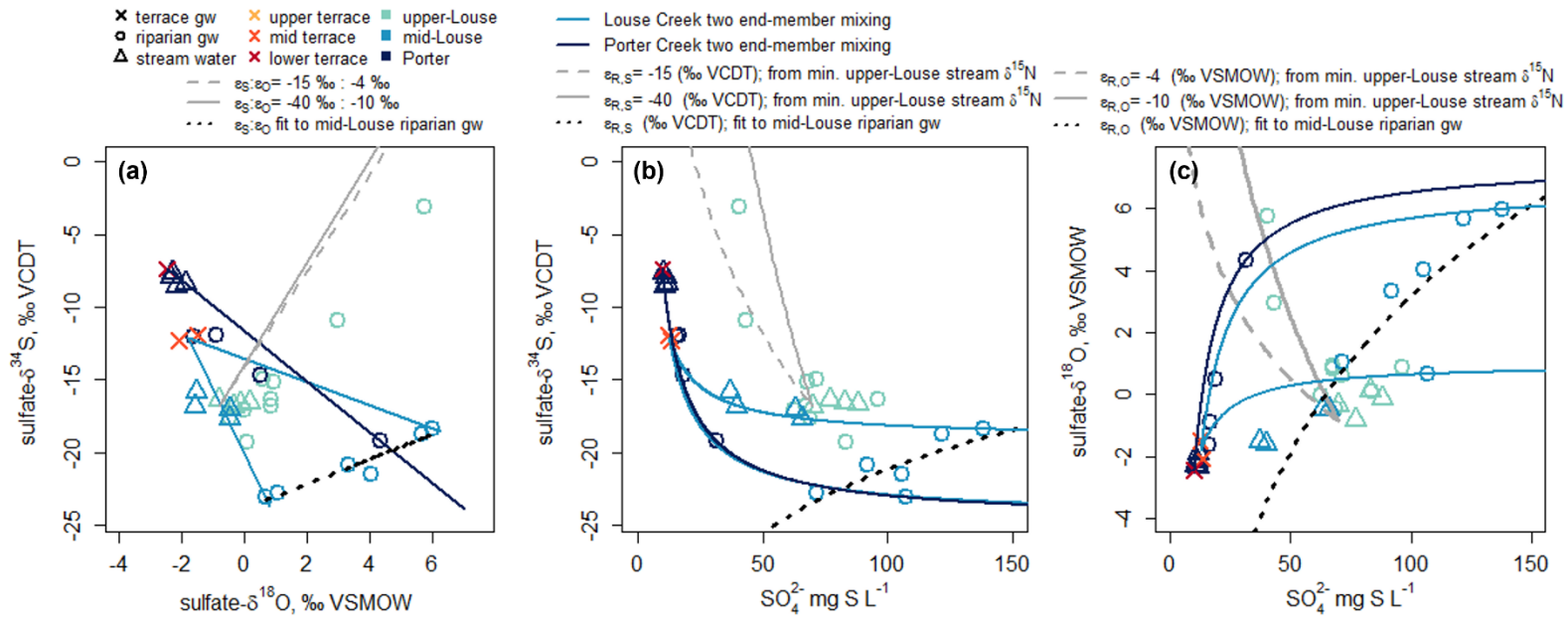
Ch.4-Figure 1. Conceptualization of riparian groundwater as an open, mixed reservoir under steady-state conditions processing mass (M) and isotopic composition (δ) of solutes in transit from terrace groundwaters to streams. Solute mass input to the reservoir M_{in} , δ_{in} includes loading from the terrace M_t , δ_t and local mass production from biogeochemical processes in the riparian substrate M_p , δ_p . Apparent isotopic effects ϵ_a from subsequent biogeochemical losses from the mixed reservoir of riparian groundwater M_l , δ_l determine the mass and isotopic composition of solutes remaining in the stream corridor M_s , δ_s and ultimately exported via the stream channel. Inset represents an alternative closed system conceptual model with Rayleigh-type fractionation associated with biogeochemical loss ϵ_R influencing mass and isotopic composition along riparian groundwater flow paths M_r , δ_r .



