Watershed Nitrogen Transport, Retention, and Fate in Dryland and Urban Ecosystems

by

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ABSTRACT

Nitrogen is an essential, often limiting, element for biological growth that can act as a pollutant if present in excess. Nitrogen is primarily transported by water from uplands to streams and eventually to recipient lakes, estuaries, and wetlands, but can be modulated by biological uptake and transformation along these flowpaths. As a result, nitrogen can accumulate in aquatic ecosystems if supply is high or if biological retention is low. Dryland and urban ecosystems offer interesting contrasts in water supply, which limits transport and biological activity in drylands, and nitrogen supply that increases with human activity. In my dissertation, I ask: What is the relative balance among nitrogen retention, removal, and transport processes in dryland watersheds, and what is the fate of exported nitrogen? My dissertation research demonstrates that water is a major control on where and when nitrogen is retained and removed versus exported to downstream ecosystems. I used a mass-balance model based on synoptic surveys to study seasonal and spatial patterns in nitrate loading to a dryland stream network. I found that irrigation diversions transport nitrate from agricultural areas to the stream network year-round, even during dry seasons, and are an important driver of nitrate loading. I further explored how seasonal precipitation influences flood nutrient export in an intermittent desert stream by coupling long-term data of flood-water chemistry with stream discharge and precipitation data. I found that higher precipitation prior to a flood fills water storage sites in the catchment, leading to larger floods. In addition, higher antecedent precipitation stimulates biological nitrogen retention in the uplands, leading to lower nitrogen concentration in floods. Finally, I evaluated the consequences of nitrogen export from watersheds on how urban wetlands attenuate nitrate through denitrification that permanently removes nitrogen, and dissimilatory nitrate reduction to ammonium (DNRA) that retains nitrogen in another biologically reactive form. I found that DNRA becomes proportionally more important with low nitrate concentration, thereby retaining nitrogen as ammonium. Collectively, my dissertation research addresses how dryland and urban ecosystems can be integrated into models of watershed nitrogen cycling.

DEDICATION

For Ellen Handler

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CHAPTER 1

INTRODUCTION: THE BALANCE OF NITROGEN TRANSPORT AND RETENTION IN DRYLAND AND URBAN ECOSYSTEMS

Nitrogen is an essential element for all organisms and has many different chemical forms, only some of which are biologically accessible to primary producers. Biologically accessible forms of nitrogen include nitrate and ammonium, collectively referred to as dissolved inorganic nitrogen (DIN). As the phrase suggests, these nitrogen forms are usually transported dissolved in water. Hydrology is strongly linked to nutrient cycling as a transport vector (Hatt et al. 2004, Kaye et al. 2006, Lewis and Grimm 2007, Walsh et al. 2009) and through the effect of water on physical and chemical conditions of the environment and rates of biogeochemical transformations (Paul and Meyer 2001, Groffman et al. 2002, Grimm et al. 2005, Walsh et al. 2005, Kaye et al. 2006). As DIN is transported downslope or downstream it is subject to retention and removal reactions. Dryland and urban ecosystems are especially good study systems for nitrogen cycling because of the contrasts in nitrogen supply and transport. In addition, these systems are not commonly included in watershed models, but are useful examples of more complex features common across watershed systems (Figure 1.1). Water availability in drylands fluctuates. Extended dry periods are interspersed with precipitation, and this mediates both nitrogen transport, retention, and removal (Noy-Meir 1973). In contrast, urban ecosystems tend to have higher DIN supply, but have altered landscapes in ways that reduce retention and removal, and increase export to downstream systems (Paul and Meyer 2001).

Dissolved inorganic nitrogen retention and removal occurs through a suite of mostly biologically mediated reactions (Figure 1.2). Retention refers to nitrogen held temporarily in the organic tissues of organisms or in soil organic matter complexes and is not available for transport while removal refers to the conversion to nitrogenous gases (N_2, N_2O, NH_3) which are lost to the atmosphere. Nitrogen enters the landscape through nitrogen fixation that transforms atmospheric dinitrogen gas to organic nitrogen in the tissues of the organisms carrying out this process. When those organisms die or exude organic materials, it is subject to mineralization to ammonium. Under oxic conditions, ammonium can be transformed to nitrate. Nitrate and ammonium are taken up by primary producers and incorporated into their organic tissues for growth. This organic material is eventually mineralized through decomposition to ammonium. Ammonium is generally considered less mobile than nitrate because its positive charge leads to its adsorption to negatively charged clay particles in soil and sediment. Ammonium can also be removed from a system by volatilization; this disproportionately occurs following precipitation in uplands (Schlesinger and Peterjohn 1991). Nitrate can be removed via denitrification to nitrogenous gases, effectively removing nitrogen from the system, or transformed to ammonium via dissimilatory nitrate reduction to ammonium (DNRA). As DIN is transported downslope and downstream, it can be subject to retention via biological uptake, removal via denitrification and volatilization, and transformation between DIN forms through nitrification and DNRA.

In drylands, the location of nitrogen processing and retention depend largely on where and when water is available to facilitate physical transport and the chemical and biological conditions necessary for transformation. During extended dry periods, nitrogen cycling is limited to locations that have available water to support biological activity such as: flowing streams, wetlands, riparian zones, and dry stream channels with hyporheic water (McClain et al. 2003, Harms and Grimm 2008). These locations are situated at topographic low points that accumulate water and materials. In addition, these locations can retain elevated moisture for extended periods relative to the surrounding hillslopes (Welter et al. 2005, Sponseller and Fisher 2008, Harms and Grimm 2012) and can therefore support nitrogen cycling during periods without precipitation. Due to water limitation, dry periods may have little biological activity in surrounding hillslopes to transform nitrogen.

Hillslopes may experience hot moments of biogeochemical activity (biological activity ‘pulses’; Ludwig and Tongway 1997) associated with precipitation events. In drylands, these events dissipate quickly with the exhaustion of soil moisture (Belnap et al. 2005, Harms and Grimm 2008). The magnitude of precipitation can prompt different amounts of biological activity that transform nitrogen; precipitation also transports water and materials across the landscape (Noy-Meir 1973, Ludwig and Tongway 1997, Belnap et al. 2005, Welter et al. 2005, Collins et al. 2008, 2014). Small amounts of precipitation can increase soil microbial activity without substantially increasing soil moisture (Belnap et al. 2005, Welter et al. 2005, Sponseller and Fisher 2008). Intermediate-scale precipitation events will activate more of the biological community (Collins et al. 2014) and may prompt transfers of water and nutrients between locations via runoff, resulting in a redistribution of material along flowpaths (Ludwig and Tongway 1997, Belnap et al. 2005, Welter et al. 2005). Large precipitation inputs can exceed the soil water storage or infiltration capacity and generate floods that transfer material faster than biological demand can retain it (Welter et al. 2005, Oldham et al. 2013). These large transport events can culminate in flushing material through stream channels, resulting in large-scale material export rather than retention and removal (Raymond et al. 2016).

Urbanization changes the magnitude, location, and timing of nutrient retention in landscapes (Figure 1.3). Human activities increase nitrogen supply in ecosystems, alter landscapes such that the biological community that is responsible for retention and removal is reduced, and build infrastructure that favors efficient flood water export rather than infiltration. As a result, large amounts of DIN may accumulate on the landscape, ultimately to be preferentially transported to recipient lowland areas such as streams and wetlands when precipitation occurs (Paul and Meyer 2001, Wollheim et al. 2005). Such large DIN influx may exceed the biological demand for growth, resulting in eutrophication of urban waterways (Carpenter et al. 1998).

Humans increase DIN supply through applying nitrogen fertilizer, cultivating plants, importing nitrogen in food and feed, and increasing atmospheric nitrogen deposition (Boyer et al. 2002). Nitrogen fertilizer is used in the context of both agricultural activities that are often closely linked to urban landscapes and residential areas for maintaining greenspaces (Kaye et al. 2006). Many agriculturally important crops are associated with nitrogen-fixing microorganisms and therefore further increase DIN supply in ecosystems (Vitousek et al. 1997). Urban areas import nitrogen in food for humans and feed for livestock (Boyer et al. 2002). Nitrogen in human food generally becomes part of the sewer system, with exceptions for cities that have combined sewage outflows when stormwater overwhelms the sewer system. Municipal effluent that is high in DIN is often directly discharged to urban waterways. Livestock and pet waste can become a non-point source of nitrogen to waterways. Fossil fuel combustion leads to higher atmospheric deposition in urban landscapes (Baker et al. 2001). As a result of these activities, DIN supply in urban ecosystems is much higher than surrounding landscapes. One consequence of greater supply is that the magnitude of retention and removal can increase; however, the proportion of retention may fall as the DIN supply saturates the ecosystem demand.

Urban ecosystems have lower capacity for DIN retention and removal due to a reduced biological community for uptake and higher runoff that lowers residence time on the landscape (Caraco and Cole 1999, Paul and Meyer 2001, Peterson et al. 2001). Headwater streams and surrounding hillslopes account for the majority of the DIN retention and removal in watersheds (Peterson et al. 2001, Wollheim et al. 2017), but urban areas develop over these parts of the landscape (Beaulieu et al. 2015). Widespread impervious surface cover in cities increases water runoff and decreases water residence time on the landscape, both of which can decrease DIN retention and removal and increase export (Caraco and Cole 1999, Paul and Meyer 2001). Traditionally, urban infrastructure was designed to quickly move water from the landscape into storm sewers and detention areas to prevent flooding hazards. As a result, storm flows in urban streams are flashy: they have higher peak flow, rapid rise, and rapid return to baseflow (Walsh et al. 2005). These powerful storm flows can scour plant, algal, and microbial communities, removing the biological demand for nutrients along flow paths. The cumulative effect of these changes is that the higher DIN supply in urban ecosystems is preferentially transported to aquatic systems, potentially impairing water quality and leading to eutrophication (Paul and Meyer 2001).

Urbanization moves the dominant site of DIN retention and removal downslope. Retention and removal of DIN in the urban landscape takes place preferentially in recipient aquatic systems rather than hillslopes and headwater streams that are important in less developed watersheds. Even small precipitation inputs result in water and DIN export to downstream recipient aquatic ecosystems rather than redistributing resources across the landscape. As a result, these downstream systems—including streams, wetlands, and lakes, as well as detention and retention basins—become the primary sites of DIN retention and removal. Dissolved inorganic nitrogen can accumulate in the systems to very high concentrations, saturating the biological demand of the system (Mulholland et al. 2008). As demand saturates, dissimilatory nitrogen transformations can become important in these systems (Burgin and Hamilton 2007), including denitrification (Newcomer et al. 2012) that permanently removes nitrogen from the system, and dissimilatory nitrate reduction to ammonium (Bernard et al. 2015) that retains nitrogen as ammonium, which is less mobile than nitrate.

My research takes place in central Arizona in the southwestern US, where a network of dryland streams is a large portion of the water supply to urban and non-urban areas. The Salt and Verde River watersheds feed several reservoirs that modulate seasonal and interannual variability in surface water supply. Just below the confluence of the two rivers and upstream of the Phoenix metropolitan area, all water in the river channel is diverted into municipal and agricultural water supply canals. As a result, the Salt River is dry for much of its length in the city (Bateman et al. 2015). The Salt-Verde water combined with groundwater and Colorado River water (from the Central Arizona Project aqueduct) supply the nearly five million people living in metropolitan Phoenix

(Guhathakurta and Gober 2007). Approximately three-quarters of residential water is used outside for swimming pools and landscape irrigation (Mayer et al. 1999). Some of this outdoor water flows into the sewer system. Phoenix has a separated sewer system and the Salt River channel forms part of the stormwater infrastructure. Some of the water applied to the urban landscape drains through the sewer system to storm drains along the Salt River (Bateman et al. 2015, Palta et al. 2017). In some locations, the leaky urban system is providing a perennial source of water to the channel, and “accidental” wetlands have developed near these drains (Bateman et al. 2015, Palta et al. 2016, 2017). Thus, in Phoenix, dryland stream networks converge upstream of the city where the water is then diverted and combined with other water sources, dispersed over the landscape with some eventually returning to the stream channel through the storm sewer system.

In this dissertation, I ask: What is the balance of nitrogen transformation, transport, and retention in dryland watersheds, and what is the fate of nitrogen export in urban ecosystems? I addressed this question from three perspectives. First, I modeled how the spatial pattern in nitrate loading to a dryland stream network varies across rainy and dry seasons. Second, I examined how biological nutrient processing in hillslopes affects flood nutrient export and concentration in a desert stream. Third, I tested how fluctuations in nitrate concentration in an urban wetland change the types of nitrate transformations.

Chapter 2 examines how seasonal precipitation affects the rate of nitrate loading from surrounding hillslopes to a dryland stream network. During rainy seasons, there is more water available to transport nitrate from the landscape to the stream; however, there is also more biological activity that may increase nitrate retention on the landscape. Such studies are common in mesic systems and ecosystems heavily affected by nitrogen pollution, but they rarely take place in dryland ecosystems (Caraco and Cole 2001). Dryland stream modeling is difficult because the water balance often violates common assumptions in hydrologic modeling such as discharge increasing with increasing drainage area. In addition, water withdrawals for irrigation and water returns make completing a water balance for these systems difficult. Globally, more than 20% of the urban population lives in areas that are classified as semiarid or drier (McDonald et al. 2011), so understanding the dynamics of water supply and quality in these regions is a pressing issue.

Chapter 3 explores how biological nutrient processing and retention between floods in an intermittent stream channel affects the nutrient concentration and export in flood water. Many temporary streams are only connected to the larger stream network during floods and floods can represent the majority of the nutrient export to downstream ecosystems (Ye and Grimm 2013, Welter and Fisher 2016). Since the biological community is water-limited, smaller water inputs that do not generate flood conditions may affect nutrient accumulation and processing in the catchment (Welter et al. 2005, Collins et al. 2014). Understanding how the biological activity between these floods tempers nutrient export is important for understanding the tremendous variability in flood nutrient loads.

Chapter 4 experimentally tests the mechanisms of nitrate attenuation in an urban wetland system impacted by high nitrate inputs from the urban landscape. Both denitrification and DNRA consume nitrate; however, denitrification permanently removes nitrogen from the system while DNRA retains nitrogen as the biologically reactive ammonium form. Both transformations require similar environmental conditions; however, DNRA has received far less research attention than denitrification (Burgin and Hamilton 2007). The balance of these two reactions determines to what extent these wetland systems remove reactive nitrogen or conserve reactive nitrogen.

In Chapter 5, I summarize the findings of this dissertation and discuss their implications for other dryland and urban ecosystems, as well as for the fields of ecology and hydrology.

Figures

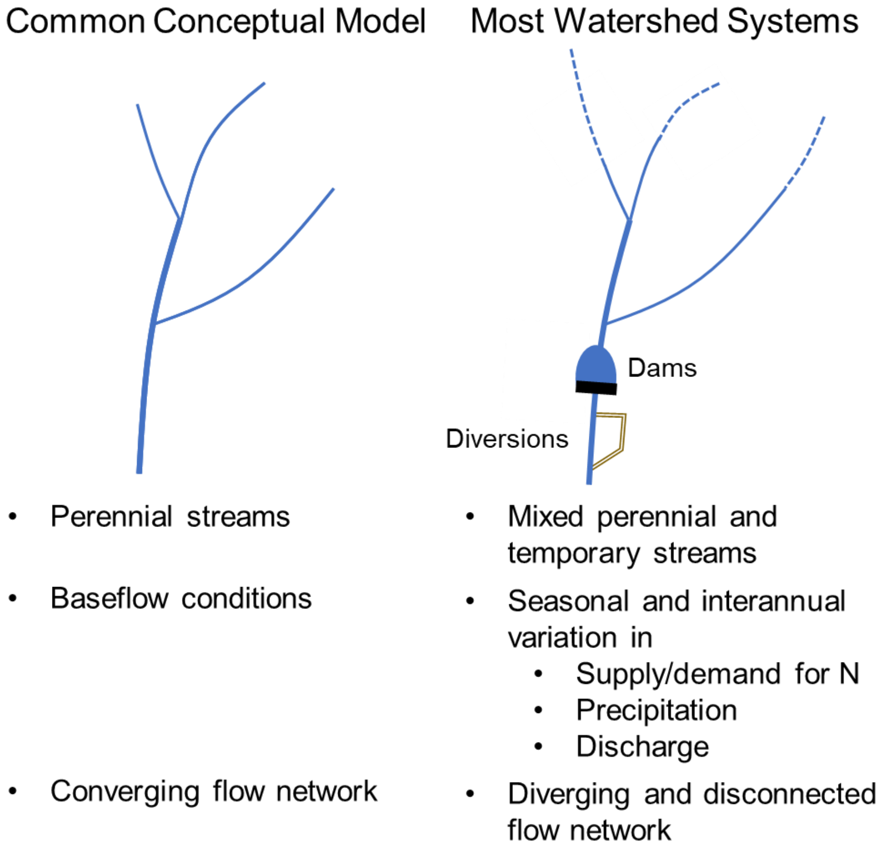

Figure 1.1. Two conceptual watershed models. While the common conceptual model of watersheds is based on a perennial stream network with baseflow discharge and a converging flow network, many, if not most, watersheds do not adhere to this model. Most watershed have a mixture of perennial and temporary sections with seasonal and interannual variation in supply and demand for nitrogen, precipitation inputs, and discharge conditions. Common human alterations to watersheds include dams and diversions for community water supply.

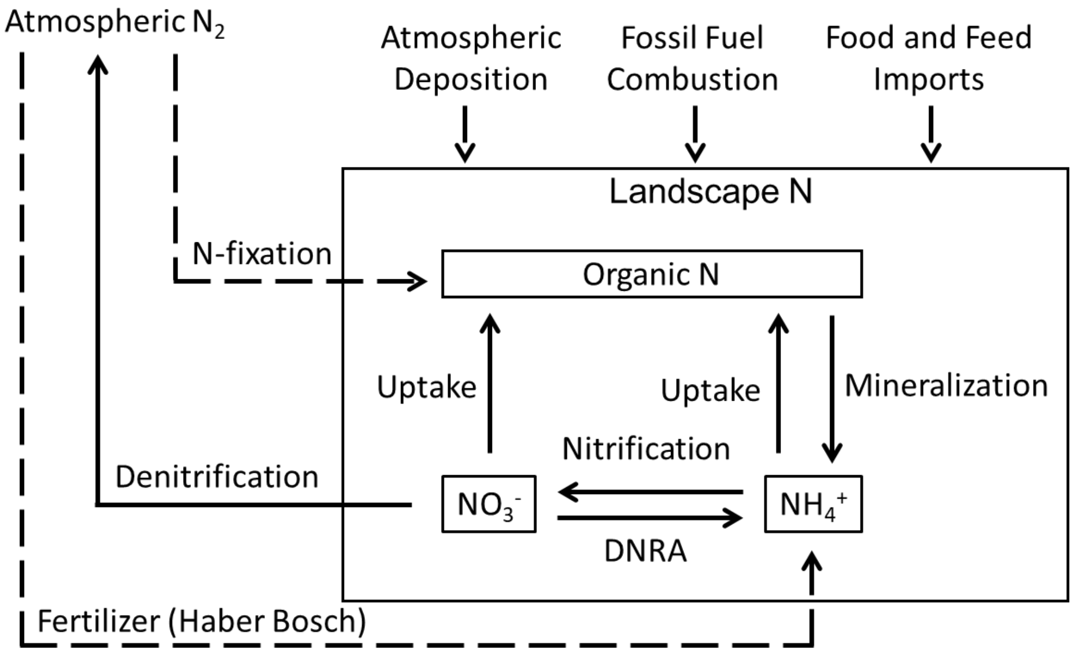

Figure 1.2. A simplified version of the nitrogen cycle. Dashed arrows represent additional or higher fluxes in human-influenced ecosystems.

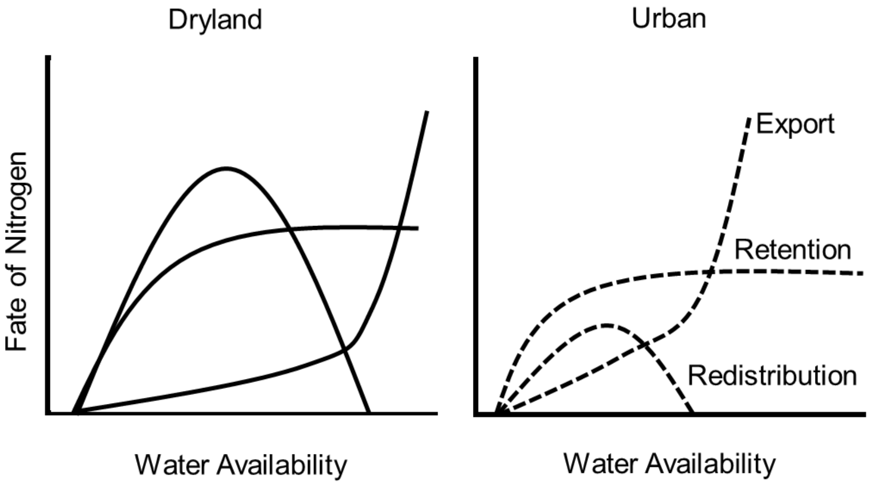

Figure 1.3. Conceptual diagram of the fate of nitrogen based on water availability in dryland (left) and urban (right) watersheds. In drylands, increasing water availability will increase biological activity and therefore processing and retention of nitrogen in the uplands and stream network. In urban areas, the biological community is reduced and therefore less retention occurs for the same water input. In drylands, storms of varying sizes redistribute nitrogen along hillslopes and from hillslopes to the stream network, connecting nitrogen to the organisms that can retain the element. Only large storms that generate floods will result in export rather than redistribution and retention of the nitrogen. In urban areas, the water infrastructure favors efficient removal of water from the landscape into streams and sewers, favoring export to downstream recipient systems rather than redistribution within the watershed. Figure modified from Welter et al. (2005).

