5-2008

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Recommended Citation

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DISCRIMINATING BETWEEN BIOLOGICAL AND HYDROLOGICAL CONTROLS OF HYPORHEIC DENITRIFICATION ACROSS A LAND USE GRADIENT IN NINE WESTERN WYOMING STREAMS

by

Andrew K. Myers

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER of SCIENCE

in

Watershed Science

Approved by:

Michelle A. Baker Major Professor	Helga Van Miegroet Committee Member
Tamao Kasahara Committee Member	Byron Burnham Dean of Graduate Studies

UTAH STATE UNIVERSITY
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2008

ABSTRACT

Discriminating Between Biological and Hydrological Controls of Hyporheic Denitrification Across a Land Use Gradient in Nine Western Wyoming Streams

by

Andrew K. Myers, Master of Science

Utah State University, 2008

Major Professor: Dr. Michelle A. Baker
Department: Watershed Sciences

I studied nine streams near Grand Teton National Park, Wyoming, covering a land use gradient (urban, agricultural, and forested) to assess influences of land use on denitrification rates and hyporheic exchange. I hypothesized denitrification in the hyporheic zone is governed by availability of chemical substrates and hydrologic transport. I tested this hypothesis by coupling measurements of denitrification potentials in hyporheic sediments with a 2-storage zone solute transport model. Denitrification potentials were lowest on average in hyporheic sediments from forested streams and highest from agricultural streams. Modeling results suggest, on average, agricultural sites are transport-limited by having the slowest exchange rate with hyporheic zone and longest transport before entering storage. Land use influences the capacity for hyporheic denitrification in two ways 1) agricultural and urban practices supply substrates that build the microbial potential for denitrification and 2) agricultural and urban activities alter channel form and substrates, limiting hyporheic exchange.

(77 pages)

ACKNOWLEDGMENTS

Special thanks to Bill Resor and the Snake River Ranch for access to study sites and cooperation in this research. Thanks to Chris Arp, Mike Gooseff, Bob Hall, Jen Tank, Roy Haggerty, and Steve Wondzell for providing context in developing this research. Special thanks to Helga Van Miegroet and Tamao Kasahara of my graduate advisory committee for their help and guidance through this wonderful experience. I would also like to thank Hank Harlow from the National Park Service – AMK Research Center for field accommodations and lab space. None of this work could have been done without Susan O'Ney and the cooperation of the National Park Service for permitting us to work in Grand Teton National Park. Additional thanks to Ian Washbourne, Keli Goodman, Erin Hotchkiss, and Lisa Kunza for their help in the field. I give thanks to Susan Durham of Utah State University for statistical guidance of denitrification analyses. Special thanks to Jo Nissembaum for her devotion to lab work and Rob Payne for modeling guidance. Finally, I would like to thank all the wonderful people in the Baker Lab, Keli Goodman, Ian Washbourne, Jo Nissemabum, Scarlett Vallaire, Sam Hochhalter, Angie Benedetto, Chelsea Crenshaw, and Evan Lytle, with whom I have been fortunate enough to work. This research was funded by the National Science Foundation (grant # EAR-0409591).

Andrew K. Myers

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

Nutrient availability affects water quality and the productivity of aquatic ecosystems. Nitrogen (N) and phosphorous (P) are important chemical constituents of aquatic systems as they are essential nutrients needed for cellular growth. When present in excess, N and P can cause eutrophication, or the over-productivity of water bodies. Historically, lakes are generally thought to be limited by P availability (Wetzel 2001), while streams can be limited by N or P, or co-limited by both N and P (Dodds 2002). Both N and P are present in streams due to natural sources such as mineralization in and transport from uplands (Wetzel 2001). Scores of studies have evaluated the effect of N and P on primary productivity in aquatic ecosystems (Elser et al. 2007). Recent research in stream ecosystems has focused on the rapid increase of anthropogenic N to streams and subsequent ecological consequences (e.g. Peterson et al. 2001; Mulholland et al. 2008).

It is increasingly acknowledged that anthropogenic activities are a principal threat to water quality and the overall integrity of aquatic ecosystems (Allan et al. 1997; Allan 2004). Activities such as fossil fuel combustion and inorganic fertilizer application over the last fifty years have doubled the amount of reactive N cycling globally (Vitousek et al. 1997). In excess, N can have negative effects on freshwater, marine, and terrestrial ecosystems, including eutrophication and creation of hypoxic environments similar to that found in the Gulf of Mexico (Rabalais et al. 2002; Fenn et al. 2003).

Land Use Practices and Stream Ecosystems

Land use practices that affect stream ecosystems are often categorized as follows: agriculture, urbanization, mining, logging, and recreation (Bryce et al. 1999). The work presented in this thesis focuses on hydrological and biogeochemical processes within agricultural, urban, and reference (forested) streams in the Intermountain shrub-steppe biome (Gooseff et al. 2007).

Agricultural practices can increase nutrient and sediment loads to streams, thus altering ecosystem functioning. Fertilizer applications in particular have been shown to increase nitrate (NO_3^-) concentrations in streams, leading to eutrophication and decreased biodiversity (Vitousek et al. 1997). High NO_3^-concentrations (>10 mg N/L) also are linked to human health risks (USEPA 1990). Agricultural practices also alter hydrologic characteristics of streams depending on the type of agriculture (i.e. crops vs. livestock) and source of irrigation water (ground water vs. stream diversion). For example, use of row crops can lead to increases in magnitude and frequency of storm flows, which can increase erosion and alter community composition (Allan 2004). Problems associated with agriculture are exacerbated due to the spatial extent that agricultural land occupies across the globe. Agricultural land often occupies the largest portion of land in developed catchments, with coverage estimates upward of 66% in areas such as Upper Mississippi Basin (Benke and Cushing 2004).

Urbanization has been recognized as a threat to aquatic ecosystems for several decades (Leopold 1968), and has received increased research attention in recent years (Grimm et al. 2005; Meyer et al. 2005). It is estimated that 75% of the world's population lives in urban areas, yet urban areas make up only 2% of the earth's surface (Paul and Meyer 2001). The foremost concern associated with urbanization is the increase in impervious surfaces, which reduces soil infiltration capacities at the same time as increasing surface runoff (Leopold 1968). This phenomenon often results in flashy stream flow and in an increase in amounts of sediment and nutrients such as NO_3^-, both of which can affect the ecological integrity of streams (Allan 2004).

Land use practices such as agriculture and urbanization are often assessed by comparing to reference sites. Establishing reference conditions is increasingly a challenge as the human footprint extends well beyond the land surface people use directly (Grimm et al. 2008). For streams, reference conditions represent the undisturbed (or minimally disturbed) state with respect to physical, chemical and biological elements (Wallin et al. 2003).

Nitrogen Cycling in Stream Ecosystems

In light of recent increases in N loading to streams world wide, recent research has focused on understanding sources, sinks and transformations of N in streams (e.g. Alexander et al. 2000; Peterson et al. 2001; Mulholland et al. 2008). Mass balance approaches have shown that only 20% to 30% of N added to land is eventually exported to the ocean (Howarth 1996). As N availability increases, biological requirements for N are met which allows for increased algal growth, and decreases biodiversity of stream communities by allowing certain taxa to out-compete other organisms for N and other nutrients. Nitrate, an important form of N in aquatic systems, comes from two main natural sources; regeneration in situ through coupled biological processes of mineralization of organic N and nitrification, and leaching from soil (Webster and

Ehrman 1996). Anthropogenic sources include atmospheric deposition and agricultural and urban runoff, as well as point sources such as waste water effluent (Allan 2004).

Denitrification is the only mechanism for permanent N loss from streams (Martin et al. 2001), and it is a source of greenhouse gasses (Sigunga 2003). As illustrated in Figure 1, denitrification is the reduction of NO_3^- to NO_2^- to N_2O to N_2 (~77% of atmospheric gas). This process is carried out by bacteria in anaerobic conditions when organic substrates are available as electron donors. Thus, the supply and quality of labile organic carbon is fundamental for denitrification to occur. Furthermore, the final reduction of N_2O to N_2 has been shown to be a direct function of dissolved organic carbon (DOC) abundance and quality (Jones 1995).

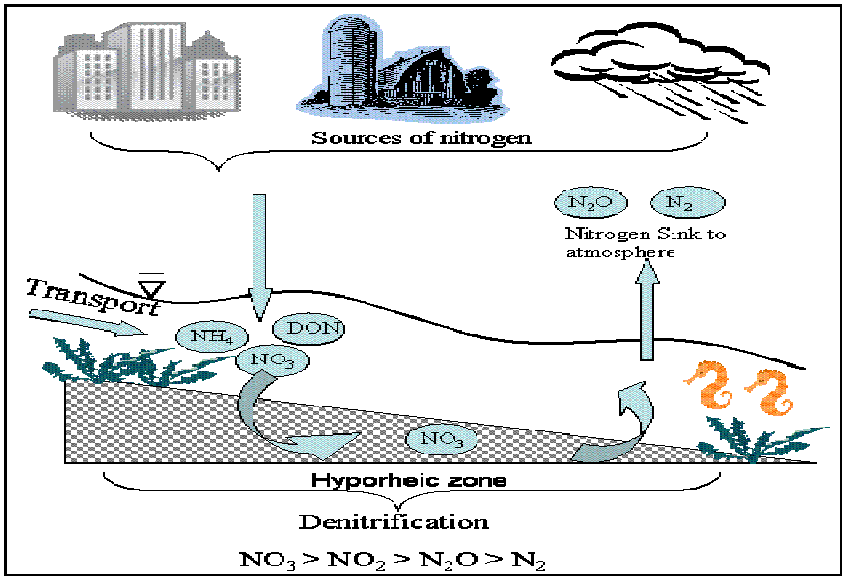

Figure 1. Conceptual diagram of denitrification occurring in the hyporheic zone.

Denitrification occurs in stream bed sediments, riparian soils, or other low oxygen environments (Rysgaard et al. 1994). Denitrifying microbes are able to use NO_3^- as the terminal electron acceptor during organic matter decomposition when O_2 is not available (Randall and Ingraham 1981). Most denitrifiers are facultative anaerobes and will preferentially use O_2 for cellular respiration if it is available (Tiedje et al. 1982) because of higher energy yields (Bohn et al. 1979; Madigan and Brock 1991).

One important area of stream biogeochemistry research is aimed at quantifying denitrification rates with respect to available NO_3^- to evaluate effectiveness of denitrification as a N loss process. Some researchers accomplish this by measuring the mass of NO_3^- that leaves streams via denitrification per unit time relative to the amount in transport. Generally, N loads can be directly related to land use practices (Grimm et al. 2005; Bernot et al. 2006). However, the relationship between land use and N cycling, and denitrification in particular, is poorly understood (Inwood et al. 2005).

Denitrification in reference stream systems (i.e. forested streams) is typically limited by NO_3^- (Martin et al. 2001), therefore denitrification may not represent a significant N sink. Conversely, streams located in agricultural and urban landscapes generally have higher concentrations of NO_3^- (i.e. NO_3^- is not a limiting factor) than undisturbed systems, and positive correlations have been observed between NO_3^- concentrations and denitrification rates (Kemp and Dodds 2001; Groffman et al. 2005; Mulholland et al. 2008). Although Royer et al. (2004) found high concentrations of stream NO_3^- and relatively high denitrification rates in the streambed of agricultural streams; denitrification did not represent a significant N sink relative to N loading.

In contrast to N availability, Groffman et al. (2003) found that denitrification in urban riparian zones was more highly correlated to carbon-related variables (i.e. microbial biomass) than nitrogen-related variables (i.e. nitrification). Similarly, Baker and Vervier (2004) found that denitrification in the hyporheic zone of the NO_3^- rich Garonne River was limited by availability of dissolved organic matter. Additional work is clearly needed to elucidate relationships between NO_3^- loading and denitrification rates across streams subject to different land use practices.

Hydrology and Biogeochemistry of Stream Hyporheic Zones

The hyporheic zone is defined as the interface between stream water and groundwater, where the stream water passes back and forth between the active channel and subsurface flow paths (Figure 2; Bencala and Walers 1983; Runkel 1998). Studies have shown that the hyporheic zone plays an important role in stream functioning with respect to physical characteristics (i.e. stream temperature, habitat) (Stanford and Ward 1988) and as an important area for nutrient uptake and transformation (Findlay 1995; Morrice et al. 1997; Baker et al. 1999; Baker et al. 2000).

Many physical attributes have been shown to drive hyporheic exchange. On large spatial scales, Morrice et al. (1997) found that parent lithology of watersheds affects hyporheic flow by controlling sediment porosity and hydraulic conductivity. At small spatial scales, bed topography (i.e. dunes and ripples in sediments) drives hyporheic exchange because of changes in local hydraulics (i.e. turbulent vs. laminar flow) (Harvey and Bencala 1993; Packman and Salehin 2003). At intermediate spatial scales, stream slope, morphology (Wondzell 2005) and bed form also influence hyporheic exchange. For example, Kasahara and Wondzell (2003) found hyporheic flow in a steep mountain stream was primarily controlled by pool-step sequences. The combination of these physical attributes at different spatial scales creates and supports hyporheic exchange.

The ecological importance of hyporheic exchange is much greater than just a hydrologic flux. Hyporheic exchange greatly increases the contact time of stream water with chemically reactive sediments and microbial communities, which creates hot spots for biogeochemical processes (Findlay 1995). Furthermore, these hot spots can be especially important for N cycling processes in streams because of strong redox gradients associated with penetration of oxygen-rich water into slower moving subsurface sediments (Baker et al. 1999). Any dissolved oxygen (DO) reaching the hyporheic zone can be quickly depleted as a result of microbial respiration, creating anaerobic conditions (Dahm et al. 1991). It is under these conditions that NO_3^- can be used as an electron acceptor, and is further reduced to N gases (Baker et al. 1999). Organic carbon is also needed for these processes and its availability may limit microbial activity in the hyporheic zone (Baker et al. 2000; Baker and Vervier 2004). Due to the complex nature of hyporheic processes, further research is needed to clarify these processes under different conditions.

Solute Transport Modeling

Solute transport models are commonly used to quantify surface water-groundwater interactions. Typically these models describe solute transport as a function of advection, dispersion, lateral inflow, and transient storage (Bencala and Walters 1983). Advection is downstream transport at the mean water velocity (Webster and Ehrman 1996), dispersion is caused by molecular diffusion and turbulent flow (Webster and Ehrman 1996), lateral inflow is groundwater inputs to stream, and transient storage is the temporary retention of water apart from the main advective flow in the stream channel

(Bencala and Walters 1983). Solute transport models rely on principles of first-order mass transfer to describe solute exchange between streams and storage zones (Fetter 1999; Worman et al. 2002). Historically, transient storage has been viewed as principally hyporheic exchange (Harvey and Fuller 1998).

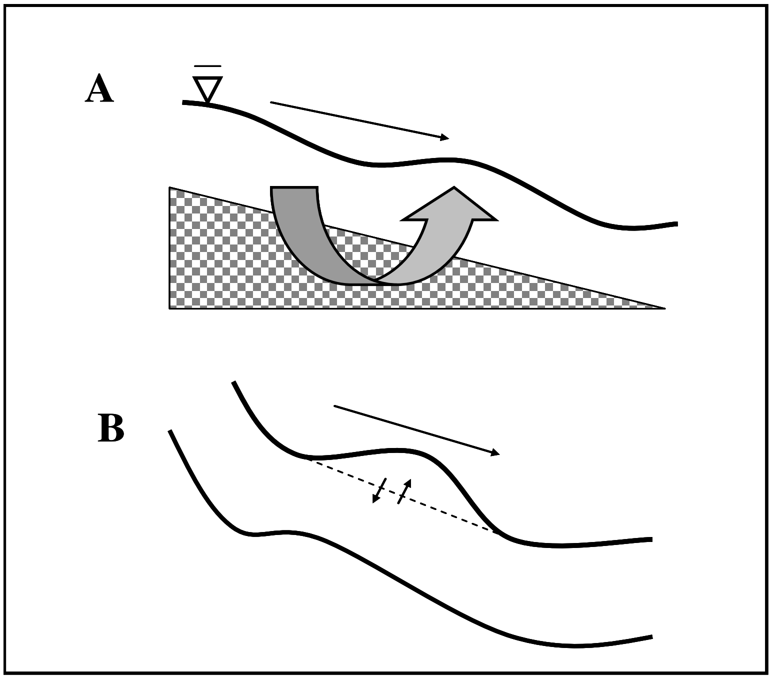

Figure 2. Illustration of transient-storage mechanisms. Transient storage occurs (*A*) when solutes leave the main channel and enter the hyporheic zone or porous areas that make up the bed or banks of the channel, and (B) arrows denote solute movement between the main channel and surface storage or areas of slow moving water. Modified from Runkel (1998).

In reality, two distinct areas of transient storage exist in streams, in-channel dead zones, and hyporheic zones. The former occur under many conditions and include areas behind logs and boulders, within submerged vegetation, in slow moving pools, and in eddies along channel margins. In contrast to these areas of transient storage in the surface water, hyporheic zones are the result of surface-groundwater exchange. Because transient storage zones have been identified as active zones for nutrient cycling (Grimm and Fisher 1984; Triska et al. 1989; Findlay 1995), measuring the relative size of the storage zone and exchange rate with the main channel is important in understanding stream processes (Hart et al. 1999).

In general, solute transport models are fit to field data obtained by the release of solute tracers into streams for a given period of time, while the concentration of the tracer is monitored downstream. The time component of these releases varies between instant releases of solution (slug) or constant rate releases. Wagner and Harvey (1997) found that constant rate releases provide more reliable parameter estimates. These releases provide concentration values over time, and are described as solute breakthrough curves (BTCs). Models fit simulated data to the BTC using solute transport parameters that describe hydraulic characteristics of the stream.

The rising limb of the BTC (left side of curve in Figure 3) is most sensitive to dispersion (D) and channel cross sectional area (A) (Harvey and Wagner 2000). The release of the water from transient storage back into the main channel is characterized by the tail or falling limb of the BTC, which is sensitive to A_S and α (Figure 3).

The One-dimensional Transport with Inflow and Storage model (OTIS) (Runkel 1998) uses Equation (1) to solve for stream flow characteristics and (2) to solve for storage parameters;

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}(C_L - C) + \alpha(C_s - C) \tag{1}$$

$$\frac{\partial C_S}{\partial t} = \alpha\frac{A}{A_S}(C - C_S) \tag{2}$$

where C = solute concentration in the stream (mg/m^3), Q = volumetric flow rate (m^3/s), A = cross-sectional area of the main channel (m^2), D = dispersion coefficient (m^2/s); q_L = lateral volumetric inflow rate (m^3/s-m) equivalent units as m^2/s), C_L = solute concentration in lateral inflow (mg/m^3), C_S = solute concentration in the storage zone (mg/m^3), A_S = cross-sectional area of the storage zone (m^2), α = stream storage exchange coefficient (/s), t = time (s), and x = distance downstream (m). Additional summary of variables presented in Table 1.