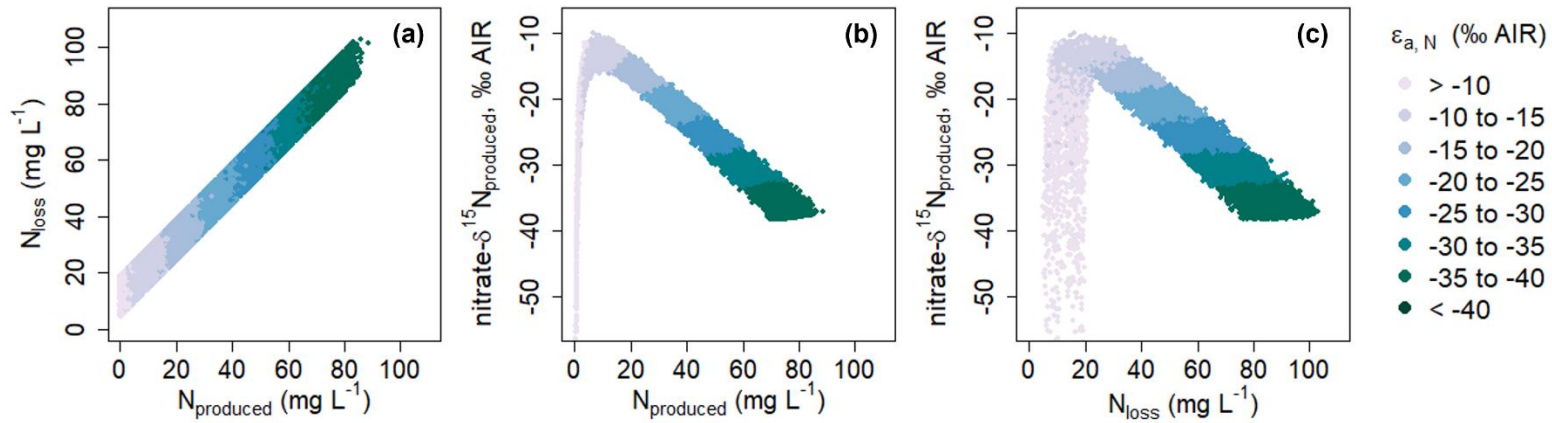
Ch.4-Figure 2. Maps and aerial imagery of the study area and sampling locations. (a) Map of the Judith River Watershed (JRW; orange outline), Montana, USA in the northern Great Plains ecoregion (NGP; maroon outline, inset). The focal area for this study is a terrace landform outlined in green. (b) Expanded map of the terrace with upland groundwater sampling locations (crosses) and study reach locations (triangles) along Louse and Porter creeks. (c-e) Sample site locations for riparian groundwater (circles) and stream water (triangles) along ca. 0.7-km (c) upper-Louse (d) mid-Louse and (e) Porter creek reaches. Data sources for the maps include: ESRI, USDA, USGS, FSA; NGP boundary obtained from World Wildlife Fund.



Ch.4-Figure 3. Comparisons of nitrate isotopic compositions and concentrations from water sampled across terrace groundwater (crosses), riparian groundwater (circles) and stream water (triangles) for samples collected in 2021 and 2012 to 2014. Colors indicate position on the terrace for terrace groundwater sites (red scale) and stream corridor sites (blue scale). Comparisons include: (a) nitrate- $\delta^{15}\text{N}$ versus nitrate- $\delta^{18}\text{O}$ values; (b) nitrate- $\delta^{15}\text{N}$ values versus nitrate concentration; and (c) nitrate- $\delta^{18}\text{O}$ values versus nitrate concentration. Thick, solid black lines (b and c) represent the linear open, mixed reservoir model fit to the stream water data. Solid and dashed light and dark grey lines represent closed system Rayleigh fractionation models based on different stream composition starting points and different fractionation effects of loss (eq. 7; Table S5).



Ch.4-Figure 4. Comparisons of sulfate isotopic compositions and concentrations from water sampled across terrace groundwater (crosses), riparian groundwater (circles) and stream water (triangles) for samples collected in 2021. Colors indicate position on the terrace for terrace groundwater sites (red scale) and stream corridor sites (blue scale). Comparisons include: (a) sulfate- $\delta^{34}\text{S}$ versus sulfate- $\delta^{18}\text{O}$ values, (b) sulfate- $\delta^{34}\text{S}$ values versus sulfate concentration, and (c) sulfate- $\delta^{18}\text{O}$ values versus sulfate concentration. Solid blue lines represent the mixing scenarios between terrace and riparian endmembers for Louse Creek (light blue) and Porter Creek (dark blue). Solid and dashed grey lines represent closed system Rayleigh fractionation models based on stream composition starting points and different fractionation effects of loss (eq. 7; Table S5). Dotted black lines represent closed system Rayleigh fractionation model for sulfate precipitation to secondary salts (e.g., gypsum), resulting in (a) ϵ_{Sp} : ϵ_{Op} of 0.85, (b) $\epsilon_{R,Sp}$ of +6.48‰, and (c) $\epsilon_{R,Op}$ of +7.26‰.



Ch.4-Figure 5. Visualization of the Monte Carlo ensemble characterizing the range of riparian production isotopic composition and concentration relative to terrace inputs that may contribute to the net loss of nitrate in the stream corridors of Louse Creek. Simulation based estimates of (a) total mass loss versus total mass produced in the riparian area, (b) nitrate- $\delta^{15}\text{N}$ of riparian production versus the total mass produced in the riparian area, and (c) nitrate- $\delta^{15}\text{N}$ of riparian production as a function of total mass loss in the riparian area. Symbols are colored by apparent isotopic effects of loss with darker color indicating higher magnitude.

Tables

Ch.4-Table 1. Monte Carlo simulation parameters based on empirical nitrate isotopic composition and concentration results.