Literature Cited

Baker, L. A., D. Hope, Y. Xu, J. Edmonds, and L. Lauver. 2001. Nitrogen balance for the Central Arizona-Phoenix (CAP) ecosystem. Ecosystems 4:582–602.

Bateman, H. L., J. C. Stromberg, M. J. Banville, E. Makings, B. D. Scott, A. Suchy, and D. Wolkis. 2015. Novel water sources restore plant and animal communities along an urban river. Ecohydrology 8:792–811.

Beaulieu, J. J., H. E. Golden, C. D. Knightes, P. M. Mayer, S. S. Kaushal, M. J. Pennino, C. P. Arango, D. A. Balz, C. M. Elonen, K. M. Fritz, and B. H. Hill. 2015. Urban stream burial increases watershed-scale nitrate export. PLoS ONE 10.

Belnap, J., J. R. Welter, N. B. Grimm, N. Barger, and J. A. Ludwig. 2005. Linkages between microbial and hydrologic processes in arid and semiarid watersheds. Ecology 86:298–307.

Bernard, R. J., B. Mortazavi, and A. A. Kleinhuizen. 2015. Dissimilatory nitrate reduction to ammonium (DNRA) seasonally dominates NO3– reduction pathways in an anthropogenically impacted sub-tropical coastal lagoon. Biogeochemistry 125:47–64.

Boyer, E. W., C. L. . Goodale, N. A. . Jaworski, and R. W. Howarth. 2002. Anthropogenic Nitrogen Sources and Relationships to Riverine Nitrogen Export in the Northeastern U.S.A. Biogeochemistry 57–58:137–169.

Burgin, A. J., and S. K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and the Environment 5:89–96.

Caraco, N. F., and J. J. Cole. 1999. Human impact on nitrate export: An analysis using major world rivers. Ambio 28:167–170.

Caraco, N. F., and J. J. Cole. 2001. Human influence on nitrogen export: a comparison of mesic and xeric catchments. Marine and Freshwater Research 52:119–125.

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8:559–568.

Collins, S. L., J. Belnap, N. B. Grimm, J. A. Rudgers, C. N. Dahm, P. D. Odorico, M. Litvak, D. O. Natvig, D. C. Peters, W. T. Pockman, R. L. Sinsabaugh, and B. O. Wolf. 2014. A multiscale, hierarchical model of pulse dynamics in arid-land ecosystems. Annual Review of Ecology, Evolution, and Systematics 45:397–419.

Collins, S. L., R. L. Sinsabaugh, C. Crenshaw, L. Green, A. Porras-Alfaro, M. Stursova, and L. H. Zeglin. 2008. Pulse dynamics and microbial processes in aridland ecosystems. Journal of Ecology 96:413–420.

Grimm, N. B., R. W. Sheibley, C. L. M. Crenshaw, C. N. Dahm, W. J. Roach, and L. H. Zeglin. 2005. N retention and transformation in urban streams. Journal of the North American Benthological Society 24:626–642.

Groffman, P. M., N. J. Boulware, W. C. Zipperer, R. V. Pouyat, L. E. Band, and M. F. Colosimo. 2002. Soil nitrogen cycle processes in urban riparian zones. Environmental Science and Technology 36:4547–4552.

Guhathakurta, S., and P. Gober. 2007. The impact of the Phoenix urban heat island on residential water use. Journal of the American Planning Association 73:317–329.

Harms, T. K., and N. B. Grimm. 2008. Hot spots and hot moments of carbon and nitrogen dynamics in a semiarid riparian zone. Journal of Geophysical Research: Biogeosciences 113:1–14.

Harms, T. K., and N. B. Grimm. 2012. Responses of trace gases to hydrologic pulses in desert floodplains. Journal of Geophysical Research: Biogeosciences 117:1–14.

Hatt, B. E., T. D. Fletcher, C. J. Walsh, and S. L. Taylor. 2004. The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environmental Management 34:112–124.

Kaye, J. P., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. 2006. A distinct urban biogeochemistry? Trends in Ecology and Evolution 21:192–199.

Lewis, D. B., and N. B. Grimm. 2007. Hierarchical regulation of nitrogen export from urban catchments: Interactions of storms and landscapes. Ecological Applications 17:2347–2364.

Ludwig, J. A., and D. J. Tongway. 1997. A landscape approach to rangeland ecology. Pages 1–12 *in* J. Ludwig, D. Tongway, D. Freudenberger, J. Noble, and K. Hodgkinson, editors. Landscape ecology: Function and management. CSIRO Publishing, Collingwood, Victoria, Australia.

Mayer, P. M., W. B. DeOreo, E. M. Opitz, J. C. Kiefer, W. Y. Davis, B. Dziegielewski, and J. O. Nelson. 1999. Residential end uses of water. AWWA Research Foundation and American Water Works Association Rep.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H. McDowell, and G. Pinay. 2003. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. Ecosystems 6:301–312.

McDonald, R. I., I. Douglas, C. Revenga, R. Hale, B. Fekete, N. Grimm, and J. Gro. 2011. Global urban growth and the geography of water availability, quality, and delivery. Ambio 40:437–446.

Mulholland, P. J., A. M. Helton, G. C. Poole, R. O. Hall, S. K. Hamilton, B. J. Peterson, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, W. K. Dodds, S. E. G. Findlay, S. V Gregory, N. B. Grimm, S. L. Johnson, W. H. McDowell, J. L. Meyer, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, L. T. Johnson, B. R. Niederlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, D. J. Sobota, and S. M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202–205.

Newcomer, T. A., S. S. Kaushal, P. M. Mayer, A. R. Shields, A. Elizabeth, P. M. Groffman, and A. J. Gold. 2012. Influence of natural and novel organic carbon sources on dentrification in forest, degraded urban, and restored streams. Ecological Monographs 82:449–466.

Noy-Meir, I. 1973. Desert ecosystems: Environment and producers. Annual Review of Ecology and Systematics 4:25–51.

Oldham, C. E., D. E. Farrow, and S. Peiffer. 2013. A generalized Damkohler number for classifying material processing in hydrological systems Solid. Hydrology and Earth System Sciences 17:1133–1148.

Palta, M., M. V. du Bray, R. Stotts, A. Wolf, and A. Wutich. 2016. Ecosystem services and disservices for a vulnerable population: Findings from urban waterways and wetlands in an American desert city. Human Ecology 44:463–47816.

Palta, M. M., N. B. Grimm, and P. M. Groffman. 2017. "Accidental" urban wetlands: Ecosystem functions in unexpected places. Frontiers in Ecology and the Environment 15:248–256.

Paul, M. J., and J. L. Meyer. 2001. Streams in the Urban Landscape. Annual Review of Ecology and Systematics 32:333–365.

Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Marti, W. B. Bowden, H. M. Vallett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from headwaters by headwater streams. Science 292:86–90.

Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. Ecology 97:5–16.

Schlesinger, W. H., and W. T. Peterjohn. 1991. Processes controlling ammonia volatilization from Chihuahuan desert soils. Soil Biology and Biochemistry 23:637–642.

Sponseller, R. A., and S. G. Fisher. 2008. The Influence of Drainage Networks on Patterns of Soil Respiration in a Desert Catchment. Ecology 89:1089–1100.

Vitousek, P. M., H. a Mooney, J. Lubchenco, and J. M. Melillo. 1997. Human domination of Earth's ecosystems. Science 277:494–499.

Walsh, C. J., T. D. Fletcher, and A. R. Ladson. 2009. Retention capacity: A metric to link stream ecology and storm-water management. Journal of Hydrologic Engineering 14:399–406.

Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan. 2005. The urban stream syndrome: Current knowledge and the search for a cure. Journal of the North American Benthological Society 24:706–723.

Welter, J. R., and S. G. Fisher. 2016. The influence of storm characteristics on hydrological connectivity in intermittent channel networks: Implications for nitrogen transport and denitrification. Freshwater Biology 61:1214–1227.

Welter, J. R., S. G. Fisher, and N. B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76:421–440.

Wollheim, W. M., G. K. Mulukutla, C. Cook, and R. O. Carey. 2017. Aquatic nitrate retention at river network scales across flow conditions determined using nested in situ sensors. Water Resources Research 53:9740–9756.

Wollheim, W. M., B. A. Pellerin, C. J. Vo, and C. S. Hopkinson. 2005. N Retention in Urbanizing Headwater Catchments. Ecosystems 8:871–884.

Ye, L., and N. B. Grimm. 2013. Modelling potential impacts of climate change on water and nitrate export from a mid-sized, semiarid watershed in the US Southwest. Climatic Change 120:419–431.

CHAPTER 2

SPATIAL PATTERN IN NITRATE LOADING CHANGES WITH STREAM NETWORK CONNECTIVITY IN A DRYLAND ENVIRONMENT

Abstract

Dryland ecosystems have high seasonal and interannual variation in precipitation and stream discharge, but their effect on stream nitrate loading is poorly understood. I investigated the role of seasonal precipitation in driving hydrologic connectivity between landscape and stream with respect to nitrate loading. I conducted four seasonal synoptic surveys of stream water discharge and chemistry (two during dry seasons and two during rainy seasons) and coupled these with experimental measurements of stream nitrate uptake. These data served as inputs to a mass-balance model of stream network nitrate to determine the landscape-to-stream nitrate flux. The spatial variation in nitrate loading within seasons exceeded across-season variation. Three of the surveys took place when only the perennial sections of the stream network had surface water, these surveys had similar spatial patterns in nitrate loading. Nitrate loading was positively correlated with agricultural land use and wetland area. Surface water irrigation diversions transport nitrate from agricultural lands to the stream network year round, even during dry seasons. During the winter rainy season survey, a higher proportion of the network had surface water, including tributaries and headwaters. This winter survey had a different pattern of nitrate loading than other seasons, likely driven by snow melt in the headwaters and a reduction in irrigation and fertilizer use near the watershed outlet. These data suggest seasonal differences in water sources can change patterns in stream nitrate loading and

that human activities, such as irrigation, can enhance hydrologic connectivity between landscapes and streams, even during dry seasons.

Introduction

Nitrogen loading to streams has consequences for stream ecosystem function and services. This is particularly important for nitrate, a biologically reactive form of nitrogen that can act as an aquatic pollutant if present in high concentrations. Understanding nitrate loading to dryland stream networks is especially important because these systems account for two-fifths of terrestrial land (Bastin et al. 2017) but have received less research focus than mesic ecosystems (Caraco and Cole 2001). Dryland stream networks are challenging to model because they do not adhere to many common assumptions in watershed modeling (Helton et al. 2011). For example, drylands are characterized by high seasonal variability in precipitation such that streams lack defined baseflow conditions and often are highly altered to supply irrigation and drinking water. As a result, we lack understanding of nitrate cycling in dryland streams at the network scale. Therefore, the challenge is to incorporate seasonal variation in hydrology and human-caused discontinuities in network structure into a watershed model to understand the controls on nitrate delivery between landscape and stream at the network scale. Understanding nitrogen cycling is drylands is critical as population, urbanization, and water modification begin to alter the nutrient and water balances of these ecosystems.

In this study, I asked how the magnitude and spatial patterns of nitrate loading to streams and uptake within streams varied across rainy and dry seasons for a dryland stream network. Across rainy and dry seasons in the summer and winter, I measured stream nitrate uptake empirically and used synoptic surveys of concentrations, empirical estimates of uptake, and a mass balance model to estimate nitrate loading rates to streams for a whole stream network.

Nitrate loading in dryland ecosystems differs from that in mesic systems because the high seasonal and interannual variability in precipitation leads to variability in hydrologic connectivity and biological nitrogen retention (Caraco and Cole 2001). Hydrologic connectivity varies over space and time due to seasonal and spatial variation in precipitation, temperature, and topography. Only the precipitation that becomes runoff can increase connectivity between landscapes and stream and the amount of runoff is sensitive to temperature and the potential evapotranspiration. During the dry and hot summer months in the U.S. Southwest, much of the precipitation input is almost immediately transferred back to the atmosphere. Any water remaining generates runoff that can carry entrained particles and dissolved nutrients from uplands to the stream network via interflow, groundwater flow, or overland flow. Seasons with high rainfall or snow melt and low evapotranspiration have high runoff and thus greater connection between terrestrial sources of nitrogen and stream ecosystems (Stieglitz et al. 2003, Jencso et al. 2009). During extended dry periods between rains, the upland–stream connection may be limited to groundwater and there can be significant lag times between water sources and eventual loading to stream (Van Meter and Basu 2015). During these periods of low connectivity to landscape sources of nitrogen, streams may rely more on internal recycling of nitrogen (Grimm 1987). Thus, variability in connectivity has consequences for nitrogen transport.

Nitrogen loading to stream ecosystems is modified by nitrogen removal along the flowpaths between source and stream. In water-limited upland ecosystems nitrogen removal is closely tied to precipitation inputs. Precipitation prompts pulses in biological activity that are generally proportional to the size of the event (Ludwig and Tongway 1997, Belnap et al. 2005, Collins et al. 2008, 2014). Larger precipitation inputs can deliver water deeper into the soils, thus generating both microbial and plant responses (Huxman et al. 2004, Sponseller 2007, Collins et al. 2008). On longer timescales, seasons with higher precipitation support high biological activity (Carbone et al. 2008). Precipitation inputs also move nutrients between landscape patches distribution to organisms that process, uptake, and retain the nutrients (Belnap et al. 2005). Thus, precipitation increases hydrologically mediated nutrient connectivity between landscape units. However, periods or seasons with higher hydrologic connectivity may not necessarily have higher nitrogen loading to streams because of elevated biological nitrogen processing and retention along upland flowpaths.

A spatially explicit approach to evaluating nitrogen loading to stream networks is important for (1) identifying control points in the watershed that are disproportionately high or low contribution to loading, and (2) identifying relationships between landscape activities and nutrient loading (Caraco and Cole 2001, Bernhardt et al. 2017). Activities such as fertilizer application, construction that promotes soils erosion, livestock operations, and fish hatcheries are all potential nitrogen sources (Carpenter et al. 1998) that vary in space and time. The variation in nitrogen pools across a watershed combined with varying connections between the sources and the stream make understanding the dynamics of nitrogen loading to stream difficult to investigate at large scales; however, this research is needed if a mechanistic understanding of the processes leading to nitrate loading is the goal.

Network modeling is increasingly used to investigate the dynamics of nitrogen cycling at the watershed scale. Many studies conducted at the river reach scale have increased our understanding of the biogeochemical reactions that retain and remove nitrogen from the water column in streams. Likewise, many studies have evaluated the extent of watershed attenuation of nitrate through mass balance via input-output budgets. Increasingly, network modeling is bridging the gap between these two approaches by applying the biogeochemical dynamics for nitrate at the reach scale to whole river networks based on the location and timing of nitrate inputs to the watershed (Helton et al. 2011). Network modeling approaches include deterministic (Mulholland et al. 2008, Helton et al. 2011) and statistical approaches (Alexander et al. 2000, Seitzinger et al. 2002).

In this study, I expected to find seasonal variation in nitrate loading due to seasonal differences in water availability for forming hydrologic connections between land and stream and for fueling biological community activity that retains and removes nitrate from flowpaths. I expected to find spatial variation in nitrate loading within seasons due to the human activities in the watershed, which alter the amount of nitrate on the landscape and connectivity between land and stream. I specifically tested three alternative hypotheses: (1) Nitrate loading to streams is higher during rainy seasons than dry seasons because hydrologic connectivity is higher; (2) nitrate loading is similar across seasons because higher hydrologic connectivity is concurrent with higher biological nitrogen processing and retention; and (3) nitrate loading differs across seasons because different sources of water connect the stream to different sources of nitrogen. I combined field survey data with experimentally determined nitrate uptake rates as inputs to a mass-balance spatial model of stream network nitrate dynamics. I applied this approach across four seasons in a dryland watershed in central Arizona, U.S.

Methods

Site description

This research was conducted in Oak Creek, a sub-watershed of the Verde River watershed in the transition zone between the Basin and Range Province and the Colorado Plateau in Arizona, U.S. The creek originates at an elevation of 2,300 m in ponderosa pine forest and descends through pinyon-juniper and high desert ecosystems to its confluence with the Verde River at 950 m elevation. Central Arizona has two rainy seasons separated by two dry seasons. The main stem of Oak Creek is perennial, as are short sections of three spring-fed tributaries. The remainder of the network is temporary, with some channels running seasonally and many others supporting surface flow only during large floods. Land use in the Oak Creek watershed is mostly undeveloped, but it does include some developed and agricultural land associated with small villages. There are two fish hatcheries in the watershed that rely on springs for water supply and then discharge water to the main channel of Oak Creek (Oak Creek Watershed Council 2012). Residential and agricultural areas are irrigated through a combination of diverted stream water and groundwater wells, which may increase the hydrologic connection between landscapes and adjacent stream segments. Portions of the creek are impaired due to elevated fecal coliform from human, pet, livestock, and wild animal waste (Southam et al. 2000). Some segments of the creek receive groundwater inputs with elevated coliform counts and phosphate concentrations derived from residential septic systems (Oak Creek Watershed Council 2012).

Synoptic sampling

I conducted four seasonal synoptic surveys of stream water chemistry and discharge across the Oak Creek watershed. Surveys took place in 2017 on February 25 and 26 (winter snow melt), June 27 and 28 (summer dry season), September 29 and 30 (post summer rainy season), and November 10 and 11 (winter dry season). During each survey, I sampled surface water at between 25 and 29 sites (depending on presence of surface water) across the Oak Creek main stem, tributaries, and irrigation ditches (Figure 2.1). I targeted locations above and below confluences and irrigation diversions. Most sites were accessed via public lands. A smaller subset was accessed via private land with permission. Often, only one site along an irrigation ditch was accessible and in these cases I assumed that discharge was uniform across the length of the diversion. At each site, I collected duplicate, field-filtered water samples (0.45 µm GFF syringe filter, Fisher Scientific). Grab samples were stored in a cooler on dry ice until returned to the lab where samples were stored at 0°C until analysis. Nitrate/nitrite and chloride concentration were analyzed using a Lachat QC 8000 flow injection analyzer (Lachat Instruments, Loveland, CO). At each water sample collection site, I estimated discharge. At sites where discharge exceeded 200 L/s I measured cross-sectional area and water velocity. In locations where discharge was <~200 L/s I used dilution gauging.

Nitrate uptake experiments

To determine the nitrate uptake rate in Oak Creek and its tributaries, I conducted seasonal nutrient-spiraling experiments (Newbold et al. 1981). Sodium chloride and sodium nitrate were dissolved in stream water in a bucket to create a concentrated solution that would raise the nitrate concentration by 50 µg/L and the chloride concentration by 6.5 mg/L at the downstream collection location when added in a single pulse. I conducted the experiments on the main stem of Oak Creek in 2017 on April 19, June 22, September 27, and November 13, and in Spring Creek, a perennial tributary, on March 22, June 21, September 18, and November 8, 2017. I did one experiment in Dry Creek on March 10, 2017, during the only period when this tributary had surface water. This was a total of nine nitrate uptake experiments. The reach lengths from the injection point to the collection point were 710, 400, and 370 m for Oak, Spring, and Dry Creeks, respectively. The chloride- and nitrate-enriched water was added to the stream instantaneously and monitored at the collection location with a conductivity meter (either YSI 556 MPS, YSI 600 XLM, YSI DSM Pro or Eureka Manta) and a SUNA nitrate sensor (Sea-Bird Scientific, Bellevue, WA). I collected background grab samples at the downstream collection point prior to the solute addition and 25-30 grab samples distributed across the breakthrough curve at the collection location. All grab samples were collected in duplicate in 500 mL HPDE Nalgene bottles; subsamples were poured into 50 mL centrifuge tubes for transport to the lab on ice and then storage at 0°C until analysis. All nitrate and chloride concentrations were determined with a Lachat QC 8000 flow injection analyzer (Lachat Instruments, Loveland, CO, USA); nitrate is reported as mass of nitrogen (i.e., nitrate-nitrogen).