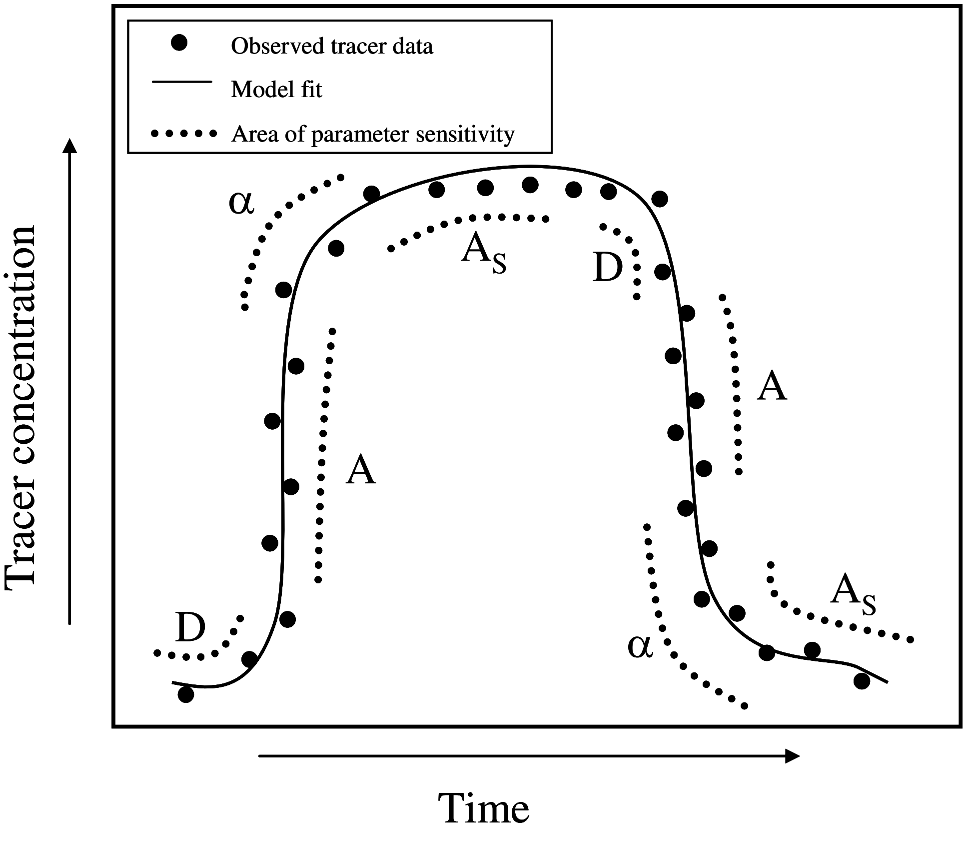

Figure 3. Illustration of observed stream tracer data, best fit line from model, and areas of the curve sensitive to different model parameters, where D is dispersion, A is cross sectional area of main channel, A_S is cross sectional are of storage zone, and a is exchange rate between channel and storage zone. Modified after Harvey and Wagner (2000).

Table 1. Model input and output variables and hydrologic parameters.

Variable	Description
C	solute concentration in stream (mg/m$^{3)}$
Q	stream discharge (m^3/s)
A	cross sectional area of channel (m^2)
D	dispersion coefficient (m^2/s)
q_L	lateral inflow (m^3/s)
C_S	solute concentration in storage zone (mg/L)
C_L	solute concentration in lateral inflow (mg/m^3)
A_S	cross sectional area of storage zone (m^2)
A_{SHZ}	cross sectional area of hyporheic zone (m^2)
A_{SDZ}	cross sectional area surface storage zone (m^2)
α	stream storage exchange coefficient (/s)
α_{SHZ}	hyporheic zone storage exchange coefficient (/s)
α_{SDZ}	surface storage exchange coefficient (/s)
t	time (hr)
% channel storage	% surface storage from Surfer
x	distance (m)
1stor RMSE	error for 1 storage zone model (OTIS P)
2 stor RMSE	error for 2 storage zone model
Tail RMSE	error for tail of 2 storage zone model
DaI	storage sensitivity metric (dimensionless)
T_{STOR_HZ}	hyporheic residence time (s)
L_{SHZ}	length solute travels before entering hyporheic storage (m)
A_{SHZ}/A	relative size of hyporheic zone to channel area

Models such as OTIS have been used extensively to estimate the timing, magnitude, duration and fate of environmentally important solutes in streams and rivers (Bencala and Walters 1983; Stream Solute Workshop 1990; Runkel 1998). Additionally, model output parameters such as α, cross sectional area of channel (A), cross sectional area of storage zone (A_s), and D are useful as comparative hydrologic metrics (Stream Solute Workshop 1990).

There are important assumptions associated with the use of these models when inferring hydrologic functioning. Runkel (1998) separates the OTIS model assumptions into two categories, main channel and storage zone. Main channel assumptions include

1) physical processes including advection, dispersion, lateral inflow and outflow, and transient storage affect solute concentrations, 2) all model parameters may be spatially variable, and 3) model parameters describing advection and lateral inflow (including volumetric flow rate, main channel cross sections, lateral inflow rates and their solute concentrations) are temporally variable. All other parameters describing physical process (dispersion and transient storage) are temporally constant (Runkel 1998). Storage zone assumptions include 1) physical processes such as advection, dispersion, lateral inflow and outflow do not occur in the storage zone, and transient storage is the only process affecting solute concentrations, 2) all model parameters describing transient storage may be spatially variable, while parameters describing transient storage are temporally constant. Finally, due to the inherent nature of these types of models, equifinality (the principle that in open systems a given end state can be reached by many potential means) and/or lack of model parameter convergence are potential problems (Ebel and Loague 2006) that can be minimized based on initial model inputs.

A significant shortcoming of models such as OTIS is that surface and hyporheic transient storage zones are lumped into single parameters α (exchange coefficient) and A_s (cross-sectional area of storage zone) (Equation 2). As described above, there are multiple storage zones in streams, in-channel and hyporheic, which can also function at different time scales and likely have different ecological and biogeochemical influence on stream ecosystem functioning.

Recent efforts have attempted to address this shortcoming in OTIS and similar models. Choi et al. (2000) recognized multiple storage processes occurring at multiple timescales and modified OTIS to describe in-channel storage and hyporheic storage.

They found that in some cases model accuracy could be improved using a two-storage zone model compared to a single storage zone model, but that in general single storage zone models accurately characterized storage processes. However, Choi et al (2000) also suggest that independent estimates of hydrologic parameters for use in multiple storage zone models, while important, are time consuming and expensive to estimate in field settings. Nonetheless, additional efforts are needed to independently characterize hyporheic processes and that multiple storage zone models can be a useful tool in doing so. Recently Briggs et al. (in review) have developed cost-effective and efficient protocols to obtain additional field data to inform multiple storage zone models. Accordingly, modeling efforts presented in this thesis build from the initial work of Choi et al. (2000), and the more recent work of Briggs et al. (in review) to quantify the role of the hyporheic zone in N losses from streams.

Research Questions and Hypotheses

Due to the potential importance of hyporheic nitrogen cycling, the following research was completed in hope of contributing to the understanding of biogeochemical and hydrologic processes. The primary goals of this project were to investigate (1) how hyporheic denitrification rates and denitrification potentials vary among streams subject to different N inputs or land use practices (forested, agricultural, urban) and (2) use a 2-storage zone model to determine how hydrologic characteristics of hyporheic flow vary across land use, and (3) examine the relative importance of hyporheic denitrification as a N sink across streams based on NO_3-N loss potential. I hypothesized the following; first, hyporheic denitrification in forested streams limited by chemical substrate availability while agricultural and urban streams are not reaction-rate limited meaning they have high enough concentrations of the essential nutrients (i.e. DOC, NO_3^-) for denitrification to take place. Therefore, denitrification rates measured in sediments from forested streams should increase in magnitude with the addition of limiting nutrients such as NO_3^- and DOC, while such pattern would be observed to a lesser extent in urban and agricultural stream sediments. Second, I hypothesized that hyporheic denitrification in agricultural and urban streams is also controlled by hydrologic processes, which will be isolated using a 2-storage zone model [(i.e., extent of hyporheic area (A_{SHZ}), exchange rate of solute between channel and hyporheic zone (α_{SHZ}), duration time exposed to biologically reactive substrate (T_{STOR_HZ}), and distance traveled before water enters hyporheic storage (L_{SHZ})]. The physical template of urban and agricultural streams may be quite different from forested streams, with respect to formation processes (i.e. alluvial vs. tractor) and substrate composition. Urban and agricultural streams are often diverted through areas of highly compacted soils and non-alluvial material with low hydraulic conductivity, conditions not conducive to drive hyporheic exchange. Therefore, I predicted that hyporheic denitrification in agricultural and urban streams is controlled hydrologically due to relatively small A_{SHZ}, slow α_{SHZ}, short T_{STOR_HZ} values, and relatively long L_{SHZ}, compared to forested streams. Finally I predicted that hyporheic denitrification relative to available NO_3^- will be greatest at forested sites because the physical setting would foster greater hyporheic exchange, than agricultural and urban sites.

CHAPTER II

STUDY SITES

All sites used in this study are located near Jackson Hole, Wyoming and Grand Teton National Park (GTNP), Wyoming. Similar to many areas in the country, this location provides the appropriate setting to examine streams subject to different land use practices (Figure 4). Our work was carried out in conjunction with the Lotic Intersite Nitrogen Experiment-II (LINX-II), whose goal was to understand NO_3^- transport and cycling processes in streams across the United States, with sites in Wyoming representing the Intermountain sagebrush-step biome (Gooseff et al. 2007; Mulholland et al. 2008). Criteria used by LINX II for the selection and designation of streams by land use type were based on characteristics such as stream order (1st to 3rd), and % of land area subject to different human uses. Forested streams have areas of human activity comprising <5% of total disturbance in watershed, whereas impaired streams were selected from watersheds with >25% of land use in either agricultural or urban categories.

All forested sites in this study are located within the boundaries of GTNP. These streams (Spread Creek, Two Oceans Creek, and Ditch Creek) are similar with respect to their physical settings (i.e. gravel bed rivers), although Two Oceans Creek is a lake outlet (Gooseff et al. 2007). All of the agricultural and urban sites are located just outside Jackson Hole (~15 km) near Teton Village, Wyoming. All agricultural sites are located on private land, which is grazed by cattle on a rotating schedule. Stream flow for Headquarters Creek and Kimball Creek is diverted from other sources, including irrigation return flow. These two sites are different from Giltner Spring Creek, as they are essentially irrigation ditches rather than a natural water way. Giltner Spring Creek is fed by both springs and irrigation return flows. The settings of urban sites vary, but all channels are man-made. Fish Creek originates as groundwater pumped through an artificial stream in Teton Village that is augmented by diverted irrigation water. Teton Pines stream flows through Teton Pines town home development. Here, stream flow is pumped groundwater, which flows through a partially lined channel adjacent to town houses and a road (Gooseff et al. 2007). Finally, Jackson Hole Golf and Tennis Club stream is water pumped through a man-made channel running through the golf course.

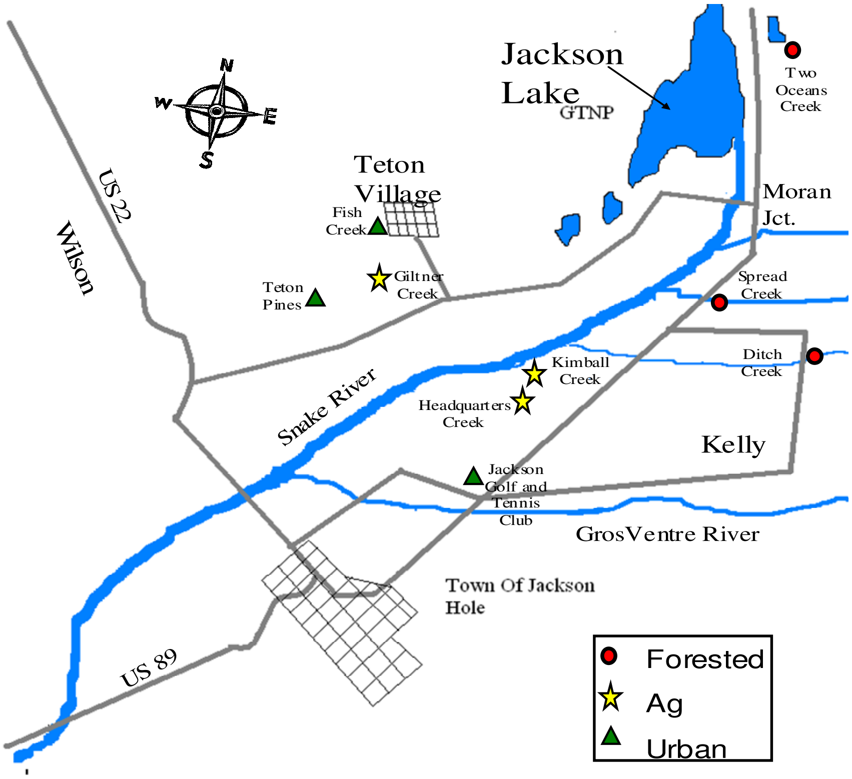

Figure 4. Map of the Jackson Hole area and study sites by land use type. This map is not to scale but intended to show relative location of study sites by land use type.

Physical and hydrologic characteristics (Table 2) were somewhat variable during our study. The highest value of stream discharge (1.00 m^3/s) was recorded in Spread Creek (forested) while the lowest (0.016 m^3/s) was measured in Teton Pines (urban) stream (Table 2). These streams also had the highest (0.43 m/s) and lowest (0.03 m/s) velocities measured in the field (Table 2). Forested streams had the largest width to depth ratios (40-99), while this ratio was generally lower and more variable (8-43) in agricultural and urban streams (Table 2). These physical characteristics are similar to those reported for six of our nine study sites in work by Gooseff et al. (2007). The hyporheic zone was generally well oxygenated in forested streams, ranging from means of 1.4-5.6 mgO_2/L (Table 3). Dissolved oxygen in agricultural and urban streams was more variable,and all but one site averaged less than 2 mg/L (Table 3). Chemical characteristics of surface and sub surface water for individual sites are outlined in Table 3, and digital orthophotos illustrating study reach and cross sections are provided in Appendix A.

Table 2. Physical characteristics of study sites by land use type.

Forested sites	Ditch Creek	Spread Creek	Two Oceans Creek
Lat (N)	43°39'48"	43°47'26"	43°52'29"
Long (W)	110°37'53"	110°32'16"	110°29'12"
Elevation (ft)	6764	6852	6844
Q (m^3/s)	0.125	1.000	0.066
mean u (m/s)	0.16	0.43	0.19
reach length (m)	187	240	252
subsurface DO (mg/L)	1.36	5.66	5.85
width to depth	89	99	40
Substrate Description	cobble	cobble	gravel
Agricultural sites	Headquarters	Kimball Creek	Giltner Creek
Lat (N)	43°34'04"	43°33'58"	43°32'43"
Long (W)	110°48'00"	110°49'01"	110°50'38"
Elevation (ft)	6284	6313	6202
Q (m^3/s)	0.375	0.175	0.183
mean u (m/s)	0.097	0.27	0.11
reach length (m)	180	259	252
subsurface DO (mg/L)	1.8	0.77	1.59
width to depth	43	9	32
Substrate Description	silt/sand/heavy veg	silt/sand/heavy veg	cobble/silt/sand
Urban sites	Fish Creek	Teton Pines	Jackson Golf and Tennis Club
Lat (N)	43°35'06"	43°31'42"	43°55'48"
Long (W)	110°49'35"	110°50'32"	110°38'14"
Elevation (ft)	6303	6200	6856
Q (m^3/s)	0.110	0.016	0.200
mean u (m/s)	0.112	0.03	0.380
reach length (m)	252	277	96
subsurface DO (mg/L)	1.6	NA	4.1
width to depth	8	20	17
Substrate Description	silt/sand	cobble/sand/partially lined/heavy veg*	sand/partially lined*

* indicates streams constructed with partail bed liner such as rubber sheeting, but only partial, did not cover whole bed.

CHAPTER III

METHODS

Field Sampling for Denitrification Assays

Sampling took place during July and August 2006. At each of the 9 stream reaches sampling sites were chosen based on visual estimates for areas of potential hyporheic exchange, which included stream gradient, bed form, and meanders. Four sites along each stream reach were selected for sampling. First, hyporheic sediment samples to be used in the denitrification assays were collected from each site at approximately 5 to 10 cm below the stream bed or water table along stream margins. This was done by digging down below water table, and manually collecting sediments. Water was removed from sampling holes and allowed to refill before subsurface dissolved oxygen (DO) was measured using a hand held YSI Dissolved Oxygen Meter. Hereafter these sites will be referred to as the hyporheic zone (i.e. chemical analyses) or sites of hyporheic denitrification. I also measured percent organic matter (%OM) from subsamples of the hyporheic sediments collected (Hauer and Lamberti 2006). Stream water samples were collected for use in the denitrification assays and for analysis of chemical constituents. Hyporheic water samples were also collected for chemical analysis after measuring DO. Note that only one discrete sample was taken from surface and subsurface for chemical analyses. All water samples were filtered through Whatman GF/F filters (pore size 0.7 µm). Chemical analyses for NO_3^-, total dissolved nitrogen (TDN), and total dissolved phosphorus (TDP) were done colorimetrically using an Astoria Auto Analyzer (Astoria Pacific International) and FASPac II data acquisition software. Dissolved organic carbon

(DOC) analyses were made using wet persulfate oxidation (Menzel and Vacarro 1964) on a model 700 Total Organic Carbon Analyzer.

Laboratory Denitrification Assays

Denitrification rates were measured in the laboratory using the chloramphenicol-amended acetylene (C_2H_2) block method (Smith and Tiedje 1979; Inwood et al. 2005). Chloramphenicol prevents bottle effects (i.e. new enzyme production) by inhibiting *de novo* enzyme synthesis; therefore denitrification estimates are more representative of *in situ* rates (Smith and Tiedje 1979). Acetylene is used to prevent the final reduction of N_2O to N_2. The N_2O product is easier to measure by gas chromatography owing to its lower ambient concentration in the atmosphere than N_2 (Chan and Knowles 1979; Inwood et al. 2005). Denitrification assays using hyporheic sediments were conducted in a lab setting within 48 hours of collection.