Header	slope	intercept	M_t	δ_t	M_s	δ_s	ϵ_a
Units	per mil, ‰ (mg L ⁻¹) ⁻¹	per mil, ‰	mg L ⁻¹	per mil, ‰	mg L ⁻¹	per mil, ‰	per mil, ‰
Summary	The change in nitrate- $\delta^{15}\text{N}$ value for a change in [nitrate-N] value, m .	Nitrate- $\delta^{15}\text{N}$ value for [nitrate-N] = 0.	Concentration of nitrate in terrace groundwater, assumed to be influenced by agricultural practices.	Delta value for nitrogen-15 in a terrace groundwater, assumed to be influenced by agricultural practices.	Concentration of nitrate in a stream water sample.	Delta value for nitrogen-15 in a stream water sample.	Apparent fractionation effect of loss.
Method	Calculated using linear regression of nitrate- $\delta^{15}\text{N}$ and [nitrate-N] observed in Louse Creek stream water.	Calculated using linear regression and 95% confidence of nitrate- $\delta^{15}\text{N}$ and [nitrate-N] observed in Louse Creek stream water.	Mean value of all terrace groundwater results.	Mean value of all terrace groundwater results.	Uniform distribution between minimum and maximum Louse stream water results.	Calculated for a given M_s using slope and intercept.	Uniform distribution between minimum accepted value (Denk et al., 2017) and maximum determined by upper terrace groundwater as the minimum input [nitrate-N] per $\epsilon_a = m \cdot C_{in}$; where $C_{in,min} = 21.9$.
Louse Creek value or range	-0.40 ± 0.05	$+11.1 \pm 0.50$	21.9	+3.8	3.07 to 17.7	+3.41 to +10.5	-40 to -8.1

Ch.4-Table 2. Minimum and maximum values of nitrate and sulfate concentration (mg L⁻¹) and isotopic compositions (‰) in terrace groundwater, riparian groundwater, and stream water by landscape position and reach.

		Nitrate-N								Sulfate-S (2021 only)					
Sample type	Period of record	n	Min. nitrate-N, mg L ⁻¹	Max. nitrate-N, mg L ⁻¹	Min. nitrate- $\delta^{15}\text{N}$	Max. nitrate- $\delta^{15}\text{N}$	Min. nitrate- $\delta^{18}\text{O}$	Max. nitrate- $\delta^{18}\text{O}$	n	Min. sulfate-S, mg L ⁻¹	Max. sulfate-S, mg L ⁻¹	Min. sulfate- $\delta^{34}\text{S}$	Max. sulfate- $\delta^{34}\text{S}$	Min. sulfate- $\delta^{18}\text{O}$	Max. sulfate- $\delta^{18}\text{O}$
Terrace groundwater															
Upper	2013-2014	8	14.3	32.3	+3.71	+6.53	-5.00	-2.63	8	50.3	66.7	NA	NA	NA	NA
Middle	2012-2014, 2021	30	15.2	25.7	+2.67	+4.96	-5.15	-3.37	2	12.3	13.4	-12.3	-11.9	-2.08	-1.51
Lower	2013-2014, 2021	11	18.6	24.9	+2.42	+3.86	-4.71	-3.40	1	NA	10.0	NA	-7.37	NA	-2.46
Riparian groundwater															
Upper-Louse	2021	7	0.4	5.05	+14.5	+39.7	+2.76	+11.8	9	40.5	96.3	-19.3	-3.15	-0.47	+5.73
Mid-Louse	2021	6	0	0.05	NA	NA	NA	NA	6	71.3	138	-23.0	-18.4	+0.65	+5.98
Porter	2021	4	1.17	14.4	+6.09	+39.1	-1.12	+14.6	4	15.9	31.4	-19.2	-11.9	-1.62	+4.33
Stream water															
Upper-Louse	2012-2014, 2021	20	3.40	18.2	+3.91	+12.3	-3.37	+1.66	4	69.7	87.9	-16.8	-16.4	-0.84	+0.14
Mid-Louse	2021	4	3.14	7.35	+6.42	+9.62	-2.08	-1.12	4	36.8	65.6	-17.7	-15.8	-1.59	-0.50
Porter	2021	4	16.2	18.8	+2.76	+4.11	-4.65	-3.16	4	10.3	11.6	-8.59	-7.61	-2.34	-1.89

Kolin	2012-2014	16	5.66	15.4	+5.30	+8.52	-2.53	-0.28	6	39.4	56.1	NA	NA	NA	NA
Porter311	2013-2014	10	15.9	20.5	+3.90	+4.83	-3.82	-2.87	2	11.2	11.5	NA	NA	NA	NA

Supporting Materials

Introduction

The supporting information included provides additional description of materials and methods, data included in the analyses for this study (Table S4 and Data Set S1), and additional data visualizations (Figures S1 to S3). Data files include nitrate and sulfate isotopic composition and concentration results and field parameters for samples collected in 2021 and from 2012 to 2014 (Data Set S1).

Text S1. Extended Description of Materials and Methods

Text S1.1 Extended Description of Study Area: Terrace landforms and river floodplains in the lower elevations of the JRW are extensively cultivated for non-irrigated cereal crop production. Cultivated crops include primarily spring wheat, winter wheat, and barley with increasing incorporation of pulse crops in cropping system rotations to replace fallow (John et al., 2017; U.S. Department of Agriculture, 2023). Producers incorporate summer fallow rotations using herbicide suppression of vegetation to maximize soil water storage for the subsequent crop rotation. Documented nutrient retention and processing in fallowed soils of the JRW suggests this practice promotes N mineralization and nitrification (John et al. 2017, Sigler et al. 2022). The non-arable riparian areas of stream corridors incised into terraces like the Moccasin are typically managed as pasture for cattle production (Figure 2; U.S. Department of Agriculture, 2023), due to prolonged forage production and water availability during the dry season.

