GROUNDWATER NITRATE TRANSPORT AND RESIDENCE TIME IN A VULNERABLE AQUIFER UNDER DRYLAND CEREAL PRODUCTION

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TABLE OF CONTENTS

TABLE OF CONTENTS – CONTINUED

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES - CONTINUED

Figure Page

ABSTRACT

Selection of agricultural management practices to reduce nitrate leaching from soils can only be successful if both nitrate loading rates from soils to shallow aquifers and groundwater residence times are quantified. Elevated nitrate concentrations in shallow unconfined aquifers are commonly observed in agricultural areas as a result of increased N inputs. In the Judith River Watershed (JRW) in central Montana, USA, notably high nitrate concentrations in groundwater and stream water have exceeded the U.S. EPA drinking water standard of 10 mg L^{-1} for at least two decades. This large (24,400 ha) watershed drains immediately into the Missouri River, a tributary of the Mississippi River. Over an eleven month period in 2012, we measured groundwater and surface water nitrate concentrations across a hydrologically isolated strath terrace. We use the resulting data to constrain nitrate accumulation dynamics in the shallow aquifer. Nitrate is relatively conservative in this location, as it is high in groundwater (17.57 +/- 4.29 mg L^{-1}; all groundwater samples pooled together), and remains high in streams and springs that drain the landform (15.67 +/- 9.45 mg L^{-1}; all surface water and spring samples pooled together). We use a numerical model to simulate the character of nitrate accumulation in the aquifer as a whole, in order to evaluate how the entire period of cultivation has contributed to current nitrate concentrations, and begin to predict response times for effects of land use change. We consider the effect of groundwater residence time and travel time on nitrate loading using particle tracking in a three dimensional model aquifer. We find no correlation with nitrate concentrations in groundwater and emerging surface waters, and suggest approaches for improving both the geometry of the model and the selection of sites in future work. Overall, our results imply that groundwater residence times are several decades at most, suggesting that similar timeframes will be needed to reduce overall nitrate concentrations in groundwater and emergent streams to below drinking water standards. Preliminary evaluation of several management scenarios suggests that both increased fertilizer use efficiency and rotational strategies may be needed to prevent the loss of soil N to groundwater.

GENERAL INTRODUCTION

Management of soil fertility for sustained agricultural production is essential for the well-being of both rural communities and local economies in the western US and globally. Often, nutrient management inefficiencies can result in increased nitrogen loading in ground and surface water, now frequently associated with agricultural land use (Bohlke 2002; Burow et al. 2010; Canfield et al. 2010; Liao et al. 2012; Nolan and Hitt 2006b; Scanlon et al. 2005). In the agricultural region of the Judith River Watershed in central Montana (Figure 1), nitrate in groundwater and surface water in many locations currently exceeds the U.S. EPA drinking water standard of 10 mg L^{-1}. Understanding how this has occurred requires improved understanding of groundwater residence times and seasonal nitrate dynamics, as well as assessment of the broader influence of land use history on N dynamics. Shallow unconfined aquifers in the region are vulnerable to contamination with dispersed recharge from infiltration of rainfall through thin, gravelly soils. This work targets an isolated but spatially extensive landform (strath terrace, 24,400 ha) supporting a shallow, unconfined aquifer with chronically high and rising nitrate concentrations. We use measured residence times, landform water balance and nitrate concentrations in groundwater and surface water to begin to (1) evaluate the influence of land management practices on the landform scale N balance over the past 100 years and (2) predict the rate of aquifer response to land management practices targeting improved drinking water quality.

LITERATURE REVIEW

Water Quality in Agricultural Landscapes of the Semi-arid Northern Great Plains and Montana

Changes in groundwater recharge as well as soil and aquifer solute chemistry have resulted from cultivation of grassland ecosystems (Bohlke 2002; Custer 1975; Davidson and Ackerman 1993; Scanlon et al. 2005). Water quality issues including elevated nitrate concentrations have been observed in agricultural regions throughout the United States (Bohlke 2002; Burow et al. 2010; Harter et al. 2002; Puckett et al. 2011; Puckett 1994; Schmidt and Mulder 2010), including cultivated systems in the northern great plains of the U.S. Though nitrogen (N) contamination is receiving attention, many soil-groundwater systems within different climate and cultivation regimes remain poorly understood

Nitrate (NO_3^--N) is a common contaminant often found in shallow groundwater below agricultural land, and has received increasing national attention because of its environmental and human health effects (Carpenter et al. 1990; Ward et al. 2005). Nitrate is highly labile and part of complex N cycling between soils, aquifers, and streams (Canfield et al. 2010; Hedin et al. 1998; Nolan 2001; Puckett et al. 2011); aquifer oxidation state, aquifer stratigraphy, microbial processes and electron donor availability all control the fate of nitrate within a groundwater-surface water system (Burow et al. 2010; Galloway et al. 2004; Hedin et al. 1998; Liao et al. 2012; Nolan and Hitt 2006b) . Thus differences in irrigation, climate, and cultivation regimes add complexity to biogeochemical N cycling.

Excess nitrate in drinking water has been shown to cause methemoglobinemia in infants and has potential links to several types of cancers and birth defects (Ward et al. 2005). Private wells are often not tested regularly for nitrate, though concentrations above the U.S. EPA drinking water standard (10 mg L^{-1} nitrate-nitrogen) are often found in agricultural areas with high N input, oxic subsurface conditions, and shallow groundwater (Burow et al. 2010; Ward et al. 2005). Nitrate contamination through agricultural land use practices is of particular concern in areas with thin soils, shallow unconfined aquifers, well-drained soils and high N inputs (Burow et al. 2010; Green and Bekins 2010; Liao et al. 2012; Lindsey et al. 2003; Nolan and Hitt 2006a; Paschke et al. 2008a; Puckett et al. 2011; Puckett 1994; Ward et al. 2005). Additionally, high nitrate in agricultural water resources represents an economic loss for farmers (Lewandowski 2008), as well as a potential target of environmental regulation.

Cereal grain production is economically critical to the northern Great Plains region; however these systems have received less specific attention with respect to water quality issues, likely due to the small population and the prevalence of non-irrigated systems. However, the areal extent of these systems is considerable – in Montana, 2.3 million ha were harvested for wheat in 2012, accounting for 6% of the land area of the state; in that same year, the state of Montana produced 8.6% of U.S. wheat, yielding $1.7 billion in revenue, and 86% of that production was non-irrigated (USDA NASS). Montana is the third-largest exporter of wheat by U.S. state, exporting 2.27 million bushels or nearly $900 million of wheat in 2012, around eighty percent of which was exported to Asian countries including Japan (50% of exported) as well as Taiwan, South

Korea, the Philippines and Indonesia (Montana Department of Commerce Office of Trade & International Relations 2011; USDA Economic Research Service 2011).

The need is clear for a better understanding of non-irrigated agricultural environments. The hydrologic and biogeochemical drivers of water quality impairment in non-irrigated agricultural systems need to be better understood to best inform agricultural management and protect local water quality from further degradation.

Changing Dynamics of the Global N Cycle

Nitrogen (N) is essential for plant growth and biotic function and is a major constituent of the Earth's atmosphere and a minor yet important constituent in the Earth's lithosphere, biosphere, and hydrosphere. World population increases have driven food demand and major resulting changes in the Earth's N cycle through crop production (Canfield et al. 2010; Smil 1999). Humans have altered the global N cycle by developing technology capable of reducing atmospheric N_2 gas into NH_4^+ (ammonium), a plant available form of N used widely in fertilizers, which is readily converted into NO_3^- (nitrate), an inorganic form of N that is highly soluble, thus prone to leaching through the subsurface (Canfield et al. 2010).

Fertilizer input, biological nitrogen fixation, and turnover of organic waste combined have doubled N inputs into the terrestrial N cycle over the past 50 years in response to food demands of a growing population (Canfield et al. 2010; Galloway et al. 2004; Smil 1999). It is widely known that inputs of nutrients to surface waters, especially phosphorus and nitrogen are high in agricultural areas, though land use and conservation changes can mitigate the pollution (Carpenter et al. 1990). Fertilizer use efficiency, or the rate that fertilizer is taken up by plants relative to the total amount applied, is estimated as 40-70% depending on agronomic practices (Canfield et al. 2010; Sebilo et al. 2013; Smil 1999). Of the residual fertilizer N that is not taken up by the crop on an annual basis, an estimated 40% may reach water resources, with the balance stored in soil (10-15%) or lost to the atmosphere (10-50%) (Engel et al. 2011; Sebilo et al. 2013; Smil 1999). Inefficiency in N use through atmospheric loss provides a set of problems and challenges relating to greenhouse gas concentrations in the atmosphere (Canfield et al. 2010); the resulting global changes have substantial secondary effect on world water resource supply and quality, including a potential decrease in water supply in the western United States (Intergovernmental Panel on Climate Change 2013). By addressing a case study of N dynamics in a region of chronic water quality issues, this work seeks to provide insight about hydrological and biogeochemical controls on water contamination with nitrate in a non-irrigated agricultural system.

Residence Time Determination and Usefulness

A residence time is the average time material spends in a reservoir. Here we conceive of groundwater residence time as the average time water spends in the shallow aquifer, or the time between recharge of water into the aquifer through infiltration of rainfall and discharge of water from the aquifer in streams (Puckett et al. 2011). Determination of mean groundwater age coupled with other chemical and isotopic analyses within groundwater sources can constrain the expected response time in ground or surface water chemistry to a land management change (Bohlke 2002). Stable and radiogenic isotopic tools can be used to date young groundwater, including tritium, chlorofluorocarbons (CFC's), Sulphur-35 and Radon-222 (Plummer 2005). Bohlke et al., (2007) found short mean residence times on the scale of 30 years in a semi-arid agricultural system with vulnerable aquifers near the North Platte River in Nebraska. In the South Platte River basin, another semi-arid agriculturally dominated system in the Western US, groundwater age was shown to increase with distance along flow paths as well with depth in the aquifer from 12 – 31 years (Paschke and Mashburn 2008). Tesoriero et al. (2013) showed that groundwater residence times may create a lag in transformation of surface water nitrate loading following a land management change. In evaluating the influence of land use on groundwater nitrate dynamics, a key step is to quantify groundwater residence time.

Judith River Watershed, Montana, USA

In the Judith River Watershed of central Montana, nitrate-N concentrations higher than the U.S. EPA standard of 10 mg L^{-1} have been documented since the late 1980's (Bauder et al. 1991) and are continuing to rise (Figure 3) yet soil-groundwater connections are not well understood in this area. Alluvial fans and fluvial terraces in the JRW support soils with shallow gravel contacts (< 1 m) but high fertility due to landform age and stability, and the long-term presence of grassland ecosystems. These soils have been cultivated for dryland cereal production since about 1900, and commercial N fertilizer has been applied since the early 1960's (Bauder et al. 1991; de Yong and Ames 2011). Shallow, unconfined aquifer materials in this context are coarse gravel and sand, with high hydraulic conductivity generally expected, and depths up to 150 m thick (Montana Bureau of Mines and Geology 2012; Perry 1933). These shallow, unconfined aquifers are perched on underlying Cretaceous age shales (Vuke et al. 2002) and are recharged by infiltrating waters that may readily transport solutes such as nitrate without substantial attenuation in an unsaturated zone. As a result, response times between soil process and aquifer recharge are expected to be short, on the order of decades or less.

Here we focus on a strath terrace in the JRW-- the Moccasin terrace (MoT) -- that is isolated from mountain front stream recharge by incision at its head (Figure 2), suggesting that recharge of its shallow aquifer occurs mainly by dispersed infiltration through soils. We evaluate the water and nitrate balance reflected in groundwater and surface water and at the scale of the entire landform (24,400 ha) to assess the expected response time of groundwater chemistry to land management and to better understand potential rates of accumulation of aquifer N in terms of aquifer residence time and historic land use. This assessment will help to understand means the by which the shallow aquifer has accumulated ~15-20 mg L^{-1} nitrate and inform future land management in other dryland cultivated areas.

Goals of Thesis Work

Through improved understanding of the hydrologic controls on surface water and shallow groundwater connection in an alluvial aquifer, my thesis work sought insight about (a) the degree to which nitrate found in groundwater and surface water is a result of farm nitrogen leaching loss and, (b) how quickly a change in management practice might be expected to improve water quality.

In order to begin to understand the relationship between hydrology and biogeochemical sourcing of nitrate, I collected and analyzed groundwater and surface water samples during 11 months in 2012, with goals of understanding 1) groundwater residence time, 2) changes in nitrate seasonally and 3) spatial variation of nitrate concentrations across the study area. I collected and analyzed over one hundred samples from streams and wells on the Moccasin landform. Based on averages and the long term record in a monitoring well on the landform, I used a numerical mass balance model to interpret the results of those measurements in the context of the landform and shallow aquifer as a whole based on a representation aimed at understanding the general nature of the aquifer system, and to begin to estimate potential future nitrate concentrations as a function of proposed management changes. Because nitrate concentrations varied more among locations than seasonally, I used the location of seeps and springs along with mean nitrate concentrations at each location to test the degree to which a simple groundwater flow model could explain the variation in concentrations among locations on the landform.

CHAPTER THREE

GROUNDWATER NITRATE TRANSPORT AND RESIDENCE TIME IN A VULNERABLE AQUIFER UNDER DRYLAND CEREAL PRODUCTION

Contribution of Authors and Co-Authors

Manuscript in Chapter 3

Author: Christine Miller

Contributions: Performed field data collection and laboratory analysis, developed ideas and compiled ideas into this manuscript.

Co-Author: Dr. Stephanie Ewing

Contributions: Created research questions and goals, developed methodology on all fronts, developed ideas, edited and compiled ideas into this manuscript.

Co-Author: W. Adam Sigler

Contributions: Developed field data methodology, performed field data collection, developed and contributed ideas on all project fronts.

Co-Author: Dr. E. N. Jack Brookshire

Contributions: Developed mass balance modeling methodology, data analysis ideas and gave advice on data representation.

Co-Author: Dr. Clain A. Jones

Contributions: Developed mass balance modeling methodology and suggested data source. Provided knowledge and information about realities of agricultural systems.

Co-Author: Dr. Douglas Jackson-Smith

Contributions: Assisted in sourcing county and state level data for nitrogen mass balance modeling and area information.

Co-Author: Dr. Gary S. Weissmann

Contributions: Developed conceptual model of the landform, assisted in groundwater flow modeling and apparent age/residence time data interpretation.

Manuscript Information Page

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Abstract

Groundwater nitrate concentrations in the Judith River Watershed (JRW) of central Montana, USA commonly exceed the U.S. EPA drinking water standard of 10 mg L^{-1}. Shallow, perched unconfined aquifers in the JRW underlie thin, gravelly soils managed for dryland cereal production, and are vulnerable to nitrate contamination. Selection of agricultural management practices to reduce nitrate leaching from soils can only be successful if both nitrate loading rates from soils to shallow aquifers and groundwater residence times are quantified. To characterize residence times and nitrate loading rates at the scale of large landforms hosting vulnerable aquifers in the JRW, we identified an extensive strath terrace isolated from mountain front stream recharge and assessed groundwater and surface water nitrate concentrations and water levels over an eleven-month period. The resulting time series suggests that shallow groundwater and surface water levels respond rapidly (within days) to increased recharge during the wet spring months, but with limited perturbation of solute concentrations reflecting the longer term accumulation of nitrate in the aquifer. Similar concentrations in surface water (15.67 +/- 9.40 mg L^{-1} nitrate-N) and groundwater (17.57 +/- 4.29 mg L^{-1} nitrate-N), suggest limited loss of N to transformation within the aquifer or in streams that drain the shallow aquifer. Water table samples collected in late summer 2012 had $^{3}H/^{3}He$ ages of ≤ 1 year, possibly reflecting aquifer stratification. A simplified water balance based on discharge measurements and estimated aquifer volume suggests mean residence times of decades for the entire aquifer volume, a result that is consistent with the large total quantity of nitrate present in the aquifer (~5 x 10^{6} kg N or 220 kg N ha-1) based on observed

concentrations. A numerical mass balance model for historic nitrate accumulation in the aquifer at the scale of the entire landform, over the period of cultivation and fertilization (since ~1900) suggests that a substantial portion of groundwater nitrate is likely derived from initial and ongoing mineralization of native soil organic matter following cultivation, and that changes in nitrate leaching with realistic changes in agricultural management practices could lead to reduced reduce groundwater nitrate concentrations over a timeframe comparable to the aquifer residence time, here estimated as decades. However, a combination of rotational strategy (replacing fallow with a third year cover crop) and increased efficiency (lower proportions of soil nitrate leached when crops are present) will be required to attain levels below the drinking water standard of 10 mg L^{-1} within decades, particularly in light of anticipated effects of climate change. Results from a simple groundwater flow model suggest that variation in nitrate-N concentrations among locations on the landform is partly related to differences in mean flow path length reaching those locations, rather than being a reflection of only land use practices in a local area.

1.0 Introduction

Agriculture has transformed the global nitrogen cycle, and the consequences of that transformation are now receiving increased attention as one of the foremost challenges to human and ecosystem health globally (Canfield et al. 2010; Rockstrom et al. 2009; Tilman et al. 2002). Elevated groundwater nitrate is commonly observed in agricultural areas with shallow unconfined aquifers; thin, well-drained soils and high N inputs (Burow et al. 2010; Green and Bekins 2010; Liao et al. 2012; Lindsey et al. 2003; Nolan and Hitt 2006b; Paschke et al. 2008b; Puckett et al. 2011; Puckett 1994; Schmidt and Mulder 2010; Ward et al. 2005). Yet actual nitrate leaching rates are poorly constrained because they depend on both management choices and regionally variable circumstances of landscape development, internal soil processes and hydrology (Bohlke 2002; Cassman et al. 2003; Puckett et al. 2011). To effectively address the mounting problem of elevated groundwater nitrate associated with agricultural systems requires approaches that efficiently combine understanding of landform scale groundwater dynamics with fundamental controls on nitrate leaching to aquifers, to better understand how to limit nutrient loss to water resources.

The semi-arid, primarily non-irrigated systems of the northern Great Plains (Montana, North Dakota, and South Dakota) produced 28% of the US wheat crop in 2012; in that same year, Montana alone produced 8.6% of U.S. wheat (USDA NASS). Because limited work has been done to evaluate N contamination of groundwater in these systems (Burow et al. 2010), we aim to better understand nitrate dynamics in local water resources in order to provide information to help land and nutrient management on a larger scale. The Judith River Watershed (JRW) is a major agricultural watershed within the northern Great Plains and drains to the Missouri River at its outlet, which eventually drains into the Mississippi River. This work can serve as a model for dryland farming regions draining into the Mississippi River. The JRW in Central Montana (Figure 1), is a region of chronic elevated nitrate in groundwater (Bauder et al. 1991) and vulnerable aquifers (Schmidt and Mulder 2010). Nitrate levels in a monitoring well completed in a shallow aquifer in the JRW have doubled in the last 20 y, rising at a rate of 0.70 mg L^{-1} y^{-}

^{1} (Figure 3; (Montana Bureau of Mines and Geology 2012)). Here we focus on an isolated but extensive landform, referred to as the Moccasin terrace (MoT) within the JRW and use nitrate concentrations and water balance in wells and streams, combined with measures of groundwater residence time, to constrain the relationship between landform-scale dispersed recharge and biogeochemical sourcing of nitrate in the shallow, perched aquifer. We evaluate these data using a combination of (a) residence time assessment with $^{3}H/^{3}He$ and the relationship of aquifer volume to total discharge; (b) a longer term mass balance model for the aquifer as a whole to evaluate temporal trends and estimate response times in ground or surface water chemistry to past and future changes in land management; and (c) a groundwater flow model to begin to assess the contribution of flow path length to nitrate accumulation in groundwater, and the resulting variation in observed concentrations with location on the landform. We hypothesize that nitrate in ground and surface water is similar, given the direct connection visible on the landform with seeps and springs draining the aquifer, and a seasonal change in aquifer and stream water nitrate, given thin soils and shallow groundwater. We pose the question, what kind of time scale will ground and surface water nitrate be seen on if a land management change that can improve water quality is implemented?