I processed data from the experiments using the TASCC method described by Covino et al. (2010). Briefly, conductivity data were interpolated to one-minute-intervals to match the nitrate data for the breakthrough curve. The first-order uptake-rate coefficient was calculated for each sample collected over the breakthrough curve by taking the log of the background-corrected ratio of nitrate to the specific conductivity in the sample divided by the same ratio in the injection solution all divided by the distance between the injection and collection points. Uptake length was calculated for each sample by taking the inverse of the uptake coefficient. A regression between the uptake length and the nitrate concentration of the sample was used to estimate uptake length at the ambient nitrate concentration by extrapolation. This ambient uptake length was used to calculate a vertical uptake velocity and an areal uptake rate for each point on the breakthrough curve. I used a travel-time correction to control for the differing amounts of time each sample had in the stream prior to collection.

Modeling

I used an inverse model to estimate spatial patterns in nitrate loading rates to streams in the Oak Creek watershed based on the synoptic survey data (Mulholland et al. 2008, Helton et al. 2011). The model estimates the loading rates necessary to reproduce the observed spatial patterns in nitrate concentration and discharge, given the experimentally determined nitrate uptake rates. The model calculates the mass of nitrate and discharge using a steady-state mass-balance approach, in which incoming fluxes are subtracted from outgoing fluxes for each stream segment. Discharge (Q, in m^3/d) for each reach is calculated by subtracting outgoing water fluxes from incoming water fluxes according to the following equations

$$Q_p = \left(\sum Q_{p-l_i} + Q_L\right) - \left(Q_w + Q_{p+l_i}\right) \qquad \text{Eq 2.1}$$

and $Q_L = A_p \cdot Y_p$, Eq 2.2

where Q_p is the discharge in stream reach p, ΣQ_{p-li} is the sum of the discharge of all upstream reaches contributing discharge to stream reach p, Q_L is the discharge from the adjacent drainage area, Q_w is water withdrawal from reach p, Q_{p-li} is the discharge to the next downstream reach $p+1$, A_p is the area of the catchment draining directly to stream reach p, and Y_p is the per unit drainage area water yield to stream reach p. Nitrate flux (N, in g/d) is modeled similarly by subtracting the outgoing dissolved nitrate flux from incoming fluxes

$$N_p = \left(\sum N_{p-l_i} + N_L\right) - \left(N_R + N_{p+l_i}\right) \qquad \text{Eq 2.3}$$

and $N_L = A_p \cdot L_p$, Eq 2.4

where N_p is the nitrate flux in stream reach p, ΣN_{p-li} is the sum the nitrate flux from all upstream reaches contributing nitrate to stream reach p, N_L is the nitrate flux from the adjacent drainage area, N_R is the in-stream nitrate uptake from reach p, N_{p+li} is the nitrate flux to the next downstream reach $p+1$, A_p is the area of the catchment draining directly to stream reach p, and L_p is the nitrate loading rate per unit drainage area to stream reach p. For each stream reach, the mass of nitrate removed (N_R, in g/d) is equal to the total nitrate flux in the stream reach times the fractional removal factor (R)

$$N_R = R * N_p. \qquad \text{Eq 2.5}$$

The fractional removal factor is determined according to the following equation from Wollheim et al. (2006)

$$R = 1 - e^{\left(-vf/_{H_L}\right)}, \qquad \text{Eq 2.6}$$

$$\text{where } H_L = {}^{Q_p}\!/_{SA_p}, \qquad \text{Eq 2.7}$$

and v_f is the experimentally determined vertical uptake rate for nitrate (in m/d). The vertical uptake is normalized by hydraulic load (H_L, in m/d), which is a measure of the rate of water passage through the stream relative to the benthic surface area. Hydraulic load is calculated by dividing the discharge (Q_p, in m^3/d) by the surface area (SA_p, in m^2, calculated as stream length times average width). Average stream width (w, in m) is estimated as

$$w = aQ^b,$$

where a and b are the width coefficient, which controls the scaling, and width exponent, which controls the rate of increase, respectively (Leopold and Maddock 1953). Both a and b were determined from field survey data within each sampling period (Table 2.1).

The model was implemented for the flowing sections of the stream network, which varied in extent between synoptic surveys. The model was implemented for subcatchments composed of the incremental drainage area for each point sampled in each synoptic survey (the entire drainage area to the sampling location minus the drainage areas to any upstream sampling locations). The stream channels (both flowing and non-flowing) in each subcatchment were further divided into 1000-m segments and the drainage areas connected to these segments. Lateral water yield to each subcatchment was calculated by subtracting the discharge at the next most upstream point from the discharge at the base of the subcatchment and dividing by the area of the sum of the flowing 1000-m subcatchments. For net losing sections, a water withdrawal term was added. To simulate gross water yield to these losing sections, I applied the water yield from the subcatchment that had the highest discharge within the survey and removed the same amount of water through the withdrawal term. Non-flowing subcatchments were assigned a lateral water yield near zero. Discharge in agricultural ditches was assumed to remain constant over their length. Once the model was parameterized to reproduce the measured discharge from each synoptic survey, I used a model-independent parameter estimator (PEST 16.0, Model-Independent Parameter Estimation & Uncertainty Analysis), to determine the nitrate loading rates necessary to reproduce each synoptic survey concentration datum.

Land cover analysis

To relate nitrate loading to land cover variables, I acquired the 2011 National Land Cover Database and the 2017 Cropland Data Layer (USDA-NASS 2017). I found the total developed, agricultural, and wetland land use/cover within the flowing subcatchment area and for each of the 1000-m stream-segment catchments. I evaluated the relationship between these land cover metrics and the stream nitrate loading through correlation analysis. All statistical analyses were performed in R (R Core Team 2018).

Results

Synoptic Surveys

The mean annual discharge for Oak Creek is highly variable with a coefficient of variation of 1. The discharge in the year of the study was 33% greater than the annual mean discharge for the period of record (1941 - 2017). The mean discharge values for the months when the surveys were conducted were similar to the mean for the period of record in June (percent difference from mean, -1) and in September (-12). The discharge in February was much higher than the monthly mean (+133) and in November was lower than average (-46; Figure 2.2). The flowing catchment area was 54% larger in February (279 km^2) than during the other campaigns (181 km^2) because a tributary and a portion of the headwaters were flowing during this campaign (Figure 2.3). Median discharge in the main channel was highest during the February campaign (2.82 m^3/s) and lowest during the June campaign (0.62 m^3/s; Figure 2.4). Similarly, the February campaign had the highest coefficient of variation in discharge across all sites including the main channel, tributaries, and irrigation ditches. June had the lowest coefficient of variation (1.53 and 0.94). Nitrate concentration varied from below the detection limit of the Lachat (< 0.005 mg/L) to 0.236 mg/L (Figure 2.5). The highest concentrations were in ditches. Chloride concentration varied from below the detection limit of the Lachat (<1.25 mg/L) to 36.7 mg/L (Figure 2.6).

Nitrate Uptake

Stream nitrate uptake velocity was high relative to other studies of nitrate uptake (Hall et al. 2009b), with a mean of 8.6 mm/min (range = 3.27 to 13.89 mm/min) and did not vary significantly based on nitrate concentration, stream size, or season in which the experiment was conducted. Areal nitrate uptake rates varied from 0.002 - 0.129 mg m^{-2} hr^{-1}.

Nitrate Loading

Nitrate loading was highly spatially variable, spanning seven orders of magnitude, including negative and positive values across the four synoptic surveys (Figure 2.7). Negative nitrate loading rates suggest there was not sufficient uptake capacity in a stream reach to achieve the measured nitrate concentration, i.e., that nitrate concentration was lower than would be predicted based on the upstream concentration and uptake rate. Nitrate loading ranged from -1.25 to +51.33 kg N km^{-2} d^{-2}. There were no significant differences for mean nitrate loadings rates across seasons (Linear regression: $F_{3,75}=0.996$, $p > 0.05$) Spatial variation in nitrate loading was higher within seasons (mean CV = 2.4) than the variation across seasons (CV = 0.68). Nitrate loading during dry seasons in June and November were significantly spatially correlated with each other (Pearson correlation: t=6.05, r=0.886, p=0; Figure 2.8). The rainy season nitrate loading September campaign was also significantly correlated to the June and November campaigns (Pearson correlation: Jun t=7.83, r=0.896, p=0; Nov t=9.7, r=0.933, p=0). There was a significant negative correlation between total subcatchment area and nitrate loading in June and September; in other words, smaller subcatchments tended to have higher nitrate loading. This relationship disappeared if the nitrate loading rates were compared to the adjacent flowing subcatchment area.

Nitrate loading was significantly related to land use and land cover in some seasons. Nitrate loading was significantly positively correlated to the proportion of wetland area in June (Pearson correlation: t=2.79, r=0.572, p=0.013), September (t=2.51, r=0.509, p=0.022), and November (t=2.7, r=0.56, p=0.016; Figure 2.9), but not in

February. Nitrate loading was also significantly correlated to the proportion of agricultural land cover in June (t=2.99, r=0.599, p=0.009), September (t=2.43, r=0.497, p=0.026), and November (t=3.1, r=0.612, p=0.007; Figure 2.10). Wetland and agricultural land cover were also significantly correlated across all seasons (Table 2.2), but a multiple linear regression that included both as explanatory variables for nitrate loading did not significantly increase the amount of variation explained (data not shown). Nitrate loading was not related to the proportion of developed land cover in any season, nor to any land-cover variable in February. Nitrate loading had a wide range of values in locations with low lateral water yield, but catchments with high lateral water yield had high nitrate loading rates (Figure 2.11).

Discussion

Seasonal variability in stream nitrate loading is a function of watershed hydrology (Fisher et al. 2004, Meixner et al. 2007), the climate and topography (Holloway et al. 1998, Howarth et al. 2006), nitrogen inputs to the landscape (Galloway et al. 2004), and the net result of uptake, retention, and release by biota. The primary goal of this study was to determine whether seasons with higher hydrologic connectivity between landscape and stream would result in higher nitrate loading to the stream network. I found that rainy seasons were not statistically different from dry seasons in terms of nitrate loading, despite variation in discharge. I also found that spatial variation was much higher than seasonal variation. Possible explanations for this finding include (1) hydrologic connectivity is higher, but biological retention of nitrogen in the uplands is also higher in wet seasons or (2) stream discharge is supported by different sources of water (of different nitrate concentration) in rainy and dry seasons.

Hydrologic connectivity varied across seasons as evident from differing lateral water yield, stream discharge, and extent of the flowing river network across seasons. There was higher precipitation during the winter snow-melt season and the summer rainy season compared to the summer and winter dry seasons. More precipitation leads to a higher potential for connectivity between the landscape and the stream. Lower temperature in the winter seasons produces less evaporative demand for water and a higher proportion of the precipitation is available to infiltrate and flow overland, potentially increasing connectivity between landscape and stream (Gardner and McGlynn 2009). Higher lateral water yield and stream discharge in the winter seasons (February and November) may be attributed to a lower rate of evapotranspiration. In addition, the extent of the network with flowing surface water was highest in the February campaign that was preceded by rain and snow inputs. Finally, less water is appropriated during the winter seasons for irrigation. In contrast, the summer dry season campaign has high irrigation demand. The discharge in the lower section of the watershed is lowest in June, whereas a sharp increase in discharge for this same section is observed in all other seasons. Therefore, hydrologic connectivity between the landscape and the stream network was likely higher in the winter seasons compared to the summer seasons.

Biological nitrate demand was high across all seasons in the stream. Rainy seasons may have more hydrologic connectivity between landscape and stream, as well as high biological nutrient retention in the uplands, which has consequences for nutrient delivery to streams (Belnap et al. 2005, Welter et al. 2005, Collins et al. 2014). Small precipitation inputs can prompt large increases in nutrient transformations and growth for the soil microbial community, with increasingly large inputs resulting in an heightened activity from progressively more components of the biological community (Collins et al. 2014). Nitrogen demand in the uplands increases with higher precipitation inputs in dryland systems (Gebauer and Ehleringer 2000). The result is that seasons with higher precipitation have higher biological demand for nitrogen on the landscape; therefore, less nitrate is available for export to the stream network (Meixner et al. 2007, Harms and Grimm 2010). In addition, this study measured high nitrate uptake capacity in streams relative to streams across the United States. Hall et al. (2009) compiled 69 measurements of nitrate uptake in U.S. streams and found a median vertical uptake flux of 0.44 mm/min with a range from 0.024 to 17.9 mm/min. In comparison, the median vertical uptake flux for this study was higher, at 9.0 mm/min, and ranged from 3.3 to 13.9 mm/min. Thus, the aquatic systems in this study had high nitrogen demand. There were no detectable differences in stream nitrate uptake or stream nitrate loading across seasons, indicating that nitrate availability is limiting in streams across all seasons.

Nitrate loading may have been different for the February campaign compared to all others because of the contribution of snow melt to stream discharge. The June, September, and November campaigns were likely drawing from similar nitrate sources because the nitrate loading rates were correlated among all pairwise comparisons of these three surveys. These surveys took place when only the perennial portions of the stream network had flowing surface water. The perennial stream comprises just 10% of the drainage network. The February survey took place during a period of snow melt and, consequently, closer to 16% of the drainage network was flowing. The nitrate loading rates for the Feb survey were not correlated to those of any other survey, demonstrating a potential difference in water source and therefore potentially nitrogen sources in different seasons.

Research in other dryland stream networks has shown distinct temporal and spatial patterns in groundwater contribution to streamflow depending on prior precipitation inputs that can affect the nitrate loading to the stream (Brooks and Lemon 2007, Dent et al. 2007, Meixner et al. 2007). Meixner et al. (2007) found that the composition of flood water depended on antecedent water inputs to the system. For floods preceded by a dry season, nitrogen accumulated on the landscape and flood events were smaller, composed mostly of groundwater and shallow soil water with higher nitrate concentrations. Floods occurring after a rainy season had a higher proportion of overland flow and lower nitrate concentrations because the higher antecedent precipitation increased biological nitrogen retention. This suggests the February campaign may have had lower nitrate loading because moisture input from the snow melt increased processing and retention of nitrate. Brooks and Lemon (2007) found that precipitation in the rainy season flushed accumulated nutrients from shallow groundwater into the stream, thereby raising the stream dissolved organic nitrogen and nitrate concentrations. In this system, groundwater was the only consistent source of water to the main stem of the stream; rainy seasons supplemented groundwater with shallow soil water inputs. In Oak Creek, each of the June, September, and November surveys took place during baseflow periods, whereas the February survey took place at a time with active snow melt. Therefore, the February campaign likely had a distinct precipitation input with a distinct nitrate signal that was not present in the other surveys.

Chloride data also support the hypothesis that different water sources were present during the February campaign. Chloride concentration increased dramatically in the lower (0-25 km from outlet) section of the watershed for the June, September, and November surveys, but stayed relatively constant through this section during the February survey. In this lower section of the watershed, the chloride may be sourced from a combination of agricultural activity, because fertilizer contains some chloride (Lowrance et al. 1985), and from groundwater inputs that tend to be higher in chloride than precipitation (Brooks and Lemon 2007). Unlike in other surveys, the tributaries and irrigation ditches in the February campaign in the lower section of the watershed were low in chloride, indicating lower influence of agriculture and groundwater. The lower chloride combined with the high discharge during the February survey suggest that snow melt was the dominant source of water during this period.

Nitrate loading was related to agricultural land cover in the June, September, and November campaigns, but not in the February campaign, and was unrelated to developed land cover in all surveys. Agricultural lands generate non-point source nitrogen pollution to aquatic ecosystems (Carpenter et al. 1998). The types of agriculture taking place in Oak Creek watershed include alfalfa and hay production (USDA-NASS 2017). Grass and pastures near the stream margin are likely used for livestock grazing. Most agricultural cover was within 200 m of the stream or an irrigation ditch. These locations will have higher hydrologic connectivity to the stream channel than do the more distant locations throughout the year because of irrigation. Water is removed from the stream via diversion and pumped from ditches or groundwater wells onto agricultural fields. As a result, some of the nitrate on these landscapes is transported back to the stream or ditch through irrigation runoff or shallow soil water. The irrigation ditches had among the highest nitrate concentrations and nitrate loading rates, supporting the hypothesis that these sites were a primary source of nitrate to the streams. Nitrate loading was not related to developed land cover in any season, meaning either that there were no substantial nitrogen pools in these areas or that they were not connected to the stream during the surveys. Most areas with a higher density of developed land cover were some distance from the flowing stream channel, indicating there was likely a lack of hydrologic connectivity between these locations and the stream channel.

Nitrate loading significantly increased with proportion wetland area, including both emergent woody and herbaceous wetlands that varied from 0 to 16% of the flowing subcatchment area. Most of the wetland area occurred directly along the stream margin. The positive correlation between wetland area and nitrate loading contradicts much previous research showing that more wetland area decreases nitrate loading to stream ecosystems (Peterjohn and Correll 1984, Hill 1996, Helton et al. 2011); however, in dryland ecosystems that are generally strongly nitrogen limited (Grimm and Fisher 1986a, 1986b), water that moves through the stream margin can be a source rather than a sink for nitrate (Holmes et al. 1994, Schade et al. 2001). Generally, wetland ecosystems are considered nitrogen sinks because of high biological nitrogen assimilation and the capacity to permanently remove nitrate through denitrification. However, in dryland streams that are strongly nitrogen limited, organic nitrogen delivered to subsurface flow paths along the stream margin can undergo mineralization and nitrification, leading to higher nitrate at outwelling locations (Jones et al. 1995, Holmes et al. 1996, Fisher et al. 1998). However, wetland and agricultural land cover were significantly positively correlated. Multiple linear regressions that included both wetland and agricultural cover as explanatory variables for nitrate loading did not significantly increase the amount of variation explained. As a result, the relationship between nitrate loading and either one of these variables may be spurious with the patterns driven by one, but not both, land cover metrics.

Comparing nitrate loading values from this study to the literature is difficult because these values represent nitrate loading from the landscape to the stream and are distinct from the stream nitrate uptake. The most comparable estimates come from the incremental total nitrogen load produced by the SPARROW model that incorporates stream-channel nitrogen retention. Nitrate can be near 90% of total nitrogen in dryland streams during stormflow but is generally closer to 0-10% at lower flows. If I conservatively assume that nitrate accounts for 20% of the total nitrogen in Oak Creek, then total nitrogen loading estimate range from 0.0005–254 kg N km^{-2} d^{-1} with a median of 1.05 kg N km^{-2} d^{-1} (Table 2.3). The median for Oak Creek is near the mean reported for Spain (Aguilera et al. 2012) and much of the US (Hoos and McMahon 2009, Brown et al. 2011, Moore et al. 2011, Rebich et al. 2011, Wise and Johnson 2011). High nitrate loading rates (>6 kg N km^{-2} d^{-1}) identified in this study are also within the range of those reported for California’s Central Valley (Saleh and Domagalski 2015) and the Great Lakes basins (Robertson and Saad 2013), California and the Great Lakes are both influenced by agriculture. Just 15% of the observations from this study are within the same order of magnitude or less than that measured for the dryland Orange River in South Africa (0.09 kg N km^{-2} d^{-1}; Caraco and Cole 2001) and below the low range for

California (0.08 kg N km^{-2} d^{-1})(Saleh and Domagalski 2015). Thus, Oak Creek supports nitrate loading rates that span a range from very low to high nitrogen inputs.

This study is among the first to quantify nitrate loading to a stream network in a dryland environment. Such investigations are common in more mesic ecosystems but are challenging to undertake in dryland contexts because these systems violate many common assumptions for hydrology and nutrient loading, such as the assumption that discharge increases with drainage area, because they often have gaining and losing reaches. Helton et al (2011a) found that representing the hydrology as a topographically driven flow accumulation failed to accurately represent the discharge of the Rio Grande River in New Mexico. The Rio Grande is dominated by flow-regulating structures such as dams, headgates, and diversions. I found that implementing discharge as a gross process, representing water both entering and leaving losing reaches, allowed simple model representation of the complex hydrology in Oak Creek. Oak Creek was chosen in part because the network has a regional aquifer that supplies flowing surface water year-round, making seasonal comparisons possible even for the dry hot season. To deal with the size of the system that had to be sampled over a short period of time, I targeted sampling at points that would capture changes in hydrology and nitrate loading including tributary confluences, irrigation diversions and returns, and spring inputs. Finally, conclusions drawn from a single season or year should be treated with caution given the high interannual variation endemic to dryland ecosystems. This study was conducted in 2017, which was the warmest year on record at the time and which had comparatively above-average precipitation in winter, but below-average precipitation in all other seasons (NOAA National Centers for Environmental Information 2018). Nitrate loading was extremely spatially variable across the watershed during 2017. This high spatial heterogeneity overwhelmed seasonal variation in nitrate loading. However, nitrate loading likely varies more among years than within years, because of the high degree of interannual variability in precipitation in this dryland ecosystem.

