

WATER QUALITY RESPONSE TO WATER AND NITROGEN MOVEMENT
THROUGH A SEMI-ARID DRYLAND AGROECOSYSTEM IN MONTANA, USA

by

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DEDICATION

This dissertation is dedicated to recognition of the responsibility that comes with privilege in its many forms; to the quest for understanding, peace, and meaning in life; to the preservation of the water resources that sustain our lives; and to my incredible family, friends, colleagues, and mentors who have been there with me along my path.

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TABLE OF CONTENTS

BACKGROUND AND MOTIVATION	1
Literature Cited	7
CONNECTIONS AMONG SOIL, GROUND, AND SURFACE WATER CHEMISTRIES CHARACTERIZE NITROGEN LOSS FROM AN AGRICULTURAL LANDSCAPE IN THE UPPER MISSOURI RIVER BASIN	10
Contribution of Authors and Co-Authors	10
Manuscript Information	12
Abstract	13
1. Introduction.....	15
2. Methods.....	19
2.1 Study Area	19
2.2 Water Sample Collection	21
2.3 Water Sample Analysis and Major Ion Composition.....	23
2.4 Groundwater Catchment Delineation, Discharge, Stream Baseflow and Area- Normalization	24
2.5 Nitrate Loading to Ground/Surface Water and Leaching Rates.....	26
2.6 Groundwater Residence Time.....	28
3. Results.....	29
3.1 Catchment Delineation and Soil Type Composition.....	29
3.2 Nitrate Concentrations in Soil Water and Groundwater	30
3.3 Major Ion Composition of Terrace Waters and Hydrologic Connectivity.....	31
3.4 Stream Discharge, Groundwater Levels and Recharge	33
3.5 Nitrate Leaching Rates and Riparian Losses	34
3.6 Groundwater Residence Time.....	36
4. Discussion	36
4.1 Connection of Soil, Ground and Surface Waters within Moccasin Terrace.....	37
4.2 Nitrogen Concentrations and Soil-Groundwater Connections.....	37
4.3 Nitrate Leaching Rates.....	39
4.4 Riparian N Losses	41
4.5 Groundwater Nitrate over Time and Expected Timescale of Response to Changing Inputs.....	42

TABLE OF CONTENTS CONTINUED

4.6 Value of Participatory Approach to Hydrologic Investigation.....	43
5. Conclusions.....	44
Acknowledgements.....	45
Figures.....	47
Tables.....	54
Supplemental Materials	59
2. Methods Supplement	59
3. Results Supplement.....	67
4. Discussion Supplement.....	67
Supplemental Figures.....	69
Literature Cited	72
WATER AND NITRATE LOSS FROM DRYLAND AGRICULTURAL SOILS IS CONTROLLED BY MANAGEMENT, SOILS, AND WEATHER	80
Contribution of Authors and Co-Authors	80
Manuscript Information	81
Abstract	82
1. Introduction.....	83
2. Methods.....	87
2.1 Study Area and Cropping.....	87
2.2 Spatial Distribution of Soils.....	89
2.3 Measuring Nitrate in Soil.....	91
2.4 Model Description	92
3. Results.....	95
3.1 Soil Water Content and Soil Nitrate	95
3.2 Spatial Distribution of Soil Thickness	96
3.3 Model Results versus Observations and Sensitivity	97
3.4 Simulated precipitation partitioning	98
3.5 Nitrate Leaching.....	100
3.6 Scaling Simulation Results to Fields and Landforms	101
4. Discussion	102
4.1 Controls on Precipitation Partitioning	103
4.2 Weather & Soils as Controls on Deep Percolation and Leaching.....	105
4.3 Fallow Expands Hot Moments and Hot Spots.....	106
4.4 Management Implications.....	108
4.5 Emergent Landscape-Scale Behavior	109

TABLE OF CONTENTS CONTINUED

5. Conclusions.....	111
Acknowledgements.....	112
Figures.....	113
Tables.....	122
Supplemental Materials	125
2. Methods.....	125
3. Results.....	146
4. Discussion	170
Data and Code.....	171
Literature Cited	172
DRIVERS OF DENITRIFICATION ACROSS A SEMIARID AGROECOSYSTEM REVEALED BY NITRATE ISOTOPIC PATTERNS	178
Contribution of Authors and Co-Authors	178
Manuscript Information	179
Abstract	180
Introduction.....	181
Materials and Methods.....	185
Study Area	185
Sampling and Analysis	186
Isotopic Signals of Denitrification	187
Results and Discussion	190
Nitrate Isotopic Composition Across Domains	190
Denitrification Signals	191
Estimating Soil Nitrification and Denitrification Rates.....	193
Implications for Landscape N Budgets	196
Author Information	199
Acknowledgements.....	199
Figures.....	200
Tables.....	204
Supplemental Materials	206
Results and Discussion	206
Data	213
Literature Cited	214
SYNTHESIS AND RECOMMENDATIONS.....	220
Literature Cited	229
REFERENCES CITED.....	231

LIST OF TABLES

Table	Page
1. Ch2-Table 1. Terrace and Catchment Characteristics	54
2. Ch2-Table 2. Nitrate-N concentration summary statistics.....	55
3. Ch2-Table 3. Annual mean major ion concentrations (mM) and principal component scores.	56
4. Ch2-Table 4. Principal component loadings for major ions.....	57
5. Ch2-Table 5. Water and nitrate-N efflux from Kolin and Porter catchments.	57
6. Ch2-Table 6. Groundwater apparent age based on tritium/helium analysis.....	58
7. Ch2-Table 7. Groundwater turnover time.....	58
8. Ch2-Sup Table 1. Analytical specifications.....	65
9. Ch3-Table 1. Lysimeter nitrate concentrations.....	122
10. Ch3-Table 2. Summary of precipitation partitioning by sequence (Seq).	122
11. Ch3-Table 3. Field scale deep percolation and leaching.	123
12. Ch3-Table 4. Deep percolation and leaching by z_f distribution and time period.	124
13. Ch3-Sup Table 2.2a - SSURGO soil series	128
14. Ch3-Sup Table 2.4a - van Genuchten parameters.	132
15. Ch3-Sup Table 2.4b - Crop growth parameters.	138
16. Ch3-Sup Table 2.4c - Root depth in soil pits.....	142
17. Ch3-Sup Table 2.4d – Field observations for comparison.....	144
18. Ch3-Sup Table 2.4e - Sensitivity analysis scenarios.	145
19. Ch3-Sup Table 3.2a - Soil pit z_f observations.....	147

LIST OF TABLES CONTINUED

Table	Page
20. Ch3-Sup Table 3.3a - Sensitivity analysis results.....	157-158
21. Ch3-Sup Table 3.4a – PSE summary.....	162
22. Ch3-Sup Table 3.4b – DP & leaching polynomial coefficients.....	168
23. Ch4-Table 1. Summary of denitrification signals.....	204
24. Ch4-Table 2. Annual soil denitrification rate estimates during the fallow year.	205
25. Ch4-Sup Table 1. $\delta^{18}\text{O}$ in Precipitation and NO_3^-	207
26. Ch4-Sup Table 2. Isotope effects for ammonification and nitrification of SON (ϵ_{nit}) and denitrification (ϵ_{den}) applied in soil denitrification rate estimates.	211

LIST OF FIGURES

Figure	Page
1. Ch2-Figure 1. Site location and conceptual terrace cross section.	47
2. Ch2-Figure 2. Landform maps with shale depth, soils and land use.....	48
3. Ch2-Figure 3. Nitrate-N concentration and water level in M1 monitoring well	49
4. Ch2-Figure 4. Nitrate-N concentration in Moccasin terrace waters.	50
5. Ch2-Figure 5. Moccasin terrace major ion concentrations.	51
6. Ch2-Figure 6. PCA of water chemistry and relationship to catchment shale soil area.	52
7. Ch2-Figure 7. Precipitation, nitrate-N concentration, discharge and nitrate-N load time series.	53
8. Ch2-Sup Figure 1. Conceptual diagram of Moccasin terrace for flux calculations.	69
9. Ch2-Sup Figure 2. Estimated stream riparian corridor N loss.	70
10. Ch2-Sup Figure 3. Dissolved oxygen at groundwater sites measured during sampling visits.....	71
11. Ch3-Figure 1. Study Area.	113
12. Ch3-Figure 2. Monthly Precipitation and rPET.....	114
13. Ch3-Figure 3. Crop rotations.	115
14. Ch3-Figure 4. Soil water and nitrate profiles by crop sequence.....	116
15. Ch3-Figure 5. Normalized Difference Vegetation Index (NDVI) and Thickness of Fines.....	117
16. Ch3-Figure 6. Simulated precipitation partitioning by crop sequence.....	118

LIST OF FIGURES CONTINUED

Figure	Page
17. Ch3-Figure 7. Deep percolation and nitrate leaching versus z_f	119
18. Ch3-Figure 8. Modeled daily deep percolation, transpiration and evaporation.....	120
19. Ch3-Figure 9. Field scale simulated DP and leaching.....	121
20. Ch3-Sup Figure 2.1a - Precipitation comparisons.....	125
21. Ch3-Sup Figure 2.4a - Bulk density profile.....	133
22. Ch3-Sup Figure 2.4b – Core samples at wilting point.....	134
23. Ch3-Sup Figure 2.4c – Core samples at field capacity	135
24. Ch3-Sup Figure 2.4d - Tower data winter wheat.....	139
25. Ch3-Sup Figure 2.4e - Tower data spring wheat	140
26. Ch3-Sup Figure 2.4f - Tower data fallow	141
27. Ch3-Sup Figure 3.1a – Lysimeter NO_3 vs z_f	146
28. Ch3-Sup Figure 3.2a – Field C NDVI vs core depth.....	149
29. Ch3-Sup Figure 3.3a – Field C observations.....	151
30. Ch3-Sup Figure 3.4a - DP vs Precipitation.....	161
31. Ch3-Sup Figure 3.4b - Daily timeseries z_f 25	164
32. Ch3-Sup Figure 3.4c - Daily timeseries z_f 50	165
33. Ch3-Sup Figure 3.4d - Daily timeseries z_f 100	166
34. Ch3-Sup Figure 3.4e - Partitioning by year	167
35. Ch3-Sup Figure 3.6a – Field scale DP & leaching.....	169
36. Ch4-Figure 1. Study area.....	200

LIST OF FIGURES CONTINUED

Figure	Page
37. Ch4-Figure 2. Comparisons of patterns in isotopic composition and concentration of NO_3^- dissolved in soil water, groundwater, and stream water across the JRW	201
38. Ch4-Figure 3. Comparisons of patterns in $\delta^{15}\text{N}$ in NO_3^- versus DO and DOC dissolved in groundwater and stream water across the JRW.	202
39. Ch4-Figure 4. Soil NO_3^- pool versus simulated $\delta^{15}\text{N}_{\text{NO}_3}$ assuming intermediate isotope effects ($\epsilon_{\text{den}} = -25\text{‰}$; $\epsilon_{\text{nit}} = -10\text{‰}$).	203
40. Ch4-Sup Figure 1. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values in precipitation.	206
41. Ch4-Sup Figure 2. Lysimeter composite plots	208
42. Ch4-Sup Figure 3. Groundwater composite plots.....	209
43. Ch4-Sup Figure 4. Stream composite plots	210
44. Ch4-Sup Figure 5. Soil NO_3^- pool versus simulated $\delta^{15}\text{N}_{\text{NO}_3}$	212

ABSTRACT

Humans have increased reactive nitrogen (N) on the planet by an order of magnitude over the past 150 years. Most of this reactive N is used for fertilizer to feed a growing population, but loss of N from cultivated soils threatens agricultural and environmental sustainability. Nitrate accumulated in soil from fertilization or decomposition of soil organic N (SON) may be lost via leaching, which can reduce soil fertility and compromise water quality. Nitrate concentrations commonly exceed human drinking standards in groundwater resources around the globe. In the Judith River Watershed (JRW) in central Montana, nitrate has been detected above the standard since the 1960s. This dissertation contributes to a more holistic understanding of the fate and transport of N in the JRW. An interdisciplinary team engaged with farmers in a participatory research project, making observations in soils, groundwater, and streams to characterize water and N movement. At the landform scale, 5 to 9 cm yr⁻¹ of the 38 cm yr⁻¹ mean annual precipitation moves through soil to recharge groundwater and leaches 11 to 18 kg ha⁻¹ yr⁻¹ of nitrate-N from soil. These leaching rates are approximately 20-30% of fertilizer rates but likely reflect inmixture of nitrate from SON decomposition. Soil modeling analyses suggested that water and N losses were dominated by intense precipitation periods on wetter soils, such that more than half of simulated deep percolation and leaching occurred in two of 14 model years. Simulations further suggest that thinner soils (<25 cm fine-textured materials) experience water and nitrate loss rates five to 16 times higher than thicker soils (>100 cm). Soil sampling demonstrated that increased soil water during fallow periods facilitates conversion of SON to nitrate. Soils are then primed for water and N loss with subsequent precipitation, resulting in disproportionately high leaching rates during and following fallow periods. Isotopic evidence from fallow periods further suggests that nitrate is lost to the atmosphere via denitrification, a gas phase loss combining with leaching losses to compromise the goal of delivering N to crops. These findings suggest that reduction of fallow increases N use efficiency and reduces nitrate loss to groundwater.

CHAPTER ONE

BACKGROUND AND MOTIVATION

The nitrogen (N) and water cycles on Earth are inextricably linked, a linkage with direct implications for our ability as humans to feed ourselves, while preserving the integrity of water resources on which our lives depend. Water and N are both critical for life, yet the largest pools of both are unavailable for use by most organisms (Grosberg et al., 2012). Inert dinitrogen gas makes up 78% of the atmosphere and is only transformed to bioavailable reactive N (N_r) with high energy input (e.g. fossil fuel combustion or lightning) or via specialized microbes through use of nitrogenase, an enzyme that evolved 3.2 Ga and likely facilitated emergence of complex life forms on Earth (Galloway et al., 2004; Mus et al., 2019). Following development of the Haber-Bosch process in the early 20th century, anthropogenic fixation of dinitrogen gas to N_r increased by an order of magnitude, the products of which are used mostly for fertilizer (Galloway et al., 2003). Today, anthropogenically fixed N is responsible for feeding half of the human population (Erisman et al., 2008). Sixty percent of N_r inputs for production of goods and services in the United States (US) are lost to inefficiency and a third of losses are routed to groundwater and surface water (Houlton et al., 2013), resulting in degradation of water quality and a cascade of disruptive effects on planetary systems (Galloway et al., 2003; Rockstrom et al., 2009). Recognition of the complex interactions among human and natural systems has led to development of frameworks such as the Water-Energy-Food Nexus (Hoff, 2011) and the Water-Soil-Waste Nexus (Hülsmann and Ardakanian, 2014; Avellan et al., 2017) for working across sectors and resource management disciplines to

pursue sustainability goals. In this dissertation, I focus on a *Soil-Water Nexus* to quantify fluxes of water and N through an agroecosystem and characterize opportunities for increased N use efficiency, pursuant to viable crop production coincident with protection of groundwater and surface water quality.

In addressing environmental concerns, wicked problems have been defined as those where (1) competing goals are at play within (2) a complex system where there is (3) information uncertainty or missing information about the social and physical controls on the system (Kirschke et al., 2018). To what degree do food production and water resource protection challenges embedded in the Soil-Water Nexus represent a wicked problem? The criterion for a complex system is readily met due to the dynamic interaction among cropping system management, soils, and weather to control the flux of water and N through soils. In a general sense, the correlation between increasing N input to soils for food production and increasing magnitude and extent of water quality issues (e.g. eutrophication) suggests competing goals, indicating a wicked problem (Reddy et al., 2018). However, the goal to minimize N loss to water does not compete with the food production goal to retain N in soil in order to maximize opportunity for uptake by crops. The path to achieving the shared fundamental goal of N use efficiency has been obscured by uncertainty about where, when and, why the largest N losses from soil are occurring. An additional obstacle to increasing N use efficiency has been low adoption rates for nutrient related conservation practices among agricultural producers (Perez, 2015; Weber and McCann, 2015). Even if farmers do adopt a practice initially, they may not continue or maintain the practice if the purpose and value is not clear to them (Jackson-Smith et

al., 2010). I assert that we can make progress on this and other wicked problems by: engaging stakeholders to identify areas of alignment among seemingly competing goals (focusing on the shared goal of N use efficiency); designing research to elucidate primary controls on system behavior that are relevant for management decisions (when, where, and why are the largest soil N losses occurring); and co-producing conceptual models that make system complexity more approachable.

An institutional framework for addressing wicked problems exists within the land-grant university system of the US and is reflected in the mission of these institutions to intertwine research, outreach, and education (Zimdahl, 2003). The importance of the tripartite land-grant mission is echoed by the self-described “leading competitive grants program for agricultural sciences” in the US (US Department of Agriculture, Agriculture and Food Research Initiative), which includes grant types for research, education, and extension, as well as integrated projects that combine the three types (USDA, 2020). In addition to integration among these types, bridging between the *fundamental* and *applied* categories of research is also likely to yield benefits beyond independent pursuit of each. With societal pressure to increase food production while both minimizing environmental impact and maintaining robust communities, agricultural researchers unsurprisingly tend to identify as focused more on “applied” than on “fundamental” questions (Bentley et al., 2015). Directly implementable applied research is unquestionably necessary for viable agriculture, but fundamental understanding of how natural and managed systems function is also essential for the creativity necessary to address the wicked problems facing agriculture (Lederman, 1984; Levin et al., 2012).

Issues surrounding the Soil-Water Nexus are exemplified in the dryland wheat farming region of central Montana where mean nitrate (NO_3^-) concentrations in shallow aquifers of the Judith River Watershed (JRW; $\sim 15 \text{ mg N L}^{-1}$; Schmidt and Mulder, 2010) are higher than median values reported for all 24 US well networks evaluated by Rupert et al. (2008). Groundwater NO_3^- concentrations above the US public drinking water standard (10 mg N L^{-1}) were detected in the JRW as early as the 1960s (Schmidt and Mulder, 2010a). A statewide private well testing campaign in 1989-90 by Bauder et al. (1993) found that Judith Basin County (western portion of the JRW) had a mean NO_3^- concentration tied for highest in the state (7.3 mg N L^{-1}), and a physiographic correlation assessment of the data partially attributed these high concentrations to the practice of summer fallow.

In 2005, shortly after starting employment with Montana State University Extension Water Quality (MSUEWQ) under Dr. Jim Bauder, I reestablished a private well owner Extension program (the Well Educated program). Similar to Bauder's previous findings, the first few years of the Well Educated program revealed that some of the most consistently high NO_3^- concentrations in Montana were in Judith Basin and Fergus counties (covering the JRW). As a result, MSUEWQ formed partnerships with Extension agents and conservation districts in the two counties in 2008-2010 to promote private well testing. Discussion with Bauder on an early drive to the JRW was formative for my early recognition of the Soil-Water Nexus and the role of summer fallow in the cropping system of the region. In 2009 the Montana Department of Agriculture sampled wells and streams within the JRW and published a report in 2010 indicating that elevated

groundwater NO_3^- concentrations in the JRW are primarily associated with gravel landforms, which host shallow aquifers perched on shale (Schmidt and Mulder, 2010). These early efforts were the underpinnings for my decision to pursue this work and engage the team of people that made it possible to address these issues, with critical initial funding from USDA-NIFA in 2011. A participatory research framework was at the core of the approach to implementing the research funded by NIFA. This work would not have been possible without extensive engagement with cooperating farmers and broader local stakeholders (Jackson-Smith et al., 2018).

In this dissertation I address the question: Where, when, and how much water and N are moving through soils, groundwater, and streams of the JRW and what are the controls on these fluxes? The question can be more simply stated as: What are the opportunities for increased N use efficiency in the farming systems of the JRW? This dissertation is largely composed (Chapters 2-4) of discrete manuscripts that merge the fields of hydrology, cropping systems, biophysics, and isotope biogeochemistry to answer questions about controls on fluxes of water and N through the soils, groundwater, and streams of the JRW agroecosystem. First, I combine measurements of groundwater chemistry and stream discharge to characterize deep percolation and NO_3^- leaching at the landscape scale (Sigler et al., 2018; Chapter 2). Second, I apply soil water modeling informed by field observations to characterize the interaction of crop rotation, weather, and soils as controls on deep percolation and NO_3^- leaching, bridging between point, field, and landform scales (Sigler et al., in revision; Chapter 3). Third, I describe use of a water and NO_3^- isotope dataset to characterize the influence of denitrification losses

across soil, groundwater, and stream riparian corridor domains (Sigler et al., in prep.; Chapter 4). Finally, the conclusions from these manuscripts are synthesized in the context of addressing issues surrounding the Soil-Water Nexus along with recommendations for future research (Chapter 5).

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CHAPTER TWO

CONNECTIONS AMONG SOIL, GROUND, AND SURFACE WATER CHEMISTRIES CHARACTERIZE NITROGEN LOSS FROM AN AGRICULTURAL LANDSCAPE IN THE UPPER MISSOURI RIVER BASIN

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Abstract

Elevated nitrate in shallow aquifers is common in agricultural areas and remediation requires an understanding of nitrogen (N) leaching at a variety of spatial scales. Characterization of the drivers of nitrate leaching at the mesoscale level (10^2 to 10^3 km²) is needed to bridge from field-scale observations to the landscape-scale context, allowing informed water resource management decisions. Here we explore patterns in nitrate leaching rates across a depositional landform in the northern Great Plains within the Upper Missouri Basin, where the predominant land use is non-irrigated small grain production, and nitrate-N concentrations above 10 mg L⁻¹ are common. The shallow Moccasin terrace (260 km²) aquifer is bounded in vertical extent by underlying shale and is isolated from mountain front stream recharge, such that aquifer recharge is dominated by infiltration of precipitation through agricultural soils. This configuration presents a simple landform-scale water balance that we leveraged to estimate leaching rates using groundwater nitrate concentrations and surface water discharge, and quantify uncertainty using a Monte Carlo approach based on spatial variation in observations of groundwater nitrate concentrations. A participatory research approach allowed local farmer knowledge of the landscape to be incorporated into the study design, improved selection of and access to sample sites, and enhanced prospects for addressing nitrate leaching through collaborative understanding of system hydrology. Mean landform-scale nitrate-N leaching rates were 11 and 18 kg ha⁻¹ yr⁻¹ during the 2012-2014 study for the two largest catchments draining the terrace. Over a standard three-year crop rotation, these leaching rates represent 19 to 31% of typical fertilizer N application rates; however, leaching

losses are likely derived not only from fertilizer but also from soil organic N mineralization, and are apparently higher during the post-fallow phase of the crop rotation. Groundwater apparent age is relatively young (0-5 yr) based on tritium-helium analysis, but whole-aquifer turnover time calculations are an order of magnitude longer (20-23 yr), suggesting changes in groundwater may lag behind changes in land management by years to decades.

1. Introduction

An estimated sixty percent of N inputs for production of goods and services in the United States (US) is lost due to inefficiency, where one third of these losses are routed to ground and surface water (Houlton et al., 2013b). Nitrogen losses associated with low N use efficiency have thus polluted drinking water sources and compromised aquatic ecosystem integrity across the globe, and N pollution is expected to increase in regions with increasing population or development (Spalding and Exner, 1993; Vitousek, 1994; Smith, 2003; Bouwman et al., 2005; Diaz and Rosenberg, 2008). Total N concentration in streams draining areas of agricultural land use are commonly six times greater than background levels (Dubrovsky et al., 2010). Such effects are particularly evident in the Mississippi Atchafalaya River Basin (MARB) where N flux to the Gulf of Mexico increased three-fold in the second half of the 20th century (Goolsby and Battaglin, 2001). These N fluxes are more than 60% nitrate-N, which is thought to be transported to ground and surface water primarily from microbial mineralization of soil organic N (SON) and fertilizer leached from agricultural soils (Goolsby et al., 1999a). In this study, we examine causes of high nitrate (NO_3^-) levels in groundwater and streams within an extensively cultivated 260 km² (26,000 ha) landform in the Upper Missouri Basin headwaters of the MARB. We link observations of water quality in cultivated soil, ground, and surface waters at this intermediate scale (mesoscale: 10² – 10³ km²) to estimate nitrate leaching rates, characterize the drivers of N loss, and suggest implications for water resource quality management in the region.

Despite the general understanding that mineralized SON and fertilizer play an important role in generating the large nitrate loads to the MARB (Goolsby et al., 1999a), there remains considerable uncertainty about the subsurface dynamics that control these fluxes. Understanding subsurface N processing and transport to groundwater is particularly important for mitigating surface water N loads in catchments with a high baseflow index, where the majority of stream flow generation is sourced from groundwater (Dubrovsky et al., 2010; Tesoriero et al., 2013). In addition, groundwater nitrate levels are above the 10 mg L⁻¹ drinking water standard (Ward et al., 2005) in 20% of shallow domestic wells in US agricultural areas (Dubrovsky et al., 2010). The number of wells exceeding the standard increased by ~5% between ~1990 and ~2000 (Dubrovsky et al., 2010) and average nitrate-N in agricultural area wells has increased 1 to 2 mg L⁻¹ per decade since the 1940s (Puckett et al., 2011). These increases have led to mounting health and economic costs borne by private well owners and municipal water suppliers (Ward et al., 2005; Bauder and Smith, 2011; Keeler and Polasky, 2014).

Nitrogen loss to ground and surface water can be characterized at a range of spatial scales, each integrating different sets of transport and loss mechanisms. In-stream N yields of <1 to 26 kg N ha⁻¹ yr⁻¹ estimated for large basins (> ~10³ km² or >~10⁵ ha) within the MARB represent an integration of all N sources and pathways, as well as processing and loss within riparian corridors during transport (Goolsby et al., 1999a). These values are highly relevant for prioritization of efforts to manage eutrophication in the Gulf of Mexico, but have limited utility for understanding the undoubtedly diverse mechanisms of N dynamics across the central North American continent. In contrast,

specific soil leaching dynamics are more readily isolated at the point-scale ($<1 \text{ m}^2$). While leaching rates measured at this scale can range over two orders of magnitude (Beaudoin et al., 2005), aggregation of point observations at the field-scale ($1\text{-}10^2 \text{ ha}$) has effectively allowed estimates of leaching rates (<5 to $69 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) that can be tied to drivers like crop type, soil character, and inter-annual variation in conditions (Beaudoin et al., 2005; Campbell et al., 2006; John et al., in revision). Thus, nitrate leaching rates and drivers identified at point- and field-scales can directly inform farm N management decisions. At the same time, there is no assurance that those rates and drivers are representative of landscape-scale ($>10^4 \text{ ha}$) variability. Conversely, nitrate observations that aggregate landscape-scale processes can identify water quality impairment and general sources, but the heterogeneity of pathways from sources along with N losses in transit impede efforts to quantify leaching rates and isolate specific drivers (Kunstmann and Kastens, 2006; Hansen et al., 2007; Dubrovsky et al., 2010; Pizzol et al., 2015). The question remains: How do N dynamics operating in soil at the point-scale ($<1 \text{ m}^2$) manifest in patterns of N fluxes observed at the spatially aggregated scale of entire agricultural catchments?

To address this central question, we evaluated mesoscale aquifer systems defined by local geomorphic and hydrogeologic context (Weissmann et al., 1999; Hancock and Anderson, 2002; Montgomery, 2004). Our study area lies within a central Montana watershed with elevated and increasing nitrate concentrations in groundwater. In particular, we sought a simplified hydrologic system, where stream flow generation is dominated by groundwater sources (i.e. minimal infiltration excess overland flow and

interflow) and groundwater recharge is dominated by infiltration from overlying soils (i.e. an aquifer with no groundwater inputs from surrounding areas). We selected a 260-km² strath terrace hosting a shallow unconfined aquifer with elevated nitrate, almost exclusively managed for non-irrigated cereal production (Miller, 2013). The terrace represents a process domain (Montgomery, 1999) with well-defined boundaries and a shallow, oxygenated, high-conductivity aquifer. The system allows landscape-scale estimates of leaching based on time series observations of nitrate concentrations in groundwater wells and surface water discharge (Q). Our first hypothesis was that ground and surface water chemistry is primarily controlled by the aggregate character of terrace soils draining to the sampling location because groundwater recharge is derived exclusively from local soils. As a result, we expected chemistry of ground and surface water to reflect chemistry of soils within a catchment. We hypothesized that the physical character of this landform promotes oxygenated conditions and short residence times in the shallow aquifer, resulting in minimal denitrification in groundwater. We further hypothesized that high N loading and biotic activity in the riparian corridors likely result in substantial denitrification. Thus, we expected groundwater nitrate concentrations would be similar to soil water concentrations measured in lysimeters during leaching periods, but that surface water concentrations would be lower than groundwater concentrations due to losses in the riparian corridors. Our approach to addressing these hypotheses and the overarching research question was to characterize soil connectivity to ground and surface water sampling locations based on chemical tracers, estimate the landscape-scale nitrate budget for the terrace aquifer, and constrain the residence time of

water in the aquifer to understand the potential time scale of nitrate concentration response to management changes. This research was framed using a community-based participatory approach described in detail in a companion paper (Jackson-Smith et al. 2018) and in the supplemental materials. Our approach engaged agricultural producers in understanding sources of nitrate in ground and surface water and testing farm management practices for effectiveness at reducing nitrate leaching (John et al., 2017).

2. Methods

2.1 Study Area

The study area is located within the Judith River Watershed (HUC 10040103), which drains 7,200 km² of central MT into the Missouri River. The Montana State University (MSU) Central Agricultural Research Center (CARC) near the center of the watershed reports an average annual precipitation of 389 mm for the period of record from 1909 to 2014 (WRCC Gage # 245761). Heaviest precipitation typically occurs in May and June with the two-month mean representing about 40% of annual precipitation. The study area is within the northern Great Plains (NGP) agroecoregion (Padbury et al., 2002), which roughly corresponds to the west-central semi-arid prairies Level II ecoregion (Fig. 1a; CEC, 2006). Annual crops in the NGP have traditionally been dominated by small grain (winter wheat, spring wheat, and barley) with whole-year summer fallow included in the crop rotation. Pulse crops (e.g. lentil, field pea) have replaced fallow in parts of the NGP (Long et al., 2014a), but small grain–fallow systems continue to dominate the study area (CropScape, 2014).

Cropland in fallow represents an elevated risk of nitrate leaching to groundwater and has been implicated as a likely cause of elevated groundwater nitrate in this region (Custer, 1976; Bauder et al., 1993; Schmidt and Mulder, 2010). Groundwater nitrate contamination in the Judith River Watershed is most evident in shallow alluvial aquifers within gravel terraces and alluvial fans at lower-elevation and lower-relief areas of the watershed (Schmidt and Mulder 2010; Fig. 1d). Terraces and fans are underlain by a relatively impermeable shale unit approximately 300 m thick (Vuke et al. 2002; Fig. 1d; supplemental materials), the top of which defines the lower boundary of the shallow gravel aquifers.

The Moccasin terrace (Fig. 1) provides a simplified case study of a gravel bench aquifer that receives recharge only from precipitation and infiltration on the terrace surface. In this system, mountain front streams are incised below the shale surface (Fig. 1c), preventing recharge from mountain front surface runoff (Covino and McGlynn, 2007) or groundwater flow (Carling et al., 2012), that occurs in other systems. Highly conductive gravel substrate and a relatively shallow aquifer thickness in the Moccasin Terrace result in relatively young groundwater, with estimated mean residence times on the order of one to ten years (Miller, 2013). Vulnerability of the aquifer to contamination is a function of its proximity to the surface (1-10 m depth to water table) and overlying soils with high infiltration capacity and low field capacity. The majority of the terrace surface (89%) is covered with clay loam soils with relatively thin zones of fine-textured horizons (ca. 30-100 cm) over horizons dominated by alluvial gravels and cobbles (ca. 1-20 cm diameter). Where the transition to these alluvial gravels is shallow, clay

accumulation is limited and soils are classified as Judith series. Where the transition is deeper, clay content is higher in B horizons and soils are classified as Danvers series. Both components exhibit high calcium carbonate below the A horizon (Soil Web; NRCS OSD website; Fig. 2b) and we refer to them here as calcareous loam soils. The largest fraction of remaining area (7%) is made up of shale-derived soils that are rich in gypsum (calcium and sulfate) and sodium (supplemental materials).

2.2 Water Sample Collection

We selected water sampling locations to capture nitrate flux and associated major ion chemistry along flow paths from soils to groundwater and surface water. Optimal sample site locations were developed in conversation with local producers and community members (supplemental materials), and through observations made during early sampling of the stream network (Miller, 2013). All water samples were field filtered at 0.45 μm , transported cold, and frozen prior to analysis, except for inorganic and organic carbon analysis, which occurred on never-frozen samples within two weeks of sample collection. See supplemental materials for a more detailed description of water sample collection methods.

Soil water sampling with porous cup tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark) was conducted within privately owned/managed fields (ca. 80 acres; 32 ha). Installation/sampling was coordinated with cooperating farmers to minimize disruption of farming operations and ensure that samples represented the outcome of uninterrupted standard field-scale farming practices. Eighteen lysimeters were installed in calcareous soils (near Grove spring, Fig. 2b) on the Moccasin terrace

and in similar nearby soils under the same management. Lysimeters were installed in fine textured material just above the gravely horizons (50 to 100 cm depth) below undisturbed upper soil horizons. During seasons when soil water content was relatively high, lysimeters were visited one to three times per month and an internal tension of approximately -100 kPa was applied with a hand pump to sample soil water. Only data from samples greater than 2.0 mL, collected within 48 hours of pressurization are reported here. Excluding samples smaller than 2.0 mL removed from consideration soil water nitrate concentrations during drier conditions when leaching was less likely to be occurring. Lysimeter samples were separated into crop rotation categories based on land use in the preceding growing season (ending 15 October). For example, a sample collected any time between 15 October 2012 and 14 October 2013 is categorized as post-fallow or post-grain depending on whether the field was in fallow or grain during the 2012 growing season.

Groundwater sampling sites (Fig. 2b) were wells and springs selected to represent subsurface contributing areas with a range of mean groundwater flow path lengths and different overlying soil types. Delineation of subsurface contributing areas to sampling sites was based on flow directions estimated from surface topography (Miller, 2013). Nitrate data from Montana Department of Agriculture (MDA) monitoring well M1 for the period 1994 – 2015 (two samples per year) were obtained from MDA (unpublished data; Schmidt and Mulder, 2010; Schmidt, 2009) and historic water level data were downloaded from the Montana Bureau of Mines and Geology (MBMG) Groundwater Information Center (MBMG 2016).

Surface water was sampled in order to capture N export from the landscape. Louse and Porter creeks were identified as the largest streams draining the terrace (Fig. 2b). We sampled Porter Creek at a single location at the outlet from the terrace (Porter site). Louse Creek was sampled at two locations: at an upstream location draining the higher elevations of the terrace (Railroad site) and at the outlet from the terrace (Kolin site). Water sampling at ground and surface water sites was conducted 12 to 15 times per year during 2012-2014. Five of the sites were established in 2012 (Miller, 2013) and the other five were established in 2013 (Table 2).

2.3 Water Sample Analysis and Major Ion Composition

Chemical analysis of all water samples was conducted in the Department of Land Resources and Environmental Sciences Environmental Analytical Laboratory (EAL) on the MSU campus. Major anions (chloride, nitrate, sulfate) were analyzed by ion chromatography (Dionex, ICS-2100, AS18 column), major cations and total sulfur by inductively coupled plasma-optical emission spectroscopy (Perkin Elmer, 5300 DV), dissolved organic and inorganic carbon by combustion (Shimadzu, TOC VCSH), and nitrate additionally by cadmium reduction and colorimetry (Lachat, QuickChem 8500; Seal, QuAAtro). See supplemental materials for detailed analytical methods and data quality assurance procedures. Differences in major ion composition were used to assess connectivity among soil, ground, and surface waters. In order to infer source waters based on relative variations in major ion composition of a given sample, dilution effects were removed by calculating ion ratios, which represent the fraction of the molar concentration of an individual ion relative to the summed molarity for all major ions. Variation in ion

ratios among sites was evaluated using principle component analysis (PCA) conducted within R statistical software with the `prcomp` function, with data scaled to unit variance (R version 2.15.2; The R Foundation for Statistical Computing, Vienna, Austria). For the PCA, ion ratios were aggregated as annual means within sites for the 2013-14 intensive data collection period. Tests for statistical difference in concentrations for different sites or domains (i.e. soil versus groundwater) were conducted with paired Kruskal-Wallis rank sum test using `kruskal.test` function within R statistical software (R version 2.15.2; The R Foundation for Statistical Computing, Vienna, Austria).

2.4 Groundwater Catchment Delineation, Discharge, Stream Baseflow and Area-Normalization

Groundwater catchments were delineated to allow normalization of volumetric stream flow observations from the Porter and Kolin sites to the area of their respective drainage and to subsequently produce leaching estimates (described in section 2.5). We interpret area-normalized stream flow at low-flow conditions as an indicator of baseflow yield and subsequently groundwater recharge, assuming that the change in storage in groundwater over the three-year study was negligible compared to the total volume of recharge or discharge over that time.

Area normalizations are based on annually cultivated catchment area alone, and the perennially vegetated catchment area is therefore excluded. See Supplemental Fig. 1 for a conceptual representation of this area normalization approach. This approach produces more accurate areal recharge rates for the cultivated soils, considering research that suggests recharge rates are much higher through annually cultivated soils than through perennially vegetated soils (Scanlon et al., 2005). Because we assume no

recharge through perennially vegetated soils, there is some possibility of over-estimating recharge rates through annually cultivated soils during the limited time when water content in perennially vegetated soils exceeds field capacity. Nitrate leaching rates for annually cultivated soils are estimated with the same area-normalization approach, but are less subject to over-estimation. This approach assumes (Section 2.5; Supplemental Fig. 1) that virtually all nitrate in groundwater comes from annually cultivated soils. This assumption is supported by both higher recharge rates driving more leaching and higher nitrate concentrations in annually cultivated soils relative to perennially vegetated soils. Consistent with this assumption, soil nitrate concentrations in the top 15 cm in three perennially vegetated fields were approximately an order of magnitude lower than those in adjacent annually cultivated fields during the fallow phase of the crop rotation (Ewing et al., unpublished data).

Delineations of groundwater catchments were derived from surface-derived topographic divides and subsurface divides determined by the topographic surface of underlying shales. Delineation by surface topography was based on a one third arc-second (~10 m) National Elevation Dataset (USGS 2012) digital elevation model (DEM) processed in ArcMap Spatial Analyst using the Flow Direction and Watershed tools based on the sample site locations. The shale surface DEM was estimated in ArcMap by kriging shale surface elevations from well logs, geologic maps coupled with aerial imagery, and mapped locations of shale-derived soil series (ordinary spherical semivariogram kriging model; supplemental materials). Ground-surface- and shale-surface-derived catchment delineations were manually combined based on assessment of

the most likely driver of flow direction in a given area. The ground-surface-derived delineation was selected where shale was near the surface and where the shale-surface-delineation was ambiguous. The shale-surface-delineation was selected in places where shale topography was unambiguous and departed from ground surface shape (most notably around the Spring 555 sample site; Fig. 2A).

Stream discharge (Q , $\text{m}^3 \text{s}^{-1}$) at the Porter and Kolin sites was measured manually during water sampling visits using the velocity cross-section method with a Marsh McBirney FloMate electromagnetic flow meter. In 2013, manual staff gages were installed along with stilling wells containing capacitance rod stage recorders (TruTrack, Inc.). For periods prior to stage recorder installation and when ice affected stage, daily Q was estimated using linear interpolation between the measured or modeled values bracketing the period.

We quantified aquifer efflux by estimating baseflow with a simple manual hydrograph separation method, using linear interpolation between inflection points identified on the rising and falling limbs of the hydrograph. This manual linear approach was used rather than a more objective approach (e.g., Lyne and Hollick, 1979; Lim et al., 2005) to ensure that allocation of flow to the groundwater source was conservatively low during high flow periods in March-June when flow data were less reliable. Selection of methods producing conservatively low values provides confidence that nitrate flux estimates produced from baseflow estimates represent a lower bound on nitrate leaching losses.

2.5 Nitrate Loading to Ground/Surface Water and Leaching Rates

To estimate cultivated soil nitrate load (kg N yr^{-1}) to the riparian corridor (NLRC) prior to hypothesized riparian losses, each daily mean aggregate groundwater nitrate concentration (mean across seven groundwater sites) was multiplied by daily stream baseflow. These loads were area-normalized to the annually cultivated land area within each catchment (described in section 2.4 and Supplemental Fig. 1) in order to estimate leaching rates ($\text{kg N ha}^{-1} \text{ yr}^{-1}$).

Daily mean aggregate groundwater nitrate concentrations used for load calculations were derived by first calculating monthly mean concentrations for each of the seven groundwater sites. Monthly mean values for the sites were then averaged to produce the monthly mean aggregate groundwater values and linear interpolation between these values produced the daily mean aggregate groundwater concentrations. During the intensive April 2013 to September 2014 sampling period, the seven groundwater sites selected to represent variability in terrace groundwater were included in this calculation. Before and after the intensive sampling period, two groundwater sites were included in the monthly mean aggregate groundwater concentration. Uncertainty in the monthly mean aggregate groundwater nitrate concentration was assessed using residual differences between the monthly mean aggregate groundwater values and monthly means for the individual sites during the 2013-14 high intensity sampling period. A Monte Carlo ensemble of groundwater concentration time series was created with 1000 randomly generated realizations from this distribution. The ensemble of groundwater concentrations in combination with daily stream baseflow values determined the ensemble of loads that provide some constraint on uncertainty in daily and annual mean

NLRC estimates. Descriptive statistics (i.e. 2.5% and 97.5% quantiles) from the resulting Monte Carlo ensembles of concentrations, daily loads, and time-aggregated loads provide a rough estimate of how error in characterizing a single aggregate nitrate concentration from the observed spatial variation in groundwater may propagate to uncertainty in the total load estimates from the terrace.

To estimate nitrate-N losses from the riparian corridor, stream concentrations were subtracted from mean groundwater concentrations during periods when the majority of stream flow was originating from longer-term storage. This calculation was conducted for stream concentrations and the set of groundwater concentrations collected on the same sampling trip.

2.6 Groundwater Residence Time

We sampled for apparent groundwater age using ^3H - ^3He (Cook and Solomon, 1997) in May 2014 at the M1 monitoring well and at two springs (Indian and Grove sites). Gas sampling was conducted with copper tube diffusion samplers deployed in the well and in flow-through buckets at the orifice of the springs, with 24 hours equilibration time before being crimp sealed (Sanford et al., 1996). At the time of gas sampler deployment, 1-L polypropylene bottles were filled with water for associated ^3H analysis. Gas and water samples were shipped to the University of Utah Stable Isotope Laboratory for analysis. Tritium analysis was performed using a Helix SFT sector-field mass spectrometer with the helium ingrowth method (Clarke et al., 1976).

Groundwater turnover time was also estimated based on a fully mixed reservoir assumption, dividing the estimated total volume of the groundwater reservoir [L^3] by the

total discharge from that reservoir [$L^3 T^{-1}$]. Steady state aquifer outflow is estimated as the average annual baseflow discharge for each catchment over the three-year study (section 2.4). Aquifer volumes for each catchment were estimated from the product of catchment area (section 2.4), specific yield of 0.3 (Anderson and Woessner, 1992), and saturated thickness. Saturated thickness was estimated by first calculating the thickness of gravel overlying shale, as the shale surface DEM subtracted from the ground surface DEM. The fraction of the gravel that was saturated was estimated using values observed in seven well logs (MBMG, 2016) within terrace boundaries where shale depth and depth of water below ground surface were available.

3. Results

3.1 Catchment Delineation and Soil Type Composition

The Kolin groundwater catchment area is the largest within the landform at 9,670 ha (37% terrace area), followed by Porter (3,630 ha and 14%), Pioneer spring (750 ha, 3%) and Spring 555 (320 ha, 1%; Fig. 2a-b, Table 1). For three of these four catchments (Kolin, Porter, Pioneer) surface topography based delineation was not notably different from the shale surface approach, while for Spring 555 the catchment area was much larger (~500%) based on inference from the shale surface. The four groundwater catchment areas combined (Kolin, Porter, Pioneer, Spring 555) capture 55% of the terrace area, indicating that the majority of water leaving the terrace is characterized by the ion chemistry data presented here. Shale soils compose 13% of the Louse Creek catchment above Railroad and 8% of the catchment above Kolin (Fig. 2b, Table 1). The

Spring 555 catchment has the highest fraction of shale-derived soils (16%) while Porter creek catchment has no shale-derived soil.

3.2 Nitrate Concentrations in Soil Water and Groundwater

The mean nitrate-N concentration observed in M1 during the three-year study ($18.6 \pm 6.7 \text{ mg L}^{-1}$) was generally consistent with predictions from the increasing trend in the well from ca. 10 to ca. 20 mg L^{-1} during the 1994-2015 observation period (Fig. 3). The three-year mean for M1 was also not significantly different (Kruskal-Wallis, $p = 0.20$) from the aggregate mean concentration for the other six groundwater sites over the three-year period ($20.9 \pm 6.6 \text{ mg L}^{-1}$). However, the mean concentration in M1 for 2014 ($9.9 \pm 4.7 \text{ mg L}^{-1}$) was notably lower than for 2012 ($21.4 \pm 0.9 \text{ mg L}^{-1}$) and 2013 ($23.4 \pm 0.9 \text{ mg L}^{-1}$) and lower than mean concentration in aggregate terrace groundwater for 2014 (17.1 mg L^{-1} , Table 2). The lower 2014 mean concentration in M1 was confirmed to be a local dilution event based on a corresponding change in specific conductance. This type of transient dilution is also suggested by the historic data in the form of occasional concentrations lower than the overall increasing trend (Fig. 3). Lower nitrate concentrations in M1 consistently occur during the January-July period when snow melt and the heaviest seasonal precipitation occurs, and only one of the other groundwater sites (Pioneer) displays a spring dilution pattern of similar magnitude. The fact that dilution effects are relatively localized in time and space suggests that they do not have a substantial influence on the long-term state of the aquifer. Given the seasonal timing of these transient dilution events, the long-term trend in aquifer status was assessed with only the concentrations for August to December samples. Concentrations during this

period tend to be more stable and presumably less subject to temporary dilution during large recharge events. Regression of nitrate concentrations from this smaller data set with time ($r^2 = 0.79$, $p < 0.05$, Fig. 3) indicates nitrate-N concentrations have generally increased by $0.67 \pm 0.09 \text{ mg L}^{-1} \text{ yr}^{-1}$ in the well for the past two decades.

The range of nitrate-N concentrations observed in groundwater ($1.5 - 33.5 \text{ mg L}^{-1}$) was approximately half that observed in lysimeters ($<1 - 61 \text{ mg L}^{-1}$), suggesting an averaging effect in groundwater with respect to incoming soil leachate concentration. However, the aggregate mean groundwater nitrate concentration ($20.4 \pm 6.4 \text{ mg L}^{-1}$) was significantly higher ($p < 0.05$) than the aggregate mean lysimeter nitrate concentration ($16.6 \pm 13.1 \text{ mg L}^{-1}$). When lysimeter samples were separated based on phase of cropping cycle, post-fallow concentrations ($25.4 \pm 14.0 \text{ mg L}^{-1}$) were significantly higher ($p < 0.05$) than post-grain concentrations ($11.6 \pm 7.7 \text{ mg L}^{-1}$). Mean groundwater nitrate-N concentration was intermediate between mean lysimeter concentrations grouped by crop phase (Fig. 4). Groundwater concentration was significantly higher ($p < 0.05$) than lysimeter concentrations post-grain, but not significantly different ($p = 0.08$) from lysimeter concentrations post-fallow. These results agreed with expectations in the simple sense that aggregate groundwater nitrate concentration was not lower than aggregate lysimeter concentration, but concentrations were similar (not significantly different) only when cropping stage was considered.

3.3 Major Ion Composition of Terrace Waters and Hydrologic Connectivity

The highest total ion concentrations observed in ground and surface waters were in the well at the Headwaters site (20.9 mM) and the spring at the 555 site (17.8 mM),

(Table 3, Fig. 5). These molar concentrations are approximately twice that of the five other groundwater sites. Higher molarities at the Headwaters site are attributable mostly to higher sodium (Na^+) concentrations, but sulfate is notably higher at both the Headwaters and 555 sites relative to the other groundwater sites. The Railroad site has the highest total ion concentration of the surface water sites (16.8 mM).