The goal of this study is to better understand the time scale of nitrate loading to vulnerable aquifers in the Judith River Watershed, in order to inform predicted outcomes of management choices thought to reduce nitrate leaching. We hypothesize that nitrate levels reflect increased fertilizer inputs and mineralization in soils, with negligible attenuation and aquifer residence times long enough to allow for nitrate accumulation to current elevated levels. Accordingly, we aim to understand seasonal and spatial nitrate patterns to gain an understanding of how prevalent high nitrate is on the terrace and to interpret residence time and groundwater age information. We can estimate the rate at which water quality effects of a land management change may be seen by first understanding the residence time of water and nitrate in the shallow aquifer, combined with information about changes in nitrate loading rate due to land management practices. To accomplish this goal, we sought to work at the scale of large fluvial strath terraces and alluvial fans that dominate the cultivated area of the Judith River Watershed (Figure 1). We predict that at this scale, in this system, nitrate concentrations in groundwater and surface water will be persistently high and similar in magnitude.

2.0 Methods

2.1 Study Design

Strath terraces in the JRW are formed from marine shales with high clay content, overlain by gravels tens of meters thick and more recent loess (Perry 1933). As a result of this stratigraphy, these landforms tend to host shallow, perched aquifers. Although absolute ages of these landforms have not been determined, they host gravelly but fertile soils derived from the long-term presence of grassland ecosystems following loess deposition that likely dates to retreat of the continental ice sheet to the north near the end of the Pleistocene epoch (10 – 20 kya) (Davis et al. 2006). For this work, we focus on a well preserved fluvial strath terrace at Moccasin, Montana (Figure 1), mantled by gravels <30 m thick and loess derived calcareous soils developed in 30-100 cm of fines (silt loam to clay loam) over gravel (USDA NRCS 1967). A shallow, unconfined aquifer is present with water table depths of 0-10 meters from the surface, and saturated thickness of 1.5 –

8.2 meters based on records for 18 well logs (MBMG 2012; Table 1). This alluvial aquifer is underlain by shale, and given the perched nature of this aquifer, water discharges from the aquifer from springs and seeps along this gravel/shale interface. A deeper confined aquifer is present at ~490 meters in the Kootenai sandstone (Vuke et al. 2002) and is accessed by two deep artesian wells on the landform (MBMG 2012). Our field observations suggest that this areally extensive (24,400 ha) landform was isolated by downcutting of the Judith River and its tributaries on all sides (Figure 2). Distinct spring and seeps drain the landform, making it an ideal target for groundwater and landform scale mass balance modeling with a uniquely closed hydrologic system (as the only aquifer recharge is in the form of precipitation and discharge in springs and seeps draining to stream), yet with scalable dryland cereal farming agricultural land use.

To understand the apparent steady increase in groundwater nitrate levels (Figure 3), we sampled groundwater and surface water at ten locations on the MoT during 2012, with higher frequency sampling during the rising and falling limbs of the wet-season (spring) hydrograph to capture seasonal fluctuations in nitrate, as well as differences in nitrate among locations on the terrace. Figure 2 shows the locations of both stream and well sampling locations. In order to derive a water balance for the landform and assess nutrient loading, we monitored discharge in the two primary streams draining the landform.

2.2 Site Description

At the Montana State University Central Agricultural Research Center, an agricultural experiment station centrally located on the MoT, mean annual temperature is

6.67° C, while mean annual precipitation is 36.0 cm (MSU CARC 2012 1909-2012). Convective storms drive early and mid-summer precipitation in the area, resulting in some variation of rainfall levels across the terrace. Total annual modified Penman Monteith potential evapotranspiration (PET) is 62.7 cm y^{-1} (average from 2002-2012) when a winter cereal crop is present, and possibly up to ~0.2 mm hr^{-1} during the growing season for fallow depending on soil hydrologic potential and assuming bare soil conditions (Bureau of Reclamation 2013; Vanderborght et al. 2010). The MoT slopes generally towards the east with an incline ~0.61%. Soils generally become more shallow in terms of depth to gravel in the downslope direction, with deeper fines in the upslope direction (south and west) in areas related to derivation from the underlying shale (USDA Natural Resources Conservation Service 1967). Small grain production (primarily spring and winter wheat) is the dominant land use on MoT, although in Judith Basin County as a whole, livestock operations (241 farms) were nearly equal to wheat production (246) in 2007 (USDA National Agricultural Statistics Service 2007). On the MoT, several farming operations include livestock, but there are no confined animal feeding operations (CAFOs). Cultivated area on the MoT is currently estimated at 21,716 ha based on 2006 National Land Cover Data (U.S. Geological Survey 2006). Grain production is almost entirely non-irrigated; only one center pivot irrigation system was in use on the landform at the time of the study (based on 2011 aerial photo interpretation (USDA FSA 2011)). Since the 1980s, almost all producers in the watershed have practiced reduced tillage due to high wind erosion in the area (Jackson-Smith and Armstrong 2012; Wichman 2012). The typical crop rotation strategy on MoT is winter wheat-spring cereal-fallow, although fallowing historically was every other year until about 1985 (USDA Census of

Agriculture; D. Wichman, personal comm.; C. Jones, personal comm.). With reduced tillage, fallowing is accomplished through herbicide application.

2.3 Water Sampling and Discharge Measurements

To understand seasonal variability in nitrate leaching and transport prior to understanding residence time and longer scale aquifer processes, water samples were collected at stream and well sites on or near the MoT (Figure 2). Site elevations for streams ranged from 1172 to 1347 m above mean sea level. We established ten water sampling locations: seven surface water locations, two wells, and one spring. Weekly sampling of these ten surface water sites scattered across the terrace took place during the wettest months of May and June; seven other sampling trips occurred approximately monthly. Stream flow point discharge measurements were made using a factory calibrated Marsh McBirney Flo-Mate 2000 flow meter. Discharge was calculated based on measures of water height and flow rate (at 40% of water height) at ten equidistant points across the stream sampling location (Dingman 2002). Water level heights in wells were recorded using absolute pressure transducers and calibrated through point measurements with an electronic tape. An atmospheric pressure logger was installed at one well to correct for ambient pressure. Wells were purged one full well casing before sampling except at MSU CARC Shallow well (CRC), which was purged as adequately as possible before water level was drawn below pump elevation. At two well sampling locations (“M-1” and “CRC”), the water table depth below the ground surface was measured before and after purging the well, and pressure loggers were installed at the beginning of the sampling season. Tubing used for pumping sample water from all sites was flushed with source water at each site to avoid cross-contamination among sites.

Temperature, dissolved oxygen, pH, conductivity, and barometric pressure were measured at each sampling point using a YSI-556 (YSI, Inc.) that was calibrated daily. Water samples for nitrate and tritium were collected in HDPE plastic bottles. Water samples for noble gas analysis were collected using stainless steel diffusion sampler devices from University of Utah Dissolved and Noble Gas Laboratory. All bottles used were triple rinsed with sample water. All samples as well as field blanks were filtered at the sampling location using 0.45 µm capsule filters (GeoTech). Duplicate samples of a groundwater well maintained by the Montana Department of Agriculture (M-1) were collected beginning in June, 2012 and used for quality assurance purposes, along with laboratory blanks. Samples were stored on ice for transport; upon returning to the laboratory, nitrate samples were frozen prior to analysis (up to 52 weeks), while tritium and noble gas samples were stored at room temperature. Nitrate test strip readings (Hach Company) were recorded at each sampling site.

Water samples were analyzed for nitrate using cadmium-reduction and colorimetry on a Lachat flow injection analyzer at Montana State University (Zellweger Analytics Lachat QuikChem FIA+, 8000 Series). Check standards ranging from 0-10 mg L^{-1} were included at the beginning and end of each run as well as every 10 to 36 samples within a run. Duplicate samples of the M-1 well and field blanks were evaluated, suggesting added uncertainty of up to 0.02 ppm,. A SPEX CertiPrep NO_3^--N 1000 mg L^{-1} external standard was used and diluted to 5 ppm and 1 ppm. Both SPEX standards were within 0.2 ppm, and the 1 ppm SPEX standard was usually within 0.02 ppm. All samples were tested with a nitrate meter and diluted to 7 ppm or less before instrumental analysis. Uncertainty in nitrate measurements was <0.10 ppm based on sample preparation error (dilution to within the range of the calibration curve), and calibration curve error (linear fit to five standards, 0-10 mg L^{-1}).

2.4 Groundwater Residence Time

Tritium abundance was used as a preliminary indicator of groundwater residence time (Bohlke 2002; McMahon et al. 2011). Tritium samples were collected three times (January, March and August) during 2012 from two shallow wells, a deep artesian well, a spring discharging from the shallow water table and two surface water sites (Table 2). Based on these results, two samples were collected for noble gases and $^{3}H/^{3}He$ age assessment in August 2012 (Plummer 2005). The noble gas samplers were pressurized to seal following equilibration with source water after a minimum of 24 hours. Unfiltered tritium samples and unfiltered noble gas samples in sampling devices were shipped to the University of Utah Dissolved and Noble Gas Lab in Salt Lake City, Utah. Analysis of ^{3}He and ^{4}He was performed on a magnetic sector-field mass spectrometer (Mass Analyzers Products, Model 215-50). Analysis of noble gases other than He, in order to to validate the sample ^{4}He data, was performed on a quadrupole mass spectrometer (Stanford Research SRS, Model RGA 300). For analysis of tritium, ^{3}He was quantified after several months of ingrowth and used to infer initial ^{3}H abundance. For noble gas samples, the observed $^{3}He/^{4}He$ ratios were used to correct the $^{3}H/^{3}He$ ratio for tritiogenic ^{3}He ($^{3}He^{*}$) assuming a lithogenic $^{3}He/^{4}He$ ratio of 2.77 x 10^{-8} (Solomon et al. 1995). A closed-equilibration model incorporating noble gases (Kr, Ar, Xe, Ne) was used to correct for excess air in the water sample, and the observed $^{3}H/^{3}He^{*}$ ratio was used to calculate the $^{3}H/^{3}He^{*}$ ratio at the time of collection. Apparent ages were calculated using Equation 1:

$$t = \lambda^{-1} \ln\left(\frac{\left[{}^{3}He^{*}\right]}{\left[{}^{3}H\right]} + 1\right) \qquad (1)$$

where *t* represents time, $[^{3}He^{*}]$ represents the tritiogenic ^{3}He concentration in tritium units, $[^{3}H]$ represents the tritium concentration in tritium units, and λ^{-1} represents the decay constant of tritium based on a half-life of 12.4 years (Solomon et al. 1995; University of Utah Dissolved and Noble Gas Lab 2012).

2.5 Groundwater Flow Modeling

Based on our starting hypothesis, we predicted that nitrate concentrations would accumulate with travel time in the aquifer, resulting in observed concentrations that would vary with groundwater movement and aquifer travel times. Therefore we developed a generalized groundwater transport in the MoT aquifer was modeled in GMS (Aquaveo, Version 9.0.4) using MODFLOW for groundwater flow and MODPATH for advective groundwater particle tracking. By building a simple groundwater flow model, we are able to look at advective travel times and assess these in the context of the scale of residence time and groundwater age data gleaned from other methods, and assess the longer term nitrogen mass balance land use information in context of these residence time/groundwater age/groundwater travel time data.

2.6 Nitrogen Mass Balance

In order to better understand groundwater nitrate concentrations and general aquifer processes on the landform as a whole over the past several decades, we used a numerical mass balance model to evaluate the influence of nitrate inputs to and losses from the shallow aquifer as a whole (kg N y^{-1}) during the period of cultivation and fertilization (1900 to present; Figure 4). Cultivated area for each Census of Agriculture between 1969 and 2007 was derived from public records for Judith Basin County, with proportion of fallow estimated using area of land harvested compared with area of land cultivated (USDA Census of Agriculture 2007).

Given one-year time-steps, we first make the simplifying assumption that the aquifer volume (V_A, m^3 y^{-1}) is constant (steady state) with recharge water volume (R_W, m^3 y^{-1}) equal to discharge water volume (D_W, m^3 y^{-1}):

$$R_w = D_w \qquad (2)$$

The residence time of the water in the aquifer can be expressed as:

$$t = \frac{V_a}{D_w} \qquad (3)$$

This steady state assumption for the water balance is coupled with N dynamics through aquifer concentration and loss of N in discharge, as discussed below.

The aquifer volume was estimated using Montana well log data and groundwater level measurements (Table 1). R_w was estimated as described in the groundwater modeling section, above, and was consistent among years at the long term average of 36.0 cm yr^{-1}. R_w likely increased upon initial cultivation and with increases in cultivated area over time (Scanlon et al. 2005).

In the model for the MoT landform, we focus on two pools: soil nitrate-N on an area basis, (S_N, kg N ha^{-1}) and groundwater nitrate-N for the entire aquifer (G_N, kg N). S_N reflects inputs of fertilizer (F_N, kg N ha^{-1} y^{-1}), net mineralization (M_N, kg N ha^{-1} y^{-1}), losses through crop yields (Y_N, kg N ha^{-1} y^{-1}), and non-harvested biomass uptake into roots and stubble that are not taken off in crop yield (B_N, kg N ha^{-1} y^{-1}). The fertilizer nitrate-N term (F_N) is equivalent to the effective fertilizer applied, assuming complete conversion to nitrate and accounting for 5% volatilization loss upon application (Engel et al. 2011; Engel and Jones). Fertilizer inputs were determined from yearly data from the U.S. Agricultural Census and state fertilizer sales reports (USDA 2007; de Yong and Ames 2011). Fertilization with N had begun but was limited in Montana in the 1950's (US Department of Commerce 1954). Fertilizer input rates are consistent with application rates reported for 2013 by several growers in the watershed: ~60-70 kg ha^{-1} (Jones 2012, pers. comm.). We assume that all fertilizer N is converted to nitrate N or taken up by the crop, and that leaching occurs as nitrate-N. Yield data were retrieved from the USDA National Agricultural Statistics Service (NASS) for non-irrigated wheat in Judith Basin County, Montana (USDA National Agricultural Statistics Service). In a scenario testing peas instead of fallow, pea yields (bu ac^{-1}) were assumed to be half those of wheat.

Wheat yield nitrogen was calculated using a test weight of 60 lbs bu^{-1}, a 12% protein concentration and a protein to N ratio of 5.7 (Jones, personal communication). Peas were assumed to have a yield that is 50% of that of wheat (2007 wheat yield used (USDA National Agricultural Statistics Service)) and no fertilizer applied. A similar test weight and protein:N ratio to that of wheat was used, though protein concentration was assumed to be 21.6%. Although the use of peas is forecasted to be potentially beneficial to groundwater nitrate contamination, in the year following a pea rotation a reduced wheat yield could possibly be seen due to water or N stress if climatic conditions are below average precipitation (John et al. 2013).

Leaching We assume that all fertilizer N is converted to nitrate N or taken up by the crop, and that leaching occurs as nitrate-N.

Additionally, leaching from the root zone is represented as a proportion (k_L) of available nitrate-N in cropped land:

$$\frac{dS_{N(cropped)}}{dt} = F_N + M_N - Y_N - B_N - k_{L(cropped)} S_{N(cropped)} \quad (4)$$

Soil nitrate-N for only the fallowed proportion of the MoT landform in a given year is represented by only net mineralization and leaching of available nitrate through the root zone:

$$\frac{dS_{N(\text{fallow})}}{dt} = M_N - k_{L(\text{fallow})} S_{N(fallow)} \quad (5)$$

On the MoT, water tables are generally shallow (0-10 meters) with limited storage potential below the rooting zone and above the water table. In zones of deeper fines with high clay content, storage in these non-irrigated systems may occur at depths as shallow as 1 m over the course of a year based on our observations of soil nitrate pools with depth (Ewing et al. 2013a; Ewing et al. 2013b). Because our focus here is groundwater nitrate, we make the simplifying assumption that annually the fraction ($k_{L,cropped}$ or $k_{L,fallow}$) of nitrate-N that is leached from soil reaches the water table within a year as recharge (R_N; kg N y^{-1}):

$$R_N = R_{N(\text{cropped})} + \mathrm{R}_{N(\text{fallow})} \qquad (6)$$

$$R_{N\,(\mathrm{cropped})}(t) = S_{N\,(\mathrm{cropped})}[(\mathrm{k}_{\mathrm{L(cropped)}})]\,\mathrm{X}_{\mathrm{cropped}} \qquad (7)$$

$$R_{N\,(\mathrm{fallow})}(t) = S_{N\,(\mathrm{fallow})}[(\mathrm{k}_{\mathrm{L(fallow)}})]\,\mathrm{X}_{\mathrm{fallow}} \qquad (8)$$

where $X_{cropped}$ is the fraction of the cultivated area that is cropped and X_{fallow} is the fraction of the cultivated area that is fallow. Estimates of the nitrate leaching fraction (k_L) relative to total soil N pool range from 2% to 60%, (Canfield et al. 2010; Liao et al. 2012), with an estimated 4% to 29% for non-irrigated crops in a location with higher N application rates and likely much thicker soils (Liao et al. 2012). In the model we use N leaching fractions of 0.4 for fallow land and 0.1 for cropped land (Table 6).

In general, limited soil water storage exists on the Moccasin terrace because the finer textured upper horizons of soils are relatively shallow (40-150 cm) over contacts with coarse material (>35% gravel, cobbles or larger) (USDA Natural Resources Conservation Service 1967).We assume that all groundwater nitrogen is gained and lost as nitrate-N in recharge and discharge, respectively, and that there is no lag time in the vadose zone between leached soil nitrate and recharged nitrate.

We estimate annual deep percolation of water from soils based on a one-dimensional modeling approach using daily time steps to assess the effects of rainfall and Penman Monteith PET (Sigler et al. 2012). Using this approach and assuming a uniform 60 cm thickness of soil fines, we infer that the cropped leaching fraction of water is 8-40%, while the fallow leaching fraction is likely much higher given no transpiration and an increase in evaporative demand (Vanderborght et al. 2010). We estimate up to twice as much precipitation could be leached (16-80%) during summer fallow with tillage, while no-till cropping has been shown to increase the water storage capacity of the soil

(Peterson et al. 1996). Hence the transition to reduced tillage and less frequent fallow has likely decreased recharge and increased groundwater residence times in recent decades. Based on available records for Judith Basin County, Montana, we assume that fallow was 50% of total cultivated area during the initial cultivation period, when most of the area was managed with a crop-fallow rotational cycle (1900-1985), and 33% of total cultivated area during the more recent period when a crop-crop-fallow rotational cycle has been the dominant management practice (1985-present) (USDA Census of Agriculture 2007). We use a discretized approach to simulate rotational sequences in each rotation cycle (crop-fallow and fallow-crop; crop-crop-fallow, crop-fallow-crop, fallow-crop-crop). While a typical rotational sequence is winter wheat-spring grain-fallow, we use uniform values (winter wheat) for all cropped area in a given year for simplicity.