For this experiment, four treatments were used, with four replicates per treatment (16 total jars per site). For each site, 250 grams (±1 g) of homogenized sediment were placed into 465 ml glass bottles. Bottles were then filled with stream water to a pre-marked 350 ml line. Slurries were stirred and lids with a rubber septum were placed on each bottle. On each bottle, two 22 gauge needles with stopcocks were placed through septa for adding gas, treatments, and for sampling. Each bottle was purged with He for five minutes to create anoxic conditions. Next, 1 ml of 0.1M chloramphenicol was added to each bottle followed by the individual treatments; 1) ambient or control, 2) 200 mg NO_3^- N/L as KNO_3 , 3) 1 gram C/L as dextrose, and 4) 1 gram C/L as dextrose + 200 mg NO_3^- N/L as KNO_3. Following addition of treatments, acetylene was bubbled through a

0.1M HCl solution, after which 6 ml of acetylene was added to each bottle. After allowing bottles to sit for 10 minutes, 3 ml headspace samples were taken and put into pre-evacuated vials, and sealed with a silicon bead. After sample collection, 3 ml of replacement gas (90% He and 10% acetylene) was added back to each bottle. Headspace sampling was repeated hourly for three hours; making sure to shake each jar vigorously for one minute prior to sampling to allow for equilibration between the wet sediment and the headspace.

Headspace gas samples from the denitrification experiment were analyzed for N_2O concentrations on a SRI 8610C gas chromatograph with an electron capture detector and Peak Simple 2000 software package. The following Equations (3a – 3f) were used to determine concentration of N_2O as μg N_2O / min;

3a) part per million (ppm) N_2O = (area determined on gas chromatograph) * (slope calibration regression),

3b) A = (ppm N_2O) * (44/22.4)

44 is the molecular weight of N_2O and 22.4 come from ideal gas law and represents L/mol of gas,

3c) B = (A) * (volume of head space or 0.113),

3d) C = (B) / (volume of water in slurry or 0.35),

3e) M = C + (C * 0.06277), where 0.06277 is the Bunsen coefficient used for assays (20° C).

Values were further corrected for gas removal during sampling following Inwood et al. (2005) using equation:

3f) $M_{cx} = M + P_h M_{c(x-1)}$

Where M_{cx} is the concentration of N_2O adjusted for previously taken samples, P_h is the proportion of headspace removed during each sampling, $M_{c(x-1)}$ is the corrected concentration of N_2O for the sample taken prior to sampling time X. N_2O production rate (µg N_2O/minute) was calculated as the slope of N_2O concentration plotted against time.

Hyporheic sediment subsamples from each site (four per stream) were analyzed for organic matter content (%OM). Estimates were made by taking the dry weights, then combusting the dry sediments in a muffle furnace at 450°C. Sediments were rewetted and then dried at 60 ºC to obtain final mass. Percent OM was calculated from four replicated from each site (n = 12 per land use) as the dry weight minus the ashed weight divided by the dry weight and multiplied by 100.

Denitrification Assay Analyses

Statistical analyses of denitrification potential rates were performed using SAS Analyst (version 8, SAS Institute, Cary, North Carolina). All data were first square root transformed to meet statistical assumptions of approximate normality and constant variance. A mixed linear analysis of variance (ANOVA), PROC MIXED, was used to model the effect of land use (forested, agricultural, and urban) and the addition of carbon and nitrogen on denitrification rates. Significance was determined at $\alpha = 0.05$. Comparisons of DO, and nutrient concentrations (i.e. NO_3^-, DOC) of surface and subsurface water were done in SAS using an ANOVA (PROC GLM) and a post hoc means comparison for differences across land use types (REGWQ). Additionally, to estimate effectiveness of the hyporheic zone as in stream N sink, a NO_3-N loss potential was calculated. This was done by dividing denitrification potential rates (treatments with added carbon and nitrogen) in mg/min by NO_3^- load (product of stream NO_3^- and average discharge). This yields a dimensionless number describing the maximum measured denitrification potential relative to available NO_3^- and stream discharge.

Conservative Tracer Additions and Field Sampling

Steady-state conservative tracer additions using NaCl were done at each reach, encompassing hyporheic sediment sampling locations for denitrification assays. At each site, between 24 and 45 kg of NaCl were added to a 208 L plastic drum, which was filled with between 94 and 189 L of stream water and mixed until salt was completely dissolved. Reach lengths across sites varied (Table 2) to best allow for adequate solute mixing and to cover a distance of at least 20 stream widths. Similarly mass of NaCl and volume of solution varied based on stream discharge, with the goal adding enough salt to increase stream electrical conductivity (EC) by a minimum of 5 µS/cm (Stream Solute Workshop 1990). A Fluid Metering Inc. (FMI) pump and tubing were used to pump the solution into the stream at a constant rate. Prior to starting the releases, two YSI 600XLM Sondes were activated at the downstream end of the reach to measure the EC in the stream thalweg and in an in-channel storage zone. In-channel storage zone was estimated to be an area in the stream where the flow was less than 0.5*mean velocity, and is discussed in greater detail in the modeling segment of the methods section. Tracer data from the in-channel storage zone was later used as an independent parameter for model input as described below. Sites of tracer tests were chosen carefully and should be an accurate representation of the stream reach, while capturing hydraulic features of both the main channel and the in-channel storage zone. Pump rate and the time the release started and stopped were noted. Pump rate was monitored periodically throughout the duration of tracer release. Sufficient time was give at each site for the EC to reach plateau and to come down after the end of the injection, as measured by monitoring with a handheld EC meter.

To estimate in-channel flow characteristics, velocity profiles were taken across each stream. Each reach was divided into six evenly spaced cross sections, where velocity measurements were taken using a Marsh-McBirney flow meter. These data were used to estimate the area of the channel defined as an in-channel storage zone, which is discussed below in more detail under the modeling approach section.

Modeling Approach

Modeling applications for this research were done using the modified version of OTIS (Equations 4,5,6) developed by Choi et al. (2000) and described by Gooseff et al. (2004), which allows for estimates of two storage zones, in-channel and hyporheic (Equations 4,5,6). Additional steps (2-4) are modified from Briggs et al. (in review), as outlined below.

$$\frac{\partial C}{\partial t} = -\frac{Q}{A}\frac{\partial C}{\partial x} + \frac{1}{A}\frac{\partial}{\partial x}\left(AD\frac{\partial C}{\partial x}\right) + \frac{q_L}{A}\left(C_L - C\right) + \alpha_{DZ}(C_{sDZ} - C) + \alpha_{HZ}(C_{sHZ} - C) \tag{4}$$

$$\frac{\partial C_{SDZ}}{\partial t} = \alpha_{DZ}\frac{A}{A_{SDZ}}(C - C_{SDZ}) \tag{5}$$

$$\frac{\partial C_{SHZ}}{\partial t} = \alpha_{HZ}\frac{A}{A_{SHZ}}(C - C_{SHZ}) \tag{6}$$

where C = solute concentration in the stream (mg/m^3), Q = volumetric flow rate (m^3/s), A = cross-sectional area of the main channel (m^2), D = dispersion coefficient (m^2/s); q_L = lateral volumetric inflow rate (m^3/s-m; equivalent units as m^2/s), C_L = solute concentration in lateral inflow (mg/m^3), C_{SDZ} = solute concentration in the dead zone storage (mg/m^3), A_{SDZ} = cross-sectional area of in channel storage zone (m^2), α_{DZ} = in-channel dead zone storage exchange coefficient (/s), t = time (s), x = distance downstream (m), A_{SHZ}=cross-sectional area of hyporheic zone storage (m^2), α_{SHZ} = hyporheic storage exchange coefficient (/s), and C_{SHZ} solute concentration in hyporheic storage (mg/m^3) (Table 1). This model implies a differential exchange rate between in-channel storage zone (fast) and hyporheic zone (slow) based on estimates of α. Field data used to inform the model included estimates of stream cross-sectional area (A), discharge (Q), in-channel exchange rate (α_{DZ}), and in-channel dead zone cross-sectional area (A_{SDZ}).

I. Single-storage zone modeling with OTIS-P

First, OTIS-P was used to model a single storage zone by iteratively solving Equation 1 and 2 to fit model parameters to the BTC of tracer injection data. However, before running the model, it was important to calculate stream discharge, and model boundary conditions. Discharge measurements were calculated by solving for the area under the BTC (which is mass of salt added) based on pump rate, solute concentration, and duration of the tracer addition. Boundary conditions are specified within model input files to describe tracer concentrations at upstream and downstream locations of the modeled system. Output from the model provides the following transport and storage parameters: A or cross section area of main channel (m^2), D or dispersion rate (m^2/s), A_s

or cross section area of storage zone (m^2), and α the exchange rate of solute between main channel and storage zone (/s) (Runkel 1998).

II. Empirical estimates of in-channel storage and storage zone separation

Second, the six velocity profiles from each site were analyzed using Surfer software (Golden, Colorado) to solve for channel areas below a given velocity. This provides estimates of two velocity populations, fast and slow. I set the cut off for in-channel dead zone at 0.5*mean velocity (u) (Briggs et al. in review). This is done in Surfer by creating a three dimensional file (width (X), depth (Y), and velocity (Z)), blanking out the area outside of the channel, selecting a Z value (0.5*(mean u)), and then creating a volume grid which solves for the area of the channel above and below the Z value (Figure 5). This provides an estimate of in-channel A_{SDZ} from cross-sectional areas with u<0.5. The six cross sections from each reach were pooled for an average area per stream. Surfer results for all sites and cross sectional areas are provided in the Appendix B.

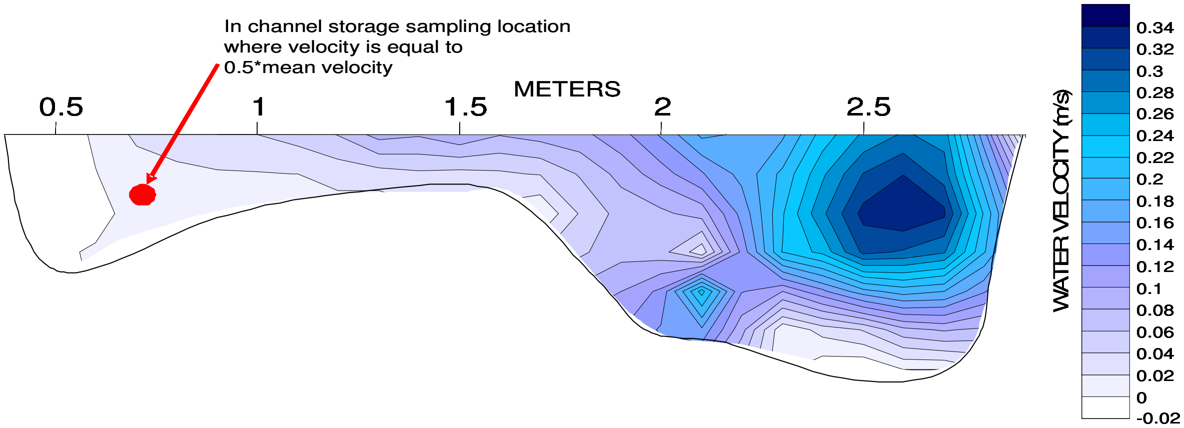

Figure 5. Representation of how Surfer was used to estimate areas of in channel storage based on velocity values. Dead zone sampling location represents where velocity < 0.5*mean velocity and used for estimate of A_{SDZ}. Here the mean velocity is 0.4m/s making in channel storage area of channel below or equal to 0.2m/s.

Third, the in-channel A_{SDZ}, as described above, was used to separate the OTIS-P storage parameter, A_S, into hyporheic (A_{SHZ}) and in-channel dead zones (A_{SDZ}). This was accomplished by converting the independent Surfer results into percent of surface flow as storage or %Storage = (area below 0.5mean velocity from Surfer / total channel area from Surfer) * 100. Then, A_{SDZ} was then estimated as A_{SDZ} = %Storage * A_S. Next, A_{SHZ} values were estimated by difference as $A_{SHZ} = A_S - A_{SDZ}$.

Fourth, estimates for in-channel storage exchange, α_{SDZ}, were taken from the slopes of the exponential decline of the tail of the storage zone tracer curves obtained from the sondes that were placed in in-channel dead zones (Figure 6). Original values of α from the single storage zone OTIS runs were then used as initial values of α_{SHZ} (Briggs et al. in review).

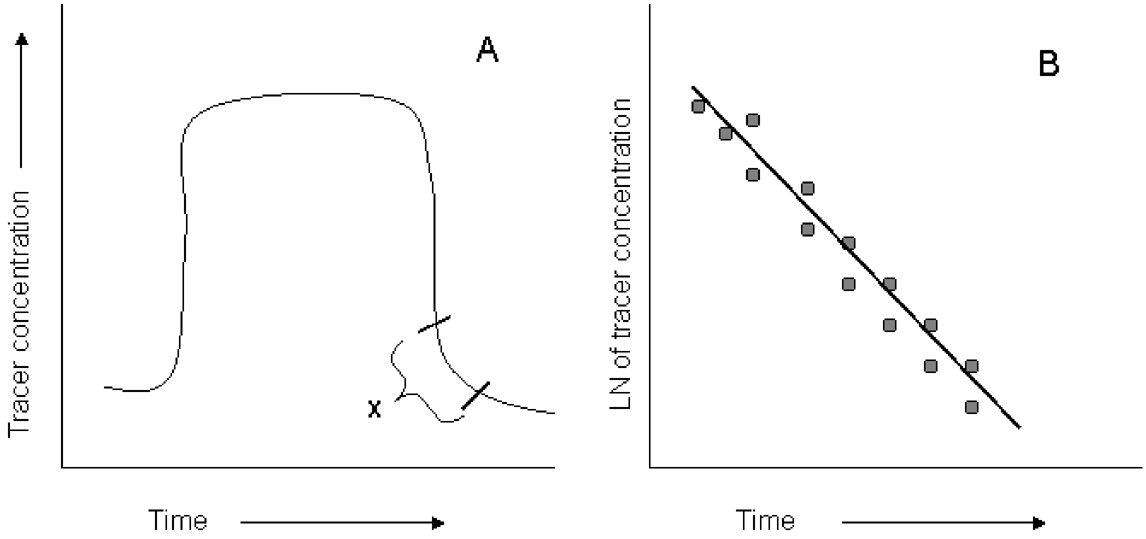

Figure 6. Method used to estimate a for in channel storage zone. (A) represents hypothetical BTC. X represents region of curve sensitive to α. (B) Observed points are then plotted as the natural log of tracer data over time. Similar to a, the slope of this line has units of s-1 and was used as starting point for α_{SDZ}.

III. Model fits using OTIS-2Stor

Using steps 3-4, these parameters were entered into OTIS-2stor as independent values for in-channel and hyporheic storage parameters. OTIS-2stor was used to solve Equation 4, 5, and 6 estimate both in-channel and hyporheic parameters. This model application uses the same inputs and boundary conditions as the single storage zone model as initial model inputs with the exception of using values of A_{SHZ} , A_{SDZ}, $\alpha_{SDZ,}$ and $\alpha_{SH.Z}$ to avoid problems of equifinality and lack of model convergence (Choi et al. 2000).

IV. Assessment of model performance

Parameter estimates were achieved by iteratively solving the model (>50 model runs) and finding the best fit between the model and tracer data based on the residual sum of squares from model output and improving the root mean square error (*RMSE*) (Equation 7) between observed and modeled data (Gooseff et al. 2005).

$$RMSE = \frac{\sqrt{\sum \ln(C_{obs} - C_{sim})^2}}{n} \tag{7}$$

where C_{obs} is the measured concentration of tracer in stream from conservative tracer additions, C_{sim} is the OTIS simulated concentration, and n is the number of C_{obs} or data points collected in the field. *RMSE* was calculated for the single storage zone (OTIS), two storage zone model, as well as the tail of the two storage zone model, which works specifically as in indicator of the fit for hyporheic characteristics (discussed further below). Additionally, the Damkohler number (*DaI*) was used to gauge the reliability of the transient storage parameters (Equation 8). This is a dimensionless number that expresses the balance between transport and storage processes from the tracer. *DaI* values near 1 indicate sensitivity to storage processes and parameter reliability at its highest, while values much smaller or much larger than 1 indicate decreased sensitivity from too long or too short of a study reach with respect to transport and storage processes (Wagner and Harvey 1997). *DaI* is expressed as:

$$DaI = \frac{\alpha\,(1 + A / A_s)\,L}{u} \tag{8}$$

where u is the mean stream velocity, L is the length of the study reach, and α, A_S, and A are the storage exchange coefficient, storage zone area and stream cross sectional areas, respectively.

For the purpose of this research, the following hydrologic parameters are used to describe hyporheic storage and exchange characteristics. First, A_{SHZ}, and α_{SHZ} output values from the two storage zone model are used. Next, hyporheic residence time, T_{STOR_HZ} (s) (Equation 9), is the average time a tracer molecule remains in the hyporheic zone before it is released back to surface water (Thackston and Schnelle 1970). Then, A_S/A, a common metric used to compare the relative sizes of the storage zone and surface area, was modified to describe relationship between surface water area and hyporheic zone (Equation 10). Finally, hydrologic turnover length, L_{SHZ} (m) (Equation 11), describes the average distance a molecule travels downstream before entering hyporheic storage (Mulholland et al. 1994).

$$T_{HZ\_STOR} = \frac{A_{SHZ}}{\alpha_{SHZ} * A} \tag{9}$$

$$Storage\ /\ surface = \frac{A_{SHZ}}{A} \tag{10}$$

$$L_{SHZ} = \frac{u}{\alpha_{SHZ}} \tag{11}$$

Model Parameter Analyses

Values of NO_3-N loss potential, *DaI,* $A_{SHZ},$ $\alpha_{SHZ},$ $T_{STOR\_HZ},$ A_{SHZ}/A and L_{SHZ} , values were compared across land use types using ANOVA methods (PROC GLM) and post hoc means comparison (REGWQ) by land use type. Difference in NO_3-N loss potential across land use was analyzed using ANOVA (PROC GLM) as described above (significance determined for $\alpha = 0.05$). Differences in *RMSE* between single storage zone model, two storage zone model, and the tail from two storage zone model were analyzed for differences using student t tests (significance determined for $\alpha = 0.05$). Finally, linear regression was used to evaluate relationships between NO_3-N loss potential and $A_{SHZ},$ α_{SHZ} $T_{STOR\_HZ},$ and L_{SHZ}, to evaluate how hydraulic characteristics of the hyporheic zone act as a control or predictor of hyporheic denitrification.