A PCA of the molar ratios resulted in 77% of the total variation in composition explained by the first two components (PC1 = 58%, PC2 = 19%). Analytes contributing the most loading on PC1 were sulfate (SO_4^{2-}) and sodium on the negative side and calcium (Ca^{2+}) and bicarbonate (HCO_3^-) on the positive side (Fig. 6a, Table 4). Analytes with the most important loading on PC2 are nitrate on the positive side and magnesium (Mg^{2+}) and bicarbonate on the negative side.

Sampling sites with the lowest mean PC1 scores (higher sodium and sulfate molar ratios) are Spring 555 and Headwaters site, which are located in the higher elevations of the terrace (Fig. 2, Table 4), with higher occurrence of shale soils. The Railroad catchment, which encompass the shale soil areas in the upper half of the terrace, also has low PC1 scores. The Kolin catchment encompasses the Railroad catchment but also drains extensive calcareous soils downstream and has a higher PC1 score than Railroad. On the other extreme of PC1, the highest scores (higher proportion calcium and bicarbonate) are for the lysimeter soil water samples and Pioneer Spring, followed by the other springs draining the downgradient half of the terrace where calcareous soils are dominant. Porter Creek, draining much of the southern regions of the terrace, has a PC1 score similar to Grove and Indian springs, which drain that portion of the terrace where

very little shale soil is present. This general alignment of PC1 score and prevalence of shale soil is consistent across the terrace, demonstrated by a strong negative relationship (slope = -0.25; $r^2 = 0.94$; $p < 0.05$) between percent shale soil within a catchment and PC1 score in surface water (Fig. 6b). Alignment of water sample site PC1 scores (sodium and sulfate versus calcium⁺ and bicarbonate) with the extent of shale soil versus calcareous soil upgradient agrees with our prediction that ground and surface water chemistry will uniquely reflect chemistry of soils within a catchment.

Differences in nitrate concentration are the next most notable driver of variation in ion ratios, reflected in PC2 scores. Soil nitrate concentrations are highly dynamic, which is why lysimeter samples produced both the highest and lowest PC2 scores. Higher nitrate concentrations in groundwater relative to surface water are evident in groundwater sites generally having higher PC2 scores, a finding consistent with our prediction of lower surface water nitrate after riparian losses.

3.4 Stream Discharge, Groundwater Levels and Recharge

Kolin and Porter Creek catchment discharges (Fig. 7d-e; Table 4) experienced annual peaks between March and June across the study period, coincident with peak water levels in the M1 well (Fig. 7a-b). Peak groundwater and stream discharge levels aligned with timing and magnitude of April-June precipitation in 2012 and 2013, while peaks in 2014 coincided with snow melt and rain-on-snow events in February-March. On Aug. 23rd of 2014, 110 mm of rain fell at the CARC Agrimet station on a single day, amounting to more than twice the previous maximum daily precipitation (41 mm on 5/24/2011) since installation of the station in 2001.

Annual average baseflow for both streams (Table 5) was highest in 2012 following high annual precipitation in 2011 and baseflow was lowest in 2013 after low annual precipitation in 2012. The lowest measured baseflow in Louse Creek was just before the 23 August 2014 rain event, which brought groundwater levels and Louse Creek flows back up to levels similar to early 2012. While groundwater and stream discharge respond to precipitation on a timescale of days to months, influence of previous year precipitation on average annual baseflow suggests that stream discharge is integrating recharge rates across the current and previous year. Therefore, while area-normalized annual average baseflows are presented (Table 5) as an estimate of annual recharge, these may be over- or under-estimated due to baseflow contributions from inter-annual storage. Therefore, we also report the three-year mean values (Kolin = 54 mm yr⁻¹, Porter = 87 mm yr⁻¹) as an estimate of average annual recharge that is less influenced by inter-annual storage.

3.5 Nitrate Leaching Rates and Riparian Losses

Daily mean NLRC values for Kolin (Fig. 7f; 11.1 ± 0.3 kg N ha⁻¹ yr⁻¹) are, on average, 60% of those for Porter (Fig. 7g; 18.4 ± 0.4 kg N ha⁻¹ yr⁻¹). The same aggregate groundwater nitrate concentrations are used to calculate the NLRC values for both catchments, so the different NLRC values stem from differences in area-normalized baseflow between the catchments. Uncertainty in concentration and NLRC values (gray shading Fig. 7c, f, g) are based on residual differences between the monthly aggregate groundwater mean and monthly means for the individual sites (normal distribution; standard deviation = 6.2 mg L⁻¹). Parallel to groundwater recharge estimates, annual

average NLRC values are presented (Table 5), but the three-year mean values provide estimates of average annual load that are less influenced by inter-annual storage.

The 2012-14 mean nitrate-N concentration for Porter Creek ($19.3 \pm 1.8 \text{ mg L}^{-1}$) was similar to that for aggregate groundwater ($20.4 \pm 6.4 \text{ mg L}^{-1}$), while three-year mean concentrations in Louse creek at both Railroad ($12.1 \pm 3.7 \text{ mg L}^{-1}$) and Kolin ($10.0 \pm 2.4 \text{ mg L}^{-1}$) were approximately half that in aggregate groundwater (Fig. 4, Table 2), a pattern also apparent in the time series data (Fig. 7c). Instantaneous nitrate-N loads were calculated for each visit to the Kolin and Porter sites (Fig. 7f-g) using measured concentration and measured Q. Values ranged from 31.3 to 373.8 with a mean of 109 kg N day⁻¹ for Kolin while values for Porter Creek ranged from 73.8 to 295.7 with a mean of 131 kg N day⁻¹. Normalizing these values to the cultivated area within the catchments produces a mean of $5.3 \pm 3.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for Kolin and a mean of $18.6 \pm 7.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for Porter (Fig. 7f-g). These values represent nitrate-N loads leaving the Moccasin terrace after potential losses in the stream-riparian system, and hence constitute a conservative lower bound on N yields from the landscape over time during the study.

Riparian nitrate loss was estimated for six site visit trips during the period from July to November 2013, when no storm related peaks in the stream hydrographs were present. Apparent riparian nitrate loss during this period averaged 53% (range: 43 to 60) for Kolin and 16% (range: 10 to 23) for Porter Creek (Supplemental Fig. 2). Apparent riparian losses normalized to cultivated area within the catchments during this period averaged $3.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (range: 3.0 to 4.3) for Kolin and $2.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (range: 1.8 to 4.8) Porter Creek, but were higher on average for Kolin (Supplemental Fig. 2).

3.6 Groundwater Residence Time

Groundwater residence time estimated by ^3H - ^3He apparent age for the open M1 well bore was 1.7 ± 0.5 yr on 9 August 2012 (Miller, 2013) and was 5.2 ± 0.57 yr on 25 May 2014 (Table 6). Depth-specific sampling in M1 using packers on 24 May 2014 produced ages of 3.9 ± 0.56 yr for the bottom of the well (5.2–5.7 m) and 1.2 ± 0.65 yr for the top of the screening interval (2.6–3.4 m). Grove and Indian springs sampled for ^3H - ^3He apparent ages on 24 May 2014 produced values of 0.8 ± 0.5 and -0.8 ± 0.9 yr (effectively zero), respectively. The mean of ^3H - ^3He apparent age values observed in 2014 in the open M1 well bore and the two springs was 1.8 yr (st dev = 3.1 yr). Estimated turnover times based on aquifer volume and discharge were approximately an order of magnitude longer at 23 and 20 yr for Kolin and Porter catchments respectively (Table 7).

4. Discussion

Our results provide a landscape-scale perspective on the fate and transport of nitrate from soils to groundwater to stream networks in a non-irrigated agrosystem. We found that N loss to nitrate leaching represents up to one third of typical fertilizer N inputs over a three-year crop rotation, but that fallow within a crop rotation may allow for a disproportionate amount of nitrate leaching to groundwater. These results allow assessment of the differences between the two largest stream catchments draining the Moccasin terrace, which were evaluated with respect to leaching rate and riparian denitrification losses. This study highlights opportunities for targeting reductions in deleterious leaching losses and enhancement of beneficial N losses due to riparian denitrification.

4.1 Connection of Soil, Ground and Surface Waters within Moccasin Terrace

Delineation of the process domains controlling nitrate dynamics in lower-relief sedimentary basins requires consideration of the relationship between stratigraphy and the land surface that characterizes the hydrogeologic and geomorphic context (Montgomery, 1999; Montgomery, 2004; Capell et al., 2011; Tesoriero et al., 2013), particularly in contrast with studies in mountain catchments where N transport to streams may be assumed to follow hydraulic gradients suggested by surface topography alone (e.g., Gardner and McGlynn, 2009). Within the Moccasin terrace process domain, the alignment between surface water chemistry and catchment soil chemistry (Fig. 6b), suggests accuracy in our approach to groundwater catchment delineation. In addition, the alignment of ground and surface water chemical composition with SSURGO map unit chemical composition for upgradient soils (Fig. 2b, Fig. 6a) provides support for our first hypothesis that ground and surface water chemical composition are primarily controlled by the aggregate character of terrace soils draining to a sampling location.

4.2 Nitrogen Concentrations and Soil-Groundwater Connections

The mean groundwater nitrate-N concentration we observed for the Moccasin aquifer (20.4 mg L^{-1}) is above the 75th percentile for a Montana statewide agricultural well network (Schmidt, 2009), is near the 95th percentile of US concentrations reported by Puckett et al. (2011), and is approximately double the highest 2000-2004 median US well network concentrations reported by Rupert (2008). It is similar, however, to mean values reported for other shallow groundwater underlying dryland small grain production in Montana (20 mg L^{-1} ; Nimick and Thamke, 1998) and Eastern Washington (19.3 mg

L^{-1} ; Kelley et al., 2013). The high concentrations are likely a function of the proximity of easily leachable soils to the shallow Moccasin aquifer, where limited volume and reduced denitrification potential result in vulnerability to nitrate pollution. Furthermore, this aquifer lacks inputs of low nitrate recharge water from mountain front stream recharge or from extensive irrigation, both of which can dilute groundwater nitrate in systems where they are present.

Consistent with global patterns of pronounced seasonality in groundwater recharge (Jasechko et al., 2014), the Moccasin aquifer receives most recharge in the pre-growing season months. This is evident from the rise in groundwater level with spring precipitation observed annually (Fig. 7), juxtaposed with a general lack of response to precipitation during the growing season. Flux to groundwater can be expected to be larger from soils with high water storage from the previous season (Nippgen et al., 2016) and soil moisture storage is purposefully created with fallow land use (Zeleeke et al., 2014). Higher recharge from post-fallow fields, coupled with higher nitrate concentrations in post-fallow soil water (25.4 mg L^{-1}) than post-grain soil water (11.6 mg L^{-1}), suggests that fallow rotations may result in disproportionately high leaching of N to groundwater. While fallow land use makes up only 25% of the cultivated terrace surface (Table 1), its importance to N leaching is supported by nitrate-N concentrations in groundwater (20.4 mg L^{-1}) that are more similar to post-fallow than post-grain soils (Figure 4). Similarity between post-fallow lysimeter and groundwater nitrate concentrations provides support for our first hypothesis, that minimal denitrification occurs in groundwater. In future work, the range of lysimeter nitrate concentrations we observed ($<1 - 61 \text{ mg L}^{-1}$; similar

to comparable studies: <0.1 to 63.3 mg L^{-1} , Kelley, 2015; <1 to $\sim 43 \text{ mg L}^{-1}$, Mariotti et al., 2015) could be coupled with daily deep percolation rates to provide more insight about crop rotation effects on leaching. In the simplest terms however, significantly lower soil nitrate concentrations observed post-grain versus post-fallow suggest that replacing fallow with continuous cropping – potentially in the form of water and N efficient cover crops or legumes - would be a step toward reducing groundwater nitrate concentrations below the drinking water standard of 10 mg L^{-1} .

4.3 Nitrate Leaching Rates

Landform-average nitrate leaching rates presented here ($11\text{-}18 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) for the Moccasin terrace are 19 to 31% of average standard fertilizer N application over a three-year rotation in the study area ($\sim 90 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for each of two crop years and zero for fallow year) during the study (John et al., 2017). However, these values should not be interpreted as applied fertilizer lost directly to leaching. Mineralization of SON during fallow periods is an important component of leaching loss at this site that remains difficult to quantify (Custer, 1976; Miller 2013; John et al., 2017). Our results agree with general findings by John et al. (2017), that leaching rates are higher post-fallow than post-crop (pea), but average leaching rates in that 2013-2014 field-scale study were notably higher ($\sim 50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) than our leaching estimates. One possible explanation for the discrepancy is the set of conservative assumptions in our approach (Section 2.4 and Supplemental Material Section 4.3), including possible denitrification at a few groundwater sites during periods where measured dissolved oxygen was below 2 mg L^{-1} (Supplemental Fig. 3). Uncertainty in the field based approach is another possible

explanation, along with the fact that our study integrates leaching losses over years to decades, while the field-scale study quantifies leaching for 2013 and 2014. The fact that our leaching values are lower than those of John et al. (2017), provides support for our suggestion that leaching estimates presented in this study are conservatively low.

Notably, values presented here are comparable to rates ($13 \pm 7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$) from a study in eastern Washington that used a 12 ha tile drainage network to delineate a process domain within a small grain landscape where leaching was 12 to 15% of applied fertilizer rates (Kelley et al., 2017).

Area-normalized baseflow in the Kolin catchment is approximately one third lower than in Porter, a result that propagates into the estimated leaching rate differences between the two catchments (Table 5). This difference may reflect greater soil water storage capacity and/or less groundwater storage capacity within the Kolin catchment relative to Porter. The Kolin catchment has a larger fraction of area mapped as the thicker (Danvers series) calcareous soils (Fig. 2b, Table 1), while the Porter catchment has a higher fraction of the thinner (Judith series) calcareous soils. More potential for water storage in the thicker soils of the Kolin catchment could retain more infiltrated precipitation within the root zone, making it available for loss to evapotranspiration and reducing deep percolation/leaching. At the same time, the mean depth to shale and associated aquifer volume is less in the Kolin catchment than the Porter catchment (Table 1). In the higher elevations of the Kolin catchment, where shale is at or near the surface, soils may be subject to saturation excess overland flow, halting the recharge of groundwater from deep percolation/leaching. The Kolin catchment is likely to have a

combination of both higher soil moisture storage capacity and less groundwater storage capacity, resulting in lower deep percolation and leaching rates relative to the Porter catchment. It is also possible that differences in riparian corridor evapotranspiration between the two catchments (i.e., more at Kolin) are contributing to lower area-normalized baseflow for Kolin.

4.4 Riparian N Losses

Our results suggest substantial losses of nitrate in the riparian corridor, as has been observed in previous studies (Lowrance et al., 1984; Hedin et al., 1998; Bohlke et al., 2002; Mulholland et al., 2009; Zarnetske et al., 2011), a finding that supports our second hypothesis. The estimated loss rate of 14% for Porter is similar to that predicted by Mulholland et al. (2008) for small streams ($> 100 \text{ L s}^{-1}$), while the 53% estimate for Louse Creek above Kolin is far higher than predicted from other studies. Higher loss rates in Louse Creek corridor may be due to difference in the fraction of groundwater discharged through more diffuse seeps versus more focused springs. Groundwater discharging through seeps has prolonged contact with soil that can facilitate denitrification (Williams et al., 2015), while higher discharge rates through coarse substrate springs likely promotes less denitrification. Persistence of losses into November (Supplemental Fig. 2) beyond the peak season for in-stream primary productivity suggests that denitrification in this riparian system may play a larger role relative to plant uptake. This dominance of denitrification is atypical across biomes (Mulholland et al., 2008), but may be common in systems not limited by N. These findings merit further exploration based on the isotopic composition of nitrate.

4.5 Groundwater Nitrate over Time and Expected Timescale of Response to Changing Inputs

The rate of increase in nitrate-N concentrations in the M1 well from 1994 to 2014 ($0.67 \pm 0.09 \text{ mg L}^{-1} \text{ yr}^{-1}$) is two- to five-fold higher than the rates of increase reported in national studies (Dubrovsky et al., 2010; Puckett et al., 2011). Over the same period, water levels in groundwater have been variable but do not show a trend (Fig. 3), suggesting that recharge rates have not changed. Therefore, the most likely explanation for increases in groundwater nitrate concentrations is that leached nitrate concentrations in recharge have increased. Apparent groundwater ages of $1.8 \pm 3.1 \text{ yr}$ based on ^3H - ^3He values are aligned with some of the youngest reported in other studies ($<2\text{yr}$ from Williams et al., 2015) and suggest that groundwater nitrate concentration only lags a few years behind changes in leachate concentration. However, the fact that apparent groundwater age is ten-fold less than calculated turnover time based on aquifer volume (20-23 yr) suggests that a substantial proportion of the aquifer is bypassed by flows that mix more slowly with the total volume. Paleo-channels carved in the shale surface during terrace formation (Hancock and Anderson, 2002) or differentially sorted gravel channels within gravel deposits (Ritter, 1967; Stamm et al., 2013) may constitute important pathways of preferential flow through the terrace aquifer. Areas of lower hydrologic conductivity - outside preferential flow paths - will turn over more slowly. Aquifer zones with longer turnover times will add to lag time in groundwater nitrate concentration response to changes in leachate concentration from management changes. Collection of ^3H - ^3He time series data for springs and wells could help characterize differences in

groundwater age distributions over seasons and different aquifer zones, which could help refine understanding of expected lag times in groundwater response to inputs.

County level data for Judith Basin County indicates that in the 1990s, the rate of N applied in fertilizer surpassed the rate of N removed in grain (Miller, 2013). The low spatial resolution of the county level data and the dynamic role of soil organic matter as a soil N storage reservoir preclude simple conclusions about nitrate concentration in leachate from the yield and fertilizer data. Nonetheless, the multi-decadal N data for yield and fertilizer input provides interesting context for interpreting the concentration trend in the M1 monitoring well and warrants further exploration.

4.6 Value of Participatory Approach to Hydrologic Investigation

For purposes of exploring hydrologic drivers of nitrate leaching in agricultural settings, the participatory approach of this work allowed us to benefit from local farmer knowledge of the landscape, provided access to sampling sites that otherwise would not have been possible, and facilitated development of effective strategies to communicate results to the agricultural community, thus potentially influencing changes in behavior to mitigate nitrate pollution in this area (Jackson-Smith et al., in review). Basins draining Montana rank below the 15th percentile of MARB basins for total N yield, but our study area includes nitrate concentrations ranking among the highest in national assessments (Goolsby et al., 1999; Dubrovsky et al., 2010; Puckett et al., 2011). Thus, while Montana's role in eutrophication of the Gulf of Mexico is small, groundwater nitrate pollution challenges are large from the perspective of communities within the state, and as reflected in an increasing number of regional studies globally (Bohlke and Denver,

1995; Flipo et al., 2007; Wong et al., 2015; Ameer et al., 2016; Niu et al., 2017). Work at the mesoscale landscape level to characterize and address groundwater contamination issues is important both from the perspective of isolating process domains within which a similar set of hydrologic and agronomic drivers are at play, but also for leveraging a scale at which management and environmental effects can be explicitly connected and effectively addressed by local communities (Wilbanks, 2015).

5. Conclusions

In conclusion, the Moccasin terrace exhibits close connections between soil water and groundwater, and between groundwater and streams. This setting provides a unique opportunity to directly observe landscape-scale movement of soil solutes as they travel through groundwater storage and are exported via stream discharge. Our results indicate nitrate leaching rates up to one third the rate of fertilizer N input over a standard three-year crop rotation, but losses may be more heavily weighted to the post-fallow period within the rotation, and mineralized SON is likely an important source of leached N. The possible influence of the practice of fallowing on groundwater nitrate concentrations suggests that replacing grain-fallow rotations with continuous-crop rotations could reduce groundwater nitrate levels. Tracer-based apparent groundwater ages ranging up to five years suggest that groundwater nitrate concentrations could respond relatively quickly to changing nitrate concentrations in leachate; however, whole-aquifer turnover times on the order of decades suggest longer lag times are possible. Reduced groundwater nitrate concentrations should directly reduce N loads to surface water, especially in catchments with high baseflow index such as those in our study area. Additional surface water

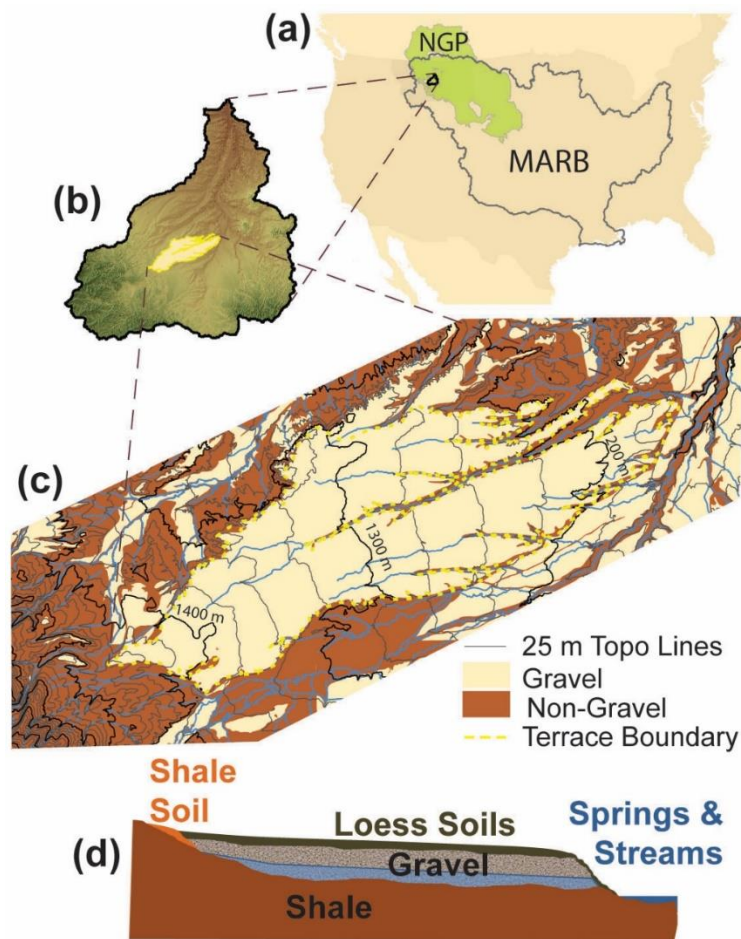
quality benefits may be achievable if drivers for the higher riparian N loss rates observed for Kolin versus Porter catchment can be further characterized and addressed with management.

Our research approach included individual profile-scale observations to infer soil processes within a field-scale management context, which we combined with ground and surface water observations to infer landscape-scale processes. This multi-scale approach allows inference about N processing that would not have been possible with observations only in soils, wells, or streams. Moreover, our participatory study design facilitated local farmer input and collaboration, resulting in improved access to and understanding of research sites. The demonstrated connection between soil, ground, and surface water in the study area became a working model in an open dialog that allowed agricultural producers to evaluate their role in landscape-scale water quality issues and to help identify management strategies that would be practical and effective. This type of multi-scale process based research, coupled with a participatory approach to developing shared understanding of both management choices and environmental consequences, could improve progress toward addressing environmental issues while sustaining farm viability across a variety of contexts (Committee on Twenty-First Century Systems Agriculture, 2010; Seitzinger et al., 2010).

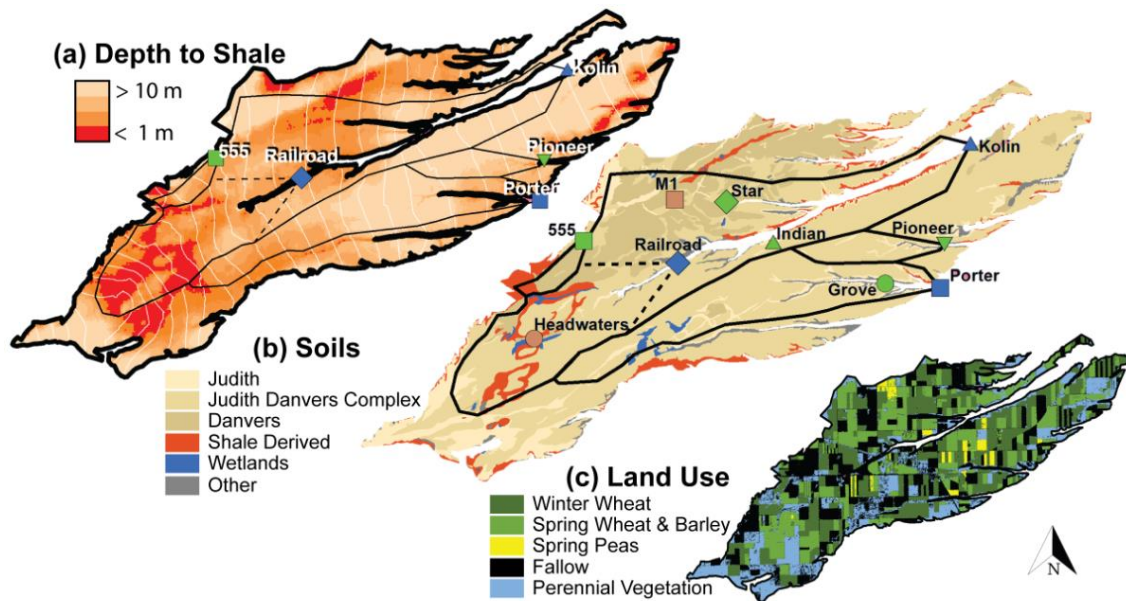
Acknowledgements

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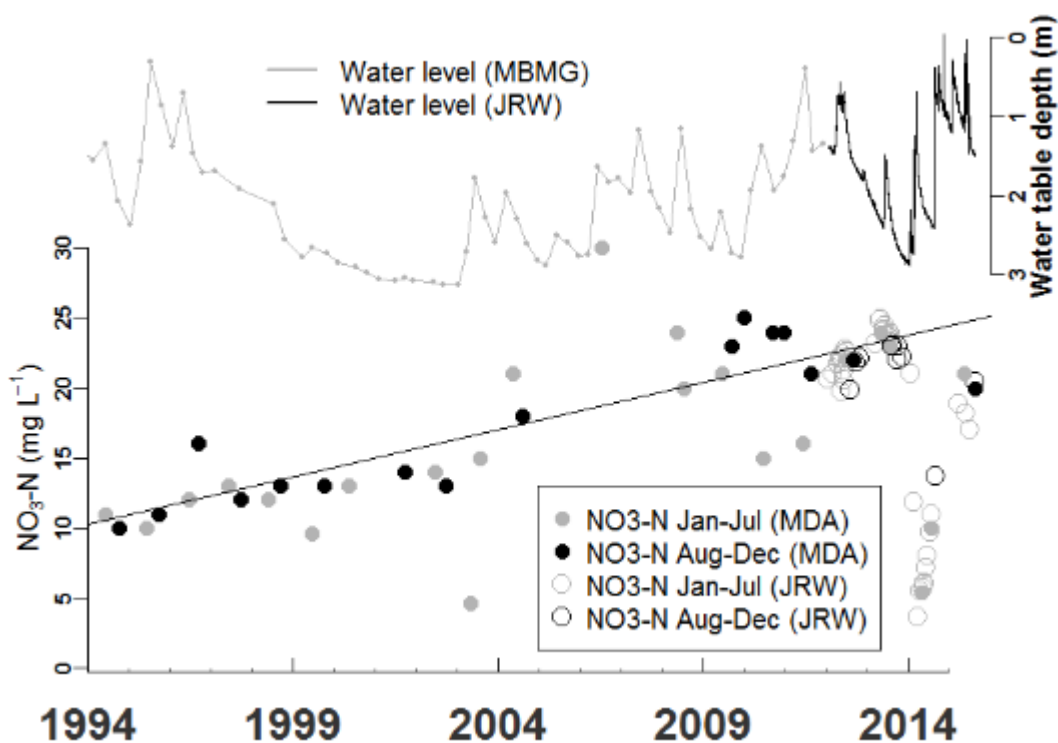
Center (CARC). CARC superintendent Dave Wichman provided assistance in the form of local contacts, vehicle and equipment use, accommodations, and knowledge of the study area. The six-member producer research advisory group (PRAG) conducted management trials on their farms and provided invaluable insights on data collected from a farm management perspective. Data collection and analysis conducted by Christine Miller from 2012-2013 for her master's thesis was foundational for framing of this work. Kyle Mehrens and Robby Robertson along with a number of MSU undergraduates helped with instrumentation and data collection. A special thank you to Simon Fordyce who was the lead field technician for the majority of the field campaign. This work was funded by the United States Department of Agriculture, National Institute of Food and Agriculture [grant number 2011-51130-31121, 2011]. Additional funding was provided by MSU Extension, the Montana Fertilizer Advisory Committee, the Montana Agricultural Experiment Station, and MSU Institute on Ecosystems.

Figures

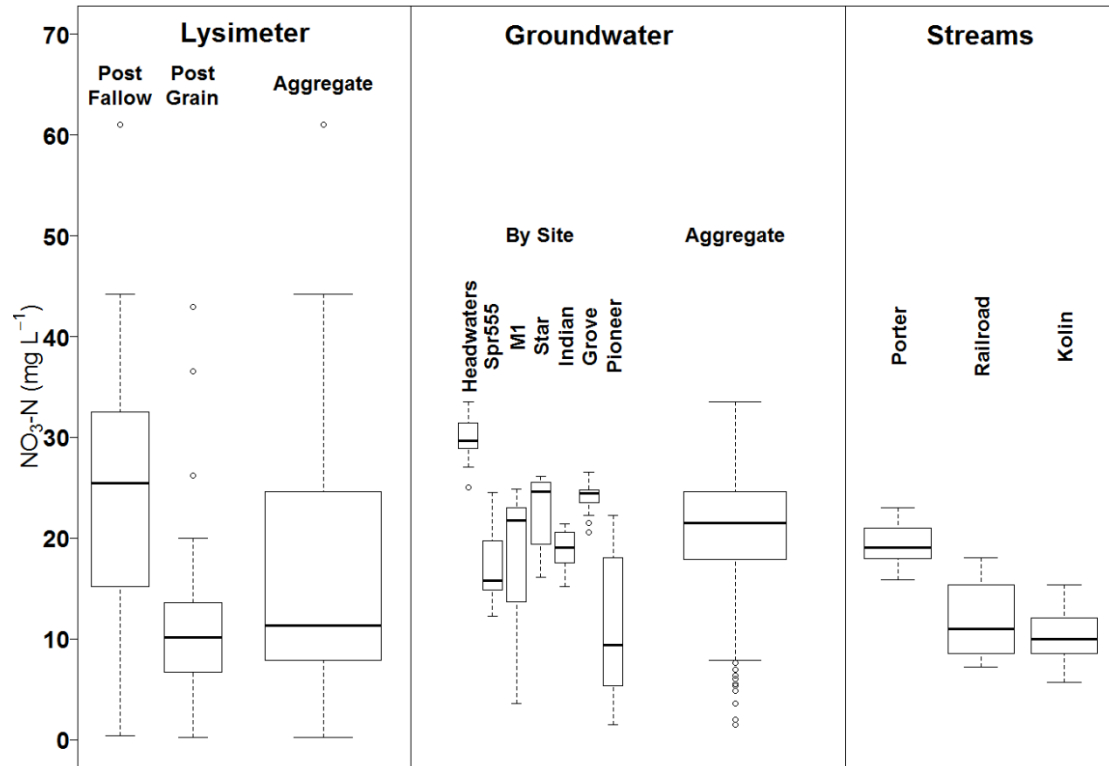
Ch2-Figure 1. Site location and conceptual terrace cross section. The Moccasin terrace (outlined in yellow in (b) and (c)), is located in the center of the Judith River Watershed (b), within the NGP, which roughly corresponds to the west-central semi-arid prairies Level II ecoregion (green in (a)) at the headwaters of the MARB (grey outline in (a)). The conceptual terrace cross section (d) is oriented parallel to the longest axis of the terrace.



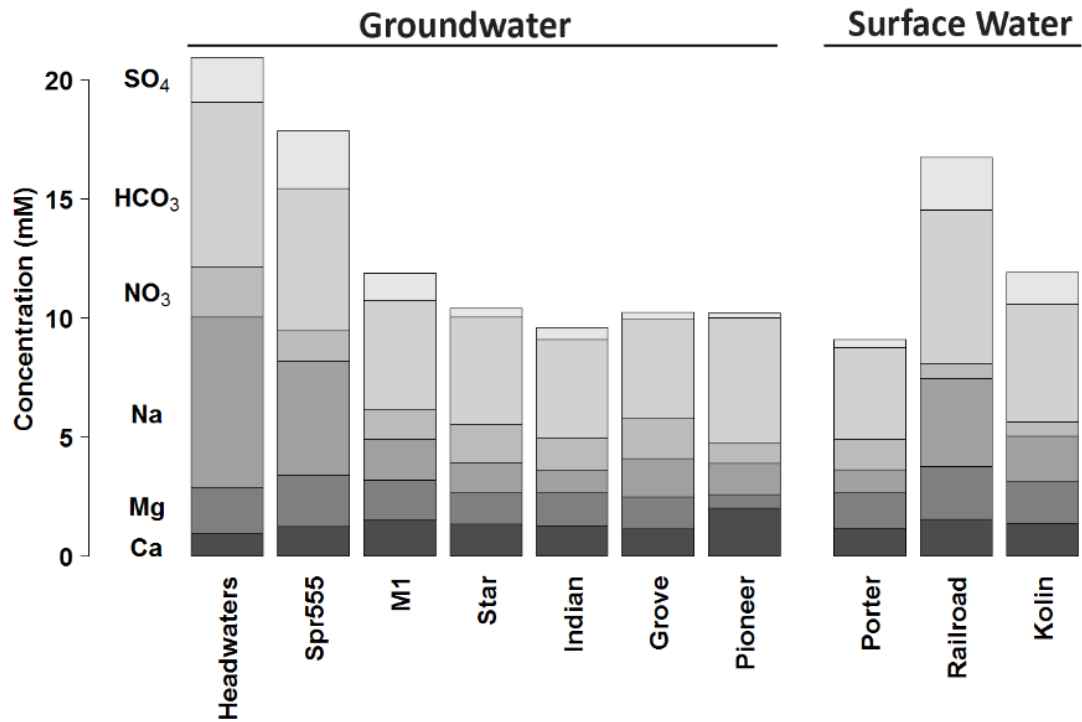
Ch2-Figure 2. Landform maps with shale depth, soils and land use. (a) Interpolated shale surface with 10 m contour lines (white) along with associated depth to shale from ground surface (shades of red). (b) Primary soils categories as groups of SSURGO map units with Judith, Danvers (and similar Tamaneen) CaCO_3 loam soils in tan and shale-derived soils in red. Lysimeters are in fields southwest of Grove spring (precise location omitted for cooperator privacy). Boundaries for the four primary catchments (Kolin, Porter, Pioneer, and 555) are depicted in (a) and (b). Green symbols are springs, brown are wells and blue are streams. (c) Land use in 2014 by major crop category.



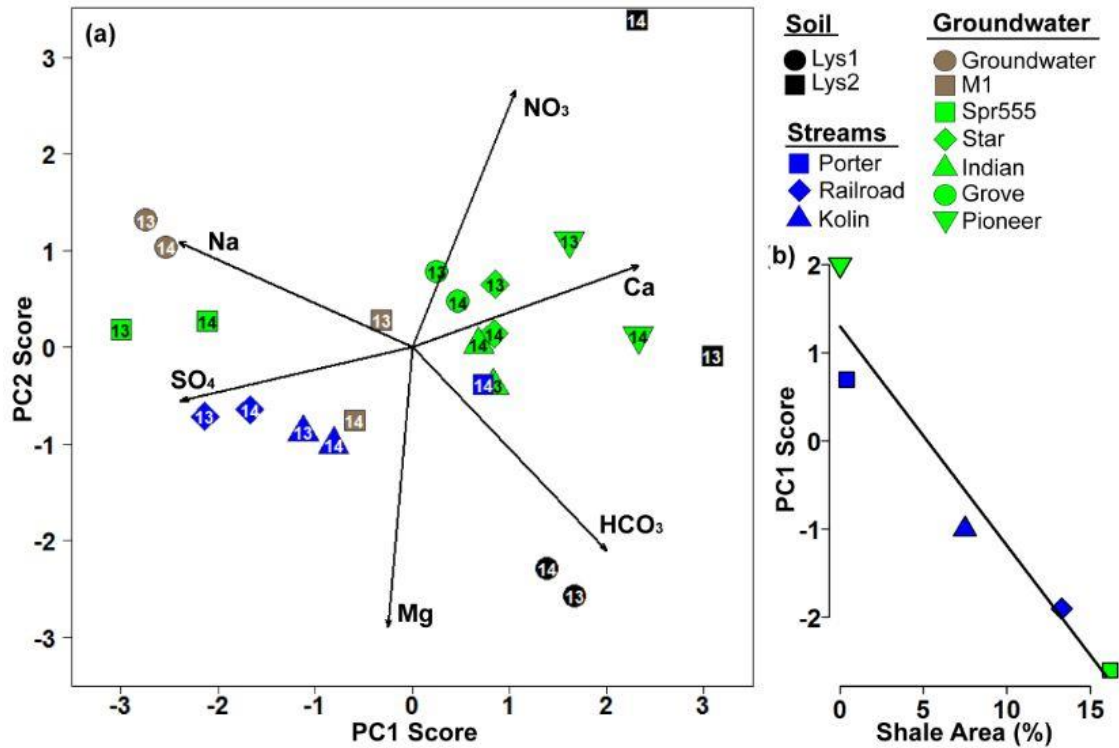
Ch2-Figure 3. Nitrate-N concentration and water level in M1 monitoring well. Nitrate-N data from the Montana Department of Agriculture (MDA) are filled circles and from this project (JRW) are open circles (grey = Jan. through July; black = Aug. through Dec.). Straight line is a linear regression through the MDA Aug. through Sept. nitrate-N points with fit $y = 0.67 \cdot \text{year} - 1328$ ($r^2 = 0.77$, $p < 0.001$). Water level data are from Montana Bureau of Mines and Geology (MBMG) visits 1994-2011 (grey line) and from hourly transducer data from this project (black line).



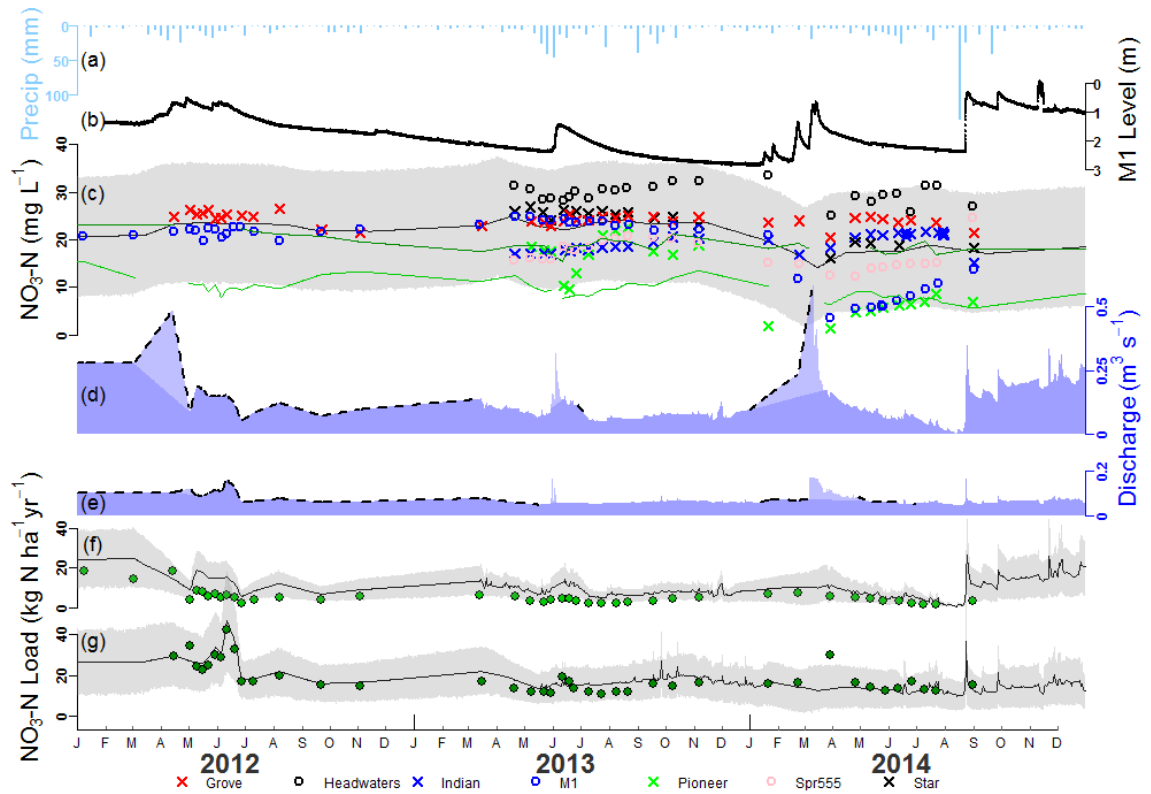
Ch2-Figure 4. Nitrate-N concentration in Moccasin terrace waters. Data were aggregated as monthly mean values by site prior to plotting. Box plot center lines are medians, boxes are 25th and 75th percentiles, whiskers extend to most extreme data point that is no more than 1.5 times the interquartile range away from the box.



Ch2-Figure 5. Moccasin terrace major ion concentrations. Mean solute concentrations (mM) for samples collected for each site during the intensive data collection period (2013-14). See supplemental materials for individual sample concentration data.



Ch2-Figure 6. PCA of water chemistry and relationship to catchment shale soil area. (a) PCA of major ion molar ratios in terrace waters. Points represent average PC scores for sites identified in the legend for years indicated by the number in the center of the symbol. Lys1 and Lys2 are two lysimeters installed near the Grove site in Figure 2b. (b) Catchment mean PC1 scores (Figure 6a; Table 3) versus percent shale area (Figure 2.B; Table 1), (slope = -0.25; $r^2 = 0.94$; $p < 0.05$). Symbology for ground and surface water sites is consistent with that in Figure 2.



Ch2-Figure 7. Precipitation, nitrate-N concentration, discharge and nitrate-N load time series. (a) Precipitation from the Agrimet station at the Central Agricultural Research Center (CARC). (b) Water depth below ground surface in the M1 monitoring well. (c) Nitrate-N concentrations for individual groundwater site measurements (colored point symbols) with stream nitrate-N concentrations linearly interpolated between visits at Porter (dark green), and Kolin (light green), excluding storm response (gaps in lines), along with average groundwater nitrate-N concentration (solid black line) and associated Monte Carlo uncertainty (2.5 to 97.5 quantile; gray shading). Discharge for (d) Kolin and (e) Porter, distinguishing baseflow (dark purple shading) from event flow (light purple shading). Times where values are interpolated are represented by a black dashed line. Nitrate-N load to the riparian corridor (NLRC) for (f) Kolin and (g) Porter catchments (black lines) with Monte Carlo uncertainty (2.5 to 97.5 quantile; gray shading), and in-stream nitrate-N loads calculated at the time of visits (green circles). Nitrate-N load values are normalized to cultivated catchment area (Table 1).

Tables

Ch2-Table 1. Terrace and Catchment Characteristics

	Terrace	Spr555	Pioneer	Porter	Kolin	Railroad*
Total area (km ²)	261.4	3.2	7.5	36.3	96.7	36.4
Total area (ha)	26,140	320	750	3,630	9,670	3,640
Terrace area (%)	100	1	3	14	37	14
Mean depth to shale (m)	7.2	4.6	11.2	8.3	5.7	3.1
Aquifer Characteristics**						
Saturated Thickness (m)	3.6	2.3	5.6	4.2	2.9	1.6
Water Volume. (m ³ ha ⁻¹)	10,800	6,900	16,800	12,450	8,550	4,650
Soils						
Judith (%)	10	0	10	10	5	3
Judith Danvers (%)	62	7	88	83	59	68
Danvers (%)	17	77	0	1	25	11
Shale derived (%)	7	16	0	0	8	13
Wetland (%)	1	0	0	2	1	3
Other (%)	3	0	2	4	2	2
Land Use						
Annual Cultivation (%)	72	93	92	70	77	71
Annual Cultivation (ha)	18,821	298	690	2,541	7,446	2,584
Fallow*** (%)	25	50	18	26	25	31
Perennial (%)	25	3	5	25	19	25
Other (%)	3	4	3	5	4	3

* Railroad is a headwater sub-catchment within Kolin catchment

** Aquifer characteristics assume 50% of gravel thickness is saturated. As a result, saturated thickness is equal to vadose zone thickness. Water volume assumes specific yield of 0.3.

*** Fallow is calculated as percent of annual cultivation area

Ch2-Table 2. Nitrate-N concentration summary statistics. Mean nitrate-N concentrations are calculated from monthly site mean values (n = site month count). Min, max and StDev are calculated with individual sample values (n = total sample count). Lysimeter (Lys) concentrations are aggregated by previous year management for the two lysimeters near Grove spring (Lys1 and Lys2) that were included in PCA (Fig. 6a) and for all lysimeters in the study. Post fallow (PF) indicates the field was in fallow the previous year. Post grain (PG) indicates the field was in grain the previous year.

Site	Period	Mean (mg L ⁻¹)	StDev (mg L ⁻¹)	Min (mg L ⁻¹)	Max (mg L ⁻¹)	Mean n (count)	Min, Max, StDev n (count)
<u>Lysimeters</u>							
Lys1	2013 PG	10.9	1.8	7.9	12.4	2	5
Lys1	2014 PF	8.8	0.8	8.3	9.4	2	2
Lys2	2013 PG	10.4	1.1	9.2	11.4	2	3
Lys2	2014 PF	61.0	NA	61.0	61.0	1	1
All Lys	PF	25.4	14.0	0.4	61.0	20	30
All Lys	PG	11.6	7.7	0.2	42.9	35	52
All Lys (Aggregate)	PF & PG	16.6	13.1	0.2	61.0	55	82
<u>Groundwater</u>							
Headwaters	2013	30.7	1.4	28.4	32.3	8	14
Headwaters	2014	29.0	2.6	25.0	33.5	7	10
Spr555	2013	18.7	1.9	15.6	20.8	8	14
Spr555	2014	15.4	3.3	12.2	24.5	8	11
M1	2012	21.4	0.9	19.8	22.8	9	16
M1	2013	23.4	0.9	22.0	24.9	9	15
M1	2014	9.9	4.7	3.6	21.0	8	13
Star	2013	25.2	1.0	23.2	26.9	8	14
Star	2014	18.4	1.4	16.1	19.5	5	5
Indian	2013	18.7	1.2	17.0	20.6	8	14
Indian	2014	19.3	1.6	15.2	21.7	8	26
Grove	2012	24.4	1.5	21.5	26.5	7	13
Grove	2013	24.2	0.7	22.9	25.3	8	14
Grove	2014	23.3	1.4	20.6	24.9	8	10
Pioneer	2013	17.6	4.0	9.6	22.6	7	13
Pioneer	2014	5.0	2.3	1.5	8.7	7	10
Aggregate GW	2012	22.7	2.1	19.8	26.5	16	29
Aggregate GW	2013	22.7	4.7	9.6	32.3	56	98
Aggregate GW	2014	17.1	7.7	1.5	33.5	51	85
Aggregate GW	2012-14	20.4	6.4	1.5	33.5	123	212
<u>Surface Water</u>							
Porter	2012-14	19.3	1.9	15.5	23.0	24	40
Railroad	2012-14	12.1	3.7	6.5	18.0	27	58
Kolin	2012-14	10.0	2.2	5.7	15.4	26	58

Ch2-Table 3. Annual mean major ion concentrations (mM) and principal component scores. Major ion concentrations for individual samples are included in supplemental materials.

variable	yr	HW*	Spr555	M1	Star	Indian	Grove	Pion.	Porter	Railrd	Kolin	Lys1	Lys2
Ca	13	0.7	1.1	1.7	1.3	1.2	1.1	2.0	NA	1.4	1.4	1.5	2.6
Ca	14	1.2	1.4	1.3	1.4	1.3	1.2	2.0	1.2	1.7	1.3	1.0	2.3
Mg	13	1.8	2.3	1.8	1.3	1.4	1.3	0.6	NA	2.4	1.8	2.5	0.8
Mg	14	2.1	2.0	1.6	1.3	1.4	1.4	0.5	1.5	2.1	1.6	1.8	0.8
Na	13	7.4	5.3	2.0	1.3	0.8	1.8	1.5	NA	3.7	2.0	0.5	0.5
Na	14	6.9	4.3	1.4	1.3	1.0	1.5	1.1	0.9	3.6	1.9	0.5	0.7
NO3-N	13	2.2	1.3	1.7	1.8	1.3	1.7	1.2	NA	0.7	0.7	0.9	0.8
NO3-N	14	2.1	1.3	0.8	1.4	1.5	1.7	0.5	1.3	0.6	0.5	0.8	3.2
HCO3	13	6.8	6.1	5.0	4.4	4.1	4.1	5.2	NA	6.2	4.9	7.0	6.4
HCO3	14	7.0	5.9	4.2	4.6	4.1	4.2	5.3	3.8	6.7	4.9	5.0	3.4
S	13	1.7	2.8	1.1	0.3	0.5	0.3	0.2	NA	2.3	1.5	0.2	0.1
S	14	2.1	2.0	1.2	0.4	0.5	0.3	0.1	0.3	2.1	1.2	0.2	0.2
sum	13	20.6	18.8	13.3	10.4	9.4	10.3	10.9	NA	16.7	12.4	12.6	11.4
sum	14	21.3	16.9	10.5	10.3	9.8	10.2	9.5	9.1	16.8	11.5	9.4	10.6
pc1	13	-2.7	-3.0	-0.3	0.9	0.8	0.2	1.6	NA	-2.1	-1.1	1.7	3.1
pc1	14	-2.5	-2.1	-0.6	0.8	0.7	0.5	2.3	0.7	-1.7	-0.8	1.4	2.3
pc2	13	1.3	0.2	0.3	0.6	-0.4	0.8	1.1	NA	-0.7	-0.9	-2.6	-0.1
pc2	14	1.0	0.3	-0.8	0.1	0.0	0.5	0.1	-0.4	-0.6	-1.0	-2.3	3.4

* Headwaters

Ch2-Table 4. Principal component loadings for major ions.