Previous research in northern high plains ecosystems suggests that initial cultivation could have mobilized 1000 kg N ha^{-1}, or 20-40% of the organic matter in surface horizons relatively rapidly (Davidson and Ackerman 1993, Custer 1975). However, this is neglected in our model and a constant leaching fraction is initiated for all cultivated land, estimated at 21,716 ha; based on the amount of total land in farms in Montana in 1920 relative to present (Table 2) (USDA National Agricultural Statistics Service 1920). Montana land in farms increased by 28% in Montana between 1920 and 2007, and harvested cropland within the state reached a first peak at 65% reflected in the 1982 U.S. Agricultural Census, and a second peak of 70% reflected in the 1997 U.S. Agricultural Census. In the model, we scaled Montana farm acreage data to the MoT to quantify the area of cultivated land in each year until 1980. From 1980- present 21,716 ha, or 89% of the terrace was estimated to be cultivated. This maximum cultivation was estimated based on 2006 land cover data (U.S. Geological Survey 2006).

In this model, a portion of the soil nitrate-N pool is lost each year (during a fallow or a cropped year), and this soil nitrate is added to the aquifer nitrate-N pool. The aquifer water volume has a simplified input and output of water in the form of precipitation and aquifer discharge (both constant among years). Nitrate-N is lost each year from the model from stream discharge outputs with nitrate-N present in those outputs. Therefore, the water balance and nitrogen mass balance models are coupled within the aquifer pool, as well as the within the stream flow output.

We use the mass-balance model to estimate future groundwater nitrate levels under four scenarios representing hypothetical altered management practices beginning in 2013. The first scenario is a business-as-usual scenario where yield and fertilizer increase according to the trends they have followed during the years of record since 1964 (fertilizer increasing at a rate of 1.38 +/- 0.07 kg N ha^{-1} y^{-1}, yields increasing at a rate of 0.35 +/- 0.04 kg N ha^{-1} y^{-1}). A second scenario with both increased efficiency and the replacement of fallow with a third year legume (peas) crop was evaluated based on increasing use of strategy in the region (Jones 2012, pers. comm.; Miller 2012, pers. comm).

In the model, leachable soil nitrate-N in a given year ($S_{N(t)}$) reflects inputs and losses in that year (t), and storage from the year before $[(1-k_L)S_{N(t-1)}]$:

$$S_{N(cropped)}(t) = F_N(t) + M_N(t) - Y_N(t) - B_N(t) + (1-k_{L(cropped)})S_N(t-1) \qquad (9)$$

$$S_{N(\mathrm{fallow})}(t) = M_N(t) + (1-k_{L(fallow)})S_N(t-1) \qquad (10)$$

Leached soil nitrate-N then is recharged to groundwater (R_N, accounting for fallow, Eq. 6). The entire aquifer volume is assumed to be well mixed annually. As described below, we observed nitrate-N in groundwater and surface water that was chronically above the U.S. EPA drinking water standard with limited difference between groundwater and surface water. Consequently, we assume that denitrification in the shallow aquifer is negligible. Therefore, our conceptual model is that groundwater nitrate (G_N) reflects inputs of N in recharge (R_N, kg N y^{-1}) and losses of N in discharge (D_N, kg N y^{-1}):

$$\frac{dG_N}{dt} = R_N - D_N \qquad (11)$$

The nitrate-N in groundwater, $G_N(t)$ (kg N) is then:

$$G_{N\,(t)} = G_{N\,(t-1)} + R_{N\,(t)} - D_{N\,(t-1)} \qquad (12)$$

In each year, the concentration of N in the aquifer ($C_{N\,(t)}$, kg N L^{-1}) is calculated as N in groundwater (G_N) per volume of the aquifer (V_A). and used to calculate D_N, (kg N discharged from the aquifer):

$$C_N(t) = \frac{G_{N(t)}}{V_A} \qquad (13)$$

$$D_{N\,(t)} = D_{W(t)} C_{N\,(t)} \qquad (14)$$

These equations link the steady state water balance and associated residence time (Equations 2 and 3, above) with the N balance for the landform as a whole.

3.0 Results and Discussion

3.1 Nitrate-N and Water Dynamics in Groundwater and Surface Water

The nature of the connection between surface water and groundwater on the Moccasin Terrace is apparent from field observations. Springs and seeps visibly drain to streams that have down cut through the gravel alluvial aquifer and are flowing on shale bedrock (Vuke et al. 2002). Based on this distinctive visible connection and the implication of high nitrate loading provided by previous observation of chronic high nitrate in groundwater and surface water (Bauder et al. 1991; Schmidt and Mulder 2010), we hypothesized that surface water chemistry would be similar to that of groundwater given the direct connection between ground and surface water.

Throughout the study period, we observed nitrate concentrations in ground and surface water that were near or above the U.S. EPA drinking water standard (Figure 5). Based on two locations on the MoT, nitrate in shallow groundwater averaged 17.57± 4.29 mg N L^{-1} (n=29; one standard deviation of the mean), while nitrate in surface water and a spring on or discharging from the terrace averaged 15.67 ± 9.45 mg N L^{-1} based on observations at eight locations (n=108) (Figure 5b). The mean concentration of nitrate-N in surface water (hereafter including spring water sampling results) was not significantly lower than that in groundwater (2-sided p-value 0.29 from a one-way ANOVA with 136 degrees of freedom).

The response of water level and nitrate in the M-1 monitoring well provides clues about seasonal nitrate dynamics in the shallow aquifer (Figure 6). During the spring, the water table rose to its maximum point in 2012 (0.85 m on April 29th) and appears to respond within 24 hours to precipitation events greater than 7.5 mm. In late June and July, however, the water table falls steadily without responding to precipitation events, suggesting storage in soils. Nitrate concentrations in M-1 well samples are steady (~21-22 mg L^{-1}) during this time (Figure 6). This suggests that nitrate concentrations in the shallow aquifer are the result of longer term accumulation and mixing.

The two shallow wells on the Moccasin terrace had significantly different nitrate concentrations during 2012 (two-Sample t-test, p-value = 6.80×10^{-14}; Figure 5), with concentrations in M-1 consistently higher than in CRC (means of 21.38 ± 0.90 and 13.47 ± 1.98 mg L^{-1} respectively) (Figure 5, 7). The M-1 and CRC wells have well completion depths of 5.41 and 9.27 m respectively, and hence the screened or open interval remains in the top half of the aquifer based on inferences about the total aquifer depth and saturated thickness drawn from state well log data for wells reaching shale (average = 9.03 m; Table 1). The M-1 and CRC wells are located within 4.5 km from one another on the landscape, but on opposite sides of Louse Creek (Figure 2). The depth to the water table at the CRC well was consistently about seven meters deeper than the depth to the water table at the M-1 well, despite a difference in ground elevation of only 2 m. Lower mean nitrate concentrations at CRC may be related to attenuation of leached nitrate with vadose depth, differences in up-gradient land use distribution contributing to heterogeneity in spatial loading of nitrate, or varying travel times in the aquifer. Notably, the CRC well is a pumping well from which the water is used for activities on the ground surface near the well, which may limit nitrate loading through changing recharge patterns. M-1 is a monitoring well located at the edge of a cultivated area near the northern landform boundary where a higher strath terrace is present (Figure 1). The lower observed mean nitrate concentration and greater depth to the water table the CRC well provide hints about aquifer variability and mixing with flow through the aquifer and recharge patterns.

When M-1 concentrations are compared to the nearest Louse Creek location (LC-C) the difference is not significant, yet when compared to most down-gradient sample point on Louse Creek (LC-E; Figure 5), M-1 concentrations are significantly higher. Our data suggest reduced variability in stream water nitrate at the most downstream site, as well as reduced nitrate concentrations between middle and lowermost sites (LC-C, LC-E; difference of 5.04 mg L^{-1}; however not significantly different with a p-value of 0.58; Figure 5; Table 3). These trends suggest spatial variation in aquifer loading, dilution of nitrate concentrations by runoff, or by hyporheic or in-stream nitrate loss. Notably, levels near the Judith River outlet into the Missouri River from Schmidt and Mulder (2010) have been consistently below detection, and one sample from 2012 at the USGS gauge (site 0611470) near the Judith River outlet was 1.90 ppm. At the scale of the Judith Watershed, other water sources of groundwater as well as surface water tributaries may effectively dilute the concentration (Frisbee et al. 2012).

Both shallow groundwater and Louse Creek stream water were somewhat responsive in water levels and stream discharge to rainfall in spring, while in early July, surface water but not groundwater responded to a rainfall event (Figure 7). This suggests that runoff contributed to flows in Louse Creek, potentially diluting nitrate concentrations. Yet we observed a general lack of seasonal variability in nitrate concentrations at all sampling sites (Figure 8), even as mean nitrate concentration varied among sites (Figure 5) in surface waters. This suggests that short flow paths, hyporheic exchange, dilution or in-stream processing are additional factors in surface water concentrations. The overall variability among mean nitrate concentrations at our sampling locations (Figure 5, Table 5) may be related to the distribution of groundwater flow path lengths driving stream nitrate inputs from groundwater, where downstream locations buffer the changes by dilution from storm events (Figure 8). Overall, the generally flat seasonal trend in surface as well as groundwater suggests that longer term drivers and groundwater mixing are influencing the consistently high nitrate concentrations observed on this landform.

Stream water nitrate and discharge were not correlated (Table 10), providing further support for the idea that aquifer mixing following in seasonal recharge outweighs any relationship between variable flow and nitrate loading in streams. Total nitrogen export in 2012 based on the average monthly discharge and nitrate concentration for LC-E and L-P combined is 7.49×10^4 kg N yr^{-1} +/- 1.50×10^4. If we assume there was negligible in-stream attenuation and that these two major streams coming off of the terrace represent 50% of all of the water and nitrogen exiting the terrace through springs and seeps, then 1.50×10^5 kg N yr^{-1} is thought to exit the aquifer.

3.2 Groundwater Residence Time

In order to understand the missing link between water quality and management and to evaluate effects of changing management on water quality at the appropriate timescale, understanding groundwater residence times is critical. We used two approaches to evaluate groundwater residence time: aquifer volume vs. stream discharge during 2012 and direct measurement of isotopic constituents in groundwater. We then used groundwater flow modeling to estimate the spatial variability of advective travel times across the landform. These evaluations provide a first estimate of the timescale over which management effects on elevated groundwater nitrate should be considered in this landscape. Understanding timescales of groundwater nitrate loading and transport on MoT, where dispersed recharge dominates, will contribute to understanding those on other landforms strongly influenced by both dispersed recharge and mountain front stream recharge.

3.2.1 Aquifer Volume vs. Stream Discharge Average 2012 discharge measurements of LC-E and L-P surface water gaging sites indicate that there was ~8.59 x 10^6 m^3 yr^{-1} of water discharged from these two locations in 2012. We assume based on the number of springs identified in aerial photos that this total is about one half of the total spring and seep discharge, thus approximately 1.72 x 10^7 m^3 yr^{-1} of water is discharged from the aquifer around the terrace. Given a 4.17 m (±1.95 m) thick saturated zone and a water filled pore space of 30%, the residence time of water in the aquifer would be 17.8 y (range 9.5-26.0 given one standard deviation of mean saturated thickness). Rainfall in 2012 was lower than average and outside of one standard deviation: 27.8 cm compared to the long term average of 38.2 ± 8.60 cm; rainfall in 2011 was 48.4 cm. The elevated water table at the beginning of 2012 (Figure 6) is likely a legacy of the above average precipitation in 2011, and may have caused increased discharge during the first part of 2012 followed by decreased discharge with below average 2012 precipitation. Hence we suggest that total discharge from the landform in

2012 was likely consistent with longer term discharge from the landform. Given a mean saturated thickness of 4.17 m, a residence time of 11.8-35.5 y is implied if ± 50% uncertainty in total discharge is considered.

3.2.2 Tritium and $^{3}H/^{3}He$ Results Tritium results indicate that all surface water and shallow well samples have "bomb" tritium (tritium ≤ 60 y, remnant from atmospheric nuclear weapons testing), or modern tritium present (greater than 5 TU) (Table 2). As discussed above, these young waters also have nitrate concentrations consistently above the U.S. EPA drinking water standard of 10 mg L^{-1}. One well sample, from a deep artesian well 494 meters deep (ART), shows nearly non-detectable nitrate and non-detectable tritium; this is consistent with the notion that deep groundwater in the confined aquifer is both less recently recharged and protected from leaching nitrate. Results for $^{3}H/^{3}He$ in samples from the two shallow groundwater wells (Table 2) indicate very recently recharged water, with model ages of 0 ± 2 years. We suspect that these especially short residence times may be related to both shallow sampling depths and precipitation in 2011 that was well above average: 48.4 cm during which 18.7 cm fell in May alone of that year (compared to 38.2 cm and 6.6 cm, respectively, on average for all other years during 1909 to 2012). The legacy of that unusually wet year can be seen in the record for M-1 (Figure 6), where the elevated groundwater level from a year with well above average precipitation (2011) transitioned into a below average year (2012). Consequently, the groundwater level in the M-1 well during the dry mid to late summer during 2012 is lower than the level during the dry winter months.

In this shallow aquifer, stratification of apparent groundwater ages where age increases with depth is expected, as well as stratification of nitrate concentrations, where concentrations decrease with depth, however our data does not resolve age or nitrate stratigraphy (Böhlke et al. 2007a, LaBolle et al. 2006, McMahon et al. 2007). Nitrate concentrations would be expected to decrease both with depth and down gradient if top-down loading into the aquifer from soil nitrate is increasing with time and losses are limited. Lack of vertical mixing in the aquifer water column must be considered as it is unlikely that the entire aquifer volume has been ‘turned over’ and replaced with modern precipitation over the past two years, given our estimates of aquifer volume and total discharge, above. This suggests that observed concentrations in M-1 may overestimate the overall concentration in the shallow aquifer as the well in screened in the top portion of the aquifer.

3.3 Spatial Variation in Groundwater Nitrate Loading: Groundwater Flow Model

Seasonal variation in nitrate-N concentration was limited in ground and surface water, yet mean concentrations varied spatially (Figure 5a). To examine this variability, a simplified model was built using the MODFLOW model in GMS. This generalized MODFLOW simulation, in combination with a MODPATH particle tracking simulation, allowed us to evaluate possible flow path travel times and assess whether there is a relationship to nitrate variability at sampling locations across the landform. The model was built using a Digital Elevation Model from the U.S. Geological Survey, interpolated as the ground surface, and the base of the aquifer was modeled as a uniform 30 m below the ground surface based on maximum depth to shale of 27 m (average of 14 meters with a standard deviation of 6 meters) and water table elevations averaging 13 m below the ground surface (Montana Bureau of Mines and Geology 2012). Aquifer discharge from springs and seeps into streams was simulated as a drain boundary in the model, and drain cell locations were selected based on ground-truth information and aerial imagery from August 2011 (USDA FSA 2011) to identify green areas around the edges of the terrace where water is discharging from springs and seeps. Drain elevations were selected from the DEM (10 m resolution) using the photo interpretation of spring locations on the terrace. Grid cells in the model were 299.5 m x 296.5 m, using a grid frame with a simple number of cells dividing the length and width in the x and y directions. Cells were assigned a recharge rate of 1.645×10^{-4} meters day^{-1} based on flow budget calculations using discharge measurements and an assumption of steady state water balance for the landform (total recharge = total discharge, annually). Recharge and drain conductance were adjusted to best represent the estimated stream output from the aquifer based on discharge measurements in gaining streams with total aquifer discharge quantified with stream discharge measurements assumed to be one half of all aquifer given discharge (see section 3.2.1 below). All drains were assigned an equal conductance of 25 m^2 day^{-1} based on this assessment. Horizontal hydraulic conductivity was assigned to the model as 5.5 meters day^{-1} for all five layers comprising the model (6 m thick each) using measured well head values at two shallow well sampling sites (Figure 2) as calibration points and to estimate this parameter. Vertical and horizontal anisotropy of 1.0 was used for simplicity, assuming a homogenous, isotropic aquifer. MODPATH reverse particle tracking for each sampling site on the terrace (e.g., wells and springs) with 12 particles per cell, from 12 equally spaced locations within the cell and a porosity of 30% was used to estimate mean travel times to the sampling location (Schwartz and Zhang 2003) (Table 4) using the following equation:

$$t = \frac{Ki \cdot cell}{n_e} \qquad (16)$$

where K is the hydraulic conductivity, *i* is the gradient, cell represents the cell area and n_e is the effective porosity. Well log information was too sparse for reliable interpolation of the subsurface boundary, thus the model surface as well as subsurface shale boundary are represented by a surface topography digital elevation model. The MODFLOW simulation in Figure 9 illustrates generally northeast groundwater flow, discharging through springs and seeps identified through aerial photo interpretation (shown in the groundwater output as grey dots representing 'drain' cells). Reverse particle tracking from sampling sites to recharge locations using MODPATH indicates variation in travel distance and therefore residence time of water sampled based on the uniform hydraulic conductivity assumed for the terrace (Table 3). Given slight variability between locations when looking at mean nitrate results, further exploration into particle travel time and mean nitrate concentrations seemed appropriate. We obtained 12 particle travel times for each site from 12 equally spaced locations within the cell that were averaged together to produce a mean advective travel time. These modeled mean advective travel times range from 25.1 to 56.5 years, with a mean of 37.2 +/- 13.8 years, consistent with estimates based on aquifer volume and discharge (which were used to calibrate the model). These travel times are within the range of ^3H mean residence times, and are within the same order of magnitude of the calculated pool/flux aquifer residence time calculations, supporting the idea that water is recently recharged and the average turnover time within the aquifer is on a decadal scale.

Figure 10 shows no correlation (p-value of 0.49 using Pearson's product-moment for a linear correlation with 6 degrees of freedom) between modeled particle flow path lengths and measured nitrate. This provides weak support of the idea that nitrate is accumulated along flow paths, through dispersed nitrate leaching to the groundwater table at annually increasing rates. The mean calculated travel times based on MODPATH (Table 3) assume advection only, and thus are underestimates in that they do not account for dispersion. However they suggest that transport times are likely long enough that nitrate concentrations tend to increase along flow paths as a result of continual nitrate leaching to the aquifer. The lack of correlation could indicate that local land use or other factors such as in stream processing or depths of soil and vadose zone may play a role in aquifer nitrate concentration variability.