CHAPTER IV

RESULTS

Background Chemistry

Average concentrations of stream water NO_3-N varied from 0.033 ± 0.006, 0.031 ± 0.018, to 0.142 ± 0.127 mg N/L in forested, agricultural, and urban streams, respectively, and stream DOC varied from 3.31 ± 0.73, 2.40 ± 0.45, to 1.7 (± 0.03) mg C/L in forested, agricultural, and urban sites (Figure 7). However, stream NO_3-N concentrations at Teton Pines was below detection limit, so subsequent calculations were assigned NO_3-N values as one half the detection limit ($4.5E^{-04}$ mg N/L). ANOVA results for stream water NO_3-N, TDN and DOC showed no significant differences among sites; however, average TDP was significantly lower at urban sites (0.01 ± 0.002 mg/L) compared to forested (0.04 ± 0.003 mg/L) and agricultural (0.04± 0.007 mg/L) sites ($p = 0.0109$) (Figure 7, Table 3). Surface water DO from single measurements per site ranged from 5.5 to10.01 mg O_2/L, but there were no significant differences across land use (Table 3).

Average concentrations of hyporheic NO_3-N and DOC from forested, agricultural and urban streams varied from 0.072 ± 0.03, 0.037 ± 0.02, to 0.096 ± 0.03 mg N/L and 5.19 ± 1.71, 5.67± 2.17, to 3.33 ± 1.53 mg C/L respectively (Figure 8). Similar to stream water samples, ANOVA results for hyporheic NO_3^- N, TDN, and DOC showed no significant difference among land uses (all p values > 0.05). Subsurface DO concentrations from single measurements per site ranged from 0.77 to 5.85 mg O_2/L (one measurement per site; Table 3) but there was no difference across land use types (all p values > 0.05).

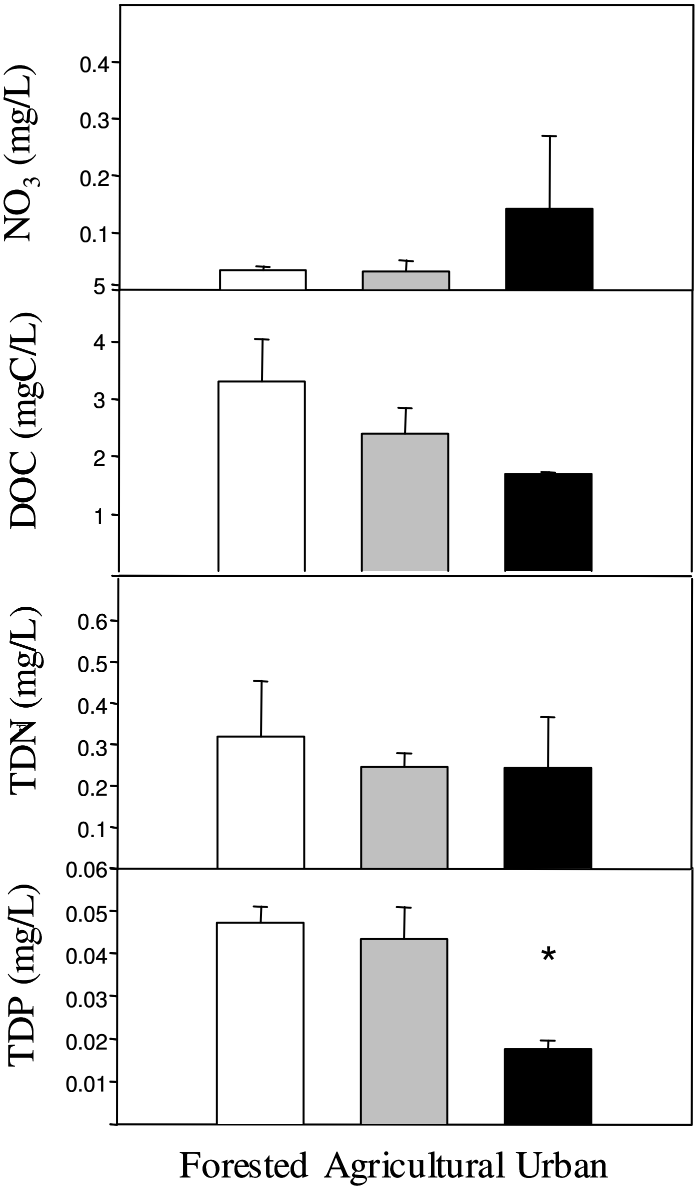

Figure 7. Mean surface water background chemistry (NO_3^-, DOC, TDN, and TDP) by land use. * indicated significant difference ($p = 0.01$).

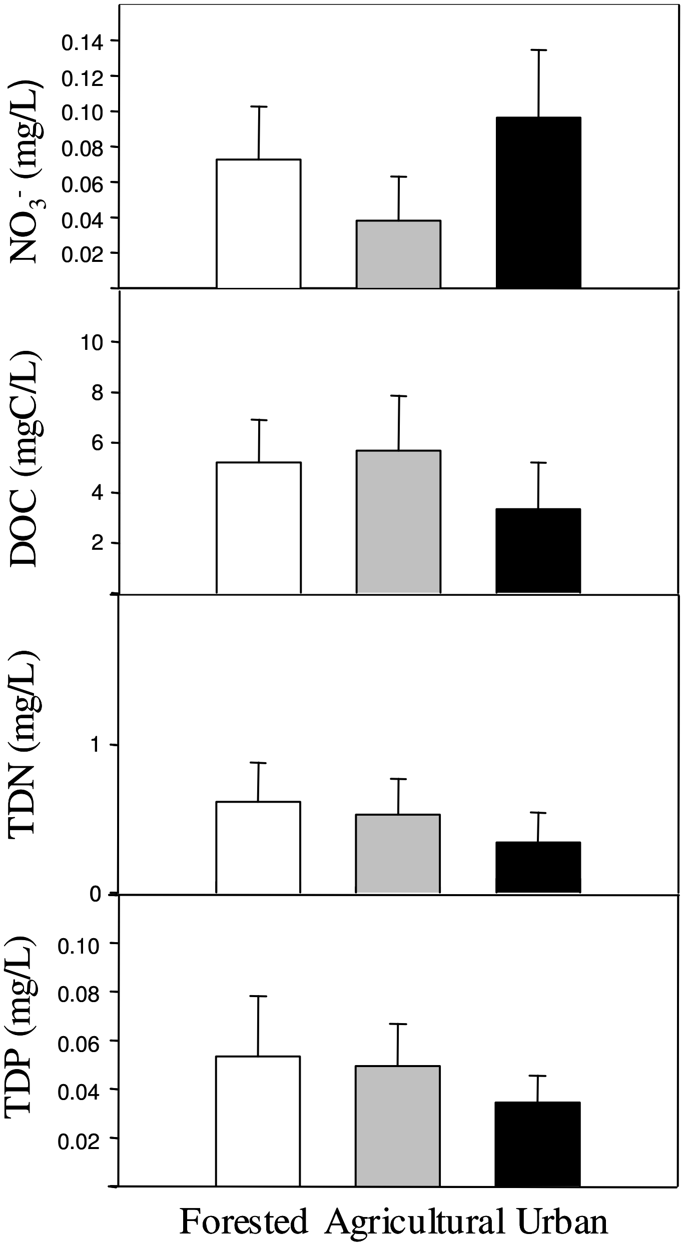

Figure 8. Mean sub surface or hyporheic water background chemistry (NO_3^-, DOC, TDN, and TDP) by land use.

Percent OM from hyporheic sediments from forested, agricultural, and urban streams were 0.42% (± 0.07), 3.44% (± 0.96), 0.42% (± 0.25), respectively (Figure 9,

Table 3) and were significantly higher at agricultural sites than forested and urban sites ($p < 0.001$).

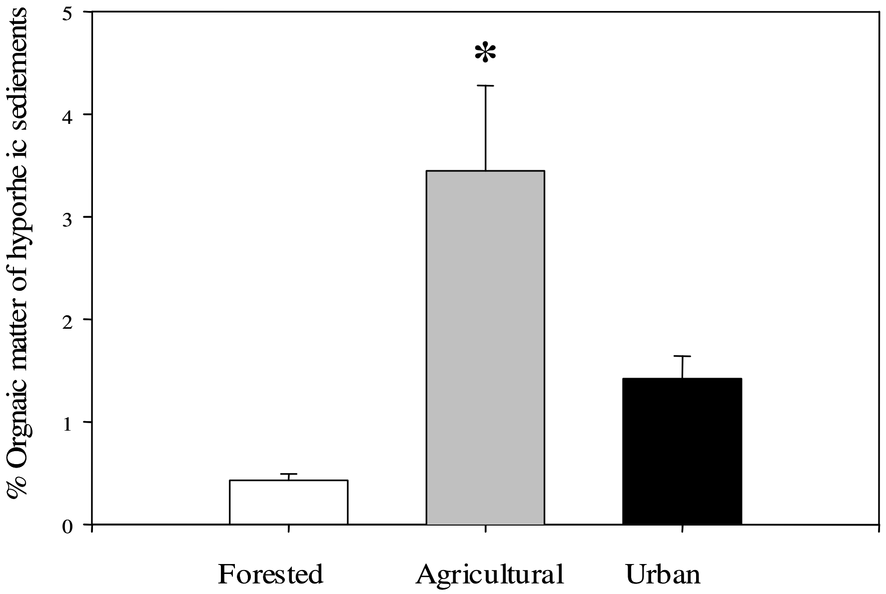

Figure 9. Average percent organic matter from hyporheic sediments by land use. * indicates significantly higher %OM ($p < 0.001$).

Denitrification and Land Use

Denitrification rates were not significantly different among treatments (with or without addition of carbon and nitrogen) or land use (all p values > 0.05). That said, ambient denitrification rates were low and increased in all cases with the addition of nitrogen and carbon + nitrogen (Figure 10). Addition of carbon alone appeared to suppress denitrification in sediments from agricultural streams, while it moderately stimulated denitrification in sediments from forested and agricultural streams (Figure 10).

Denitrification rates increased from forested and urban to agricultural sites, with similar trends across treatments, except carbon (Figure 10). Results from the individual replicates are presented in the Appendix C.

Table 3. Chemical characteristics of study site by stream type for surface and subsurface water.

Forested Streams	Ditch Creek	Spread Creek	Two Oceans Creek
Surface water NO_3^-N (mg/L)	0.0453	0.225	0.0329
Surface water TDN (mg/L)	0.5857	0.2126	0.1577
Surface water TDP(mg/L)	0.0516	0.0499	0.0397
Surface water DOC (mgC/L)	4.436	3.569	1.925
Surface DO (mg/L)	6.87	10.01	7.00
Surface temperature (°C)	20.00	5.40	10.80
Subsurface NO_3^-N (mg/L)	0.0351	0.0505	0.1324
Subsurface TDP (mg/L)	1.057	0.1397	0.6365
Subsurface TDP (mg/L)	0.0422	0.0173	0.1008
Subsurface DOC (mgC/L)	8.204	2.274	5.097
Subsurface DO (mg/L)	1.36	5.66	5.85
Sub surface temperature (°C)	21.3	9.6	13.8
Agricultural Streams	Headquarters	Kimball Creek	Giltner Creek
Surface water NO_3^-N (mg/L)	0.0014	0.0266	0.0665
Surface water TDN (mg/L)	0.2817	0.1765	0.2787
Surface water TDP(mg/L)	0.0555	0.0447	0.0298
Surface water DOC (mgC/L)	3.30	1.99	1.91
Surface DO (mg/L)	5.50	6.02	6.27
Surface temperature (°C)	21.70	14.80	11.30
Subsurface NO_3^-N (mg/L)	0*	0.0854	0.0284
Subsurface TDP (mg/L)	0.3791	0.1985	0.998
Subsurface TDP (mg/L)	0.0729	0.0151	0.0597
Subsurface DOC (mgC/L)	4.82	2.398	9.80
Subsurface DO (mg/L)	1.80	0.77	1.59
Sub surface temperature (°C)	18.20	9.90	13.80
Urban Streams	Fish Creek	Teton Pines	Jackson Golf and Tennis Club
Surface water NO_3^-N (mg/L)	0.3968	0*	0.0319
Surface water TDN (mg/L)	0.4906	0.1025	0.1363
Surface water TDP(mg/L)	0.0216	0.0162	0.0147
Surface water DOC (mgC/L)	1.64	1.70	1.75
Surface DO (mg/L)	8.64	7.50	7.50
Surface temperature (°C)	12.40	10.00	13.40
Subsurface NO_3^-N (mg/L)	0.0581	NA**	0.1345
Subsurface TDP (mg/L)	0.1353	NA**	0.5414
Subsurface TDP (mg/L)	0.0231	NA**	0.0454
Subsurface DOC (mgC/L)	1.45	NA**	5.21
Subsurface DO (mg/L)	1.60	NA**	4.10
Sub surface temperature (°C)	14.20	NA**	14.00

* Indicates concentration below detection limit for NO_3^- (0.0009 mg/L).

** No measurements were made on subsurface water, because we couldn't find any.

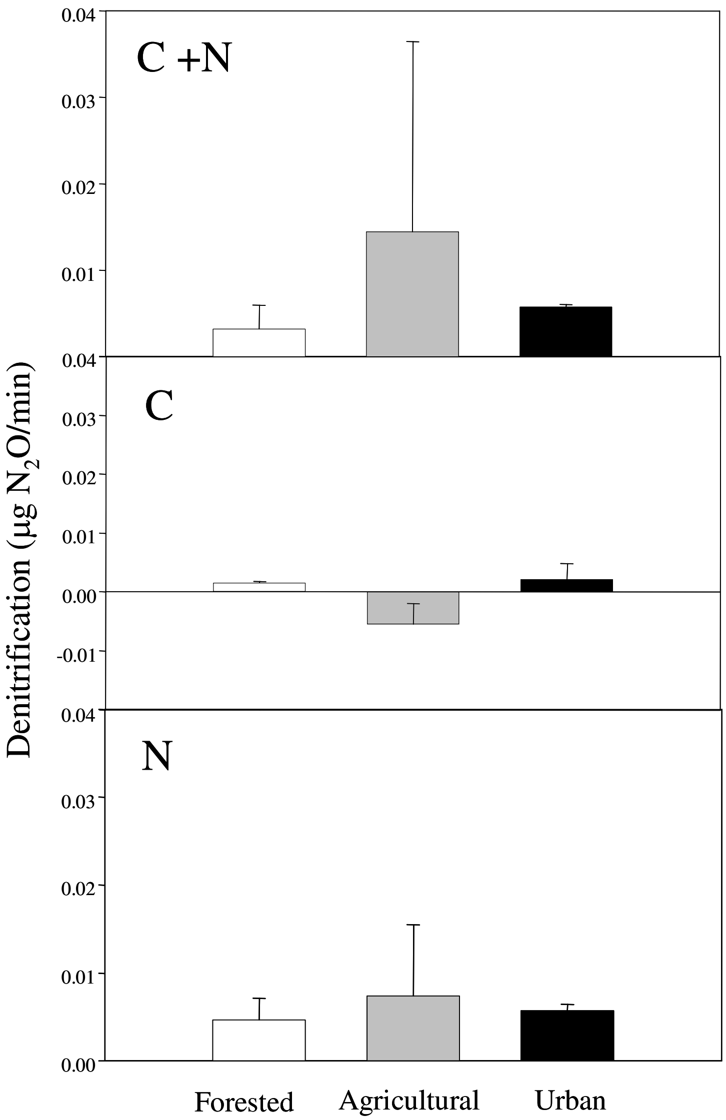

Figure 10. Denitrification rates normalized to control rates by treatment and land use.

Modeling Results

Model inputs and outputs are presented in Table 4. Model fits between the single storage zone and two storage zone models were generally similar (Figure 11), with slightly better fits in most cases using the single storage zone model based on the *RMSE*

(Table 5). At five of the nine sites, the *RMSE* from the two storage zone was higher than the single storage zone model; however increases were typically very small. *RMSE* on the two storage zone model ranged from 0.084 at Fish Creek to 1.074 at Teton Pines. Error values on the tail of the two storage zone model alone range from 0.066 at Fish Creek to 1.198 at Teton Pines (Table 5). High *RMSE* values at Teton Pines can be partially explained by the modeling difficulties from tracer concentration not reaching steady state. Results from t-tests showed no significant differences between *RMSE* from single storage zone, two storage zone, and tail or two storage zone model runs.

Table 4. Model inputs and outputs for 1storage zone and 2storage zone model by land use type.

Site	Ditch Creek	Spread Creek	Two Oceans Creek
A (m^2)	4.806E-01	3.550E+00	3.800E-01
D (m^2/s)	9.125E-01	3.492E-01	4.481E-01
% Channel Storage	3.600E+01	2.700E+01	1.600E+01
A$_s$ (m^2)	4.869E-02	1.392E-01	3.434E-02
A$_{SHZ}$ (m^2)	3.120E-02	1.020E-01	2.880E-02
A$_{SDZ}$ (m^2)	1.753E+00	3.758E+00	5.494E-01
a (s^{-1})	2.676E-03	2.736E-03	1.317E-04
a$_{SHZ}$ (s^{-1})	2.676E-03	2.736E-03	1.317E-04
a$_{SDZ}$ (s^{-1})	5.000E-04	2.300E-03	4.200E-03
Site	Headquarters	Kimball Creek	Giltner Creek
A (m^2)	2.308E+00	8.308E-01	1.519E+00
D (m^2/s)	1.974E+00	3.977E-01	1.365E+00
% Channel Storage	6.000E+01	1.900E+01	4.300E+01
A$_s$ (m^2)	9.590E-01	4.540E-03	4.767E-04
A$_{SHZ}$ (m^2)	3.480E-01	3.680E-03	2.720E-04
A$_{SDZ}$ (m^2)	5.754E+01	8.625E-02	2.050E-02
a (s^{-1})	9.202E-05	1.575E-05	1.923E-03
a$_{SHZ}$ (s^{-1})	9.202E-05	1.575E-05	1.923E-03
a$_{SDZ}$ (s^{-1})	1.300E-03	1.400E-03	3.600E-03
Site	Fish Creek	Teton Pines	Jackson Golf and Tennis Club
A (m^2)	1.007E+00	3.933E-01	7.409E-01
D (m^2/s)	5.878E-01	1.082E-01	1.188E-02
% Channel Storage	2.600E+01	4.500E+01	1.800E+01
A$_s$ (m^2)	1.363E-02	8.913E-02	1.071E-01
A$_{SHZ}$ (m^2)	1.010E-01	4.900E-02	8.780E-02
A$_{SDZ}$ (m^2)	3.543E-01	4.011E+00	1.927E+00
a (s^{-1})	1.743E-05	1.175E-04	9.218E-04
a$_{SHZ}$ (s^{-1})	1.743E-05	1.175E-04	9.218E-04
a$_{SDZ}$ (s^{-1})	3.010E-01	9.400E-05	7.000E-03

Table 5. Root mean square error and DaI for all sites from 1stor, 2stor, and tail model runs.