Major Ion	PC1	PC2
Na ⁻	-0.51	0.23
SO ₄ ²⁻	-0.51	-0.12
Ca ²⁺	0.50	0.18
HCO ₃ ⁻	0.43	-0.45
Mg ²⁺	-0.05	-0.62
NO ₃ ⁻	0.22	0.57

Ch2-Table 5. Water and nitrate-N efflux from Kolin and Porter catchments. Base flow is the annual mean of daily baseflow (Figure 7d-e) for each catchment. Base flow total is mean annual baseflow normalized to the entire catchment area (Table 1). Base flow cultivated is annual baseflow normalized to cultivated catchment area (Table 1). NLRC is the mean of the daily NLRC values (normalized to cultivated area) in Figure 7F-G with 2.5 and 97.5 quartile values in parentheses.

Stream	Year	Baseflow (L s ⁻¹)	Area Normalized Baseflow (mm yr ⁻¹)	NLRC (kg N ha ⁻¹ yr ⁻¹)
Kolin	2012	150	63	14.1 (Q2.5=15.7; Q97.5=16.7)
	2013	94	40	9.2 (Q2.5=10.0; Q97.5=10.6)
	2014	136	57	10.1 (Q2.5=11.3; Q97.5=12.2)
	3 yr mean	127	54	11.1 (Q2.5=10.9; Q97.5=11.4)
Porter	2012	84	104	23.4 (Q2.5=22.7; Q97.5=24.1)
	2013	62	77	17.9 (Q2.5=17.4; Q97.5=18.4)
	2014	64	79	14.0 (Q2.5=13.5; Q97.5=14.5)
	3 yr mean	69	87	18.4 (Q2.5=18.1; Q97.5=18.8)

Ch2-Table 6. Groundwater apparent age based on tritium/helium analysis.

Site	Sample Date	Apparent Age (yr)	Uncertainty (yr)
M1 (no packer)	8/9/2012	1.7	0.5
M1 (no packer)	5/25/2014	5.22	0.57
M1 top (2.6-3.1 m)	5/24/2014	1.23	0.65
M1 bottom (5.2-5.7 m)	5/24/2014	3.91	0.56
Indian Spring	5/25/2014	-0.78	0.91
Grove Spring	5/25/2014	0.84	0.5

Ch2-Table 7. Groundwater turnover time. Calculated as estimated aquifer volume [L^3] (assuming 50% of gravel thickness is saturated) divided by baseflow [$L^3 T^{-1}$].

Catchment	Aquifer Volume (m^3)	Mean Baseflow ($m^3 y^{-1}$)	Turnover Time (y)
Porter	5.0 E+07	2.21 E+06	23
Kolin	8.0 E+07	3.99 E+06	20

Supplemental Materials

2. Methods Supplement

2 Participatory Research Context Three questions guided this research and the broader body of companion research efforts. 1) What are the sources of elevated nitrate in groundwater in the Judith River Watershed? 2) What agricultural management practices could be effectively implemented to reduce leaching? 3) Can a participatory research approach enhance outcomes?

To address these questions, a participatory research framework was designed that included a six-member Producer Research Advisory Group (PRAG). The university research team met with the PRAG multiple times per year between Fall 2011 and Spring 2015 and the three research questions were revisited at each of these meetings. More detail on the participatory research framework, results from interviews with cooperating farmers, and pre- versus post-study watershed scale farmer surveys are presented in Jackson-Smith et al. (in review).

An overarching approach for addressing the three research questions was the adoption of a hierarchical spatial scale where three PRAG farmer fields were identified on three different landforms within the Judith River Watershed. Extensive field based research was conducted on the three PRAG fields, which included the lysimeter sampling included in this manuscript. Results of field scale soil and crop analysis to evaluate effectiveness of management practices for reducing nitrate leaching are presented in a companion paper (John et al. 2017).

In the spring of 2012, the research team toured the landscapes surrounding the three PRAG study farms. Conversations on these tours included discussion of stream and groundwater behavior, crop rotations, N management, broader land management, practices to reduce nitrate leaching, property ownership and sample site access, logistics for installation of instruments, and research approaches/questions. Selection of PRAG study fields hinged on PRAG member identification of fields representing standard grower practices. The outcomes from the conversations on these tours and the PRAG meetings was formative in refining research approaches. Interactions with PRAG members (and other community members they introduced us to) informed and facilitated the layout of landscape scale water and solute observations on each of the three landforms hosting the PRAG study fields. This extensive information exchange and data collection effort helped refine hydro-geomorphic understanding of the study area, and provided the research team with key insight about specifics of landscape processes based on local observations.

2.1 Study Area The Judith River Watershed falls within the northern Great Plains (NGP) ecoregion and ranges in elevation from 2,700 m in the headwaters to 760 m at the confluence with the Missouri River.

Cultivation of annual crops in the NGP has traditionally been dominated by small grain (winter wheat, spring wheat, and barley) with whole-year summer fallow included in 2 to 4-yr crop rotations. In portions of the NGP region (northeast Montana in particular), pulse crop (e.g. lentil, field pea) production has increased in the past decade while fallow has decreased (Long et al., 2014b). Despite small increases in pulse

production, wheat–fallow systems continue to dominate in Judith Basin (Fallow = 25%; Pulse = 2%) and Fergus (Fallow = 31%; Pulse = 1%) counties (CropScape, 2014). From the 1930s through the 1970s, in the area surrounding the MSU Central Agricultural Research Center, the typical crop rotation was to fallow a field every other year (a two-year rotation). In the 1980s, producers began more continuous cropping and adopted no-till and chem-fallow management, which meant a transition to controlling weeds during fallow years with herbicide rather than tillage (Wichman, personal comm.). On average, producers currently fallow a field every third or fourth year (PRAG, personal communication; CropScape).

The Moccasin terrace at the center of the Judith River Watershed is mantled primarily with clay loam, derived from loess, alluvium and underlying shale. These soils have relatively thin fine-textured zones (~30-100 cm) above and within coarse-textured alluvium, hosting thick, dark surface horizons and subsurface horizons with elevated clay and calcium carbonate. The soils with shallowest gravel contacts are classified as Typic Calciustolls of the Judith series and those with deeper gravel contacts as Vertic Argiustolls of the Danvers series (Soil Web; NRCS OSD website; Fig. 2b). Complexes of these two soil series along with the similar Typic Argiustolls of the Tamaneen series make up 89% of the Moccasin terrace area. The next largest fraction of terrace area (7%) is made up of gypsum and sodium-rich shale-derived soils including four series: Entic Haplustolls of Winifred series, Ustertic Natrargids of the Arvada series, Typic Haplustert of the Promise series, and Aridic Natrustolls of the Beckton series. The latter three series

indicate zones of high clay and sodium, consistent with soils derived from saline marine shales.

The Moccasin terrace is mapped as Quaternary and/or Tertiary age alluvium and braided plains. Material is moderately to well-sorted sand and gravel (dominantly limestone clasts) from the Little Belt Mountains. The gravel is underlain by approximately 300 m of shale, mapped as various members of the Marias River and Telegraph Formations (Porter and Wilde, 1999; Vukobratovic et al., 2002).

2.2 Water Sample Collection Lysimeters were installed in fields identified with cooperating farmers that were in chemical fallow land use at the beginning of the project in 2012. Selection of fallow fields allowed for excavation of soil pits for instrumentation without disrupting farming operations. Soil pits were excavated and refilled immediately following soil description, sampling, and instrumentation, with surface and subsurface materials separated and replaced in sequence, in order to minimize effects on subsequent farming. Lysimeter installations on the Moccasin terrace were in soils mapped as a complex of Judith and Danvers series where soil profiles revealed depth to horizons with >50% gravel (2Bk or 2C horizon) ranging from 41 to 105 cm. Data are also included from lysimeters installed nearby that were installed in similar soils mapped as a complex of Doughty, Sipple and Judith series. All lysimeters were installed in fine textured material just above the gravelly horizons (50 to 100 cm depth) below undisturbed upper soil horizons at the edge of the pits. Access to lysimeters was via boxes housing collection bottles. These access boxes were buried during seeding, spraying, and harvesting operations. During seasons when soil water content was relatively high,

lysimeters were visited one to three times per month. On each sampling trip, lysimeters were pressurized to internal vacuum of approximately -100 kPa on two consecutive days, resulting in up to two samples per lysimeter per trip.

Groundwater sampling sites included two wells and five springs (Fig. 2b). The Headwaters well is 4.3 m deep with unknown screening interval and a submersible pump in place. The M1 well is a monitoring well installed by the Montana Bureau of Mines and Geology in 1993 and monitored by the Montana Department of Agriculture (MDA). The well is 5.7 m deep and is screened from 2.6 meters below surface to the bottom. The drilling log reports 0.6 m of clayey silt loam soil over gravel with varied fines intermixed and a water table at 2.4 meters below ground surface (MBMG 2016). During sampling, wells were purged for a minimum of three well volumes and until field parameters (specific conductance, temperature, pH and dissolved oxygen) stabilized before sample collection. Springs were sampled at the orifice except at Star and Pioneer springs, which had stagnant water at the orifice so were sampled with shallow 2.5 cm PVC wells installed 1-2 meters up-gradient from the orifice. Shallow spring wells were pumped until field parameters stabilized before sample collection.

Water sampling at ground and surface water sites was conducted 12 to 15 times per year during 2012-2014. Five of the sites were established in 2012 (Miller, 2013; Table 2) and the other five were established in 2013 (Table 2).

All sampling visits were more frequent during the May to June high rainfall period and were approximately monthly otherwise. Field parameters were measured with a YSI 556 multi-meter, which was calibrated daily according to manufacturer's suggested

methods (YSI Incorporated; Yellow Springs, OH). Water samples were filtered in the field through 0.45 μm capsule filters (Geotech Environmental Equipment, Inc; Denver, CO) and preserved on ice during transportation. Duplicate and blank samples were collected in the field periodically for data quality assurance.

2.3 Water Sample Analysis and Major Ion Composition Chemical analysis was conducted on all water samples in the Department of Land Resources and Environmental Sciences Environmental Analytical Laboratory (EAL) on the MSU campus. Analysis for nitrate on ground and surface water samples was conducted on a Lachat QuickChem 8500 (Lachat Instruments; Loveland, CO) using flow injection automated colorimetric cadmium reduction method. Analysis for nitrate and sulfate on lysimeter and select groundwater and surface water samples was conducted with ion chromatography on a Dionex ICS-2100 (Thermo Fisher Scientific; Waltham, MA) using an AS18 column. Select lysimeter samples were also analyzed on a SEAL QuAAtro (SEAL Analytical Inc.; Mequon, WI) using cadmium reduction. Samples for total carbon (TC) and non-purgeable organic carbon (NPOC) collected with zero headspace were analyzed by combustion on a Shimadzu TOC VCSH analyzer (Shimadzu America Inc.; Columbia, MD) within 15 days of collection. Inorganic carbon was calculated by difference (TC-NPOC) and assumed to be predominantly bicarbonate based on the neutral to somewhat basic pH levels (7 to 9) typically observed in the field. Remaining analytes (Na, Mg, Ca, S) were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP) on Perkin Elmer 5300 DV instrument (Perkin Elmer; Waltham, MA) on samples acidified with trace metal grade nitric acid. Sulfate was estimated from sulfur by ICP

assuming sulfur is predominantly present as sulfate. Select samples run for sulfate using ion chromatography produced similar $\text{SO}_4\text{-S}$ values as those produced using ICP for total sulfur. Upper and lower limits of quantitation are given in the following table. Samples with concentrations above the quantitation limit were diluted to within quantitation range.

Ch2-Sup Table 1. Analytical specifications

Analyte	Instrument	Quantitation Limits	Units
Nitrate	Lachat	0.02 – 10	ppm $\text{NO}_3\text{-N}$
Nitrate	SEAL	0.005-0.750	ppm $\text{NO}_3\text{-N}$
Nitrate	Dionex	0.02-30	ppm $\text{NO}_3\text{-N}$
TC	Shimadzu	2-50	ppm C
NPOC	Shimadzu	0.05-5	ppm C
Sulfur	Perkin Elmer	1-50	ppm S
Sulfate	Dionex	0.05-50	ppm $\text{SO}_4\text{-S}$
Na	Perkin Elmer	5-50	ppm Na
Mg	Perkin Elmer	1-50	ppm Mg
Ca	Perkin Elmer	1-50	ppm Ca

Matrix effects were evaluated through dilution series on the ICP and where possible, by comparison among instruments. Analytical results were evaluated based on agreement among replicates, comparison of working standards between runs, absence of detection in blanks, charge balance closure, and analyte ionic strength agreement with specific conductivity measured in the field. Samples that did not exhibit charge balance

closure within 10% of total negative charge were not included in geochemical assessment (~40% of samples). Our closure threshold is higher than those previously suggested (Snoeyink, 1980) and was chosen because it is commensurate with collective propagated uncertainty on major ion concentrations used to assess charge balance, including assessment of sample matrix and sample handling steps. Some of the charge balance closure issues arose due to precipitation of calcium carbonate in samples. This precipitate formed upon freezing of samples that occurred after bicarbonate analysis (TC and DOC) but prior to calcium analysis.

2.4 Catchment Delineation, Stream Baseflow and Groundwater Recharge Shale

surface interpolation: The shale surface DEM was estimated in ArcMap with Ordinary Spherical semivariogram model kriging using shale surface elevations from three sources. The first source was points representing the shale/gravel contact around the edge of the terrace, which were selected from the geologic map. Points were only selected where spatial resolution could be refined using springs, seeps, or green (vegetation) lines on NAIP aerial imagery indicating water being forced to the surface by exposed shale. The shale elevation at these 51 outcrop locations was determined from the DEM. A second set of 12 points came from well logs where depth of the first occurrence of shale was subtracted from the DEM to get shale elevation. A third set of 46 points were selected within areas mapped as shale soils (SSURGO), where shale was set at 1 m below ground surface (DEM), a depth found to be consistent with field observations. Hourly stage recording began on 5/22/2013 for Porter and on 3/13/2013 for Kolin. For Kolin, 26 observations were used for the linear model rating curve ($r^2 = 0.87$; $p < 0.005$).

For Porter, the bank near the stilling well was deformed by livestock during May 2014, so it was necessary to build separate rating curves before and after livestock disturbance. The pre-disturbance period included 17 observations used for the 4th degree polynomial rating curve ($r^2 = 0.92$; $p < 0.005$). The post-disturbance period included six observations for the linear fit rating curve ($r^2 = 0.86$; $p = 0.007$).

3. Results Supplement

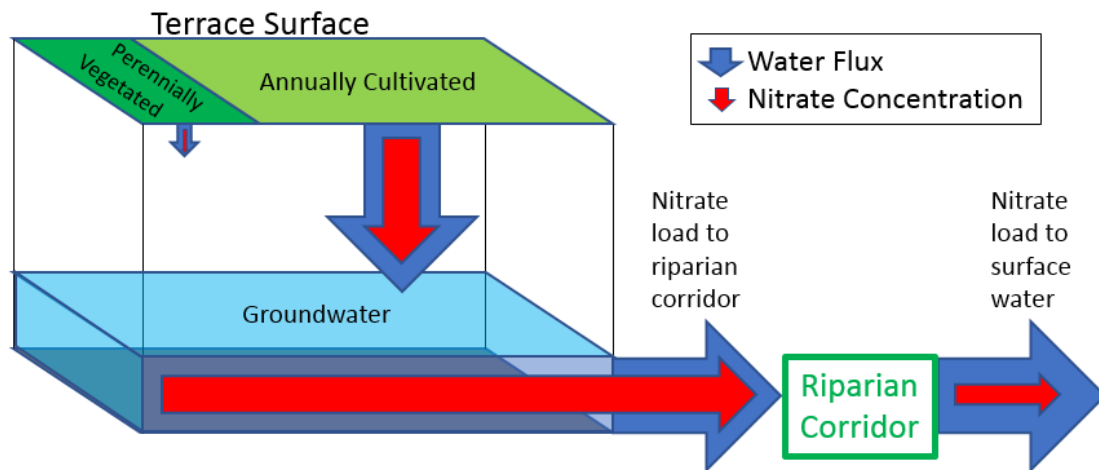
3.1 Catchments Catchment delineation with the shale surface approach produced only slightly larger catchments for Kolin (2% larger) and Porter (7% larger) relative to the surface delineated catchments. In contrast, for Spring 555, delineation with surface topography produced a catchment area of approximately 65 ha, while that with the shale surface approach produced a 320 ha catchment (~500% larger; 1% of terrace area). The catchment for Pioneer spring was not notably affected by delineation approach and has a catchment area of 750 ha (3% terrace area).

4. Discussion Supplement

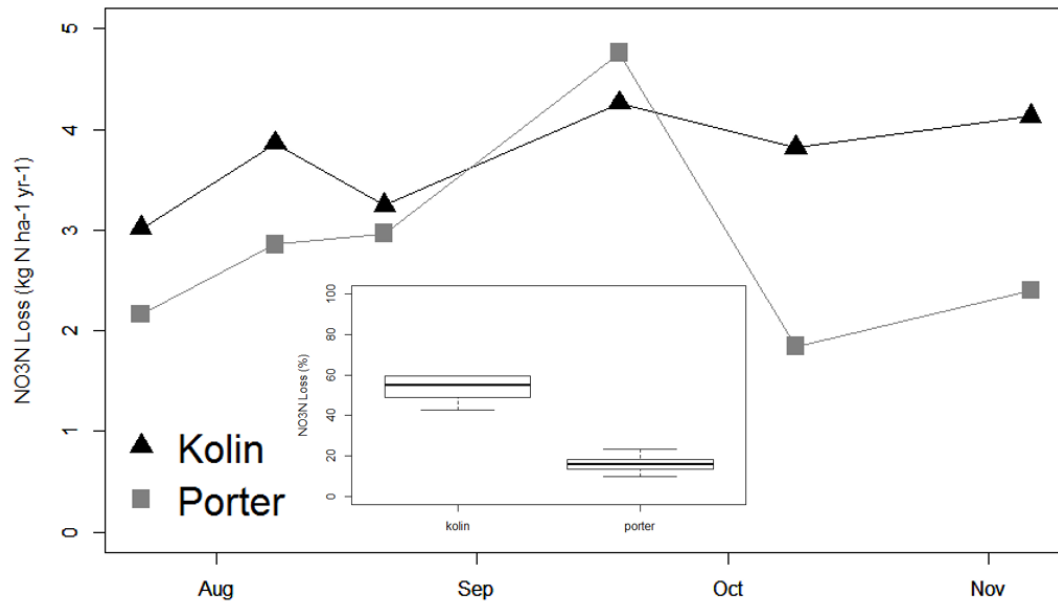
4.3 Nitrate Leaching Rates Our approach to estimating nitrate leaching from presumed baseflow loads produces conservatively low values for three reasons. First, the nitrate observed in groundwater may be diminished relative to soil leachate due to denitrification in transit from soil to groundwater and/or in groundwater. While terrace aquifer dissolved oxygen was greater than 2 mg L⁻¹ for the majority of sites and sampling times, many dissolved oxygen readings at Pioneer spring and a few at M1 and Headwaters sites were less than 2 mg L⁻¹ (Supplemental Fig. 3). Second, as described in section 2.4, the linear baseflow separation method removes the entire March-June runoff

peak from baseflow quantification. Overland flow on the well-drained calcareous soils of the Moccasin terrace is rare, so some of the excluded spring runoff response is likely derived from groundwater. Higher temporal resolution of nitrate quantification during peak flows would be required to determine how much of the March-May peak is sourced from groundwater and is carrying nitrate load for which we have not accounted. Third, flow reductions within the riparian corridor due to evapotranspiration and irrigation withdrawal would result in underestimates of recharge using our simplified approach. Evapotranspiration rates in the riparian corridor were not quantified but are assumed to be small relative to total annual baseflow. The single irrigation withdrawal on the terrace is from Louse Creek for a center pivot sprinkler which removes less than 4% of the total annual baseflow from the creek. Therefore, evapotranspiration and withdrawals are not likely to have a major effect on measured baseflow and associated leaching estimates. Our leaching estimates should also be considered in the context of uncertainty associated with the accuracy of catchment delineation and percent area with annual cropping. Use of the shale surface catchment delineation approach produced slightly larger areas than the surface delineation approach, which conservatively produced slightly lower area normalized NLRC values.

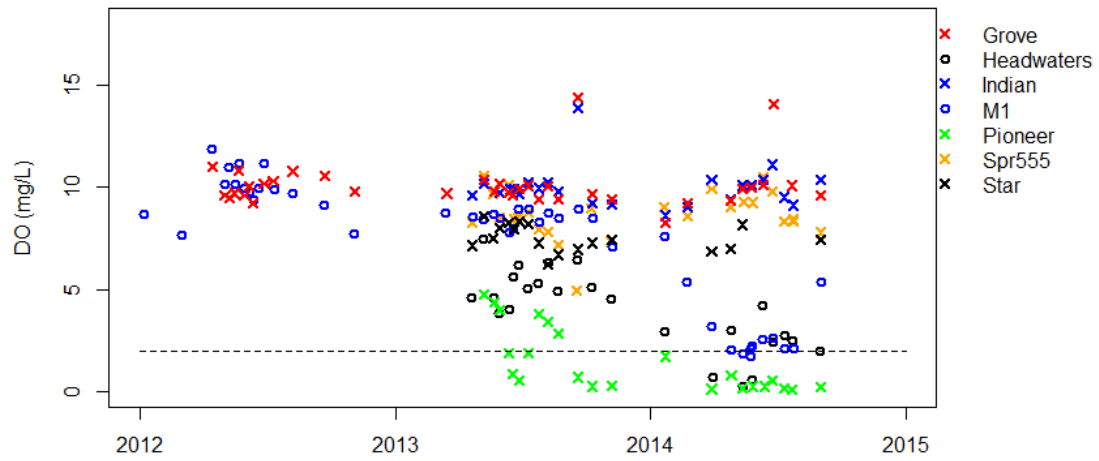
Supplemental Figures



Ch2-Sup Figure 1. Conceptual diagram of Moccasin terrace for flux calculations. Conceptual contrast in magnitude of water flux is represented by size of blue arrows (less recharge from perennially vegetated soils than annually cultivated soils; Scanlon et al., 2007). Conceptual contrast in level of nitrate concentrations within water flux are represented by size of red arrow within blue arrows. In support of this expected difference, we observed much lower nitrate inventories in perennially vegetated soils than in annually cultivated soils (Ewing et al., unpublished). Nitrate load to the riparian corridor (NLRC; defined in section 2.5 of the manuscript) is normalized to the annually cultivated terrace surface (light green) within each catchment to estimate nitrate leaching rates ($\text{kg N ha}^{-1} \text{ yr}^{-1}$).



Ch2-Sup Figure 2. Estimated stream riparian corridor N loss. The estimated percent nitrate-N loss in the stream riparian corridor (inset boxplot), calculated by subtracting nitrate-N concentrations measured in-stream at Kolin and Porter from mean groundwater concentration on the same trip. The time series plot combines the percent concentration loss values with measured stream discharge and cultivated catchment area to normalize losses to contributing area.



Ch2-Sup Figure 3. Dissolved oxygen at groundwater sites measured during sampling visits.

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CHAPTER THREE

WATER AND NITRATE LOSS FROM DRYLAND AGRICULTURAL SOILS IS CONTROLLED BY MANAGEMENT, SOILS, AND WEATHER

Contribution of Authors and Co-Authors

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Contributions: PI on project, designed the study, collected data, trained technicians to collect data, conducted the analysis, wrote the manuscript.

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Contributions: Lead PI on project, made significant contributions to design of the study, provided mentorship for framing the manuscript, conducted extensive editing on the manuscript.

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Contributions: Provided extensive guidance on coding to conduct analysis including various analysis that did not ultimately make it into the manuscript, extensively edited the manuscript.

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Contributions: Consulted about the management implications of the work, provided key references, edited the manuscript.

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Contributions: Provided guidance on model calibration and optimization that ultimately did not make it into the manuscript but were important for understanding model behavior, edited the manuscript.

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Abstract

The vast majority (82%) of the earth's cultivated area is not irrigated, and half is in semi-arid regions where water tends to limit crop growth. In dryland semi-arid agroecosystems, any precipitation not transpired indicates crop yield that is below potential and precipitation that is partitioned to deep percolation can transport nitrate out of the root zone, reducing nitrogen use efficiency and potentially contaminating groundwater. To mitigate risk of crop loss to drought, the practice of summer fallow (suppressing plant growth for a full growing season) has been common in semi-arid regions to store water for the following growing season. However, precipitation losses during fallow tend to exceed the amount of precipitation stored, and fallow tends to increase nitrate leaching. We present model simulations informed by field observations that explore the interaction of crop rotation, weather, and soils as controls on precipitation partitioning and nitrate leaching. Simulations reveal that high intensity precipitation periods produce hot moments of deep percolation and nitrate leaching such that 54% of deep percolation and 56% of leaching occurs in two of 14 model years. Simulations indicate that thin soils produce hot spots for deep percolation and nitrate leaching such that thinner soils (<25 cm) experience water and nitrate loss rates five to 16 times higher than thicker soils (>100 cm). The practice of fallow facilitates mineralization of soil organic nitrogen to nitrate and increases deep percolation, magnifying the interaction of hot moments and hot spots. Simulations suggest that a field with fallow in rotation once every three years experiences 55% of its deep percolation and 43% of its leaching losses during fallow years.

1. Introduction

Fifteen million square kilometers of the earth's surface is cultivated (Ramankutty et al., 2008). Of that cultivated area, 82% is not irrigated (Siebert et al., 2005), and approximately 50% is in semi-arid regions (Ramankutty et al., 2008; Safriel and Adeel, 2005). Definitions vary, but the climate is generally considered semi-arid where annual precipitation is approximately 20 to 50% of potential evapotranspiration (PET), and the regions classified as semi-arid are expanding with global-scale changes in climate (Huang et al., 2016). Without irrigation (dryland), crops grown on cultivated lands in semi-arid areas tend to be water limited, meaning that partitioning of precipitation to evaporation, overland flow, and percolation below the root zone can result in crop yields below potential (Rockstrom and Falkenmark, 2000). This *yield gap* between actual and potential crop production is a loss of economic opportunity and more generally inhibits the ability to meet the challenges of feeding a growing human population (Cassman et al., 2003; Nielsen et al., 2005; Foley et al., 2011). Deep percolation may also transport nutrients out of the root zone, simultaneously reducing nitrogen (N) use efficiency and potentially degrading downgradient water quality (Spalding and Exner, 1993; Goulding, 2000; Di and Cameron, 2002; Smith, 2003; Tesoriero et al., 2013; Sigler et al., 2018). Cropping system management can influence efficient use of both water and N in food production, by regulating water storage and movement in soil. Thus, improved understanding of the interactions of dryland cropping systems with water and solute dynamics in soils is required to achieve reliable crop yields and protection of water resources.

In semi-arid agricultural regions like the northern Great Plains (NGP) of North America, chemical summer-fallow is a common rotational practice of suppressing plant growth over a full growing season to encourage water storage in the soil for crops grown the subsequent year. Fallow practices strongly influence the partitioning of water and N in soils. Water stored in the rooting zone during fallow periods can mitigate risk of poor yields due to drought during the following season (Nielsen et al., 2002; Nielsen et al., 2005; Lawrence et al., 2018). However, extended periods of higher soil water content during fallow may also promote in-soil formation of nitrate with decomposition of soil organic matter, creating conditions primed for loss of both water and nitrate from the root zone (John et al., 2017). The benefit to yield resulting from water storage during fallow is quantified as the fraction of stored precipitation available for use by the subsequent crop (precipitation storage efficiency; PSE). Since the adoption of no-till and crop-residue management practices starting in the 1970s, the maximum PSE value observed in the Great Plains region has been ca. 40%, but PSE is commonly less than 20% (Peterson et al., 1996; Farahani et al., 1998; Nielsen et al., 2005). In addition to increasing subsequent yields, enhanced soil water content during fallow periods facilitates ammonification of soil organic N rapidly followed by nitrification of ammonium to nitrate, which we collectively term *mineralization*. Mineralization provides an added N supply available to the following year's crop, but mineralized nitrate may also be lost to leaching when subsequent precipitation exceeds the field capacity of the soil. In our study area of dryland wheat production in central Montana, Sigler et al. (2018) found evidence that

fallow strongly influenced nitrate leaching rates estimated to be 11 to 18 kg N ha⁻¹ yr⁻¹ for a 260-km² terrace landform. In a companion study examining soil mass balance, John et al. (2017) found higher nitrate leaching (nitrate-N loss) rates at the field scale (ca. 80 acres or 0.32 km²) post-fallow in a fallow-wheat sequence (54 kg N ha⁻¹ yr⁻¹) than post-pea in a pea-wheat sequence (18 kg N ha⁻¹ yr⁻¹). Similarly, in another study of crop management in semi-arid systems, Campbell et al. (2006) found higher nitrate leaching rates over a 37-yr period with a wheat-fallow rotation (ca. 5 kg N ha⁻¹ yr⁻¹) than with a continuous cropping rotation (ca. 0 kg N ha⁻¹ yr⁻¹). Characterizing the connections between fallow practices and nitrate leaching in dryland systems requires holistic understanding of the coupling of soil water and N dynamics. This understanding in turn can inform land management decisions that influence the efficiency of water and nutrient use by crops in dryland agriculture.

Research on N dynamics and plant use efficiency in agricultural soils has been extensive, but we are aware of few studies that have integrated variation in crop rotation, soil properties, and weather to identify the particular times and places where water and N are not being used efficiently. Field trials have been conducted for decades to explore the effects of fallow on precipitation use efficiency (PUE) in the Great Plains region (Farahani et al., 1998 ; Anderson et al., 1999; Nielsen and Vigil, 2017), and to a lesser degree, field trials have investigated the effects of fallow on nitrate leaching (Campbell et al., 2006; John et al., 2017). The few related studies that have used modeling approaches have focused on predicting yield and water use for various crop rotations (Anapalli et al., 2005; Saseendran et al., 2010). Modeling work has yet to address interactions of crop

rotation, weather, and soils as controls on precipitation partitioning and nitrate leaching in the context of water quality implications. This gap in the literature underscores our limited understanding of the vulnerability of these agroecosystems to the increasing pressure for intensified agricultural production in a changing climate (Cassman et al., 2003; Lanning et al., 2010; Siebert et al., 2010).

We employed a hydrologic model informed by field data to explore how changes in evapotranspiration (ET) due to fallow practices interact with variable soil depths and weather patterns to control nitrate leaching via episodic deep percolation. A one-dimensional soil water model based on Richard's equation (Hydrus-1D v4.16; Simunek et al., 2013) was used to characterize precipitation partitioning and nitrate leaching across a combination of crop rotation and soil water holding capacity scenarios for a 14-yr period in the Judith River Watershed, central Montana (Figure 1). We hypothesize that the reduction of ET by fallow practices increases soil water storage and mineralization of soil organic N. While these stored resources can benefit the subsequent crop, they also hydrologically prime soils for higher rates of deep percolation and biogeochemically prime soils for nitrate leaching in response to springtime precipitation the following year. More generally, we suggest that long-term use of fallow rotations is effectively a manipulative experiment that has created a shifting mosaic (Bormann and Likens, 1979) within dryland agroecosystems, where the larger-scale water and N budgets of the landscape emerge from an interaction of "hot spots" defined by areas with shallow soils and "hot moments" defined by periods of rain on soils primed for water and nitrate loss (McClain et al., 2003). We therefore hypothesize that the overlap of these key locations

and key events for water and N transport has created predictable ecological control points (Bernhardt et al., 2017) that are the primary determinants of N use inefficiency of the agroecosystem as a whole.

2. Methods

2.1 Study Area and Cropping

The study area (Figure 1) is located within the Judith River Watershed (HUC 10040103), which drains 7,200 km² of central Montana into the Missouri River. Nitrate-N concentrations in shallow aquifers underlying farmland in the watershed are commonly above 20 mg L⁻¹ (U.S. EPA drinking water standard: 10 mg L⁻¹; Ward et al., 2005), and trends suggest concentrations approximately doubled from 1994 to 2011 (Sigler et al., 2018; Schmidt and Mulder, 2010). These relatively high nitrate concentrations have been associated with the common practice of summer fallow, precipitation patterns, and soil characteristics (Bauder et al., 1993a). Most soils overlying shallow aquifers in the area have relatively thin (ca. 30-100 cm) fine-textured horizons (typically clay loams) overlying relatively coarse subsurface horizons (>40% gravel/cobble), resulting in modest water holding capacity and thus a vulnerability of underlying shallow aquifers to contamination from infiltrating waters.

Annual crops in the region are typically dominated by small grains including winter wheat (*Triticum aestivum* L.), spring wheat, and barley (*Hordeum vulgare* L.) with a year of fallow included in rotation every two to four years (Sigler et al. 2018). Irrigation is not common in the area, so production tends to be water-limited and variation in yields tend to vary with the distribution of precipitation its storage in soils. Near the center of

the study area, mean annual precipitation at the Montana State University Central Agricultural Research Center (CARC) is 39 cm (1909-2016 period of record at Western Regional Climate Center Station: WRCC 245761), with 37% of mean annual precipitation occurring in May and June (Figure 2). Precipitation measured during non-freezing months at fields selected for this study ranged from 50 to 140% of the values reported for the WRCC gage at CARC between 2012 and 2014 (Sup Figure 2.1a). Mean annual reference PET (rPET) at CARC is 144 cm (2001-2016 at Agrimet Station: MWSM), resulting in an average precipitation to rPET ratio of 0.26 during the 15-yr period of the Agrimet record.

Three study fields (Field A near Stanford, MT; Field B near Moccasin, MT; Field C near Moore, MT; Figure 1) with similar soils were selected from areas managed by collaborating farmers on three different depositional landforms in the study area (Figure 1; detailed field and management descriptions in John et al. 2017). Two crop *rotations* are addressed in this modeling work, based on practices currently employed in wheat production in the region. The 3-yr rotations include winter wheat, followed by spring grain, followed by either fallow (“with-fallow”) or a second spring grain (“without-fallow”). Within each rotation are three possible *rotational sequences*, each offset by one year for a total of 6 rotational sequences (Figure 3) that represent every combination of annual weather and crop or fallow. Crop years are delineated starting 1 April, reflecting approximate timing of winter wheat emergence in the area (Agrimet; start date for winter wheat crop coefficients), as well as initiation of spring grain seeding. We present results in the context of each 2-yr crop *sequence* within each rotation, designated by the field use

in consecutive years (e.g., Fallow-Crop, Crop-Crop, Crop-Fallow), where the underlined descriptor indicates land use during the crop year of analysis and the prefix indicates land use during the previous crop year (Figure 3).

The without-fallow rotation simulated in this work represents a continuous small grain rotation, which is not generally recommended due to pest control issues. However, the simulation of spring grain in place of fallow is expected to represent roughly similar hydrologic behavior as other fallow alternatives such as pulse crops (e.g., pea, lentil, chickpea). Research is suggesting that pulse crops may provide more sustainable diversification of crop rotations in at least some areas of Montana (Burgess et al., 2012; Miller et al., 2015).

2.2 Spatial Distribution of Soils

We characterized the spatial distribution of soil architecture using a combination of soil maps, direct observation from soil pits, and aerial imagery. The pertinent soil series from the SSURGO database (USDAb) have well drained, fine-textured clay loam surface horizons, underlain by coarser textured gravelly loam horizons (Sup Section 2.2). For these soil series and for our own soil pits, we define the thickness of fine-textured soil (z_f) as the depth at which the fine-textured horizons transition to coarser textured subsurface horizons with more than 40% rock. More than seventy soil pits were excavated and described within the three study fields between 2012 and 2013. Field C soils were further characterized using an aerial image from 24 July 2011 (USDAC), which depicts variable greenness across the field in a barley crop. Variation in greenness was hypothesized to be correlated with water availability as a function of z_f . Soil pits were

dug at 19 locations within Field C (Figure 1) during fallow in 2012. The z_f values observed from these pits were plotted versus a normalized difference vegetation index (NDVI) value calculated from the NAIP image for a 2-m buffer area around each soil pit. This relation was used to estimate the spatial distribution of z_f based on a 1-m resolution NDVI raster. The frequency distribution of z_f observed in soil pits and inferred from NDVI for Field C was used to characterize an example spatial distribution of z_f to estimate field-scale deep percolation and nitrate leaching.

Previous landscape scale characterizations of deep percolation and nitrate leaching rates for two catchments of the study area (Sigler et al. 2018; Figure 1D) are revisited for comparison to model results from this study, applying z_f values from SSURGO soil series mapped in the catchments and soil pit observations. Soils information from SSURGO data compiled by Sigler et al. (2018) indicates both catchments are dominantly (>80%) comprised of Judith and Danvers soil series. Mean z_f values for the two series were characterized based on soil series descriptions (USDAa). Mean z_f for the Judith series is assumed to be 61 cm, corresponding to the mean depth to the gravel horizon (2Bk3). Mean z_f for the Danvers series is assumed to be 112 cm, corresponding to the minimum thickness of the 2C horizon (Sup Table 2.2a). The Kolin catchment has a higher fraction of Danvers series and the Porter catchment has a higher fraction of Judith series (Figure 1D), so model results based on z_f values for those soil series as well as z_f distributions observed in soil pits are evaluated against Sigler et al. (2018) catchment scale values.

2.3 Measuring Nitrate in Soil

Soils were sampled from 36 pits excavated in Fields B and C in 2012 and 2013. Twenty-four pits were excavated and sampled in July-August during fallow years (fallow since harvest approximately one year prior) and 12 were excavated and sampled in August-September following harvest (four winter wheat, eight barley) in cropped years. Soil volumes ($1,500 \text{ cm}^3$) were sampled at 15-cm depth increments along 10x10 cm square columns. Total depth of sampling was ca. 120 cm, depending on the depth to gravel. Soils were weighed in the field, chilled during transport to the lab, and then frozen until analyzed. Solutes were extracted from weighed subsamples with 1M KCl and the resulting solutions were analyzed for nitrate concentration by cadmium reduction and colorimetry (Lachat, QuickChem 8500). The mass of nitrate-N per unit area (kg N ha^{-1}) and the volume of soil water per unit area (cm) were determined using wet and dry mass, measured nitrate-N concentrations, and bulk density.

Soil water sampling was conducted using tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark). Eighteen lysimeters were installed in Fields B and C at the bottom of the fine-textured soil (depths ranging from 40 to 120 cm), and where conditions were representative of overall field management. Lysimeters were visited one to three times per month during wetter conditions. Approximately 100 kPa of tension was applied with a hand pump to one-liter sample bottles attached to lysimeters and any water in the bottle was collected within 48 h after applying the tension. A total of 550 water samples were collected from lysimeters over a period of four years (2013-2016). Samples larger than 2 mL (319 samples) were analyzed by ion chromatography (Dionex, ICS-2100, AS18 column) and/or cadmium reduction and colorimetry (Lachat, QuickChem

8500; Seal, QuAAtro). Nitrate concentrations for each lysimeter were aggregated by monthly mean. The threshold for outlier concentrations within each 2-yr sequence was calculated as three times the interquartile range (IQR) plus the value for the 75th percentile, and outliers above this threshold were not included in the analysis. Tests for differences in lysimeter nitrate concentration among 2-yr sequences were conducted with paired Kruskal-Wallis rank sum analyses using R statistical software (kruskal.test function; R version 3.4.3; The R Foundation for Statistical Computing, Vienna, Austria).

2.4 Model Description

Simulations of soil water movement with Hydrus-1D were used to assess the potential response of deep percolation to crop rotation, soil architecture, and precipitation. Deep percolation is defined as water exiting the lower boundary of the model, simulated at a depth of 1.75 m. Simulated deep percolation was multiplied by the median observed nitrate concentration for each 2-yr sequence to assess potential rates of nitrate leaching. Modeling included various rotational sequence and z_f values applied over the model period for which daily meteorological data were available (2001-10-01 to 2017-03-31). The first 17 months of simulation were used as a spin-up period to establish appropriate initial conditions specific to each rotational sequence before the start of the 14-yr model reporting period (2003-04-01 to 2017-03-31). We report the mean annual results aggregated over the model reporting period. For all simulations, the model was driven by precipitation data from the WRCC weather station and rPET data from the Agrimet station. Agrimet rPET values were calculated with the Kimberly-Monteith method, which uses an established perennial grass without water limitation as the

reference crop (Dockter and Palmer, 2008). The evaporation and transpiration composing rPET were allocated using crop coefficients. Crop coefficients were calculated based on crop growth stage estimated from growing degree day C (GDD) and the ratio of ET measured by eddy covariance to rPET (Table 1; Sup Section 2.4; Vick et al., 2016). Maximum rooting depth was informed by soil pit observations and root growth rates were estimated as a function of cumulative GDD after seeding. The root growth rate function followed the approach of Thorup-Kristensen et al. (2009) with rate adjusted based on preliminary simulation results (Table 1; Sup Section 2.4).

The Hydrus model was configured with two materials to simulate soils commonly observed in the study area: a shallow fine-textured horizon overlying a deeper coarse-textured horizon. The van Genuchten soil hydrology parameters used for the lower horizon were the default values for sand from Rosetta Lite v. 1.1 embedded in Hydrus (parameters listed and defined in Sup Table 2.4a). For the upper fine-textured horizon, the residual water content value (θ_R , 0.12) was based on volumetric water content (VWC) measured in soils near wilting point and the saturated water content value (θ_s , 0.5) was based on porosity calculated from bulk density measurements (Sup Table 2.4a). A value of 0.5 was used for the pore connectivity parameter l (Mualem, 1976). Remaining van Genuchten parameters for the fine-textured horizon were set to default values for clay loam from Rosetta Lite v. 1.1. Volumetric water content at field capacity for the fine-textured soil horizon was calculated to be 0.33 within Hydrus according to Twarakavi et al. (2009). Deep percolation can occur at VWC below field capacity (Twarakavi et al., 2009; Flury et al., 1994), but we apply a simplification and define soils as *primed* for

deep percolation when simulated daily VWC (at a depth 2 cm shallower than the z_f depth) was greater than field capacity. Maximum soil water storage potential was estimated as the difference between field capacity and wilting point for the fine-textured horizon multiplied by z_f . Precipitation storage efficiency was calculated as the fraction of measured annual precipitation that was not lost to modeled deep percolation, evaporation, or runoff in fallow years.

The influence of fine-textured soil horizon thickness on soil water storage capacity and deep percolation was assessed by varying z_f from 5 to 150 cm in increments of 5 cm (30 z_f values). The hydrologic effect of fallow on deep percolation was assessed using model scenarios simulating the six rotational sequences depicted in Figure 3, such that all combinations of rotational sequence and annual weather were represented. Thirty z_f values for each of six rotational sequences produced a total of 180 model simulations.

To assess whether the model produced reasonable predictions of soil water content dynamics, additional simulations were configured for comparison to field observations and coefficients of determination (R^2) were calculated for simulated versus observed values (Sup Section 2.4). The sensitivity of model results was manually assessed for different values of: scaling of mean annual precipitation, maximum root depth, root growth rate, fallow crop coefficient, spring grain seeding date, crop development rates, and van Genuchten parameters for the fine-textured horizon (10 texture scenarios assessed; Sup Table 2.4c).

3. Results

3.1 Soil Water Content and Soil Nitrate

Soil water contents observed during August and September of fallow years were consistently higher than those observed following harvest (Figure 4A). Volumetric water content in fallow soils was up to 0.18 higher than post-harvest across 15-cm depth increments. The total water stored in soil to a depth of 105 cm was 10.1 cm post-harvest and 23.3 cm in fallow (Figure 4A). Total nitrate-N pools (kg N ha^{-1}) in the top 15 cm of soil were seven times higher in fallow than post-harvest and total nitrate-N pools in deeper soils were at least three times greater in fallow than post-harvest for all but the deepest 15-cm increment. The total mass of soil nitrate-N to a depth of 105 cm was 12 kg ha^{-1} after harvest and 46 kg ha^{-1} during fallow (Figure 4B). Apparent dissolved nitrate-N concentrations (mg L^{-1} ; calculated as nitrate-N pool from soil extractions / water pool) were 1.3 to 2 times higher in fallow than post-harvest for all but the deepest profile increment (Figure 4C). The depth-weighted mean nitrate-N concentrations over the profile were 12 mg L^{-1} for post-harvest and 19 mg L^{-1} for fallow.

Nitrate-N concentration values observed in lysimeter samples over the 2013-2016 period ranged from 0.03 to 347 mg N L^{-1} . Six values from one field in the Crop-Fallow sequence were removed as extreme outliers reducing the maximum value to 45.5 mg N L^{-1} , with a median of 12.0 mg N L^{-1} (IQR 8.1 to 20.2 mg N L^{-1}). Median concentrations were significantly higher for Fallow-Crop years (19.4; IQR 9.9 to 28.0 mg L^{-1}) than for Crop-Fallow years (9.8; IQR 6.1 to 15.7 mg L^{-1} ; $p < 0.05$) and Crop-Crop years (11.1;

IQR 7.6 to 17.5 mg L⁻¹; $p = 0.06$; Table 1). Lysimeter nitrate concentrations did not vary with z_f ($R^2 = 0.01$, $p = 0.33$; Sup Figure 3.1a).

3.2 Spatial Distribution of Soil Thickness

Soil pits in Field B ($n = 18$) had z_f values ranging from 26 to greater than 142 cm (z_f transition not observed in one pit, 142 cm deep; Sup Table 3.2a), with a median value of 48 cm. This field is primarily mapped as Danvers-Judith complex, with series descriptions suggesting z_f ranges from 58-150 cm with mean z_f values for the two series of 61 and 131 cm (Sup Table 2.2a). Additionally, a portion of Field B includes Tamaneen series, which is described as having a minimum z_f of 43 cm.

The z_f measured in soil pits from Field C ($n = 26$) ranged from 16 to 125 cm with a median value of 86 cm. In this field, values of z_f up to 55 cm ($n = 9$ soil pits) showed a positive relationship with NDVI from the 2011 NAIP image ($R^2=0.46$; Figure 5B). Soil pits with z_f values greater than 55 cm all had NDVI values near 0.15, so extrapolation of the z_f :NDVI relationship was inappropriate for deeper soils. A subsequent soil core sampling campaign targeting validation of this relationship found 68 of 72 core locations falling within the NDVI-predicted z_f value category (Sup Section 3.2). This field is mapped as a Doughty-Sipple-Judith complex. The Doughty, Sipple, and Judith series have mean z_f values of 81, 132, and 61 cm respectively, with a range of 51 to 152 cm across the three series (Sup Table 2.2a). Lower values for z_f observed in pits (on both Fields B and C) and across Field C based on the z_f relationship to NDVI suggest that soil mapping for the fields do not capture the thinnest fine-textured soils, nor do they characterize the distribution of z_f necessary for mechanistic hydrologic modeling. We

adopted an example z_f distribution (“standard- z_f ”) with mean z_f of 50 cm based on NDVI for Field C and soil pits on Field B, and standard deviation of 30 cm based on soil pits in both fields.