Text S1.2 Extended Description of Sample Collection and Handling

Terrace Groundwater. Sites in the lower terrace category were at lower elevations and considered representative of groundwater contributing to the Porter Creek reach. Middle terrace sites were at intermediate elevations and considered representative groundwater contributing to the Louse Creek reaches. Upper terrace sites were at higher elevations and considered representative of groundwaters farther from stream drainages. We included samples collected from the Montana Department of Agriculture at groundwater monitoring well M-1 (site identification # 133047 and name MOS-1 in MBMG, 2024). Two hillslope springs sampled from 2013 to 2014 required sampling from shallow PVC wells installed 1-2 meters up-gradient from the orifice due to stagnant water at the spring orifice (Sigler et al., 2018).

Riparian Groundwater. Casings for riparian groundwater sampling wells were constructed from 2.54-cm internal diameter PVC installed to ca. 1-m depth in riparian soils and sediments. Thin (< 5 mm) slots were cut into the bottom of the casings to provide 30 to 50 cm of screening. We monitored dissolved oxygen (DO) concentrations continuously while pumping through a flow cell.

In Situ Sensor Calibration. We calibrated the DO sensor to water saturated air each day prior to collecting samples and measurements. We calibrated specific conductance and pH once prior to the start of each multi-day sampling campaign, within 24 hours of the first measurement. We performed a 3-point calibration of the pH sensor using standards of pH 10, pH 7, and pH 4. Specific electrical conductivity (corrected to a water temperature of 25 °C) was calibrated to a standard of 1412 $\mu\text{S cm}^{-1}$.

Text S1.3 Extended Description of Chemical Analysis: Samples were collected into combusted 24-mL glass vials without headspace for organic and inorganic carbon. We analyzed dissolved organic and inorganic carbon (Shimadzu TOC VCSN) within two weeks of sample collection (Table S2). Chloride (Dionex Thermo Scientific ICS-2100) was analyzed within one year of sampling and used to inform sulfate isotopic composition analysis.

Text S1.4 Extended Description of Water Isotopic Composition Analysis: Water samples were analyzed for isotopic compositions of water (d^2H and $d^{18}O$) at the Montana State University EAL (Bozeman, Montana). Water isotopic composition was determined using integrated cavity output spectroscopy (Los Gatos Research; Mountain View, CA). Isotopes of water were normalized to the global standard of ocean water (Vienna Standard Mean Ocean Water, VSMOW; Craig, 1961; Dansgaard, 1964). Analytical uncertainty was constrained using repeated measurements of USGS-certified standards and a groundwater sample from the Gallatin River watershed, Montana over the last five years ($n=80$, EAL unpublished data) had a standard deviation of 0.9 ‰ for water- d^2H and 0.6 ‰ for water- $d^{18}O$ (see detailed methods in Mayernik et al. (2024)).

Text S1.4 Extended Description of Monte Carlo Analysis: We define the fractionation effect of transforming the isotopic composition of the total input ($\delta_{in} = M_{terr} + M_p$) to the isotopic composition of export in the stream (δ_s) as a consequence of the apparent isotopic change (ϵ_a). Interpretation of values of ϵ_a are more clearly understood by expressing it as a function of the isotopic change and fraction of solute lost (equation 5b), showing that ϵ_a is a metric of the effectiveness of the fractional loss at changing the isotopic composition of the total input before export by the stream. For example, a higher ϵ_a would arise from a given mass

fraction of loss having a larger effect on the isotopic composition, or a higher ϵ_a would arise from a given effect on the isotopic composition being created by a smaller mass fractional of loss.

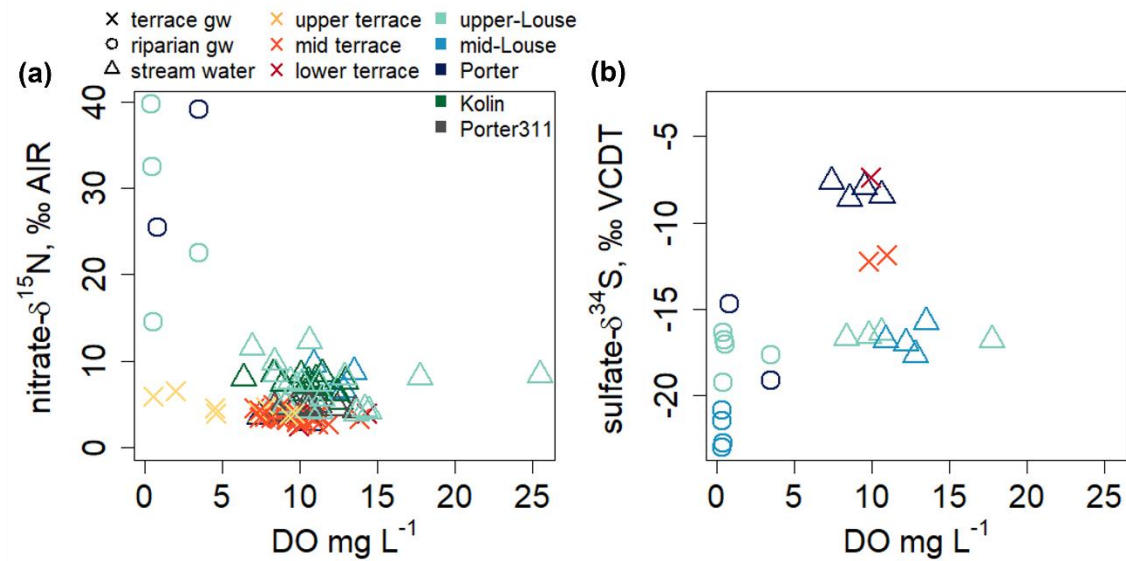
After deriving δ_p and C_p , we calculated δ_{in} using equation 4a and observed terrace groundwater values. We also determined C_l from equation 4b to determine the relative mass loss to mass produced, which we further express as a ratio of mass loss to mass produced (r_{loss}):