Site	1stor RMSE	2stor RMSE	2stor tail RMSE	DaI
Ditch Creek	0.396	0.397	1.004	34.00
Spread Creek	0.167	0.167	0.134	40.48
Two Oceans Creek	0.889	0.825	0.906	2.11
Headquarters	0.080	0.201	0.306	0.58
Kimball Creek	0.220	0.219	0.680	2.78
Giltner Creek	0.129	0.129	0.250	14037.47
Fish Creek	0.086	0.084	0.066	2.94
Teton Pines	0.237	1.074	1.198	5.87
Jackson Golf and Tennis Club	0.469	0.475	1.075	1.84

DaI or the balance between transport and storage was used to gauge the reliability of the transient storage parameters based on the. With the exception of Giltner Creek, all *DaI* values are within a reasonable range (0.58 to 40.48), suggesting the model was sensitive to transport and storage process (Table 5). Giltner Creek has an exceptionally high *DaI* value, 14037, which may partially be explained by a high volume of lateral surface (spring) and subsurface flows, diluting tracer concentrations and decreasing model sensitivity.

A_{SHZ} (reach-averaged cross sectional area of the hyporheic zone) was useful for comparing the relative extent of hyporheic zone across streams. Model results show average A_{SHZ} values at forested and urban streams are similar (0.05 m^2 ± 0.02 m^2 and 0.04 m^2 ± 0.02 m^2), while larger hyporheic extent is found at agricultural sites (0.12 m^2 ± 0.12 m^2). When comparing hyporheic storage zone size relative to channel cross sectional area (A_{SHZ}/A), mean values were similar across all land uses (Table 6), thus making comparison of other storage parameters across streams subject to land use more informative.

The hyporheic exchange rate α_{SHZ} was approximately 3 times slower at agricultural (0.0006 s^{-1} ± 0.0006 s^{-1}) and urban sites (0.0004 s^{-1} ± 0.0002 s^{-1}) than at forested sites (0.0018 s^{-1} ± 0.0008 s^{-1}).

Table 6. Results from hydrologic parameter analyses. Values are averages by stream type ± 1SE.

Stream Type	α_{HZ} (-s)	A_{SHZ}/A	T_{STOR_HZ} (s)	L_{SHZ} (m)
Forested	0.0018 (±0.0008)	0.05 (±0.014)	203 (±186)	533 (±445)
Agricultural	0.0006 (±0.0006)	0.05 (±0.05)	695 (±560)	6086 (±5537)
Urban	0.0003 (±0.0002)	0.08 (±0.03)	587 (±269)	2364 (±2030)

This influenced average hyporheic residence times T_{STOR_HZ} which were greatest at agricultural sites (695 s ± 560 s) decreasing at urban (588 s ± 199 s) and forested sites (203 s ± 186.39). Finally, L_{SHZ} values were at least 4 times greater at agricultural (6086 m ± 5538 m) and urban sites (2364 m ± 2031 m) than at forested sites (533 m ± 445). Additional values from single storage and two storage zone model are listed in Table 5.

NO_3-N loss potentials averages were greatest at urban sites. However, this was driven by one outlier, Teton Pines. Otherwise, NO_3-N loss potentials were highest at agricultural sites decreasing to urban and then forested sites. There were no significant differences detected between NO_3-N loss potential and land uses (all p values > 0.05). Maximum NO_3-N loss potentials (C + N treatment) were regressed over the hydrologic parameters A_{SHZ}, α_{SHZ}, T_{STOR_HZ}, and L_{SHZ}, to determine the best hydrologic predictor of NO_3-N loss potentials (Figure 12). T_{STOR_HZ} was the best predictor of NO_3-N loss potentials across land use ($r^2 = 0.354$), but none of these relationships are statistically significant.

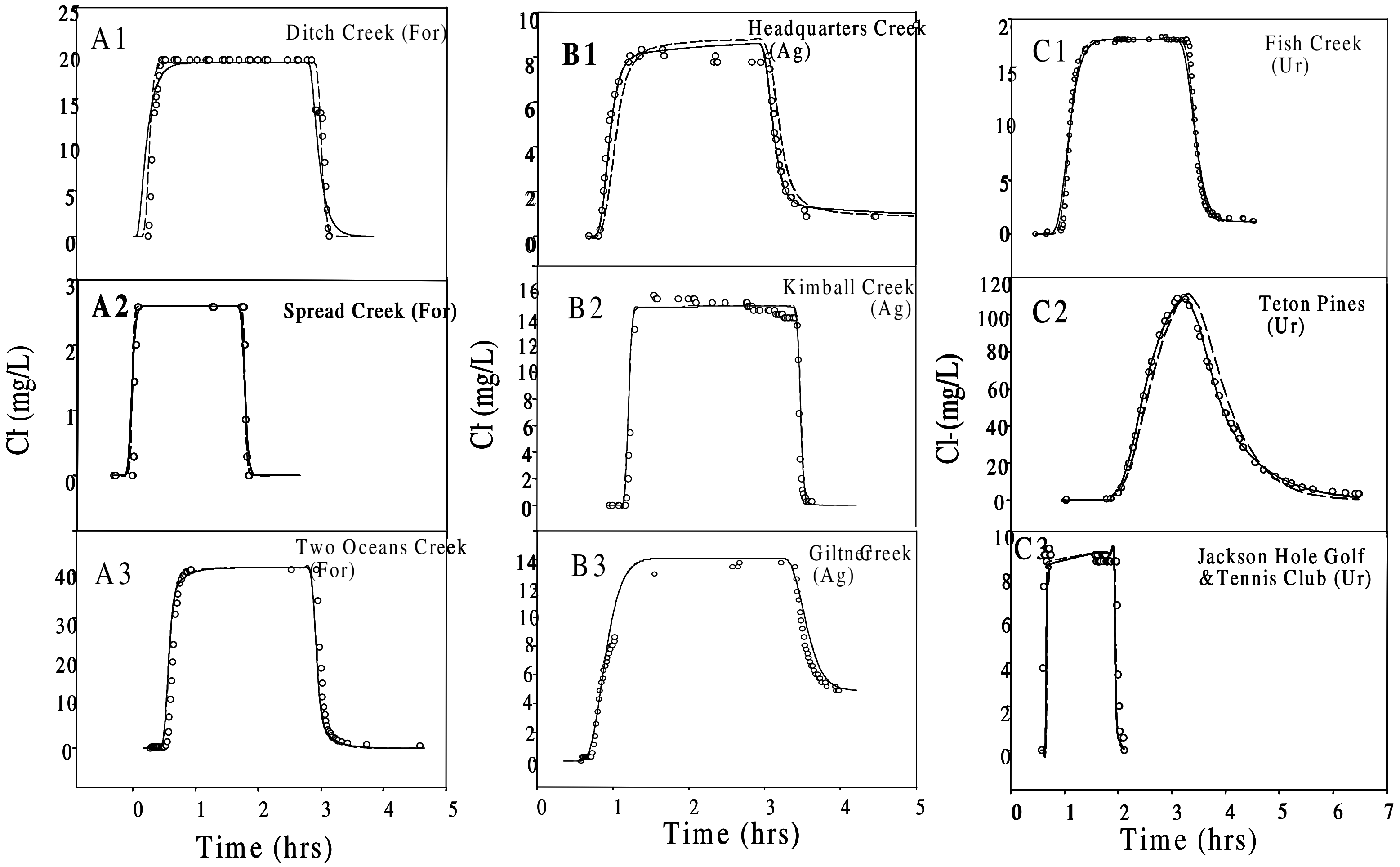

Figure 11. Observed data from conservative tracer additions (open circles), and results from single storage zone model (solid line) and two storage zone model (dashed line) by land use type (Forested A1-3; Agricultural B1-3; Urban C1-3).

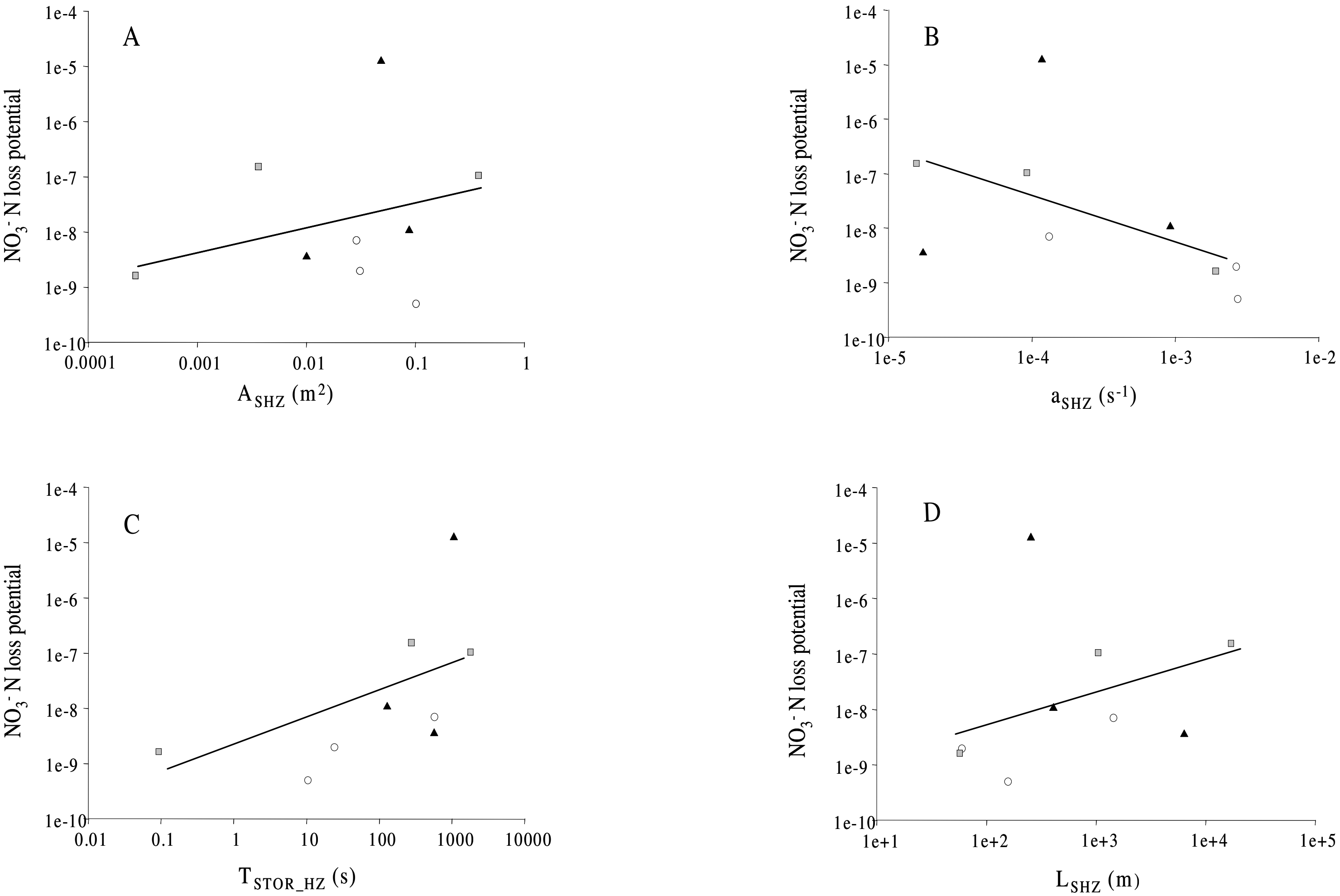

Figure 12. Regression analyses of NO_3- N loss potentials and hydrologic parameters, A_{SHZ} (A) ($r^2 = 0.043$), a_{SHZ} (B) ($r^2 = 0.278$), T_{STOR_HZ} (C) ($r^2 = 0.354$), and L_{SHZ} (D) ($r^2 = 0.076$), (all p values > 0.05).

CHAPTER V

DISCUSSION

Denitrification Across a Land Use Gradient

Streams, viewed at a landscape scale, are strongly influenced by their surroundings (Hynes 1975). Varying land uses at this scale produce dissimilar sources, forms, and amounts of nutrients that can eventually be transported to ground or surface waters. Therefore, understanding linkages between land use and stream nutrient concentrations and transport is of vital importance. In this study, I evaluated denitrification rates and potentials across a land use gradient from forested, agricultural, and urban streams.

I hypothesized that ambient rates of denitrification would be lowest at forested sites and higher in agricultural and urban sites. At the same time, I hypothesized that hyporheic denitrification rates at forested sites would be reaction rated limited or stimulated more with addition of nutrients than at agricultural and urban sites. This was based on the idea that in forested stream settings, NO_3^- and DOC are generally the limiting factors for denitrification based on lower inputs of both from only natural sources (i.e. mineralization) (Inwood et al. 2005). On the other hand, agricultural and urban sites typically have greater inputs of NO_3^- and DOC, or some other carbon source (Allan 2004), based on land use practices (i.e. fertilizer, manure, etc), thus denitrification rates should be greater as chemical limitations decrease. Consequently, I expected that forested streams would have the highest denitrification potentials once all reaction rate limitations were eliminated.

Mean ambient denitrification rates followed the expected trend, albeit differences among land use categories were not statistically significant. Similarly, substrate additions were highly variable, and the highest denitrification potentials were measured in agricultural streams. These results were unexpected but may be explained by spatial heterogeneity of sediments used in the assays, small sample size ($n = 4$) and limited statistical power. Furthermore, agricultural sites had highest %OM and maybe have highest microbial biomasses.

Additional work has focused on denitrification in streambed sediments from single land use categories. Martin et al. (2001) found significant increases in denitrification rates following similar nutrient additions in forested headwaters streams of the Appalachian Mountains. Additionally, Royer et al. (2004) found a significant increase in nitrate amended stream sediments from agricultural streams compared to ambient and DOC amended treatments. Rates as high as 15 mg N m^2 hr^{-1} were reported, which is much greater than those seen in this study.

There have been few studies looking at hyporheic denitrification (Holmes et al. 1996, Crenshaw 2007; Pinay et al. 2007), which presents an important research need. Holmes et al (1996) found that hyporheic denitrification in a desert stream was primarily N limited and secondarily limited by carbon, as denitrifiers depended on surface derived organic matter. Holmes et al. (1996) found higher denitrification potentials using stream bank sediments (150 μg m^{-2} h^{-1}) than parafluvial sediments (<5μg m^{-2} h^{-1}). Crenshaw (2007) investigated N_2O production using nitrogen isotopes across a similar land use gradient as used in this study and showed greatest N_2O production in human altered streams than reference streams. Finally, Pinay et al. (2007) found soil moisture to be the best predictor of denitrification in alluvial soils across a very large spatial gradient in Europe. The variability and range in spatial and temporal conditions under which we have information on hyporheic denitrification indicates a need for additional studies.

A variety of factors are required for denitrification to occur and include a NO_3^- source, carbon source, and anoxic conditions (Rysgaard et al. 1994). One commonality across many of the studies done on stream denitrification is the positive relationship observed between denitrification and stream NO_3^- concentration, which has been observed in streams across this land use gradient (Martin et al. 2001; Inwood et al. 2005; Arango et al 2007; Mulholland et al. 2008). However, I observed a poor relationship between denitrification rates and stream NO_3^- ($r^2 = 0.17$), improving slightly with subsurface NO_3^- concentrations ($r^2 = 0.33$). It is important to note that the studies mentioned above had a larger range and much higher concentrations of NO_3^- (>5 mg NO_3-N / L) (Inwood et al. 2005; Arango et al. 2007), than in this study. In this study, both stream and subsurface concentrations did not exceed 0.2 mg NO_3^- N / L, with most sites having considerably lower concentrations. Interestingly, stream NO_3^- concentrations at forested sites were within the range of published data. However my agricultural and urban sites are, with the exception of Fish Creek (0.4 NO_3-N mg/L), an order of magnitude less than what has been reported in the literature (Inwood et al. 2005). Given such low NO_3^- concentrations at these Wyoming sites, and trends in the nitrogen amended denitrificaiton rates, these results suggests NO_3^- limits hyporheic denitrificaiton at all land use locations.

The differences between denitrification rates seen in this study versus those reported by Inwood et al. (2005) can be partially explained by the management practices of the Wyoming streams used in this study and those in the Illinois setting of Inwood et al. (2005). Although a clear description on the sties used by Inwood et al. (2005) was not included they likely were heavily fertilized crop land. Additionally, there could be large differences based on the setting of the urban sites and whether they were subject to industrial effluent or if they ran though a city park. All the agricultural sites used in this study are used for cattle grazing only, and are set up on a rotating schedule to reduce time cattle spend on a given patch of land in order to reduce physical and chemical impact to streams. All of our urban streams are quite diverse and range from a golf course (Jackson Hole Golf and Tennis Club) setting to a town house development (Teton Pines). Golf course managers expressed their intention of keeping all fertilizer runoff out of the stream in an effort to mitigate water quality issues, which is reflected in measured NO_3^- concentrations (0.031 NO_3-N mg/L). While Teton Pines stream looks very productive (abundance of macrophytes, etc), NO_3^- N concentrations were below our detection limit (0.0009 NO_3-N mg /L). These results suggest that management practices geared towards keeping excess nutrients out of surface waters in both agricultural and urban sites may contribute to low denitrification rates and trends in rates that do not follow published studies.

Limitations of Denitrification Methods

Denitrification assays can be a useful tool and metric in aquatic sciences, but obtaining accurate rates of denitrification is difficult and methods are hindered by high spatial and temporal variability (Groffman et al. 2007). Here we used the C_2H_2 inhibition technique, which inhibits N_2O reduction to N_2, allowing measurement of N_2O as the final product of denitrification. Typically, the C_2H_2 inhibition technique underestimates denitrification rates especially in situations where NO_3^- is present in low concentrations (Bernot et al. 2006) or denitrification is coupled with nitrification (Seitziniger et al. 1993; Groffman et al. 2007). Our amendments with carbon and nitrate alleviate this problem and represent maximum potential rates under optimal conditions. Finally, as suggested by the literature, I added chloramphenicol to our slurries to counter over estimates due to new enzyme production (Inwood et al. 2005).