3.3 Model Results versus Observations and Sensitivity

The model explained 72% of the variation in observed VWC during winter wheat and spring grain years, 53% of variation in observed ET during the winter wheat year, 19% of variation in observed ET during the spring grain year, and exhibited a negative coefficient of determination with observed ET during the fallow year (i.e., the chosen parameterization did not allow the mechanistic model to outperform the statistical mean during fallow, $R^2 = -0.28$; Sup Figure 3.3a). Fallow year ET was calculated by scaling rPET with a coefficient (i.e. the fallow coefficient) that was empirically derived from the median ratio of measured ET to rPET (0.22). While simulations with a fallow coefficient value of 0.22 reproduce the variation in moderate ET rates reasonably well, the highest ET rates could not be reproduced by simulations constrained by that value, resulting in a negative R^2 value. The implications of these episodically higher evaporation rates evident in a subset of ET measurements during fallow (Sup Fig 2.4f) were evaluated with sensitivity analysis scenarios where the fallow coefficient was set to 0.5 (scenario 24; Sup Table 3.3a). Simulation results with the higher fallow coefficient produced patterns similar to the primary simulation, but with decreased PSE, time above field capacity, overall deep percolation, and difference in deep percolation between crop and fallow years; the higher fallow coefficient increased the fraction of deep percolation occurring on thinner soils. More broadly, the sensitivity analysis identified the rescaling factor for

precipitation and the fallow coefficient as the parameters with the most influence on simulated water movement and that general patterns in model results were robust across likely parameterization scenarios.

3.4 Simulated precipitation partitioning

Model results suggest that shallower fine-textured soil horizons spend a larger fraction of time with VWC above field capacity, representing soils that are more regularly "primed" for deep percolation (z_f of 25 cm = 39% of time primed, z_f of 50 = 33% , and z_f of 100 = 24%; Figures 3.4b-d). Thinner soils spending more time primed for water loss resulted in higher rates of deep percolation for thinner z_f soils (Figures 6-7). Simulated mean annual deep percolation rates varied more across z_f values (within a 2-yr sequence) than among 2-yr sequences for any given z_f value. The range of deep percolation rates across z_f values was largest for the Crop-Fallow sequence with a spread of 13.6 cm yr⁻¹ (2.8 to 16.4 cm yr⁻¹; Figure 7A; Table 2). The range in deep percolation rates across z_f values was 7.9 cm yr⁻¹ for Fallow-Crop (1.9 to 9.7 cm yr⁻¹) and 10.9 cm yr⁻¹ for Crop-Crop (0.6 to 11.6 cm yr⁻¹). The difference in deep percolation rates among 2-yr sequences was largest (6.9 cm yr⁻¹) between Crop-Fallow and Fallow-Crop for z_f = 30 cm and the range across 2-yr sequences was smallest (2.2 cm yr⁻¹) at the largest z_f values. The dependence of deep percolation on z_f was strongest at lower z_f values (< 100 cm), while deep percolation was relatively insensitive to z_f at higher values (> 100 cm).

Across 2-yr sequences, the thinnest soils (z_f < 25 cm, Figure 6) had 14-yr mean simulated water loss rates approximately equal to mean annual precipitation (38 cm yr⁻¹) indicating that on average, no net precipitation storage occurred regardless of crop

presence/absence. Mean PSE during Crop-Fallow years (white space below 38 cm line in Figure 6B) for the model reporting period plateaued at a maximum value of 9.1 cm, or 23% of mean annual precipitation (Sup Table 3.4a). The mean PSE for Crop-Fallow given the standard- z_f distribution was 8%. The maximum annual PSE during our modeling period was 46% for the thickest soils ($z_f = 150$) in 2013 when 22.3 of the 48 cm of annual precipitation was stored, a value 71% of theoretical maximum of 31.5 cm (0.21 VWC times 150 cm; Sup Figure 3.4e).

Simulated transpiration rates during Fallow-Crop years were higher with deeper z_f , resulting in mean annual combined losses exceeding mean annual precipitation by up to 9.5 cm yr⁻¹ for the thickest soils (Figure 6C; Table 2). This increased loss of stored water with increasing z_f in Fallow-Crop years mirrors the increase in water storage (PSE in Figure 6B) with increasing z_f in Crop-Fallow years. The simulated mean annual transpiration rates for thickest soils ($z_f = 150$ cm) in Fallow-Crop years (34.6 cm yr⁻¹) were approximately 10 cm higher than rates in Crop-Crop years (24.5 cm yr⁻¹), due to the water stored during fallow years. The transpiration rate difference between cropped years was less pronounced for thin soils ($z_f \leq 25$ cm), where mean annual simulated transpiration was 16.5 cm yr⁻¹ in Fallow-Crop years and 13.0 cm yr⁻¹ in Crop-Crop years.

While annual deep percolation was strongly correlated with annual precipitation for the thinnest soils ($z_f = 10$ cm; $R^2 = 0.77$, $p < 0.005$), this relationship breaks down with increasing z_f . For soils with $z_f > 40$ cm, less than 33% of annual deep percolation was independently explained by annual precipitation (Sup Figure 3.4a); the rate and timing of precipitation in the current and previous year were also important explanatory

variables for precipitation partitioning. For example, 2010 and 2011 had virtually identical annual precipitation (47.8 and 47.6 cm respectively), but 2010 had only 4.6 cm of deep percolation ($z_f = 50$) in contrast to 24.4 cm in 2011. Higher deep percolation in 2011 occurred due to above normal precipitation occurring prior to peak PET, on soils with high antecedent VWC from above average precipitation the preceding fall (Figures 3 and 8; Sup Section 3.4).

3.5 Nitrate Leaching

As a result of the modeling approach, the shape of the relationship between simulated nitrate leaching and z_f (Figure 7C) was identical to that for deep percolation (Figure 7A) for each 2-yr sequence, but nitrate leaching rates were shifted relative to deep percolation due to different nitrate concentrations observed for each 2-yr sequence (Table 1). Modeled nitrate leaching rates were lowest in the Crop-Crop sequence, which has the lowest deep percolation rates and intermediate nitrate concentrations. The Crop-Fallow sequence had the highest modeled nitrate leaching rates for mid-range z_f values, but at low and high z_f values the Fallow-Crop sequence had the highest leaching rates.

Simulated deep percolation and nitrate leaching rates for all three rotational sequences with fallow were higher than rates for all three rotational sequences without fallow (Figure 7B and 7D). While all rotational sequences without fallow group tightly across z_f values for deep percolation and nitrate leaching, the three rotational sequences with fallow have variable deep percolation and nitrate leaching rates for the same z_f value. Mean nitrate leaching rates for the two rotations differ by $3.8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at low z_f values, but the difference decreases to $2.0 \text{ kg ha}^{-1} \text{ yr}^{-1}$ at z_f values greater than 100 cm

(Figure 7D). The z_f weighted difference between the rotations (assuming standard- z_f) was $2.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (without-fallow = 4.2; with-fallow = 7.0 $\text{kg N ha}^{-1} \text{ yr}^{-1}$). Overall nitrate leaching rates for the rotational sequences range from $0.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for thick z_f soils in without-fallow rotational sequences to $16.9 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for thin z_f soils in with-fallow rotational sequences.

3.6 Scaling Simulation Results to Fields and Landforms

While only 43% of Field C has $z_f < 50 \text{ cm}$ (Figure 5C), model results indicate 61% of deep percolation and 59% of nitrate leaching occurs through those thinner soils (Table 3; Sup Figure 3.6a). The fraction of the field with $z_f < 25 \text{ cm}$ (13%) accounts for 25% of the mean annual deep percolation, while field areas with z_f of 25-50 cm and $> 50 \text{ cm}$ account for 36 and 41% of deep percolation, respectively. The Crop-Fallow sequence represents one-third of the time in the 3-yr rotation but produces 55% of the deep percolation and 43% of nitrate leaching (Table 3). The model approach produces similar distributions of deep percolation and nitrate leaching across the field, the largest difference being the larger fraction of nitrate leaching occurring in Fallow-Crop years (35%) relative to deep percolation (23%) occurring in those years (Table 3, Figure 9, Sup Figure 3.6a). This difference in nitrate leaching is due to the higher nitrate concentration accumulated from mineralization during fallow years and resulting from fertilizer application during crop years (Table 1).

Application of the deep percolation and nitrate leaching rate relationships to z_f for the with-fallow rotation (upper polynomial line in Figure 7B and 7D) to various observed z_f distributions produced a range of estimates presented in Table 4. The combinations of

z_f distributions and model time periods produce deep percolation rates ranging from 2.0 to 10.8 cm yr⁻¹ and nitrate leaching rates ranging from 2.2 to 13.8 kg N ha⁻¹ yr⁻¹.

4. Discussion

Periods of fallow in a dryland crop rotation interacted with both rainfall and variation in water storage capacity associated with soil architecture to exert a strong influence on patterns of simulated episodic nitrate leaching. We suggest that the first step in predicting leaching is to understand the controls on partitioning of precipitation to soil storage, evapotranspiration, and deep percolation. Subsequently, we develop the concept that more intense precipitation on wetter soils defines hydrologic hot moments of deep percolation. Wet soil conditions promote accumulation of nitrate mineralized from soil organic matter, contributing to biogeochemical hot moments of potential leaching. Areas with thinner soils exceed field capacity more frequently, hence defining hot spots for deep percolation. Hot moments of meteorological phenomena interact with hot spots of low soil water storage capacity to define ecological control points that can be used to predict the episodic nature of deep percolation and nitrate leaching across the system. The ability to predict nitrate leaching control points suggests management practices that may help to increase N use efficiency, and points to future research that may further inform sustainable farming practices.

4.1 Controls on Precipitation Partitioning

Our simulation results for a dryland system demonstrate the interactions of weather, crop rotation, and thickness of fine-textured soil horizons (z_f) as primary controls on the partitioning of precipitation in soils. Weather and land use exert control on partitioning by altering the timing of supply and demand for meteoric water, while z_f determines the size of the storage buffer that can retain soil water against gravity, allowing for subsequent use by plants or loss via evaporation.

A motivation for the practice of fallow is to store water for the subsequent crop, an outcome that our model results suggest is controlled primarily by spatial variation in the thickness of fine-textured surface soil, a proxy for water storage potential (z_f ; Figures 6 and 7). Our 14-yr mean modeled PSE values ranged from zero for the thinnest soils to 9.1 cm (23% of 38 cm mean annual precipitation) for thicker z_f (> 100 cm) soils. These values were low relative to values of 15-45% compiled by Nielsen et al. (2005), but relatively consistent with other observations in Montana (Miller and Holmes, 2005). We found that the highest deep percolation rates tend to be associated with thinner z_f (Figure 7), which is parallel to Wang et al. (2009) who found that deep percolation was negatively correlated with soil water storage potential related to variation in soil texture.

Within limits dictated by soil water storage potential, factors affecting gains and losses of water emerge as important controls on PSE and may include tillage/stubble management, crop type, fallow duration (Nielsen et al., 2005), and timing of precipitation. The maximum PSE observed during our modeling period (46%) occurred in 2013, when unusually high precipitation rates occurred in the months after peak PET (Figure 2). Under more typical conditions when the highest precipitation rates occurred in

May and June, large fractions of annual precipitation were subject to high evaporative losses from fallow fields during summer months ($> 0.1 \text{ cm d}^{-1}$; Sup Figures 3.4b-d). In cases of fallow during drier years (2004 and 2012) or in years preceded by above-normal fall precipitation (2011 and 2015), evaporation and/or deep percolation far exceed storage, even for soil with the thickest z_f , resulting in little to no net change in water storage over the year. Evaporation during fallow years is approximately twice that of cropped years (Figure 6; Table 2), and was influenced by the capacity of soils to transport water upward to the surface in our simulations. The simulation of upward water transport is heavily influenced by the van Genuchten pore size distribution parameter n , where the maximum upward flux potential occurs in soils with n values around 1.5 (Or et al., 2013). Values of n for clay loam soil textures (ca. 1.4) fall near the 1.5 value for maximum upward water transport potential, suggesting that soils such as those in our study area may be highly prone to evaporative losses, which can extract water efficiently to a depth of approximately 50 cm (Or et al., 2013). Our finding that water losses during fallow exceed storage agrees with previous work in the Great Plains (Peterson et al., 1996) and prompts questions about sustainability of the practice in the context of pressure to increase “crop per drop” to meet food requirements for a growing global population (Rockstrom, 2003).

4.2 Weather & Soils as Controls on Deep Percolation and Leaching

The relatively large amounts of deep percolation simulated during spring storms on wet soils (2011 versus 2010; Figure 8) underscore the potential for relatively short periods of time to have a disproportionate effect on whole-system behavior (i.e. “hot moments” in time; McClain et al., 2003). In semi-arid climates such as our study area, where rPET exceeds precipitation on both a mean annual (148 versus 38 cm) and a mean monthly (Figure 2) basis, soils are typically below field capacity and poised to store precipitation. Periods of relatively high intensity precipitation are necessary for soil water to exceed storage potential and simulation results indicate that the majority of deep percolation occurs when VWC is above field capacity. These periods when VWC is above field capacity hence represent hot moments of disproportionate importance for controlling cumulative long-term groundwater recharge rates. With lysimeter nitrate-N concentrations ranging up to 45 mg L⁻¹, hot moments for deep percolation represent the temporal control points for nitrate leaching that must be quantified to understand aggregate ecosystem behavior (McClain et al., 2003; Bernhardt et al., 2017). The propensity for intense precipitation to drive export of water and solutes from soils was demonstrated by 54% of deep percolation and 56% of leaching over the 14-yr period occurring in just the two years associated with the largest monthly precipitations in May 2011 and August 2014 (Figure 2, 8 and Sup Figures 3.4b-d). As a result, a two or three year study (e.g. 2012-2014; John et al., 2017) may capture highly variable rates of deep percolation, leaching, and economic outcomes that are distinct from approaches that aggregate longer term responses (Sigler et al., 2018).

The influence of thin fine-textured soil horizons on deep percolation suggests that even if thin soils are limited in spatial extent, they may be disproportionately important to whole-system leaching behavior (i.e. a “hot spot” in the landscape; McClain et al., 2003). Thinner z_f soils have less water holding capacity and reach field capacity more readily, hence thinner soils are primed for water loss after smaller precipitation events and may be defined as hot spots, with a propensity to exaggerate the influence of deep percolation hot moments. In fact, simulation results indicate that thinner soils spend more time primed compared to thicker soils (z_f of 25 = 38.5%; z_f of 100 = 23.6% time; Sup Figures 3.4b and 3.4d). This pattern was reflected in deep percolation and nitrate leaching rates that were five times higher for z_f from 0-25 cm compared to z_f from 100-150 cm under the with-fallow rotation (Figure 7B and 7D). This pattern is even stronger during the without-fallow rotation, such that thinner soils lose 16 times more water and nitrate than thicker soils, a more punctuated difference due to very low loss rates from the thickest soils with crop present. These findings of disproportionately high deep percolation rates through thinner soils agree with our prediction that thicker z_f soils mediate losses of water and nitrate to groundwater.

4.3 Fallow Expands Hot Moments and Hot Spots

The relatively high rates of deep percolation simulated during fallow periods, along with observed accumulation of nitrate from mineralization within soil profiles during fallow, provides support for our hypothesis that fallow primes soils for loss of water and nitrate. The propensity of the Crop-Fallow sequence to generate more deep percolation than the Fallow-Crop or Crop-Crop sequences was apparent across z_f values

and was exemplified during high precipitation periods in 2011 and 2014 (Sup Materials 3.4). In addition to higher deep percolation, the warm and moist conditions during fallow periods facilitate mineralization of soil organic N to nitrate (Figure 4; Vigil and Kissel, 1995; John et al., 2017), resulting in high leaching rates during the intense precipitation period (May-June) the following year. We observed the highest nitrate concentrations in lysimeters during Fallow-Crop years (Table 1), suggesting biogeochemical nitrate priming of soils in fallow years augments the fertilizer applied during the subsequent year to promote nitrate loss even when deep percolation rates are lower. This priming due to mineralization suggests that the duration of fallow influence extends beyond one third of the crop rotation. We observed an average of 34 kg ha^{-1} of nitrate-N accumulated from mineralization approximately half-way through the fallow period (difference between profiles in Figure 4B). This rate of nitrate accumulation aligns with modeled mineralization rates ranging from 61 to $77 \text{ kg ha}^{-1} \text{ yr}^{-1}$ for the full fallow period, reported by John et al. (2017), which equate to 70-90% of N rates applied as fertilizer by our farmer-collaborators (83 to $91 \text{ kg ha}^{-1} \text{ yr}^{-1}$).

Simulations also suggest that fallow practices increase the spatial extent of soils that experience high rates of deep percolation (i.e. expand hot spots). The z_f value for a given deep percolation rate was always higher for Crop-Fallow than for the Fallow-Crop or Crop-Crop sequences, suggesting that the threshold z_f depth for soils subject to priming was increased by fallow practices (Figure 7A). Comparing the Crop-Fallow and Crop-Crop sequences, the difference in z_f value for a given mean deep percolation rate ranges from 25 cm to greater than 50 cm (horizontal distance between circles and crosses

in Figure 7A). Applying this example to Field C, only 10% of the field ($z_f < 19$ cm) exceeded 7.5 cm yr^{-1} deep percolation during Crop-Crop years compared to Crop-Fallow years where 60% of the field ($z_f < 56$ cm) exceeds 7.5 cm yr^{-1} deep percolation. The spatial expansion of high deep percolation rate areas during the Crop-Fallow sequence (Sup Figure 3.6a, panel C versus A & E) extends the duration of hot moments during fallow, such that 55% of deep percolation in Field C was simulated during the fallow year.

4.4 Management Implications

The thickest soils and the rotation without fallow produce the highest transpiration and the lowest nitrate leaching rates. The general relationship between transpiration and crop yield (Musick et al., 1994; Rockstrom, 2003) suggests that crop-rotation and soil architecture scenarios that produce the highest transpiration rates may also produce the highest PUE (Hatfield et al., 2001). The PUE to transpiration correlation is complicated by non-linear reductions in yield depending on timing of water stress (Lehane and Staple, 1962; Campbell et al., 1977). Nonetheless, our model results highlight soil architecture (z_f) and rotation-related management opportunities to reduce nitrate leaching and increase PUE, simultaneously protecting groundwater quality and enhancing economic sustainability of agricultural operations. Reducing fallow periods and transitioning to continuous cropping or perennial vegetation on the thinnest z_f soils show the most promise for reducing nitrate leaching losses. These results also suggest that precision agriculture approaches that align seeding rates and fertilizer N application with spatially variable transpiration potential (a surrogate for yield potential) could

reduce nitrate leaching. While the soils for the study area are abnormally thin on the spectrum of cultivated soils, simulations for thicker (>100 cm) z_f scenarios may approximate patterns expected for thicker soils in similar semi-arid locations. In addition, sensitivity analysis results for different soil textures and alternate values for other input parameters may facilitate extrapolation of results to additional scenarios. This type of broadly applicable tool for identifying control points may become increasingly important for sustainable agriculture, given climate projections for warmer temperatures and more intense precipitation events (Whitlock et al., 2017), which are likely to exacerbate hot moments of water and N use inefficiency.

4.5 Emergent Landscape-Scale Behavior

We assess the concept that whole-system water and N flux behavior can be predicted with a shifting mosaic of fallow land use overprinted on soil and precipitation derived control points, by comparing simulation results with emergent landscape scale patterns in deep percolation and nitrate leaching presented by Sigler et al. (2018). Deep percolation estimates by Sigler et al. (2018) were 8.7 cm yr^{-1} for the Porter catchment (thin soils) and 5.4 cm yr^{-1} for the Kolin catchment (thick soils; Figure 1), values bracketed by our model results applied with relevant z_f distributions and time periods (Table 4; Sup Section 4.5). The Sigler et al. (2018) estimates were based on stream flow measurements over the 2012-14 period, with estimates that groundwater-fed stream flows may lag behind precipitation patterns by up to one year. This suggests that the relevant period for comparison to modeling work here begins sometime in 2011 and runs through 2014. Exceptionally high precipitation in 2011 produced notably higher simulated deep

percolation rates when that year was included (Table 4). The Sigler et al. (2018) deep percolation estimate for the Porter catchment (8.7 cm yr^{-1}) falls between the 2011-2014 and the 2012-14 estimates from this work for z_f distributions based on both the Judith soil series ($5.0 - 9.2 \text{ cm yr}^{-1}$) and the median of Field B soil pits ($6.7 - 10.8 \text{ cm yr}^{-1}$).

Similarly, the Sigler et al. (2018) deep percolation estimate for the Kolin catchment (5.4 cm yr^{-1}) falls between the 2011-2014 and the 2012-14 estimates from this work for z_f distributions based on both the Danvers soil series ($2.0 - 5.7 \text{ cm yr}^{-1}$) and the median of Field C soil pits ($3.0 - 7.1 \text{ cm yr}^{-1}$). This agreement between our simulation results and an independent large-scale assessment of deep percolation lends credence to the idea that predictions of control points of episodic behavior may lead to reasonable estimates of landscape-scale phenomena.

Nitrate leaching rates estimated here from deep percolation weighted by z_f ranged from 2.2 to $13.8 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Table 4) and were somewhat lower than those from Sigler et al. (2018) at the catchment scale ($11.1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ Kolin; $18.4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ Porter). Relatively low nitrate leaching rates estimated here, in the context of deep percolation estimates that align with previous work, point to characterization of N concentration in leachate as an important avenue for future work. Mean nitrate concentrations for all three 2-yr sequences were lower than the mean nitrate concentration in groundwater, suggesting that the higher nitrate concentrations observed in lysimeters during the Fallow-Crop sequence may be more representative of concentrations reaching groundwater. A fraction of N loss from soils may have also occurred as reduced N species not quantified in our lysimeter samples (ammonium or dissolved organic

nitrogen). Reduced N species in leachate could be oxidized in the vadoze zone, augmenting the nitrate load reaching groundwater (Lorite-Herrera et al., 2009). In addition to enhanced biogeochemical analysis and modeling, future work incorporating snowmelt and the role of macropores as controls on deep percolation may increase model predictive power as well.

5. Conclusions

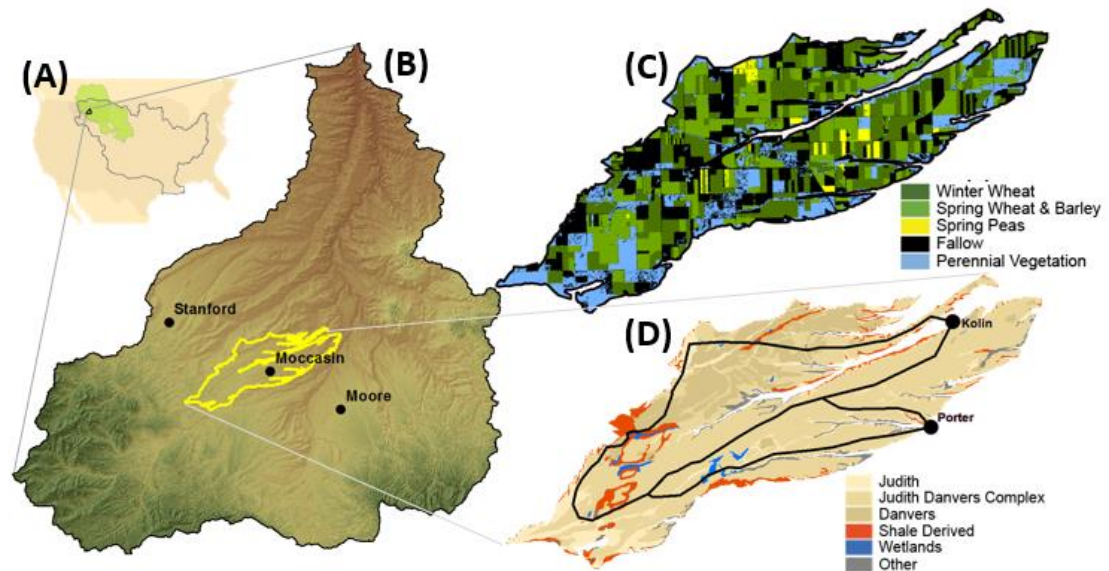
Understanding of the interactions among rotation management, soil structure, and weather is necessary to increase PUE and nitrogen use efficiency in dryland agriculture. In northern Great Plains agroecosystems, increased soil water storage during fallow periods facilitates mineralization of soil organic N to nitrate, resulting in elevated soil water and nitrate pools until the following growing season. Soil profiles that are near maximum water storage capacity and have higher nitrate concentrations are primed for both water and N losses. This priming effect happens more readily in soils with lower water storage capacity, here due to thinner fine-textured soil horizons (z_f). Fields in summer-fallow and especially those with thinner soils contribute to higher landscape-scale deep percolation and nitrate leaching at rates disproportionate to their areal extent.

This work highlights opportunities to increase water and N use efficiency for enhanced sustainability of agricultural yields that can also contribute to protection of environmental quality. In this work, soils with z_f values thinner than 25 cm have PSE values of zero and confer no water storage benefits to the crop following fallow, while facilitating nitrate leaching rates five to 16 times higher than thicker soils ($z_f > 100$ cm). While there can be motivations for including fallow in rotation other than water storage,

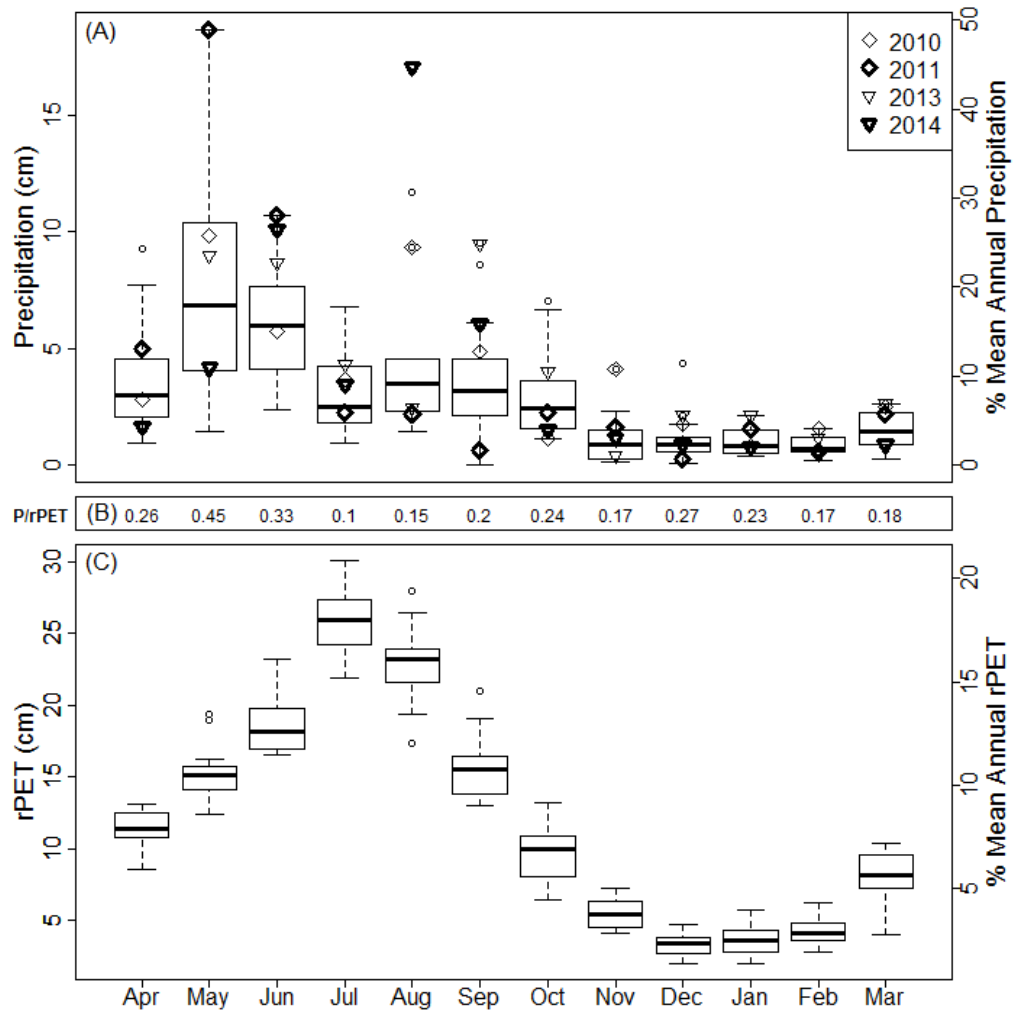
these areas with the lowest z_f values may be attractive candidates for conversion to perennial forage production, or for annual cropping with lower N application rates.

Acknowledgements

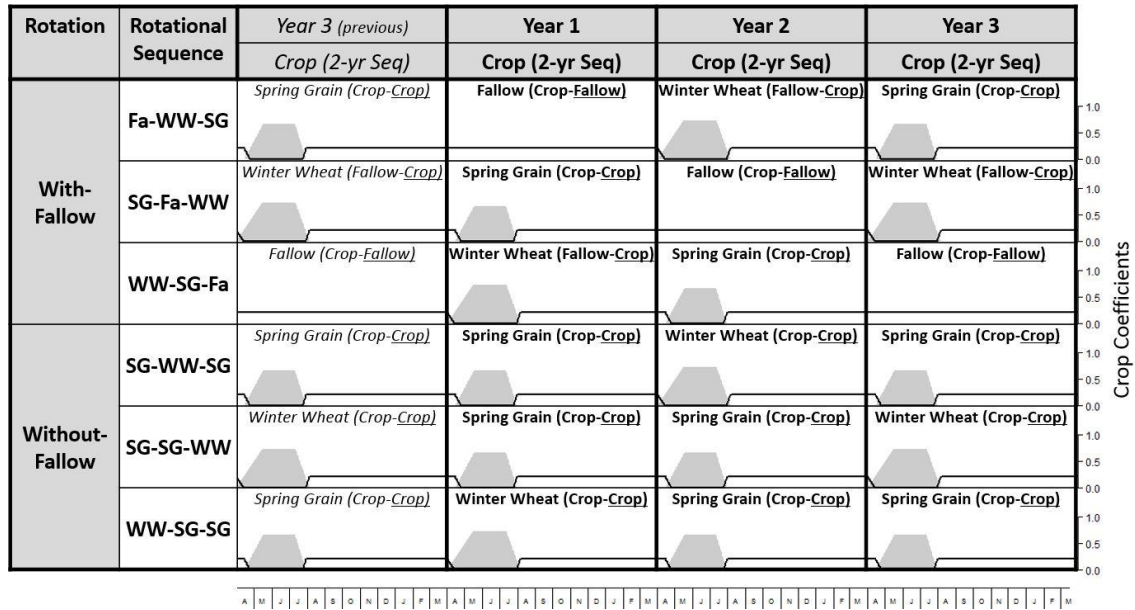
The authors would like to thank cooperating farmers, local partners, and the MSU Central Agricultural Research Center (CARC). Thank you to field technicians Kyle Mehrens, Robby Robertson, Mike Bestwick, Joe Capella and a special thank you to Simon Fordyce who was the lead field technician for the majority of the field campaign. This work was funded by the United States Department of Agriculture, National Institute of Food and Agriculture [grant number 2011-51130-31121, 2011] and USDA NIFA grant number 2016-67026-25067. Additional funding was provided by MSU Extension, Montana Fertilizer Advisory Committee, the Montana Agricultural Experiment Station, MSU Vice President of Research, MSU College of Agriculture, and the Montana Institute on Ecosystems. This work was supported in part by the National Science Foundation EPSCoR Cooperative Agreement OIA-1757351, as well as NSF EPSCoR Track 1 award numbers OIA-1443108 and EPS-1101342.

Figures

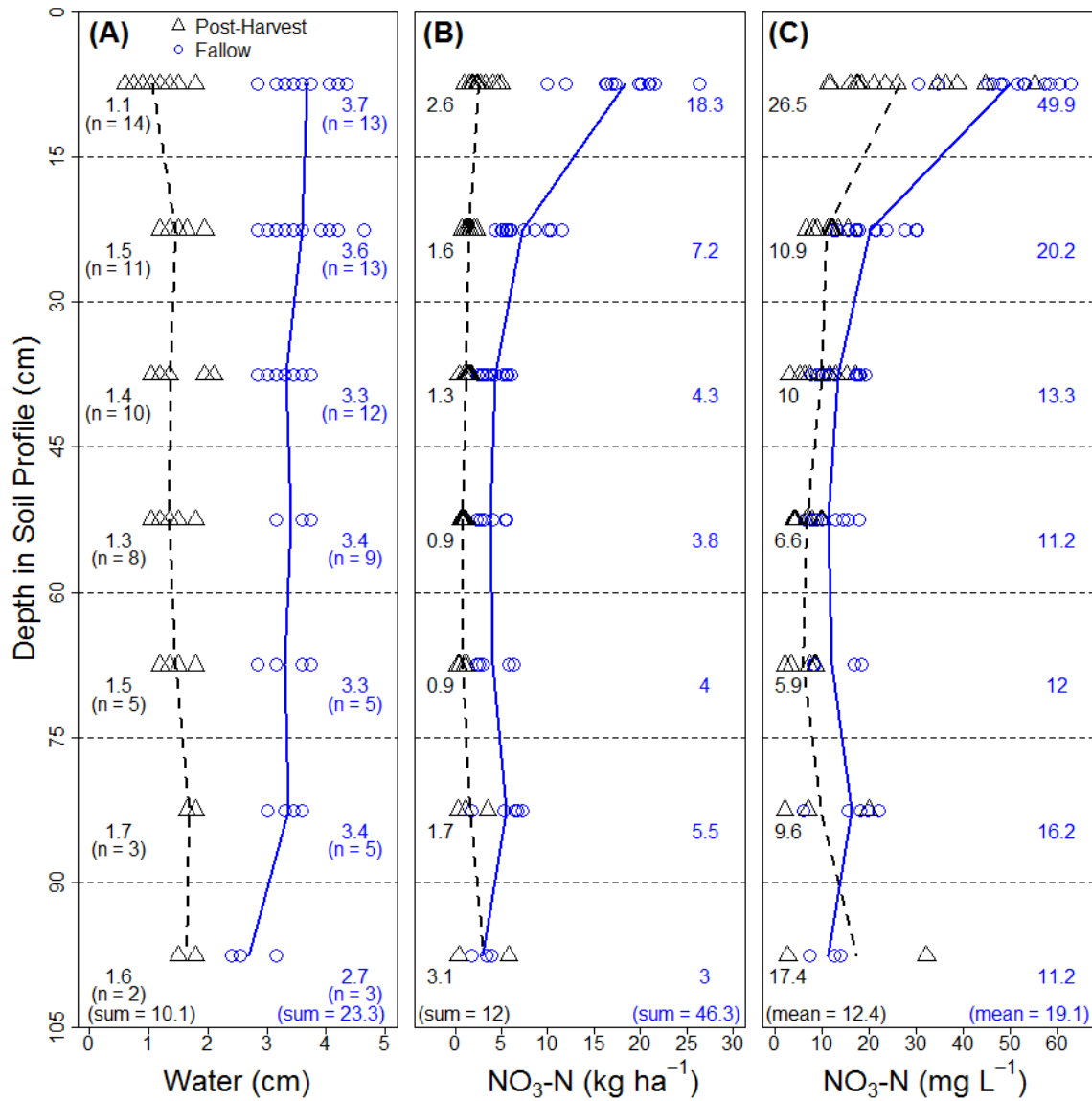
Ch3-Figure 1. Study Area. (A) the location of the Judith River Watershed (JRW) study area within the northern Great Plains (green) and the Mississippi Atchafalaya River Basin (gray outline); (B) the locations of the Moccasin terrace and towns nearest to the study fields within the JRW; (C) land use on the Moccasin terrace in 2014; and (D) soils and sample sites for catchments (outlined with black lines) on the Moccasin terrace.



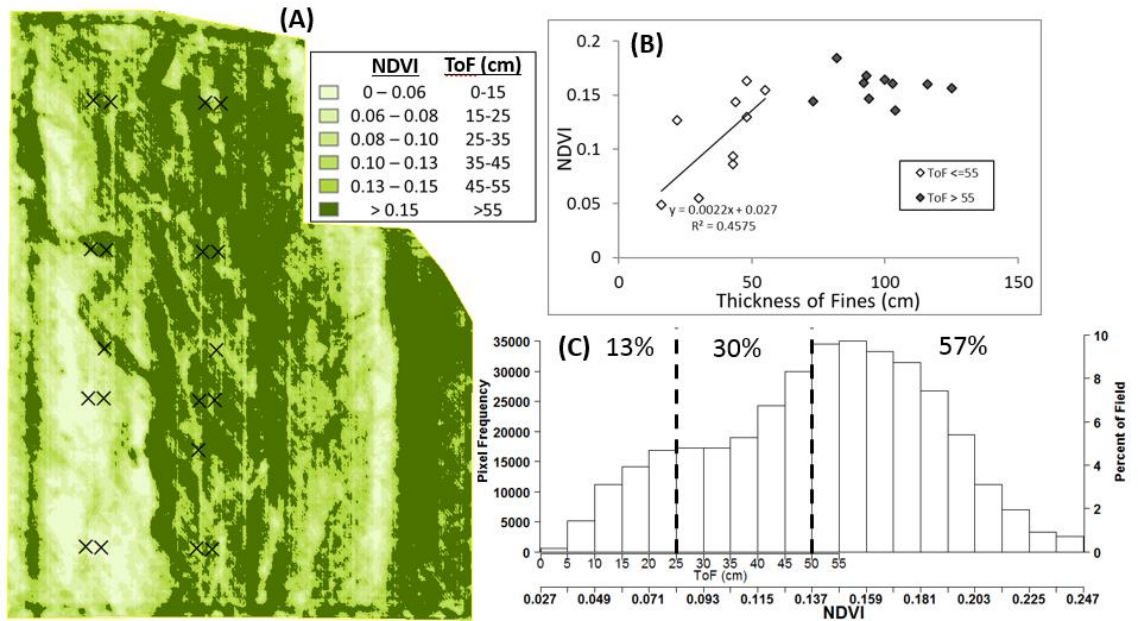
Ch3-Figure 2. Monthly Precipitation and rPET. (A) distributions of monthly precipitations at CARC (WRCC Gage: 245761) for the modeling period (2001-10-01 to 2017-05-30). Symbols for top four precipitation years are noted in the legend. (B) Ratio of monthly median precipitation over monthly median rPET. (C) distributions of monthly reference potential evapotranspiration at CARC (Agrimet Gage: MWSM) for the modeling period. Lines within boxes are medians; boxes represent the interquartile range; whiskers extend to the value furthest from the median within one interquartile range of the box.



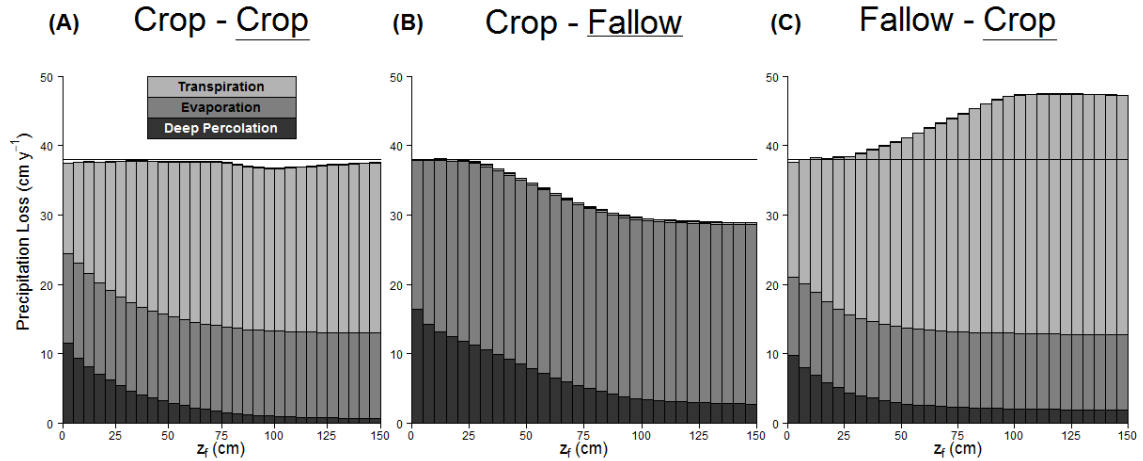
Ch3-Figure 3. Crop rotations. The two crop rotations with the three associated rotational sequences. The first year for each phase is the year 2000 (for example, with-fallow phase Fa-WW-SG is fallow in 2000, 2003, 2006, etc.). The crop for each year is listed along with the 2-yr crop sequence in parentheses, indicating crop versus fallow for the current year (underlined) and the previous year. The gray polygons are the transpiration coefficients and the black lines are evaporation coefficients for scaling and dividing rPET into E and T. Coefficient values correspond to the y axes on the right side of the figure. The WW-SG-Fa rotation was fallow in 2014, which is the land use year represented in Figure 1D where fallow fields are in black.



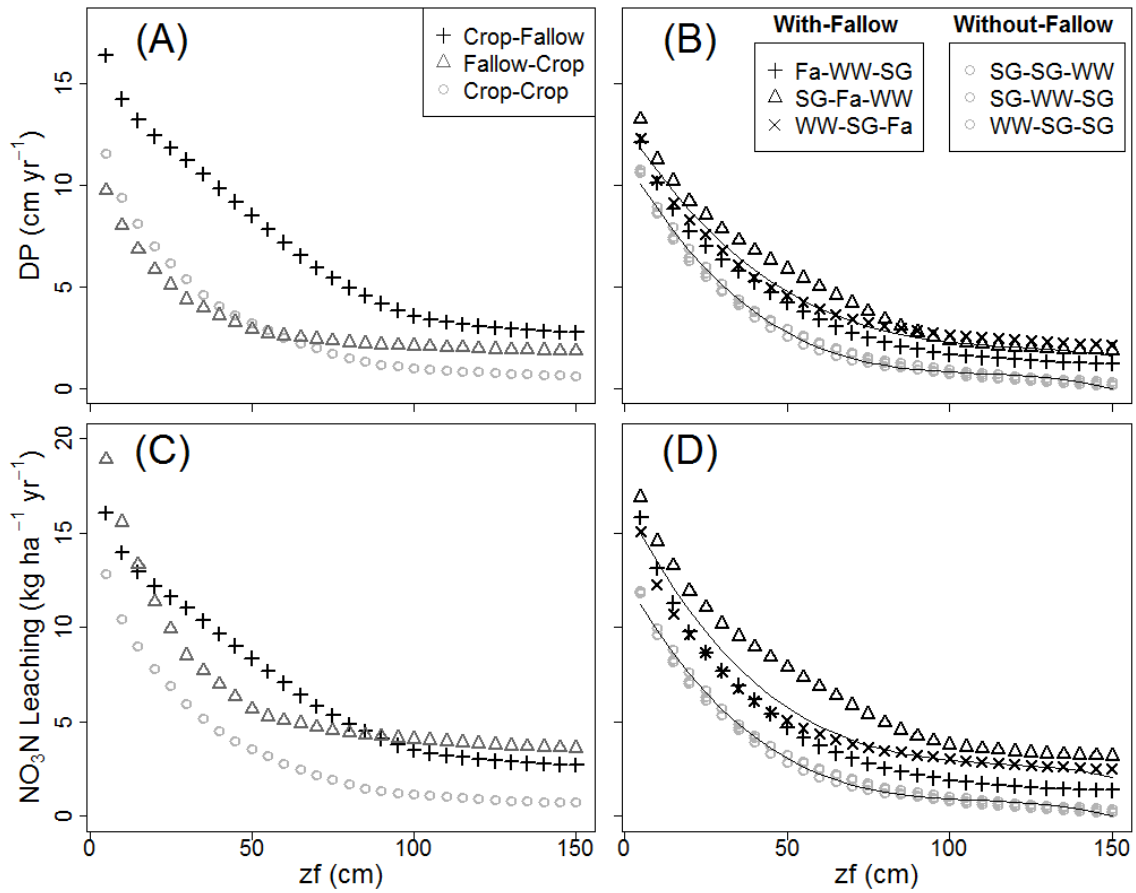
Ch3-Figure 4. Soil water and nitrate profiles by crop sequence. (A) Water pools for soil profile samples collected at 15 cm increments in August and September 2012 in fields fallow for a year (blue) and fields immediately post-harvest (black). Values on left side of the plot for each depth increment are mean water pools for samples post-harvest and values in parentheses are sample sizes. Values on the right are parallel for fallow field samples. Black dashed line is mean values for post-harvest and blue line is mean values for fallow. (B) Nitrate pools for the same samples in panel A with parallel symbology and mean values by depth increment. Sum of profile means are at the bottom. (C) Apparent nitrate concentrations calculated with nitrate and water pools from panels A and B with symbology and mean values parallel to panel A. Mean of profile means are at the bottom.



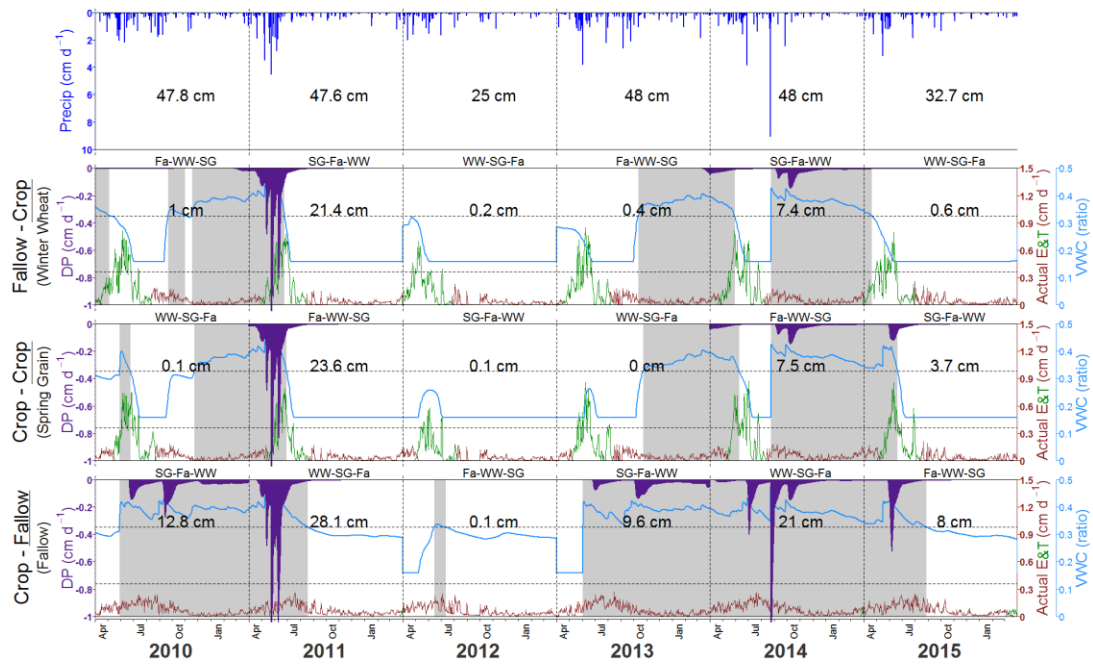
Ch3-Figure 5. Normalized Difference Vegetation Index (NDVI) and Thickness of Fines. (A) NDVI values calculated for Field C using a one-meter resolution National Agricultural Imagery Program (NAIP) image captured on July 24, 2011. Cross symbols are locations of soil pits excavated in 2012. (B) relationship between mean NDVI for pixels touching a two-meter radius around soil pits and thickness of fines (z_f) observed in the pit. (C) Pixel frequency histogram for NDVI values and corresponding z_f . Values near top of the plot are the percent of the field in depth categories separated by dashed lines (0-25, 25-50, > 50 cm).



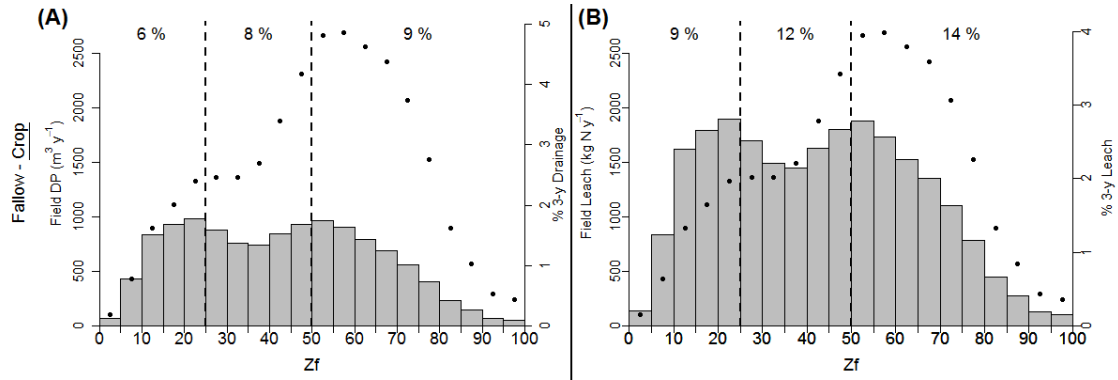
Ch3-Figure 6. Simulated precipitation partitioning by crop sequence. Mean annual precipitation partitioning results for 14-y model reporting period for the three with-fallow rotations. (A) is data from model years with crop sequence Crop-Crop (field is in crop and was crop last year). (B) is data from fallow years (Crop-Fallow). (C) is data from Fallow-Crop years. Each bar represents mean 14-y water loss to transpiration, evaporation, and deep percolation, with total bar height representing total losses (cm). Total values greater than 38 cm indicate total annual losses exceeding 14-y mean annual precipitation and thus include losses of stored water that was carried over from the previous year. Total values less than 38 cm (white area below line) indicate annual precipitation exceeding losses, and thus precipitation is stored for the following year.