$$r_{loss} = \frac{f_l}{f_p} = \frac{M_l}{M_p} \quad (S1)$$

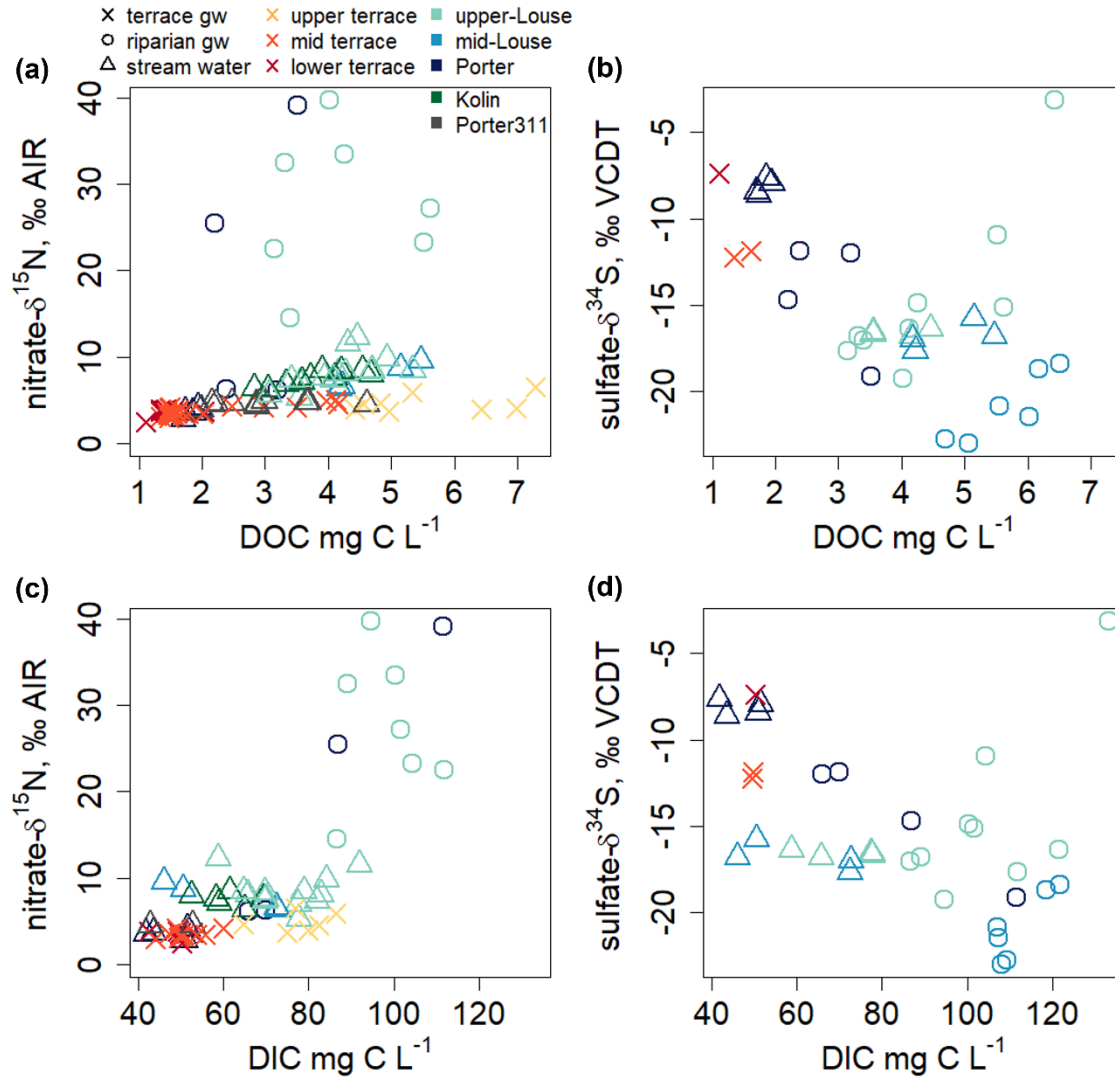
By conservation of mass at steady state, gross losses cannot exceed total mass inputs, so f_l must be less than 1 ($0 < f_l < 1$). For N, the mass fraction produced must be less than the mass fraction lost because we observed net losses from the terrace aquifer to the stream channel.

Therefore, $r_{loss} \geq 1$.