Transient Storage Comparison Across Land Uses

Solute transport models provide a way for investigators to quantify and compare transient storage parameters across streams (Morrice et al. 1997). I hypothesized that hyporheic denitrification at agricultural and urban sites is controlled by hydrologic processes. More specifically, I suspected that the physical template of agricultural and urban streams relative to forested streams (i.e. man-made vs. alluvial) would hydrologic exchange between surface and ground water. In part, this idea is driven by the substrate (bed material) characteristics across land uses. The bed and banks of forested streams is made up of sorted alluvial material and abandoned channels, which should be more conducive to hyporheic exchange than not sorted, fine material comprising the bed and banks of agricultural and urban sites. Furthermore, I speculated that the parameters calculated from the two storage zone model could be used to identify hydrologic controls of hyporheic denitrification across land uses.

I believe parameters derived from the two storage zone transport model (α_{HZ}, T_{STOR_HZ}, and L_{SHZ}) provide some evidence to support my original hypothesis that hyporheic denitrification at agricultural and urban streams is limited by hydrologic processes. Although high variability was observed for all of these parameters, which maybe be compounded by such a small sample size. However, on average agricultural and urban sites had an order of magnitude longer L_{SHZ} values than forested sites. This suggests that on average a water molecule travels 6,086 m at agricultural sites, and 2,364 m at urban sites before even entering hyporheic storage. Agricultural and urban streams are not long enough for hyporheic exchange to affect stream NO_3^- loads. Thus, solutes at agricultural and urban sites may never reach the hyporheic zone and come in contact with reactive substrates, despite the potential for long T_{STOR_HZ}. Finally, it is important to note that T_{STOR_HZ} and L_{SHZ} are driven by α_{SHZ} values (equation 10 and 12), which are lowest at agricultural and urban sites and ultimately is the limiting hydrologic factor. Together, these data support the conclusion that agricultural and urban streams are transport limited compared to forested streams.

Figure 13 conceptualizes the average surface and subsurface transient storage processes based on our results. Channel complexity cecreased from forested to agricultural and to urban streams (Figure 13; A1, B1, and C1). Surface storage (% channel storage from Surfer) was greatest at agricultural sites and similar at forested and urban sites. This trend was also recognized during field work, especially at agricultural sites. As depicted by cross sections in Figure 13 (A2, B2, and C2), agricultural streams are exceptionally wide and deep, while forested streams are also wide but much shallower. Stream margins of agricultural streams consisted of thick grassy areas of shallow, slow moving water. These areas of slow, shallow water were often much wider, laterally, than the main area of the channel (Figure 13; B2) Forested sites were typically wide and shallow with urban sites being an intermediate with respect to their cross sections, surface storage and hyporheic exchange rates. L_{SHZ} for each land use type are described by the length of the arrows in (A1, B1, and C1), which is longest at agricultural sites which decreases at urban and finally forested sites. Additionally, the width of the same arrows describes hyporheic residence times (T_{STOR_HZ}), which decreases following the same trend across land uses as L_{SHZ}.

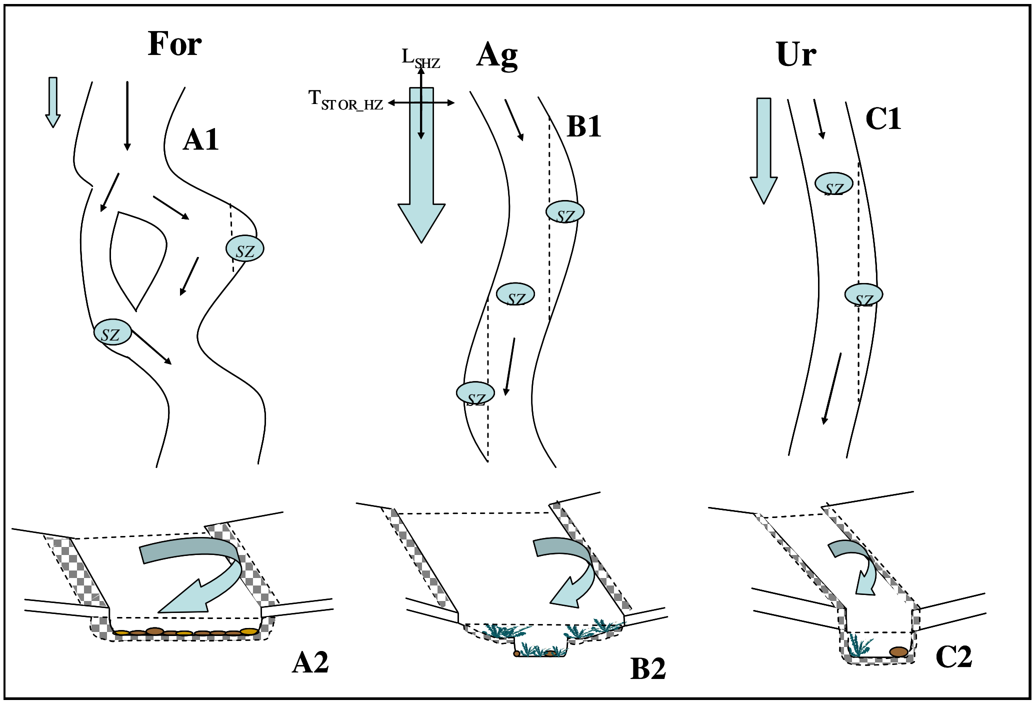

Figure 13. Conceptual diagram of transient storage across land use gradient based on results and filed observations (For A; Ag B; Ur C). A1,B1,C1 represent plan form for different stream types and extent of in channel storage zones (oval with SZ). A2, B2, and C2 represent basic cross section of each stream type. Checkered area represents size and extent of hyporheic zone. Size of curved arrows represent hyporheic exchange rate (α_{SHZ}), while length of straight arrows(A1,B1,C1) represent L_{SHZ} or distance traveled before solute enters hyporheic storage zone, while the width of the arrows represent T_{STOR_HZ} or hyporheic residence times.

Model Assumptions

There are a variety of parameters that can be calculated to describe transient storage based on OTIS outputs, thus it is important to note a couple of key assumptions. Although A_S/A is the most commonly used metric to compare relative sizes of transient storage zone and surface stream, there is not a single metric used as a "standard" for comparison. The second important assumption associated with this research concerns the methods used for independently estimating A_{SDZ}, α_{SDZ}, and subsequent estimates of A_{SHZ} and α_{SHZ}. For example, estimates of A_{SDZ} are based on a % of channel area below an arbitrary velocity value. First, using a value equal to half the mean velocity seems like a reasonable value to define in channel dead zones, but could be improved through more research on transient storage processes. Second, this method assumes that A_S minus in-channel dead zone storage from Surfer is all A_{SHZ}. Values for % in-channel dead zones range from 16 to 60% (Table 4) meaning that 84 and 40% of A_S is assumed to be A_{SHZ}. While this seems like a reasonable starting place, additional studies would be beneficial to support these assumptions.

Nitrogen Sink Analyses

A significant amount of work and effort has been focused on understanding denitrification rates in terrestrial and aquatic systems. This study is unique by focusing on hyporheic denitrification across a land use gradient rather than in stream or riparian denitrification of a single land use (i.e. urban streams). However, these findings are consistent with other studies based on individual land uses, which have shown that hyporheic denitrification in undisturbed streams, can be limited by low concentrations of

NO_3^- in subsurface environments (Holmes et al. 1996). Holmes et al. (1996) showed that hyporheic denitrification in a desert stream can be a significant nitrogen sink relative to available NO_3^-, however they did not compare denitrification across land uses (Holmes et al. 1996). Kasahara and Hill (2006) found the hyporheic zone of urban and agricultural streams to be a nitrogen sink, but, again, their study does not include a more broad land use spectrum.

Our transient storage analyses were designed with two purposes in mind: first, to explore new methods to gain independent estimates of surface water and hyporheic zone storage characteristics; and second, to evaluate the importance of hyporheic denitrification to stream N loss across land use types.

Many studies have attempted to quantify the relative importance of denitrification as a N sink in streams. However, many of these previous studies has focused on denitrification in stream bed sediments (~first 10mm of sediment) or in riparian zones (Martin et al. 2001; Royer et al. 2004; Inwood et al. 2005; Arango et al. 2007), with little attention to hyporheic denitrification (see Crenshaw 2007). Metrics used to describe the importance of denitrification relative to available NO_3^- vary and range from proportion of NO_3-N load removed via denitrification scaled to stream depth and velocity (Inwood et al. 2005) to the % NO_3-N load lost per day (Royer et al. 2004). Inwood et al. (2005) found the amount of NO_3-N removed via denitrification was significantly higher in forested streams than agricultural or urban streams, while Royer et al. (2004) determined that denitrification in stream sediments of agricultural streams did not represent a substantial N sink. The metric used in this study to describe NO_3-N loss potential

(Equation 4) is similar to those mentioned above, but applied to hyporheic processes rather than in-stream processes.

My results show that on average, urban sites denitrified the highest proportion of stream NO_3^-, followed by agricultural, then forested sites, it's important to note that NO_3-N loss potentials were exceptionally high at Teton Pines, which can be partially explained by the low NO_3-N value used (0.00045 mg/L) in the of NO_3-N loss potential calculation, which is driving this result. Ignoring this data point, shows that NO_3-N loss potential at urban sites are on the same order of magnitude as at forested sites, both of which function as a less effective sink for N compared to agricultural sites. However, these NO_3-N loss potentials cannot be viewed independently of hydrologic process identified from the two storage zone model and transient storage analysis. Values of α_{SHZ} and L_{SHZ} for agricultural and urban sites suggest limited hyporheic exchange and stream length insufficient for hyporheic exchange. In summary, the combination of N sink and transient storage analysis support my original hypothesis that agricultural and urban streams are transport limited relative to forested streams.

I chose to focus on the relationship between NO_3-N loss potential and α_{SHZ}, T_{HZ_STOR}, L_{SHZ} to evaluate the role of the hyporheic zone as a N sink. The negative trend observed for α_{SHZ} supports the hyporheic exchange limitations hypothesis in NO_3-N loss potentials are highest at lower α_{SHZ} values. This makes sense; the faster NO_3^- enters the hyporheic zone, the sooner it is available to be denitrified. This concept also applies to the relationship seen between T_{HZ_STOR} values and NO_3-N loss potential. This positive trend shows NO_3-N loss potential increasing with the amount of time water or NO_3^- resides in the hyporheic zone and is exposited to biologically reactive substrates. These results show that T_{HZ_STOR} is the best predictor of NO_3-N loss potentials based on the hydrologic parameters used in this study, however its important to keep in mind that many of the hydrologic parameters used here are not independent as they are calculated using common variables (i.e α_{SHZ}). Hyporheic exchange rate seems to be the key driver.

CHAPTER VI

CONCLUSIONS AND CONTRIBUTIONS TO WATERSHED SCIENCE

It is well known that stream water has the potential to exchange laterally andr vertically between hyporheic zone. These exchanges have the potential to alter stream water chemistry based on contact with biologically reactive substrates (Findlay 1995). However, few studies have focused on hyporheic denitrification and on quantifying hydrologic characteristics of the hyporheic zone and the potential control those characteristics have on biogeochemical processes. The objectives of this study were to evaluate hyporheic denitrification rates and potentials over a land use gradient of forested, agricultural, and urban streams. Furthermore, I aimed to distinguish between reaction rate and transport rate limitations on hyporheic denitrification across land uses.

My analyses of reaction rate limitations of hyporheic denitrification were somewhat inconclusive. While no significant differences were observed between individual treatments or across land uses, there were consistent trends in the data. Land use appears to influence the capacity for hyporheic denitrification at agricultural and urban sites by supplying substrates that build the microbial potential for relatively high denitrification potentials, while forested sites have lower denitrification potentials. The differences in denitrification rates between land uses may be due to differences in microbial communities. For example, the sediment composition of the bed and banks of agricultural and urban streams was very fine (i.e. silt and clay) relative to forested streams (i.e. cobble, gravel, sand). This suggests that sediments at agricultural and urban sites have greater surface areas that could support a greater number of denitrifying microbes. While speculative, this may be supported further by the significantly greater organic matter content found at agricultural sites. Furthermore, our data suggests that denitrification across these sites is more sensitive to available NO_3^- than DOC, which could be attributed to land management strategies.

In general, the trends in denitrification rates and NO_3^- match well with hyporheic storage characteristics discussed earlier and which are illustrated in Figure 13. That is, slower exchange and long residence times found at agricultural sites are conditions conducive for higher denitrification rates and ultimately greater NO_3-N loss potentials. Additionally, lower denitrification potentials, fast exchange, and short transport lengths at forested sties suggest these streams have greater hydrologic potential for hyporheic processes to play an important biogeochemical role relative to agricultural streams or urban streams. I originally expected NO_3-N loss potential and hyporheic residence time to be greatest at forested sites, decreasing to agricultural and finally to urban sites. However, my results show forested streams to have the highest NO_3-N loss potential and agricultural streams to have the longest hyporheic residence times. While the results are different from what was expected, the results provide important insight into biogeochemical and hyporheic transport processes, which should be considered in concert rather than as independent entities of steam ecosystems.

Due to the inherent and widespread implications that land use practices are having on aquatic ecosystems, it is important take a step back and examine how our actions potentially affect the surrounding landscape. I believe that the results from this study have applications in both natural resource management and for future biogeochemical and hydrologic studies.

Natural resource managers all over the world struggle with water quality problems. As discussed here, N is an important contributor to eutrophication and declines in water quality, due in part to management practices of land adjacent to streams and rivers. The results from this study suggest that a conscious effort by land managers can reduce NO_3^- inputs to surface waters, thus maintaining higher water quality and ecosystem integrity. For example, on average the forested and agricultural streams used in this study had approximately the same stream NO_3^- concentrations, which was and is unexpected. I believe this can be attributed to two things. First, these forested streams are rather remote (in GTNP), where atmospheric deposition of N is relatively low compared to streams located near large cities with high air pollution problems. Additionally, such low NO_3^- in these agricultural streams is due to the management strategy used which rotates cattle between lots, which lowers nutrient inputs (i.e. manure).

Physical attributes of streams also need to be incorporated in management practices. Here we saw T_{HZ_STOR} and α_{SHZ}, were the best predictors of NO_3-N loss potentials, with α_{SHZ} being the common factor. Therefore, it is to design channels with high hydraulic conductivity to increase α_{SHZ}, and A_{SHZ} with subsequent increaseing T_{HZ_STOR}. This concept is further supported by examining drivers NO_3-N loss potentials. In order to maximize NO_3^- N loss potentials, discharge values would need to rapidly decrease to almost zero, or increase the flux or proportion of stream water going through the hyporheic zone and being exposed to reactive substrates. This can also be accomplished through stream design methods, and maximizing NO_3-N loss potentials through α_{SHZ} and T_{HZ_STOR} values.

Finally, it was my goal to contribute to contemporary biogeochemical and hyporheic literature, and to provoke new discussions on these topics. This study covered biological and physical processes over a relatively large spatial scale. The results presented here provide valuable insight into poorly understood processes across a large land use gradient. Additionally, this study succeeded in employing new and useful methods to gain independent estimates of transient storage for both surface and subsurface waters. Between these two areas of study, hyporheic N cycling and hyporheic storage processes, there is a insufficiency in the literature and understanding of these processes across spatial and temporal scales, which needs to be addressed through additional research. In conclusion, I feel the relationship between biological and physical (hydrogeomorphic) processes should be explored further and that biological processes in streams cannot be considered independent of hydrologic processes.