Ch3-Figure 7. Deep percolation and nitrate leaching versus z_f . (A) 14-y mean deep percolation versus z_f aggregated by crop sequence. This is the same DP data in Figure 7. (B) 14-y mean deep percolation versus z_f aggregated by crop rotation. Lines are third degree polynomial relationships for mean deep percolation aggregated by rotation type (with-fallow and without-fallow; Sup Table 3.4b). (C) 14-y mean nitrate leaching versus z_f aggregated by crop sequence. (D) 14-year mean nitrate leaching versus z_f aggregated by rotation. Lines are third degree polynomial relationships parallel to panel B.



Ch3-Figure 8. Modeled daily deep percolation, transpiration and evaporation. The top panel is daily precipitation from CARC (WRCC Gage: 245761); the value for each year is the annual precipitation total. The bottom three panels are model results for z_f of 50 cm, organized by crop sequence year with rotations printed above for each year. Red polygons represent deep percolation and correspond to the left axis. Green lines represent transpiration and correspond to the right axis. Black lines represent evaporation and correspond to the right axis. Values printed in the panels are the annual deep percolation (cm y^{-1}). Extended versions of this plot with all model years for different z_f values are included in the supplemental materials.



Ch3-Figure 9. Field scale simulated DP and leaching. (A) Mean DP volume for the full field area by z_f category the Fallow-Crop sequence. Each bar is the mean annual DP of three with-fallow rotations, for the 14-y model reporting period. Values near the top of the plots are the percent of the total DP volume summed over the three crop sequence years for the 0-25, 25-50, and 50-100 cm z_f ranges. (B) Mean nitrate leaching mass for the for the full field area, configured parallel to DP in panel (A). Black dots show the relative distribution of z_f of Field C (bar heights in Figure 6C). See supplemental materials for parallel plots for all 2-yr crop sequences.

Tables

Ch3-Table 1. Lysimeter nitrate concentrations. Summary statistics for lysimeter nitrate-N concentrations (mg L^{-1}) with extreme outliers removed (data included as supplement).

2-yr Seq	Mean	StDev	Median	0.25 and 0.75 Quartiles	Sample Size
Crop-Crop	14.0	9.3	11.1	7.6, 17.5	34
Crop-Fallow	11.2	6.4	9.8	6.1, 15.7	23
Fallow-Crop	19.9	13.0	19.4	9.9, 28.0	36

Ch3-Table 2. Summary of precipitation partitioning by sequence (Seq). Maximum (max), minimum (Min), and range (Rng) of mean annual partitioning losses (cm y^{-1}) across zf values, presented as bar heights in Figure 7. Runoff values were all ≤ 0.1 and are not shown. Small values for transpiration in the Crop-Fallow sequence are due to modest early season growth of winter wheat prior to 1 April, which is aggregated within the Crop-Fallow sequence.

Seq	Evaporation			Transpiration			Deep Percolation			Total Losses		
	Min	Max	Rng	Min	Max	Rng	Min	Max	Rng	Min	Max	Rng
Crop-Crop	12.3	13.6	1.3	13.0	24.5	11.6	0.6	11.6	10.9	36.8	37.8	1.0
Crop-Fallow	21.5	26.6	5.1	0.1	0.2	0.1	2.8	16.4	13.6	29.0	38.1	9.2
Fallow-Crop	10.9	12.1	1.2	16.5	34.6	18.1	1.9	9.7	7.9	37.6	47.5	9.9

Ch3-Table 3. Field scale deep percolation and leaching. Percentage of deep percolation and leaching for the mean 3-yr with-fallow rotation attributed to each 2-yr sequence for thin (0-25 cm), intermediate (26-50 cm) and thick (> 50 cm) z_f soils on Field C. The bottom row is the percentage of 3-yr deep percolation and leaching attributed to each z_f category. Percentages in parentheses below the depth ranges are the portion of the field area in that depth range. Subtle deviations from 100% in sum of bottom row values and sum of right column values within Deep Percolation and Leaching are due to rounding.

Period within Rotation	Deep Percolation			All depths
	0 - 25 cm (13 %)	26 - 50 cm (30 %)	> 50 cm (57 %)	
Crop-Crop	7%	9%	8%	24%
Crop-Fallow	12%	19%	24%	55%
Fallow-Crop	6%	8%	9%	23%
Full Rotation	25%	36%	41%	100%

Period within Rotation	Leaching			All depths
	0 - 25 cm (13 %)	26 - 50 cm (30 %)	> 50 cm (57 %)	
Crop-Crop	6%	8%	7%	21%
Crop-Fallow	9%	15%	19%	43%
Fallow-Crop	9%	12%	14%	35%
Full Rotation	24%	35%	40%	100%

Ch3-Table 4. Deep percolation and leaching by z_f distribution and time period. Deep percolation and leaching rates based on z_f distributions characterizing Field B, Field C, the Judith, and Danvers soil series for different time periods. z_f distributions are normal with the centers and standard deviations specified. Deep percolation and leaching rates for 14-y estimates are based on relationships depicted in Figure 9B and 9D for the with-fallow rotation. Rates are also provided for the abnormally wet 2011-14 period and the more average 2012-2014 period. Standard deviations for soil series were not available and are set equal to that for Field B pits.

z_f Scenario	z_f Distribution (cm)		Deep Percolation (cm y^{-1})		
	z_f center	z_f SD	14-y	2011-14	2012-14
Field B Pit Median	48	30	6.2	10.8	6.7
Field B Pit Mean	63	30	4.8	9.2	5.0
Field C Pit Median	86	31	3.2	7.1	3.0
Field C Pit Mean	76	31	3.8	8.0	3.8
Judith Series	61	30	4.8	9.2	5.0
Danvers Series	112	30	2.3	5.7	2.0

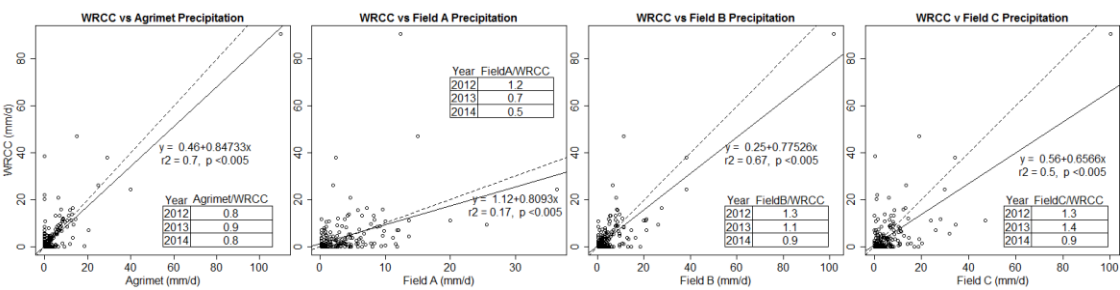
z_f Scenario	z_f Distribution (cm)		Leaching (kg N $ha^{-1} y^{-1}$)		
	z_f center	z_f SD	14-y	2011-14	2012-14
Field B Pit Median	48	30	7.7	13.8	8.3
Field B Pit Mean	63	30	5.9	11.7	6.0
Field C Pit Median	86	31	3.9	9.1	3.4
Field C Pit Mean	76	31	4.8	10.2	4.5
Judith Series	61	30	5.9	11.8	6.0
Danvers Series	112	30	2.9	7.5	2.2

Supplemental Materials

Content in this supplement is organized and numbered according to the section within the main text that is being supplemented. As a result, section numbers may be missing from the supplement if there is no supplemental material for a section in the main narrative.

2. Methods

2.1 Study Area and Cropping



Ch3-Sup Figure 2.1a - Precipitation comparisons. Comparisons between precipitation reported for the Western Regional Climate Center Station (WRCC 245761) and precipitation for other weather stations in the study area. Dashed lines are 1:1 lines and solid lines are linear regression lines fit through the data. Equations for linear regression lines, r², and p values are printed on plots. The WRCC and Agrimet stations are located within a few hundred meters of one another at the MSU Central Agricultural Research Center. Comparisons with study fields A-C are for non-freezing months when tipping buckets were active. Precipitation for days with data from both stations within comparisons was summed annually to calculate the ratios in the tables on the plots.

2.2 Spatial Distribution of Fine-Textured Soil Thickness Five SSURGO soil

series are present in the study fields (SSURGO Judith Basin and Fergus Counties) and dominate the study catchments (Sup Table 2.2a). All five series are characterized as well

drained. Four of these series (Judith, Sipple, Doughty, and Tamaneen) are formed in calcareous alluvium and are characterized by finer-textured clay loam horizons ($\leq 10\%$ gravel/cobble) overlying coarser-textured gravelly loam horizons ($\geq 40\%$ gravel/cobble) (USDA NRCS Official Soil Series Descriptions). The finer-textured shallow horizons make up the primary water holding capacity zone of the soil profile in contrast with the coarser-textured deeper horizons that drain easily. The Danvers series has thicker finer-textured horizons, with clay loam and clay texture extending through the deepest horizon (2C; 112-152 cm). The Danvers 2C horizon has 20% gravel/cobble on average but has gravel/cobble/stone content ranging up to 65%.

Soils information is informed from sampling on three study fields (A, B and C), managed by cooperating farmers during the study. Detailed management information is available in John (2015).

Field A consists of subfields totaling 128 ha near Stanford Montana. Field A is mapped as a complex of Danvers and Judith soil series. There were no lysimeters installed in Field A, but soil core data from this field is included in calculations of θ_R and θ_S for soil modeling.

Field B consists of subfields totaling 64 ha near Moccasin Montana. Field B is mapped primarily as a complex of Tamaneen, Judith, and Danvers series, with a small amount of Windham.

Field C near Moore Montana consists of subfields totaling 32 ha plus additional field C4 which was used solely for measurement of evapotranspiration by eddy covariance during fallow in 2014 (Vick et al., 2016). Field C soils are mapped as a

complex composed primarily of the Doughty series but including Sipple and Judith series (SSURGO Fergus County). Twelve of the 18 lysimeters for the project were installed in Field C.

Ch3-Sup Table 2.2a - SSURGO soil series. Gravel horizons are identified as the shallowest horizon with 40% or more rock. Depths are to the top of the gravel horizon in all cases except Danvers which does not have a horizon with mean gravel content greater than 20%. Minimum depth for Danvers is to the top of 2C which ranges up to 65% rock. Maximum for Danvers is maximum depth modeled and mean is half-way between minimum and maximum.

Series	Gravel Horizon	Gravel Horizon Texture	Min Depth (cm)	Mean Depth (cm)	Max Depth (cm)	Overlying Horizon	Overlying Horizon Texture
Doughty	2Ck1	extremely gravelly loam; 65% rock	51	81	102	Bk2	loam, clay loam; 10% rock
Sipple	2C	very gravelly loam; 55% rock	102	132	152	Bk3	clay loam; 10% rock
Judith	2Bk3	extremely gravelly loam, sandy clay loam; 75% rock	58	61	97	Bk2	clay loam; 10% rock
Danvers	2C	gravelly clay loam; 20% limestone pebbles	112	131	150	2C	Loam, silty clay loam, clay
Tamaneen	2Bk2	very gravelly loam; 40% rock	43	56	102	Bk1	clay loam; 10% rock

2.4 Hydrus Model Configuration All precipitation was routed into the model as rain rather than accounting for snow accumulation, a simplification assumed to have minimal effects on model results due to relatively low rates (2.9 cm or < 10%) of annual precipitation occurring when soils are prone to freezing (December through February).

For all periods without active plant growth, rPET was allocated entirely to evaporation. Potential transpiration during crop periods were calculated by multiplying rPET by crop coefficients associated with crop growth stage. Crop growth stage was estimated using cumulative growing degree days (GDD) Celsius since end of dormancy for winter wheat and since seeding for spring grain (Sup Table 2.4b). Crop coefficients start at zero in the spring prior to crop growth, increase with GDD to a maximum value at crop canopy closure, remain at maximum until crop maturity, and then decrease with GDD to zero on the date of harvest (Main Figure 2). Maximum crop coefficients for winter wheat and spring grain are calculated based on the ratio of actual ET (measured with eddy covariance; Vick et al., 2016) to rPET for the period between canopy closure and depleted VWC (Sup Figures 2.4c and 2.4d). When crop is not present, potential evaporation is calculated by multiplying rPET by a fallow evaporation coefficient (fallow coefficient), which was set equal to the median ratio of actual ET (measured with eddy covariance; Vick et al., 2016) to rPET (Sup Figure 2.4f). The fallow coefficient is conceptually parallel to a crop coefficient, except rather than accounting for variable water extraction effectiveness at different crop stages, it accounts for PET lower than rPET because transpiration is absent and evaporation is being controlled by soil physical properties.

To conform to the implementation of dynamic root depths in Hydrus, the spatial distribution of the removal of water from the soil by transpiration was simulated as a trapezoidal pattern specified by Hoffman and Van Genuchten (1983). This distribution function specifies maximum uptake from the soil surface to a depth of 0.2 of root depth at the current timestep, below which uptake drops linearly to zero at maximum root depth for the current timestep. Root growth is simulated at a rate of 0.665 mm per growing degree (C) day (GDD) starting on the seeding date, a rate half of that reported by Thorup-Kristensen et al. (2009). The root growth rate was adjusted down by half because the lower rate produced a notably higher coefficient of determination value (0.19 increased from -0.64) for spring grain ET on Field C in 2014. Initial model scenarios with a root growth rate of 1.33 mm per GDD, resulted simulated ET values close to zero (due to depleted soil water), while measured ET still showed high rates. Presumably the tower was measuring transpiration from spring wheat growing on portions of the field with zf deeper than the 46 cm VWC sensor, which indicated dry conditions before tower ET rates dropped off. Root rate is the only model parameter that was calibrated based on simulation results. Root growth stops when it reaches a maximum depth of 107 cm for winter wheat and 81 cm for spring grain based on mean values for deepest roots observations in soil pits (Sup Table 2.4b).

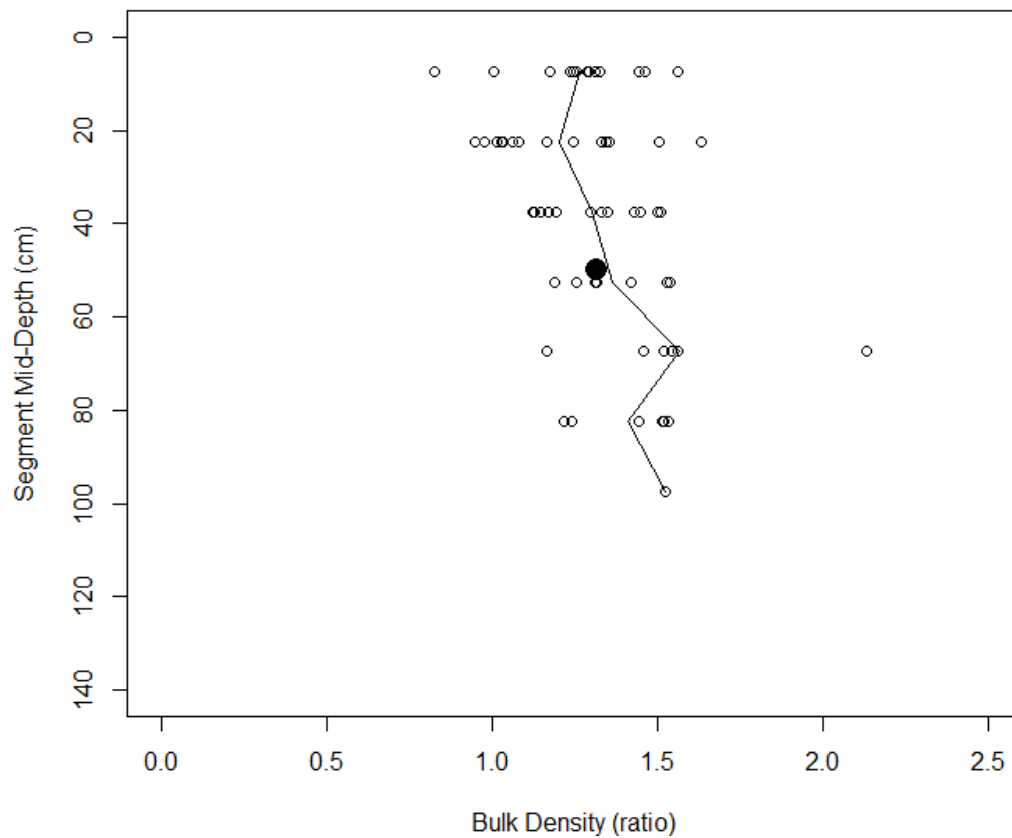
Winter wheat root growth stops in the fall with the onset of dormancy and initiates in the spring with the end of dormancy, but dates based on temperature. Start of dormancy is on the first day in the fall when the maximum daily temperature drops below 0 C for the first time and begins again in the spring when the 7-day moving average

maximum daily temperature comes above 0 C for the last time. These dormancy ‘rules’ were determined by trial and error using the daily minimum and maximum temperature data. Soil temperature data would have been preferable, but was only available starting in 2006. The rules based on air temperature produced reasonable ranges of dates in the fall and the spring and did a fair job of predicting days when soils defrosted in the spring (based on years when soil temperature data was available).

Ch3-Sup Table 2.4a - van Genuchten parameters. van Genuchten parameters for the fine textured surface horizon and the underlying coarse textured horizon used in model simulations.

Symbol	Parameter	Fine Textured Horizon		Coarse underlying material	
		Fine Textured	Source	Value	Source
θ_R	Residual soil moisture ($\text{cm}^3 \text{cm}^{-3}$)	0.12 ± 0.02	VWC observations near wilting point	0.053	Rosetta Lite 1.1 (sand)
θ_s	Saturation soil moisture ($\text{cm}^3 \text{cm}^{-3}$)	0.498 ± 0.08	calculated from bulk density observations	0.3747	Rosetta Lite 1.1 (sand)
α	Inverse air entry (cm^{-1})	0.0158	Rosetta Lite 1.1 (clay loam)	0.0353	Rosetta Lite 1.1 (sand)
n	Pore size distribution index (dimensionless)	1.4145	Rosetta Lite 1.1 (clay loam)	3.1798	Rosetta Lite 1.1 (sand)
K_s	Saturated hydraulic conductivity (cm d^{-1})	8.18	Rosetta Lite 1.1 (clay loam)	642.98	Rosetta Lite 1.1 (sand)
	Field Capacity	0.33	Hydrus	0.06	Hydrus

The value of θ_s was estimated as porosity, calculated from 60 soil bulk density measurements (Sup Figure 2.4a) divided by an assumed particle density of quartz (2.648 g cm^{-3}). Mean bulk density is $1.32 \pm 0.21 \text{ g cm}^{-3}$, resulting in mean porosity of $0.498 \pm 0.08 \text{ cm cm}^{-1}$ for the fine textured soil horizons ($\pm$ values are one standard deviation).

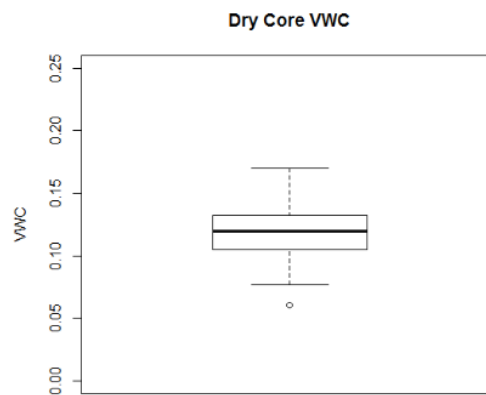


Ch3-Sup Figure 2.4a - Bulk density profile. Bulk density measurements (x axis) plotted with depth in cm (y axis) for field samples rated with the highest quality by field technicians. Mean bulk density by depth is plotted as a line and the overall mean bulk density is plotted as a solid point at the average depth of the samples.

Bulk density was measured by removing 1500 cm³ of soil from the wall of a soil pit at 15 cm depth increments. Accurate volumetric sampling was facilitated by steel forms fabricated from 1/8" steel which were 15 cm tall, and 10 cm in each horizontal direction. At the time of collection, each sample was given an accuracy rating based on precision in capturing the target 1500 cm³. Only the top ranked samples were used for calculation of mean bulk density. It was not possible to achieve high precision in

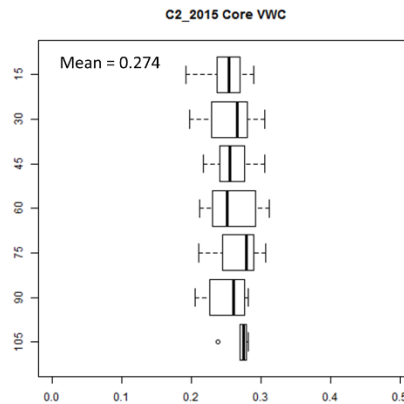
volumetric sampling in the gravel layer, so top ranked samples were all in the fine textured soil horizons. Field moist samples were transported to the lab in Ziplock bags where subsamples were removed for chemical analysis with mass quantified. Samples were dried at 50 degrees Celsius until weight change stopped. Dry weight accounting for subsample removal was divided by 1500 cm^3 to calculate bulk density. The dataset includes 60 samples from 19 soil pits from three field locations (Fields A,B,C) ranging in depth to 105 cm.

θ_R was estimated as volumetric water content (VWC) measured in soil core samples collected when soils were assumed to be near wilting point. The 100 core samples used were collected in August of 2012 from two fields (A6-7 and B3-4) immediately following harvest, following an abnormally dry growing season. The mean VWC was $0.12 \pm 0.02 \text{ cm cm}^{-1}$ (see Dry Core VWC Figure).



Ch3-Sup Figure 2.4b – Core samples at wilting point. Volumetric water content for the 100 soil core samples collected in August of 2012 used to determine θ_R .

Volumetric water content at field capacity (0.274) was calculated as the mean of gravimetric VWC measurements on core samples collected from Field C after a relatively wet summer during a fallow year in 2015 (Sup Figure 2.4c).



Ch3-Sup Figure 2.4c – Core samples at field capacity. Soil depth (y axis) and volumetric water content (x axis) for soil core samples collected during conditions when soils were expected to be near field capacity.

Description of source information for crop growth parameter values (Main Table 2).

Winter Wheat

Seeding Date: 1 October is the approximate median date that cooperating farmers seeded winter wheat during the study (John, 2015).

GDD to Emergence: 140 is the mid-range GDD value for emergence of Hard Red Wheat in the northern Great Plains (Miller et al., 2001). This GDD value occurred on 5 April in 2013 (Sup Figure 2.4d) and Field C winter wheat emergence near this date is corroborated by plant-cam photos from that field.

GDD to Canopy Close: 500 was the accumulated GDD value in 2013 (dormancy ended 18 January that year based on temperature) on 25 May, which is the first day the Tower-AET/Agrimet-rPET value for Field C winter wheat exceeded 0.7 and began to plateau (Sup Fig 2.4c). Plant cam images from Field C provide visual support that the crop canopy began obscuring most of the soil surface near this date. This GDD value falls during the stem elongation stage of barley and Hard Red Wheat (Miller et al., 2001), which is associated with leaf area index (LAI) in the range of 2-4 (Boys and Geary, 2015). Maximum crop canopy closure values (~80%) for wheat in the Great Plains have been observed to occur at LAI values of 2-3 (Nielsen et al., 2012), suggesting the wheat canopy should be reaching maximum closure by the stem elongation stage.

GDD to Mature: 1600 is the mid-range GDD value for complete maturity for Hard Red Wheat in the northern Great Plains (Miller et al., 2001).

GDD to Harvest: 1730 GDD is the value for 2013 on 7 August, which is the day winter wheat was harvested on Field C by the cooperating farmer.

Max Root Depth: 107 is the mean of maximum depths of root observation in soil pits following winter wheat during the study (Sup Table 2.4c).

Max Crop Coefficient: 0.75 is the slope of the Tower-AET versus Agrimet-rPET linear regression line for 2013 on Field C when winter wheat was growing (Sup Figure 2.4d)

Spring Grain

Seeding Date: 17 April is the median spring seeding date barley and wheat at CARC for 2016-2018 (personal communication with CARC staff).

GDD to Emergence: 130 is the mean of mid-range GDD emergence values for barley and Hard Red Wheat in the northern Great Plains (Miller et al., 2001). This GDD value occurred on 19 April in 2014 (Sup Figure 2.4e) and emergence of spring wheat on Field C near this date is supported by field photos.

GDD to Canopy Close: 400 was the accumulated GDD value in 2014 (seeding on Field C on 2 May) on 8 June, which is the best estimate of canopy closure based on the Tower-AET/Agrimet-rPET ratio and field photos. While the Tower-AET/Agrimet-rPET ratio went above 0.7 for the first time on 28 May, field photos indicate the canopy was clearly not closed on this date, while the canopy appears visually closed when the ratio goes above 0.7 for the second time on 8 June. The 8 June cutoff also produces a larger R² value than the May 28th date in the Tower-AET/Agrimet-rPET linear regression (Sup Figure 2.4e). The 400 GDD value falls within the tillering phase for Hard Red Wheat but between tillering and stem elongation phases for barley for the northern Great Plains (Miller et al., 2001).

GDD to Mature: 1500 is the mean of mid-range GDD values for complete maturing for barley and Hard Red Wheat in the northern Great Plains (Miller et al., 2001).

GDD to Harvest: 1700 GDD is the value for 2014 on 19 August, which is the day the spring wheat on Field C was harvested by the cooperating farmer. The median date for spring grain harvest at CARC for 2016-18 was 16 August (personal communication with CARC staff).

Max Root Depth: 81 is the mean of maximum depths of root observation in soil pits following spring grain during the study (Sup Table 2.4c).

Max Crop Coefficient: 0.65 is the slope of the Tower-AET versus Agrimet-rPET linear regression line for 2014 on Field C when spring wheat was growing (Sup Figure 2.4e)

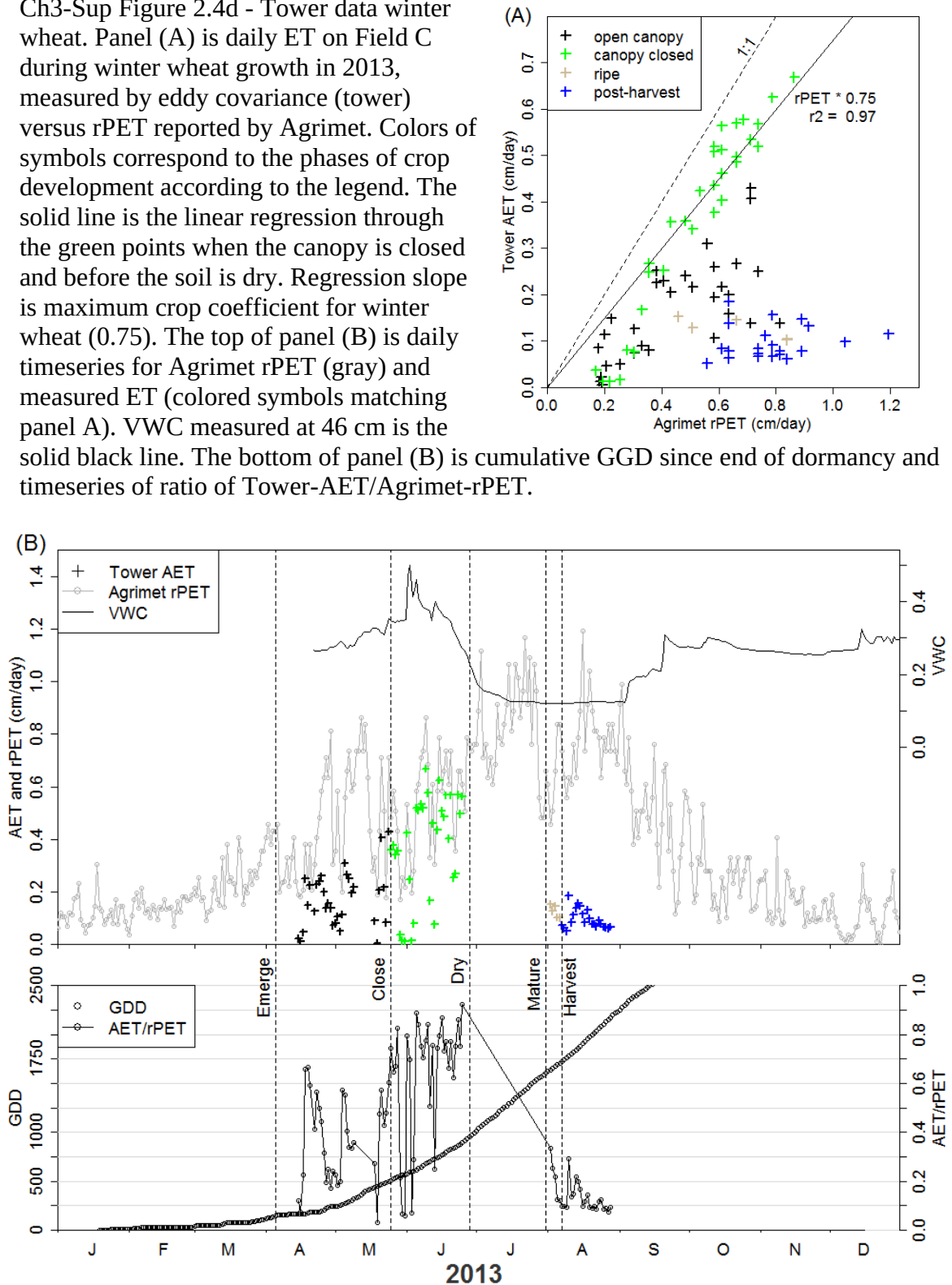
Fallow**Seeding Date:** not applicable**GDD to Emergence:** not applicable**GDD to Canopy Close:** not applicable**GDD to Mature:** not applicable**GDD to Harvest:** not applicable**Max Root Depth:** not applicable

Max Crop Coefficient: 0.22 is the median Tower-AET/Agrimet-rPET value for all fallow periods; this includes data from Field C4 in 2014 when the field was fallow and post-harvest data from Field C in 2013 and 2014 (Sup Figure 2.4f)

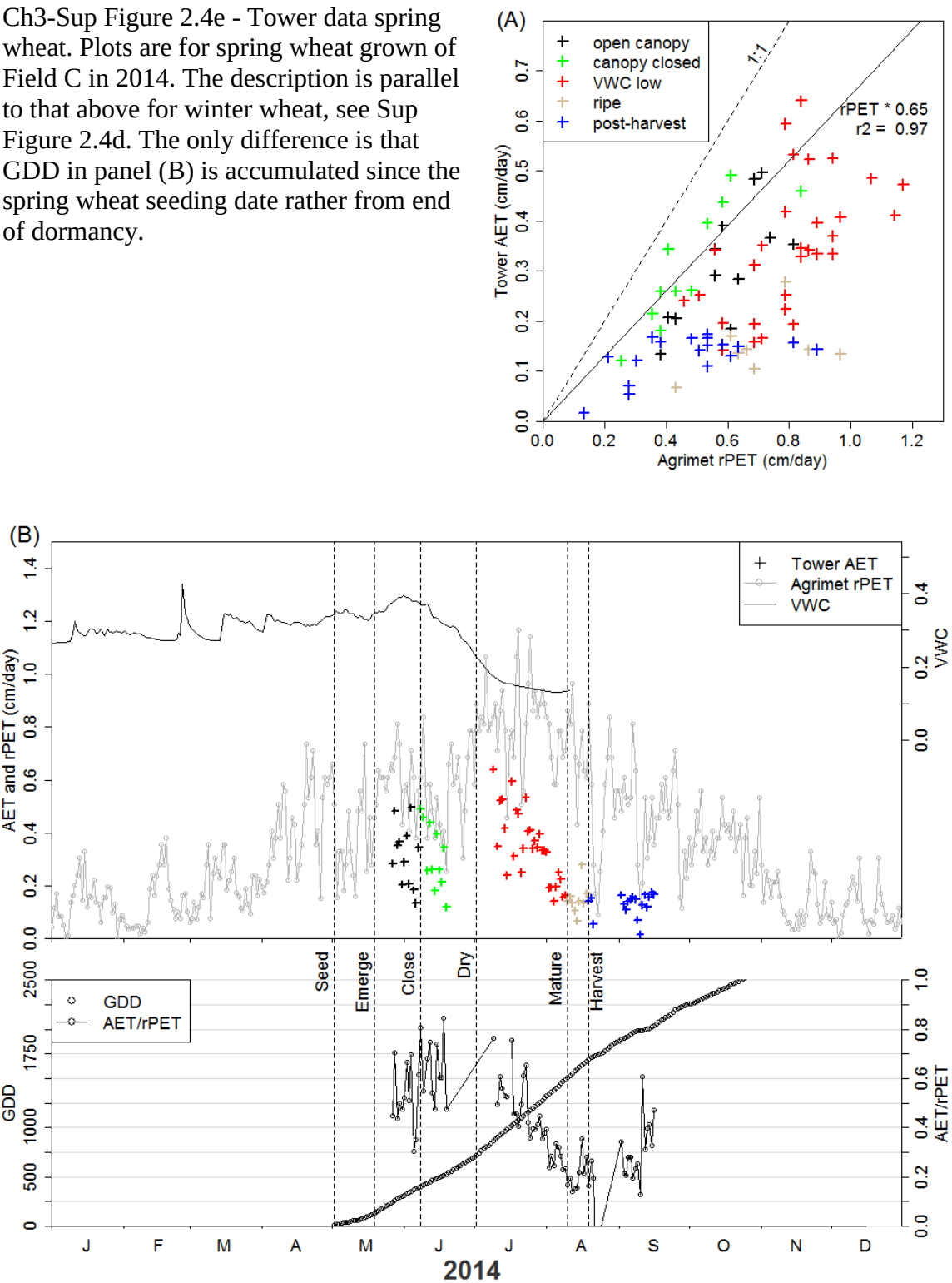
Ch3-Sup Table 2.4b - Crop growth parameters. For winter wheat, growing degree day (GDD) values are cumulative degrees above 0 C from the end of dormancy following winter, the date for which is dynamic with temperature (rules described above). For spring grain, GDD values are cumulative from seeding date.

Crop	Seed Date	GDD to Emergence	GDD to Canopy Close	GDD to Mature	GDD to Harvest	Max Root Depth (cm)	Max Crop Coef
W.Wheat	1 Oct	140	500	1600	1730	107	0.75
S.Grain	17 Apr	130	400	1500	1700	81	0.65
Fallow	NA	NA	NA	NA	NA	NA	0.22

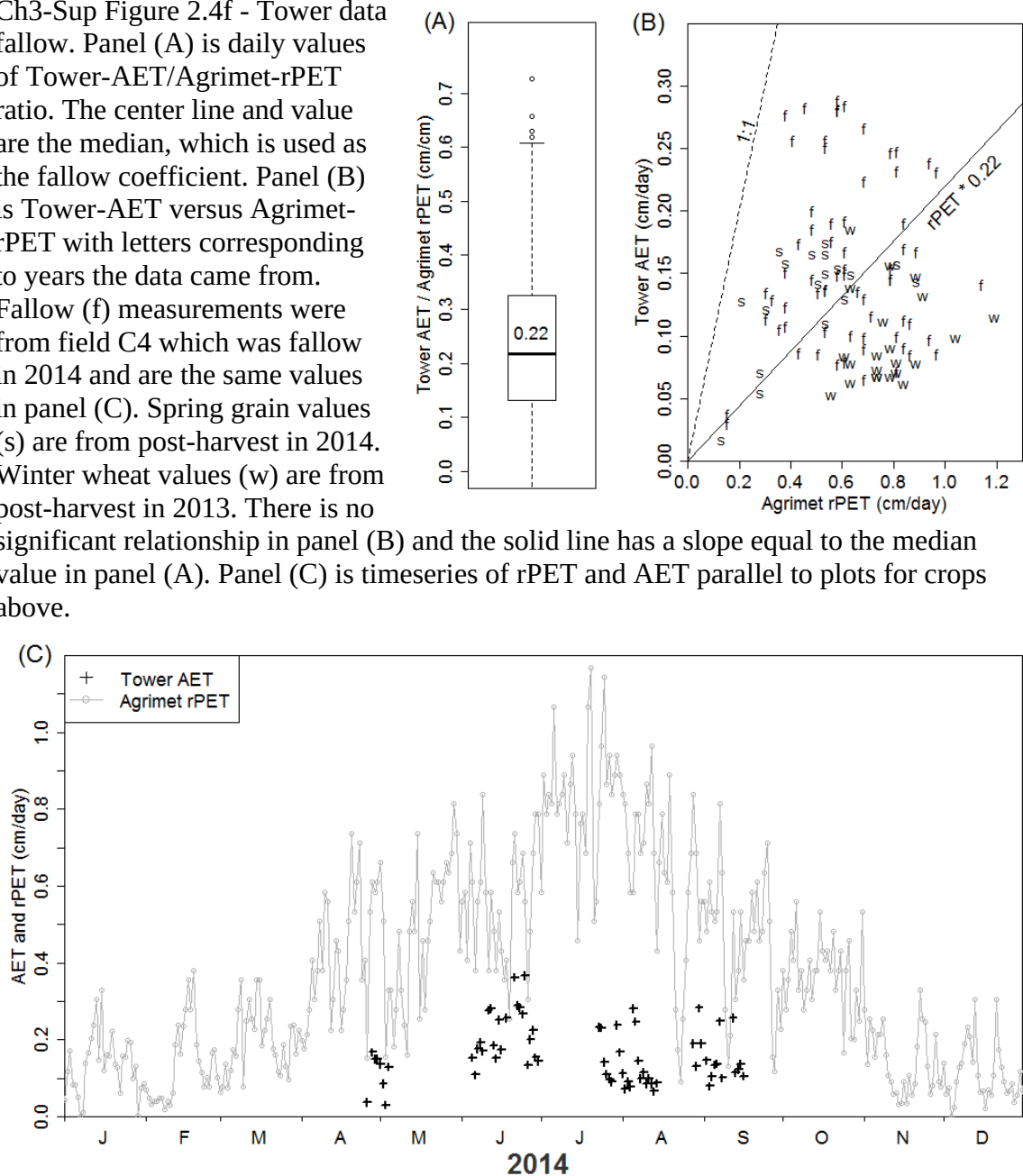
Ch3-Sup Figure 2.4d - Tower data winter wheat. Panel (A) is daily ET on Field C during winter wheat growth in 2013, measured by eddy covariance (tower) versus rPET reported by Agrimet. Colors of symbols correspond to the phases of crop development according to the legend. The solid line is the linear regression through the green points when the canopy is closed and before the soil is dry. Regression slope is maximum crop coefficient for winter wheat (0.75). The top of panel (B) is daily timeseries for Agrimet rPET (gray) and measured ET (colored symbols matching panel A). VWC measured at 46 cm is the solid black line. The bottom of panel (B) is cumulative GGD since end of dormancy and timeseries of ratio of Tower-AET/Agrimet-rPET.



Ch3-Sup Figure 2.4e - Tower data spring wheat. Plots are for spring wheat grown of Field C in 2014. The description is parallel to that above for winter wheat, see Sup Figure 2.4d. The only difference is that GDD in panel (B) is accumulated since the spring wheat seeding date rather from end of dormancy.



Ch3-Sup Figure 2.4f - Tower data fallow. Panel (A) is daily values of Tower-AET/Agrimet-rPET ratio. The center line and value are the median, which is used as the fallow coefficient. Panel (B) is Tower-AET versus Agrimet-rPET with letters corresponding to years the data came from. Fallow (f) measurements were from field C4 which was fallow in 2014 and are the same values in panel (C). Spring grain values (s) are from post-harvest in 2014. Winter wheat values (w) are from post-harvest in 2013. There is no significant relationship in panel (B) and the solid line has a slope equal to the median value in panel (A). Panel (C) is timeseries of rPET and AET parallel to plots for crops above.



Ch3-Sup Table 2.4c - Root depth in soil pits. Maximum depth of roots observed in soil pits, grouped by crop.

Location	Root Depth (cm)	Crop	Mean Depth (cm)	Sample Size by Crop
C2W.04-2013	88	winter wheat	107	4
C2E.10-2013	115	winter wheat		
C3W.01-2013	110	winter wheat		
C3W.04-2013	118	winter wheat		
B1E.01-2012	70	pea	77.5	4
B1E.04-2012	70	pea		
B1E.07-2012	85	pea		
B1E.10-2012	85	pea		
B3E.01-2012	85	barley	81	9
B3E.03-2012	70	barley		
B3E.04-2012	92	barley		
B3E.07-2012	98	barley		
B3E.10-2012	41	barley		
B4W.01-2012	80	barley		
B4W.04-2012	60	barley		
B4W.07-2012	124	barley		
B4W.10-2012	75	barley		

Assessment of model performance based on comparison to field observations was facilitated by aligning input parameters with conditions on Fields C and C4 for a 3-yr period (2012-2014) where field observations were available (Sup Table 2.4d). Observations included Field C in 2013 during winter wheat, Field C 2014 during spring grain, and Field C4 during 2014 during fallow. Fields C and C4 were in separate rotations and hence modeled separately. A spin-up period of one year was included for each scenario to allow for development of crop rotation context within the modeled results. Volumetric water content was measured over two growing seasons (2013-04-15 to 2014-08-15) on Field C with Decagon dielectric 10HS moisture probes (Decagon Devices, Pullman, WA) and Onset data loggers (Onset, Bourne, MA). VWC observations were calibrated using the three-point retroactive method described by Gasch et al. (2017) using porosity (0.50), field capacity (0.27), and wilting point (0.12) VWC sample measurements described above. Precipitation for the comparison period came from a tipping bucket on Field C during non-freezing periods and from the WRCC weather station (27 km away) during freezing periods.

Ch3-Sup Table 2.4d – Field observations for comparison. Summary of field observation data used for evaluation of model simulation results.

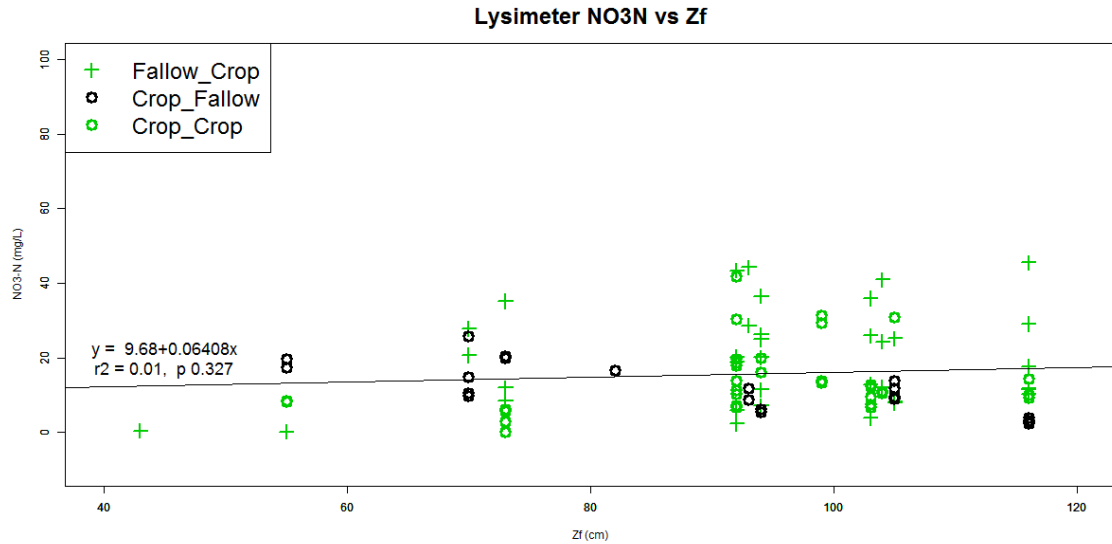
Simulation Year	Sim 1 Year 1	Sim 1 Year 2	Sim 1 Year 3	Sim 2 Year 1	Sim 2 Year 2
Actual Year	2012	2013	2014	2013	2014
Crop	Fallow	Winter Wheat	Spring Grain	Spring Grain	Fallow
Simulated Field	C	C	C	C4	C4
Purpose	Establish Conditions	Comparison	Comparison	Establish Conditions	Comparison
Precipitation	CARC and Field C	CARC and Field C	CARC and Field C	CARC and Field C	CARC and Field C
rPET	Agrimet	Agrimet	Agrimet	Agrimet	Agrimet
Seeding Date	Not Applicable	2012-10-17 (date farmer seeded)	2014-05-02 (date farmer seeded)	2013-04-02 (parallel to sim year 3)	Not Applicable
Harvest Date	Not Applicable	2013-08-07 (date farmer harvested)	2014-08-19 (date farmer harvested)	2013-08-19 (parallel to sim year 3)	Not Applicable
Tower AET	Not Applicable	2013-04-13 to 2013-08-29	2014-05-26 to 2014-09-17	Not Applicable	2014-04-25 to 2014-09-17
VWC	Not Applicable	Field Location C2E.10 2013-04-15 to 2013-12-31	Field Location C2E.10 2014-01-01 to 2014-08-15	Not Applicable	No Data

Ch3-Sup Table 2.4e - Sensitivity analysis scenarios. Parameters that were assessed with sensitivity analysis and summary of rational.

#	Scenario Name	Change to input	Rational for including
1	Primary	No change	Results in the paper are based on this set of model inputs
2	Clay Loam	fine texture van Genuchten parameters	effect from custom ThetaR and ThetaS values in primary scenario
3	Clay	fine texture van Genuchten parameters	effect assuming different texture of fines
4	Loam	fine texture van Genuchten parameters	effect assuming different texture of fines
5	Silty Clay	fine texture van Genuchten parameters	effect assuming different texture of fines
6	Loamy Sand	fine texture van Genuchten parameters	effect assuming different texture of fines
7	Sandy Clay Loam	fine texture van Genuchten parameters	effect assuming different texture of fines
8	Sandy Loam	fine texture van Genuchten parameters	effect assuming different texture of fines
9	Silt	fine texture van Genuchten parameters	effect assuming different texture of fines
10	Silty Clay Loam	fine texture van Genuchten parameters	effect assuming different texture of fines
11	Silt Loam	fine texture van Genuchten parameters	effect assuming different texture of fines
12	Rain 0.5	daily precipitation multiplied by 0.5	effect of dramatically reduced precipitation
13	Rain 0.75	daily precipitation multiplied by 0.75	effect of somewhat reduced precipitation
14	Rain 1.25	daily precipitation multiplied by 1.25	effect of somewhat increased precipitation
15	Rain 1.5	daily precipitation multiplied by 1.5	effect of dramatically increased precipitation
16	Max Root 0.75	max root depth (WW and SG) multiplied by 0.75	effect of somewhat shallower roots
17	Max Root 1.25	max root depth (WW and SG) multiplied by 1.25	effect of somewhat deeper roots
18	Root Rate 0.50	root growth rate multiplied by 0.5	effect of root growth rate half of modeled
19	Root Rate 0.75	root growth rate multiplied by 0.75	effect of root growth rate somewhat less than modeled
20	Root Rate 1.25	root growth rate multiplied by 1.25	effect of root growth rate somewhat more than modeled
21	Root Rate 1.50	root growth rate multiplied by 1.5	effect of root growth rate 1.5 times modeled
22	Root Rate 2.00	root growth rate multiplied by 2	This is the rate reported by Thorup-Kristensen et al. 2009
23	Fallow Coef Set 0.1	fallow coefficient reduced from 0.22 to 0.1	effect of less effective evaporation during fallow periods
24	Fallow Coef Set 0.5	fallow coefficient increased from 0.22 to 0.5	effect of more effective evaporation during fallow periods
25	Crop Coefs Set 0.7	mean crop coef (0.7) for winter and spring crops	effect of both spring and winter crops having same max crop coefficient
26	↓ Crop Coef 0.75	crop and fallow coefficients multiplied by 0.75	effect assuming crop/fallow coefficients are 25% less than calculated
27	↑ Crop Coef 1.25	crop and fallow coefficients multiplied by 1.25	effect assuming crop/fallow coefficients are 25% higher than calculated
28	↓ GDDs 0.75	all GDD values for crop growth multiplied by 0.75	effect of earlier crop growth development
29	↑ GDDs 1.25	all GDD values for crop growth multiplied by 1.25	effect of later crop growth development
30	Spring Seed Late	spring seeding date 2 weeks earlier	effect of earlier spring seeding
31	Spring Seed Early	spring seeding date 2 weeks later	effect of later spring seeding

3. Results

3.1 Soil Water Content & Soil Nitrate



Ch3-Sup Figure 3.1a – Lysimeter NO₃ vs z_f . Lysimeter nitrate-N concentrations (mg/L) on the y axis versus z_f (cm) on the x axis. Green symbols were collected during crop years, black symbols were collected during fallow years. Samples collected post-fallow are represented by a “+” and post crop by a circle. Statistics for linear fit model on the plot are for all data together. Lysimeters are installed at each location immediately above the z_f depth.