3.4 Groundwater Nitrate Over Time with Cultivation and Fertilization

Residence times of decades in groundwater suggest that longer term changes in land management can be seen in spatial and temporal variation ground and surface water quality. However, given likely stratigraphy of groundwater ages (thus nitrate concentrations), we are likely to see water quality changes locally while the aquifer as a whole may require decades for an overall nitrate decrease to be seen. Within the last century two major land management changes have occurred on the MoT: the inception of cultivation and the inception of fertilization. Publically available data sets for major nitrogen inputs to and outputs from the system during this time (wheat yield and nitrogen fertilizer use) provide informative constraint for a century scale model of nitrate fluxes. Motivated by rising nitrate-N concentrations in the M-1 well during the past two decades and the observation of seasonally steady ground and surface water nitrate concentrations, we used a numerical mass balance model to better understand general aquifer processes and to see if using available data we could simulate decadal scale patterns of N accumulation in the shallow aquifer. Available data show that fertilizer rates and yields have increased steadily (USDA Economic Research Service; USDA National Agricultural Statistics Service), with rates of wheat yield N increasing at 0.35 ± 0.04 kg ha^{-1} $year^{-1}$ and for the period of record (1945-2008) (Figure 11). This rate of N yield increase is outpaced by rates of fertilization increase (1.38 ± 0.07 kg ha^{-1} $year^{-1}$ during the period of record (1964-2009)). Hence the rate of fertilizer N increase in excess of yield N increase has been 1.03 ± 0.08 kg ha^{-1} $year^{-1}$. We assume that mineralization has remained constant (approximating yield levels when fertilization began; 40 kg ha^{-1} in 1964). Using constant proportions of nitrate leaching from soil during cropping ($k_{L,cropped} = 0.1$) and fallow ($k_{L,fallow} = 0.4$), we find an increasing rate of groundwater nitrate accumulation over time since fertilization was initiated (1964-present; Figure 11), as a result of cultivation and increased fertilizer application. This result is averaged for the entire landform and is qualitatively consistent with the observed increase in the M-1 well.

An important source of uncertainty in this evaluation is the volume of the aquifer, which we have estimated using the maximum observed saturated thickness based on well logs (Table 1). Our field observations and the number of well logs indicating a reduced saturated thickness (12 out of 18 well log records indicated a saturated thickness <5m;

Table 1) suggesting that a 10 m estimate may overestimate the aquifer volume by a factor of 2.

Another major source of uncertainty is the leaching proportion, estimated at 10% in cropped years and at 40% in fallow years. Because the literature range shows 2% to 60% leaching loss, we assume this entire range of values and apply it to our modeling scenarios. This sensitivity analysis is shown in Figure 11, where the 2% leaching proportion was applied to cropped years and 60% was applied to fallow years. The general trends resulting from the various scenarios remains similar, however the modeled concentrations vary.

For the landform as a whole on an annual basis, the steady state discharge rate (equal to total recharge for the landform, Equation 1), implies a mean residence time of water in the aquifer of 17.8 years depending on volume estimates described above (9.5 – 26.0 years depending on aquifer saturated thickness uncertainty, or 11.5 – 35.5 years depending on discharge uncertainty). These agree with the groundwater flow model particle tracking results: 25.1 to 56.5 years, with a mean of 37.2 +/- 13.8 years.

The results in nitrate-N concentration change in the aquifer based on three modeling scenarios are shown in Figure 11. Scenario 1 shows the results in aquifer nitrate-N concentration with constantly increasing yield and fertilizer rates based on historic data. Scenario 2 is increased N use efficiency where fertilizer is 110% of the increasing (at historic rates) yield after 2012. Scenario 3 combines increased N use efficiency and a harvested pea crop in place of fallow. Our modeled projections (Figure 11) suggest that groundwater nitrate levels will continue to increase but the rate of increase can be dramatically limited if fertilizer levels remain constant relative to expected yield. Groundwater nitrate-N concentrations may potentially be reduced over decades if fertilizer inputs are limited relative to yield and peas or another shallow rooted legume are introduced into a three year rotation in place of fallow.

Given the results of the groundwater solute trend following inception of the use of peas, it appears that replacing a third year fallow with a harvestable crop should be considered and may potentially help reduce aquifer nitrate, however the range of likely aquifer residence times and thus when to expect a change in local water quality (within several years) versus the water quality of the entire aquifer (decades) should be considered when assessing the effects of a land management change on water quality.

4.0 Conclusions

In this study, we evaluated nitrate-N dynamics and residence time in groundwater and surface water from an isolated shallow aquifer in the Judith River Watershed in Montana, USA. Nitrate concentrations were commonly above the drinking water limit (in 80 of 109 surface water samples and 28 of 29 shallow groundwater samples). Water levels in groundwater and surface water responded rapidly to rainfall during spring, but only surface water was responsive in late summer. Nitrate concentrations in streams were highest during the winter months at two downstream locations, and in two locations, minor (~3 mg L^{-1}) increases in nitrate concentrations were seen during the wetter spring months. However, the overall trend in nitrate concentrations during 2012 was flat, with no major increase or decrease in nitrate concentrations throughout the year. All mean nitrate concentrations for locations across the year were above the U.S. EPA drinking water standard of 10 mg L^{-1}. Our combined modeling results indicate that a management change limiting leachable soil nitrate may be detectable in shallow groundwater in few (less than ten) years, whereas rapid reduction of nitrate concentrations in the aquifer as a whole is unlikely given probable aquifer residence times. However, a combination of approaches maintaining current efficiency and limiting leaching through rotational strategies has the potential to decrease aquifer nitrate levels over the next few decades. The evidence of direct connection between ground and surface water nitrate concentrations, suggests that surface water nitrate will remain elevated in tandem with high ground water concentrations, but could be slowly reduced through strategies targeting longer term N use efficiency.

Interannual variability in precipitation and spatial variability in leaching potential are likely important drivers of overall nitrate leaching rates, suggesting that identification and protection of vulnerable locations could contribute to effective attenuation of nitrate leaching.

Soil-groundwater systems in dryland cultivated areas have been minimally studied, but are vulnerable to contamination. We suggest that effective management decisions can be made for protection of soil and water resources and the sustainability of agricultural production, especially in light of uncertain future climate conditions.

5.0 Manuscript Acknowledgements

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6.0 Tables

Table 1. Well log information for 18 wells on the Moccasin Terrace. Saturated thickness is calculated using depth to shale-static water level at the time of drilling (Montana Bureau of Mines and Geology 2012).

	Well Log Information for MoT			
	Depth to Shale (m)	Saturated Thickness (m)	Static Water Level (m)	Drilling Date
1	10	3	6	5/28/1969
2	11	2	8	6/3/1986
3	8	3	5	7/31/1971
4	16	5	10	5/16/1985
5	12	3	8	9/4/1981
6	9	5	4	4/28/1969
7	5	4	2	7/26/1983
8	7	2	5	7/30/1983
9	8	5	3	7/15/1983
10	8	8	0	7/16/1983
11	5	2	4	3/19/1998
12	12	8	4	12/1/1998
13	5	2	4	3/19/1998
14	9	5	4	4/7/1999
15	5	5	0	5/31/2000
16	11	4	7	12/18/2000
17	13	7	6	10/3/2002
18	10	3	7	4/19/2004
Average		4.2	4.86	

Table 2. Tritium, noble gas, and nitrate data. Tritium and noble gas data from the University of Utah, nitrate data from Montana State University. Tritium (TU) concentrations are back calculated using decayed tritium and daughter ^{3}He concentrations. R/Ra ratio less than 1.0 indicates radiogenic helium is present, and an R/Ra ratio of greater than 1.0 indicates tritiogenic helium is present.

Groundwater Age Data for MoT										
ID	Sampling Date	Site Elevation (m above msl)	Tritium Conc (TU)	Tritium (error +/-)	Nitrate-N (mg L-1)	Nitrate Uncertainty (mg L-1)	N2 total (ccSTP/g)	Ar total (ccSTP/g)	Ne total (ccSTP/g)	Kr total (ccSTP/g)
Artesian	Jan-12	1297	0.08	0.05	0.0	0.00				
CRC	Jan-12	1297	8.19	0.38	12.9	0.05				
CRC	Aug-12	1297	8.52	0.32	14.3	0.02	1.25E-02	3.37E-04	1.79E-07	8.30E-08
M-1	Jan-12	1295	10.49	0.47	20.7	0.04				
M-1	Aug-12	1295	10.59	0.39	20.6	0.44	1.55E-02	3.97E-04	2.36E-07	8.78E-08
SPR	Apr-12	1225	8.57	0.42	25.0	0.08				
LC-B	Jan-12	1331	10.76	0.38	12.9	0.01				
LC-D	Jan-12	1172	9.94	0.40	15.4	0.05				

ID	Sampling Date	Xe total (ccSTP/g)	He4 (ccSTP/g)	R/Ra	Tritium (TU) (submitted with noble gas)	Tritium (error +/-) (submitted with noble gas)	Age - using Ne only (yrs)	Age error +/- (using Ne)	Age - using EA (yrs)	Age error +/- (using EA)
Artesian	Jan-12									
CRC	Jan-12									
CRC	Aug-12	1.17E-08	4.06E-08	0.97	8.52	0.32	-3.32	1.00	-2.12	0.5
M-1	Jan-12									
M-1	Aug-12	1.20E-08	5.60E-08	1.02	10.59	0.39	-3.57	1.07	1.73	0.5
SPR	Apr-12									
LC-B	Jan-12									
LC-D	Jan-12									

Table 3. Advective maximum particle travel time used in a MODPATH reverse particle tracking simulation and nitrate. Nitrate (mg L^{-1}) means and standard deviations are shown for each site sampled in 2012.

2012 MoT Sample Site Information							
Location	Mean Nitrate (mg/L)	Std Dev Nitrate (mg/L)	n	Mean Advective Travel Time (years)	Std Dev Advective Travel Time (years)	Site Description	Measurements made
LC-A	12.84	4.49	13	25.09	17.20	Stream	Field Parameters, nitrate, discharge
LC-B	8.18	5.34	14	25.09	17.20	Stream	Field Parameters, nitrate, discharge
LC-C	15.80	2.12	17	47.88	17.69	Stream	Field Parameters, nitrate, discharge
LC-D	10.15	1.67	8	53.39	26.24	Stream	Field Parameters, nitrate, discharge
LC-E	10.75	1.87	16	39.63	39.22	Stream	Field Parameters, nitrate, discharge
SPR	24.82	1.52	12	56.49	20.06	Spring	Field Parameters, nitrate
LP	21.62	1.42	14	nd	nd	Stream	Field Parameters, nitrate, discharge
TribA	20.28	19.66	15	nd	nd	Stream	Field Parameters, nitrate, discharge
M1	21.38	0.90	15	25.09	17.20	Well	Field Parameters, nitrate, water level
CRC	13.47	1.98	14	25.09	17.20	Well	Field Parameters, nitrate, water level

Table 4. Parameters and assumptions used.

	Assumption	Value Used	Reference
	Assumptions and Parameters Used		
Aquifer characteristics	Aquifer area is equivalent to terrace area	24,400 ha	(U.S. Geological Survey 2006)
	Aquifer saturated thickness	4.17 m	(Montana Bureau of Mines and Geology 2012)
	Aquifer porosity	0.2 (groundwater model) 0.3 (mass balance model)	(Dingman 2002; Montana Bureau of Mines and Geology 2012; Schwartz and Zhang 2003)
Water balance	Stream discharge measurements relative to total annual water loss from aquifer	50%	Aerial photo interpretation (USDA FSA 2011)
	Precipitation	360 mm yr^{-1}	(Montana State University Central Agricultural Research Center 2012)
Land area and N mass balance	Proportion of land fallow/cropped	0.5/0.5 (1900-1985 0.4/0.6 (1986-present)	(USDA National Agricultural Statistics Service 2007; USDA National Agricultural Statistics Service; Wichman 2012)
	k_L fallow/k_L cropped	0.4/0.1	(Canfield et al. 2010; Liao et al. 2012)
	Constant mineralization rate	40 kg ha^{-1}	Observation of yield when fertilization was initiated (USDA National Agricultural Statistics Service)

7.0 Figures

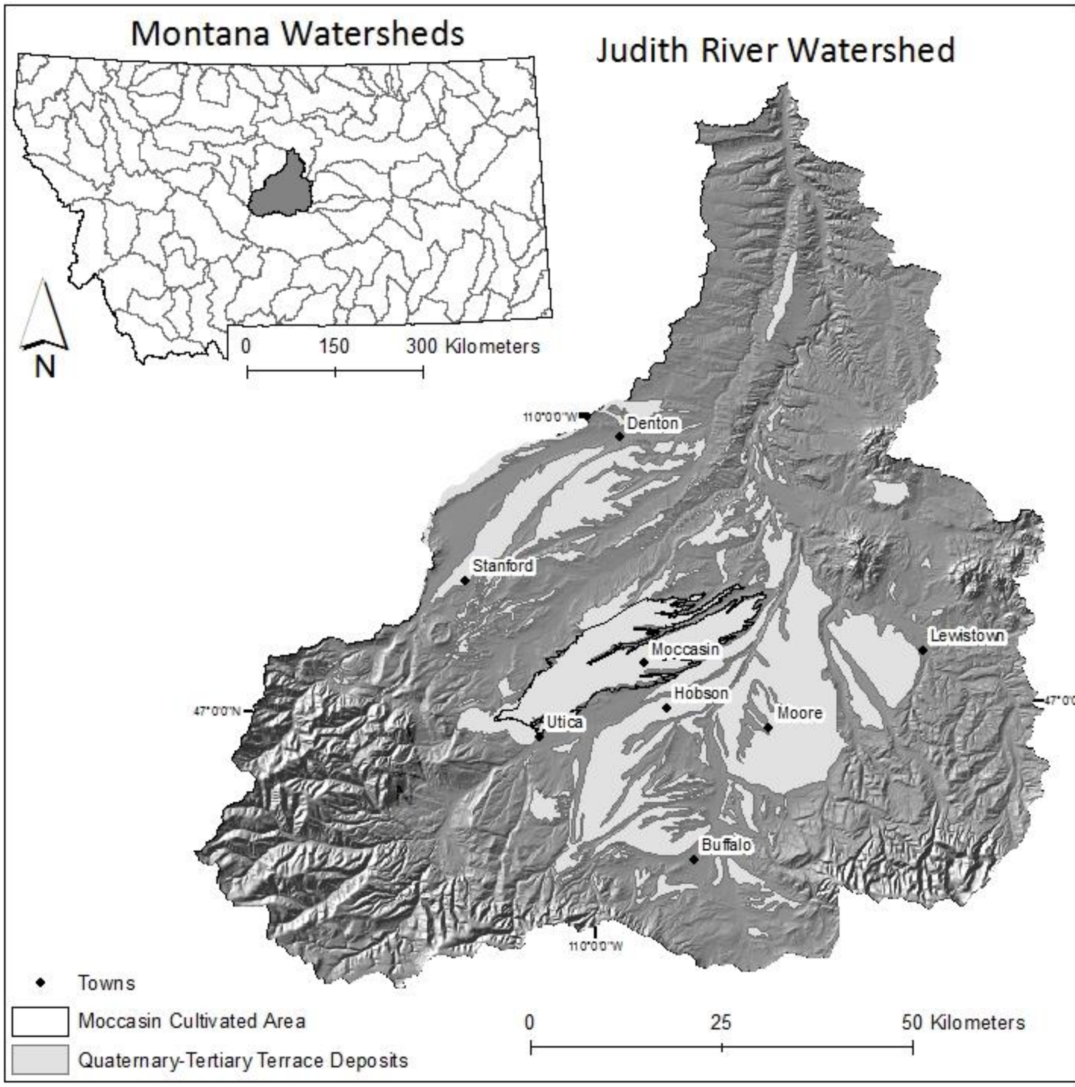

Figure 1. The Judith River Watershed in central Montana, USA. Towns are shown as black dots, and cultivated area is shown as highlighted polygons. Black line indicates extent of cultivated area on the MoT. (Data Source: Montana Natural Resource Information Systems, USGS National Elevation Dataset)

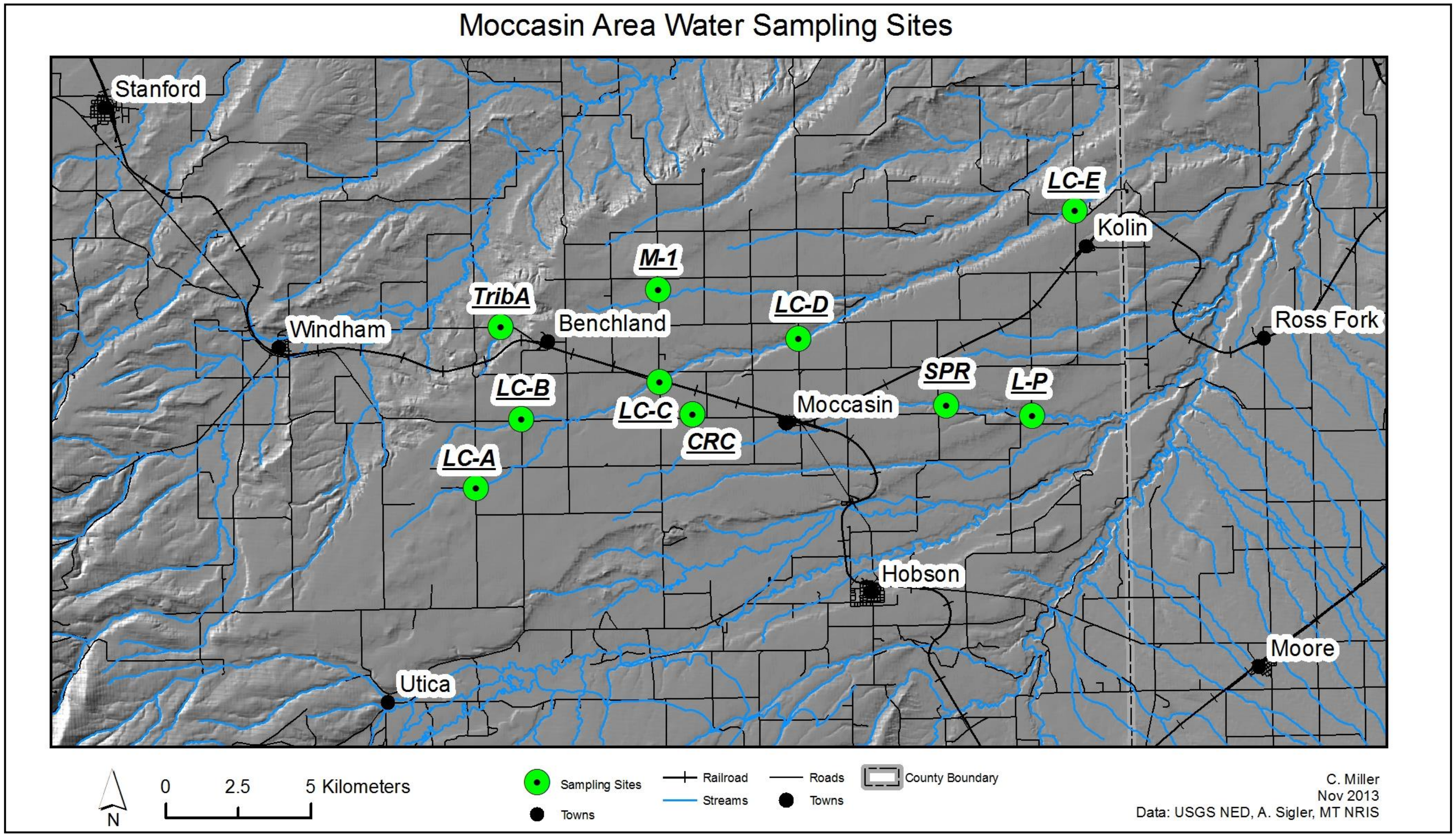

Figure 2. Water sampling sites on the Moccasin terrace (MoT), a strath terrace near Moccasin, Montana used in this study. Both streams ("S-") and wells ("W-") are shown on the map. See Table 4 for location information.