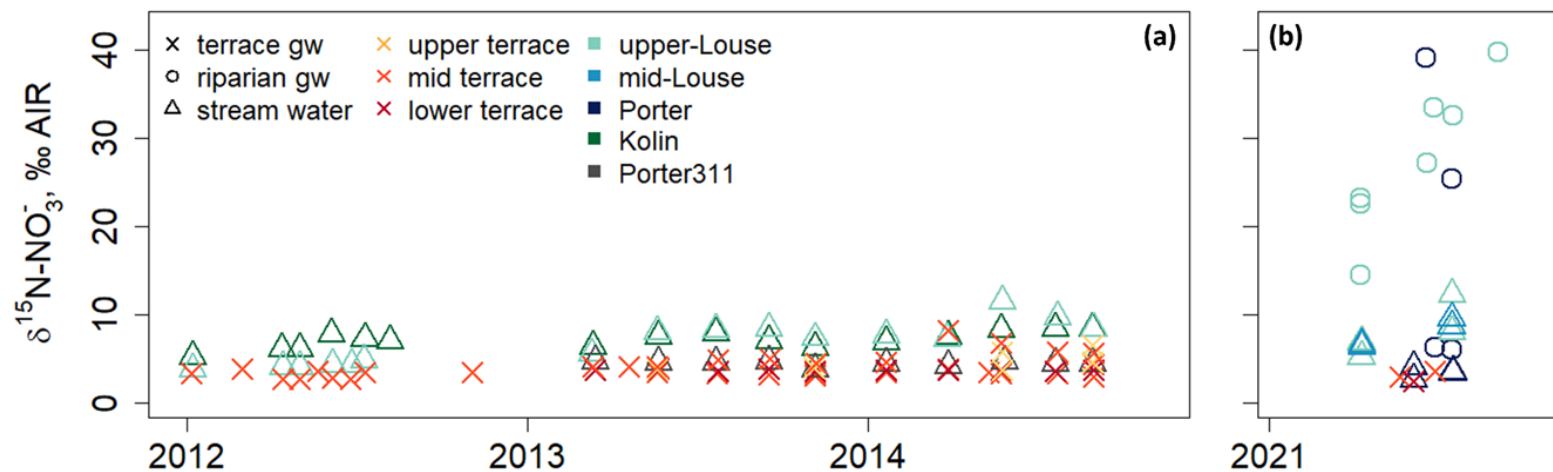
Supporting Figures



Ch.4-Figure S1. Isotopic compositions versus dissolved oxygen. (a) Nitrate- $\delta^{15}\text{N}$ values and (b) sulfate- $\delta^{34}\text{S}$ values versus dissolved oxygen (DO) across terrace groundwater (crosses), riparian groundwater (circles) and stream water (triangles). Colors indicate position on the terrace for terrace groundwater sites (red scale; Figure 2) and stream corridor sites (blue-green scale). Samples collected in 2021 and from 2012 to 2014.



Ch.4-Figure S2. Isotopic compositions versus dissolved carbon species. (a) Nitrate- $\delta^{15}\text{N}$ values versus dissolved organic carbon (DOC), (b) sulfate- $\delta^{34}\text{S}$ values versus DOC, (c) Nitrate- $\delta^{15}\text{N}$ values versus dissolved inorganic carbon (DIC), and (d) sulfate- $\delta^{34}\text{S}$ values versus DIC across terrace groundwater (crosses), riparian groundwater (circles) and stream water (triangles). Colors indicate position on the terrace for terrace groundwater sites (red scale; Figure 2) and stream corridor sites (blue-green scale). Samples collected in 2021 and from 2012 to 2014.



Ch.4-Figure S3. Nitrate- $\delta^{15}\text{N}$ over time from (a) 2012 to 2014 and (b) 2021 across terrace groundwater (crosses), riparian groundwater (circles) and stream water (triangles). Stream water at Kolin and Porter311 was only sampled from 2012 to 2014. Stream water at mid-Louse and Porter was only sampled in 2021. Colors indicate position on the terrace for terrace groundwater sites (red scale; Figure 2) and stream corridor sites (blue-green scale). (Sigler et al., 2022).

Supporting Tables

Ch.4-Table S1. Detailed site description, geographic location, and sample collection frequency for geochemical and nitrate and/or sulfate isotopic composition analyses.

Site	SiteType	YearSampled	AnnualCounts	Latitude	Longitude	Comments
RW01	Riparian groundwater	2021	2	47.0672	-109.9661	Groundwater sampled from shallow well within riparian floodplain
RW06	Riparian groundwater	2021	4	47.0683	-109.9633	Groundwater sampled from shallow well within riparian floodplain
RW08	Riparian groundwater	2021	3	47.0681	-109.9639	Groundwater sampled from shallow well within riparian floodplain
LW03	Riparian groundwater	2021	2	47.0779	-109.9096	Groundwater sampled from shallow well within riparian floodplain
LW04	Riparian groundwater	2021	2	47.0792	-109.9089	Groundwater sampled from shallow well within riparian floodplain
LW05	Riparian groundwater	2021	2	47.0788	-109.9087	Groundwater sampled from shallow well within riparian floodplain
PW01	Riparian groundwater	2021	2	47.0571	-109.8335	Groundwater sampled from shallow well within riparian floodplain
PW02	Riparian groundwater	2021	2	47.0578	-109.8321	Groundwater sampled from shallow well within riparian floodplain
IS01	Middle terrace groundwater	2013, 2014, 2021	5, 5, 2	47.0758	-109.9048	Terrace spring; also identified as 'Indian'
PS01	Lower terrace groundwater	2013, 2014, 2021	5, 5, 1	47.0570	-109.8336	Terrace spring
Headwaters	Upper terrace groundwater	2013, 2014	2, 2	47.0350	-110.0591	Louse Creek Headwaters Well at Mudsprings Road; at diesel shop