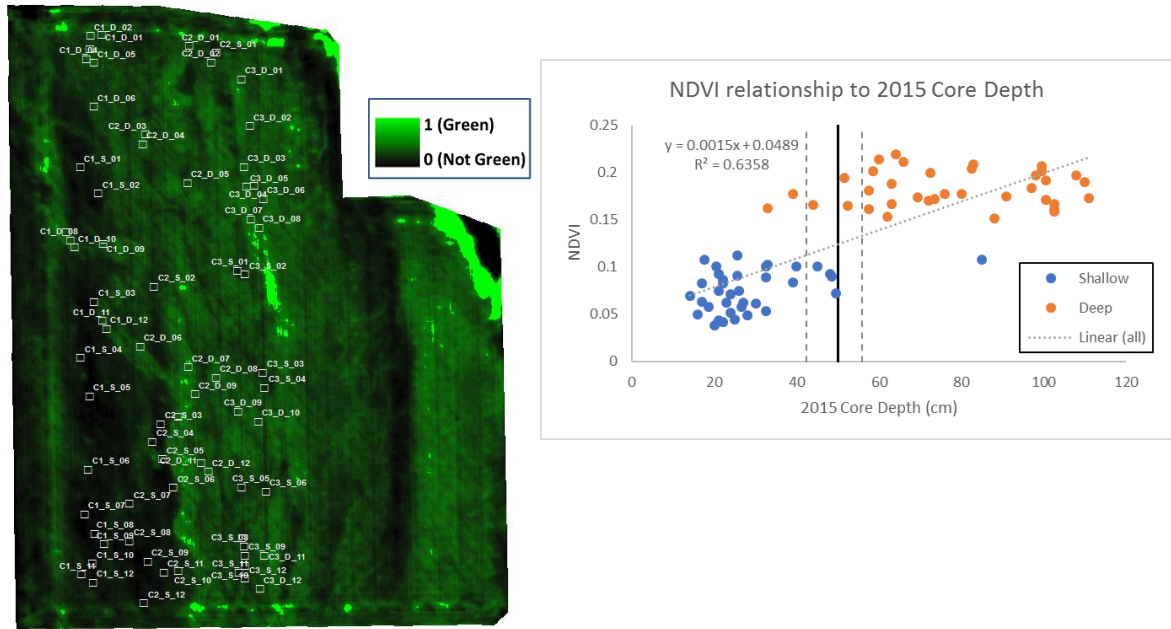
3.2 Spatial Distribution of Soil Thickness

Ch3-Sup Table 3.2a - Soil pit z_f observations. Observed thickness of fine textured soil horizons in pits dug on study Fields B and C. Pit B2W.01 was 142 cm deep and the fine textured soil extended below the bottom of the pit.

Field B				Field C			
Count	Pit ID	Date	z_f (cm)	Count	Pit ID	Date	z_f (cm)
1	B1E.01	8/9/2012	26	1	C1E.01	7/11/2012	104
2	B1E.04	8/9/2012	44	2	C1E.04	8/6/2012	103
3	B1E.07	8/9/2012	48	3	C1E.07	8/6/2012	30
4	B1E.10	8/9/2012	42	4	C1E.10	8/6/2012	43
5	B2W.01	8/9/2012	>142	5	C2E.01	8/7/2012	82
6	B2W.04	8/9/2012	46	6	C2E.04	8/7/2012	48
7	B2W.06	8/9/2012	48	7	C2E.07	8/7/2012	116
8	B2W.07	8/9/2012	97	8	C2E.08	8/7/2012	94
9	B2W.10	8/9/2012	38	9	C2E.08	8/13/2013	72
10	B3E.01	9/8/2012	62	10	C2E.10	8/7/2012	73
11	B3E.03	9/8/2012	105	11	C2E.10	8/13/2013	73
12	B3E.04	9/8/2012	70	12	C2W.01	7/11/2012	44
13	B3E.07	9/8/2012	57	13	C2W.04	8/6/2012	93
14	B3E.10	9/8/2012	41	14	C2W.04	8/13/2013	105
15	B4W.01	9/8/2012	75	15	C2W.06	8/6/2012	55
16	B4W.04	9/8/2012	51	16	C2W.07	8/8/2012	43
17	B4W.07	9/8/2012	99	17	C2W.10	8/6/2012	16
18	B4W.10	9/8/2012	45	18	C3W.01	8/7/2012	92
				19	C3W.01	8/13/2013	105
				20	C3W.04	8/7/2012	100
				21	C3W.04	8/13/2013	90
				22	C3W.06	8/7/2012	22
				23	C3W.07	8/7/2012	125
				24	C3W.10	8/7/2012	103
		Minimum	26			Minimum	16
		Median	48			Median	86
		Maximum	>142			Maximum	125
		Mean	63			Mean	76
		SD	30			SD	31

As a means to evaluate accuracy of z_f values on Field C predicted by NDVI, results are presented here for a 2015 soil core sampling campaign. For the sampling campaign, coring locations were randomly selected within predicted shallow versus deep thickness of fines (z_f) zones, based on NDVI relationship to z_f observed in soil pits ($z_f = \text{NDVI} \cdot 0.0022 - 0.027$; main paper Figure 5). An intermediate depth of 50 cm was designated as the threshold separating shallow from deep z_f with a corresponding NDVI value of 0.137. Field areas with NDVI values between 0.12 (predicted $z_f = 42$ cm) and 0.15 (predicted $z_f = 56$ cm) were excluded from categorization to decrease likelihood of inaccurate categorization.

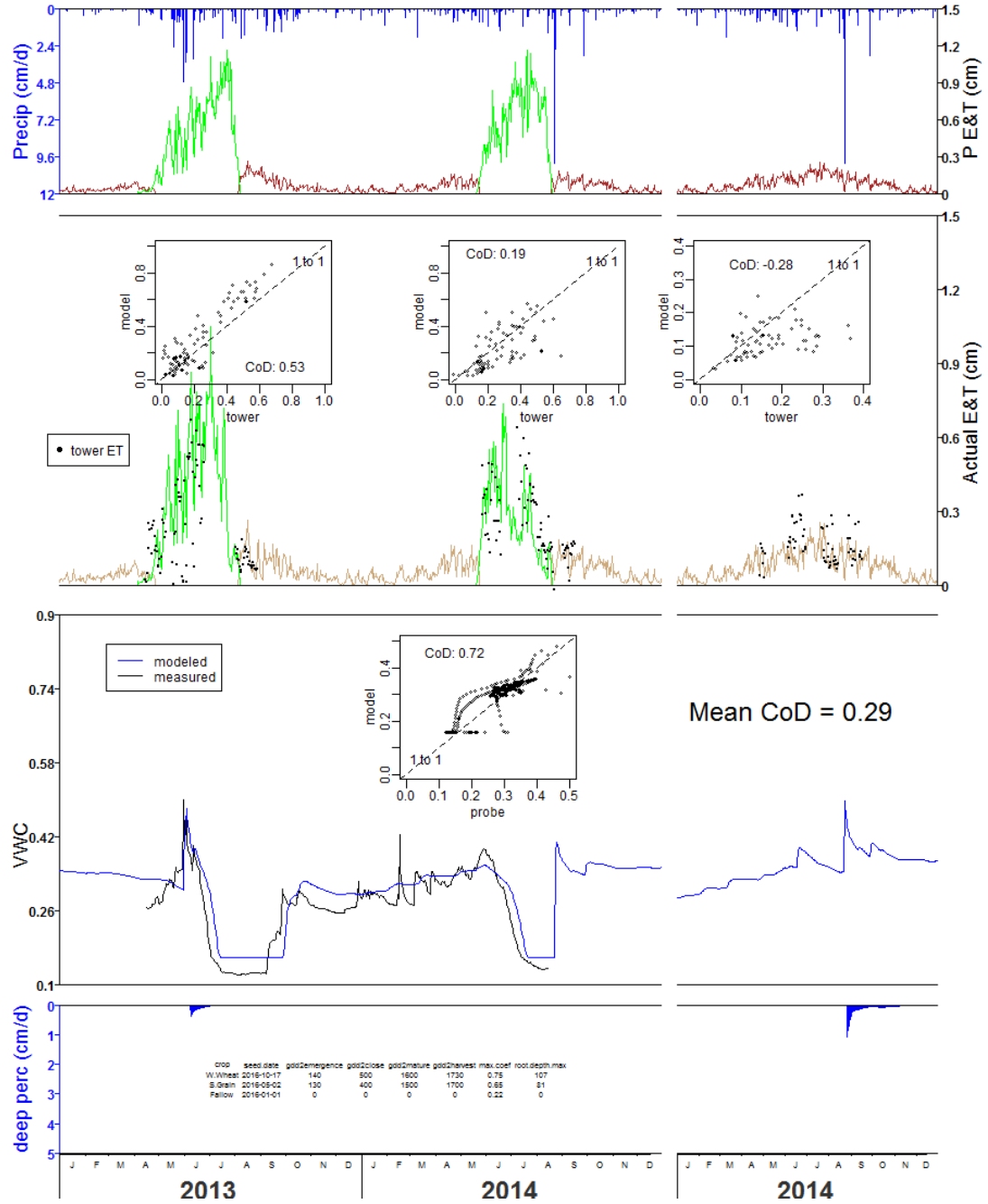
During the field campaign 97% (35/36) of locations predicted to have shallow z_f had core depths less than 50 cm and 92% (33/36) of locations predicted to have deep z_f had core depths greater than 50 cm (Sup Figure 3.2a).



Ch3-Sup Figure 3.2a – Field C NDVI vs core depth. Left panel is NDVI for Field C calculated from National Agricultural Imagery Program (NAIP) aerial image captured on July 24, 2011 when a barley crop was present. White squares are locations of core sample collection using a truck mounted hydraulic probe. Right panel is 2011 NDVI versus 2015 core depths. Core locations predicted to be shallow are blue and those predicted to be deep are orange. The vertical black line is at $z_f = 50$ cm and the dashed lines are at 42 and 56 cm (z_f predicted by NDVI values 0.12 and 0.15 respectively).

3.3 Model Results versus Observations and Sensitivity Modeled results for ET

during winter wheat growth on Field C in 2013 produced a positive coefficient of determination (CoD) value in relation to ET measured by eddy covariance on that field (CoD = 0.53; Sup Figure 3.3a). Modeled results for spring grain on Field C in 2014 also produced a positive CoD value (0.19) with measured values, but modeled ET during fallow on Field C4 in 2014 produced a negative CoD value (-0.28). Modeled volumetric water content produced a positive CoD value (0.72) with measured values on Field C for the 2013-14 years combined. The mean of the four CoD values is 0.29.



Ch3-Sup Figure 3.3a – Field C observations. Field C observations (Sup Table 2.4d) and corresponding model results. Two years on the left are Field C and the year on the right is Field C4. Top panel is precipitation and potential transpiration and evaporation. Second panel is modeled transpiration (green) and evaporation (brown), with tower ET (black dots). Inset xy scatter plots and coefficient of determination (CoD; R^2) values are for each year. The third panel is measured and modeled volumetric water content. Inset xy scatter and CoD is for all daily values. The “mean CoD” in the third panel is simply the mean of the four CoD values. Bottom panel is modeled deep percolation.

Sensitivity Analysis

Results of sensitivity analysis presented in Sup Table 3.3a were manually assessed and are summarized below, first by result parameters and then by input parameters. In general, model output metrics supporting primary conclusions in our work were robust across sensitivity scenarios. The largest deviations in results came from scaling of precipitation and changes in fallow coefficients.

Deep percolation (results)

Mean deep percolation (DP) of 5.9 cm/yr (Sup Table 3.3a A) for the primary scenario was most sensitive to precipitation scaling and the fallow coefficient. Highest modeled DP was from precipitation 1.5 scenario and lowest DP was from the precipitation 0.5 scenario.

The ratio of DP during Crop-Fallow relative to that during Crop-Crop was 2.1 (Sup Table 3.3a D) for the primary scenario and varied from 1.5 to 2.5 across scenarios. Scenarios that notably increased the difference were: 0.5 precipitation, 2x root growth rate, fallow coefficient 0.1, lower GDD for crop development, and earlier spring seeding. Scenarios that notably decreased the difference were: fallow coefficient 0.5 and later spring seeding.

The effect of z_f on DP was such that DP was 3.4x higher with z_f 25 compared to z_f 100 and was 2.2x higher with z_f 50 compared to z_f 100 cm for the primary scenario (Sup Table 3.3a E-F). Scenarios that notably increased effect of z_f on DP include low precipitation, high fallow coefficient, and silt texture. Scenarios that notably decreased effect of z_f on DP include sandy soils and high precipitation.

Precipitation storage efficiency (results)

Precipitation storage efficiency (PSE) ratio for standard- z_f of 0.08, maximum ratio of 0.23, and volume of 9.1 cm for the primary scenario are not notably increased by any scenario, but are dramatically reduced for a few scenarios (Sup Table 3.3a G-I). PSE is the lowest for loamy sand and for the other coarse textured horizons, but is also reduced in low precipitation, low root growth rate, and high fallow coefficient scenarios. It is also reduced for the low GDD crop development scenario, but that is likely the result of earlier winter wheat growth resulting in crop water use before April 1st, which is considered to be within the fallow year, a reduction in PSE that is not representative of water storage difference.

Time primed (results)

Mean time primed for the primary scenario was 38% for z_f 25 and 24% for z_f 100 cm, with a difference of 15% (Sup Table 3.3a K,L,O). Time primed for z_f 25 was somewhat more consistent across scenarios than for z_f 100. Highest time primed

scenarios were for high precipitation and low fallow coefficient. Lowest time primed scenarios were for low precipitation and high fallow coefficient. Thinner soils spending more time primed than thicker soils was consistent across all but 2 scenarios (loamy sand and half root rate). The difference in primed time for thin versus thick soils was higher for the 75% rain and low fallow coefficient scenarios and the difference was lower for coarse textures, 0.5 precipitation, 0.75 root rate, and lower GDD values.

Differences in time primed between Crop-Fallow and Crop-Crop sequences were 16% for z_f 25 and 38% for z_f 100 for the primary scenario (Sup Table 3.3a M,N). Scenarios that notably increased the difference were: high precipitation, low fallow coefficient, and low crop coefficients; low max root depth and slow root growth increased the difference only in thicker soils. Scenarios that notably decreased the difference were: low precipitation and high fallow coefficient.

Texture of the z_f horizon (inputs)

- Clay loam, clay, loam, and silty clay (scenarios 2-5) produced results roughly similar to the primary model scenario across all metrics.
- Coarser textured soils (loamy sand, sandy clay loam, and sandy loam; scenarios 6-8) produced higher deep percolation (DP) rates than the primary scenario but ratios of DP in Crop-Fallow versus Crop-Crop years were similar to the primary scenario. Coarse texture scenarios had less pronounced differences in DP across z_f than the primary scenario. Coarse textured soils had lower precipitation storage efficiency (PSE) than the primary scenario, and loamy sand produced the lowest PSE of any scenario. Loamy sand thick soils spent far more time primed than other textures. The largest differences in time primed between Crop-Fallow and Crop-Crop sequences were in thick z_f for coarse texture scenarios. The primary scenario higher time primed for thin (z_f 25) versus thick (z_f 100) soils was reduced for coarse textured soils and reversed for loamy sand where thicker soils spent more time primed.
- Silt textures (silt, silty clay loam, and silt loam; scenarios 9-11) produced lower deep percolation values than the primary scenario but ratios of DP in Crop-Fallow versus Crop-Crop years were similar to the primary scenario. Silt texture scenarios had more pronounced differences in DP across z_f than the primary scenario. Silt textured scenarios had PSE similar to the primary scenario. Silt textured scenarios spent somewhat more time primed than the primary scenario, but differences in time primed between 2-yr sequences and z_f were similar to the primary scenario.

Precipitation scaling (inputs)

- Scenarios where precipitation was scaled up and down (scenarios 12-15) produced some of the most dramatic departures from the primary scenario results.
- As precipitation was scaled down (scenarios 12-13), DP was reduced and approached zero when precipitation was half of the primary scenario but ratios of DP in Crop-Fallow versus Crop-Crop years similar to the primary scenario. The effect of z_f on deep percolation was much higher with lower precipitation rates than for the primary model scenario and the half precipitation rate produced the most dramatic z_f effect on DP. While PSE as a ratio was roughly similar for low precipitation as for the primary scenario, the volume of water stored (cm) was far lower with lower precipitation. Time primed was far lower with reduced precipitation, especially for thick z_f soils, which spent zero time primed. Differences in time primed between Crop-Fallow and Crop-Crop sequences were much less pronounced with low precipitation than for the primary scenario. Differences in time primed for thin (z_f 25) versus thick (z_f 100) surface horizon approached zero with half precipitation but at 75% precipitation the difference was larger than for the primary scenario.
- As precipitation was scaled up (scenarios 14-15) DP increased and the 1.5 precipitation scenario produced the highest DP of all scenarios. The ratios of DP in Crop-Fallow versus Crop-Crop years were similar to the primary scenario. The effect of z_f on deep percolation was lower with higher precipitation rates than for the primary model scenario. PSE both as a ratio and as volume was lower for high precipitation than for the primary scenario. Time primed was higher with higher precipitation than for the primary scenario. Differences in time primed between Crop-Fallow and Crop-Crop sequences were more pronounced with high precipitation than for the primary scenario. Differences in time primed for thin (z_f 25) versus thick (z_f 100) surface horizon were less pronounced with higher precipitation than for the primary scenario.

Root rate and depth (inputs)

- Scenarios with maximum root depth reduced and half growth rate produced notable differences in results, while other root related scenarios had minimal effect on results.
- DP rates and ratio of DP in Crop-Fallow versus Crop-Crop years was similar to the primary scenario across root scenarios. In the scenario where root growth rate was reduced by half, the effect of z_f on DP was less

pronounced. PSE in the reduced maximum depth and the half growth rate scenarios was lower than the primary scenario. Time z_f 100 soils spent primed for the half root rate scenario was 2x the primary scenario.

- Differences in time primed for thin (z_f 25) versus thick (z_f 100) surface horizon were less pronounced than the primary scenarios for the lower maximum root depth and for the lower root rate scenarios, and with the half root rate scenario thicker soils spent more time primed than thin soils .

Fallow coefficient (inputs)

- Scenarios with high and low fallow coefficient values produced some of the most extreme departures from primary model scenario results.
- DP increased with a smaller fallow coefficient and decreased with larger fallow coefficient. DP difference between Crop-Fallow versus Crop-Crop years was increased with the low fallow coefficient and reduced with the high fallow coefficient. The effect of z_f on DP was decreased with a low fallow coefficient and increased with a high fallow coefficient. PSE increased with a low fallow coefficient and decreased with a higher fallow coefficient. Time primed increased with the low fallow coefficient and decreased with the high fallow coefficient. Differences in time primed between Crop-Fallow and Crop-Crop sequences were much more pronounced with a low fallow coefficient and much less pronounced with a high fallow coefficient than for the primary scenario. Differences in time primed for thin (z_f 25) versus thick (z_f 100) surface horizon were more pronounced with the low fallow coefficient and less pronounced with the high fallow coefficient than for the primary scenario.

Crop coefficients (inputs)

- The scenario with spring and winter grain crop coefficients set to a mean value of 0.7 produced results almost identical to the primary scenario.
- Smaller crop coefficients increased DP while larger crop coefficients decreased DP but the ratio of DP in Crop-Fallow versus Crop-Crop was similar to the primary scenario. The effect of z_f on DP was decreased with lower crop coefficients and increased with higher crop coefficients. PSE increased with lower crop coefficients and decreased with higher crop coefficients. Time primed increased with lower crop coefficients and decreased with larger crop coefficients. Differences in time primed between Crop-Fallow and Crop-Crop sequences were much more pronounced with lower crop coefficients and somewhat less pronounced with a high fallow coefficient than for the primary scenario. Differences in

time primed for a thin ($z_f 25$) versus thick ($z_f 100$) surface horizon were not notably different than for the primary scenario.

GDD scaling (inputs)

- Scaling GDD values for crop growth stage development up and down by 25% did not have a large effect on DP. Smaller GDD slightly increased the difference in DP between Crop-Fallow versus Crop-Crop while larger GDD slightly decreased the difference relative to the primary scenario. The effect of z_f on DP was decreased with lower GDD values and increased with higher GDD values. PSE decreased with lower GDD values and increased with higher GDD values. Scaling GDD values did not affect percent time primed for $z_f 25$, but in $z_f 100$ soils, time primed did increase for lower GDD values and decrease for larger GDD values. Differences in time primed between Crop-Fallow and Crop-Crop sequences were not affected in $z_f 25$ soils or in $z_f 100$ soils for increased GDD values, but time primed did increase in $z_f 100$ soils for lower GDD values relative to the primary scenario. Differences in time primed for thin ($z_f 25$) versus thick ($z_f 100$) surface horizon were less pronounced for small GDD values and slightly more pronounced for higher GDD values than for the primary scenario.

Spring seeding (inputs)

- Later spring seeding slightly increased DP, while earlier spring seeding slightly decreased DP. Later seeding resulted in less punctuated differences in DP between Crop-Fallow versus Crop-Crop while earlier seeding produced more punctuated differences relative to the primary scenario. None of the other results metrics were notably affected by spring seeding date.

Ch3-Sup Table 3.3a - Sensitivity analysis results. Sensitivity scenarios 1-31 are described in Table 2.4e. The first group of columns indicate what model inputs were used for each scenario; a blank cell indicates use of the primary model value. Remaining columns are 14-yr model reporting period mean annual values for comparison of: deep percolation (DP) related to sequence effect (A-D), DP related to z_f (E-F), precipitation storage efficiency (PSE; G-I), and % time above field capacity (J-M). Columns A-D and G are z_f weighted means assuming z_f distribution standard- z_f (mean 50; StDev 30 cm). (A) is mean DP across sequences and can be considered a grand mean across space and time for the with-fallow rotation. (B) is mean annual DP for the Crop-Crop sequence. (C) is mean annual DP for the Crop-Fallow sequence. (D) is the ratio of DP for Crop-Fallow over Crop-Crop. (E) is the ratio of mean annual DP for z_f 25 over DP for z_f 100. (F) is the ratio of mean annual DP for z_f 50 over DP for z_f 100. (G) is the z_f weighted PSE ratio. (H) is the maximum 14-yr mean PSE ratio and (I) is the maximum PSE as a volume (these maximum values are effectively PSE for the thickest soils). (J) is volumetric water content at field capacity for the fine textured horizon. (K) is the mean time primed for z_f 25 across sequences. (L) is the mean time primed for z_f 100 across sequences. (M) is the % time the Crop-Fallow sequence spends above field capacity (primed) minus the % time the Crop-Crop sequence spends primed assuming z_f 25 cm. (N) is parallel to the previous, assuming z_f 100 cm. (O) is the % time primed for z_f 25 minus % time primed for z_f 100 across sequences.

#	Scenario Name	Sensitivity Inputs										DP Comp across Seq				DP Comp		PSE			% time above field capacity						
		Texture for van Gennuthen	Rain Scaler	Root Max Scaler	Root Growth Rate	Fallow Coef	WW coef	SG coef	GDD scaler	Seed Date	mean of 2-yr sequences CC,CF,FC (cm/yr)	CC (cm/yr)	CF (cm/yr)	CF/CC (ratio)	mean of sequences zf25/zf100 (ratio)	mean of sequences zf50/zf100 (ratio)	Zf wght (ratio)	Max Mean (ratio)	Max Mean (cm/yr)	Field Cap. (ratio)	zf 25 (%)	zf 100 (%)	zf 25; CF - CC (%)	zf 100; CF - CC (%)	mean of sequences zf 25 - Zf 100 (%)		
1	Primary	Cust	1	1	0.67	0.22	0.75	0.65	1.00	17-Apr	5.9	4.3	9.1	2.1	3.4	2.2	0.08	0.23	9.1	0.33	38	24	16	38	15		
2	Clay Loam	Clay									6	4.5	9.2	2.0	3.2	2.1	0.08	0.22	8.7	0.28	39	27	15	46	12		
3	Clay	Clay									6.3	5	9.6	1.9	2.9	2	0.06	0.19	7.8	0.33	38	25	13	41	13		
4	Loam	Loam									5.9	4.9	8.7	1.8	3.3	2.1	0.06	0.20	8.3	0.23	43	30	14	49	13		
5	Silty Clay	SiCl									6.3	5.1	9.5	1.9	3.2	2.1	0.07	0.21	8.6	0.34	37	25	15	41	13		
6	Loamy Sand	LoSa									9	7.4	13.8	1.9	2.5	1.3	0.02	0.06	2.1	0.14	41	55	14	54	-14		
7	Sandy Clay Loam	SaCL									7	5.3	10.9	2.0	2.5	1.7	0.06	0.17	6.8	0.25	36	31	14	52	5		
8	Sandy Loam	SaLo									6.9	5.4	10.6	2.0	2.4	1.7	0.05	0.16	6.2	0.20	38	33	13	54	5		
9	Silt	Silt									4.1	3.1	5.8	1.9	6.6	3.4	0.08	0.21	9.1	0.19	47	30	17	40	17		
10	Silty Clay Loam	SiCL									5	3.9	7.2	1.8	4.6	2.7	0.08	0.23	9.5	0.27	43	25	16	40	19		
11	Silt Loam	SiLo									4.5	3.5	6.4	1.9	5.4	2.9	0.07	0.21	9.0	0.20	47	33	15	42	15		
12	Rain 0.5		0.5								0.4	0.2	0.6	2.5	75.9	10.4	0.10	0.15	3.1	0.33	5	0	7	0	5		
13	Rain 0.75		0.75								2.2	1.6	3.3	2.0	11.4	5.5	0.10	0.22	6.7	0.33	28	5	12	9	23		
14	Rain 1.25		1.25								10.8	8.6	16.7	1.9	2.3	1.7	0.07	0.18	8.4	0.33	51	43	23	60	8		
15	Rain 1.5		1.5								17.4	14.4	25.3	1.8	1.7	1.4	0.04	0.12	6.5	0.33	67	53	25	56	14		
16	Max Root 0.75			0.75							5.9	4.4	9	2.0	2.8	1.8	0.07	0.18	7.2	0.33	38	31	16	52	8		
17	Max Root 1.25			1.25							5.7	4.4	8.6	2.0	3.6	2.3	0.09	0.24	9.8	0.33	38	23	16	36	16		
18	Root Rate 0.50				0.33						6.4	4.9	9.8	2.0	2.1	1.3	0.05	0.11	4.6	0.33	39	50	15	51	-11		
19	Root Rate 0.75				0.50						5.9	4.5	9.1	2.0	2.9	1.8	0.07	0.19	7.5	0.33	38	32	16	48	7		
20	Root Rate 1.25				0.83						5.7	4.3	8.9	2.0	3.6	2.3	0.08	0.24	9.6	0.33	39	22	16	36	17		
21	Root Rate 1.50				1.00						5.7	4.1	9.1	2.2	3.7	2.3	0.08	0.24	9.8	0.33	39	21	16	37	18		
22	Root Rate 2.00				1.33						5.7	4.1	9.1	2.2	3.7	2.4	0.08	0.25	10.0	0.33	40	21	15	37	19		
23	Fallow Coef Set 0.1					0.1					11.6	7.8	19.6	2.5	2.1	1.6	0.11	0.27	10.0	0.33	67	43	44	66	24		
24	Fallow Coef Set 0.5					0.5					2.4	2.1	3.1	1.5	9.7	4.5	0.05	0.14	5.7	0.33	14	5	6	9	10		
25	Crop Coefs Set 0.7						0.70	0.70			6	4.6	9.2	2.0	3.4	2.2	0.08	0.23	9.1	0.33	38	24	16	38	15		
26	↓ Crop Coef 0.75					0.17	0.56	0.49			7.7	5.6	12.4	2.2	2.8	1.9	0.10	0.25	9.8	0.33	48	32	23	51	16		
27	↑ Crop Coef 1.25					0.28	0.94	0.81			4.5	3.5	6.6	1.9	4.3	2.5	0.07	0.21	8.4	0.33	32	19	12	36	13		
28	↓ GDDs 0.75							0.75			5.9	4.2	9.6	2.3	2.7	1.8	0.06	0.17	6.8	0.33	38	31	16	49	7		
29	↑ GDDs 1.25							1.25			5.7	4.3	8.4	1.9	4.1	2.4	0.10	0.27	10.7	0.33	39	20	16	40	19		
30	Spring Seed Late								1-May		6.2	5.4	9.2	1.7	3.5	2.2	0.08	0.22	9.0	0.33	39	26	14	43	13		
31	Spring Seed Early								3-Apr		5.6	3.7	9.1	2.4	3.3	2.1	0.08	0.22	9.0	0.33	38	24	17	38	14		
	mean										6.3	4.8	9.6	2.0	6.1	2.5	0.07	0.20	8.0	0.30	39	28	16	42	12		
	stdev										3.0	2.4	4.6	0.2	13.1	1.7	0.02	0.05	2.0	0.05	11	12	6	14	8		
	min										0.4	0.2	0.6	1.5	1.5	1.3	0.02	0.06	2.1	0.14	5	0	6	0	-14		
	max										17.4	14.4	25.3	2.5	75.9	10.4	0.11	0.27	10.7	0.34	67	55	44	66	24		

3.4 Precipitation Partitioning The 2010 and 2011 crop years both had ~48 cm of precipitation, but DP was 1.5 to >10 times higher in 2011 depending on z_f (Sup Figure 3.4b-d). With a z_f value of 50 cm, modeled DP averaged over the three with-fallow rotational sequences was 4.6 cm yr⁻¹ in 2010 and 24.4 cm yr⁻¹ in 2011 (Sup Figure 3.4c). While 2010 had three months with outlier high precipitation, these all occurred after peak ET (July) and no month had more than 10 cm of precipitation (Main Figure 3). The abnormally large amount of precipitation late in the 2010 growing season resulted in wet soils at the start of the 2011 crop year, followed by 17.1 cm of precipitation in May 2011, which was the highest monthly rate for the 15-yr Agrimet data period and occurred before peak-seasonal ET rates.

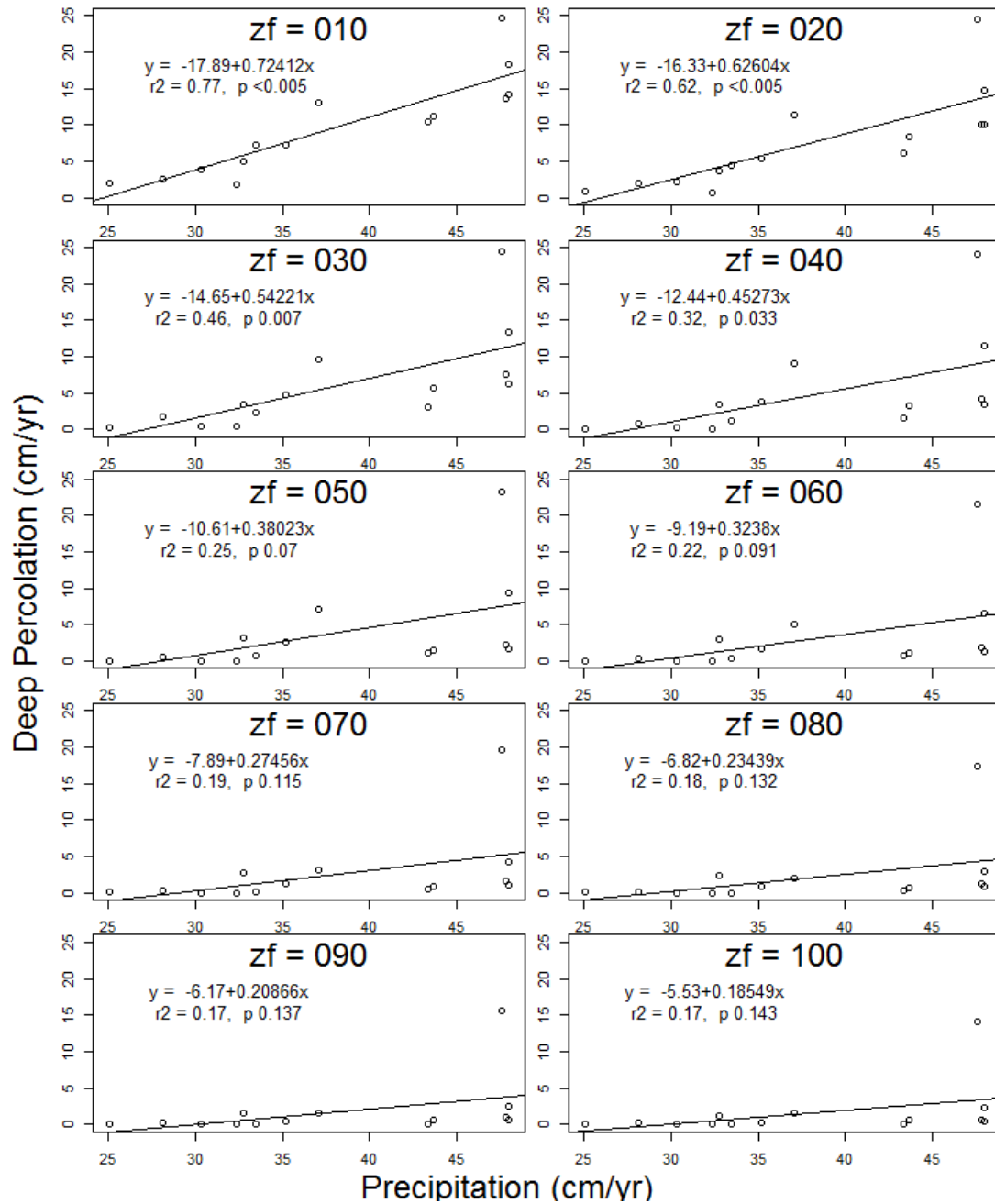
The 2013 and 2014 crop years also both had 48 cm of precipitation but the simulated DP (z_f of 50 cm) averaged over the three with-fallow rotational sequences was 3.3 cm in 2013 and 12 cm in 2014. No month in 2013 had precipitation high enough to be classified as an outlier, but similar to 2010, there were multiple months with above normal precipitation after July. Soils were relatively wet at the start of the 2014 crop year, but below normal precipitation in April and May of 2014 resulted in relatively low DP rates. While the majority of DP in the average year occurs in April-June, the highest DP in 2014 occurred when 11.0 cm of precipitation fell on 23 August, producing the highest daily precipitation and the second highest monthly precipitation for the 15-yr Agrimet data period. For intermediate soil thickness (z_f = 50 cm), 36% of DP for the 14-yr model reporting period (for the mean of the three with-fallow rotational sequences)

occurred in 2011 and 18% occurred in 2014 for a combined 54% occurring in two of 14 years.

High DP rates during intense precipitation in 2011 and 2014 were compounded under the Crop-Fallow sequence. Specifically, fields which were in the Crop-Fallow sequence in 2014 remained primed with soil water throughout the summer resulting in far higher DP losses with the intense August precipitation than for either cropped 2-yr sequence (2014 annual DP: 21 cm for Crop-Fallow versus 7.4 and 7.5 cm; $z_f = 50$ cm; Sup Figure 3.4c). A similar result from plant growth suppression was seen in 2011 where fields in the Crop-Fallow sequence had higher DP rates (28.1 cm) than either cropped 2-yr sequence (21.4 and 23.6 cm); these examples demonstrate the amplification of DP from suppression of plant growth during the fallow year.

More nuanced than differences between crop and fallow years are precipitation partitioning differences between cropped 2-yr sequence years, where effects from 1) antecedent wetness from fallow in Fallow-Crop, and 2) later timing of transpiration onset during Crop-Crop can offset one another. In 2011, the later onset of transpiration was the more dominant of the two drivers and the Crop-Crop sequence had higher DP (23.6 cm) than the Fallow-Crop sequence (21.4 cm), a phenomenon also occurring in 2003, 2007, and 2015 ($z_f = 50$ cm; Sup Figure 3.4c). In 2004, however, the influence of wet soil conditions following fallow was more influential and DP was higher in Fallow-Crop (1.1 cm) than in Crop-Crop (0.1 cm).

DP versus Precip



Ch3-Sup Figure 3.4a - DP vs Precipitation. Annual modeled deep percolation versus annual precipitation for z_f values 10 to 100. Statistics on plots are for linear regression.

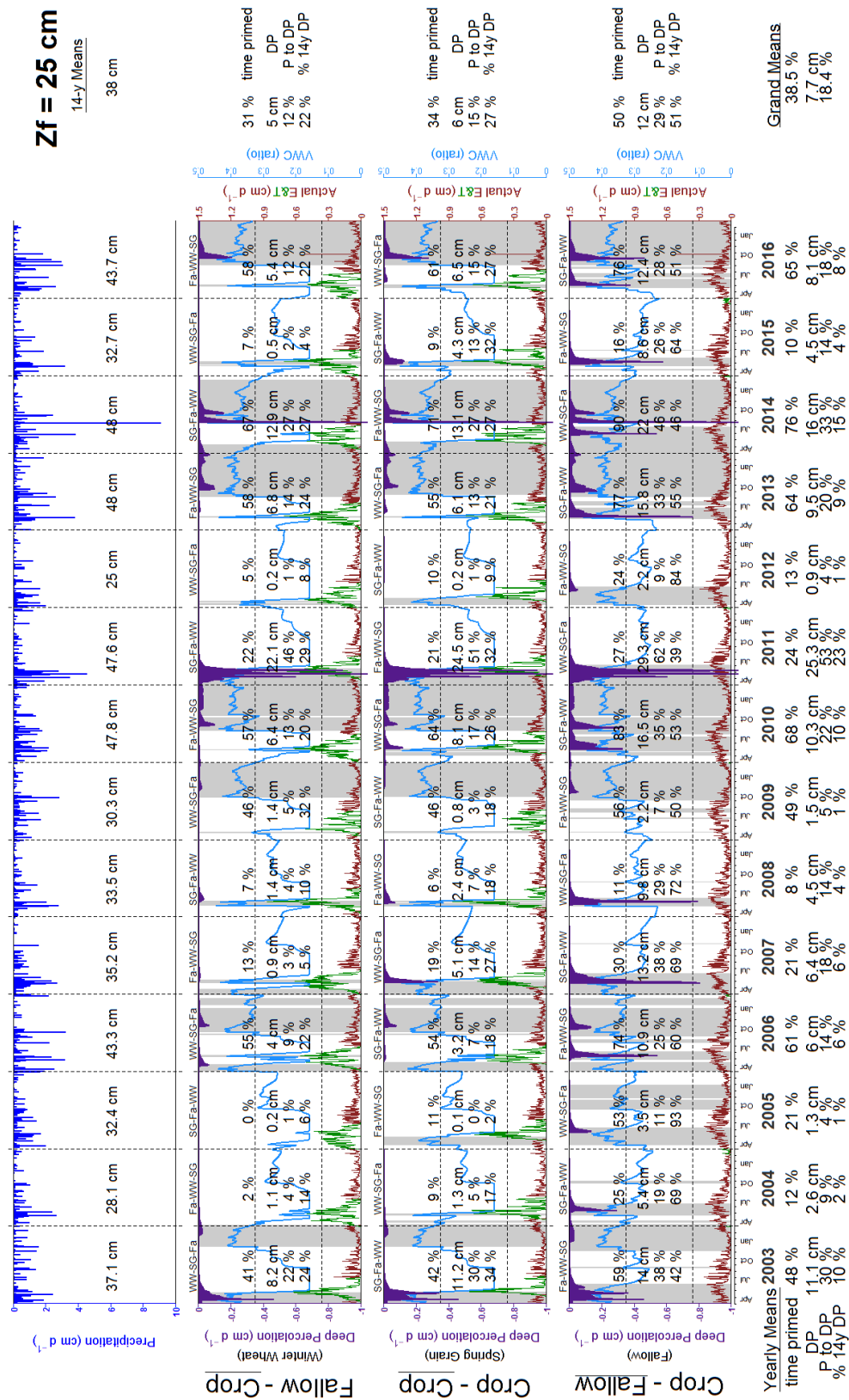
Ch3-Sup Table 3.4a – PSE summary

	Minimum	Maximum	Range
PSE (cm yr⁻¹)	-0.1	9.1	9.2
PSE (ratio)	0.00	0.23	0.23

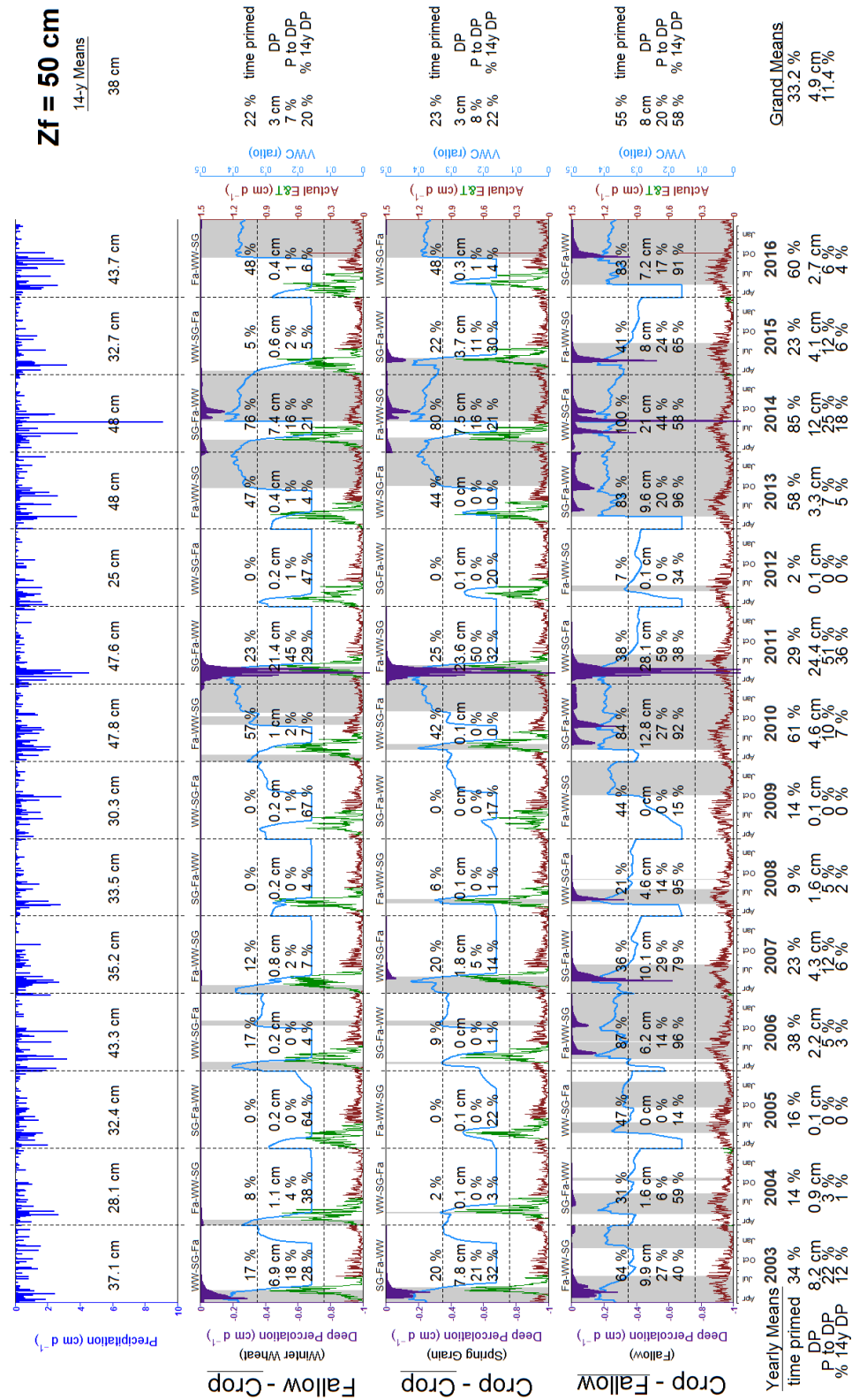
Timeseries of simulation results

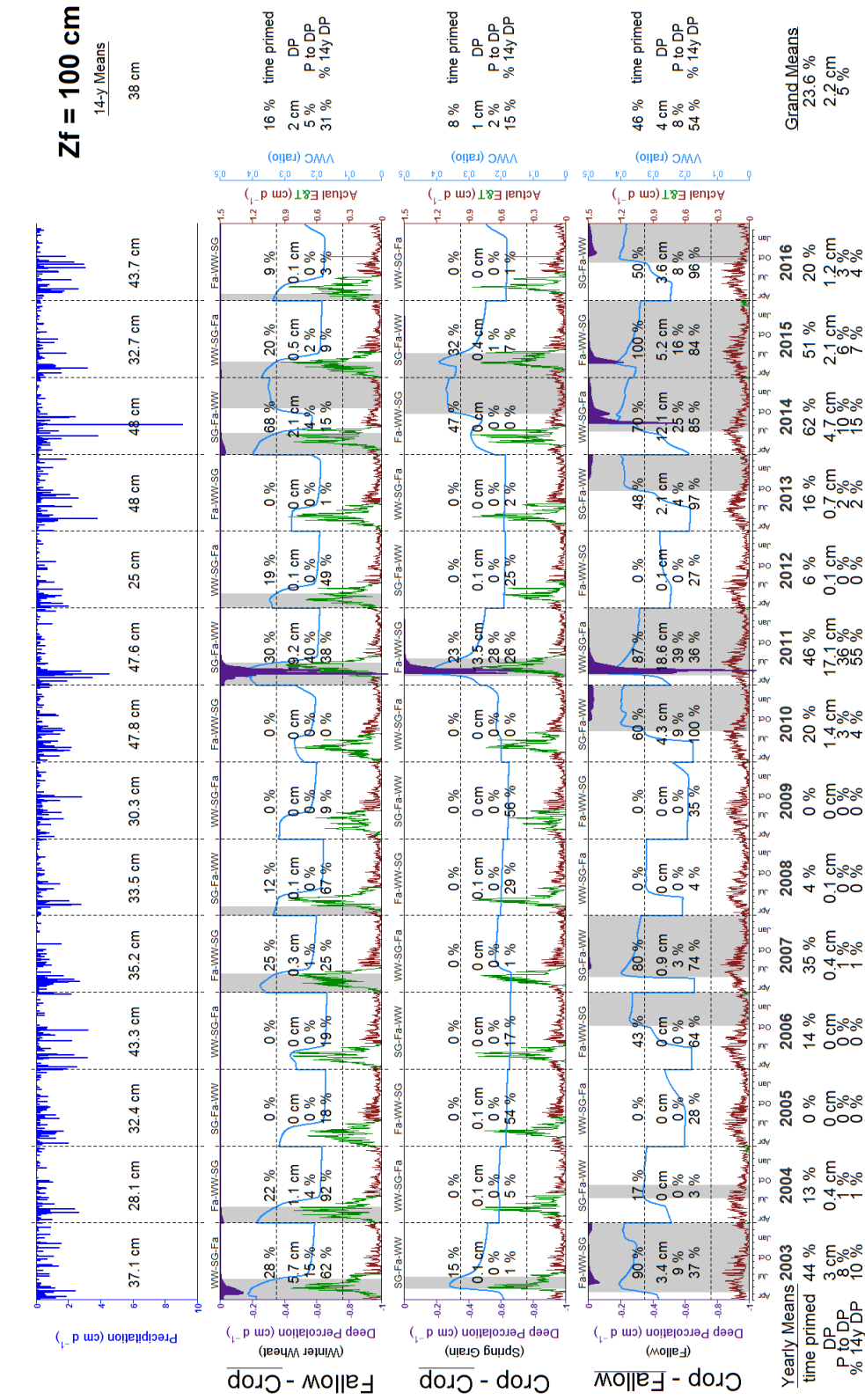
Daily timeseries data for z_f 25,50, and 100 are presented in Sup Figures 3.4b-d. These plots have parallel configuration where the top panel is daily precipitation for the 14-yr model reporting period with annual precipitation values within the panel for each year. Panels 2-4 are results for the three with-fallow rotational sequences organized by 2-yr sequence. The rotational sequence that each panel year is associated with is indicated at the top of the panel (ex: WW-SG-Fa). The second panel is modeled values for the Fallow-Crop sequence years including: modeled DP (purple corresponding to left axis), modeled VWC (blue corresponding to second right axis), modeled evaporation (brown) and modeled transpiration (green) corresponding to the right axis. The top number printed within each panel year is the percent time soils spent primed that year, the second number is modeled DP for that year, the third number is the percent of precipitation lost to DP that year, the fourth number is the percent of 14-yr DP for that 2-yr sequence that was lost that year. Mean values and labels for these values are in the right margin of the plot. The third panel is modeled results for the Crop-Crop sequence year with layout parallel to the second panel. The fourth panel is modeled results for the Crop-Fallow sequence year with layout parallel to the second panel. Values in the bottom plot margin are annual mean values across sequences for: percent time primed, annual DP, percent annual precipitation lost to DP, percent of 14-yr DP lost that year. Values in the bottom right are grand means across sequences across the 14-yr period.