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Tables and Figures

Table 2.1. Estimated value and standard error in parentheses of the relationship between stream width and discharge calculated for each synoptic survey. The width coefficient and exponent correspond to the *a* and *b* terms in equation 2.7. Significance levels are indicated with asterisks: p<0.05 (*), p<0.01 (**), p<0.001(***).

Season	Month	Width Coefficient	Width Exponent
Summer Dry	June	13.9 (1.4)***	0.646 (0.175)**
Summer Rainy	September	0.002 (0.003)	0.719 (0.091)***
Winter Dry	November	0.016 (0.014)	0.558 (0.072)***
Winter Rainy	February	0.084 (0.082)	0.412 (0.076)***

Table 2.2. Relationship between proportion agriculture and proportion wetland area cover for each synoptic survey as quantified by Pearson's correlations.

Season	**Month**	**t**	**r**	**p-value**
Summer Dry	June	3.559	0.653	0.002
Summer Rainy	September	4.243	0.707	<0.001
Winter Dry	November	3.567	0.654	0.002
Winter Rainy	February	4.038	0.680	<0.001

Table 2.3. Total nitrogen (TN) loading to streams from adjacent catchment area (lateral area draining to a stream segment, excluding any area draining to upstream segments) compared across literature values and to this study. Incremental total nitrogen (TN) load is the amount of nitrogen drained from the adjacent catchment minus the stream nitrogen uptake. Land-to-stream nitrogen load is the amount of nitrogen delivered to the stream prior to any stream uptake.

Location	**Method**	**Metric**	**Measure**	**TN Load (kg N km^{-2} d^{-1})**	**Reference**
Orange River, S Afr	Mass Balance	Land to Stream Load	Mean	0.09	Caraco and Cole 2001
Missouri River	SPARROW	Incremental Load	Mean	0.92	Brown et al. 2011
South-Central US	SPARROW	Incremental Load	Mean	1.01	Rebich et al. 2011
Spain	SPARROW	Incremental Load	Mean	1.1	Aguilera et al. 2012
Pacific Northwest	SPARROW	Incremental Load	Mean	1.3	Wise and Johnson 2011
Southeast US	SPARROW	Incremental Load	Range	1.40 - 1.70	Hoos and McMahon 2009
Northeast US	SPARROW	Incremental Load	Range	0.55 - 3.48	Moore et al. 2011
California	SPARROW	Incremental Load	Range	0.08 - 795	Salah and Domalgaski 2015
Great Lakes Basins	SPARROW	Incremental Load	Range	0.002 - 1263	Robertson and Saad 2011
Oak Creek, Arizona	Mass Balance	Land to Stream Load	Range	5×10^{-4} - 254	This study
Oak Creek, Arizona	Mass Balance	Land to Stream Load	Mean	12.05	This study

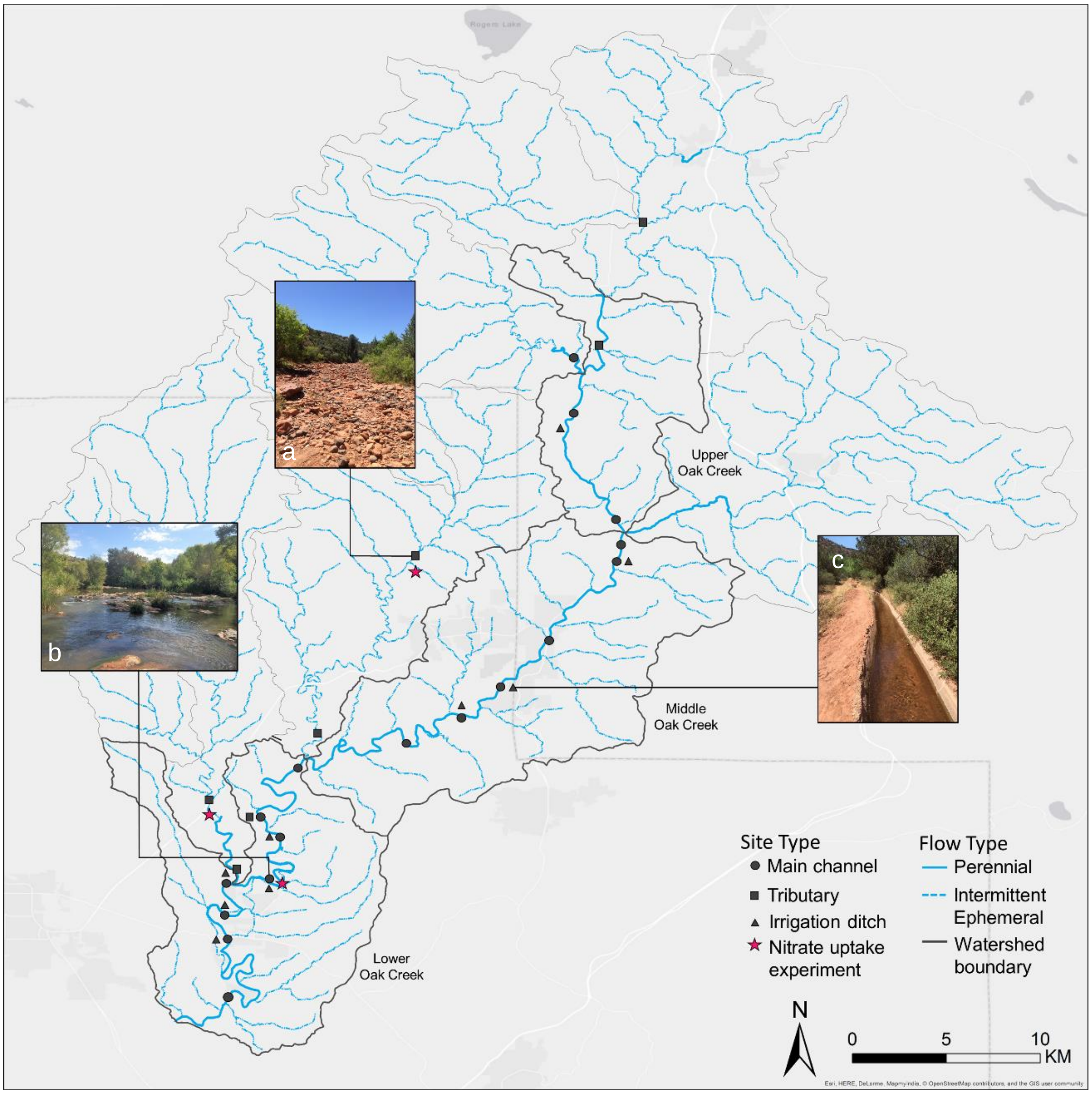

Figure 2.1. Sampling locations across Oak Creek watershed and locations for nitrate uptake experiments. Between 25 and 29 sites were sampled each survey depending on presence of surface water and access. Insets show a) Dry Creek is a season without surface water Cr, b) the mainstem of Oak Creek, and c) an irrigation ditch.

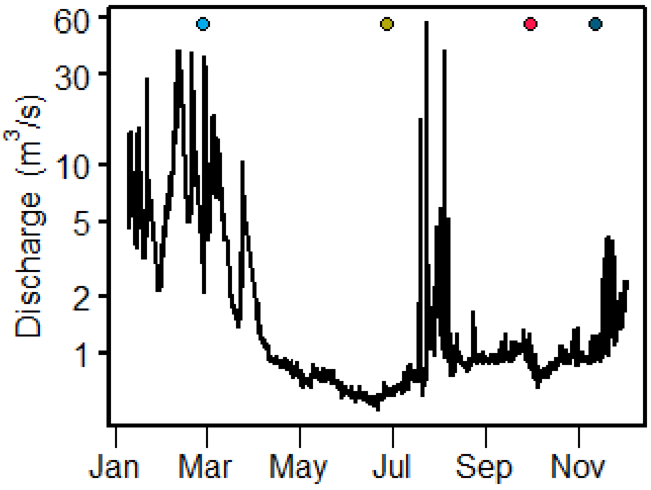

Figure 2.2: Discharge on the main stem of Oak Creek (USGS Gauge #09504500). Dots indicate when each sampling campaign took place.

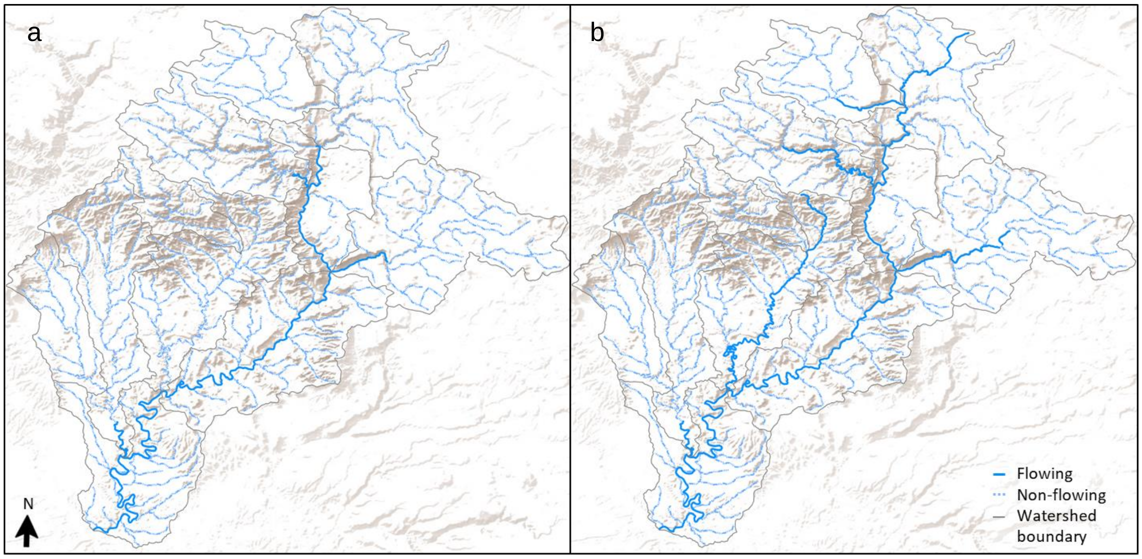

Figure 2.3. Maps of Oak Creek watershed indicating the portions of the stream network that had flowing surface water during the (a) June, September, and November and (b) the February synoptic surveys.

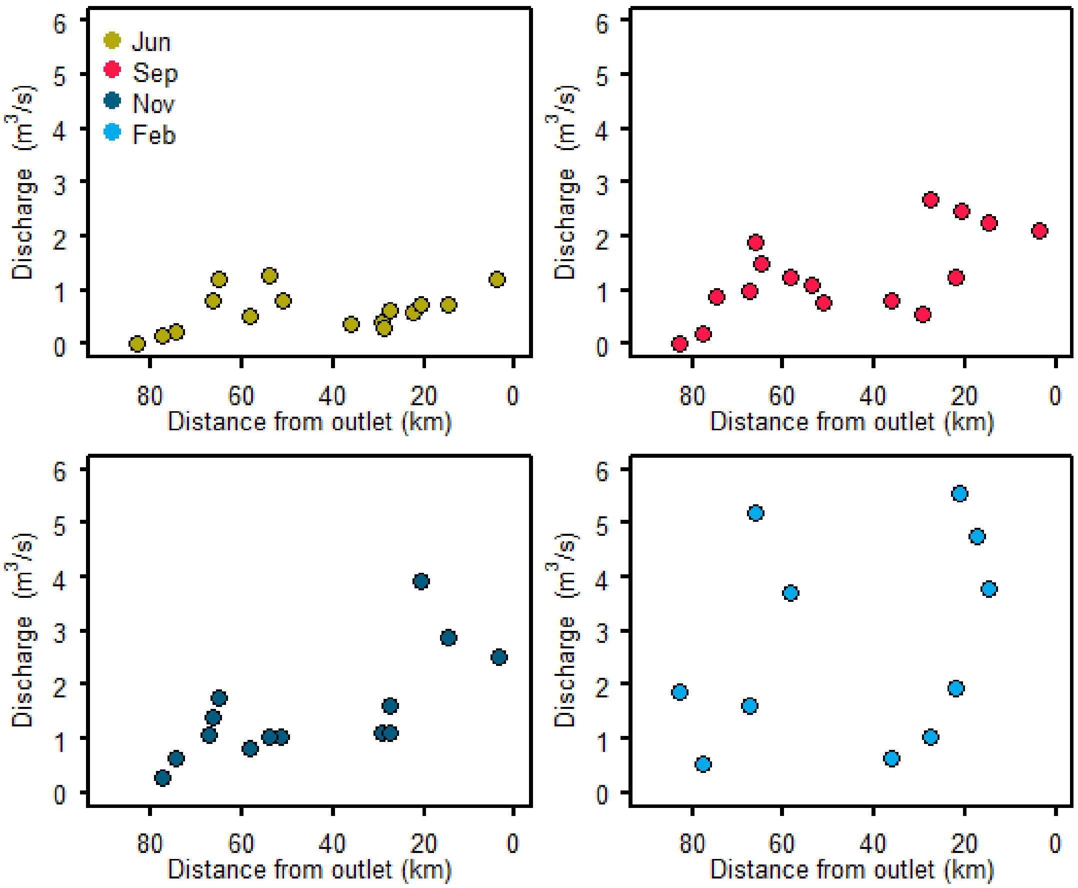

Figure 2.4: Discharge in the main stem of Oak Creek for the (a) June, (b) September, (c) November, and (d) February surveys as a function of distance from the watershed outlet.

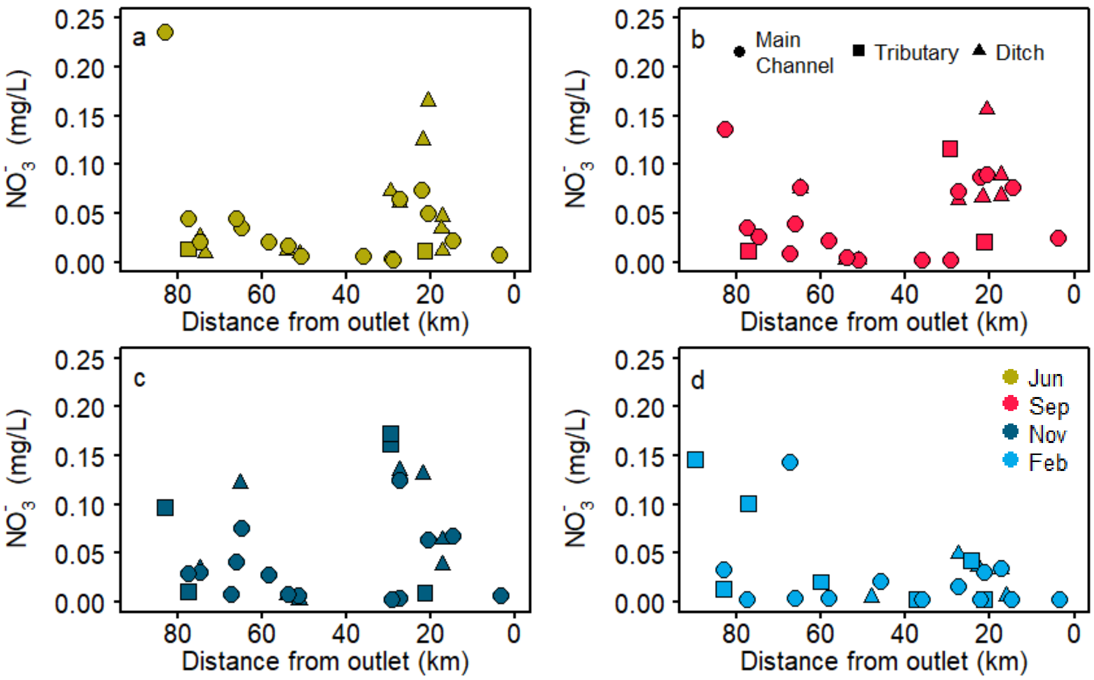

Figure 2.5: Nitrate concentration in the Oak Creek main stem (circles), tributaries (squares), and irrigation ditches (triangles) for the (a) June, (b) September, (c) November, and (d) February surveys as a function of distance from the watershed outlet.

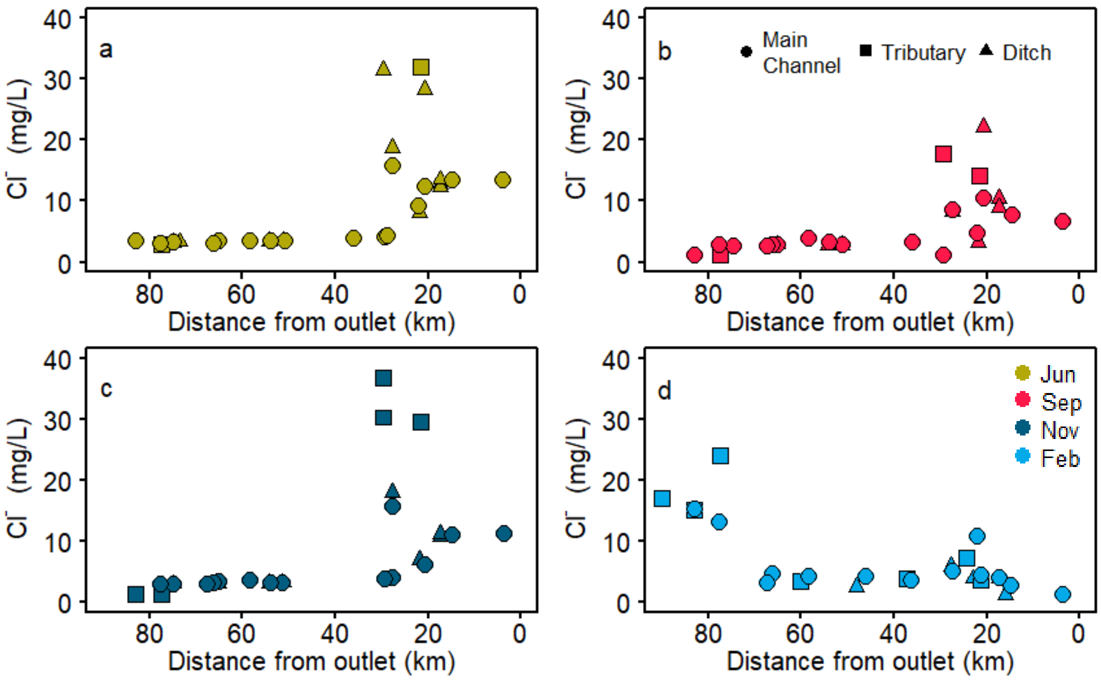

Figure 2.6: Chloride concentration in the main stem (circles), tributaries (squares), and irrigation ditches (triangles) for the (a) June, (b) September, (c) November, and (d) February surveys as a function of distance from the watershed outlet.

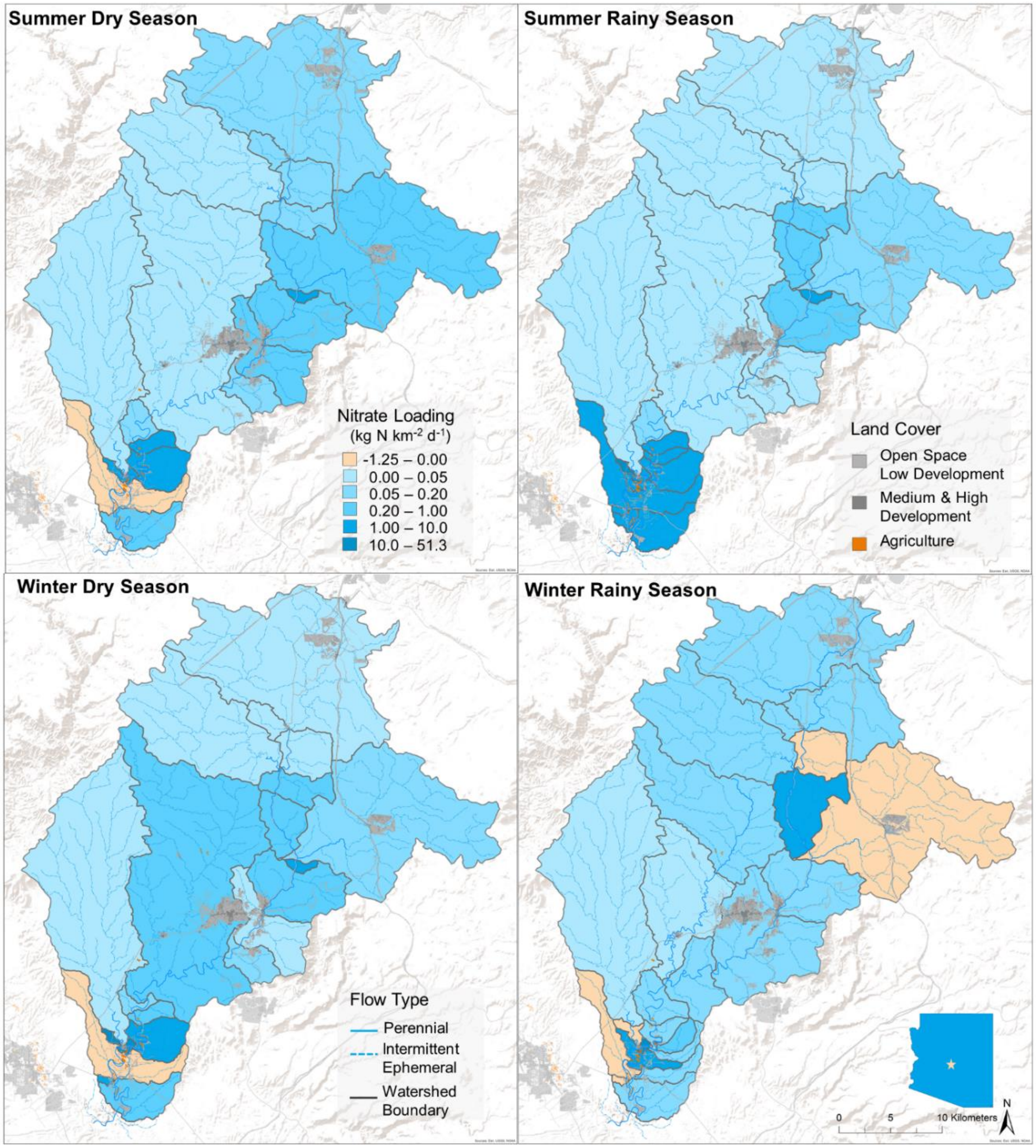

Figure 2.7: Spatial distribution of nitrate loading rate for the summer dry season (June, top left), summer rainy season (September, top right), winter dry season (November, bottom left), and winter rainy season (February, bottom right).