M1	Middle terrace groundwater	2012, 2013	9, 5	47.0950	-109.9676	MDA M1 Monitoring Well #133047
Spr555	Upper terrace groundwater	2013, 2014	2, 2	47.0775	-110.0265	Terrace spring trib 555 near Benchland, MT
Star	Middle terrace groundwater	2013, 2014	2, 2	47.0937	-109.9351	Terrace spring at Star Road
RR01	Stream water	2012, 2013, 2014, 2021	6, 5, 5, 2	47.0673	-109.9665	Upgradient stream water site at upper-Louse reach, also identified as 'Railroad' (Sigler et al., 2022)
RR04	Stream water	2021	2	47.0696	-109.9604	Downgradient stream water site at upper-Louse reach
LL01	Stream water	2021	2	47.0778	-109.9126	Upgradient stream water site at mid-Louse reach, includes LL03 and LL04 due to very close proximity
LL02	Stream water	2021	2	47.0787	-109.9059	Downgradient stream water site at mid-Louse reach
PC01	Stream water	2021	2	47.0572	-109.8333	Upgradient stream water site at Porter reach
PC02	Stream water	2021	2	47.0575	-109.8296	Downgradient stream water site at Porter reach
Porter	Soil	2013, 2014	5, 5	47.0548	-109.7985	Downgradient stream water site in Porter Creek at County Road 311
Kolin	Soil	2012, 2013, 2014	6, 5, 5	47.1178	-109.7778	Downgradient stream water site in Louse Creek at Kolin Road

Ch.4-Table S2. Summary of the measured water quality and chemistry parameters and the methods used to measure them.

Parameter	Sample collection device	Analytical method	Reported unit	Uncertainty	Limit of detection
Dissolved oxygen	Measured in situ	Electrochemical (YSI Incorporated, Yellow Springs, OH)	mg L ⁻¹	± 0.2 mg L ⁻¹	0.1
pH	Measured in situ	Glass combination electrode (YSI Incorporated, Yellow Springs, OH)	N/A	± 0.2	0.01
Temperature	Measured in situ	Thermistor (YSI Incorporated, Yellow Springs, OH)	°C	± 0.2°C	N/A
Specific conductance	Measured in situ	Four electrode cell (YSI Incorporated, Yellow Springs, OH)	µS cm ⁻¹	± 0.5%	10 µS
Nitrate, as nitrogen	ashed 24 mL glass, no head space	Colorimetry (Lachat QuickChem 8500)	mg L ⁻¹	± 5%	0.01 to 0.06
Sulfate, as sulfur	Acid-washed 60 mL HDPE	Ion chromatography (Dionex, ICS-2100)	mg L ⁻¹	± 10%	0.003 to 0.9
Chloride	Acid-washed 60 mL HDPE	Ion chromatography (Dionex, ICS-2100)	mg L ⁻¹	± 10%	0.004 to 0.2
Dissolved Organic Carbon	ashed 24 mL glass, no head space	Liquid combustion (Shimadzu, TOC-VCSN for 2020 and 2021 and Shimadzu, TOC-L for 2022)	mg L ⁻¹	± 10%	0.15 to 0.4
Dissolved Inorganic Carbon	ashed 24 mL glass, no head space	Liquid combustion (Shimadzu, TOC-VCSN for 2020 and 2021)	mg L ⁻¹	± 10%	0.1 to 1.2

Ch.4-Table S3 Nitrate and sulfate isotopic values of certified and working standards used in analysis.

Standard	sulfate-$\delta^{18}\text{O}$ (‰)	sulfate-$\delta^{34}\text{S}$ (‰)	nitrate-$\delta^{15}\text{N}$ (‰)	nitrate-$\delta^{18}\text{O}$ (‰)
USGS 34	NA	NA	-1.8 ± 0.1	-27.9 ± 0.3
USGS 35	NA	NA	NA	$+57.5 \pm 0.3$
EGC 17	NA	NA	$+25.6 \pm 0.5$	NA
IAEA-SO-5	$+12.13 \pm 0.3$	$+0.49 \pm 0.3$	NA	NA
IAEA-SO-6	-11.35 ± 0.3	-34.05 ± 0.3	NA	NA
NBS-127	$+8.59 \pm 0.3$	$+21.1 \pm 0.3$	NA	NA

Ch.4-Table S4. Input values (observed and derived) for mixing and loss models of nitrate and sulfate isotopic composition and concentration.

Model	Site(s)	Reach	Parameter	Observed endmember value	Observed intermediate value	Derived endmember value
Closed system (eq. 7)	Stream water (maximum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate- $\delta^{15}\text{N}$	+9.62‰	NA	NA
Closed system (eq. 7)	Stream water (maximum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate- $\delta^{18}\text{O}$	-1.12‰	NA	NA
Closed system (eq. 7)	Stream water (maximum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate concentration	3.07 mg N L ⁻¹	NA	NA
Closed system (eq. 7)	Stream water (minimum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate- $\delta^{15}\text{N}$	+5.26‰	NA	NA
Closed system (eq. 7)	Stream water (minimum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate- $\delta^{18}\text{O}$	-2.77‰	NA	NA
Closed system (eq. 7)	Stream water (minimum nitrate- $\delta^{15}\text{N}$)	Louse (upper and mid)	nitrate concentration	8.14 mg N L ⁻¹	NA	NA
Mixing (eq. 4)	Middle terrace groundwater, Riparian groundwater (high sulfate concentration)	Mid-Louse	sulfate- $\delta^{34}\text{S}$	-12.1‰	-18.4‰	-19.0‰
Mixing (eq. 4)	Middle terrace groundwater, Riparian groundwater (high sulfate concentration)	Mid-Louse	sulfate- $\delta^{18}\text{O}$	-1.80‰	+5.98‰	+6.78‰
Mixing (eq. 4)	Middle terrace groundwater, Riparian groundwater (high sulfate concentration)	Mid-Louse	sulfate concentration	12.9 mg S L ⁻¹	138 mg S L ⁻¹	Infinity