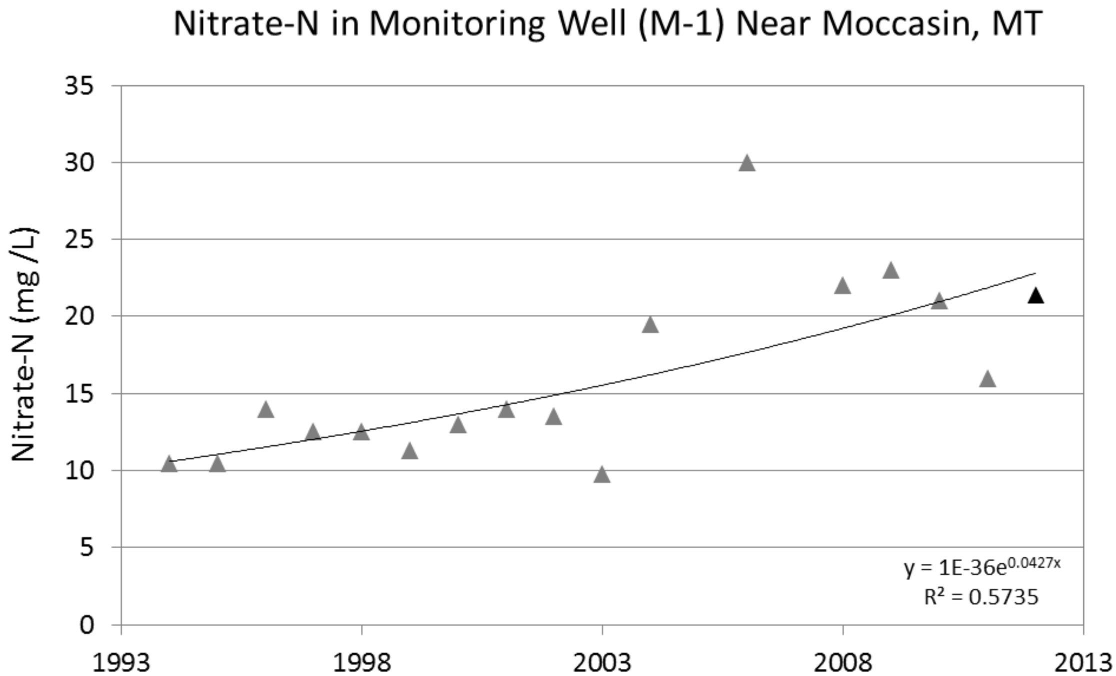

Figure 3. Historic nitrate data in a monitoring well near Moccasin, Montana compiled from Montana State University, Montana Department of Agriculture, and the Montana Bureau of Mines and Geology. Grey triangles represent historic data while black triangles represent samples taken during 2012. The mean of sample analyses in 2012 was used in exponential and linear fits to the data. A linear regression of these data to the sample year produced a slope of 0.70+/- 0.17 mg N y^{-1}, and had a calculated R^2 of 0.52 and a zero intercept in 1979. We argue that the exponential fit is more consistent with the known trajectory of inputs and losses (Figure 19) and the assumption that leaching occurs in proportion to the soil nitrate-N pool.

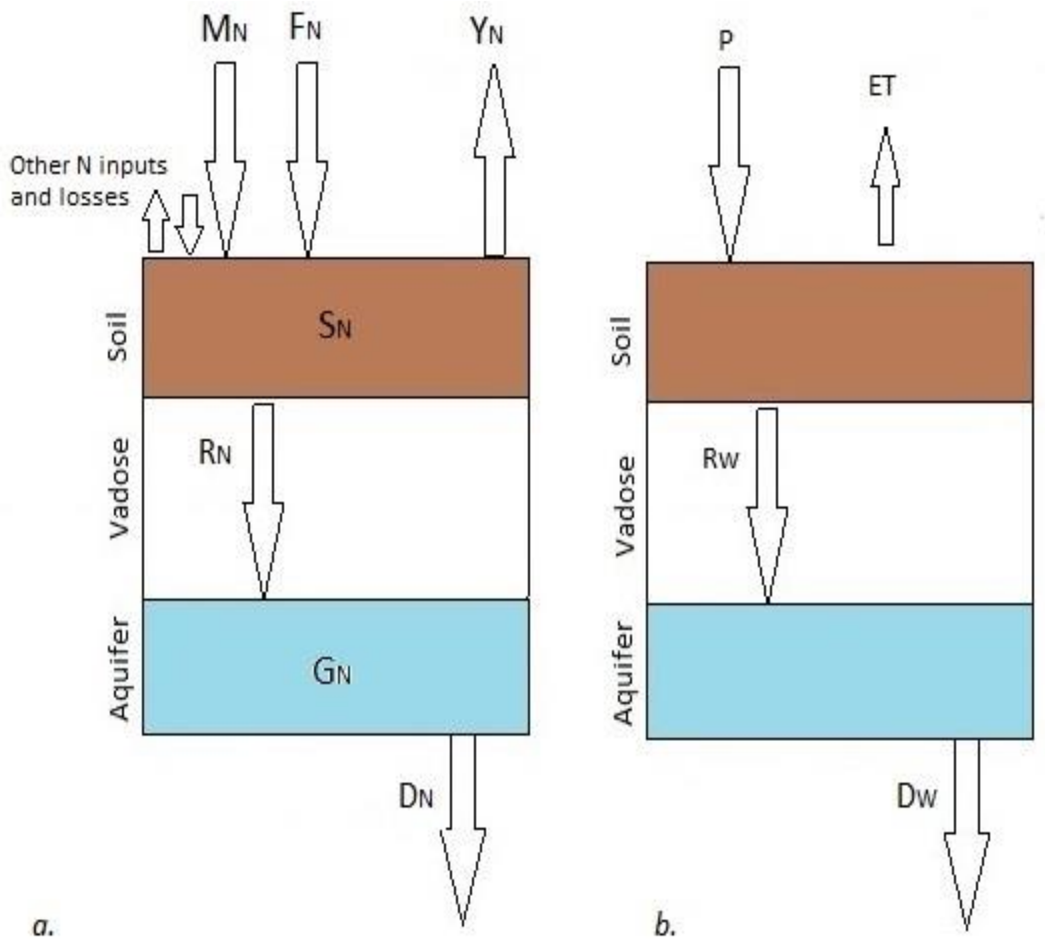

Figure 4. Schematic of mass balance model for nitrate-N (left, part a) and water (right, part b) in soil (S) and groundwater (G). In the nitrogen mass balance model M_N = mineralized nitrogen, F_N = fertilizer nitrogen, Y_N = crop yield, R_N = concentration of nitrogen in recharge water, G_N = groundwater nitrogen, and D_N = discharge nitrogen. "Other nitrogen inputs and losses" (assumed negligible) include wet and dry atmospheric deposition, septic efflux, denitrification and biological nitrogen fixation; loss of N to volatilization is assumed constant relative to fertilizer input (Engel et al., 2011). In the water balance model P = precipitation, ET = evapotranspiration, Rw = recharge water, Dw = discharge water.

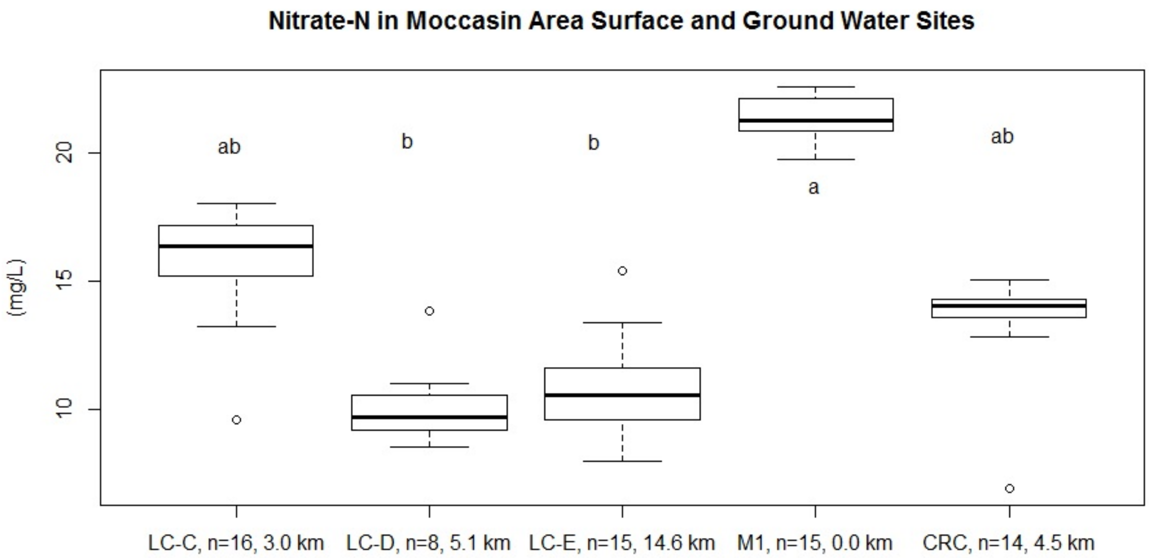

Figure 5. Boxplots of stream and well nitrate-N concentrations across the Moccasin terrace. Louse Creek (LC) longitudinal samples are shown from left to right in most-upstream to most-downstream order, followed by additional sites as well as data from two shallow wells. Significant differences found using a Tukey HSD Test are denoted by small letters above boxplots. Refer to Figure 2 for sampling locations. Distances listed under boxplots represent the lateral distance from the M-1 well.

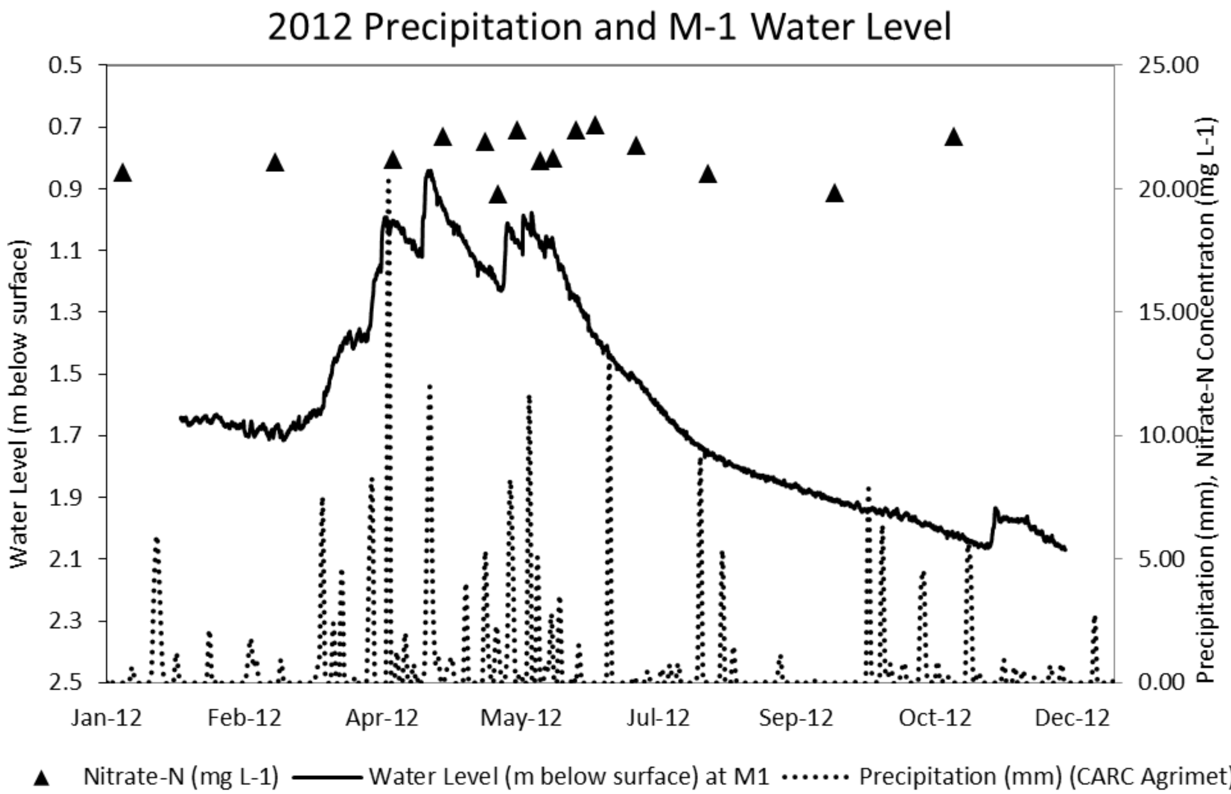

Figure 6. Groundwater level (m) below the surface in the M-1 monitoring well shown with the solid black line, precipitation (mm) shown with the dotted black line, and nitrate concentrations in the M-1 well, shown in black triangles. The legacy of a wet year (2011) is shown with an elevated water table in the early part of 2012, eventually transitioning to a deeper water table in the mid and late summer of 2012. Nitrate concentrations are related to wet season (spring) precipitation but reach a second peak after the growing season ends. The grey box is the time period highlighted in Figure 7 (below).

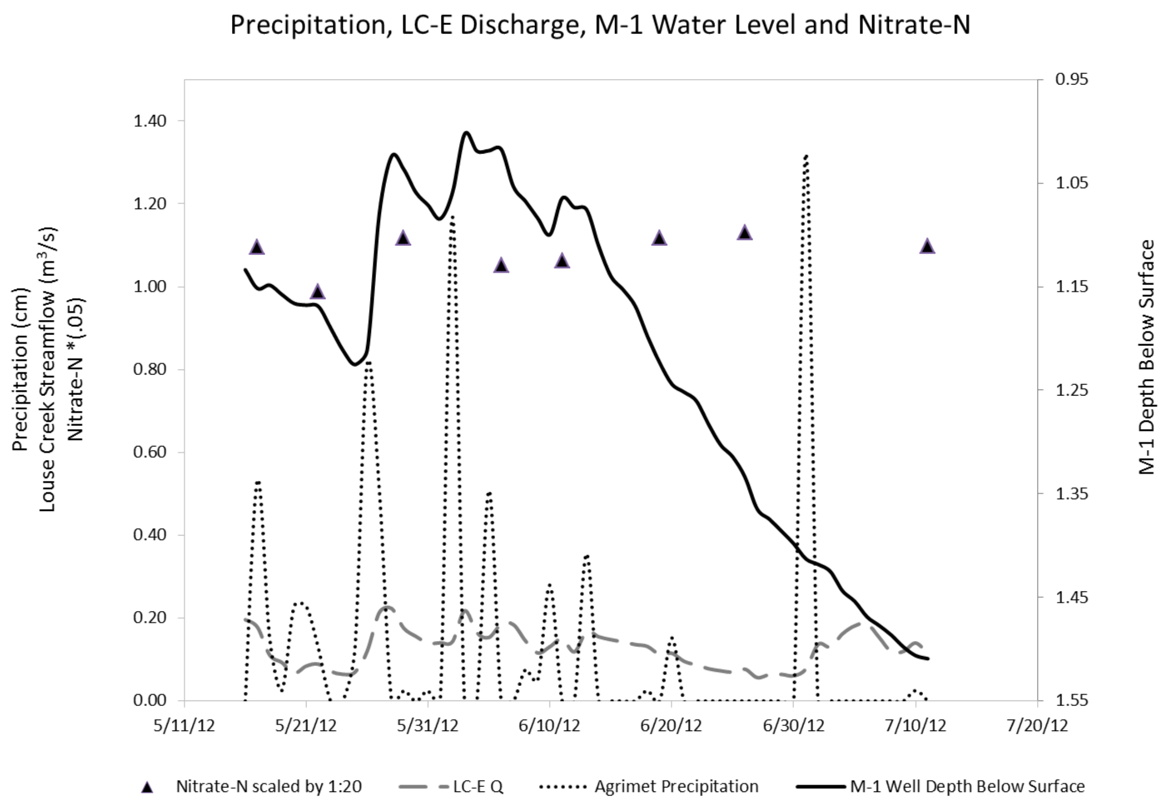

Figure 7. The time period during part of the wet season (spring) highlighted in the grey box on Figure 6 (above). The black solid line represents the groundwater level in a key monitoring well (M-1), while the dotted black line represents precipitation, and the dashed grey line represents stream response to precipitation at the farthest downstream site. A rapid response is seen in stream discharge, while a slightly slower but still rapid response to precipitation is seen in groundwater. Once the growing season is underway, little or no response to precipitation is seen in groundwater while a response is seen in stream discharge.

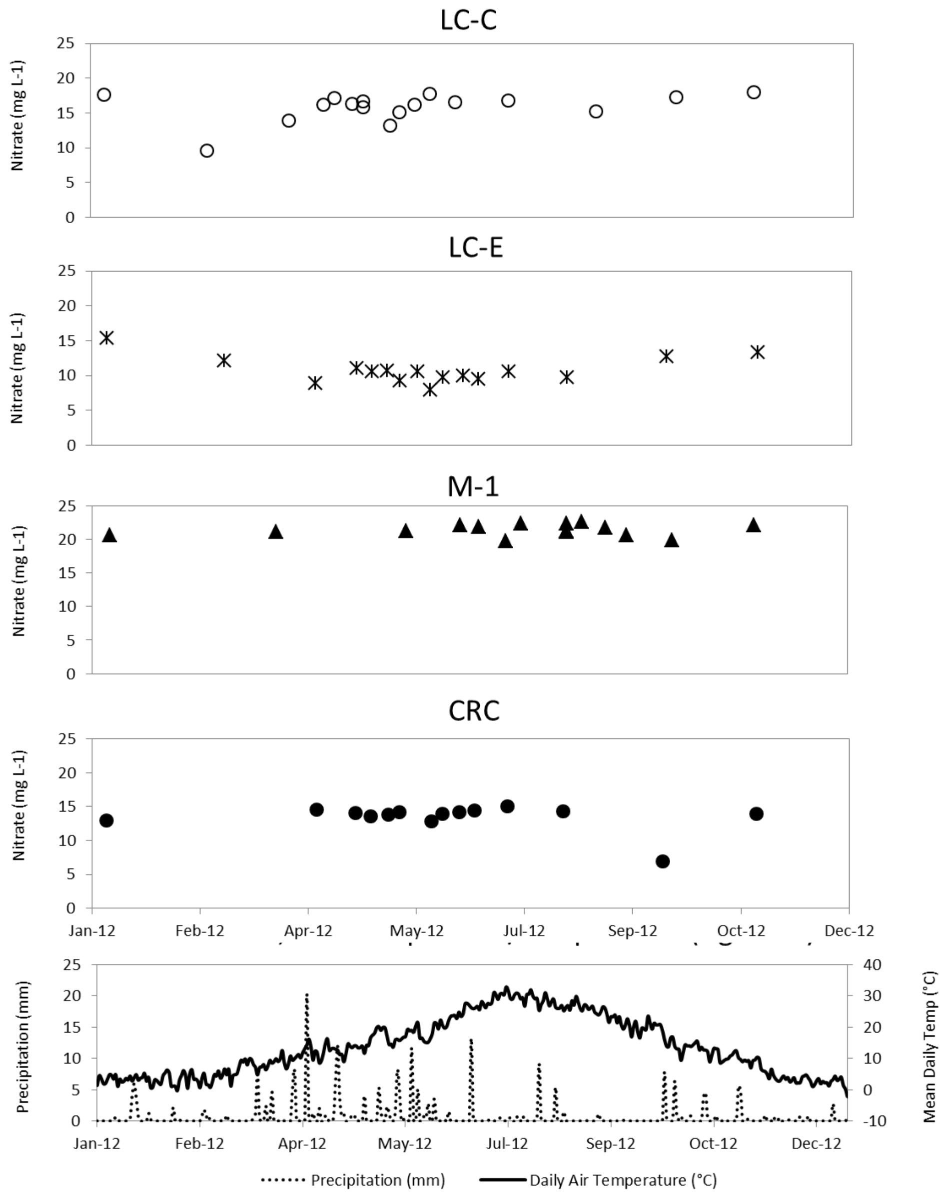

Figure 8. Seasonal changes in nitrate-N concentrations at sampling locations.