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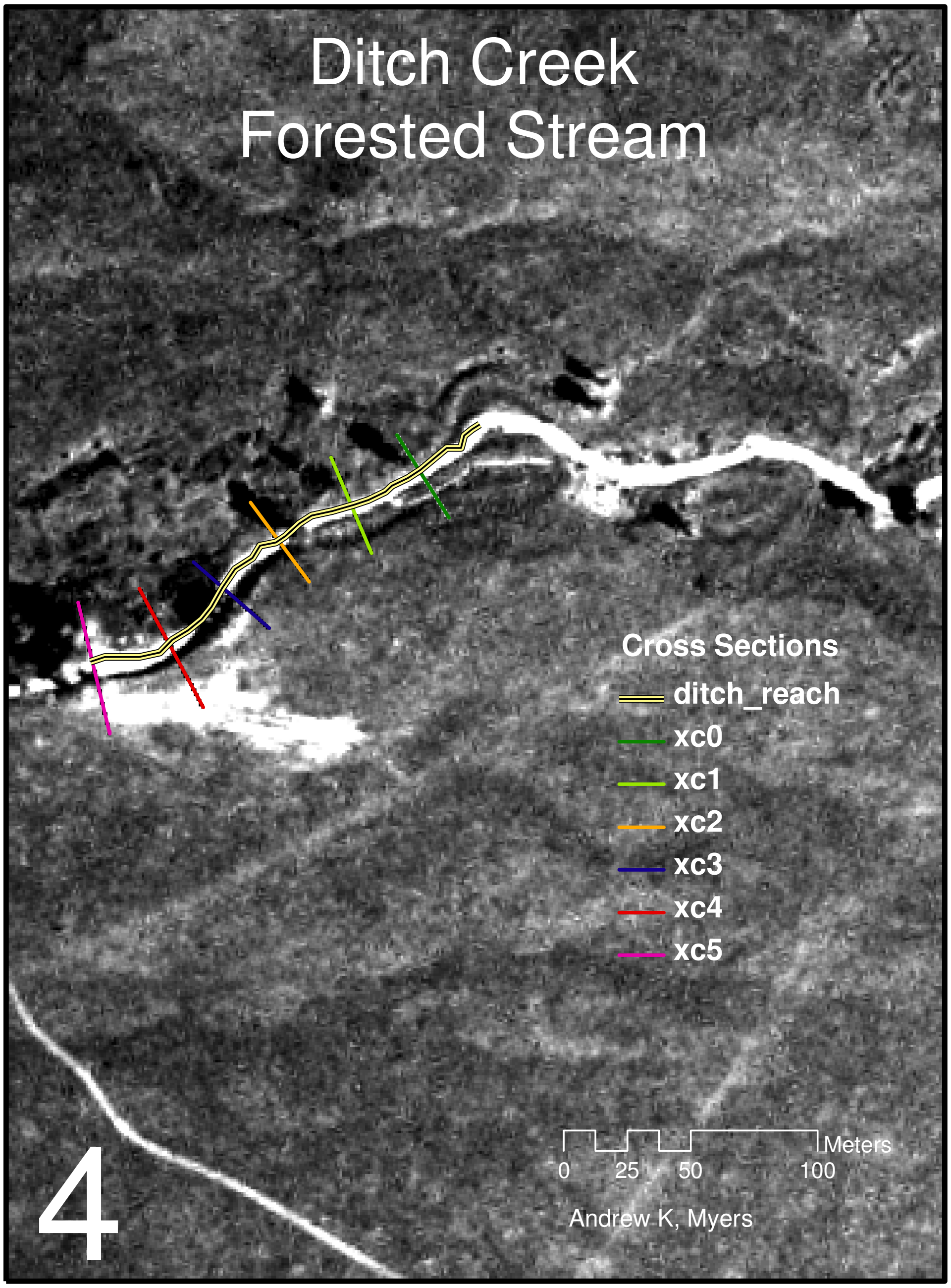
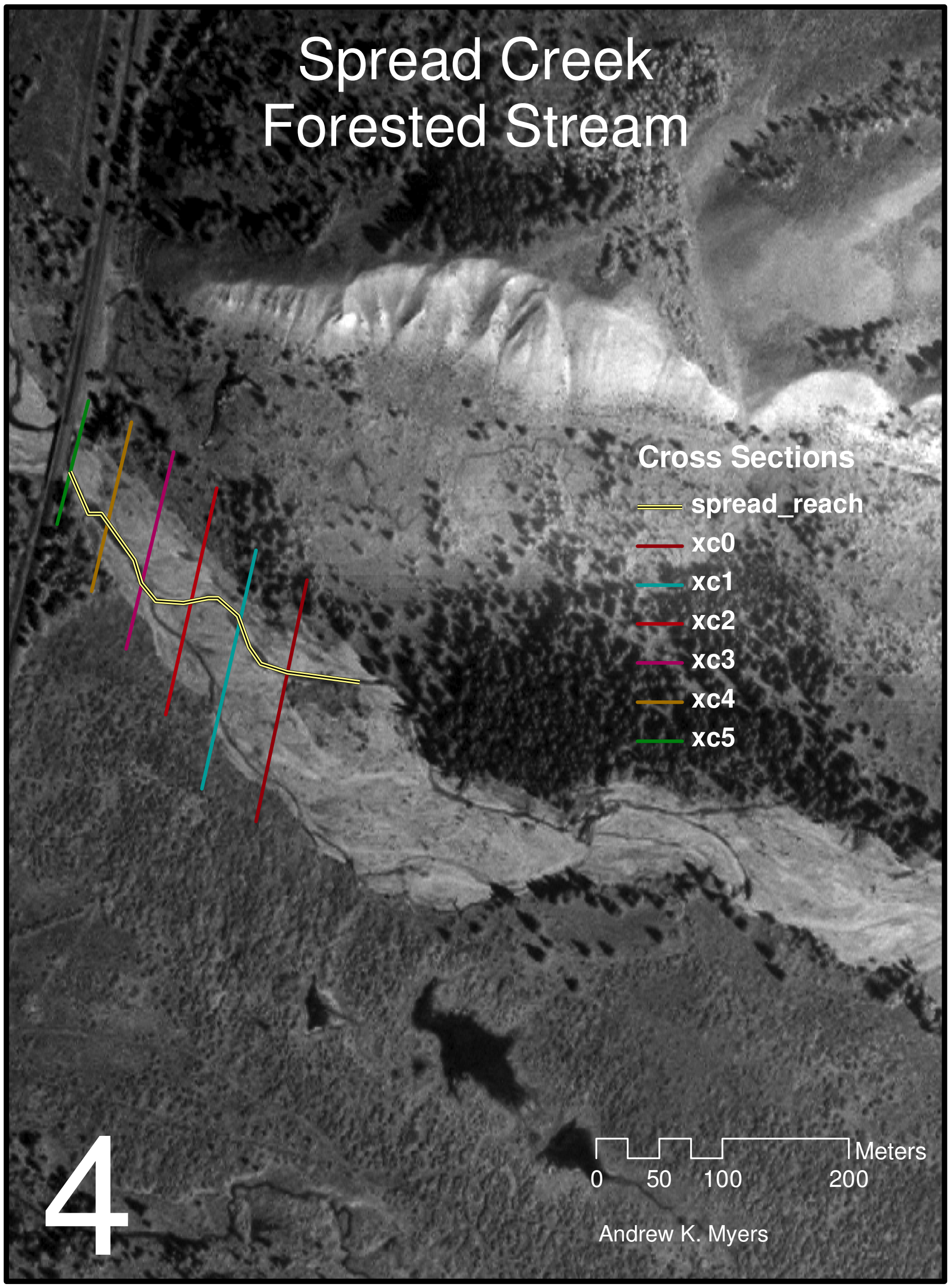
APPENDIXES

Appendices

Appendix A. Digital orthophotos of study reaches and cross sections.




Spread Creek
Forested Stream
Cross Sections
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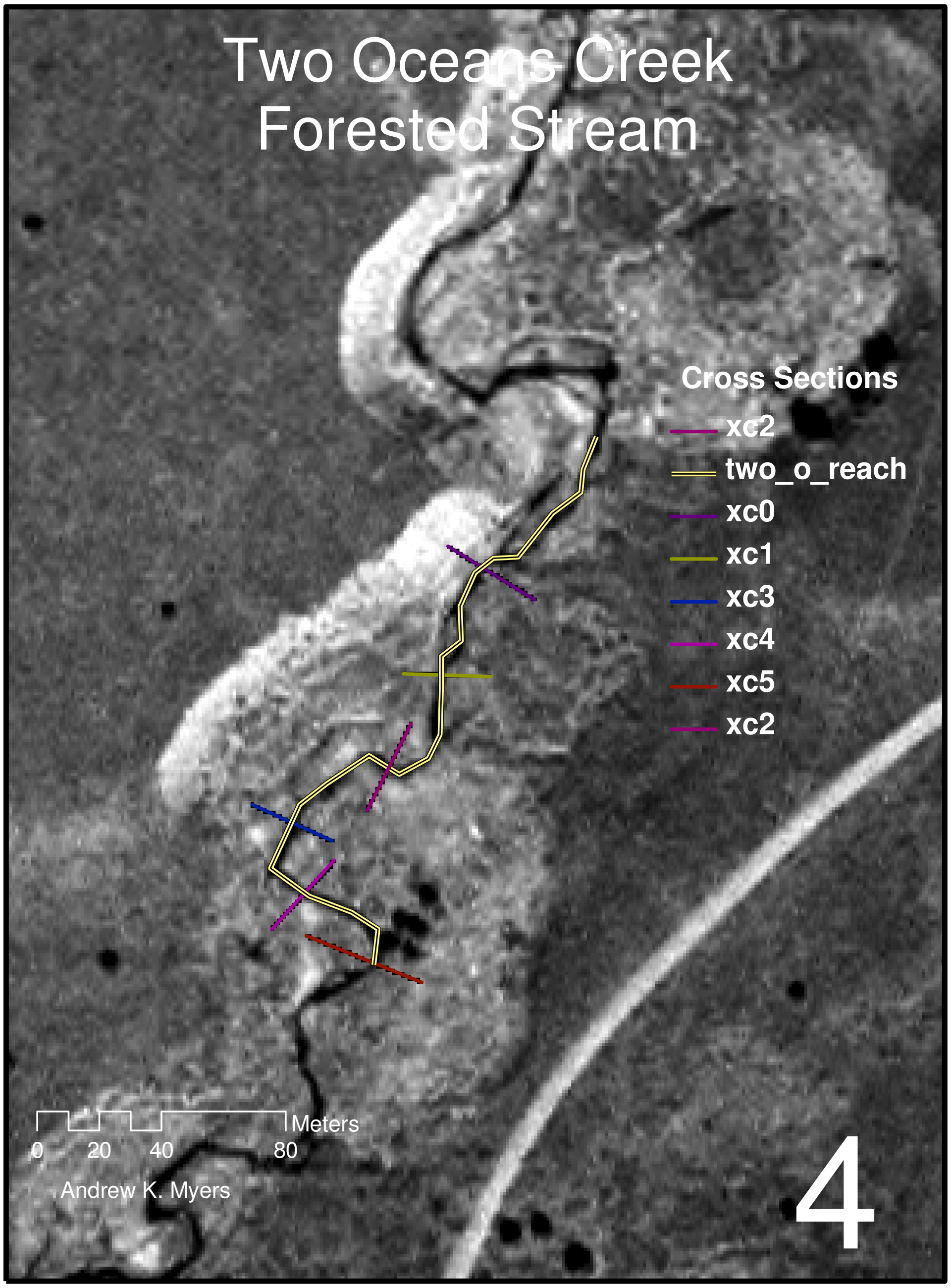
xc1
xc2
xc3
xc4
xc5
0
50
100
200
Meters
4
Andrew K. Myers


Two Oceans Creek
Forested Stream
Cross Sections
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two_o_reach
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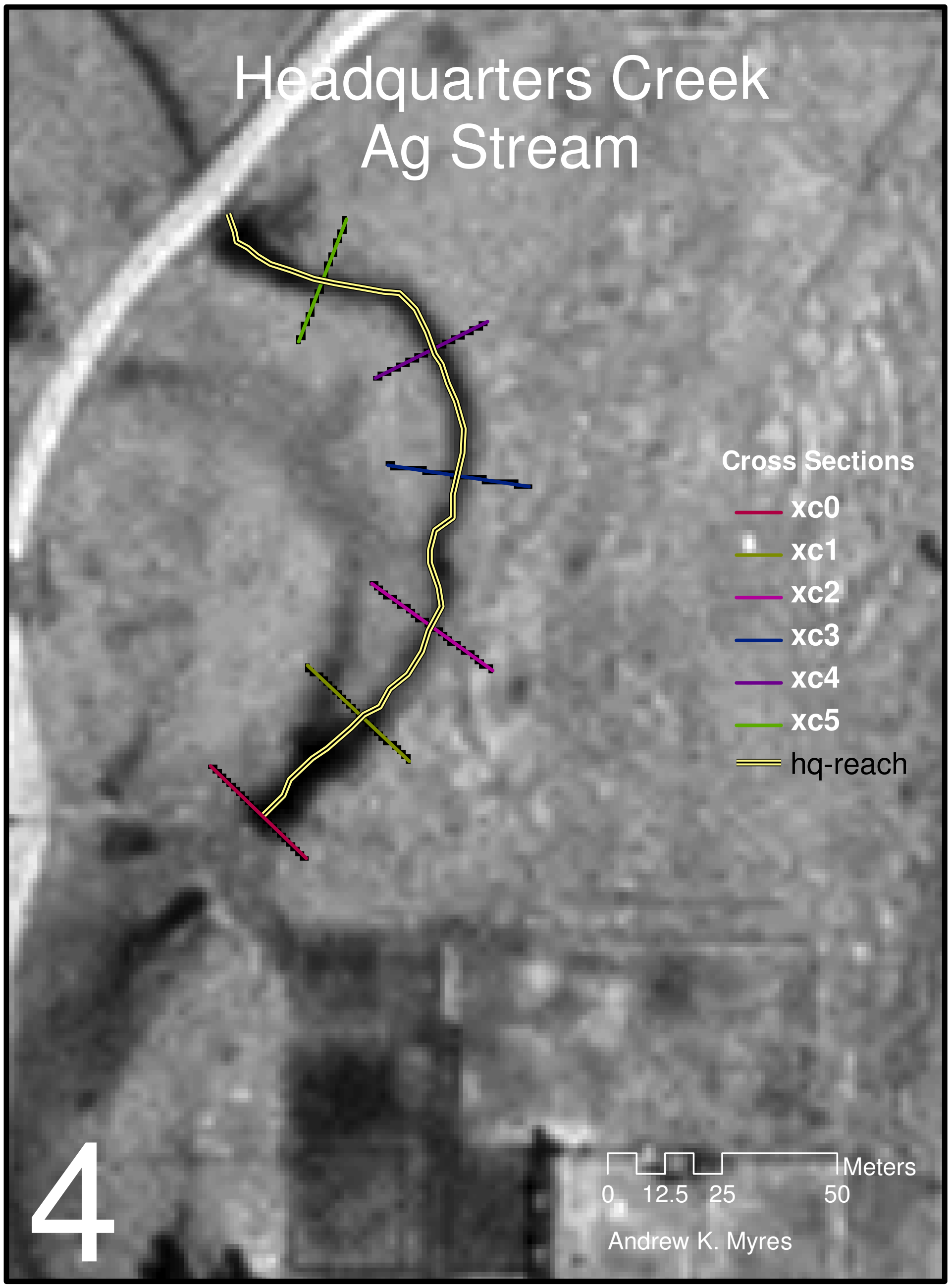
Meters
Andrew K. Myers
4


Headquarters Creek
Ag Stream
Cross Sections
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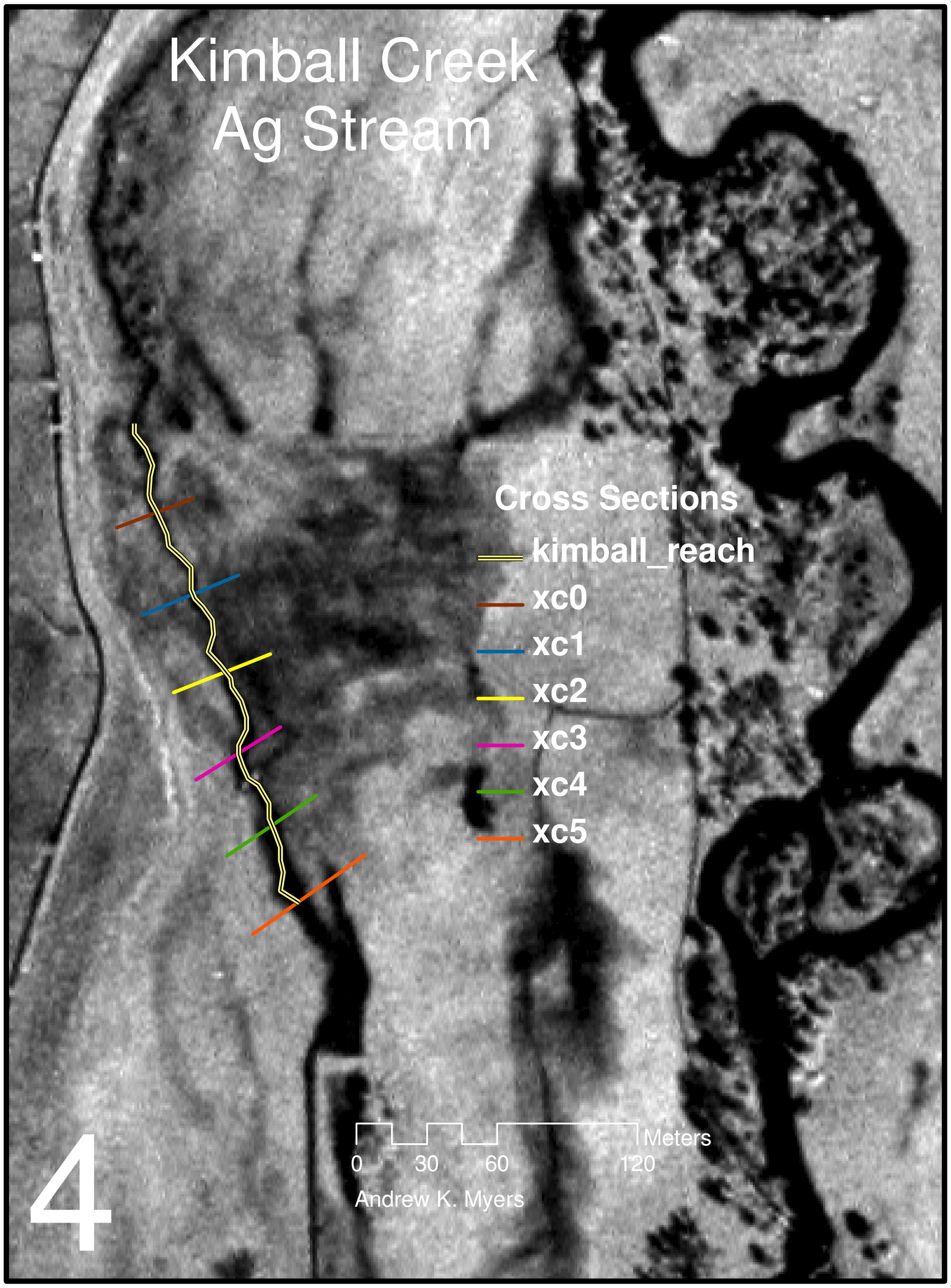
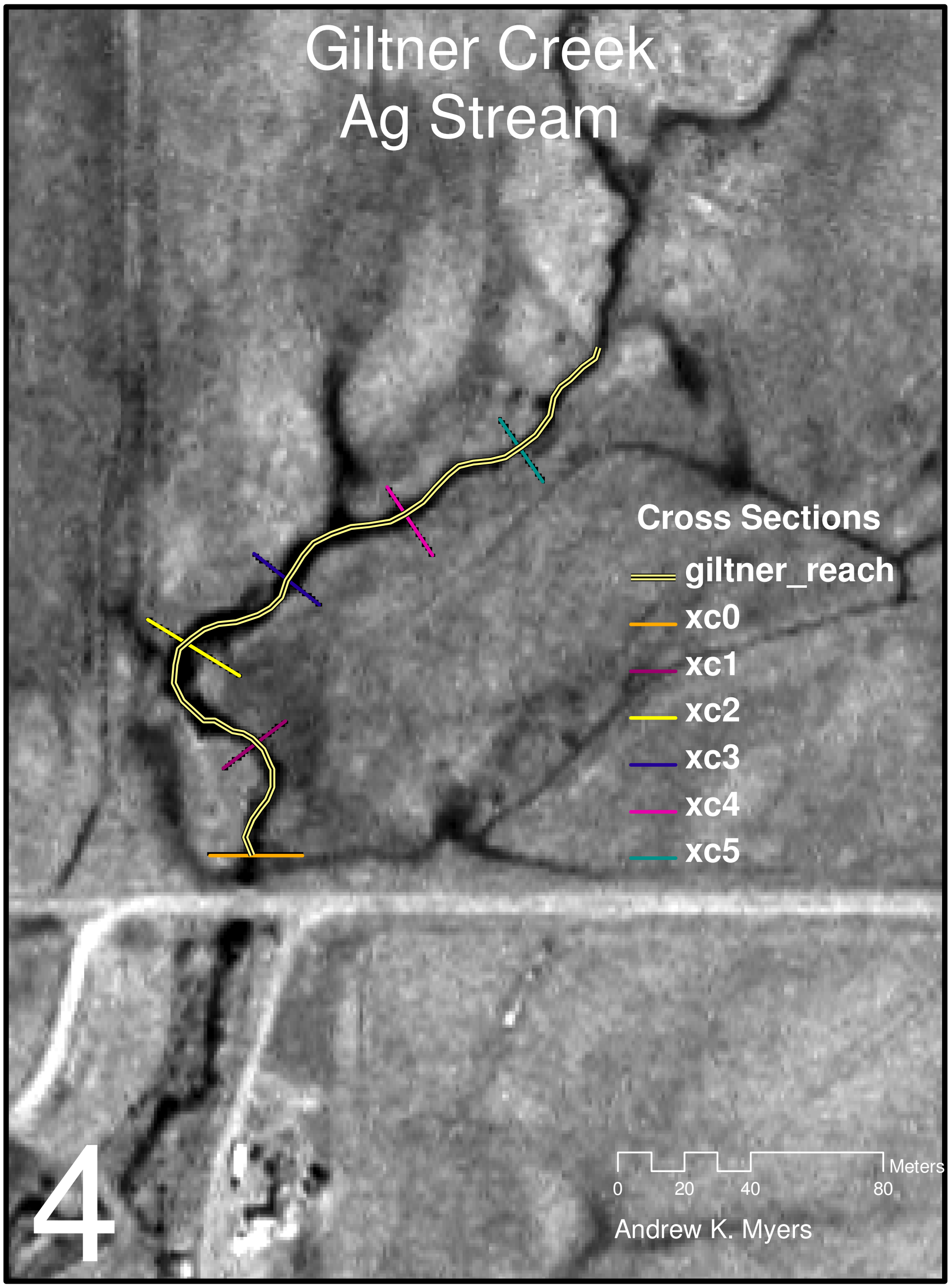
xc1
xc2
xc3
xc4
xc5
hq-reach
4
0
12.5
25
50
Meters
Andrew K. Myres