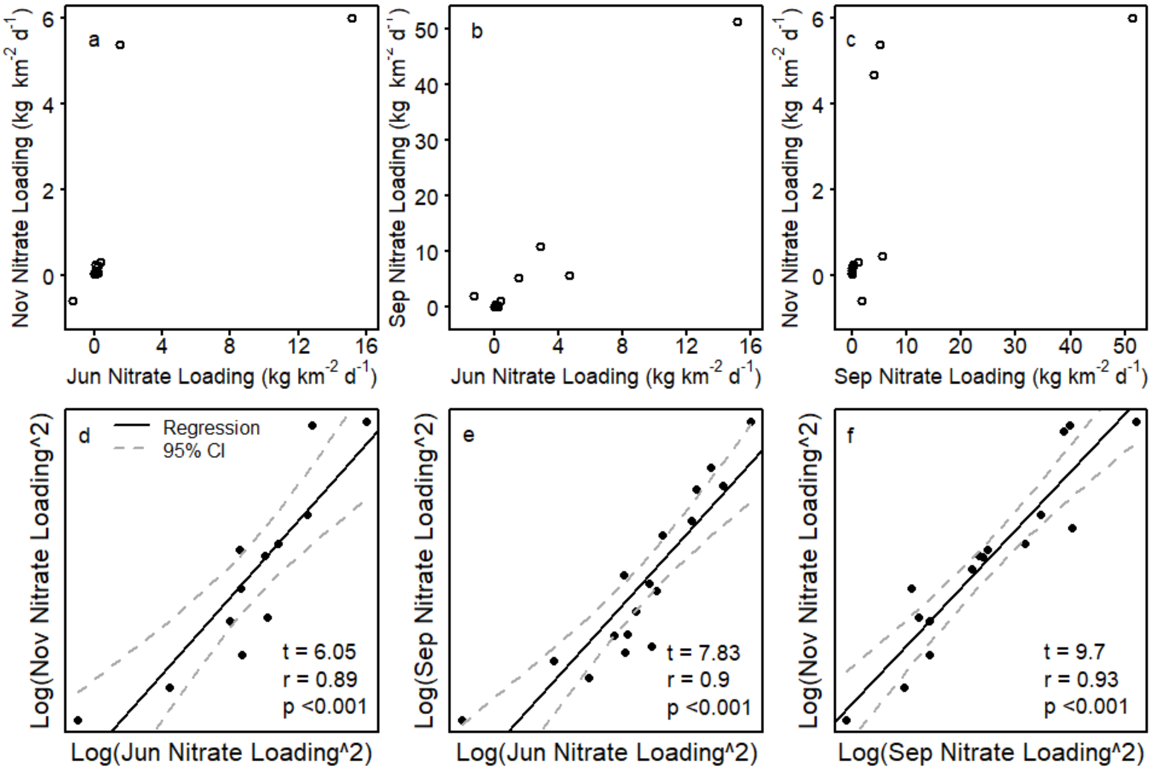

Figure 2.8: Pairwise comparisons of seasonal nitrate loading rates for June, September, and November. Non-significant correlations with February survey data are not shown. Top panels are untransformed data, bottom panels are log-square transformed with Pearson’s correlation statistics and linear trendline with 95% confidence intervals.

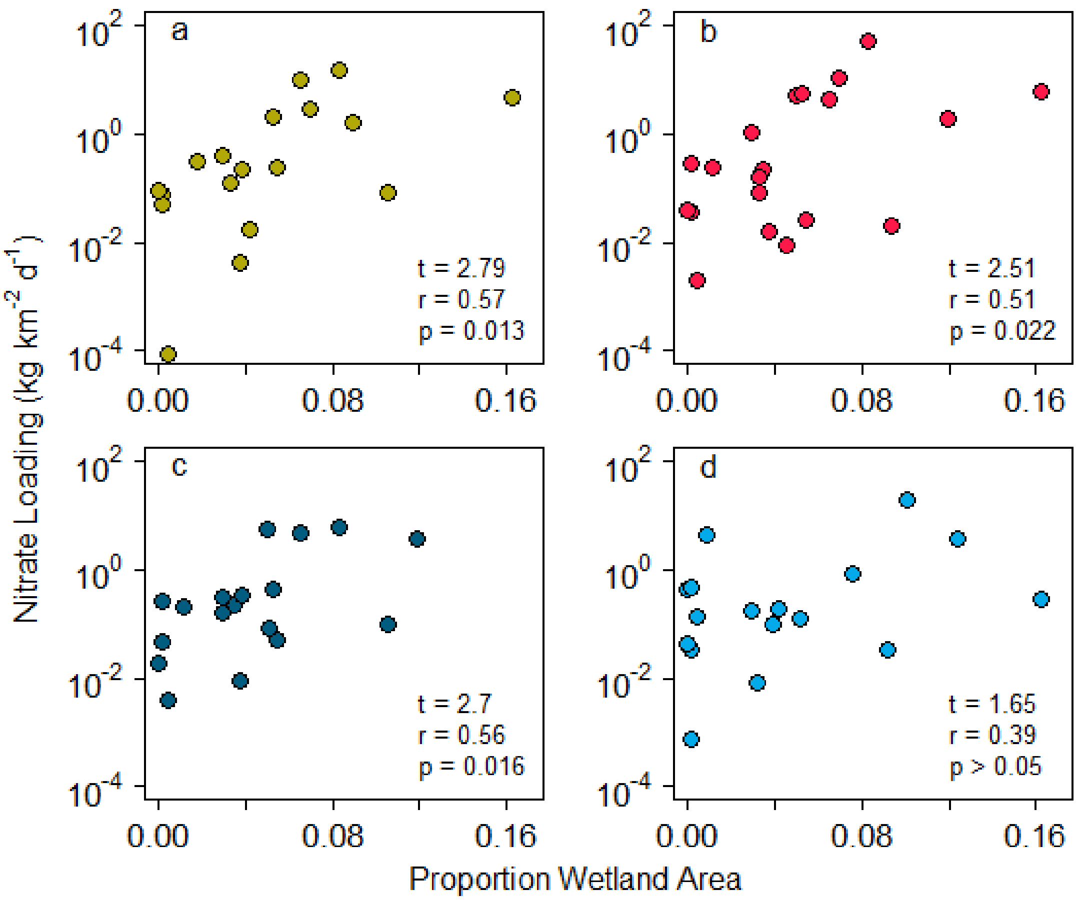

Figure 2.9: Nitrate loading as a function of wetland area within the flowing subcatchment area for the (a) June, (b) September, (c) November, and (d) February surveys. Pearson’s correlation statistics for log-transformed nitrate loading rates are reported on each figure.

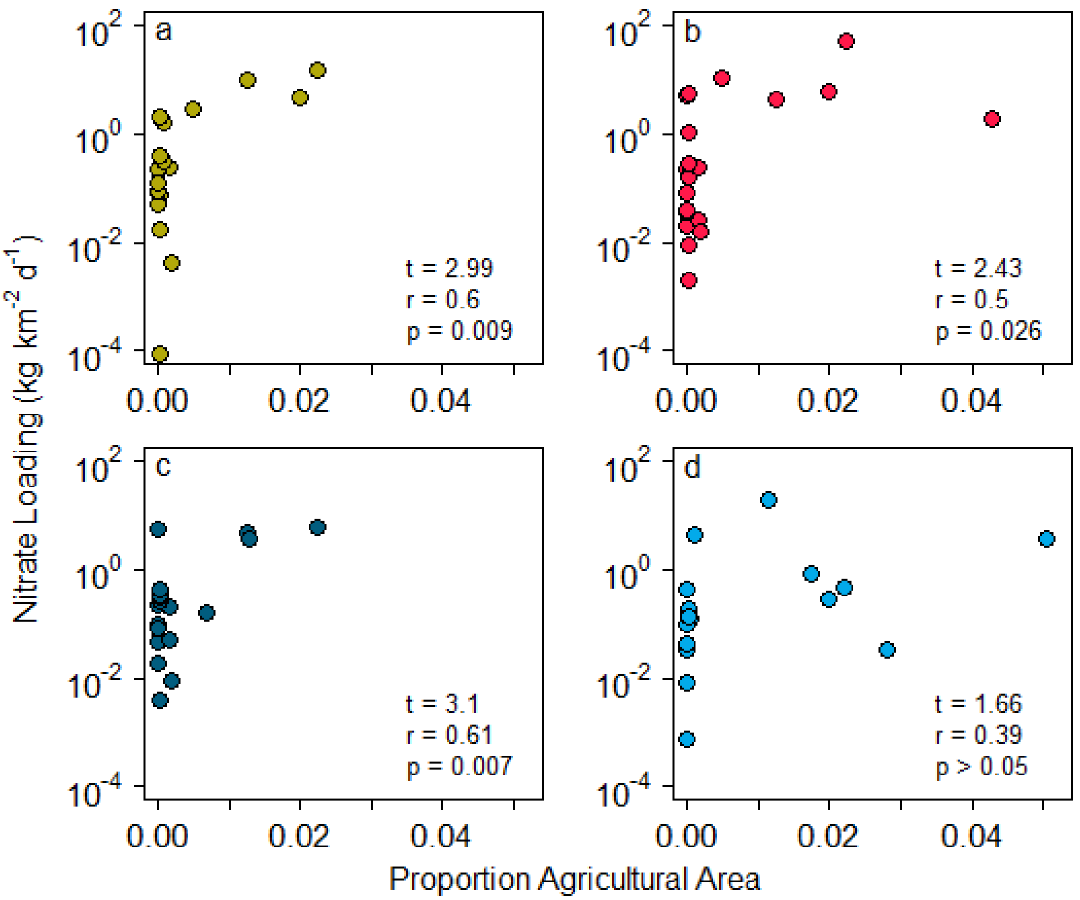

Figure 2.10: Nitrate loading as a function of proportion agricultural land use within the flowing subcatchment area for the (a) June, (b) September, (c) November, and (d) February surveys. Pearson's correlation statistics for log-transformed nitrate loading rates are reported on each figure.

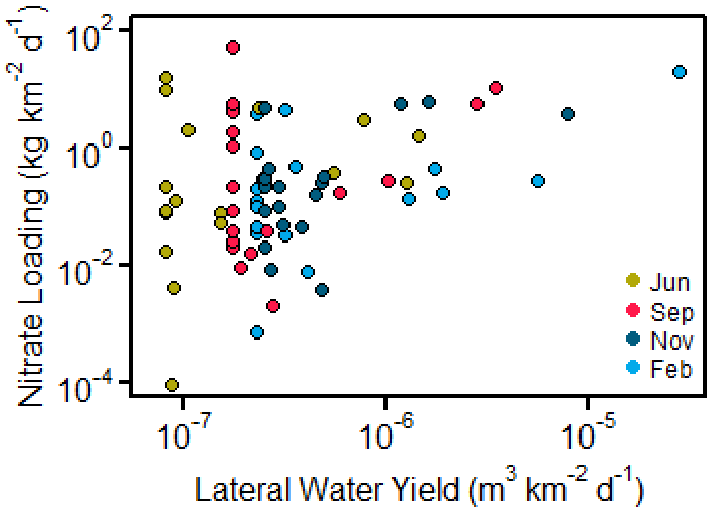

Figure 2.11: Nitrate loading as a function of lateral water yield.

Literature Cited

Aguilera, R., R. Marcé, and S. Sabater. 2012. Linking in-stream nutrient flux to land use and inter-annual hydrological variability at the watershed scale. Science of the Total Environment 440:72–81.

Alexander, R. B., R. A. Smith, and G. E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403:758–762.

Bastin, J., N. Berrahmouni, A. Grainger, D. Maniatis, D. Mollicone, R. Moore, C. Patriarca, N. Picard, B. Sparrow, E. M. Abraham, K. Aloui, A. Atesoglu, F. Attore, A. Bey, M. Garzuglia, L. G. García-montero, N. Groot, G. Guerin, L. Laestadius, A. J. Lowe, and B. Mamane. 2017. The extent of forest in dryland biomes. Science 638:635–638.

Belnap, J., J. R. Welter, N. B. Grimm, N. Barger, and J. A. Ludwig. 2005. Linkages between microbial and hydrologic processes in arid and semiarid watersheds. Ecology 86:298–307.

Bernhardt, E. S., J. R. Blaszczak, C. D. Ficken, M. L. Fork, K. E. Kaiser, and E. C. Seybold. 2017. Control points in ecosystems: Moving beyond the hot spot hot moment concept. Ecosystems 20:665–682.

Brooks, P. D., and M. M. Lemon. 2007. Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Brown, J. B., L. A. Sprague, and J. A. Dupree. 2011. Nutrient sources and transport in the Missouri River Basin with emphasis of the effect of irrigation and reservoirs. Journal of the American Water Resources Association 47:1034–1060.

Caraco, N. F., and J. J. Cole. 2001. Human influence on nitrogen export: a comparison of mesic and xeric catchments. Marine and Freshwater Research 52:119–125.

Carbone, M. S., G. C. Winston, and S. E. Trumbore. 2008. Soil respiration in perennial grass and shrub ecosystems: Linking environmental controls with plant and microbial sources on seasonal and diel timescales. Journal of Geophysical Research: Biogeosciences 113:1–14.

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8:559–568.

Collins, S. L., J. Belnap, N. B. Grimm, J. A. Rudgers, C. N. Dahm, P. D. Odorico, M. Litvak, D. O. Natvig, D. C. Peters, W. T. Pockman, R. L. Sinsabaugh, and B. O.

Wolf. 2014. A multiscale, hierarchical model of pulse dynamics in arid-land ecosystems. Annual Review of Ecology, Evolution, and Systematics 45:397–419.

Collins, S. L., R. L. Sinsabaugh, C. Crenshaw, L. Green, A. Porras-Alfaro, M. Stursova, and L. H. Zeglin. 2008. Pulse dynamics and microbial processes in aridland ecosystems. Journal of Ecology 96:413–420.

Covino, T. P., B. L. McGlynn, and R. A. McNamara. 2010. Tracer additions for spiraling curve characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation. Limnology and Oceanography: Methods 8:484–498.

Dent, C. L., N. B. Grimm, E. Martí, J. W. Edmonds, J. C. Henry, and J. R. Welter. 2007. Variability in surface-subsurface hydrologic interactions and implications for nutrient retention in an arid-land stream. Journal of Geophysical Research: Biogeosciences 112:1–13.

Fisher, S. G., N. B. Grimm, E. Martí, and R. Gómez. 1998. Hierarchy, spatial configuration, and nutrient cycling in a desert stream. Australian Journal of Ecology 23:41–52.

Fisher, S. G., R. A. Sponseller, and J. B. Heffernan. 2004. Horizons in stream biogeochemistry: Flowpaths to progress. Ecology 85:2369–2379.

Galloway, J. N., F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vo. 2004. Nitrogen cycles: Past, present, and future. Biogeochemistry 70:153–226.

Gardner, K. K., and B. L. McGlynn. 2009. Seasonality in spatial variability and influence of land use/land cover and watershed characteristics on stream water nitrate concentrations in a developing watershed in the Rocky Mountain West. Water Resources Research 45:1–14.

Gebauer, R. L. E., and J. R. Ehleringer. 2000. Water and nitrogen uptake patterns following moisture pulses in a cold desert community. Ecology 81:1415–1424.

Grimm, N. B. 1987. Nitrogen dynamics during succession in a desert stream. Ecology 68:1157–1170.

Grimm, N. B., and S. G. Fisher. 1986a. Nitrogen limitation potential of Arizona streams and rivers. Journal of the Arizona-Nevada Academy of Sciences 21:31–44.

Grimm, N., and S. G. Fisher. 1986b. Nitrogen limitation in a Sonoran Desert stream. North American Benthological Society 5:2–15.

Hall, R. O., J. L. Tank, D. J. Sobota, P. J. Mulholland, J. M. O’Brien, W. K. Dodds, J. R. Webster, H. M. Valett, G. C. Poole, B. J. Peterson, J. L. Meyer, W. H. McDowell, S. L. Johnson, S. K. Hamilton, N. B. Grimm, S. V Gregory, C. N. Dahm, L. W. Cooper, L. R. Ashkenas, S. M. Thomas, R. W. Sheibley, J. D. Potter, B. R. Niederlehner, L. T. Johnson, A. M. Helton, C. M. Crenshaw, A. J. Burgin, M. J. Bernot, J. J. Beaulieu, and C. P. Arango. 2009. Nitrate removal in stream ecosystems measured by 15N addition experiments: Total uptake. Limnology and Oceanography 54:653–665.

Harms, T. K., and N. B. Grimm. 2010. Influence of the hydrologic regime on resource availability in a semi-arid stream-riparian corridor. Ecohydrology 3:349–359.

Helton, A. M., G. C. Poole, J. L. Meyer, W. M. Wollheim, B. J. Peterson, P. J. Mulholland, E. S. Bernhardt, J. A. Stanford, C. Arango, L. R. Ashkenas, L. W. Cooper, W. K. Dodds, S. V. Gregory, R. O. Hall, S. K. Hamilton, S. L. Johnson, W. H. McDowell, J. D. Potter, J. L. Tank, S. M. Thomas, H. M. Valett, J. R. Webster, and L. Zeglin. 2011. Thinking outside the channel: Modeling nitrogen cycling in networked river ecosystems. Frontiers in Ecology and the Environment 9:229–238.

Hill, A. R. 1996. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25:743–755.

Holloway, J. M., R. A. Dahlgren, B. Hansen, and W. H. Casey. 1998. Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature 395:785–788.

Holmes, R. M., S. G. Fisher, and N. B. Grimm. 1994. Parafluvial nitrogen dynamics in a desert stream ecosystem. Journal of the North American Benthological Society 13:468–478.

Holmes, R. M., J. B. Jones, S. G. Fisher, and N. B. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry 33:125146.

Hoos, A. B., and G. McMahon. 2009. Spatial analysis of instream nitrogen loads and factors controlling nitrogen delivery to streams in the southeastern United States using spatially referenced regression on watershed attributes (SPARROW) and regional classification framworks. Hydrological Processes 23:2275–2294.

Howarth, R. W., D. P. Swaney, E. W. Boyer, R. Marino, N. Jaworski, and C. Goodale. 2006. The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Pages 163–186 *in* L. A. Martinelli and R. W. Howarth, editors. Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. Springer, Dordrecht.

Huxman, T. E., K. A. Snyder, D. Tissue, A. J. Leffler, K. Ogle, W. T. Pockman, D. R.

Sandquist, D. L. Potts, and S. Schwinning. 2004. Precipitation pulses and carbon fluxes in semiarid and arid ecosystems. Oecologia 141:254–268.

Jencso, K. G., B. L. McGlynn, M. N. Gooseff, S. M. Wondzell, K. E. Bencala, and L. A. Marshall. 2009. Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale. Water Resources Research 45:1–16.

Jones, J. B., S. G. Fisher, and N. B. Grimm. 1995. Nitrification in the hyporheic zone of a desert stream ecosystem. Journal of the North American Benthological Society 14:249–258.