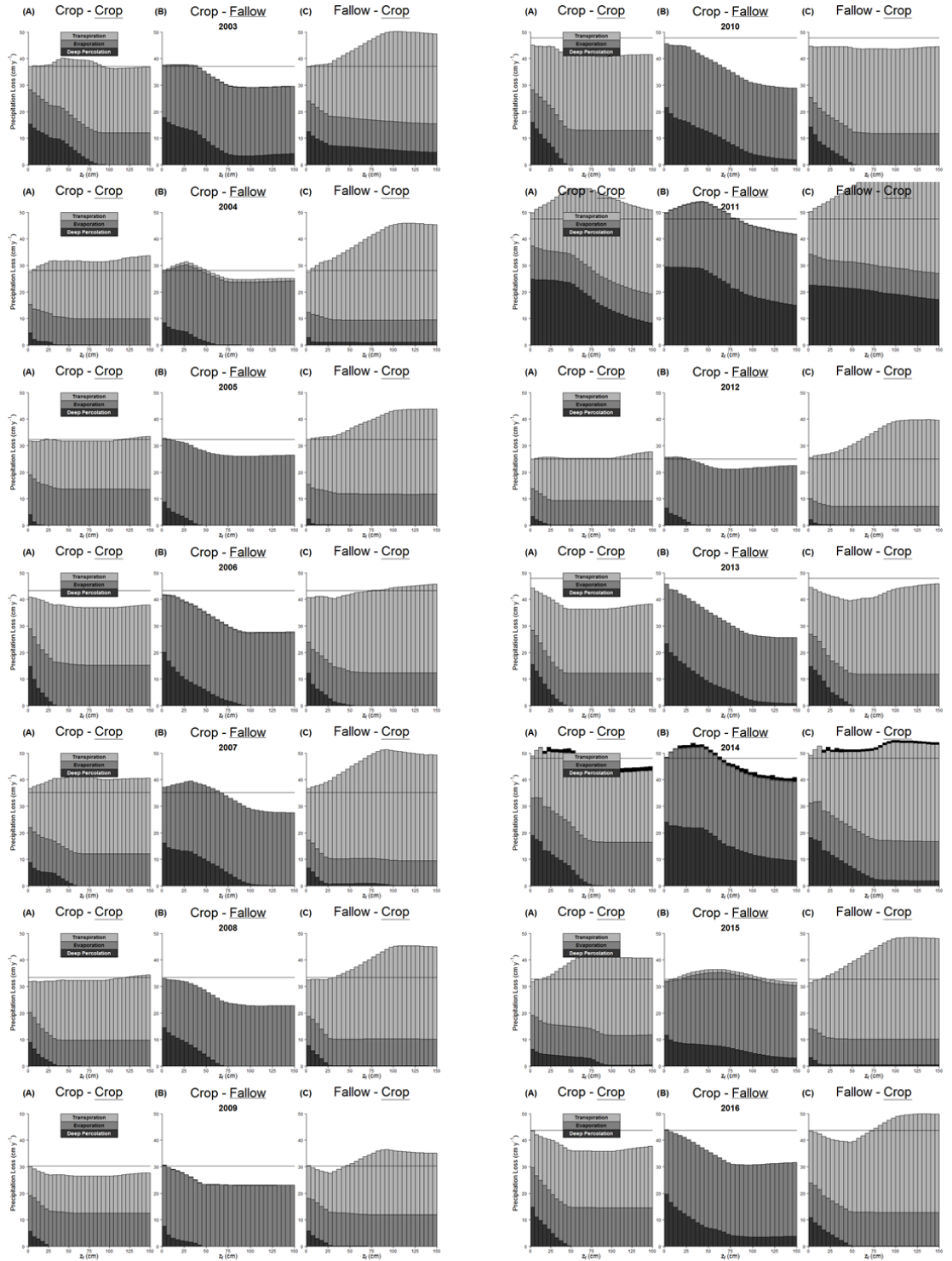
Ch3-Sup Figure 3.4b - Daily timeseries z_f 25



Ch3-Sup Figure 3.4c - Daily timeseries z_f 50







Ch3-Sup Figure 3.4e - Partitioning by year. Precipitation partitioning for each year (parallel to 14-yr mean partitioning results in Main Figure 6); years 2003-09 on left; 2010-16 on right.

Deep percolation and leaching relationships to z_f (polynomial fits for main Figure 7).

DP values produced by these polynomial equations are in units of cm per day.

Equations take the form of: $DP = \text{Coef1} + \text{Coef2} * z_f + \text{Coef3} * z_f^2 + \text{Coef4} * z_f^3$.

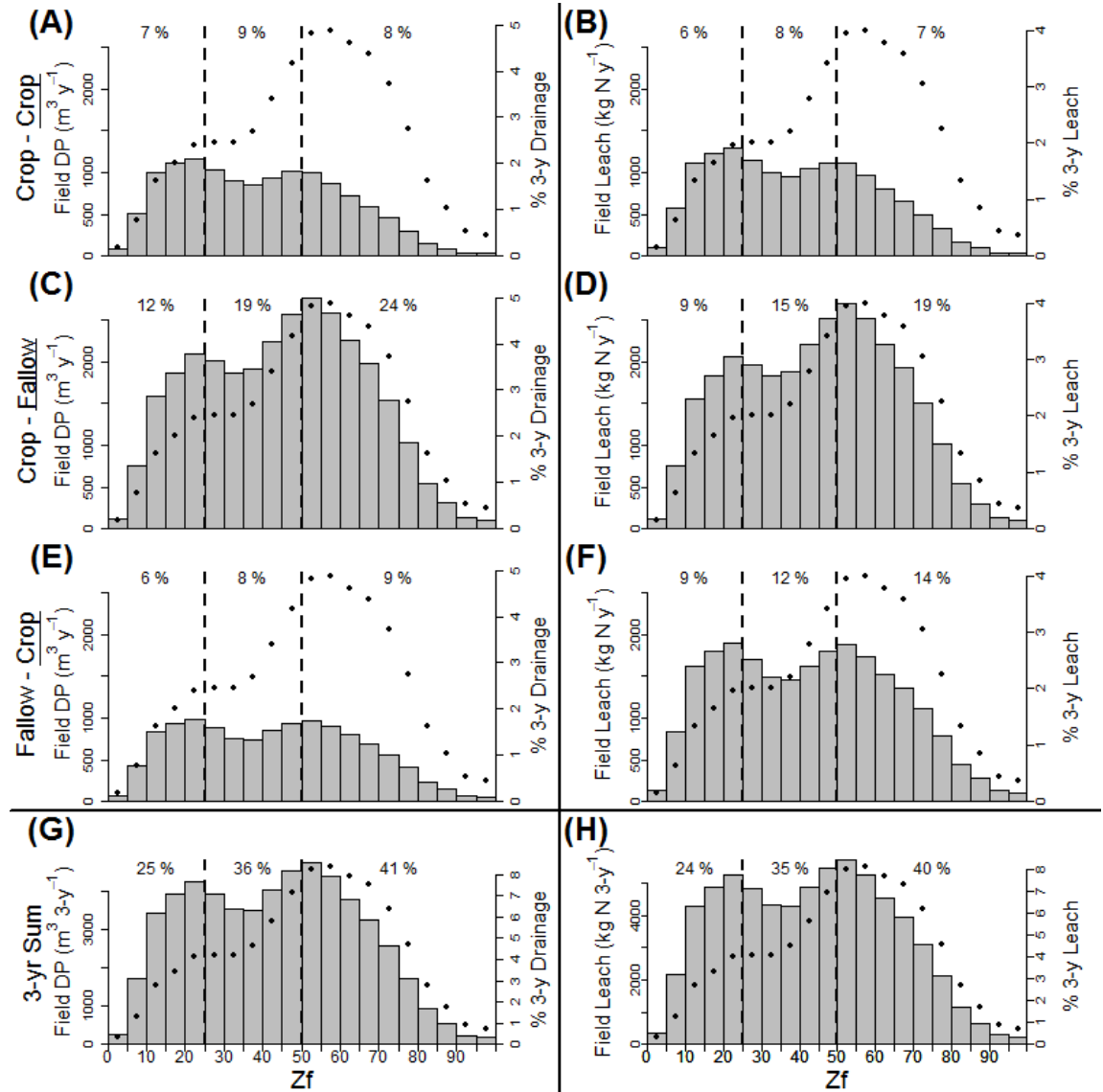
Leaching polynomial equations are parallel to those for DP and are in units of kg-N per day. Values produced by these equations can be multiplied by 365 to get annual values.

Ch3-Sup Table 3.4b – DP & leaching polynomial coefficients

Variable	2-yr Sequence	Figure	Coef1	Coef2	Coef3	Coef4
DP	Crop-Crop	7A	0.033365	-0.00079	6.92E-06	-2.05E-08
	Fallow-Crop		0.028189	-0.0007	7.02E-06	-2.30E-08
	Crop-Fallow		0.04558	-0.00056	2.08E-06	-6.55E-11
Leaching	Crop-Crop	7C	0.037036	-0.00088	7.68E-06	-2.28E-08
	Fallow-Crop		0.054686	-0.00135	1.36E-05	-4.46E-08
	Crop-Fallow		0.044668	-0.00055	2.04E-06	-6.42E-11

Variable	Rotation	Figure	Coef1	Coef2	Coef3	Coef4
DP	With-Fallow	7B	0.035711	-0.00068	5.34E-06	-1.45E-08
	Without-Fallow		0.03129	-0.00076	6.74E-06	-2.04E-08
Leaching	With-Fallow	7D	0.045463	-0.00093	7.78E-06	-2.25E-08
	Without-Fallow		0.034732	-0.00084	7.48E-06	-2.26E-08

3.6 Scaling Simulations to Fields and Landform



Ch3-Sup Figure 3.6a – Field scale DP & leaching. (A,C,E) Mean DP volume for the full field area by z_f category, plotted separately for each 2-yr sequence. Each bar is the mean annual DP of three with-fallow rotational sequences, for the 14-yr model reporting period. Vertical dashed lines separate 0-25, 25-50, and 50-100 cm z_f ranges. Values at the top of the plots are the percent of the 3-yr total field DP attributed to each 2-yr sequence for each depth range. (B,D,F) Mean nitrate-N leaching mass for the full field area, configured parallel to panels for DP. (G) The sum of DP volume for the three 2-yr sequences by z_f category. (H) The sum of nitrate-N leaching mass for the three 2-yr sequences by z_f category. Black dots in each panel show the relative distribution of z_f of Field C (bar heights in Figure 5C).

4. Discussion

4.3 Fallow Expands Hot Moments and Hot Spots While higher rates of deep percolation during Crop-Fallow years than cropped years are relatively consistent, differences between cropped 2-yr sequence years are more nuanced, where effects from 1) antecedent wetness, and 2) timing of transpiration onset can offset one another. Relative to Crop-Crop, the Fallow-Crop sequence year tends to have relatively higher antecedent wetness because it follows fallow, but this can be countered by a relatively early start of crop growth in the spring due to fall seeding of the winter wheat crop (Sup Figure 3.4c). Conversely, the Crop-Crop sequence year tends to have relatively lower antecedent wetness because it follows crop, but this can be countered by a relatively late start of crop growth in the spring with spring planted grain.

4.5 Emergent Landscape-Scale Behavior The Porter catchment is more dominated by thinner z_f Judith soil series and the Kolin catchment is more dominated by the thicker z_f Danvers series. Field B is within the Porter catchment. A majority of soil pits in Field B have descriptions aligned with Judith series. Field C has thicker mean z_f values and approximately half of pits in Field C have descriptions aligned with the Danvers series. In addition to z_f values, alignment between pits and soil series descriptions was assessed based on presence of clay accumulation at depth (t designation in horizon description). Clay accumulation at depth is absent in the Judith series and present in the Danvers series.

Data and Code

All data and code necessary for the analysis in this manuscript is available as a *resource* on CUAHSI HydroShare. A link to the current resource is provided below and access can be granted by the author upon request. Once the peer review process is complete for the associated manuscript, a finalized version of the resource will be created along with a DOI to accompany the published manuscript.

Sigler, W. A. (2020). Cultivated soil water dynamics with many Hydrus 1D simulations using R, HydroShare,

<http://www.hydroshare.org/resource/32c0e2ca9fbd4bd882efc95fe25de8cc>

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CHAPTER FOUR

DRIVERS OF DENITRIFICATION ACROSS A SEMIARID AGROECOSYSTEM
REVEALED BY NITRATE ISOTOPIC PATTERNSContribution of Authors and Co-Authors

Manuscript in Chapter 4

Author: W. Adam Sigler

Contributions: PI on project, designed the study, collected data, trained technicians to collect data, conducted the analysis, wrote the manuscript.

Co-Author: Stephanie A. Ewing

Contributions: Lead PI on project, facilitated involvement of Dr. Wankel, made significant contributions to design of the study, facilitated sample analysis, provided extensive mentorship on isotopic biogeochemistry, provided mentorship for framing the manuscript, conducted extensive editing on the manuscript.

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Contributions: Conducted nitrate isotopic analysis, provided input for framing the paper, edited the manuscript.

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Contributions: PI on project, contributed to study design, provided input for framing the paper, provided feedback and review of data and analysis at various stages, edited the manuscript.

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Abstract

Nitrogen loss from cultivated soils threatens the economic and environmental sustainability of agriculture. Nitrate (NO_3^-) derived from fertilization or nitrification of ammonified soil organic nitrogen (SON) may be lost from soils directly to denitrification, producing N_2 or the greenhouse gas N_2O . Nitrate that accumulates in soils is also subject to leaching loss, which can degrade water quality and make NO_3^- available for downstream denitrification. Here we use patterns in the isotopic composition of NO_3^- to characterize N loss to denitrification within soils, groundwater, and stream riparian corridors of a non-irrigated agroecosystem in the northern Great Plains. We find evidence for denitrification across these domains, expressed as positive correlation between $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in NO_3^- , as well as increasing $\delta^{15}\text{N}$ values with decreasing NO_3^- concentration. In soils, isotopic evidence of denitrification is present during fallow periods (no crop growing), even as accumulation of NO_3^- through ammonification of SON and subsequent nitrification is outpacing denitrification to produce a net increase in the soil NO_3^- pool. We combine previous results for soil NO_3^- mass balance with $\delta^{15}\text{N}$ mass balance to estimate denitrification rates in soil relative to groundwater and streams. Substantial denitrification from soils during fallow periods may be masked by nitrification of ammonified SON, representing a hidden loss of SON and an under-quantified flux of N as N_2 or N_2O to the atmosphere.

Introduction

Over the last ca. 150 years, anthropogenic fixation of dinitrogen (N_2) gas into reactive N (N_r) has increased by an order of magnitude (annual total mass estimates of 15 Tg N in 1860 to 165 Tg N in 2000; Galloway et al., 2003). Approximately 85% of N fixed by humans becomes fertilizer that has increased crop production to feed a growing population. However, global-scale fertilization has also resulted in a cascade of disruptive side effects on planetary systems (Galloway et al., 2003; Erisman et al., 2008; Rockstrom et al., 2009). Nitrogen fertilizer is typically applied to agricultural soils in a reduced form such as ammonium or urea, which is subject to biogeochemical transformations and loss from soil that can compromise the goal of N delivery to plants. The generally oxidizing conditions common in cultivated soils favor transformation of reduced N compounds to nitrate (NO_3^-), a fully oxidized N species susceptible to export via leaching due to its limited potential to sorb to soils (Sparks, 2003). Nitrate often dominates the loads of N transported through groundwater and surface water flows and is a primary agent for local- to continental-scale degradation of water quality in aquifers, river networks, and estuaries (Vitousek et al., 1997; Caraco and Cole, 1999; Goolsby et al., 1999; Smith, 2003; Puckett et al., 2011; Tesoriero et al., 2013). Observed variation of isotopic indicators has dramatically advanced understanding of these N cycling dynamics across diverse systems (Firestone and Davidson, 1989; Kendall and McDonnell, 1998; Burgin and Hamilton, 2007). Here, we explore insights about NO_3^- loss using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values in NO_3^- in a non-irrigated wheat production system within the Northern Great Plains.

The transport of N from terrestrial to aquatic systems as NO_3^- may be reduced by denitrification, which is a form of anaerobic microbial respiration that transforms NO_3^- back to non-reactive N_2 or to the greenhouse gas N_2O . Among other factors, anoxia and organic matter (i.e., energy) availability are thought to be primary controls on denitrification across domains from soils to the sea (Firestone and Davidson, 1989; Taylor and Townsend, 2010; Davis et al., 2019). High spatial and temporal variability in these controls along with high background concentration of N_2 in the environment make quantification of denitrification challenging, and isotopic tools are commonly brought to bear for this task given the large associated isotopic effects on the residual NO_3^- pool (Groffman et al., 2006). Synthesis of research across ecosystem types suggests that approximately 60% of global denitrification occurs in oceans and 40% occurs in freshwater and soils (Seitzinger et al., 2006). Terrestrial denitrification of 96 Tg y^{-1} is parsed among riparian areas (5%), groundwater (25%), and soils (ca. 70%) based on estimates by Bouwman et al. (2013). The global soil N budget surplus (inputs minus withdrawal by plants) has increased by about 70% over the last century (118 to 202 Tg y^{-1} from 1900 to 2000), where parallel increases in terrestrial denitrification (52 to 96 Tg y^{-1}) equate to ca. 45% of the surplus (Bouwman et al., 2013).

The general controls on denitrification in soils are well understood, though specific predictions of denitrification rates are complicated by a poor understanding of the influence of heterogeneity within the soil environment (Schlüter et al., 2019). Soils commonly host nitrifying conditions adjacent to denitrifying conditions in space or time, and accordingly can produce high denitrification rates by providing an abundant supply

of NO_3^- for denitrifiers. Presence of high dissolved oxygen (DO) as the preferred electron acceptor often limits denitrification in soil, and DO concentration is typically mediated by soil water content (Smith et al., 1997). When not suppressed by oxic conditions, the abundance of dissolved organic carbon (DOC) and NO_3^- can limit rates of denitrification (Firestone and Davidson, 1989).

Denitrification studies have been abundant in irrigated agricultural soils, where anthropogenic controls on soil water mediated rates of denitrification are directly evident (Rolston et al., 1982; DeKlein and VanLogtestijn, 1996; Scheer et al., 2008; Liu et al., 2011). Studies of the controls on denitrification in non-irrigated systems are much less common, despite the fact that non-irrigated agriculture accounts for about 80% of global cultivated land area and having equal (if not greater) challenges with N use efficiency (Foley et al., 2011; Siebert et al., 2005). Periods of fallow (lack of vegetation between crops) represent ca. 50% of a given year across cultivated land area globally (Siebert et al., 2010), and the lack of transpiration during these periods leads to a seasonal increase in soil water content (Probert et al., 1998; Nielsen et al., 2005). While fallow periods and associated seasonal increases in soil water content have been linked to higher NO_3^- leaching losses (Campbell et al., 2006; John et al., 2017; Sigler et al., in revision), few studies have explored the extent to which these periods of higher soil water content also influence denitrification in soils and downgradient aquifers or riparian corridors. Application of natural abundance isotopic methods using $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ in NO_3^- as a means of tracing N transport through soils, groundwater, and streams emerges as a promising approach for addressing this understudied question.

Leaching and denitrification losses indicate N use inefficiencies that are prevalent in agricultural production, but perhaps particularly with fallow. These inefficiencies challenge sustainability in agroecosystems, which seeks to balance crop production needs with protection of soil and water resources, while mitigating anthropogenic N loading that leads to N₂O related climate forcing (Committee on Twenty-First Century Systems Agriculture, 2010b). Minimizing these distinct environmental harms resulting from inefficient use of N_r in agricultural production requires detailed knowledge of the interactions between agricultural management practices such as fallowing, and the drivers of denitrification. To better understand the role of denitrification as a pathway of N_r loss in non-irrigated agricultural systems, we ask: *How do key drivers of denitrification throughout a non-irrigated agricultural landscape dictate N_r losses and transfers from soils to groundwater to riparian corridors?* To answer this question, we explore patterns in DOC, DO, and NO₃⁻ concentration along with isotopic composition of water and NO₃⁻ within a non-irrigated, semi-arid agroecosystem in central Montana, USA. We use δ¹⁵N and δ¹⁸O values in NO₃⁻ across soil water, groundwater, and stream water samples to infer conditions and rates of N_r loss to denitrification across these domains.

We hypothesize that in soils, DOC supply, consumption of DO, and production of NO₃⁻ support substantial denitrification during fallow periods when high soil water content is sustained, despite the semi-arid environment. More broadly, we use our isotopic results to examine hypotheses (Sigler et al. 2018) that denitrification is minimal in groundwater due to high DO and short residence times (Tesoriero and Puckett, 2011), and that denitrification is substantial in riparian corridors (Vidon and Hill, 2006), in

instances where groundwater interacting with stream flow travels slowly through saturated, carbon-rich riparian soils.

Materials and Methods

Study Area

The study area is in central Montana within the Judith River Watershed (HUC 10040103). The Judith River is a headwater tributary to the Missouri River, and streams and shallow aquifers in the lower elevations of the watershed have chronically elevated NO_3^- concentrations that are controlled by variable rainfall, soil characteristics, and agricultural land management practices (Sigler et al., 2018; Sigler et al. in revision; Ewing et al. in prep). The area is in the northern Great Plains region, with a semi-arid climate and mean annual precipitation of 389 mm (1909-2014 period at WRCC Gage # 245761). Cultivated soils in the area are generally well drained, with relatively thin (30-100 cm) zones of clay loam textures overlying horizons dominated by gravel or coarser material. Unconfined aquifers are perched on shale and generally shallow (1-10 m below ground surface), with a saturated thickness of 2-6 m and mean groundwater residence times ranging from <1 to 20 years (Sigler et al. 2018). Here we focus on the aquifer within the Moccasin strath terrace (Figure 1), where topography, stratigraphy, and water chemistry observations suggest that groundwater recharge occurs exclusively via infiltration of precipitation through terrace soils, and where 72% of the area is used for annual cultivation (Sigler et al. 2018). This system is well-suited to addressing the controls on denitrification because the terrace has well-defined hydrologic boundaries and hosts soil with variable thickness and water holding capacity, dictating a range of soil

water and biogeochemical conditions (Sigler et al. 2018; Sigler et al. in revision). Sigler et al. (2018) provides a more detailed characterization of the terrace and its aquifer and Sigler et al. (in revision) provides a detailed description of soils.

Sampling and Analysis

We infer fate and transport of N_r through components of the agroecosystem by sampling soil water, groundwater, and stream water across space and time. Soil solution chemistry was characterized in samples from tension lysimeters (PTFE/silica; Prenart Equipment; Frederiksberg, Denmark) installed in two non-irrigated fields operated by cooperating farmers (Field B near Moccasin, and Field C near Moore, Figure 1). Lysimeters were installed near the bottom of the fine textured soil horizons, with nine in relatively thin soils (40-80 cm; shallow) and nine in relatively thick soils (80-120 cm; deep). Soil water and NO_3^- isotopic compositions were measured in samples from six lysimeters, which represented a subset of 18 lysimeters that were characterized for a broader range of water chemistry over a four-year period (2013-2016). Groundwater and stream water chemistry were previously characterized with samples from two wells, five springs, and three stream sites (Sigler et al. 2018) distributed across the Moccasin terrace (Figure 1). Precipitation samples were collected at three study fields (Figure 1) with receptacles containing mineral oil (to avoid evaporation) during non-freezing months and by collection and melting of snow on one occasion (Mar 2014). Precipitation samples were analyzed for hydrogen and oxygen isotopic composition in water relative to Vienna Standard Mean Ocean Water (VSMOW), using off-axis integrated cavity output spectroscopy (Los Gatos Research, Mountain View, CA; Baer et al., 2002). Water

isotope analysis was conducted in the Montana State University Environmental Analytical Laboratory, based on reference materials USGS 46, USGS 48, LGR #2C, and LGR #3C. A working local groundwater standard included after every fourth sample across eight runs had one standard deviation of 0.4‰ for $\delta^{18}\text{O}$ and 0.6‰ for $\delta^2\text{H}$; we estimate total uncertainty in these samples is two-fold higher. Nitrate isotope analyses were conducted in the Wankel Laboratory at the Woods Hole Oceanographic Institution, using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002). Nitrate isotopic values were corrected for drift and linearity, and referenced to N_2 in air ($\delta^{15}\text{N}$) and VSMOW ($\delta^{18}\text{O}$) using reference materials USGS 32, USGS 34 and USGS 35. Analytical reproducibility of NO_3^- isotope values was calculated from replicate analysis of samples or reference materials and had one standard deviation of 0.2‰ for $\delta^{15}\text{N}$ and 0.5‰ for $\delta^{18}\text{O}$.

Isotopic Signals of Denitrification

The N isotopic composition of N-bearing phases is potentially subject to fractionation during all transformations within the N cycle (Sharp, 2017; Denk et al. 2017). In this work, we focus on fractionation during ammonification, nitrification and denitrification as the primary processes influencing isotopic composition of NO_3^- . We characterize N_r losses to denitrification using observed isotopic values and the NO_3^- mass balance, applying a range of isotope effects (ϵ) based on literature and observed isotopic values in reactant and product pools. We apply a net $\delta^{15}\text{N}$ isotope effect for conversion of SON to NO_3^- by ammonification and nitrification and consider values ranging between -2 and -18‰, indicating that the light isotope (^{14}N) is favored in the resulting NO_3^- (Sup

Material; Denk et al., 2017). For denitrification, we consider values ranging between -13 and -31‰ for an $\delta^{15}\text{N}$ isotope effect, indicating that loss increases $\delta^{15}\text{N}$ values in the residual NO_3^- pool (Sup Material; Houlton et al., 2006; Denk et al., 2017). The $\delta^{18}\text{O}$ in NO_3^- ($\delta^{18}\text{O}_{\text{NO}_3}$) resulting from nitrification reflects the isotopic composition of O_2 and ambient water, along with a negative fractionation effect with denitrification that increases $\delta^{18}\text{O}$ values in residual NO_3^- (Kendall and McDonnell, 1998; Boshers et al., 2019). The expression of $\delta^{18}\text{O}_{\text{NO}_3}$ fractionation via denitrification is also influenced by the $\delta^{18}\text{O}$ value of ambient water due to isotopic exchange with NO_2 (Granger and Wankel, 2016; Sup Material).

Evidence for a denitrification isotopic effect was assessed using the slope, coefficient of determination (R^2), and probability of falsely identifying a trend (p value) derived from linear regressions of $\delta^{18}\text{O}_{\text{NO}_3}$ versus $\delta^{15}\text{N}_{\text{NO}_3}$ ($\delta^{18}\text{O}:\delta^{15}\text{N}$) and $\delta^{15}\text{N}_{\text{NO}_3}$ versus NO_3^- concentration ($\delta^{15}\text{N}:\text{NO}_3^-$). While plenty of evidence indicates the $\delta^{15}\text{N}:\text{NO}_3^-$ relationship is not linear (Kendall and McDonnell, 1998; Bohlke et al., 2002), the regression statistics provide simple objective metrics for assessing confidence in the presence of an isotopic effect consistent with denitrification. Signals from these statistics indicating a meaningful positive $\delta^{18}\text{O}:\delta^{15}\text{N}$ slope (Granger and Wankel, 2016) and a meaningful negative $\delta^{15}\text{N}:\text{NO}_3^-$ slope (Kendall and McDonnell, 1998) were interpreted as a primary line of evidence for a denitrification effect. The expected influence of oxygen and organic carbon concentrations were explored as corroborating lines of evidence for a denitrification effect. A signal of a negative slope in the $\delta^{15}\text{N}_{\text{NO}_3}$ versus DO relationship ($\delta^{15}\text{N}:\text{DO}$) was interpreted as corroborating evidence that denitrification was suppressed

by oxygen. A signal of a positive slope in the $\delta^{15}\text{N}_{\text{NO}_3}$ versus DOC relationship ($\delta^{15}\text{N}:\text{DOC}$) was interpreted as corroborating evidence that denitrification was energy limited. For the sake of transparent reporting, isotopic values that appear to be outliers were retained in plots and analysis. To facilitate interpretation of data that reduces the influence of outliers, the range of values between the 5% and 95% quantiles are presented here as a Q_{5-95} range.

Results and Discussion

We observed evidence of denitrification in soils, groundwater, and stream riparian corridors within our study area, based on positive $\delta^{18}\text{O}:\delta^{15}\text{N}$ correlations and negative $\delta^{15}\text{N}:\text{NO}_3^-$ correlations (Figure 2, Table 1). Variation in the strength of these relationships across domains provides evidence of competing processes influencing net isotopic dynamics. Generally, we observe patterns consistent with denitrification suppression by DO (negative $\delta^{15}\text{N}:\text{DO}$ correlations) or limitation by DOC (positive $\delta^{15}\text{N}:\text{DOC}$ correlations) that would be expected in these domains (Figure 3, Table 1).

Nitrate Isotopic Composition Across Domains

Across all soil, groundwater, and stream samples, we observed $\delta^{15}\text{N}_{\text{NO}_3}$ values ranging from 0.4 to 21.1‰, $\delta^{18}\text{O}_{\text{NO}_3}$ values ranging from -9.1 to 6.7‰, and NO_3^- concentrations ranging from 0.2 to 52.6 mg N L⁻¹, with unique patterns within each domain (Figure 2). The Q₅₋₉₅ range of $\delta^{15}\text{N}_{\text{NO}_3}$ values for soil lysimeter samples was 2.3 to 6.3‰, falling within the 2 to 8‰ range conventionally expected in soils (Kendall and McDonnell, 1998). The Q₅₋₉₅ range of $\delta^{18}\text{O}_{\text{NO}_3}$ values was -8.7 to -1.1‰ and extends below the -5 to 15‰ range conventionally expected in soils (Kendall and McDonnell, 1998). However, these lower $\delta^{18}\text{O}_{\text{NO}_3}$ values are reasonable for NO_3^- resulting from nitrification using atmospheric oxygen ($\delta^{18}\text{O}_{\text{O}_2} = 24\text{‰}$) and precipitation with an observed $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ range of -3.3 to -24.7‰ (Sup Figure 1; Sup Table 1). Isotopic values in NO_3^- for high DO (> 6 mg L⁻¹) groundwater, where denitrification is not expected, cluster tightly in the middle of the soil values with a $\delta^{15}\text{N}_{\text{NO}_3}$ Q₅₋₉₅ range of 2.7 to 4.7‰ and a $\delta^{18}\text{O}_{\text{NO}_3}$ Q₅₋₉₅ range of -4.8 to -3.4‰. In addition, the mean isotopic NO_3^- values for high

DO groundwater ($\delta^{15}\text{N}_{\text{NO}_3} = 3.7\text{‰}$; $\delta^{18}\text{O}_{\text{NO}_3} = -4.0\text{‰}$) align with those of lysimeter samples ($\delta^{15}\text{N}_{\text{NO}_3} = 3.9\text{‰}$; $\delta^{18}\text{O}_{\text{NO}_3} = -4.9\text{‰}$). Similarities in the isotopic composition of groundwater and soil water agree with findings that the solute composition of groundwater within the Moccasin terrace is primarily controlled by the character of the terrace soil water (Sigler et al. 2018). This similarity extends in part to groundwater fed streams, where the lowest NO_3^- isotopic values ($\delta^{15}\text{N}_{\text{NO}_3} 3.9\text{‰}$; $\delta^{18}\text{O}_{\text{NO}_3} -5.1\text{‰}$) resemble mean soil and groundwater values. We interpret isotopic composition in downstream samples with similar isotopic composition to high DO groundwater as having undergone limited denitrification.

Denitrification Signals

Both the clearest presence and absence of denitrification signals were observed in groundwater, with differentiation apparently related to oxygen availability (Figure 2; Table 1). Four of the seven riparian groundwater sites indicated no $\delta^{18}\text{O}:\delta^{15}\text{N}$ or $\delta^{15}\text{N}:\text{NO}_3^-$ signals of denitrification (Table 1; Indian, Star, Grove, Spr555). Denitrification signals for the two non-riparian wells (M1 and Headwaters) were unclear, with mixed signals for $\delta^{18}\text{O}:\delta^{15}\text{N}$, $\delta^{15}\text{N}:\text{NO}_3^-$, and corroborating $\delta^{15}\text{N}:\text{DO}$ and $\delta^{15}\text{N}:\text{DOC}$ relationships (Table 1; Sup Figure 3). Across all groundwater samples, DO explains 73% ($R^2 = 0.73$, linear regression of $\delta^{15}\text{N}_{\text{NO}_3}$ vs $\ln[\text{DO}]$) of the observed variation in $\delta^{15}\text{N}_{\text{NO}_3}$, consistent with the common observation that DO is a key control on denitrification in groundwater. One riparian groundwater site (Pioneer) where DO concentrations were consistently low displayed clear $\delta^{18}\text{O}:\delta^{15}\text{N}$ and $\delta^{15}\text{N}:\text{NO}_3^-$ signals of denitrification along with a $\delta^{15}\text{N}:\text{DOC}$ corroborating signal. The clear denitrification signal at one riparian

groundwater site juxtaposed to absence of denitrification signal at four riparian groundwater sites underscores high variability in riparian denitrification rates and extent, similar to findings in other studies (Hedin et al., 1998b; McClain et al., 2003; Vidon and Hill, 2006).

Further assessment of riparian corridor denitrification based on stream water column samples, suggests denitrification is occurring substantially more in Louse Creek than in Porter Creek. While DO concentration data were collected along with stream samples (Sup Figure 4), we assume that minimal denitrification occurred in the water column where those values are relevant. However, corroborating evidence is provided for denitrification in Louse Creek, from the $\delta^{15}\text{N}:\text{DOC}$ signal (Table 1). Porter Creek samples indicate no isotopic signals of denitrification, when assessed independently. However, when samples from a spring feeding Porter Creek (Grove Spring) are grouped with those from Porter Creek, $\delta^{18}\text{O}:\delta^{15}\text{N}$, $\delta^{15}\text{N}:\text{NO}_3^-$, and $\delta^{15}\text{N}:\text{DOC}$ denitrification signals emerge as significant (Table 1). Denitrification signals evident between groundwater and stream water, support the interpretations, based on the mass balance analysis by Sigler et al (2018), that riparian corridor NO_3^- losses for Louse (50%) and Porter (15%) creeks are at least partially attributable to riparian denitrification.

Denitrification signals across soil waters are weak to non-existent for the full sample set collected from tension lysimeters, but the signal is stronger when samples from the fallow period are considered independently and stronger still for deep lysimeters during fallow (Table 1). In the simplest terms, presence of the strongest denitrification signals in soil during fallow is consistent with findings by Sigler et al. (in revision) that

soil moisture is higher during fallow than in cropped years. Higher water content in the presence of soil organic matter increases the chances of regions with low DO, which would facilitate denitrification (DeKlein and VanLogtestijn, 1996; Smith et al., 1997). The concomitant increases in soil NO_3^- concentrations during the fallow year, observed in both lysimeter samples (Sigler et al. 2018) and soil profile inventories (Sigler et al. in revision; John et al. 2017), indicate that nitrification is out-pacing denitrification and leaching during this period. Nitrate with the highest $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values occurs early (March-April) in the fallow year when NO_3^- concentrations are low and isotopic values decrease over the fallow year. These patterns are consistent with denitrification favored by anoxic conditions in more saturated soils associated with snowmelt early in the season, followed by nitrification favored by more oxic conditions and moderate soil water content during the warmer and drier season. Decreases in $\delta^{15}\text{N}_{\text{NO}_3}$ values with nitrification are presumably due to preference for the light isotope as NO_3^- is derived from SON with a $\delta^{15}\text{N}$ value of $\sim 5\%$. Decreases in $\delta^{18}\text{O}_{\text{NO}_3}$ values with nitrification are presumably due to incorporation of oxygen from water with relatively low $\delta^{18}\text{O}_{\text{NO}_3}$ values that is stored in soil from snowmelt and used for nitrification through the summer fallow period.

Estimating Soil Nitrification and Denitrification Rates

To further explore the potential magnitude of soil denitrification coincident with nitrification during fallow, we compared observed soil $\delta^{15}\text{N}_{\text{NO}_3}$ values to values expected given different simplified scenarios of nitrification and denitrification rates and isotopic fractionation. For the net isotope effect of ammonification and nitrification of SON, we

considered minimum (-2‰), intermediate (-10‰), and maximum (-18‰) isotopic effects favoring the light isotope in the resulting NO_3^- (rationale for values selected is in Sup Table 2). Similarly, for denitrification we present scenarios applying three isotopic effects favoring loss of the light isotope and retention of the heavy isotope in the residual NO_3^- (-13‰, -25‰, and -31‰; Sup Table 2). Observed lysimeter $\delta^{15}\text{N}_{\text{NO}_3}$ values during fallow ranged from 2.3 to 7.1‰, values assumed to constrain the range of net isotopic effects conferred by nitrification and denitrification. We assume an SON pool with steady-state isotopic composition such that the NO_3^- derived from SON also has a constant isotopic composition, a reasonable assumption given relatively large inventories of SON (31,000 kg ha⁻¹; Sup Materials). Isotopic composition of N in the residual NO_3^- pool after denitrification losses is calculated assuming Rayleigh fractionation. The size of the N pool at time t (N_t) is a function of incremental inputs from nitrification (N_{nit}) and subsequent removal by denitrification (N_{den}) at each time step, which together define the net change in NO_3^- ($\Delta N = N_{nit} - N_{den}$).

$$\text{(Equation 1)} \quad N_t = N_{t-1} + N_{nit} - N_{den} = N_{t-1} + \Delta N$$

Total denitrification ($N_{den,T}$) over the period of interest is a function of change in NO_3^- pool size over the period of interest (ΔN_T) and the ratio of denitrification to nitrification ($r_{den} = \frac{N_{den}}{N_{nit}}$).

$$\text{(Equation 2)} \quad N_{den,T} = \frac{\Delta N_T}{\left(\frac{1}{r_{den}} - 1\right)}$$

The $\delta^{15}\text{N}_{\text{NO}_3}$ value for each timestep is a function of N pool variables, the $\delta^{15}\text{N}$ isotope effects associated with nitrification (ε_{nit}) and denitrification (ε_{den}), and the $\delta^{15}\text{N}$ value for SON ($\delta^{15}\text{N}_{\text{SON}} = 5\text{‰}$, Ewing et al., in prep) (Mariotti et al., 1981; Houlton et al., 2006; Denk et al., 2017). The $\delta^{15}\text{N}$ value for NO_3^- entering the soil pool, produced from SON ($\delta^{15}\text{N}_{\text{NO}_3,\text{nit}}$) is a function of $\delta^{15}\text{N}_{\text{SON}}$ and ε_{nit} ($\delta^{15}\text{N}_{\text{NO}_3,\text{nit}} = \delta^{15}\text{N}_{\text{SON}} + \varepsilon_{\text{nit}}$). The initial value for $\delta^{15}\text{N}$ of soil NO_3^- ($\delta_{t_0}^{15}\text{N}_{\text{NO}_3}$) is the mean soil $\delta^{15}\text{N}$ value observed across all lysimeter samples (4‰; n = 112). The initial size of the soil NO_3^- pool (N_{t_0}) is 10 kg ha⁻¹, the approximate mean observed in 14 soil pits at the start of the fallow period. The final size of the pool is 45 kg N ha⁻¹ based on observations in 13 soil pits at the end of a one year fallow cycle, representing an ΔN_T value of 35 kg ha⁻¹ yr⁻¹ (Sigler et al. in revision). Two equations then describe the net isotopic effect of nitrification and denitrification:

$$\text{(Equation 3; temporally resolved)} \quad \delta_t^{15}\text{N}_{\text{NO}_3} \approx \varepsilon_{\text{den}} \cdot \ln\left(\frac{N_t - N_{\text{den}}}{N_t}\right) + \left(\delta_{t-1}^{15}\text{N}_{\text{NO}_3} \left(\frac{N_{t-1}}{N_t}\right) + (\delta^{15}\text{N}_{\text{NO}_3,\text{nit}}) \left(\frac{N_{\text{nit}}}{N_t}\right)\right)$$

$$\text{(Equation 4; steady state)} \quad r_{\text{den}} \approx \left(\frac{\delta^{15}\text{N}_{\text{NO}_3,\text{nit}} + \delta^{15}\text{N}_{\text{NO}_3}}{\varepsilon_{\text{den}}}\right)$$

Equation 3 here is parallel to Equation 8 in Denk et al. (2017) as described by Mariotti (1981) and demonstrates progression toward steady state over time (Figure 4, Sup Figure 5). The solution to the steady state condition is approximated by Equation 4 here, parallel to Equation 14 in Denk et al. (2017) as described by Fry (2006).

Annual denitrification rates estimated using this approach for the fallow period range from zero to $62 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Table 2). The scenario applying intermediate isotope effects suggests denitrification loss rates between 15 and $35 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, or approximately 30 to 50% of the NO_3^- entering the soil pool from SON (Figure 4, Table 2).

Previous field measurements of soil denitrification vary widely from less than 1 to more than $60 \text{ kg ha}^{-1} \text{ d}^{-1}$ (Stevens and Laughlin, 1998; Mathieu et al., 2006).

Denitrification estimates across ecosystem types reported for annual timeframes range between zero and $239 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ (Phillips, 2008), while Seitzinger et al. (2006) report a value of $8 \text{ kg ha}^{-1} \text{ yr}^{-1}$ across all soils at the global scale. Our estimates suggesting denitrification rates ranging between zero and $62 \text{ kg ha}^{-1} \text{ yr}^{-1}$ (Table 2) are well within these previously reported values.

Implications for Landscape N Budgets

Isotopic composition of NO_3^- suggests that denitrification is occurring in both riparian soils and cultivated soils of our study area, a finding widely supported in the literature (Bouwman et al., 2013; Hedin et al., 1998; Billen et al., 2020). While riparian area samples produced the strongest isotopic denitrification signals, with some samples approaching 100% NO_3^- removal, these losses normalized to the catchment area ($1\text{-}5 \text{ kg ha}^{-1} \text{ yr}^{-1}$; Sigler et al. 2018) are small relative to potential losses directly from more spatially extensive cultivated soils. In groundwater and riparian corridors, loss of N to denitrification can act to enhance water quality, while in soils it can compromise goals to maximize plant uptake. Across domains the fraction of denitrification routed to the

greenhouse gas N_2O (ca. 0.015) brings deleterious effects associated with climate forcing (Stevens and Laughlin, 1998; Billen et al., 2020). These results suggest that accurate accounting of N use efficiency requires dramatically improved understanding of denitrification loss rates from soils in these semi-arid, non-irrigated settings.

Our estimates of denitrification rates during fallow ranging from zero to $62 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ are well within the range of previous estimates in the literature (0 to $239 \text{ kg N ha}^{-1} \text{ yr}^{-1}$; Phillips, 2008). These estimates imply that large gross losses of NO_3^- to denitrification are occurring during fallow, when they are masked by net NO_3^- accumulation from SON. As a result, these losses may be obscured in mass balance approaches where denitrification is not directly quantified (Bouwman et al., 2013; John et al., 2017). A $62 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ loss of NO_3^- during fallow years might be expected to result in a measurable loss of SON over time. However, given uncertainty on SON values of approximately $3,100 \text{ kg ha}^{-1}$ (Sup Materials), denitrification losses of $30 \text{ kg ha}^{-1} \text{ yr}^{-1}$ could occur for 100 years without being distinguishable from noise, or losses of $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$ could occur for 30 years unnoticed. If the soil denitrification rate is $30 \text{ kg ha}^{-1} \text{ yr}^{-1}$, this loss is 1.7 to 2.7 times higher than estimated leaching rates (11 to $18 \text{ kg ha}^{-1} \text{ yr}^{-1}$; Sigler et al. 2018) and up to half of common fertilizer rates (60 to $100 \text{ kg ha}^{-1} \text{ yr}^{-1}$; John et al. 2017). Loss of N_r from soils represents lost fertility, and SON derived losses will ultimately be offset by increased fertilizer application, likely enhancing fertilizer N use inefficiencies.

Our finding of concurrent nitrification and denitrification during fallow is consistent with previous work indicating that the two processes can be tightly coupled in

space (mm) and time (minutes) in soils (Seitzinger et al., 2006). Decades of work has suggested that nitrification occurs in oxygenated macropores while NO_3^- diffusion into adjacent anoxic micropores drives denitrification (Parkin, 1987; Parkin and Berry, 1999; Schlüter et al., 2018). This scenario of oxic and anoxic conditions adjacent in space may explain part of the concurrent nitrification and denitrification in our study area soils.

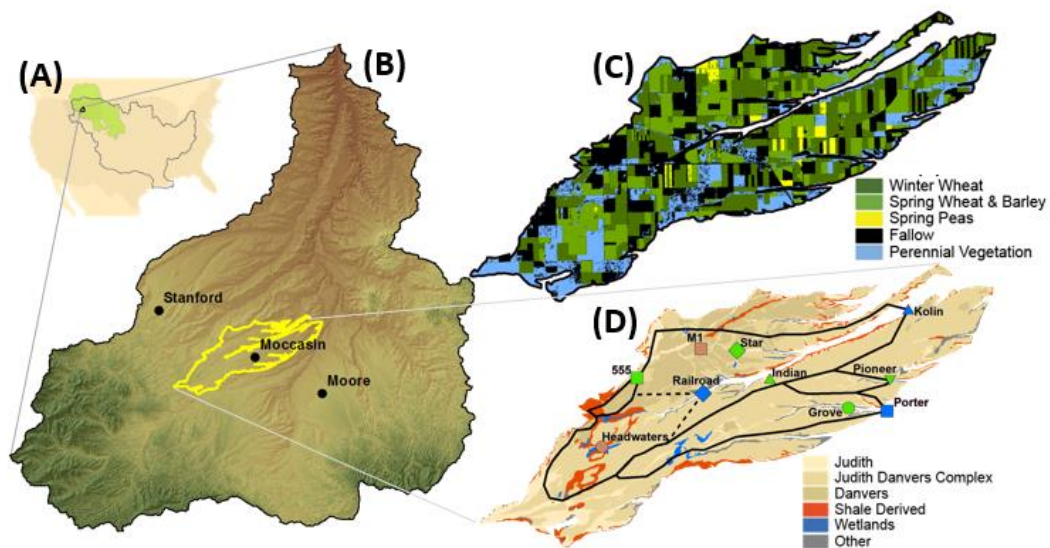
Perhaps more striking, however, is the sequence of alternating oxic and anoxic conditions created during dry and wet periods, adjacent in time as a result of fallow in an annual cultivation system (Sigler et al. in revision). In this sense, fallow may create the perfect storm for maximum denitrification losses in soils. This possibility in the context of global cultivated land spending 50% of time in fallow suggests additional work is needed to understand denitrification rates during fallow and implications for global N budgets.