Mixing (eq. 4)	Middle terrace groundwater, Riparian groundwater (low sulfate- $\delta^{34}\text{S}$ value)	Mid-Louse	sulfate- $\delta^{34}\text{S}$	-12.1‰	-23.0‰	-24.5‰
Mixing (eq. 4)	Riparian groundwater (low sulfate- $\delta^{34}\text{S}$ value)	Mid-Louse	sulfate- $\delta^{18}\text{O}$	-1.80‰	+0.65‰	+0.99‰
Mixing (eq. 4)	Riparian groundwater (low sulfate- $\delta^{34}\text{S}$ value)	Mid-Louse	sulfate concentration	12.9 mg S L ⁻¹	107 mg S L ⁻¹	Infinity
Mixing (eq. 4)	Lower terrace groundwater, Riparian groundwater (high sulfate concentration)	Porter	sulfate- $\delta^{34}\text{S}$	-7.38‰	-19.2‰	-24.7‰
Mixing (eq. 4)	Lower terrace groundwater, Riparian groundwater (high sulfate concentration)	Porter	sulfate- $\delta^{18}\text{O}$	-2.46‰	+4.33‰	+7.51‰
Mixing (eq. 4)	Lower terrace groundwater, Riparian groundwater (high sulfate concentration)	Porter	sulfate concentration	10.0 mg S L ⁻¹	31.4 mg S L ⁻¹	Infinity
Closed system (eq. 7)	Riparian groundwater (maximum concentration)	mid-Louse	sulfate- $\delta^{34}\text{S}$	NA	-18.4‰	-18.6‰
Closed system (eq. 7)	Riparian groundwater (maximum concentration)	mid-Louse	sulfate- $\delta^{18}\text{O}$	NA	+5.98‰	+6.23‰
Closed system (eq. 7)	Riparian groundwater (maximum concentration)	mid-Louse	sulfate concentration	NA	138 mg S L ⁻¹	200 mg S L ⁻¹
Closed system (eq. 7)	Stream water (minimum sulfate- $\delta^{34}\text{S}$)	upper-Louse	sulfate- $\delta^{34}\text{S}$	-16.8‰	NA	NA
Closed system (eq. 7)	Stream water (minimum sulfate- $\delta^{34}\text{S}$)	upper-Louse	sulfate- $\delta^{18}\text{O}$	-0.83‰	NA	NA
Closed system (eq. 7)	Stream water (minimum sulfate- $\delta^{34}\text{S}$)	upper-Louse	sulfate concentration	67.6 mg N L ⁻¹	NA	NA

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CHAPTER FIVE

CONCLUSION

Ecosystems are comprised of complex processes influenced by thermodynamic and kinetic favorability at the scale of microbial metabolic processes (Hedin et al., 1998; Payn et al., 2014), yet the ecosystem scale is the most vulnerable and consequential to human communities (Odum, 1964). To understand how human activities transform ecosystem functions, we must understand the various processes that contribute to a single environmental observation – both how these individual processing pathways work, and how they feed back on one another and become integrated into ecosystems at the scale we experience, observe, and measure.

The research encompassed in this dissertation highlights the importance of soils and sediments for water storage and movement, and for solute production and loss. The results of Chapter Two suggest that soils are important for retaining cold-season precipitation and integrating precipitation sources across timescales, which can influence crop production and biogeochemical processes. These findings contribute to improved understanding of soil water storage dynamics, important to anticipating and mitigating consequences of climatic shifts on crop production and water quality across non-irrigated agricultural and grassland ecosystems. The results of Chapter Three suggest that riparian areas both mitigate nitrate and augment sulfate, but these influences on streams may be masked by hydrologic connectivity between upland aquifers and stream channels, as dictated by geomorphic setting. These findings suggest that multiple ecosystem components (e.g., managed soils, substrate stratigraphy, bedrock) contribute to riparian biogeochemical processes and the extent to which stream corridors integrate these processes. The results of Chapter Four emphasize the solute production and loss

capacity of stream corridors and the extent to which we can use isotopic composition to inform and quantify these processes. These results allow us to decipher relative contributions from co-occurring hydrologic and biogeochemical processes of solute production, mixing, and loss. These findings present an important conceptualization grounded in fundamental mass balance principles and constrained by empirical observations.

My research approach integrates a foundational knowledge of soil and hydrologic processes with geochemical and isotopic analysis techniques to understand the effects of human perturbations on the quality of ground and surface waters. I recognize that in addition to integrating multiple hydrologic and biogeochemical processes, a single ecosystem function conjures many diverse human perspectives, all of which hold value to an individual or community. With this work, I cultivated a more holistic understanding of the relationship between humans and ecosystems, particularly with regard to the competing demands on water quality and quantity as ecosystem services.

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