Leopold, L. B., and T. Maddock. 1953. The hydraulic geometry of stream channels and some physiograhpic implications. Page Geological Survey Profession Paper.

Lowrance, R. R., R. A. Leonard, L. E. Asmussen, and R. L. Todd. 1985. Nutrient budgets for agricultural watersheds in the southeastern coastal plain. Ecology 66:287–296.

Ludwig, J. A., and D. J. Tongway. 1997. A landscape approach to rangeland ecology. Pages 1–12 *in* J. Ludwig, D. Tongway, D. Freudenberger, J. Noble, and K. Hodgkinson, editors. Landscape ecology: Function and management. CSIRO Publishing, Collingwood, Victoria, Australia.

Meixner, T., A. K. Huth, P. D. Brooks, M. H. Conklin, N. B. Grimm, R. C. Bales, P. A. Haas, and J. R. Petti. 2007. Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Van Meter, K. J., and N. B. Basu. 2015. Catchment legacies and time lags: A parsimonious watershed model to predict the effects of legacy storage on nitrogen export. PLoS ONE 10:1–22.

Moore, R. B., C. M. Johnston, R. A. Smith, and B. Milstead. 2011. Sources and delivery of nutrients to the receiving water in the Northeastern and Mid-Atlantic regions of the United States. Journal of the American Water Resources Association 47:965–990.

Mulholland, P. J., A. M. Helton, G. C. Poole, R. O. Hall, S. K. Hamilton, B. J. Peterson, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, W. K. Dodds, S. E. G. Findlay, S. V Gregory, N. B. Grimm, S. L. Johnson, W. H. McDowell, J. L. Meyer, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, L. T. Johnson, B. R. Niederlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, D. J. Sobota, and S. M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202–205.

Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. Van Winkle. 1981. Measuring nutrient spiralling in streams. Canadian Journal of Fisheries and Aquatic Sciences 38:860–863.

NOAA National Centers for Environmental Information. 2018. State of the Climate: National Climate Report for Annual 2017.

Oak Creek Watershed Council. 2012. Improvement plan for the Oak Creek Watershed, Arizona.

Peterjohn, W. T., and D. L. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. Ecology 65:1466–1475.

R Core Team. 2018. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Rebich, R. A., N. A. Houston, S. V Mize, D. K. Pearson, P. B. Ging, and C. E. Hornig. 2011. Sources and delivery of nutrient to the Northwestern Gulf of Mexico from stream in the South-Central United States. 2011 47:1061–1086.

Robertson, D. M., and D. A. Saad. 2013. Nutrient inputs to the Laurentian Great Lakes by source and watershed estimated using SPARROW watershed models. Journal of the American Water Resources Association 49:725–734.

Saleh, D., and J. Domagalski. 2015. SPARROW modeling of nitrogen sources and transport in rivers and stream of California and adjacent states, U. S. Journal of the American Water Resources Association 51:1483–1507.

Schade, J. D., S. G. Fisher, N. B. Grimm, and J. Seddon. 2001. The influence of a riparian shrub on nitrogen cycling in a Sonoran Desert stream. Ecology 82:3363–3376.

Seitzinger, S. P., R. V Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. Breemen. 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochemistry 57/58:199–237.

Southam, G., P. Keim, and C. Keys. 2000. The Oak Creek Canyon Escherichia coli genotyping project. Flagstaff, AZ.

Sponseller, R. A. 2007. Precipitation pulses and soil CO2 flux in a Sonoran Desert ecosystem. Global Change Biology 13:426–436.

Stieglitz, M., J. Shaman, J. P. McNamara, V. Engel, J. Shanley, and G. W. Kling. 2003. An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biogeochemical Cycles 17:1–15.

USDA-NASS. 2017. USDA National Agricultural Statistics Service Cropland Data Layer. https://nassgeodata.gmu.edu/CropScape/.

Welter, J. R., S. G. Fisher, and N. B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76:421–440.

Wise, D. R., and H. M. Johnson. 2011. Surface-water nutrient conditions and sources in the United States Pacific Northwest. Journal of the American Water Resources Association 47:1110–1135.

CHAPTER 3

STORM CHARACTERISTICS AND ANTECEDENT CONDITIONS DETERMINE FLOOD NUTRIENT EXPORT IN A DESERT STREAM

Abstract

Temporary streams are common in all ecosystems but form the majority of streams in dryland ecosystems. These streams have limited connectivity to downstream ecosystems. Most of the annual export of water and nutrients to downstream ecosystems may occur during floods. I explored the variability in flood nutrient export based on how biological activity mediates the pool of potentially mobile nutrients and storm characteristics. We coupled flood water nutrient data with stream discharge and radar precipitation data from Sycamore Creek, an intermittent watershed in the Sonoran Desert of central Arizona, US. Nutrient export was primarily driven by water export rather than concentration. Flood water export increased with larger and more intense storms, which tended to occur in the winter months. Floods were also larger following higher antecedent precipitation inputs to the watershed, indicating channel water storage is substantial in the catchment. Larger storms resulted in higher dissolved organic carbon and total dissolved nitrogen export, likely because of effects of larger storms on flood water export. Likewise, nitrate loads were higher with more antecedent precipitation inputs. Biological nutrient removal and retention lowered the concentrations and loads of DOC and TDN in flood water when there were higher precipitation inputs, which alleviate water limitation of biological activity, in the season prior to the flood. Nitrate, ammonium, and soluble reactive phosphorus concentrations in stream water were insensitive to storm

characteristics and biological activity at seasonal timescales. This may indicate that these nutrients are sensitive to factors at shorter timescales, perhaps with transformations occurring during the floods. Increasing temperature in the region is expected to decrease flow conditions, which will make floods an even greater proportion of the annual budget of nutrient export to downstream ecosystems. Understanding the variability in flood nutrient export will be key to understanding future impacts on downstream water resources.

Introduction

Temporary streams may account for 30% of river length globally and more than half of the river length in the United States (Tooth 2000, Larned et al. 2010, Datry et al. 2014). These streams are especially common in headwaters but can also occur in lower reaches due to water extraction (Larned et al. 2010). In drylands, temporary streams comprise much more than half of stream length (Meybeck et al. 2006, von Schiller et al. 2017), making these ecosystems the predominant stream type of drylands. Despite the widespread distribution of temporary streams, only recently have these systems received a marked increase in research focus, especially relating to biogeochemistry (Larned et al. 2010, Butman and Raymond 2011, Datry et al. 2014, Marcé et al. 2018, Arce et al. 2019), though there is a long history of ephemeral and intermittent stream research (Fisher et al. 1982, 1998, Grimm and Fisher 1986b, Grimm 1987). This work demonstrates that over wetting and drying cycles temporary streams are a large source of carbon and nitrogen gases (Butman et al. 2018) and carbon, nitrogen, and phosphorus export in water (Ye and Grimm 2013, Arce et al. 2014). Indeed, temporary streams may be a large contributor of greenhouse gas emissions from inland waters (von Schiller et al. 2014, Butman et al. 2018, Marcé et al. 2018), and the carbon and nutrients (nitrogen and phosphorus) exported from temporary streams during floods can fuel primary productivity in downstream ecosystems and adversely affect water quality. The ubiquity of these streams across the globe make integrating them into our understanding of watershed biogeochemistry essential. In addition, warming due to climate change is expected to increase the global extent of temporary streams (Larned et al. 2010).

Organisms are limited primarily by water in drylands. As a result, research in these systems has focused on pulses in activity associated with precipitation (Noy-Meir 1973, Davidson 1992). Rain inputs can prompt increases in decomposition of organic matter (Schlesinger et al. 1990) and gaseous emissions of carbon (Xu et al. 2004) and nitrogen (Davidson 1992). Rainfall also stimulates microbial and plant productivity (Reynolds et al. 2004, Collins et al. 2008) resulting in higher nutrient assimilation (Belnap et al. 2005, Collins et al. 2008). The size of the precipitation event mediates the size of the response (Ludwig and Tongway 1997, Reynolds et al. 2004, Belnap et al. 2005, Collins et al. 2008). Conceptual models have been developed that describe the sequence and relative rates of processes that are prompted by these water inputs (Ludwig and Tongway 1997, Belnap et al. 2005, Welter et al. 2005, Collins et al. 2008, 2014). However, these models were largely developed for the patch or hillslope scale, and are seldom applied to the watershed scale (but see Collins et al. 2014). Applying these models to the watershed scale may illuminate how pulse dynamics can lead to patterns of carbon and nutrient export in flood water from temporary dryland streams.

The extent of accumulation of potentially mobile carbon and nutrients on watershed hillslope surfaces, compared to that retained or removed through biological uptake, may be related to the number and size of rain pulses producing biological activity between floods. In the absence of rain, organic matter, carbon, and nutrients accumulate in the watershed from litter production, atmospheric deposition, and cell death (Austin et al. 2004, Belnap et al. 2005). Small amounts of precipitation can prompt a large change in activity on hillslope soils (Belnap et al. 2005). A sudden change in soil water potential from dry to wet conditions releases soil and intracellular labile carbon and nutrients to the soil community that fuels the activity pulse (Fierer and Schimel 2003). These microorganisms increase their rates of decomposition (Birch 1958, Jarvis et al. 2007, Kurc and Small 2007) and nitrogen mineralization (Yahdjian and Sala 2010), transforming nutrients among organic and inorganic forms. These transformations can increase plant available nitrogen (Schwinning and Sala 2004), which is available for use during the following rain pulse (Ludwig and Tongway 1997, Belnap et al. 2005). Gaseous losses of carbon through soil respiration (Fierer and Schimel 2003, Jarvis et al. 2007, Sponseller!) and nitrogen through denitrification (Yahdjian and Sala 2010) and ammonium volatilization (Schlesinger and Peterjohn 1991, McCalley and Sparks 2008) reduce extant soil nutrient and organic matter pools.

Progressively larger storms can penetrate the soils more deeply and raise the soil moisture such that the plant community responds (Ogle and Reynolds 2004, Reynolds et al. 2004, Collins et al. 2008). Different plants will respond to precipitation by increasing root activity, nutrient uptake, and net primary productivity depending on the antecedent soil moisture, the size of the rain input, and the community composition (Ogle and

Reynolds 2004, Reynolds et al. 2004). Based on the depletion of water, carbon, and nutrients, plant and microbial activity will slow in the aftermath of storms (Ogle and Reynolds 2004, Belnap et al. 2005, Sponseller 2007, Collins et al. 2008). The depletion rate will depend on soil cover such as plants and biological soil crusts, evapotranspiration rate, and depth to which the soil moisture increased. For example, surface soils will be the first to dry and surface microbial communities, such as biological soil crusts, will be first to down-regulate activity (Collins et al. 2008). Subsurface microbial and plant activity may be able to continue for a longer period because these communities rely on deeper soil moisture reserves that are slower to deplete (Ogle and Reynolds 2004, Collins et al. 2008). These processes continue until water, carbon, or nutrients limits community activity (Belnap et al. 2005, Collins et al. 2008).

The pulse dynamics have been generalized further to incorporate water-mediated transfers of carbon and nutrients across the landscape when precipitation events are sufficiently large to generate overland and subsurface flow (Belnap et al. 2005, Welter et al. 2005, Collins et al. 2014). Intermediate-sized storms can redistribute materials across landscape patches, which are then subject to the potentially new biogeochemical conditions of the new patch (Belnap et al. 2005, Welter et al. 2005). Large storms can connect all landscape components, flushing any accumulated nutrients on the landscape into flood water (Welter et al. 2005, Welter and Fisher 2016). The transport rate for flood water generally exceeds the uptake and transformation rates for carbon and nutrients; therefore, high carbon and nutrient export in flood water results (Oldham et al. 2013). However, a high transport rate does not preclude any transformations from occurring during floods. For example, Welter et al. (2005) measured a loss in ammonium and an increase in nitrate without a substantial change in DIN concentration in sheet flow, indicating that nitrification can be substantial during floods. Regardless of transformation, organic matter, carbon, and nutrient pools remaining at the end of these pulses can be subject to large scale transport across landscape patches when large flood-generating storms occur (Ludwig and Tongway 1997, Belnap et al. 2005, Welter et al. 2005, Collins et al. 2008, 2014, Raymond et al. 2016).

When scaling these concepts to the watershed scale, it is important to consider how the activity in the stream channel is unique from hillslope responses. While hillslope soils can experience pulses, or hot moments, in activity associated with rain, stream channels act as biogeochemical hotspots of the landscape (McClain et al. 2003, Harms and Grimm 2008). Stream channels' position at topographic low points in the landscape means that they accumulate water and materials (Welter et al. 2005, Datry et al. 2014). As a result, these systems support higher microbial and plant activity than surrounding hillslopes during periods without precipitation (von Schiller et al. 2017). For example, fragmented pools in drying stream channels accumulate ammonium (von Schiller et al. 2017), alter dissolved organic matter composition (von Schiller et al. 2015), remove nitrate via denitrification (von Schiller et al. 2011), and release phosphate from sediments due to anaerobic conditions (Baldwin et al. 2000). Stream channels without surface water can retain elevated sediment moisture for an extended period relative to the surrounding hillslopes (Welter and Fisher 2016). Dry stream channels support nitrogen mineralization, nitrification, and denitrification, depending on the penetration of oxygen into sediments (Lillebø et al. 2007, McIntyre et al. 2009, Austin and Strauss 2011, Gómez et al. 2012, Arce et al. 2014, Merbt et al. 2016). Respiration rates of dry channels may account for between 0.4 and 9% of global carbon dioxide emissions from stream channels (von Schiller et al. 2014). As the stream dries, evaporation concentrates nutrients in sediments (McLaughlin 2008). The net results of biogeochemical processes during drying/rewetting cycles are subject to export in floods (Arce et al. 2014).

The extended periods that stream channels are active following precipitation may limit the applicability of pulse dynamics concept to watersheds (Collins et al. 2014); however, hillslopes constitute the vast majority of watershed area and may overwhelm the processes in stream channels with respect to nutrient export during floods. In this study, I investigated if the pulse dynamics concept applies to the watershed scale by examining the patterns in flood carbon (dissolved organic carbon, DOC) and nutrient (nitrate, ammonium, total dissolved nitrogen [TDN], soluble reactive phosphorus [SRP]) export from a 5th order watershed in the Sonoran Desert of Arizona. I hypothesized that floods following prolonged dry periods would have higher carbon and nutrient export because of accumulation of materials on hillslopes with limited biological retention and removal due to lack of precipitation. Conversely, I hypothesized that floods following periods with more precipitation will have lower carbon and nutrient export because the precipitation inputs will prompt biological transformation, uptake, and removal of carbon and nutrients from soils, reducing the pool of potentially mobile nutrients. I used a long-term dataset of carbon and nutrient concentrations in flood water combined with publicly available datasets on stream discharge and precipitation to test these hypotheses.

Methods

Site Description: Sycamore Creek is a tributary of the lower Verde River in central Arizona, USA. The watershed is 505 km^2 with elevation ranging from 420 to 2160 m (Thomsen and Schumann 1968). Sycamore Creek encompasses Sonoran Desert scrub, pinyon-juniper woodland, and spruce-fir forest depending on the elevations. Sycamore Creek is a spatially intermittent stream with regular floods that account for the majority of nitrogen export from the system (Ye and Grimm 2013). Summer and winter precipitation patterns and temperature differ substantially in the Sonoran Desert (Thomsen and Schumann 1968). The summer monsoon season is characterized by high-intensity, short-duration storms with limited spatial extent. Given the high summer air temperatures, evapotranspiration rates are high and limit soil moisture accumulation from storms (Reynolds et al. 2004). In contrast, winter storms derived from Pacific frontal systems have lower intensity, usually longer durations, and can have a much broader spatial extent. Lower winter temperatures are associated with lower evapotranspiration rates, longer persistence of elevated soil moisture, and an extended period of microbial and plant activity following precipitation (Welter et al. 2005, Sponseller 2007, Collins et al. 2008).

Sample collection and data processing: From 2010 to 2016 flood water samples were collected using a combination of grab samples and an automated water sampler (ISCO, Teledyne ISCO, Lincoln, Nebraska) at multiple locations along the stream channel. The time interval for sample collection varied from 10 minutes to 24 hours. The automated sampling program was designed to sample flood water every 10-30 minutes for the first 2-4 hours of collection in order to increase the chances of collecting sample at the maximum discharge for the flood. Then the sampler was programed to sample every hour until there were no more sample bottle remaining (N=24). Lab personnel retrieved the samples at the end of the program. If the stream was continuing to flood at the time of retrieval, lab personnel would reset the autosampler to collect every hour. Samples were returned to the lab, vacuum filtered using 0.45 µm Whatman GF/F (Whatman, Maidstone, United Kingdom) and stored frozen until analysis. Samples for ammonium were centrifuged at 12,000 rpm for 10 minutes prior to decanting in order to avoid volatilization during filtering. Nitrate/nitrite, ammonium, chloride, and SRP were run on a Lachat QuickChem 8000 (Hach Company, Loveland, Colorado). Non-purgible organic carbon (DOC) and TDN were run on a Shimadzu TOC-V (Shimadzu, Columbia, Maryland). Discharge from a United States Geological Survey (USGS) stream gauging station (USGS gauge #09510200) was retrieved for the period of flood data from 2010 to 2016.

I determined the cumulative flood discharge by taking the integral discharge from the start to the end of the flood. A flood constituted any flow that had maximum discharge >1 m^3/s; a flow sufficient to start automated stormwater collection. The start of a flood was identified as either the time that discharge transitioned from zero to a non-zero value, or when discharge changed from decreasing to increasing. The end of flood was defined as either (1) the cessation of flow (discharge = 0), (2) the arrival of a separate flood pulse (e.g., a switch from decreasing to increasing discharge), or (3) a three-hour period of stable discharge. I determined the nutrient in export in the flood water from the daily mean concentration (kg/m^3) for each day of the flood. The daily mean flood concentration (kg/m^3) was multiplied by the daily cumulative flood water export (m^3) to determine the daily flood nutrient export (kg). These daily export totals were summed to determine the cumulative nutrient export (kg) for each flood. For floods that spanned multiple dates but lacked nutrient concentration data for one of the dates, I used a concentration that was the midpoint between the mean concentration for the day prior to and the day following the date that lacked nutrient concentration data. If the final tail of the flood lacked nutrient data, I applied the mean nutrient concentration from the last day for which we had concentration. I determined the flood nutrient export (kg) by multiplying the mean flood concentration (kg/m^3) by the cumulative flood water export (m^3).

I was unable to use a flow-integrated method for concentration because (1) some flood samples lacked time information associated with their collection point and (2) the automated stormwater sampler was located 12 km upstream of the discharge gauging station. The latter limitation meant discharge and concentration may not have been the same at the two locations. Since the water velocity varies between floods, applying a time correction was not possible. When I did have time information for flood nutrient samples, a flow-integrated export was 1-5% lower than the estimate generated by the process described above. I therefore conclude that our method using daily means was sufficient to characterize flood chemistry.

I used the Next Generation Weather Radar (NEXRAD) Level III one-hour precipitation accumulation (product code N1P) data product for information about seasonal and storm precipitation. Radar sweeps were collected every 4-6 minutes and recorded any precipitation rate greater than 0.1 mm/hr (Figure 3.1). We used the NOAA Weather and Climate Toolkit to convert files from the native binary format into shapefile format. The shapefiles were clipped to the outline of the Sycamore Creek watershed boundary. Precipitation for each file was calculated as the precipitation rate for each location in the file (mm/hr) multiplied by the total area for which the precipitation rate was active (m^2) and the interval since the prior file (hr). The precipitation was summed and divided by the total area of the watershed to yield total precipitation for the file interval (mm). These precipitation numbers were summarized into daily and seasonal totals. Seasons were defined as summer from May to September and winter from October to April (Welter et al. 2005). I also calculated cumulative precipitation up to the flood date for the season in which the flood occurred. I summarized the spatial extent of the storm by finding the area of the watershed that had detectable precipitation in each NEXRAD sweep and taking the mean area (km^2) over the duration of the storm. I determined the event precipitation intensity (mm/hr) by dividing the storm total precipitation (mm) by the duration of the storm (hr).

I evaluated the extent to which precipitation at seasonal and event scales affected flood cumulative discharge, nutrient concentration, and nutrient load using linear regressions. Response variables were evaluated for normality by testing whether the skewness and kurtosis of the distribution of each variable were significantly different from that of a normal distribution. I log-transformed variables if necessary to achieve a distribution sufficiently close to normal. I regressed each of the independent variables against the dependent variables. In cases where multiple variables were related to the response variable, I performed multiple linear regressions to see if the combination of variables improved the prediction. I performed an F test to determine if the addition of extra variables significantly increased the explanatory power of the model. All spatial and statistical analyses were performed in R (R Core Team 2018).