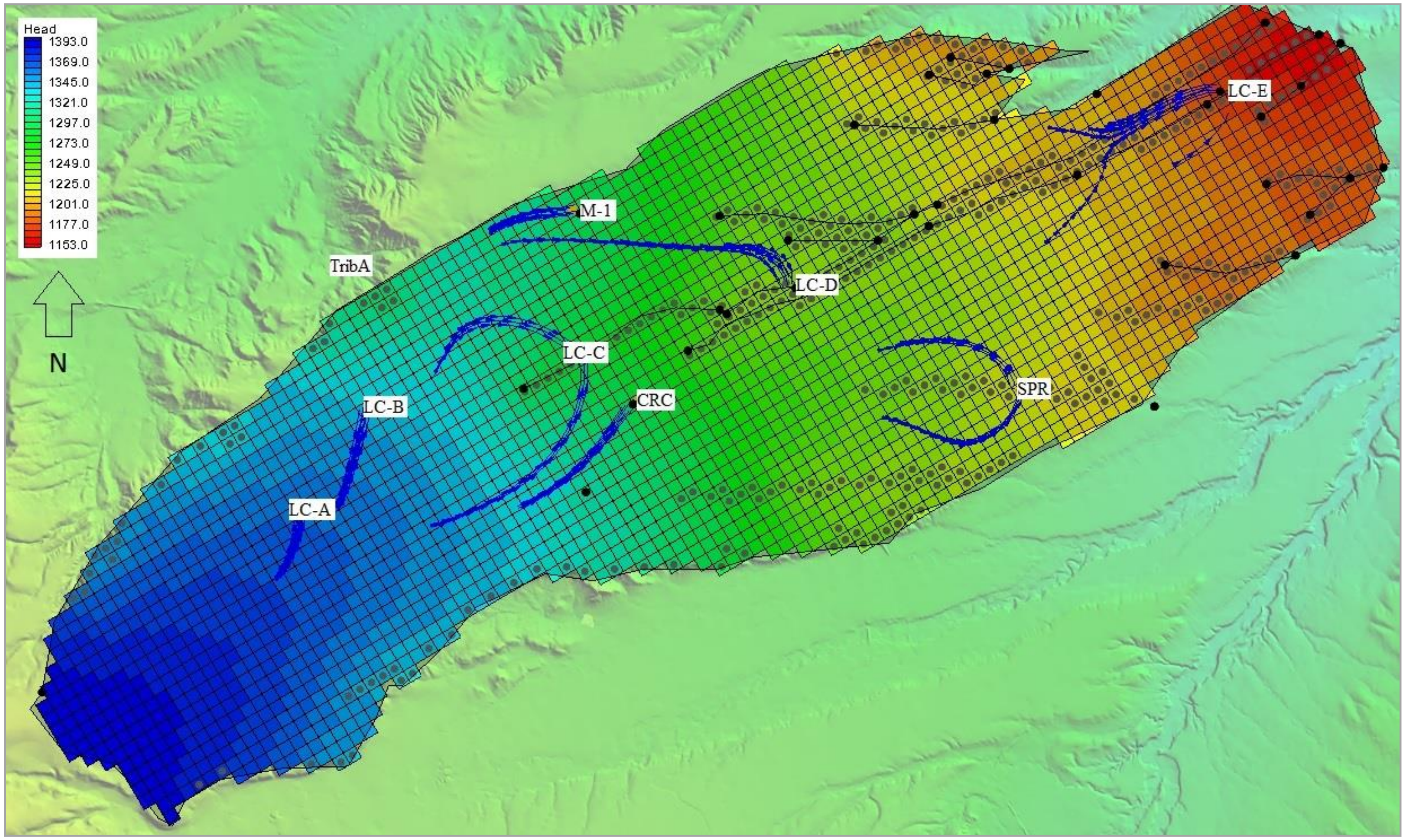

Figure 9. Groundwater flow model with backwards-particle tracking (12 particles each) from area of recharge to sampling sites**.** Grey dots indicate drain locations where springs and seeps exist. Groundwater flow is generally northeast, with springs and seeps causing more complex flow paths.

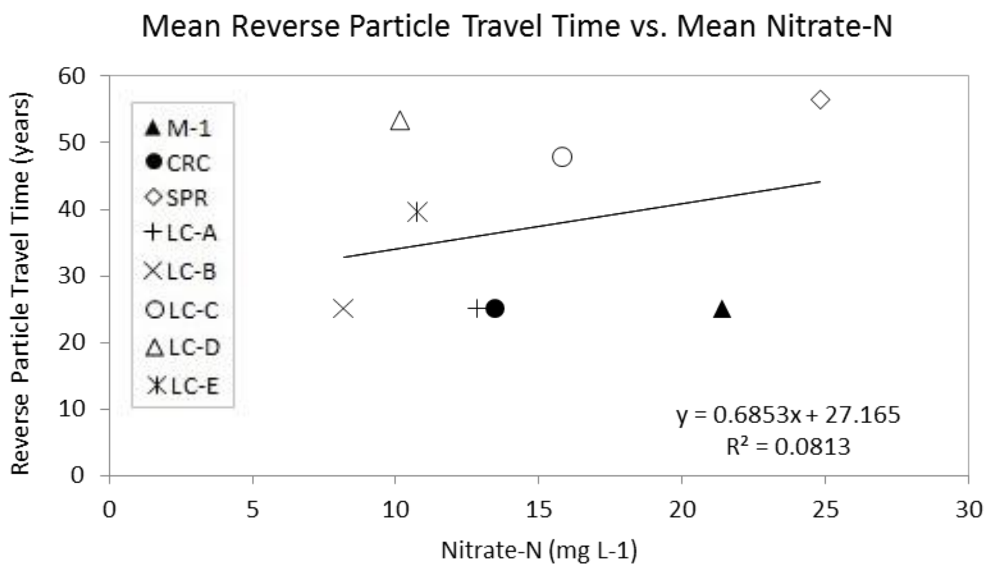

Figure 10. Mean reverse particle travel time (backwards particle tracking travel time using MODPATH with 12 particles**)** versus mean nitrate-N for sampling locations. Solid symbols represent groundwater, and open symbols represent SPR and surface water sampling locations. SPR, the only spring location sampled has the highest mean nitrate concentration as well as the longest particle tracking time. An insignificant linear correlation is shown (R^2 = 0.08, Pearson's product-moment correlation p-value = 0.49).

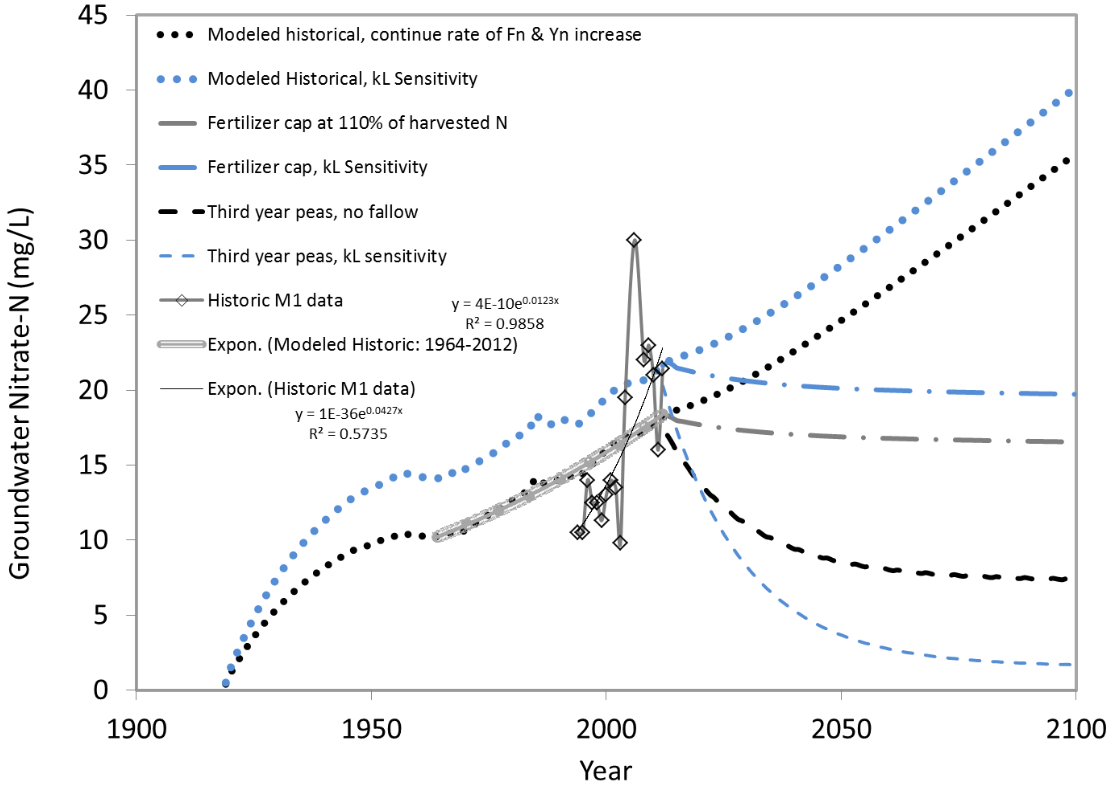

Figure 11. Model output for three nitrogen mass balance scenarios and two leaching conditions. (black/grey lines) moderate leaching intensity (kL = 0.4 in fallow and 0.1 in crop) and (blue lines) enhanced leaching intensity in fallow (0.6) and crop (0.02). Scenarios are as follows (see text for assumptions): (scenario 1) Fertilizer and wheat yields follow their historic trajectories and continue to saturate the aquifer with nitrate-N. (scenario 2) Fertilizer is capped at 110% of wheat yields, which continue to increase following the historic trajectory. Given assumptions of the model (see text), nitrate-N concentrations would initially decrease and then increase only very slowly as a function of the increasing yield and proportional fertilizer cap. (scenario 3) Fallow is eliminated across the terrace and replaced with a third-year pea crop. Given assumptions of the model (see text), concentrations would decrease substantially and become asymptotic at a level below the U.S. EPA drinking water standard with a third-year pea crop.

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GENERAL CONCLUSION

Nitrogen dynamics and residence time were evaluated in streams and wells in or draining from an isolated shallow aquifer in the Judith River Watershed in Montana, USA. Rapid residence times in groundwater indicate that nitrate leaching from soils through the vadose zone is quick and results in young groundwater being seen in the shallow groundwater. Nitrate in stream water shows a response to flushing during the wettest part of the year in the springtime, though nitrate concentrations in streams were highest during the winter months. A decrease in denitrification driven by the colder stream temperatures or winter leaching following the growing season may be related to this pattern. During the warmer months, a decrease in nitrate concentrations is seen with the exception of the period during peak flow where a flushing effect of soil nitrate occurs and nitrate is carried through the vadose zone to the aquifer. Concentrations in stream water are generally slightly less than that in the shallow groundwater, indicating dilution or some hyporheic or in-stream nitrate loss. Certain stream sites with on-the-ground indications of an increase in groundwater flux show higher average concentrations that other sites, indicating areas of well-connected ground and surface water. Modeling and isotopic tracer results indicate that a management change limiting leachable soil nitrate will likely show results in groundwater in few years (less than 10), though it will take decades to centuries to reduce nitrate by half in the aquifer. Lack of vertical mixing in the aquifer water column must be considered as it is physically impossible for the entire aquifer volume to have been ‘turned over’ and replaced with modern precipitation over the past two years.

We suspect continuous increasing nitrogen inputs to the aquifer if soil organic matter content remains the same or increases and fertilizer increases and a continuous input of nitrate to an already nitrate-rich aquifer, resulting in an exponential increase of concentrations in the groundwater. Because of the direct connection and generally well tracking nature of the ground and surface water nitrate, and possibly limited denitrification potential (given dissolved oxygen levels >2 mg L^{-1}), surface water concentrations are expected to stay elevated for at least as long as ground water concentration are.

Because no major nitrate loss is seen either in streams or in groundwater, this is unlikely to ever be a “self-remediating” system. We predict that the problem is likely to persist unless management steps can be taken to reduce soil nitrate leaching, and even then, concentrations will stay elevated for an extended period of time, though more research is needed to better understand management practice change on soil and groundwater nitrate pools.

There is likely annual variation in nitrate leaching to the aquifer since we know that even with below average precipitation in a year there is an increase in ground and surface water nitrate during the wet season. Though aquifer recharge and thus leaching was seen to discontinue as the growing season began in 2012, continuous or heavy precipitation into the growing season may saturate the soil enough for nitrate leaching to be ongoing until soil nitrate is depleted. Inter-annual variability in precipitation is likely an important driver of nitrate leaching, though the average nitrate concentration in the shallow aquifer would need decades to centuries of sustained decreases in nitrate inputs to substantially decrease concentrations.

This work indicates that more work must be done to assess nitrate leaching from the soil profile seasonally through altered management practices. With these practices, attenuation of nitrate will likely occur on a century or greater time scale, but without attention to nitrogen leaching minimization in practices, the problem is only expected to get worse. In light of unknown future climate conditions, the hydrologic framework should remain an imperative part of the research on soil nitrogen leaching. Future research needs include establishing more long-term monitoring wells, more careful consideration of locations for stream water sampling, an improved understanding of aquifer recharge and discharge rates.

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APPENDICES

APPENDIX A

TABULATED DATA

Table 5. USDA Montana Wheat Yield Information from 1945-2008 (USDA National Agricultural Statistics Service).

USDA Wheat Yield		
Year	Value (bu/acre)	kg N/ha
1945	14.3	14.3
1946	14.3	14.3
1947	16	16
1948	20.5	20.5
1949	17.1	17.1
1950	18.6	18.6
1951	14.3	14.3
1952	15.6	15.6
1953	15.9	15.9
1954	20.3	20.3
1955	21.5	21.5
1956	12.4	12.4
1957	27.2	27.2
1958	27.9	27.9
1959	26.2	26.2
1960	21.8	21.8
1961	23.6	23.6
1962	21.8	21.8
1963	28.4	28.4
1964	31.1	31.1
1965	22.9	22.9
1966	27.8	27.8
1967	29.1	29.1
1968	34.4	34.4
1969	19.1	19.1
1970	22.5	22.5
1971	26	26
1972	27.7	27.7
1973	24.3	24.3
1974	26.5	26.5
1975	26.7	26.7
1976	31	31
1977	31	31

Table 5 Continued. USDA Montana Wheat Yield Information from 1945-2008 (USDA National Agricultural Statistics Service).

1979	29.9	29.9
1980	31.3	31.3
1981	32.7	32.7
1982	30.7	30.7
1983	30.2	30.2
1984	27.3	27.3
1985	13.5	13.5
1986	31.9	31.9
1987	40.7	40.7
1988	24	24
1989	36.4	36.4
1990	27.7	27.7
1991	nd	nd
1992	nd	nd
1993	43.3	43.3
1994	27.6	27.6
1995	nd	nd
1996	23.6	23.6
1997	nd	nd
1998	nd	nd
1999	nd	nd
2000	32	32
2001	27.4	27.4
2002	25.5	25.5
2003	24.9	24.9
2004	36.2	36.2
2005	33.2	33.2
2006	35.4	35.4
2007	35.4	35.4
2008	27.5	27.5
2009	nd	nd
2010	nd	nd
2011	nd	nd
2012	nd	nd
2013	nd	nd

Table 6. Montana nitrogen fertilizer application rates from 1964-2009 (de Yong and Ames 2011).

Montana Fertilizer Application	
Year	Rate (kg/ha)
1964	5.60
1965	11.21
1966	12.33
1967	6.73
1968	10.09
1969	8.97
1970	11.21
1971	13.45
1972	15.69
1973	15.69
1974	14.57
1975	12.33
1976	19.05
1977	22.42
1978	26.90
1979	31.38
1980	25.78
1981	25.78
1982	40.35
1983	35.87
1984	44.83
1985	31.38
1986	33.63
1987	42.59
1988	42.59
1989	38.11
1990	49.32
1991	36.99
1992	35.87
1993	39.23
1994	52.68
1995	49.32

Table 6 Continued. Montana nitrogen fertilizer application rates from 1964-2009 (de Yong and Ames 2011).

1996	48.97
1997	56.64
1998	50.76
1999	61.87
2001	63.84
2003	48.70
2004	59.40
2006	60.53
2007	nd
2008	nd
2009	62.77

Table 7. Montana historical cropland data, harvested and total. This data was used to estimate when the proportion of fallow cropland decreased (USDA Census of Agriculture 2007; USDA National Agricultural Statistics Service 2007).

Montana Historical Harvested Cropland			
Year	Total Cropland (ac)	Harvested Cropland (ac)	% Harvested
1969	330142	154570	47%
1974	302021	168940	56%
1978	286886	156222	54%
1982	289738	187043	65%
1987	306262	179771	59%
1992	280291	159838	57%
1997	288532	201215	70%
2002	306553	179511	59%
2007	285022	185601	65%

Table 8. Nitrate-N data for water samples taken during 2012.

Surface and Ground Water Nitrate-N			
Site	Date	NO_3^--N	Uncertainty NO_3^--N ppm
		mg/L	mg/L
CRC	1/8/2012	12.94	0.05
CRC	4/14/2012	14.50	0.00
CRC	5/2/2012	14.06	0.12
CRC	5/9/2012	13.59	0.26
CRC	5/17/2012	13.81	0.24
CRC	5/22/2012	14.19	0.00
CRC	6/6/2012	12.81	0.04
CRC	6/11/2012	13.99	0.11
CRC	6/19/2012	14.16	0.02
CRC	6/26/2012	14.46	0.01
CRC	7/11/2012	15.03	0.06
CRC	8/6/2012	14.30	0.02
CRC	9/21/2012	6.89	10.34
CRC	11/3/2012	13.91	0.02
LC-A	4/13/2012	15.64	0.03
LC-A	5/2/2012	19.08	0.17
LC-A	5/8/2012	18.30	0.06
LC-A	5/16/2012	13.83	0.06
LC-A	5/23/2012	13.62	0.04
LC-A	6/6/2012	4.27	0.04
LC-A	6/11/2012	14.21	0.32
LC-A	6/19/2012	13.21	0.01
LC-A	6/26/2012	8.15	0.01
LC-A	7/11/2012	8.70	0.07
LC-A	8/7/2012	8.37	0.03
LC-A	9/23/2012	11.51	0.00
LC-A	11/3/2012	18.07	0.00
LC-B	1/8/2012	12.92	0.01
LC-B	4/13/2012	0.32	0.00
LC-B	5/2/2012	1.61	0.00
LC-B	5/8/2012	3.90	0.00

Table 8 Continued. Nitrate-N data for water samples taken during 2012.