Author Information

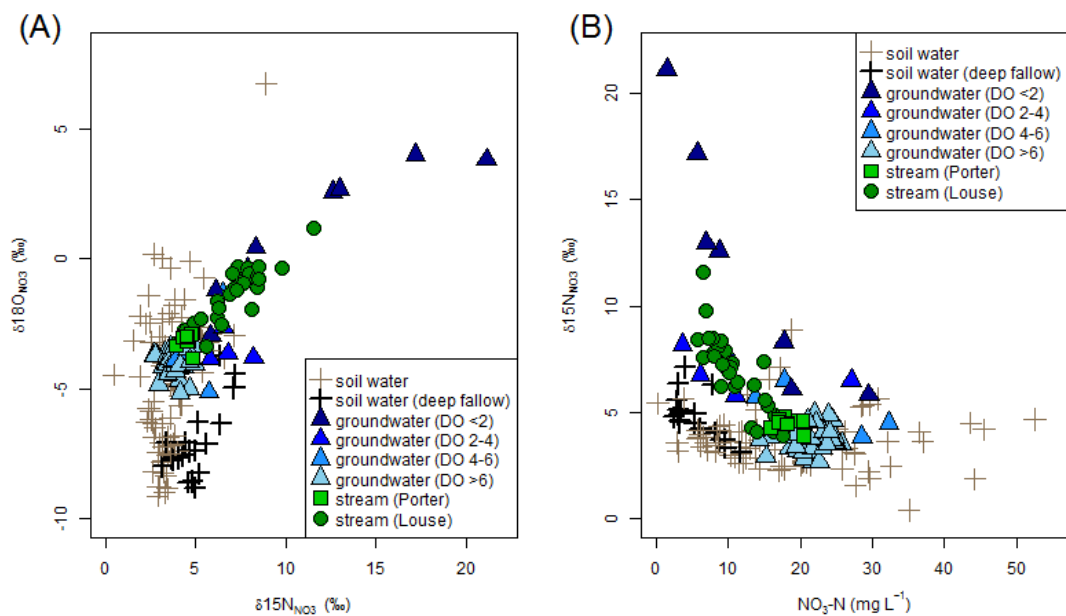
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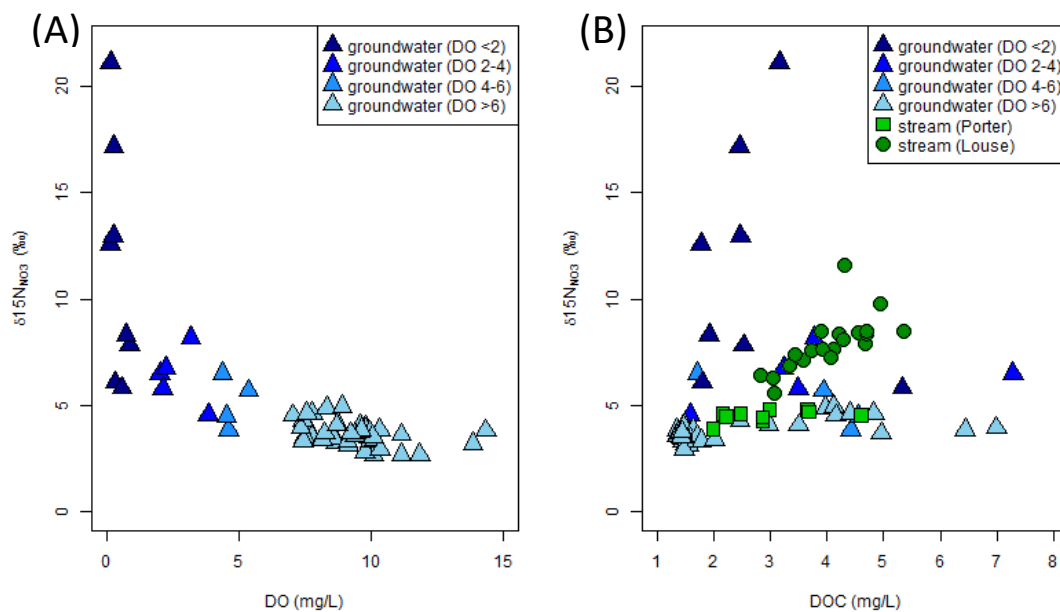
The authors would like to thank cooperating farmers, local partners, and the MSU Central Agricultural Research Center (CARC). Thank you to field technicians Kyle Mehrens, Robby Robertson, Mike Bestwick, Joe Capella and a special thank you to Simon Fordyce who was the lead field technician for the majority of the field campaign. This work was funded by the United States Department of Agriculture, National Institute of Food and Agriculture [grant number 2011-51130-31121, 2011] and USDA NIFA grant number 2016-67026-25067. Additional funding was provided by MSU Extension, Montana Fertilizer Advisory Committee, the Montana Agricultural Experiment Station, MSU Vice President of Research, MSU College of Agriculture, and the Montana Institute on Ecosystems. This work was supported in part by the National Science Foundation EPSCoR Cooperative Agreement OIA-1757351, as well as NSF EPSCoR Track 1 award numbers OIA-1443108 and EPS-1101342.

Figures

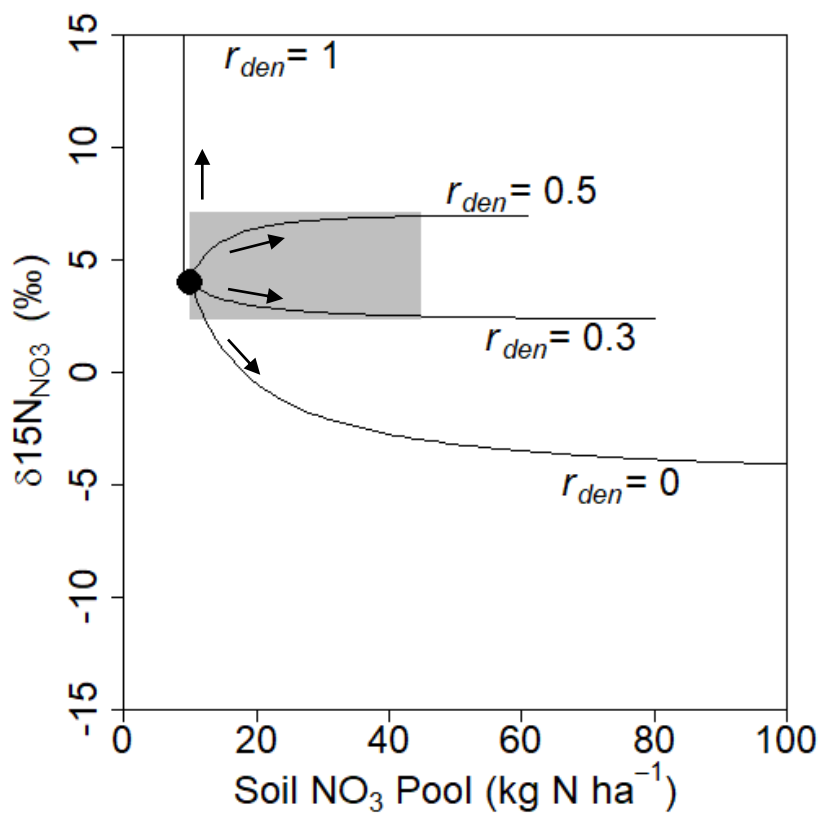
Ch4-Figure 1. Location and character of the Judith River Watershed (JRW) and Moccasin terrace in the context of: (A) the location of the study area within the United States, the northern Great Plains (green shaded area), and the Mississippi Atchafalaya River Basin (gray outline); (B) the locations of the Moccasin terrace and towns nearest to the study fields; (C) land use on the Moccasin terrace in 2014; and (D) soil series and sample sites for catchments (black outlines) on the Moccasin terrace.



Ch4-Figure 2. Comparisons of patterns in isotopic composition and concentration of NO_3^- dissolved in soil water, groundwater, and stream water across the JRW. Data from groundwater samples are differentiated by DO concentration (shades of blue as denoted in the legend with units of mg L^{-1}). (A) $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ in NO_3^- . (B) $\delta^{15}\text{N}$ in NO_3^- versus NO_3^- concentration.



Ch4-Figure 3. Comparisons of patterns in $\delta^{15}\text{N}$ in NO_3^- versus DO and DOC dissolved in groundwater and stream water across the JRW. Data from groundwater samples are differentiated by DO concentration (shades of blue as denoted in the legend with units of mg L^{-1}). (A) $\delta^{15}\text{N}$ in NO_3^- versus DO (B) $\delta^{15}\text{N}$ in NO_3^- versus DOC.



Ch4-Figure 4. Soil NO_3^- pool versus simulated $\delta^{15}\text{N}_{\text{NO}_3}$ assuming intermediate isotope effects ($\epsilon_{\text{den}} = -25\text{‰}$; $\epsilon_{\text{nit}} = -10\text{‰}$). The shaded area indicates the range of $\delta^{15}\text{N}_{\text{NO}_3}$ observed in lysimeters during fallow (2.3 to 7.1‰) and the range of soil NO_3^- pool sizes observed over one fallow year. The soil NO_3^- pool at the beginning of fallow was 10 kg N ha^{-1} and after one year of fallow it had increased to 45 kg N ha^{-1} . The black dot represents a starting value for the simulation with a $\delta^{15}\text{N}_{\text{NO}_3}$ value of 4‰. Black lines (derived from Equations 1 and 3) depict $\delta^{15}\text{N}_{\text{NO}_3}$ values for the soil NO_3^- pool over time (in the direction of the arrows) from starting conditions (black circle) for different r_{den} values (labels near lines). A value of $1 \text{ kg ha}^{-1} \text{ t}^{-1}$ was used for N_{nit} for this simulation. Maximum and minimum r_{den} values (0.3 and 0.5) produce simulated values for $\delta^{15}\text{N}_{\text{NO}_3}$ within the range observed in lysimeters according to Equation 4 and are presented in Table 2.

Tables

Ch4-Table 1. Summary of denitrification signals. Summary statistics for linear relationships associated with primary and corroborating denitrification signals. Highlighted cells (gray) are interpreted as “clear” signals where slope has the expected sign and statistical values exceed an arbitrarily designated threshold ($R^2 \geq 0.5$ and p value < 0.05).

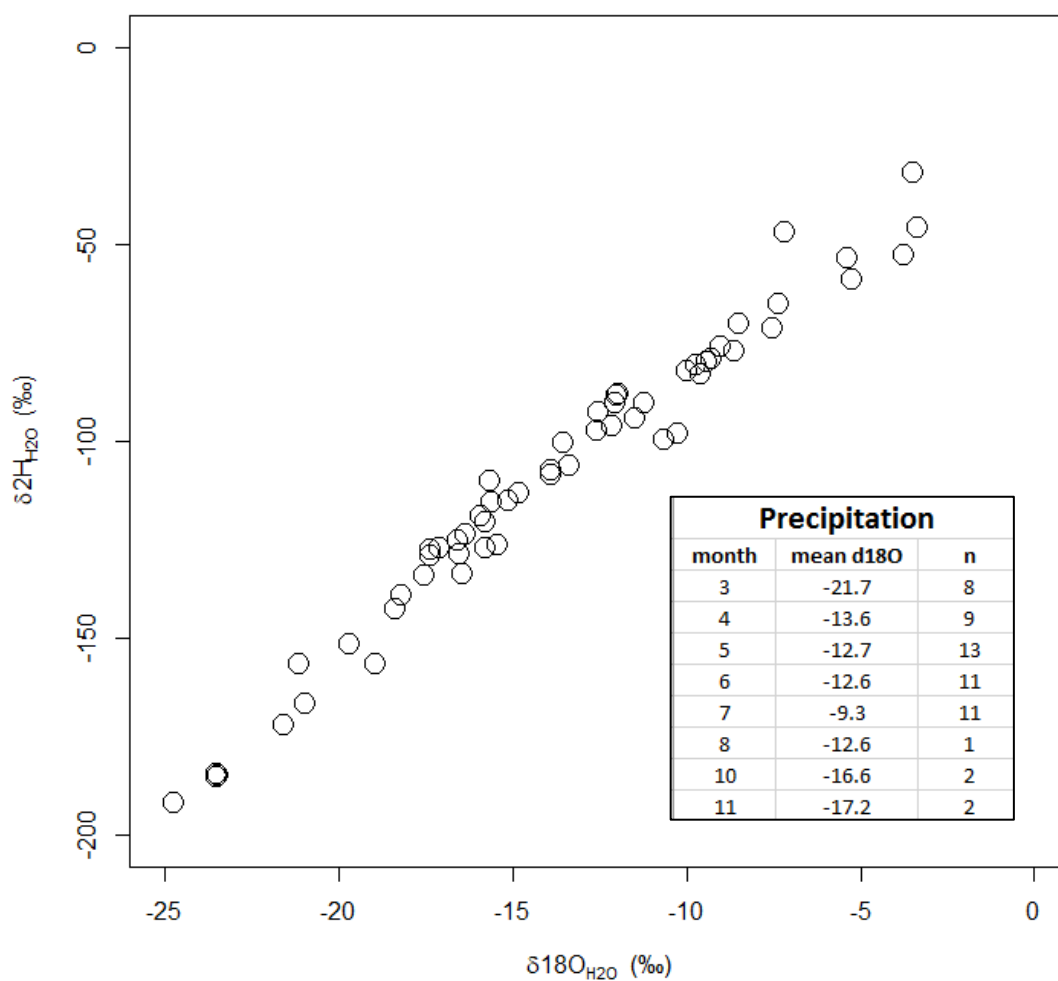
	Sites	Primary Signals				Corroborating Signals			
		$\Delta\delta^{18}\text{O}:\Delta\delta^{15}\text{N}_{\text{NO}_3}$		$\Delta\delta^{15}\text{N}:\Delta\text{NO}_3\text{N}$		$\Delta\delta^{15}\text{N}:\Delta\text{DO}$		$\Delta\delta^{15}\text{N}:\Delta\text{DOC}$	
		R^2	p value	R^2	p value	R^2	p value	R^2	p value
Soil	Lys All	0.04	0.025	0.08	<0.005	ND	ND	ND	ND
	Fallow	0.09	0.064	0.56	<0.005	ND	ND	ND	ND
	Fallow Deep	0.5	<0.005	0.38	0.005	ND	ND	ND	ND
Groundwater	Pioneer	0.88	<0.005	0.85	<0.005	0.36	0.09	0.65	0.01
	M1	0.01*	0.69*	0.81	<0.005	0.76	<0.005	0.01*	0.80*
	Headwaters	1.00	<0.005	0.23	0.52	0.70	0.16	0.82	0.10
	Indian	0.02	0.66	0.04	0.59	0.04	0.58	0.01	0.78
	Star	0.00*	0.96*	0.32	0.44	0.14	0.63	0.78	0.12
	Grove	0.23*	0.16*	0.02	0.67	0.19*	0.29*	0.01*	0.83*
	Spr555	0.85*	0.08*	0.94*	0.03*	0.33	0.42	0.15	0.62*
Stream	Porter	0.00	0.94	0.12	0.33	NA	NA	0.23	0.16
	Kolin	0.83	<0.005	0.72	<0.005	NA	NA	0.74	<0.005
	Railroad	0.82	<0.005	0.56	<0.005	NA	NA	0.36	0.07
Groups	Louse Creek								
	(Kolin & Railroad)	0.84	<0.005	0.73	<0.005	NA	NA	0.49	<0.005
	Porter & Grove	0.45	<0.005	0.73	<0.005	NA	NA	0.68	<0.005

* slope is in the opposite direction as predicted for denitrification

Ch4-Table 2. Annual soil denitrification rate estimates during the fallow year. Each scenario represents denitrification rate estimates assuming different combinations of isotope effect values for nitrification (ϵ_{nit}) and denitrification (ϵ_{den}). Scenarios A-D represent combinations of maximum and minimum isotope effect values and the last scenario (Int) represents intermediate values for isotope effects. Values for the ratio of denitrification to nitrification ($r_{\text{den}} = \frac{N_{\text{den}}}{N_{\text{nit}}}$) are calculated with steady state Equation 4, with requisite $\delta^{15}\text{N}_{\text{NO}_3, \text{nit}}$ values assuming $\delta^{15}\text{N}_{\text{SON}} = 5\text{‰}$. For each scenario, the minimum r_{den} value is calculated using the minimum $\delta^{15}\text{N}_{\text{NO}_3}$ value observed in soil (2.3‰) and the maximum r_{den} value is calculated using the maximum $\delta^{15}\text{N}_{\text{NO}_3}$ value observed in soil (7.1‰). The denitrification rates ($N_{\text{den}, T}$) associated with minimum and maximum r_{den} values are calculated with Equation 2 for a one year period assuming $\Delta N_T = 35 \text{ kg ha}^{-1} \text{ yr}^{-1}$. Visualization of the progression to steady state (based on Equation 3) is presented for the intermediate (Int) scenario in Figure 4 and for scenarios A-D in Sup-Figure 6.

Scenario	Isotope effects		Denitrification			
	$\epsilon_{\text{nit}} (\text{‰})$	$\epsilon_{\text{den}} (\text{‰})$	Minimum		Maximum	
			r_{den}	$N_{\text{den}, T}$ ($\text{kg ha}^{-1} \text{ yr}^{-1}$)	r_{den}	$N_{\text{den}, T}$ ($\text{kg ha}^{-1} \text{ yr}^{-1}$)
A	-2	-13	0*	0*	0.32	17
B	-18	-13	1.18	0*	1.55	0*
C	-2	-31	0*	0*	0.15	6
D	-18	-31	0.49	34	0.65	62
Int	-10	-25	0.3	15	0.5	35

0* indicates no solution; the value was a negative number, which is not meaningful

Supplemental MaterialsResults and DiscussionNitrate Isotopic Composition Across Domains

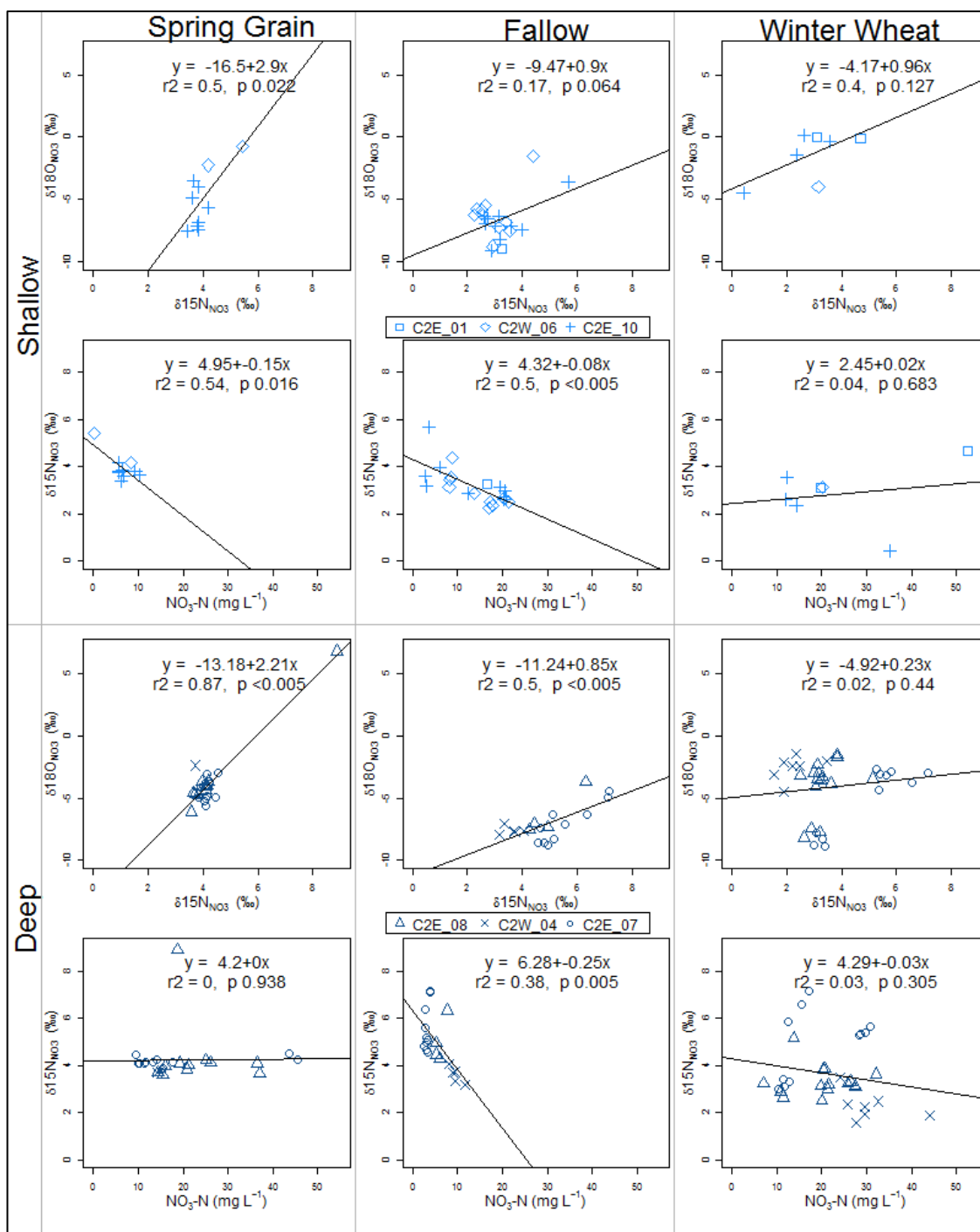
Ch4-Sup Figure 1. $\delta^{18}\text{O}$ versus $\delta^2\text{H}$ values in precipitation. See methods for details of sample collection.

The mean $\delta^{18}\text{O}_{\text{NO}_3}$ value observed in lysimeters (-5.0‰) is bracketed by values predicted from mean $\delta^{18}\text{O}_{\text{H}_2\text{O}}$ values in precipitation assuming 2/3 (-1.1‰) and 5/6 (-7.4‰) of oxygen comes from H_2O , with remaining oxygen coming from O_2 ($\delta^{18}\text{O}_{\text{O}_2} = 24\text{‰}$; Kendall and McDonnell, 1998). At least some of this variation in empirically determined ratios of oxygen derived from H_2O versus O_2 has been shown to derive from isotopic exchange between ^{18}O in ambient water and intermediate NO_2 during nitrification (Granger and Wankel, 2016).

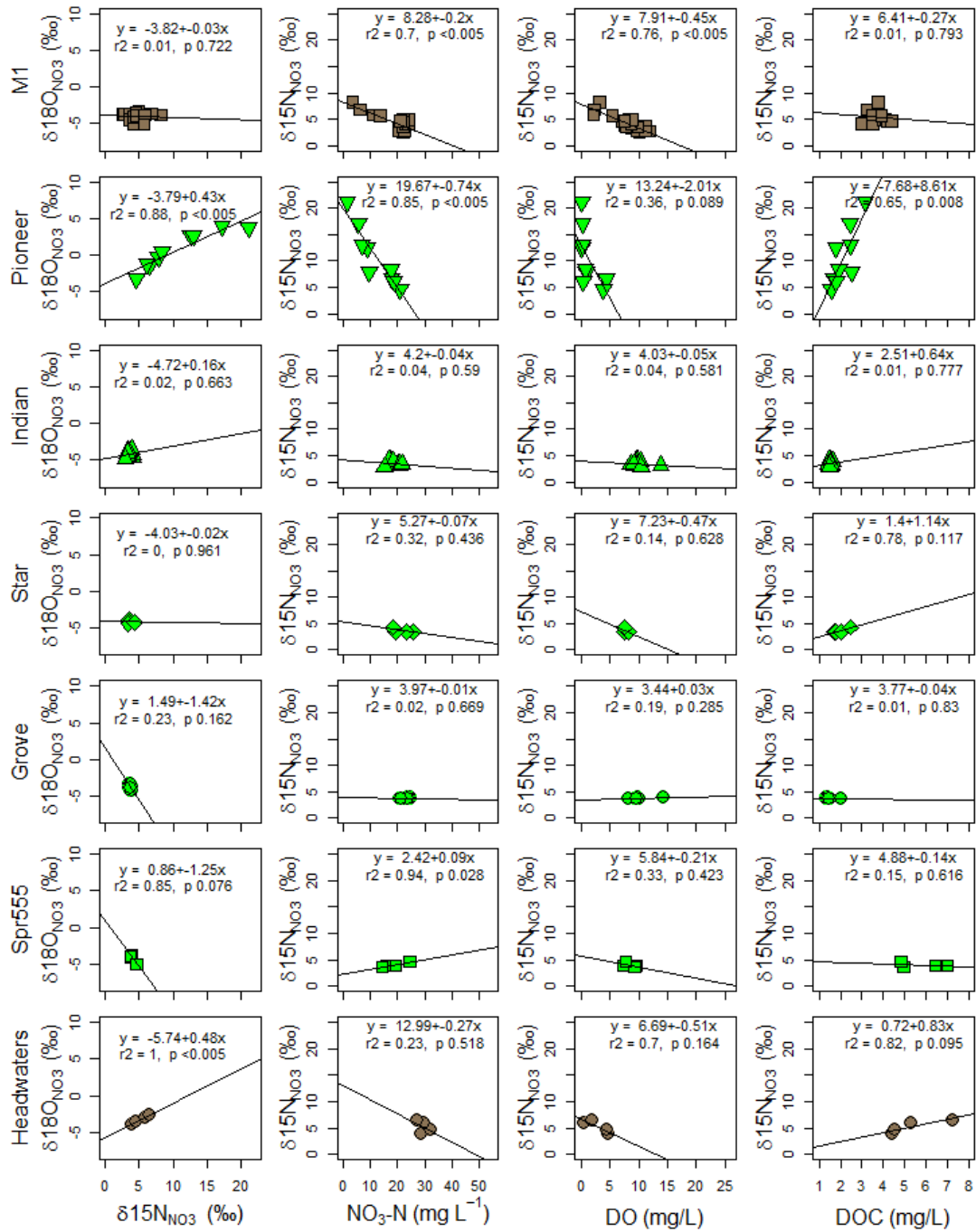
Ch4-Sup Table 1. $\delta^{18}\text{O}$ in Precipitation and NO_3^-

	Precipitation Observations	Predicted $\delta^{18}\text{O}_{\text{NO}_3}$		Lysimeter Observations
	$\delta^{18}\text{O}_{\text{H}_2\text{O}}$	2/3 O from H_2O	5/6 O from H_2O	$\delta^{18}\text{O}_{\text{NO}_3}$
Max	-3.3	5.8	1.2	6.7
Q0.95	-4.9	4.7	-0.1	-1.1
Mean	-13.7	-1.1	-7.4	-5.0
Median	-13.9	-1.3	-7.6	-4.8
Q0.05	-23.5	-7.7	-15.6	-8.7
Min	-24.7	-8.5	-16.6	-9.1

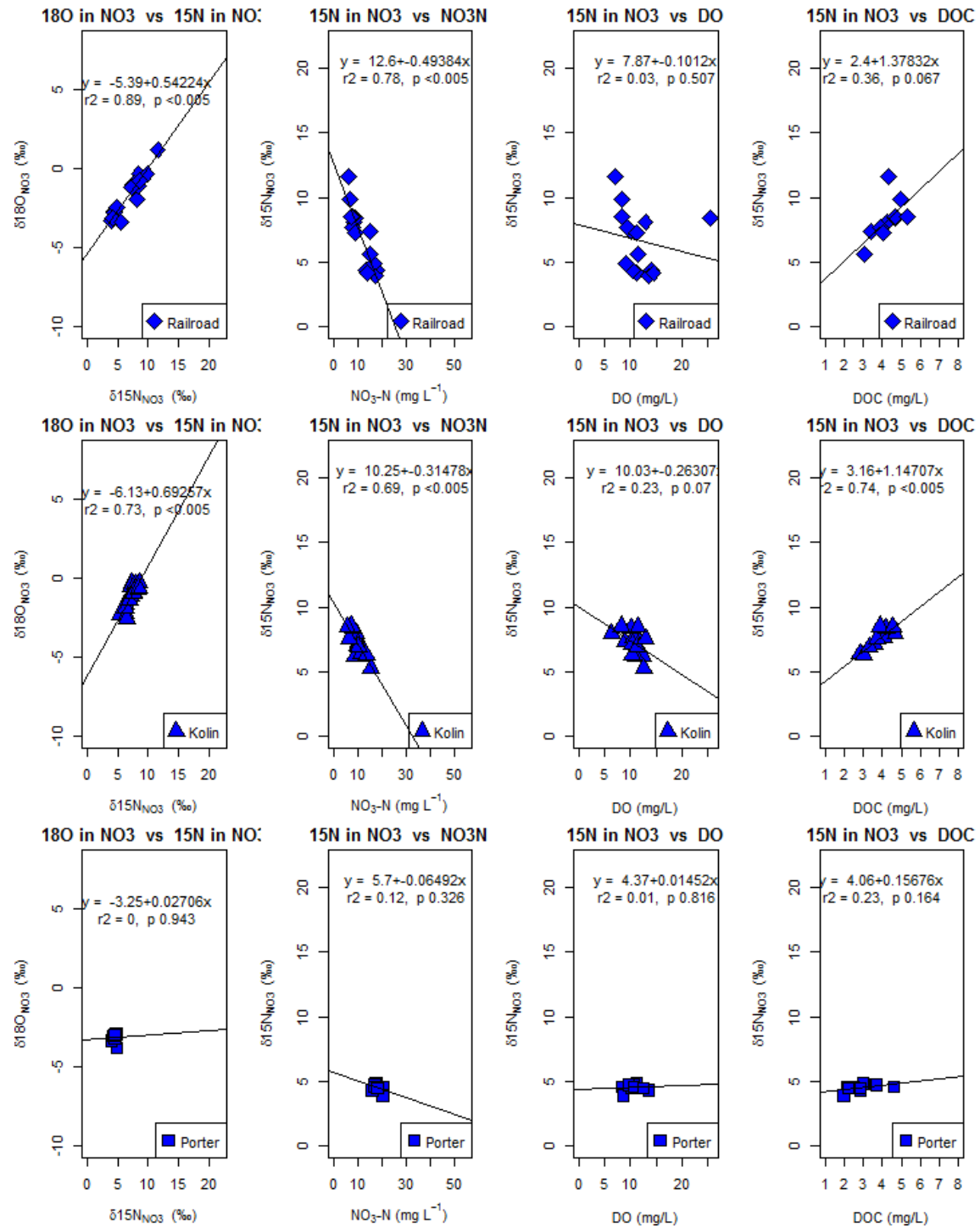
Denitrification Signals



Ch4-Sup Figure 2. Lysimeter composite plots



Ch4-Sup Figure 3. Groundwater composite plots



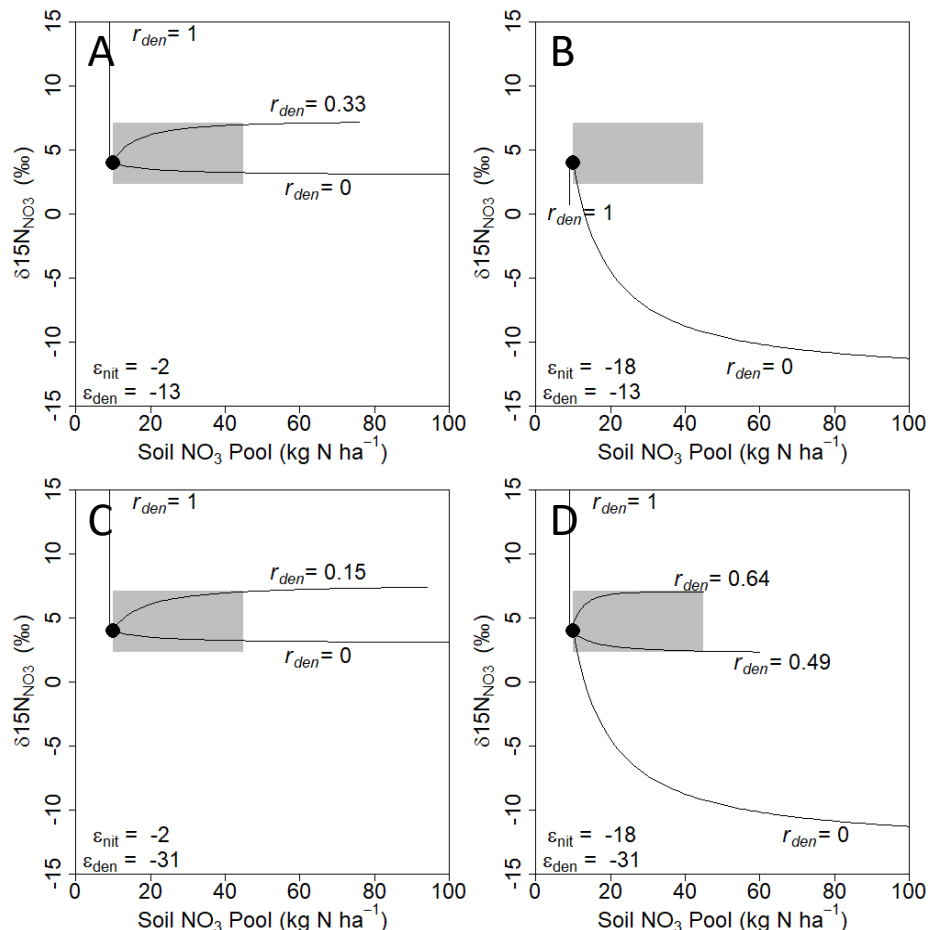
Ch4-Sup Figure 4. Stream composite plots

Estimating soil nitrification and denitrification rates

The size of the SON pool was estimated for the soils of the study area based on previous studies. The estimate assumes total N of 1.6 g N kg^{-1} (John et al. 2017) and bulk density of 1.3 (Sigler et al., in Revision). Assuming uncertainty around 10% based on standard deviations in total N observations suggests that SON is $31,000 \pm 3,100 \text{ kg ha}^{-1}$ in the top 15 cm.

Ch4-Sup Table 2. Isotope effects for ammonification and nitrification of SON (ϵ_{nit}) and denitrification (ϵ_{den}) applied in soil denitrification rate estimates.

Isotope effect	Value (‰)	Source
ϵ_{nit} (Large)	-18	The sum of isotope effects for the steps between SON and NO_3^- from Denk et al. 2017: ammonification = -1.7‰ ; NH_4 oxidation to $\text{NO}_2 = -29.6\text{‰}$; NO_2 oxidation to $\text{NO}_3^- = 13.0\text{‰}$. Expression of the isotope effect for each step likely depends on the persistence of a standing pool of the intermediate reactants.
ϵ_{nit} (Intermediate)	-10	This value is the mean of the large and small values. A value of this magnitude or larger is supported by $\delta^{15}\text{N}$ observations in soil as low as -20‰ (Hall et al. 2016).
ϵ_{nit} (Small)	-2	This is the value compiled by Denk et al. (2017) for ammonification (the first step in the chain of converting SON to NO_3^-). A value of at least this magnitude is supported by our minimum $\delta^{15}\text{N}_{\text{NO}_3}$ observation of 2.3‰ in lysimeters during fallow, which is more than 2‰ lower than the SON source (5‰).
ϵ_{den} (Large)	-31	Mean value reported by Denk et al. (2017) for reduction of NO_3^- to NO_2 (the first step of the denitrification chain) in soils.
ϵ_{den} (Intermediate)	-25	This value is intermediate between the maximum and minimum values and is near the 25 th quartile for soil incubation studies compiled by Denk et al. (2017).
ϵ_{den} (Small)	-13	Value applied by Houlton et al. 2006



Ch4-Sup Figure 5. Soil NO_3^- pool versus simulated $\delta^{15}\text{N}_{\text{NO}_3}$. Configuration is parallel to Ch4-Figure 4. Panels A-D depict results for different isotope effect values (ϵ_{nit} and ϵ_{den}) as indicated in the bottom left corner of each panel. The shaded area indicates the range of $\delta^{15}\text{N}_{\text{NO}_3}$ observed in lysimeters during fallow (2.3 to 7.1‰) and the range of soil NO_3^- pool sizes observed over one fallow year. The soil NO_3^- pool at the beginning of fallow was 10 kg N ha^{-1} and after one year of fallow it had increased to 45 kg N ha^{-1} . The black dot represents a starting value for the simulation with a $\delta^{15}\text{N}_{\text{NO}_3}$ value of 4‰. Black lines (derived from Equations 1 and 3) depict $\delta^{15}\text{N}_{\text{NO}_3}$ values for the soil NO_3^- pool over time (moving from left to right) from starting conditions for different r_{den} values (labels near lines). A value of 1 kg $\text{ha}^{-1} \text{t}^{-1}$ was used for N_{nit} for this simulation. Maximum and minimum r_{den} values (e.g. 0.49 and 0.64 for panel D) produce simulated values for $\delta^{15}\text{N}_{\text{NO}_3}$ within the range observed in lysimeters according to Equation 4 and are represented in Table 2. Minimum r_{den} is interpreted as zero for scenarios where the $r_{\text{den}} = 0$ line does not intersect the bottom of the shaded area (panels A and C). Panel B does not have a solution because no values of r_{den} between 0 and 1 produce lines within the shaded area.

Data

All data for the analysis in this manuscript is available as a *resource* on CUAHSI HydroShare. A link to the current resource is provided below and permission to access it can be granted by the author upon request. Once the peer review process is complete for the associated manuscript, a finalized version of the resource will be created along with a DOI to accompany the published manuscript.

Sigler, W. A. (2020). Sigler et al. Judith Watershed Denitrification Paper Data, HydroShare,
<http://www.hydroshare.org/resource/96e55a7386b8496c9139d2d9eb261ec1>

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CHAPTER FIVE

SYNTHESIS AND RECOMMENDATIONS

This work was made possible by a participatory research framework, in which an interdisciplinary research team worked closely with local farmers and other stakeholders to address questions about agricultural management effects on water quality in the Judith River Watershed (JRW). Cooperating farmers were engaged throughout the field research process and worked with the academic research team to identify management practices with potential to reduce nitrate (NO_3^-) leaching that were also logistically feasible for farmers to implement (John et al. 2017). Cooperating farmers not only implemented farming practices and participated in research on their own property, but they also facilitated access to the property of friends and neighbors for water sampling. In addition to land access, conversations with stakeholders provided insights from decades of local observations about where and when water moves through the landscape. These conversations helped refine a conceptual model of landscape hydrology from which hypotheses were formed, hypotheses that were logistically feasible to test via access to land also facilitated through stakeholder engagement.

Benefits of the participatory research approach extend beyond enhanced research quality to broader impacts associated with enhanced potential for adoption of management practices (Jackson-Smith et al. 2018). However, these benefits also must be placed in the context of the extensive time investment required on the part of local stakeholders and the academic research team. The participatory process required flexibility on the part of the academic research team to allocate resources to addressing

the questions of local stakeholders. This requisite flexibility diverted resources and contributed to extended timelines, but also carried intangible rewards of insights, personal understanding, and relationships gleaned from genuinely participatory work.

This body of work integrates findings across spatial scales from landforms to soil profiles in order to characterize both aggregate landscape scale water and nitrogen (N) fluxes and the interaction of weather, management (field scale) and soils (profile scale) to control those fluxes. This work leverages the natural laboratory of the Moccasin strath terrace (260 km²), which hosts a shallow aquifer that is isolated from mountain front stream recharge. Water enters the aquifer exclusively by infiltration through the terrace surface, where annual cultivation is the primary land use. Soil profile and field scale work was conducted within fields managed by cooperating farmers. The study area and approach provided a unique opportunity to advance fundamental understanding of how water and N move through non-irrigated small grain production systems.

The motivation for this work was to address the (perhaps ostensibly) wicked problem of balancing nutrient input requirements to grow crops while protecting the quality of water resources. I approached this in the context of a Soil-Water Nexus, integrating considerations from soil fertility and water quality management perspectives. Nitrogen fertilizer is commonly among the highest input costs for cultivated agriculture (USDA, 2020), making retention of N in soil against gas and leaching loss an important goal for economically sustainable agriculture. Nitrogen is also a leading cause of impairment in groundwater and surface water from local to continental scales, making an understanding of N sources and sinks within watersheds a top priority for water resource

management (EPA, 2017; Nolan and Hitt, 2006). Nitrate leached from soils contributes to elevated NO_3^- concentrations in groundwater, which subsequently dominate stream N loads in catchments with a large fraction of flow originating from groundwater, such as those in the study area (Tesoriero et al., 2013). In groundwater and riparian corridors, loss of N to denitrification can act to enhance water quality, while in soils it can compromise goals to maximize plant uptake, and across these domains the fraction of denitrification routed to the greenhouse gas N_2O brings deleterious effects associated with climate forcing.

The N and water cycles within agroecosystems are inextricably linked, not only due to physical transport of dissolved NO_3^- but also because of controls exerted by water on microbially mediated N cycling in soils. Characterization of the coupled water and N cycles was initiated at the landform scale with observations of water and NO_3^- concentrations in streams. Stream observations facilitated load calculations that were used to estimate lower limits on NO_3^- leaching from the soils of the Moccasin terrace at $5.3 \pm 3.7 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for the Louse Creek catchment and $18.6 \pm 7.5 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for the Porter Creek catchment (Chapter 2). Adjusting stream loads based on apparent riparian losses of N, provides improved landscape scale NO_3^- leaching estimates of 11–18 $\text{kg N ha}^{-1} \text{ yr}^{-1}$ or 19–31% of average standard fertilizer N application over the three-year rotation during the study ($\sim 90 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ for each of two crop years and zero for fallow year; John et al., 2017). These landscape scale estimates were notably lower than field scale NO_3^- leaching estimated by John et al. (2017) at $\sim 50 \text{ kg N ha}^{-1} \text{ yr}^{-1}$, prompting follow up work to model NO_3^- leaching and assess denitrification losses from soils.

Simulations indicate deep percolation is predominantly associated with periods of relatively intense precipitation (hot moments) and occurs with thin soils (hot spots) at rates five to 16 times higher than with thicker soils (Chapter 3). The practice of suppressing vegetation growth during summer fallow eliminates transpiration and expands both hot moments and hot spots of deep percolation due to hydrologic priming. High soil moisture and warm summer temperatures during fallow also facilitate accumulation of NO_3^- from ammonification and nitrification of soil organic N (SON), geochemically priming soils for NO_3^- leaching.

In addition to increased leaching losses during and following fallow periods, denitrification losses also occur during fallow periods (Chapter 4). Isotopic evidence of denitrification was observed in fallow years, during a period when a net accumulation of NO_3^- was observed, indicating that nitrification was ultimately outpacing denitrification. Soil N loss to denitrification occurring concurrent with net nitrification is masked when traditional mass balance approaches are applied because gas efflux of N_2 is difficult to measure and rarely conducted in field trials. These concealed gas losses of N from soil are poorly understood and potentially represent losses of NO_3^- derived from SON with important implications for soil health.

The shallow and relatively young groundwater within the JRW gravel deposits generally has high dissolved oxygen and shows little sign of denitrification, resulting in high NO_3^- concentrations in groundwater. High NO_3^- groundwater with minimal denitrification results in close to 100% of NO_3^- loss from soils being delivered to riparian corridors (Chapter 2 and 4). Within riparian corridors, denitrification is highly variable,

with no evidence of denitrification in springs with coarse substrate and little vegetation, but with extensive denitrification in seeps where roots of riparian vegetation intersect the water table to provide a DOC source. Strength of the denitrification signal is highly variable in samples from Louse Creek while the denitrification signal is consistently low in Porter Creek (Chapter 4). While differences in denitrification rates between Louse and Porter creeks explain at least part of the large difference in NO_3^- concentrations between the two creeks, the extent to which denitrification is occurring in riparian areas versus benthic stream sediment is an open question. Observation of riparian denitrification rates ranging from near zero in some locations to almost 100% in other locations suggests opportunities to improve surface water quality by promoting riparian vegetation as a source of DOC and a means of slowing water movement in areas with saturated soils. Current riparian NO_3^- losses for Porter and Louse creeks are estimated at 15 to 50% (Chapter 2 and 4), while rates of denitrification observed in other studies range from 30 to 95% NO_3^- removal (Vidon and Hill, 2006; Davis et al., 2019). Potential to increase riparian denitrification rates suggests that observed stream NO_3^- yields could be reduced from their current levels of 5 to 18 kg N ha⁻¹ yr⁻¹ (Chapter 2).

Research embodied in this dissertation significantly enhances the framework of knowledge around the Soil-Water Nexus within the JRW agroecosystem and points to a number of future research opportunities.

1. The hydrologic isolation of the Moccasin terrace, such that all groundwater derives from infiltration on the terrace surface, provides a unique opportunity for landscape scale quantification of NO_3^- leaching. The hydrostratigraphy of

the terrace could be further characterized, potentially using ground penetrating radar or other geophysical techniques to enhance the map of depth to shale or to identify paleo-channels. The three years of landscape scale water and NO_3^- flux data presented here (Chapter 2) could be extended and enhanced with high frequency in-situ NO_3^- sensing and installation of flumes at stream sample sites. Higher resolution landscape scale water and N flux data along with better resolved hydrostratigraphy information could be coupled with detailed land use and weather information (Chapter 3) to test hypotheses about how hot moments and hot spots of water and N loss from soils manifest in landscape scale losses.

2. The role of macropores in deep percolation and leaching was not addressed in this work. Macropores could provide preferential flow paths for precipitation to bypass the soil matrix, exerting an important control on timing and magnitude of deep percolation. Macropores could affect the interaction of infiltrating water with soluble N from fertilizer and mineralized SON sources. Macropore structure and frequency could be similar across thickness of fines (z_f) or could vary systematically with z_f . Understanding of the degree to which macropores may affect patterns of deep percolation and leaching across z_f (Chapter 3) will be important to more effective predictive models of N dynamics in agricultural soils.
3. Simulation results indicate a steep inverse relationship between crop transpiration and z_f for relatively thin fine textured soils (Chapter 3). Given the

generally positive relationship between transpiration and crop yield, yield could be predicted for different weather years as a function of z_f . Different scenarios for input costs, commodity prices, z_f , and crop rotation could be combined in a model to generate economic returns and inform z_f thresholds below which economic returns are commonly negative. A model of this type could provide a useful framework for farmers to determine which land areas might be converted to perennial vegetation or farmed with lower fertilizer input and variable seeding rates to enhance profitability and reduce NO_3^- leaching.

4. Denitrification rates in soil are highly variable across time and space and are poorly constrained in the literature. Suppression of plant growth during fallow periods in annually cultivated fields provides a unique manipulative experiment to couple isotopic approaches, observed NO_3^- accumulation rates, and potentially N_2O and/or N_2 gas flux to clarify the links between nitrification and denitrification in predicting N losses from soils.
5. The notable differences in denitrification signals between Louse and Porter creeks begs for explanation of the controls on denitrification in these two riparian corridors. Observations of low denitrification rates in springs (flow over the surface) and almost complete denitrification in seeps (flow through saturated soil) suggest that quantifying the ratio of stream water sourced from springs versus seeps could partially explain denitrification differences between streams. Stream morphology and velocity characteristics associated

with channel gradient may also explain denitrification differences between streams. Preliminary assessment of channel gradient using aerial imagery and a digital elevation model indicated steeper gradient in Porter Creek (0.6%) than Louse Creek (0.5%), which could result in slower velocities and more benthic sediment deposition, facilitating more benthic denitrification. A coarse initial assessment based on aerial imagery also suggests that Louse Creek may be wider and more braided than Porter Creek.

6. Modeling work by Granger and Wankel (2016) suggests that the difference between $\delta^{18}\text{O}$ in NO_3^- and ambient water can explain differences in the slope of $\delta^{18}\text{O}$ versus $\delta^{15}\text{N}$ in residual NO_3^- with progressive denitrification. I saw this prediction strongly supported ($R^2 = 0.92$, $p = 0.04$) with four observations at a riparian groundwater site. Leveraging the occurrence of large variation in $\delta^{18}\text{O}$ in water within this system driven by snowmelt and the relatively stable $\delta^{18}\text{O}$ in NO_3^- in groundwater feeding seep sites provides an opportunity to make empirical observations to validate the modeling work by Granger and Wankel (2016).
7. Predicted increases in frequency of intense precipitation and seasonal shifts in precipitation with climate change are likely to exacerbate hot moments of deep percolation and NO_3^- leaching. Building on the modeling approach presented here (Chapter 3), hypothetical shifts in weather could be applied within simulations to identify potential shifts in patterns of deep percolation and NO_3^- leaching controlled by management and z_f . Understanding potential

future shifts in patterns of water and N use efficiency could inform research on alternative management strategies to mitigate deleterious effects of climate change.

This research has not altered the complexity of the wicked problems embedded within the Soil-Water Nexus, but it has contributed to the reduction of information uncertainty and has illustrated how the seemingly competing goals of viable crop production and protection of water resources may not be so incompatible. While increased understanding of how water and N move through semiarid agroecosystems is essential to address the soil fertility and water quality issues manifest in the JRW, action toward addressing these challenges cannot occur without engagement of the people poised to effect change. The tripartite Research-Outreach-Education mission of the land-grant university system provides a structure that is poised to accomplish this. While outreach via the traditional information dissemination pathways may be effective, more active community engagement approaches are likely to gain more traction (Prokopy et al., 2008; Busse et al., 2015; Jackson-Smith et al. 2018). The existing relationships and a history of trust between researchers and the farming community of the JRW may provide a foundation for future outreach to help convert scientific findings into more widespread management change. More generally, productive conversations between practitioners and scientists to identify actionable solutions to wicked problems are increasingly critical in the face of a growing human population and a changing climate.

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