Results

We sampled 22 floods on Sycamore Creek between 2010 and 2016. Of these floods, 20 floods included nitrate/nitrite data (hereafter referred to as “nitrate”); 18 floods included ammonium data, 13 had SRP data, 17 had DOC data, and 17 had TDN data. Of the 22 floods, 17 had discharge information. Discharge was missing for three of the floods because of a gap in the gauging station data and two of the floods had no discharge data because the water from the flood never reached the discharge gauging station location 12 km downstream from the automated stormwater sampler. Seventeen floods occurred in the winter season and 5 occurred in the summer. Flood water export ranged from 19×10^2 m^2 to over 18×10^6 m^3 (Table 1). Storm precipitation inputs ranged from zero to > 3×10^6 m^3. The extent of the watershed area experiencing precipitation varied within each storm, but mean storm area ranged from 30 to 280 km^2 (6 to 55% of the 505 km^2 watershed). Storm size characteristics including storm total precipitation, mean storm spatial extent, and precipitation intensity were all positively correlated (Figure 3.2).

Nutrient export was determined primarily by the flood cumulative discharge rather than the flood water nutrient concentration. The amount of water export during floods varied by more than five orders of magnitude. Most nutrient concentrations varied over two or three orders of magnitude. Cumulative flood discharge was positively correlated with cumulative precipitation in the season of the flood ($F = 6.73$, $R^2 = 0.264$, $p = 0.02$) and mean spatial extent of the storm ($F = 8.01$, $R^2 = 0.319$, $p = 0.013$; Figure

3.3); discharge was higher in winter than in summer (F = 8.97, R^2 = 0.332, p = 0.009; Figure 3.4a). A best fit model of cumulative discharge during floods included season (coefficient mean ± standard deviation: 2.29 ± 0.86), cumulative precipitation in the season leading up to the flood (0.34 ± 0.12), and precipitation intensity (2.18 ± 0.88; full model: F = 9.77, p = 0.002, R^2 = 0.64).

The winter season had significantly higher DOC and TDN export (F = 6.44, R^2 = 0.312, p = 0.028 and F = 7.56, R^2 = 0.354, p = 0.019; Figure 3.5b, c). Higher precipitation intensity resulted in higher DOC and TDN export (F = 5.63, R^2 = 0.312, p = 0.039 and F = 5.23, R^2 = 0.278, p = 0.045; Figure 3.5). Mean storm spatial extent significantly increased DOC and TDN export (F = 7.26, R^2 = 0.363, p = 0.023 and F = 8.46, R^2 = 0.404, p = 0.016; Figure 3.5b, e). The cumulative precipitation in the season prior to the flood had a significant negative effect on the amount of DOC and TDN export (F = 6.34, R^2 = 0.308, p = 0.029 and F = 7.28, R^2 = 0.344, p = 0.021; Figure 3.5b, e). Higher cumulative precipitation in the season leading up to the flood resulted in higher export of nitrate (F = 5.54, R^2 = 0.245, p = 0.035; Figure 3.6). None of the seasonal precipitation variables nor the storm characteristics correlated with ammonium or SRP export (data not shown). The ratio of nitrate to ammonium export was significantly higher in the winter (73.8 ± 3.9) than in the summer (12.7 ± 2.4).

The concentration of DOC and TDN decreased with higher precipitation in the season prior to the flood (F = 8.37, R^2 = 0.315, p = 0.011 and F = 8.37, R^2 = 0.315, p = 0.011; Figure 3.7).

Discussion

High variability in flood nutrient loads is characteristic of many aquatic ecosystems. Floods can account for the majority of the annual surface nutrient export budget (Meyer and Likens 1979, McKee et al. 2000, Ye and Grimm 2013). Under future climate conditions, low- or zero-flow conditions are expected to increase and floods may increase in size in the U.S. Southwest (Barnett et al. 2008) and Sycamore Creek (Ye and Grimm 2013). The anticipated increase in flood flows for the region necessitates a better understanding of the variability in nutrient loading from intermittent streams because these flows will increasingly be responsible for any connectivity between headwaters and downstream ecosystems. The goal of this project was to determine the relative importance of biological nutrient processing during dry periods and storm characteristics for nutrient export during floods in an intermittent desert stream. We found that nutrient loads in flood water were determined primarily by the amount of water exported in the flood. As a result, variables associated with higher flood water export also increased nutrient export in some cases. Floods in winter, storms with higher mean spatial extent, and higher current season precipitation led to high flood water export. Export of DOC and TDN were similarly higher for floods occurring in winter and with higher storm spatial extent. Higher precipitation in the prior season decreased DOC and TDN concentration and export in flood water; this may indicate a biological influence on the carbon and nitrogen pools available for export. Higher precipitation inputs in the prior season will have prompted pulses in microbial and plant community activity such as decomposition and dissolved inorganic nitrogen (DIN; nitrate and ammonium) uptake. This activity reduces the pool of DOC and TDN on the landscape that is available for export. Interestingly, few to none of the independent variables were related to nitrate, ammonium, and SRP concentration or export in flood water.

Cumulative water export during floods was higher in the winter than in the summer season and increased with higher mean area and higher current season precipitation. A best-fit model of flood water export included season, precipitation in the current season, and storm intensity. All measures of storm characteristics (size, spatial extent, intensity) were intercorrelated and higher in the winter season as compared to the summer season. Winter storms result in larger floods because temperatures are lower in the winter season and evapotranspiration water losses are lower, leaving more water available for export in floods. However, the intercorrelation among storm characteristics mean that the relationship between any one of these variables and flood characteristics should be interpreted with caution.

Channel water storage likely explains the positive relationship between current season precipitation and flood water export. Sycamore Creek is spatially intermittent because there are alternating stream segments that are relatively constrained within bedrock canyons and wider segments with substantial alluvial deposits that allow infiltration (Stanley et al. 1997). During extended dry periods, surface water only persists in the constrained sections of the canyon while the wider sections only have water below ground. This configuration gives rise to patterns in water chemistry (Dent et al. 2007) and wetland development (Dong et al. 2016). When there is more precipitation prior to a flood, this channel storage is filled and subsequent floods are lower because less water allocated toward filling the channel storage (Welter and Fisher 2016). This finding is consistent with results from the San Pedro River, where storms occurring later in the season after numerous other floods had higher peak discharge (Meixner et al. 2007). Indeed, there are two examples of floods that were detected by the automated stormwater sampler (so flooding conditions did exist in this section of the watershed), but ultimately no discharge from the flood reached the gauging station 12 km downstream. When water flow is attenuated by alluvial channel storage, nutrients are retained and stored with it.

In most cases, nutrient loads in flood water were determined by cumulative flood discharge rather than by the nutrient concentrations. As a result, some of the factors that led to high flood water export also led to higher nutrient export. Larger storms, with higher precipitation intensity and spatial extent, and storms that occurred in the winter had significantly higher DOC and TDN export. The relationship among storm characteristics and DOC/TDN export indicates that the transport and export of these nutrients during floods is driven primarily by physical processes. This finding is consistent with studies showing that floods generated from overland flow flush nutrients from the surrounding landscape into the stream channel (Fisher et al. 1982, Brooks and Lemon 2007, Meixner et al. 2007).

In addition to physical transport, DOC and TDN may also be sensitive to interflood decomposition and removal, because both concentration and export decreased with higher precipitation in the prior season. Higher precipitation in the prior season would have increased soil moisture, reducing litter due to from desiccation of the plant community. Elevated soil moisture would also support higher rates of organic matter decomposition, producing pulses of CO_2 efflux and denitrification that decrease the pools of DOC and TDN (Austin et al. 2004, Belnap et al. 2005, Welter et al. 2005). Higher precipitation may prompt vegetation community growth (Schwinning and Sala 2004) and increase uptake of DIN from the soil, further reducing the pool of TDN. Harms and Grimm (2010) found that microbial carbon uptake and nitrogen mineralization rates increased with higher antecedent precipitation. Precipitation prior to floods may therefore reduce the pool of DOC and release nitrogen from particulate or dissolved organic forms, which can be subject to uptake or removal. Less TDN with higher precipitation complements the finding that nitrate export in flood water increased with current season precipitation. On average nitrate accounted for 72% of the TDN in floodwater samples and the nitrate to ammonium ratio was highest in the winter season. As precipitation in the season increased, mineralization of organic matter and nitrification increased the pool of nitrate that was then available for export during flooding. Higher nitrate export with higher current season precipitation could also be an indirect effect of higher current season precipitation increasing flood water export. Since nutrient export was primarily driven by water export, this result could also be a result of physical transport by flood water.

My results suggest a series of direct and indirect effects on nutrient export due to storm characteristics and prior precipitation input (Figure 3.8). Water export increased with larger storms and higher precipitation in the current season. Both DOC and TDN export increased with larger storms and higher precipitation in the current season. Since large storms generate more flood water, the relationship between export and large storms may be an indirect effect of physical transport by flood water. Similarly, higher precipitation in the current season increased nitrate export, which also may be an indirect effect of higher discharge on this same variable. Finally, higher precipitation in the season prior to the flood decreased DOC and TDN concentrations in flood water and export, indicating an indirect effect on export of carbon and nitrogen that is mediated by biological processes that mineralize and remove or retain them in the watershed.

Nitrate, ammonium, and SRP export rates were not significantly related to storm characteristics and, except for nitrate export, were unrelated to antecedent precipitation. Although nutrient export was determined primarily by the amount of water exported during the flood, we expected antecedent factors to play a role in the amount of nutrients exported. We did not find any such relationships. This may indicate that nitrate, ammonium, and SRP concentrations are driven by factors at shorter timescales. For example, Harms and Grimm (2010) found that SRP concentrations in stream water were significantly related to cumulative precipitation over the prior 6-8 weeks rather than to other timescales. Further, they found no relationship between nitrate and ammonium and previous precipitation inputs. Brooks and Lemon (2007) also could not find consistent relationships between inorganic nitrogen concentration and discharge in a desert river. Since inorganic nitrogen is highly biologically reactive, these nutrients may be modified by biological activity during storms that produce floods. For example, Welter et al. (2005) found that the ratio of nitrate to ammonium increased along hillslope overland flowpaths during storms, while TDN concentration remained constant. Welter et al. concluded that nitrification of accumulated ammonium in soil occurred quickly during storms, thus altering the ratio of nitrate and ammonium. Therefore, if these nutrient pools change on event timescales, then the effect of biological activity over the current and prior season may not be detectable in stormflow.

Taken together, my results demonstrate that the pulse dynamics concept often used to understand biogeochemical fluxes in hillslope soils does apply to the watershed scale, with some modification. High precipitation in the season prior to the flood presumably led to more pulses in decomposition and transformation of carbon and nutrients. With more water available, there may have been higher productivity in microbial and plant communities, causing more uptake of carbon and nutrients from the soil. As a result, rain-driven pulses in activity prior to flooding reduced the size of the potentially mobile pool of DOC and TDN, reducing both the concentration and, ultimately, the export. However, many of the dissolved constituents in flood water were also related to storm characteristics. Therefore, pulse dynamics at the watershed scale must consider how physical processes such as the spatial extent of a storm, total storm precipitation, and channel water storage can modulate the amount of carbon and nutrients exported.

Regional climate change for the Southwest U.S. projects a warmer future. This warming is expected to decrease low and medium flow conditions in streams regardless of the changes in precipitation (which are not well constrained) because higher temperature increases evapotranspiration (Barnett et al. 2008, Ye and Grimm 2013). However, there are also projections that suggest increases in the magnitude of storms (Barnett et al. 2008). One consequence of these changes will be that more of the nutrient export from watersheds in this region will occur during floods Further understanding of the variability in flood nutrient loads is necessary to understand how future flow regimes may affect downstream ecosystems such as reservoirs and has associated implications for recreation and drinking water quality.

Acknowledgments

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Tables and Figures

Table 3.1. Flood water export and storm characteristics for 22 storm in the Sycamore Creek watershed. Some floods lacked discharge data (i.e., ND).

Season	Water Export (10^6 m^3)	Storm Volume (10^6 m^3)	Runoff Ratio	Storm Area (km^2)	Storm Intensity (mm/hr)	Current Season Precipitation (mm)	Prior Season Precipitation (mm)
Summer	0.01	0.35	0.02	60	0.3	2.3	12.9
Summer	0.00	0.05	0.04	30	0.1	2.9	12.9
Summer	0.52	0.63	0.83	180	1.3	6.0	12.9
Summer	0.04	0.67	0.06	140	0.6	3.2	4.6
Summer	0.41	0.46	0.89	170	0.9	4.7	4.6
Winter	18.43	3.34	5.52	280	1.8	7.1	5.4
Winter	2.10	0.29	7.25	170	0.9	11.0	5.4
Winter	4.48	0.76	5.90	190	0.6	12.0	5.4
Winter	0.19	0.63	0.31	190	0.6	2.0	2.3
Winter	0.11	0.08	1.36	150	0.8	2.3	2.3
Winter	8.13	0.75	10.83	150	0.7	3.2	2.3
Winter	0.05	1.06	0.04	250	1.0	2.1	2.7
Winter	2.68	0.82	3.26	210	1.3	3.4	2.7
Winter	0.20	0.57	0.36	180	0.7	3.1	3.4
Winter	1.57	0.39	4.01	160	0.5	3.8	3.4
Winter	1.60	0.07	22.91	90	0.1	9.6	5.4
Winter	0.82	0.00	NA	NA	NA	9.5	5.4
Winter	ND	0.15	NA	100	0.4	0.9	6.1
Winter	ND	0.04	NA	50	0.1	0.1	5.1
Winter	ND	0.39	NA	160	0.7	1.8	5.1
Winter	ND	0.00	NA	NA	NA	12.5	5.4
Winter	ND	0.00	NA	NA	NA	12.9	5.4
Means							
Summer	0.20	0.43	0.37	116	0.6	3.8	9.6
Winter	3.36	0.55	5.62	166	0.7	5.7	4.3

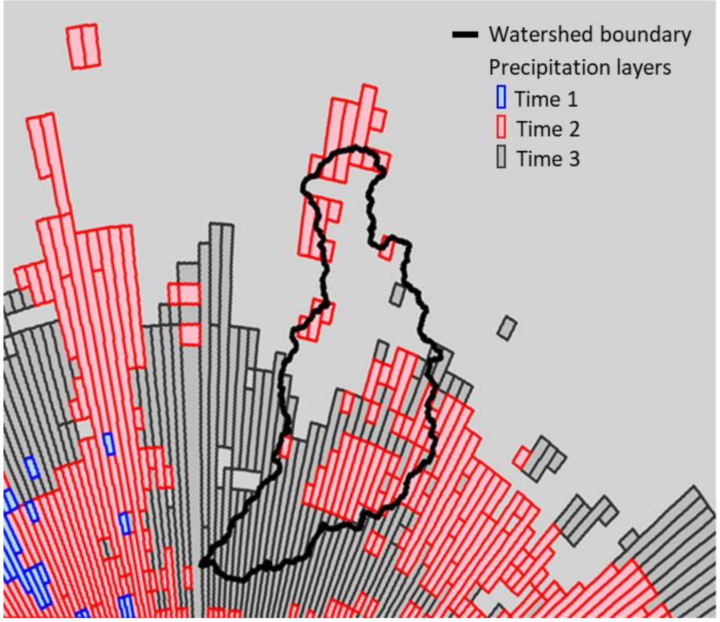

Figure 3.1. Next Generation Radar (NEXRAD) 1-hour precipitation (N1P) data layers at three timepoints for a storm with the Sycamore Creek watershed boundary. Each data layer contains polygons with unique 1-hour precipitation accumulation rates. Precipitation was calculated as the sum of the area of each polygon multiplied by the precipitation rate, summed across all polygons, and multiplied by the time interval between files (4-5 minutes).

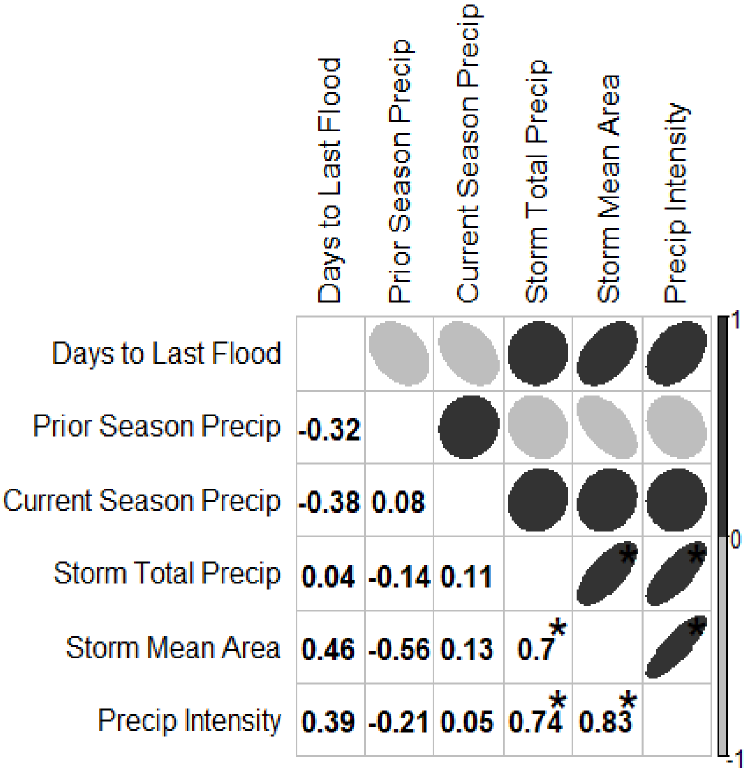

Figure 3.2: Correlation matrix of explanatory variables showing the strength of the relationship between variable in the form of the Pearson’s product moment correlation coefficient (lower triangle) and width of the ellipse (upper triangle), which shows the strength of the correlation. Dark grey indicates positive relationships and light grey are negative relationships. Asterisks indicate statistically significant relationships.

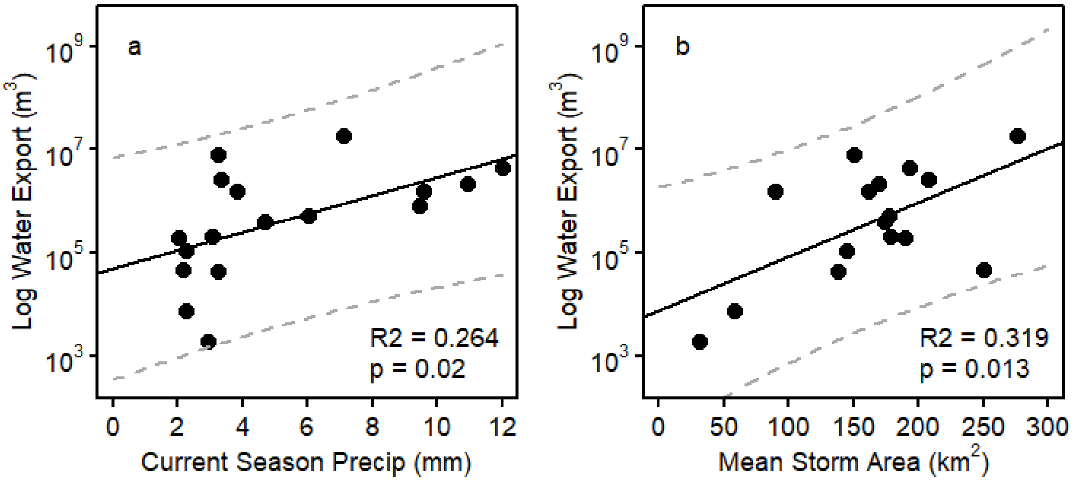

Figure 3.3: Cumulative flood water export as a function of (a) current season cumulative precipitation and (b) mean area of the storm. Solid lines are the regression relationship between the two variables and dashed lines are the 95% confidence intervals.

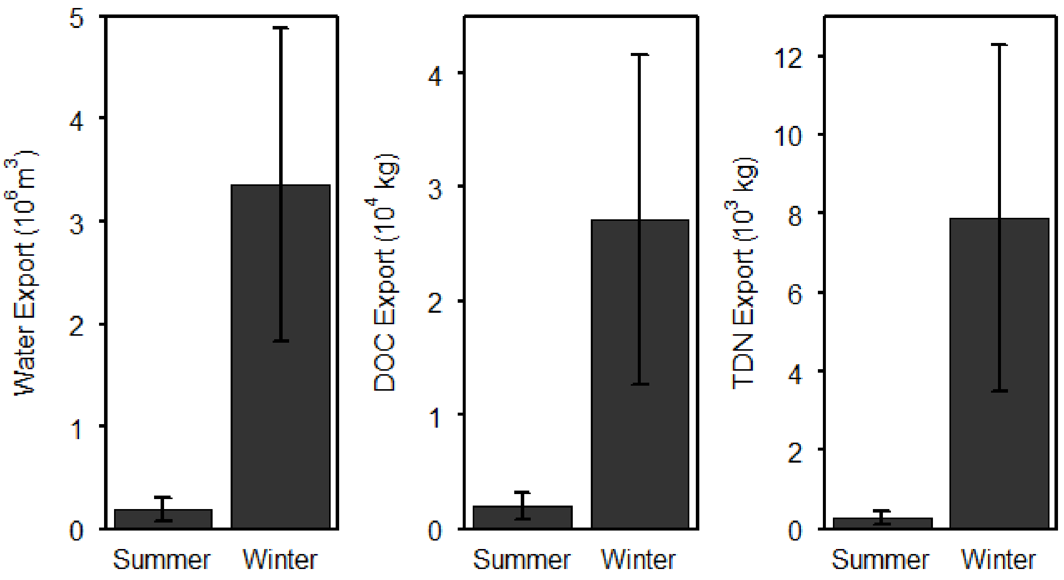

Figure 3.4: Mean flood export of (a) water, (b) dissolved organic carbon (DOC), and (c) total dissolved nitrogen (TDN) by season. Bars are ± one standard error of the mean.