Kimball Creek
Ag Stream
Cross Sections
kimball_reach
xc0
xc1
xc2
xc3
xc4
xc5
0
30
60
120
Meters
Andrew K. Myers
4


Giltner Creek
Ag Stream
Cross Sections
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0
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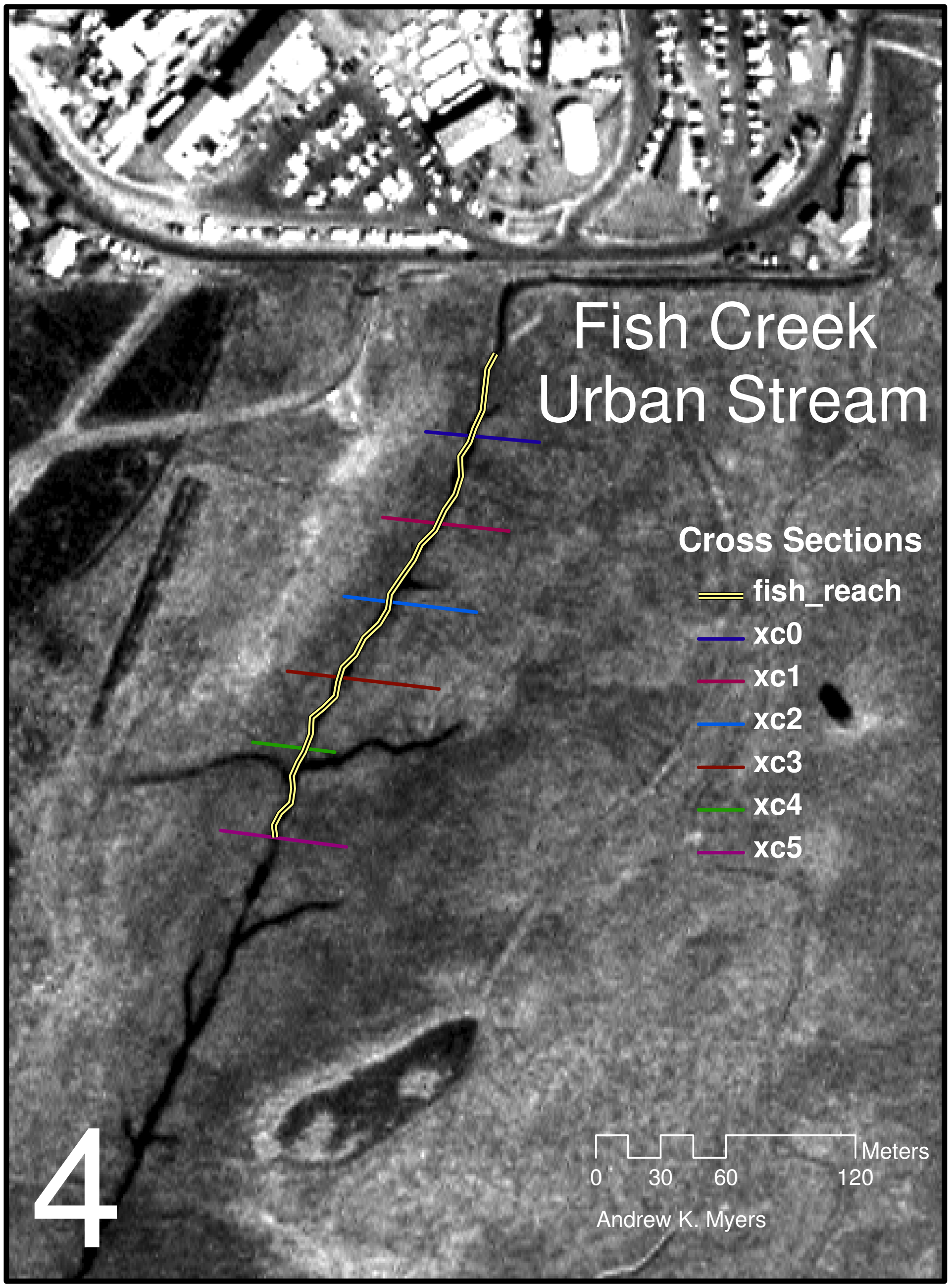
80
Meters
Andrew K. Myers
4


Fish Creek
Urban Stream
Cross Sections
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xc1
xc2
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xc4
xc5
0
30
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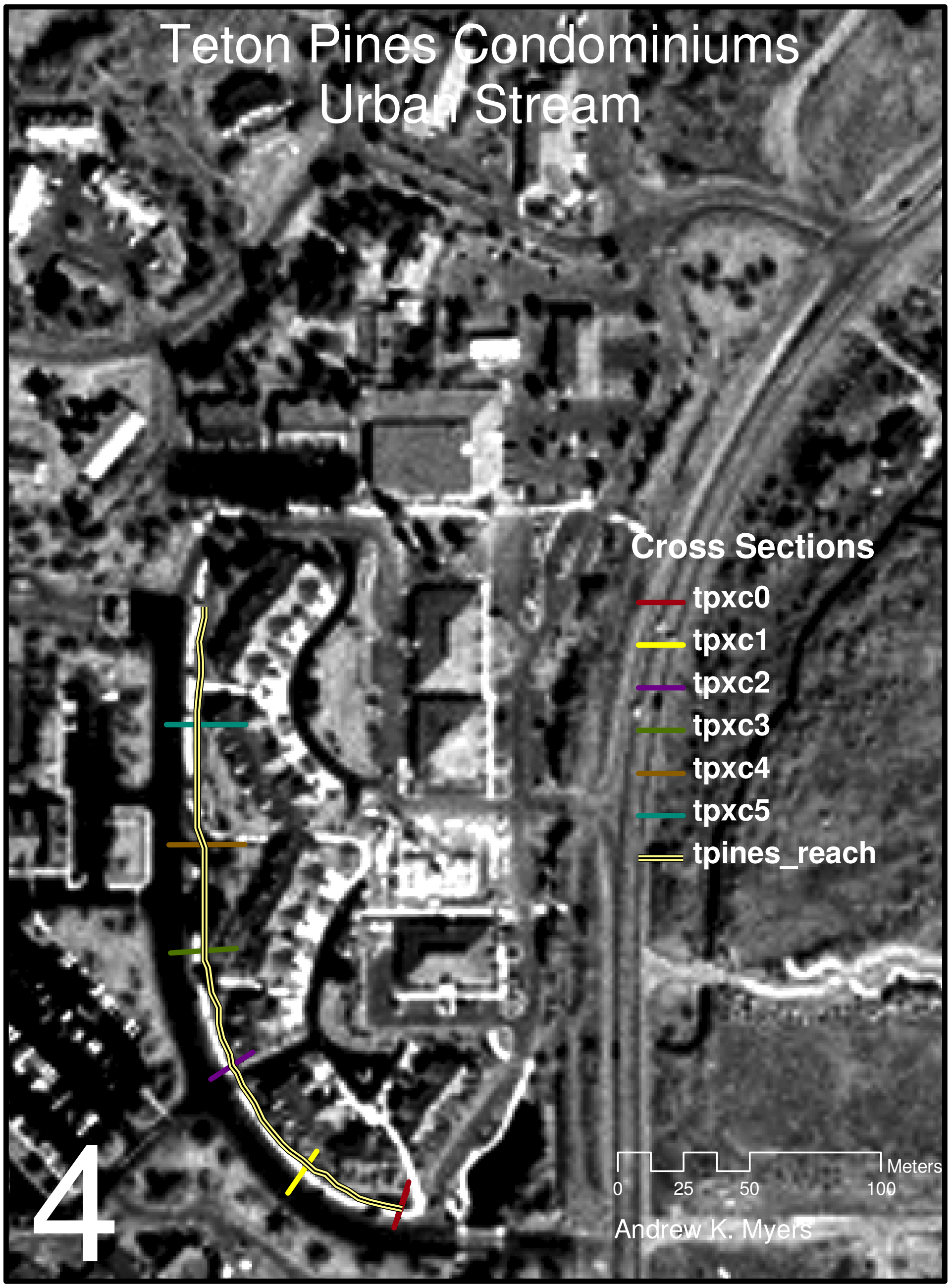
120
Meters
Andrew K. Myers
4


Teton Pines Condominiums
Urban Stream
Cross Sections
tpxc0
tpxc1
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tpxc3
tpxc4
tpxc5
tpines_reach
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25
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Meters
Andrew K. Myers
4

Jackson Hole Golf and Tennis Club photo and cross sections not available. Site was recently reconstructed and current orthophoto was not available.

Appendix B Tables

Forested Sites				
Spread Creek	**0.5Mean(V)**	**Postitive Area**	**Negative**	total area
XC1	0.250	**0.81**	**0.418**	1.23
XC2	0.226	1.11	0.341	1.45
XC3	0.073	2.57	1.28	3.85
XC4	0.108	2.34	0.65	2.99
XC5	0.201	1.67	0.04	1.71
XC6	0.495	1.21	0.87	2.08
mean total		2.22		
Mean Neg	A_{SDZ}	0.598833333		
%Channel Storage		26.9947408		
Ditch Creek	**0.5Mean(V)**	**Postitive Area**	**Negative**	
XC1	0.057	**0.41**	**0.141**	0.56
XC2	0.120	0.36	0.057	0.41
XC3	0.087	0.39	0.079	0.47
XC4	0.056	0.44	0.123	0.57
XC5	0.110	0.47	0.227	0.69
XC6	0.061	0.44	0.79	1.23
mean total		0.65		
Mean Neg	A_{SDZ}	0.236166667		
%Channel Storage		36.06515653		
Two Oceans		**Postitive Area**	**Negative**	
XC1	0.098	**0.16**	**0.012**	0.17
XC2	0.104	0.14	0.06	0.19
XC3	0.087	0.15	0.04	0.19
XC4	0.056	0.30	0.06	0.36
XC5	0.173	0.10	0.02	0.12
XC6	0.006	0.24	0.02	0.26
mean total		0.21		
Mean Neg	A_{SDZ}	0.034166667		
%Channel Storage		15.9038014		

Appendix B continued

Agricultural Sites

Gilter	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.0314	0.876	1.406	2.28
XC2	0.0964	0.715	0.376	1.09
XC3	0.0955	0.810	0.253	1.06
XC4	0.0363	0.995	0.717	1.71
XC5	0.0513	0.933	0.778	1.71
XC6	0.0689	0.965	0.398	1.36
mean Pos		0.882	0.655	1.537
Mean Neg	A_{SDZ}	0.655		
%Channel Storage		42.591		
HQ	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.0580	**0.899**	**0.483**	1.382
XC2	0.0520	0.980	0.860	1.840
XC3	0.0710	0.826	0.672	1.498
XC4	0.0590	1.023	0.701	1.724
XC5	0.0280	1.399	4.924	6.323
XC6	0.0240	2.346	3.645	5.991
mean total	3.1263			
Mean Neg	1.8808	A_{SDZ}		
%Channel Storage	60.1610			
Kimball	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.2370	**0.705**	**0.235**	0.940
XC2	0.2000	0.317	0.034	0.351
XC3	0.0691	0.628	0.211	0.839
XC4	0.1490	0.373	0.067	0.440
XC5	0.1050	0.514	0.034	0.548
XC6	0.0560	0.704	0.178	0.882
mean total	0.6667			
Mean Neg	0.1265	A_{SDZ}		
%Channel Storage	18.9750			

Appendix B continued

Urban Sites				
Fish Creek	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.130	**0.12**	**0.052**	0.18
XC2	0.020	0.79	0.52	1.31
XC3	0.043	0.99	0.05	1.04
XC4	0.020	1.05	0.45	1.50
XC5	0.068	0.57	0.149	0.72
XC6	0.090	0.44	0.154	0.59
mean total		0.89		
Mean Neg	A_{SDZ}	0.229166667		
%Channel Storage		25.82644628		
Teton Pines	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.009	**0.19**	**0.252**	0.44
XC2	0.013	0.13	0.093	0.22
XC3	0.015	0.13	0.074	0.20
XC4	0.015	0.06	0.023	0.08
XC5	0.015	0.18	0.044	0.23
XC6	0.003	0.18	0.23	0.41
mean total		0.26		
Mean Neg	A_{SDZ}	0.119333333		
%Channel Storage		45.17350158		
JG&TC	**0.5*mean V**	**Postitive Area**	**Negative**	**Total**
XC1	0.290	**0.24**	**0.044**	0.28
XC2	0.234	0.33	0.008	0.34
XC3	0.124	0.35	0.08	0.43
XC4	0.182	0.32	0.054	0.38
XC5	0.228	0.25	0.012	0.26
XC6	0.130	0.38	0.227	0.61
mean totoal		0.38		
Mean Neg	A_{SDZ}	0.070833333		
%Channel Storage		18.48629839		

Appendix C

Appendix C. Denitrification assay results (mg N_2O/min) by site, treatment, and replicate. Negative results are presents as zero

Sites	Treatment	Rep 1	Rep 2	Rep 3	Rep 4	Mean
Ditch Creek (For)	Control	0.002	0	0	0	0.0005
Spread Creek (For)	Control	0.0058	0	0.0017	0	0.001875
Two Oceans Creek (For)	Control	0.00008	0	0.0036	0.0008	0.00112
Ditch Creek (For)	Carbon	0.0006	0	0.0087	0	0.002325
Spread Creek (For)	Carbon	0.0022	0	0.0009	0.0096	0.003175
Two Oceans Creek (For)	Carbon	0.0109	0	0	0	0.002725
Ditch Creek (For)	Nitrogen	0.0005	0	0.0009	0	0.00035
Spread Creek (For)	Nitrogen	0.0257	0	0.0146	0	0.010075
Two Oceans Creek (For)	Nitrogen	0.0262	0	0.0008	0.0008	0.00695
Ditch Creek (For)	Carbon & Nitrogen	0.00370	0.00000	0.00050	0.00000	0.00105
Spread Creek (For)	Carbon & Nitrogen	0.01080	0.01550	0.01010	0.00610	0.010625
Two Oceans Creek (For)	Carbon & Nitrogen		0.00430	0.00000	0.00000	0.001433333
Headquarters Creek (Ag)	Control	0.0072	0.002	0.0324	0.0027	0.011075
Kimball Creek (Ag)	Control	0.0127	0.0017	0.0215	0	0.008975
Giltner Creek (Ag)	Control	0.001	0.0003	0	0.0002	0.000375
Headquarters Creek (Ag)	Carbon	0	0.0005	0.001	0	0.000375
Kimball Creek (Ag)	Carbon	0.0018	0.0027	0.0028	0	0.001825
Giltner Creek (Ag)	Carbon	0	0	0	0.0067	0.001675
Headquarters Creek (Ag)	Nitrogen	0	0	0.0023	0.0279	0.00755
Kimball Creek (Ag)	Nitrogen	0.0157	0.0316	0.0646	0.0166	0.032125
Giltner Creek (Ag)	Nitrogen	0	0.0037	0.003	0.0049	0.0029
Headquarters Creek (Ag)	Carbon & Nitrogen	0.0039	0.0103	0.0065	0	0.005175
Kimball Creek (Ag)	Carbon & Nitrogen	0.00445	0.0325	0.2284	0.0041	0.0673625
Giltner Creek (Ag)	Carbon & Nitrogen	0.0006	0.0044	0.0025	0	0.001875
Fish Creek (Ur)	Control	0.0362	0	0	0	0.00905
Teton Pines Creek (Ur)	Control	0.0049	0	0.002	0.0049	0.00295
Jackson Golf and Tennis Club (Ur)	Control	0.0001	0	0	0	0.000025
Fish Creek (Ur)	Carbon	0.0295	0.0016	0	0.0019	0.00825
Teton Pines Creek (Ur)	Carbon	0.0041	0.0006	0.003	0.0041	0.00295
Jackson Golf and Tennis Club (Ur)	Carbon	0	0.0032	0.0267	0	0.007475
Fish Creek (Ur)	Nitrogen	0.005	0	0.0417	0.0162	0.015725
Teton Pines Creek (Ur)	Nitrogen	0	0.0182	-0.0006	0.0186	0.00905
Jackson Golf and Tennis Club (Ur)	Nitrogen	0.0024	0	0.0102	0.0046	0.0043
Fish Creek (Ur)	Carbon & Nitrogen	0	0.0382	0.0131	0.0066	0.014475
Teton Pines Creek (Ur)	Carbon & Nitrogen	0.0035	0.0068	0.0189	0.004	0.0083
Jackson Golf and Tennis Club (Ur)	Carbon & Nitrogen	0.0039	0	0.0145	0.0071	0.006375