LC-B	5/17/2012	12.04	0.03
LC-B	5/23/2012	13.12	0.29
LC-B	6/5/2012	0.61	0.01
LC-B	6/11/2012	1.06	0.01
LC-B	6/19/2012	11.49	0.01
LC-B	6/26/2012	10.98	0.03
LC-B	7/11/2012	11.85	0.03
LC-B	8/7/2012	8.85	0.03
LC-B	9/23/2012	13.51	0.01
LC-B	11/4/2012	12.21	0.02
LC-C	1/8/2012	17.59	0.05
LC-C	3/2/2012	9.58	0.00
LC-C	4/14/2012	13.87	0.02
LC-C	5/2/2012	16.14	0.01
LC-C	5/8/2012	17.11	0.07
LC-C	5/23/2012	15.81	1.63
LC-C	5/23/2012	16.69	0.20
LC-C	6/6/2012	13.23	0.05
LC-C	6/11/2012	15.16	0.09
LC-C	6/19/2012	16.17	0.03
LC-C	6/27/2012	17.70	0.05
LC-C	7/10/2012	16.51	0.06
LC-C	8/7/2012	16.76	0.01
LC-C	9/22/2012	15.21	0.00
LC-C	11/3/2012	17.22	0.01
LC-C	12/14/2012	18.01	0.02
LC-D	6/5/2012	9.00	0.00
LC-D	6/11/2012	9.32	0.01
LC-D	6/19/2012	9.75	0.01
LC-D	6/27/2012	8.50	0.01
LC-D	7/10/2012	10.10	0.09
LC-D	8/7/2012	11.02	0.00
LC-D	9/22/2012	9.64	0.00
LC-D	11/3/2012	13.85	0.00
LC-E	1/8/2012	15.40	0.05
LC-E	3/2/2012	12.14	0.01
LC-E	4/13/2012	8.88	0.04

Table 8 Continued. Nitrate-N data for water samples taken during 2012.

LC-E	5/2/2012	11.04	0.15
LC-E	5/9/2012	10.57	0.05
LC-E	5/16/2012	10.73	1.11
LC-E	5/22/2012	9.24	0.01
LC-E	5/30/2012	10.58	0.01
LC-E	6/5/2012	7.94	0.00
LC-E	6/11/2012	9.70	0.01
LC-E	6/20/2012	9.96	0.02
LC-E	6/27/2012	9.45	0.02
LC-E	7/11/2012	10.56	0.01
LC-E	8/7/2012	9.78	0.01
LC-E	9/22/2012	12.75	0.00
LC-E	11/3/2012	13.37	0.00
L-P	4/14/2012	25.44	5.11
L-P	5/2/2012	23.02	0.19
L-P	5/9/2012	22.20	0.11
L-P	5/16/2012	20.66	0.22
L-P	5/22/2012	20.47	0.01
L-P	5/30/2012	20.88	0.00
L-P	6/5/2012	22.26	2.30
L-P	6/11/2012	21.19	0.05
L-P	6/20/2012	20.87	0.06
L-P	6/27/2012	22.32	0.15
L-P	7/10/2012	21.75	0.07
L-P	8/7/2012	21.20	0.22
L-P	9/22/2012	20.78	0.00
L-P	11/3/2012	19.59	0.03
M-1	1/7/2012	20.66	0.04
M-1	3/2/2012	21.06	0.32
M-1	4/14/2012	21.20	0.01
M-1	5/2/2012	22.11	0.53
M-1	5/8/2012	21.91	0.04
M-1	5/17/2012	19.76	1.16
M-1	5/22/2012	22.37	5.62
M-1	6/6/2012	21.13	0.07
M-1	6/11/2012	21.25	0.14
M-1	6/19/2012	22.36	0.02

Table 8 Continued. Nitrate-N data for water samples taken during 2012.

M-1	6/26/2012	22.60	0.03
M-1	7/11/2012	21.76	0.03
M-1	8/7/2012	20.64	0.44
M-1	9/21/2012	19.81	4.03
M-1	11/3/2012	22.13	0.01
SPR	4/14/2012	24.95	0.08
SPR	5/2/2012	26.32	0.03
SPR	5/9/2012	25.42	0.18
SPR	5/22/2012	26.28	0.03
SPR	5/30/2012	24.48	0.07
SPR	6/5/2012	24.71	0.26
SPR	6/11/2012	25.30	0.23
SPR	6/27/2012	25.08	0.07
SPR	7/10/2012	24.94	0.22
SPR	8/7/2012	26.54	2.71
SPR	9/22/2012	22.29	0.01
SPR	11/3/2012	21.50	0.00
TribA	1/8/2012	54.44	0.02
TribA	3/2/2012	45.91	0.65
TribA	4/14/2012	50.92	1.10
TribA	5/2/2012	26.15	0.28
TribA	5/8/2012	12.86	0.05
TribA	5/17/2012	5.37	0.14
TribA	5/22/2012	26.87	0.13
TribA	6/5/2012	25.83	0.03
TribA	6/11/2012	38.98	0.12
TribA	6/19/2012	10.69	0.12
TribA	6/26/2012	2.55	0.00
TribA	7/11/2012	0.75	0.01
TribA	8/7/2012	0.13	0.00
TribA	9/23/2012	0.01	0.00
TribA	11/4/2012	2.79	0.00

Table 9. Pearson's product-moment correlation of Nitrate-N and stream discharge (Q) for five surface water sites. All p-values are not-significant (p-value > 0.05), indicating there is no evidence that correlations are not equal to zero.

	D.f.	p-value	R-value
LC-A Q vs. NO3-N	11	0.16	-0.42
LC-C Q vs. NO3-N	13	0.29	-0.29
LC-D Q vs. NO3-N	6	0.56	-0.24
LC-E Q vs. NO3-N	14	0.90	0.03
L-P Q vs. NO3-N	12	0.62	0.15

Table 10. Tukey Honest Significant Difference (HSD) procedure results for nitrate in stream and well sites. Grey highlighted rows indicate stream nitrate means that are significantly different (p-value <0.05).

Tukey HS Pairwise Comparison		
Site Comparison	p-value	Significantly Different? (p-value < 0.05)
L-P-CRC	0.08	N
LC-A-CRC	1.00	N
LC-B-CRC	0.60	N
LC-C-CRC	1.00	N
LC-D-CRC	0.99	N
LC-E-CRC	0.99	N
M1-CRC	0.08	N
SPR-CRC	0.00	Y
TribA-CRC	0.23	N
LC-A-L-P	0.05	Y
LC-B-L-P	0.00	Y
LC-C-L-P	0.42	N
LC-D-L-P	0.01	Y
LC-E-L-P	0.00	Y
M1-L-P	1.00	N
SPR-L-P	0.98	N
TribA-L-P	1.00	N
LC-B-LC-A	0.78	N

Table 10 Continued. Tukey Honest Significant Difference (HSD) procedure results for nitrate in stream and well sites. Grey highlighted rows indicate stream nitrate means that are significantly different (p-value <0.05).

LC-C-LC-A	0.98	N
LC-D-LC-A	1.00	N
LC-E-LC-A	1.00	N
M1-LC-A	0.05	N
SPR-LC-A	0.00	Y
TribA-LC-A	0.15	N
LC-C-LC-B	0.10	N
LC-D-LC-B	1.00	N
LC-E-LC-B	0.99	N
M1-LC-B	0.00	Y
SPR-LC-B	0.00	Y
TribA-LC-B	0.00	Y
LC-D-LC-C	0.70	N
LC-E-LC-C	0.58	N
M1-LC-C	0.45	N
SPR-LC-C	0.03	Y
TribA-LC-C	0.75	N
LC-E-LC-D	1.00	N
M1-LC-D	0.01	Y
SPR-LC-D	0.00	Y
TribA-LC-D	0.04	Y
M1-LC-E	0.00	Y
SPR-LC-E	0.00	Y
TribA-LC-E	0.01	Y
SPR-M1	0.96	N
TribA-M1	1.00	N
TribA-SPR	0.81	N

APPENDIX B

ADDITIONAL FIGURES

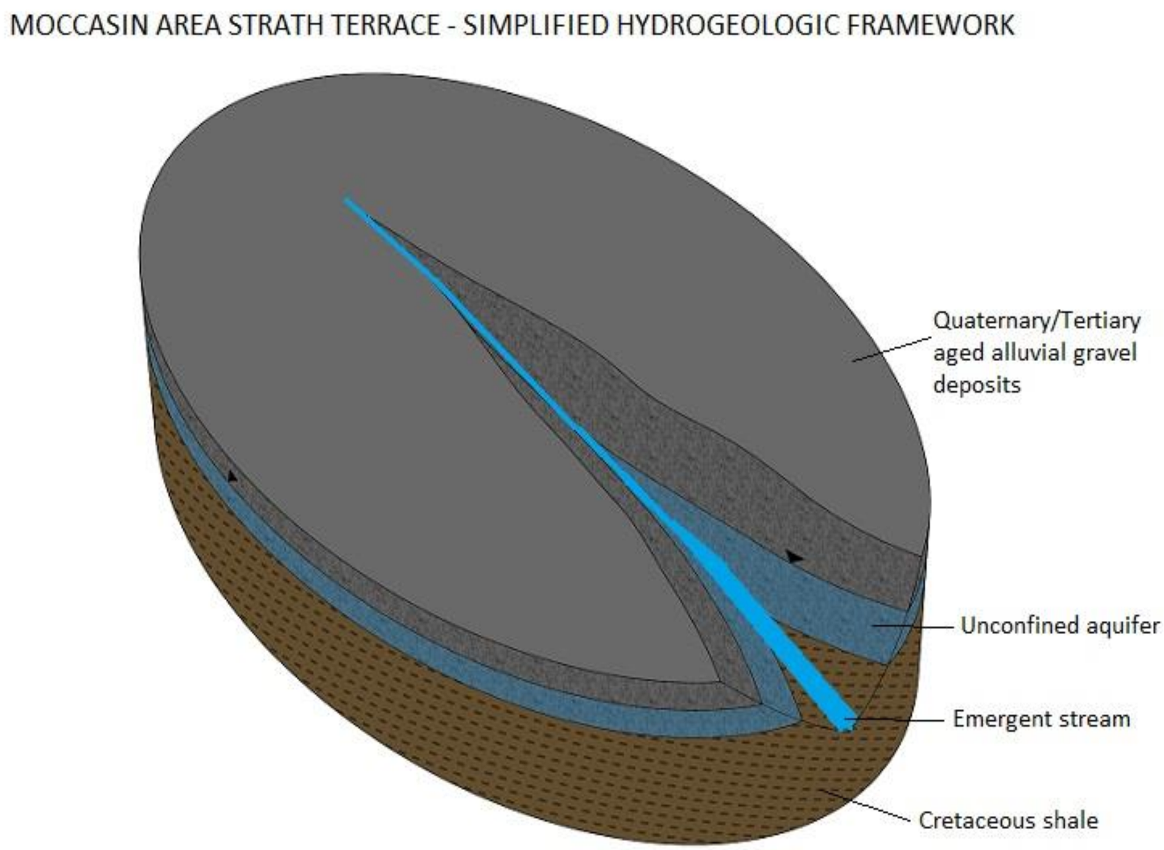

Figure 12. Simplified hydrogeologic framework of the Moccasin, Montana area strath terrace. Quaternary/Tertiary aged alluvial gravels hold the shallow, unconfined aquifer, confined below by Cretaceous aged shale. Emergent streams are present on this landform which downcut through the alluvial gravels into the shale. (Source: J. Switzer)

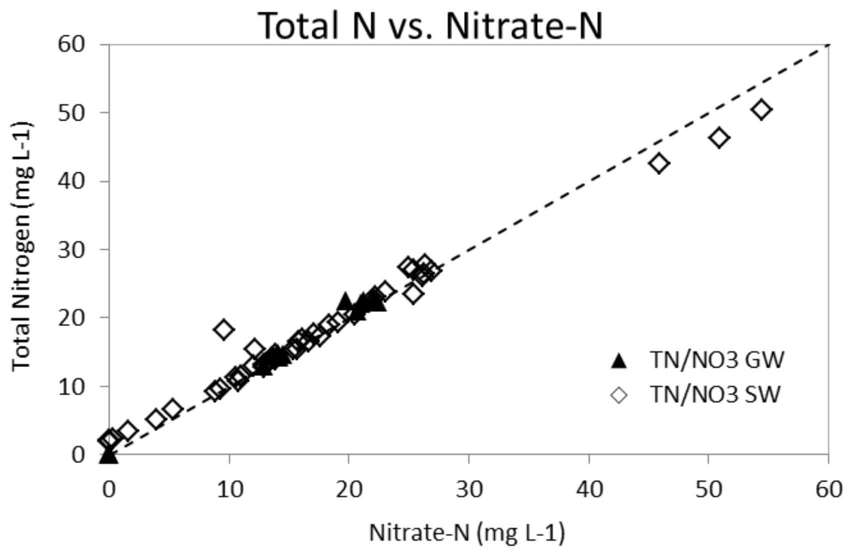

Figure 13. Total nitrogen and nitrate-N for all samples in ground and surface water in the study area during 2012. Nearly all points fall along a 1:1 line, with some scatter due to analytical uncertainty. This indicates that nitrate is the dominant species of nitrogen in the samples collected.

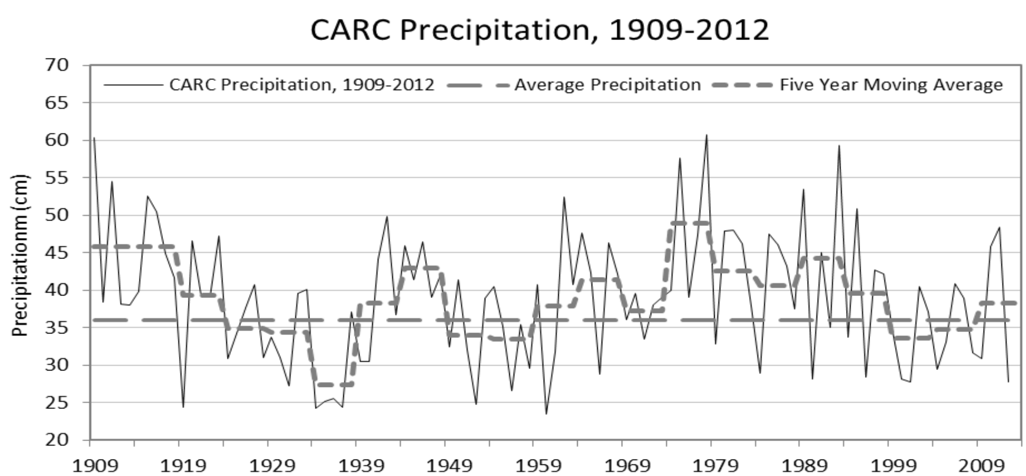

Figure 14. Precipitation at the Montana State University Central Agricultural Research Center in Moccasin, Montana between 1909 and 2012 shown in the solid black line. The grey long dashed line represents the average precipitation over this time (36.0 cm) and the short dashed line represents a five year moving average of precipitation. Data Source: (Montana State University Central Agricultural Research Center 2012)

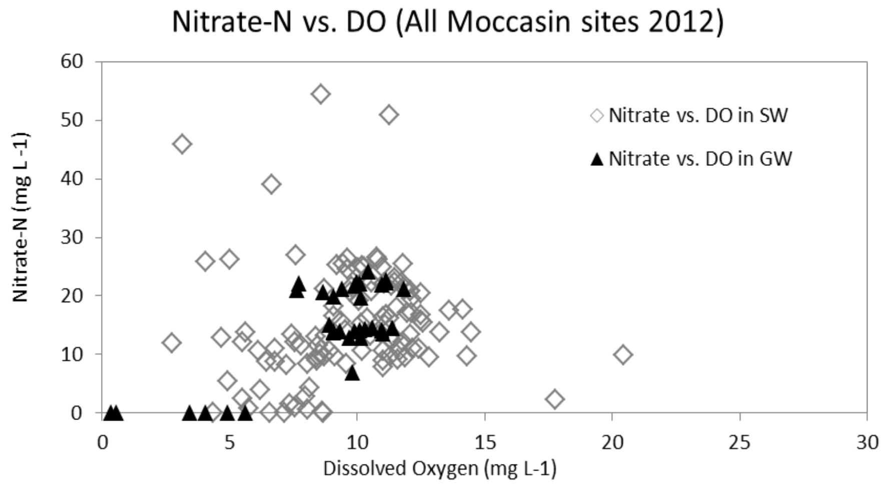

Figure 15. Nitrate-N versus dissolved oxygen at all sites measured shows wide scatter of DO concentrations in surface water and more limited scatter within groundwater.

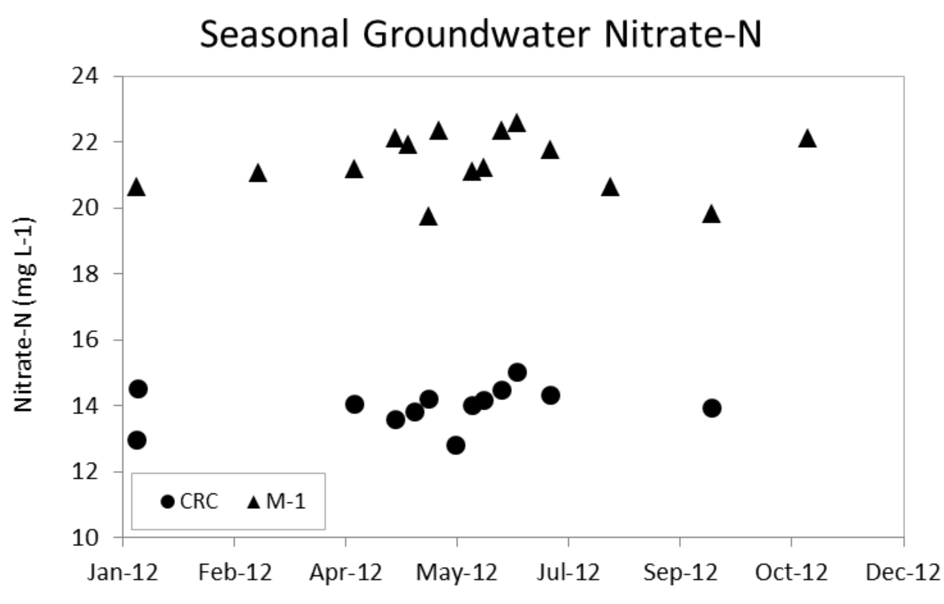

Figure 16. Seasonal groundwater nitrate-N in water samples from two shallow wells on the Moccasin terrace**.** The nitrate-N in M-1 appears to have generally higher nitrate concentrations than the CARC shallow well, with greater seasonal fluctuations.

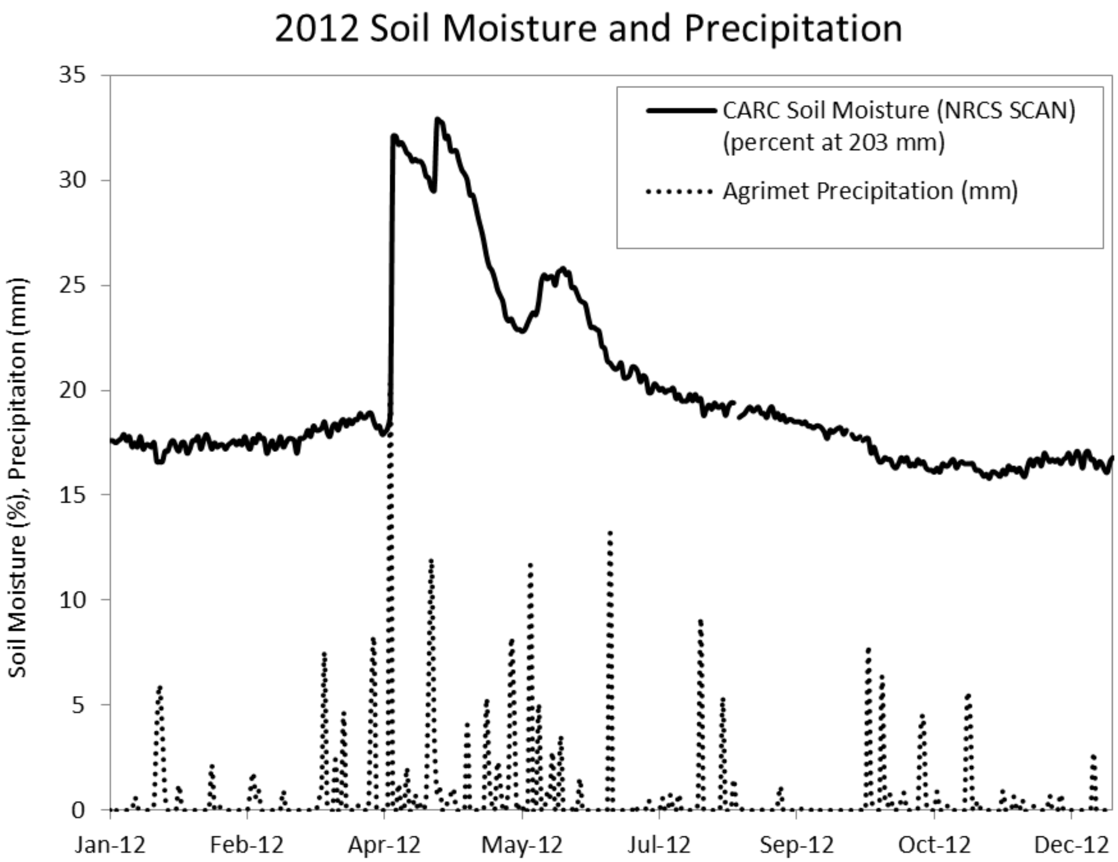

Figure 17. Soil moisture (Natural Resources Conservation Service SCAN site #2119) and AgriMet precipitation at the Central Agricultural Research Center (CARC). A major increase in soil moisture is seen during a large precipitation event. Nitrate leaching to groundwater as a function of precipitation amount is likely to depend largely on existing soil moisture status and soil thickness.

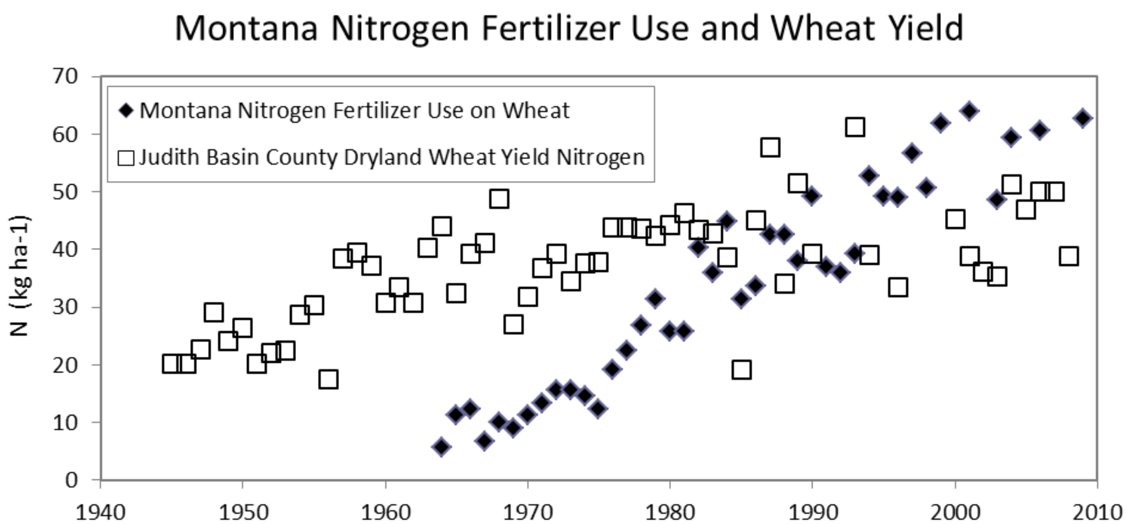

Figure 18. Rates of Montana nitrogen fertilizer application (an increase of 0.35 kg ha^{-1} yr^{-1}, $R^2 = 0.3485$) are outpaced by nitrogen removal in Judith Basin County dryland wheat yields (an increase of 1.38 kg ha^{-1} yr^{-1}, $R^2 = 0.92$).

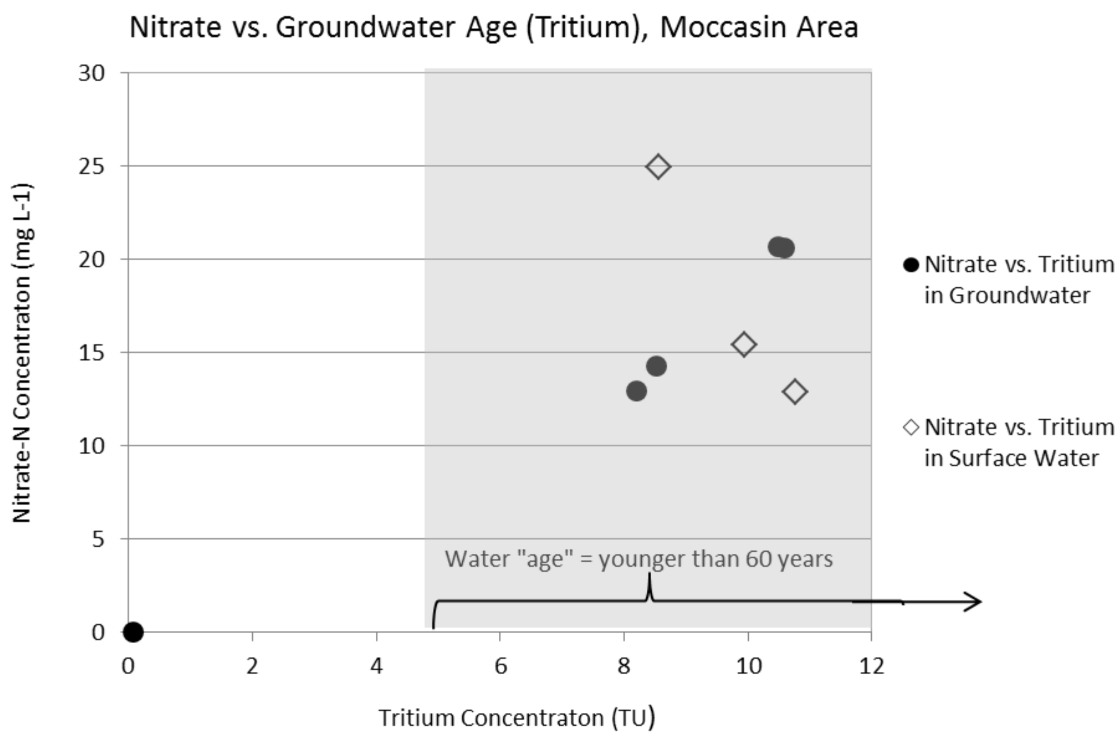

Figure 19. Tritium analyses show that shallow well or surface water samples have "modern" tritium (less than 60 years old, bomb tritium present). These samples are where high nitrate is found shows a much older signature and has nearly non-detectable nitrate (lower left corner of plot).

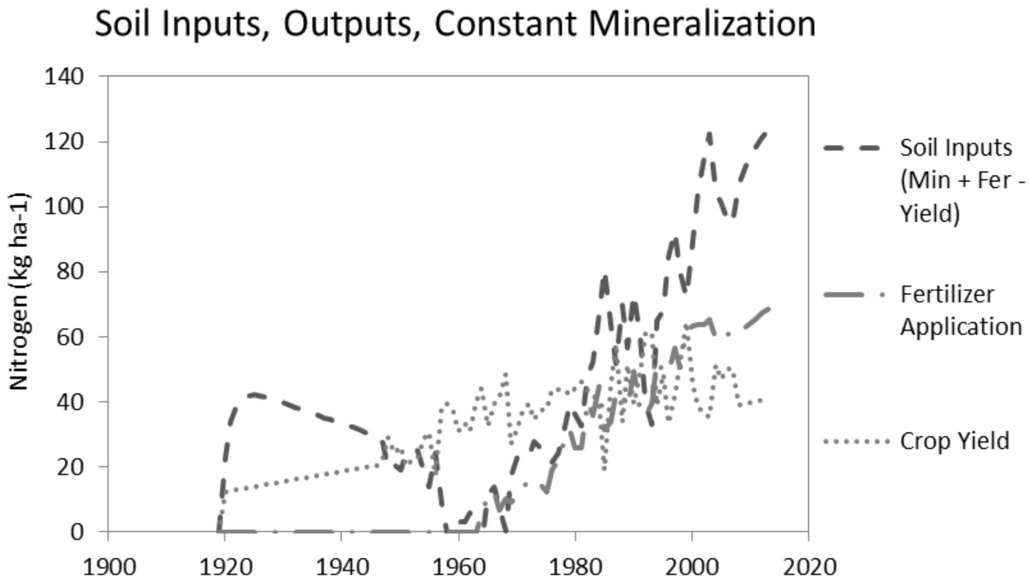

Figure 20. Known and estimated inputs and outputs to the agricultural system. Soil mineralization input (M in) is estimated at 35 kg ha-1 (Jones, unpublished data), Fertilizer Application and Crop Yield are known with relative certainty (USDA Economic Research Service; USDA National Agricultural Statistics Service). Soil nitrogen (S_N) is a summation of mineralization (M_N) and fertilizer application (F_N), and Wheat Yield (Y_N) was subtracted off. For the period of record, data indicate that wheat yield nitrogen has increased 0.39 kg ha^{-1}, while for the period of record, fertilizer application nitrogen used on wheat has increased 1.46 kg ha^{-1} , more than threefold faster than whet yield has increased.

APPENDIX C

ADDITIONAL SAMPLE ANALYSIS INFORMATION

Nitrate

Calibration standards were prepared individually by single dilution (using a digital pipette and 50 or 100 mL volumetric flask for each standard) from a stock standard of 100 ppm NO_3^--N or NO_2^--N, either the day of the sample run or a maximum of two days prior to the sample run. The stock solutions were prepared in July 2012 using solid $NaNO_2$ or KNO_3 and ultrapure water (18 MOhm, LJH 824 Millipore ultrapure water for all sample runs through September, 2012; Brookshire Lab Millipore water purification system for sample runs in November, 2012). Calibration with seven levels (10.0, 5.0, 2.0, 1.0, 0.5, 0.2, 0.0 mg L^{-1}) was performed at the onset of each run (see attached sample run results) and a quadratic fit was used. An external check standard (SPEX CertiPrep 1000 mg/L NO_3^--N diluted to 10 mg L^{-1} no more than two days prior) was used after August 15, 2012 and was included at least once in each sample run. A cadmium column efficiency check was used after August 15, 2012 and included a 10 mg/L NO_2^--N and 10 mg L^{-1} NO_3^--N made from the stock standard described above. Results were considered acceptable when (a) the calibration curve had an R^2 of at least 0.990, (b) check standards were within 11% of known concentrations, and (c) the external check standard result was within 11% of the theoretical value. Laboratory blanks were used in each run (LJH 824 Millipore ultrapure water for all runs through September, 2012; Brookshire Lab Millipore water for the November, 2012 sample run). Field blanks (Millipore water from LJH 824) were collected and filtered using the standard procedures used for sample collection, beginning in the second week of sampling in May, 2012.

<u>Dissolved Organic Carbon and Total Nitrogen</u>

Aliquots of 20 mL were transferred from the pre-sample vials into Shimadzu clear glass vials that had been washed and combusted. The samples were acidified to 2% with 6 N hydrochloric acid upon analysis using the auto-acidification capability on the instrument. A historic calibration curve using three standards: 0.1, 1.0 and 10 mg/L DOC and TN, (file name 080211_DOC_TN_BROOK) with an R^2 value of 1.000 for a linear fit was used for each run. Check standards (standards run as unknowns) were prepared the day of each run by serial dilution from a stock standard (100 mg L^{-1} KHP and 100 mg L^{-1} KNO_3 prepared August 2010) with four levels (for DOC and TN: 10.00, 1.00, 0.10, 0.00 mg/L) and analyzed at the start of each run (see attached sample output). These check standards were prepared using ultrapure water from Leon Johnson Hall Room 824 Millipore water purification system for all sample runs to date. An external check standard (SPEX CertiPrep 1000 mg L^{-1} NO_3^--N diluted to 10 mg L^{-1} no more than two days prior) was used after August 15, 2012 and was included at least once in each sample run. Laboratory blanks were collected from the Leon Johnson Hall 824 Millipore water purification system and ran for all runs to date. Field blanks (Leon Johnson Hall 824 Millipore water) were collected and filtered using the standard procedures used for sample collection, beginning in the second week of sampling in May, 2012. Check standards for DOC and TN on the Shimadzu varied from theoretical values for the 0.1 mg L^{-1} standard by up to 80% (four analyses), while the 1.0 mg L^{-1} standard varied by 3.5% or less (four analyses), and the 10.0 mg L^{-1} varied by 2% or less (two analyses).

APPENDIX D

DATA LOCATION INFORMATION FOR FIGURE REPRODUCTION

Data Location Information for Figure Reproduction

- Map of Judith River Basin, with or without Moccasin Polygon

  Miller Data -> Figures, Images -> "UpdatedJudithMapForThesis_20120610.jpg" OR "UpdatedJudithMapForThesis_NoMoccPoly_20131112.jpg"

- Sample site coordinates: (Adam Sigler also has all additional GIS data used in site location map)

  Miller Data -> Reference Data, GPS, GIS -> "Judith_Water_Sampling_SiteCoordinates20131118.xls"

- Historic (and current) nitrate in M-1 Data:

  Miller Data -> M-1 Historical Data + 2012 Nitrate Data -> "M-1 Level and Nitrate 2013-11-18.xls"

- Schematic of mass balance and water balance model

  Miller Data -> Figures, Images -> "boxANDwaterbalance_model_20120416_0006.jpg"

- Boxplots of stream and well nitrate-N (copy the code into R and run)

  Miller Data -> Statistical Code for Moccasin -> "Boxplots_Ttests_M1_CRC_LCC_LCD_LCE_20121119.txt"

- Groundwater level in M-1 with precipitation and nitrate

  Miller Data -> M-1, Agrimet, Nitrate, LouseCreekQ -> "Precip_M1WaterLevel_Agrimet20131118.xls" -> Sheet titled "M-1_Depth,Precip,Nitrate_Plot"

- Groundwater level in M-1 with precipitation and nitrate and LC-E discharge

  Miller Data -> M-1, Agrimet, Nitrate, LouseCreekQ -> "Precip_M1WaterLevel_Agrimet20131118.xls" -> Sheet titled "Data Summary, May-June Plot"

- Seasonal nitrate-N changes at sampling locations

Miller Data -> Field_Data_Summary_and_Nitrate_Figures -> "FieldData_Nitrate_Figures_AdditionalReferenceInformation_20131121.xls" -> sheet titled "Figures"

- Groundwater flow model image

  Miller Data -> Figures, Images -> "Gw_Flow_withBackwardsParticles_20130429.jpg" sourced from groundwater model (Data -> Groundwater Modeling -> "Moccasin2013Apr23_BackwardsParticles_SampleSites.gpr")

- Mean reverse particle travel time vs. mean nitrate-N

  Miller Data -> Groundwater Modeling -> "ParticleSet_Check_Moccasin_20131119.xls", see sheet titled "Summary"

- Nitrogen mass balance plot with cropping scenarios as well as k_L sensitivity

  Miller Data -> N Mass Balance Data -> "Miller_N_MassBalance_20131119.xls", which references sensitivity analysis data from -> Data -> N Mass Balance Data -> "Miller_N_MassBalance_kL_Sensitivity_20131119.xls"

- Moccasin area strath terrace schematic

  Miller Data -> Figures, Images -> "Louse Creek Reference.jpg." (for the unlabeled schematic), or "Louse Creek Reference_20130404_1106.jpg" (for the labeled version)

- Total N vs. Nitrate-N

  Miller Data -> Field_Data_Summary_and_Nitrate_Figures -> "FieldData_Nitrate_Figures_AdditionalReferenceInformation_20131121.xls" -> sheet titled "TN and NO3"

- CARC Precipitation 1909-2012

  Miller Data -> Precip, Soil Moisture, ET -> "Moccasin_Precip_20130602_1931.xls" -> sheet titled "CARC Precipitation Summary"

- Nitrate-N and Dissolved Oxygen

Miller Data -> Field_Data_Summary_and_Nitrate_Figures -> "FieldData_Nitrate_Figures_AdditionalReferenceInformation_20131121.xls" -> sheet titled "Figures"

- Seasonal Groundwater Nitrate –N

  Miller Data -> Field_Data_Summary_and_Nitrate_Figures -> "FieldData_Nitrate_Figures_AdditionalReferenceInformation_20131121.xls" -> data for figure exists in sheet titled "MoccasinGW_UpdatedNO3"

- CARC Soil Moisture and Precipitation

  Miller Data -> Precip, Soil Moisture, ET -> "Moccasin_Precip_20130602_1931.xls" -> sheet titled "CARC_Soil_Moisture_Precip_20130410.xls" -> sheet titled "2119_SMS_YEAR=2012"

- Montana Nitrogen Fertilizer use and Wheat Yield

  Miller Data -> N Mass Balance Data -> "Miller_N_MassBalance_20131119.xls" -> sheet titled "MontanaFertilizerUse", data is sourced from this sheet and from sheet titled "Yearly_USDA_Grain_Yield"

- Tritium and Nitrate-N Plot

  Miller Data -> Tritium, Noble Gas Data -> "Tritium_NobleGas_NO3_Summary_20121118.xls" -> sheet titled "Tritium, Noble Gas, NO3 Summary"

- Soil Inputs, Outputs, Constant Mineralization

  Miller Data -> N Mass Balance Data -> "Miller_N_MassBalance_20131119.xls" -> data is source from sheet titled "MontanaFertilizerUse" as well as from sheet "Yearly_USDA_Grain_Yield". Actual figure has been eliminated from mass balance data file.