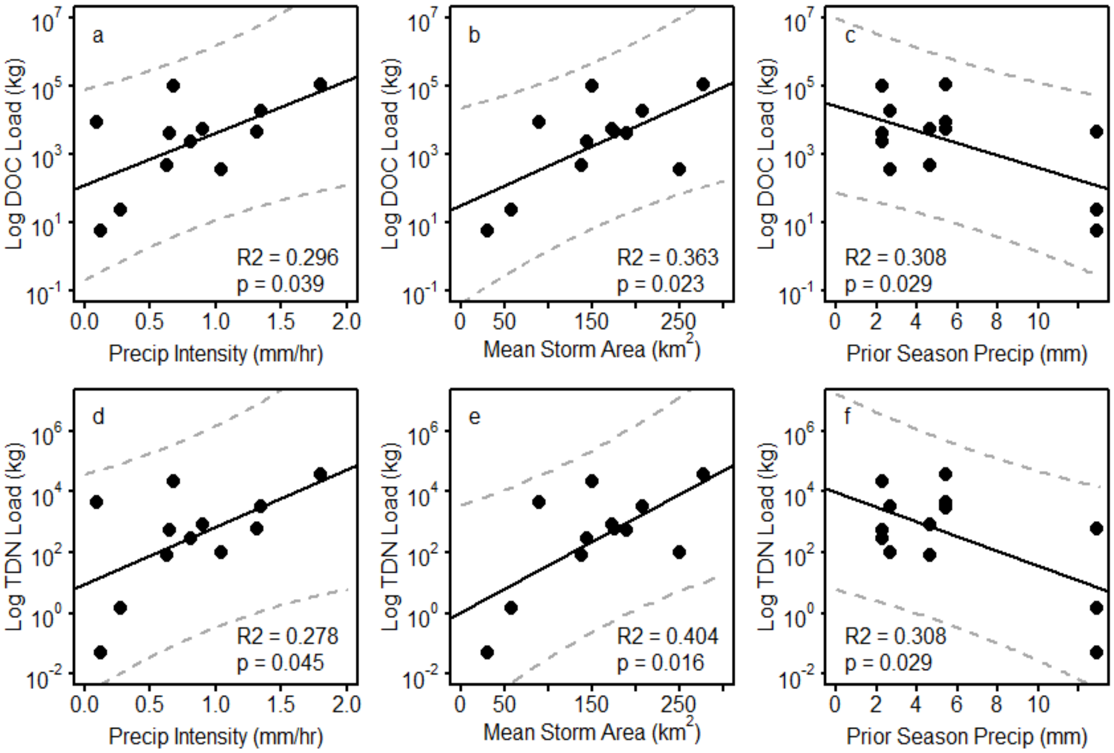

Figure 3.5: Log transformed dissolved organic carbon load (DOC; top) and log-transformed total dissolved nitrogen load (TDN; bottom) versus precipitation intensity(a,d), mean area(b,e), and prior season precipitation (c,f). Solid lines are the regression relationship between the two variables and dashed lines are the 95% confidence intervals.

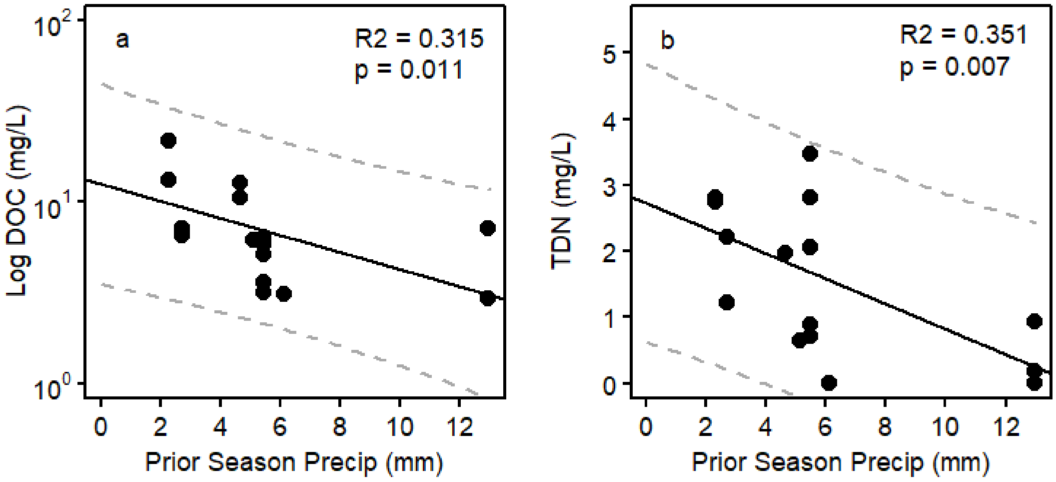

Figure 3.6: Dissolved organic carbon (DOC, a) and total dissolved nitrogen (TDN, b) as a function of prior season precipitation. Solid lines are the regression relationship between the two variables and dashed lines are the 95% confidence intervals.

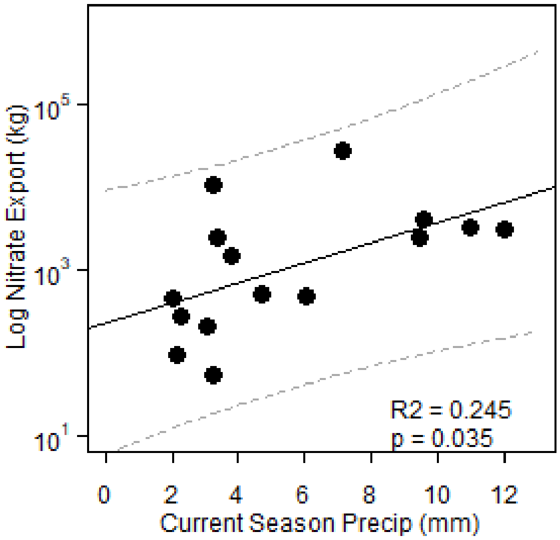

Figure 3.7: Nitrate export as a function of current season precipitation. Solid line is the regression relationship between the two variables and dashed lines are the 95% confidence intervals.

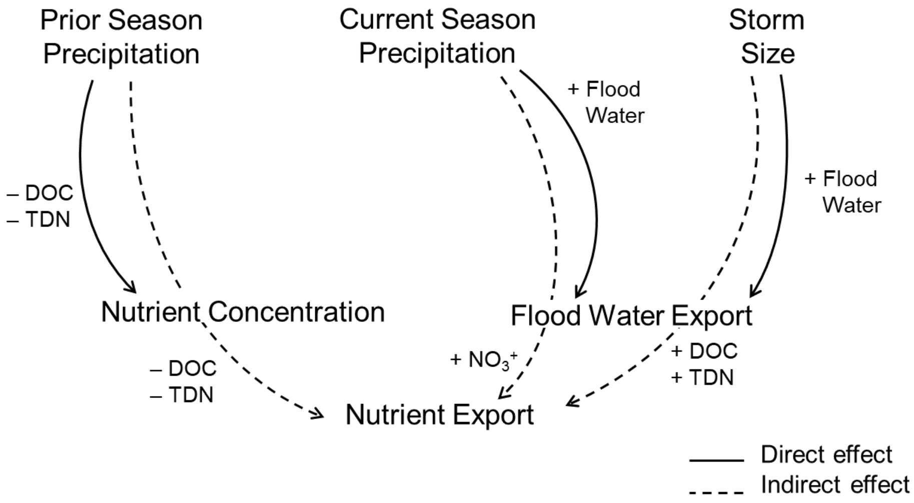

Figure 3.8. Proposed direct (solid arrows) and indirect (dashed arrows) effects of prior precipitation inputs and storm characteristics on discharge, dissolved organic carbon (DOC), total dissolved nitrogen (TDN), and nitrate (NO_3^-) concentrations and export in flood water for Sycamore Creek. Storm characteristics were all positively correlated and higher in the winter season and are grouped together as one factor as a result.

Literature Cited

Arce, M. I., C. Mendoza-lera, M. Almagro, N. Catalán, A. M. Romaní, E. Martí, R. Gómez, S. Bernal, A. Foulquier, M. Mutz, R. Marcé, A. Zoppini, G. Gionchetta, G. Weigelhofer, C. T. Robinson, A. Gilmer, M. Rulik, B. Obrador, O. Shumilova, S. Zlatanović, S. Arnon, P. Baldrian, G. Singer, T. Datry, N. Skoulikidis, B. Tietjen, and D. Von Schiller. 2019. A conceptual framework for understanding the biogeochemistry of dry riverbeds through the lens of soil science. Earth-Science Reviews 188:441–453.

Arce, M. I., M. del M. Sánchez-Montoya, M. R. Vidal-Abarca, M. L. Suárez, and R. Gómez. 2014. Implications of flow intermittency on sediment nitrogen availability and processing rates in a Mediterranean headwater stream. Aquatic Sciences 76:173–186.

Austin, A. T., L. Yahdjian, J. M. Stark, J. Belnap, A. Porporato, U. Norton, D. A. Ravetta, and S. M. Schaeffer. 2004. Water pulses and biogeochemical cycles in arid and semiarid ecosystems. Oecologia 141:221–235.

Austin, B. J., and E. A. Strauss. 2011. Nitrification and denitrification response to varying periods of desiccation and inundation in a western Kansas stream. Hydrobiologia 658:183–195.

Baldwin, D. S., A. M. Mitchell, and G. N. Rees. 2000. The effects of in situ drying on sediment-phosphate interactions in sediments from an old wetland. Hydrobiologia 431:3–12.

Barnett, T. P., D. W. Pierce, H. G. Hidalgo, C. Bonfils, D. Benjamin, T. Das, G. Bala, A. W. Wood, T. Nozawa, A. A. Mirin, D. R. Cayan, and M. D. Dettinger. 2008. Human-induced changes United States in the hydrology of the western United States. Science 319:1080–1083.

Belnap, J., J. R. Welter, N. B. Grimm, N. Barger, and J. A. Ludwig. 2005. Linkages between microbial and hydrologic processes in arid and semiarid watersheds. Ecology 86:298–307.

Birch, H. F. 1958. The effect of soil drying on humus decomposition and nitrogen availability. Plant and Soil 10:9–31.

Brooks, P. D., and M. M. Lemon. 2007. Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Butman, D., and P. A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geoscience 4:839–842.

Butman, D., R. Striegl, S. Stackpoole, P. del Giorgio, Y. Prairie, D. Pilcher, P. Raymond, and F. P. Pellat. 2018. Inland Waters. Pages 568–595 State of the Carbon Cycle 2.

Collins, S. L., J. Belnap, N. B. Grimm, J. A. Rudgers, C. N. Dahm, P. D. Odorico, M. Litvak, D. O. Natvig, D. C. Peters, W. T. Pockman, R. L. Sinsabaugh, and B. O. Wolf. 2014. A multiscale, hierarchical model of pulse dynamics in arid-land ecosystems. Annual Review of Ecology, Evolution, and Systematics 45:397–419.

Collins, S. L., R. L. Sinsabaugh, C. Crenshaw, L. Green, A. Porras-Alfaro, M. Stursova, and L. H. Zeglin. 2008. Pulse dynamics and microbial processes in aridland ecosystems. Journal of Ecology 96:413–420.

Datry, T., S. T. Larned, and K. Tockner. 2014. Intermittent rivers: A challenge for freshwater ecology. BioScience 64:229–235.

Davidson, E. A. 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Science Society of America Journal 56:95–102.

Dent, C. L., N. B. Grimm, E. Martí, J. W. Edmonds, J. C. Henry, and J. R. Welter. 2007. Variability in surface-subsurface hydrologic interactions and implications for nutrient retention in an arid-land stream. Journal of Geophysical Research: Biogeosciences 112:1–13.

Dong, X., N. B. Grimm, K. Ogle, and J. Franklin. 2016. Temporal variability in hydrology modifies the influence of geomorphology on wetland distribution along a desert stream. Journal of Ecology 104:18–30.

Fierer, N., and J. P. Schimel. 2003. A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil. Soil Science Society of America Journal 67:798–805.

Fisher, S. G., L. J. Gray, N. B. Grimm, and D. E. Busch. 1982. Temporal succession in a desert stream ecosystem following flash flooding. Ecological Monographs 52:93–110.

Fisher, S. G., N. B. Grimm, E. Martí, and R. Gómez. 1998. Hierarchy, spatial configuration, and nutrient cycling in a desert stream. Australian Journal of Ecology 23:41–52.

Gómez, R., I. M. Arce, J. J. Sánchez, and M. del Mar Sánchez-Montoya. 2012. The effects of drying on sediment nitrogen content in a Mediterranean intermittent stream: A microcosms study. Hydrobiologia 679:43–59.

Grimm, N. B. 1987. Nitrogen dynamics during succession in a desert stream. Ecology 68:1157–1170.

Grimm, N., and S. G. Fisher. 1986. Nitrogen limitation in a Sonoran Desert stream. North American Benthological Society 5:2–15.

Harms, T. K., and N. B. Grimm. 2008. Hot spots and hot moments of carbon and nitrogen dynamics in a semiarid riparian zone. Journal of Geophysical Research: Biogeosciences 113:1–14.

Harms, T. K., and N. B. Grimm. 2010. Influence of the hydrologic regime on resource availability in a semi-arid stream-riparian corridor. Ecohydrology 3:349–359.

Jarvis, P., A. Rey, C. Petsikos, L. Wingate, J. Pereira, J. Banza, J. David, F. Miglietta, M. Borghetti, G. Manca, and R. Valentini. 2007. Drying and wetting of Mediterranean soils stimulates decomposition and carbon dioxide emission: The "Birch effect." Tree Physiology 27:929–940.

Kurc, S. A., and E. E. Small. 2007. Soil moisture variations and ecosystem-scale fluxes of water and carbon in semiarid grassland and shrubland. Water Resources Research 43:1–13.

Larned, S. T., T. Datry, D. B. Arscott, and K. Tockner. 2010. Emerging concepts in temporary-river ecology. Freshwater Biology 55:717–738.

Lillebø, A. I., M. Morais, P. Guilherme, R. Fonseca, A. Serafim, and R. Neves. 2007. Nutrient dynamics in Mediterranean temporary streams: A case study in Pardiela catchment (Degebe River, Portugal). Limnologica 37:337–348.

Ludwig, J. A., and D. J. Tongway. 1997. A landscape approach to rangeland ecology. Pages 1–12 *in* J. Ludwig, D. Tongway, D. Freudenberger, J. Noble, and K. Hodgkinson, editors. Landscape ecology: Function and management. CSIRO Publishing, Collingwood, Victoria, Australia.

Marcé, R., B. Obrador, L. Gómez-Gener, N. Catalán, M. Koschorreck, M. I. Arce, G. Singer, and D. von Schiller. 2018. Emissions from dry inland waters are a blind spot in the global carbon cycle. Earth-Science Reviews 188:240–248.

McCalley, C. K., and J. P. Sparks. 2008. Controls over nitric oxide and ammonia emissions from Mojave Desert soils. Oecologia 156:871–881.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H. McDowell, and G. Pinay. 2003. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. Ecosystems 6:301–312.

McIntyre, R. E. S., M. A. Adams, and P. F. Grierson. 2009. Nitrogen mineralization potential in rewetted soils from a semi-arid stream landscape, north-west Australia. Journal of Arid Environments 73:48–54.

McKee, L., B. Eyre, and S. Hossain. 2000. Intra- and interannual export of nitrogen and phosphor us in the subtropical Richmond River catchment, Australia. Hydrological Processes 14:1787–1809.

McLaughlin, C. 2008. Evaporation as a nutrient retention mechanism at Sycamore Creek, Arizona. Hydrobiologia 603:241–252.

Meixner, T., A. K. Huth, P. D. Brooks, M. H. Conklin, N. B. Grimm, R. C. Bales, P. A. Haas, and J. R. Petti. 2007. Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Merbt, S. N., L. Proia, J. I. Prosser, E. Marti, E. O. Casamayor, and D. Von Schiller. 2016. Stream drying drives microbial ammonia oxidation and first-flush nitrate export. Ecology 97:2192–2198.

Meybeck, M., H. H. Dürr, and C. J. Vörösmarty. 2006. Global coastal segmentation and its river catchment contributors: A new look at land-ocean linkage. Global Biogeochemical Cycles 20:1–15.

Meyer, J. L., and G. E. Likens. 1979. Transport and transformation of phosphorus in a forest stream ecosystem. Ecology 60:1255–1269.

Noy-Meir, I. 1973. Desert ecosystems: Environment and producers. Annual Review of Ecology and Systematics 4:25–51.

Ogle, K., and J. F. Reynolds. 2004. Plant responses to precipitation in desert ecosystems: Integrating functional types, pulses, thresholds, and delays. Oecologia 141:282–294.

R Core Team. 2018. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. Ecology 97:5–16.

Reynolds, J. F., P. R. Kemp, K. Ogle, and R. J. Fernández. 2004. Modifying the "pulse-reserve" paradigm for deserts of North America: Precipitation pulses, soil water, and plant responses. Oecologia 141:194–210.

von Schiller, D., V. Acuña, D. Graeber, E. Martí, M. Ribot, S. Sabater, X. Timoner, and K. Tockner. 2011. Contraction, fragmentation and expansion dynamics determine nutrient availability in a Mediterranean forest stream. Aquatic Sciences 73:485–497.

von Schiller, D., S. Bernal, C. N. Dahm, and E. Martí. 2017. Nutrient and oganic matter dynamics in intermittent rivers and ephemeral streams. Pages 135–160 Intermittent Rivers and Ephemeral Streams. Elsevier Inc.

von Schiller, D., R. Marcé, B. Obrador, L. Gómez-Gener, J. P. Casas-Ruiz, V. Acuña, and M. Koschorreck. 2014. Carbon dioxide emissions from dry watercourses. Inland Waters 4:377–382.

Schlesinger, W. H., and W. T. Peterjohn. 1991. Processes controlling ammonia volatilization from Chihuahuan desert soils. Soil Biology and Biochemistry 23:637–642.

Schlesinger, W. H., J. F. Reynolds, G. L. Cunningham, F. Laura, W. M. Jarrell, R. A. Virginia, W. G. Whitford, S. Science, N. Series, N. Mar, W. H. Schlesinger, G. L. Cunningham, R. A. Virginia, W. G. Whitford, L. F. Huenneke, and W. M. Jarrell. 1990. Biological feedbacks in global desertification. Science 247:1043–1048.

Schwinning, S., and O. E. Sala. 2004. Hierarchy of responses to resource pulses in arid and semi-arid ecosystems. Oecologia 141:211–220.

Sponseller, R. A. 2007. Precipitation pulses and soil CO2 flux in a Sonoran Desert ecosystem. Global Change Biology 13:426–436.

Stanley, E. H., S. G. Fisher, and N. B. Grimm. 1997. Ecosystem expansion and contraction in streams. Bioscience 47:427–435.

Thomsen, B. W., and H. H. Schumann. 1968. Water resources of the Sycamore Creek watershed, Maricopa County, Arizona. Page United States Geological Survey Water-Supply Paper.

Tooth, S. 2000. Process, form and change in dryland rivers: A review of recent research. Earth Science Reviews 51:67–107.

Welter, J. R., and S. G. Fisher. 2016. The influence of storm characteristics on hydrological connectivity in intermittent channel networks: Implications for nitrogen transport and denitrification. Freshwater Biology 61:1214–1227.

Welter, J. R., S. G. Fisher, and N. B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76:421–440.

Xu, L., D. D. Baldocchi, and J. Tang. 2004. How soil moisture, rain pulses, and growth alter the response of ecosystem respiration to temperature. Global Biogeochemical Cycles 18:1–10.

Yahdjian, L., and O. E. Sala. 2010. Size of precipitation pulses controls nitrogen transformation and losses in an arid Patagonian ecosystem. Ecosystems 13:575–585.

Ye, L., and N. B. Grimm. 2013. Modelling potential impacts of climate change on water and nitrate export from a mid-sized, semiarid watershed in the US Southwest. Climatic Change 120:419–431.

CHAPTER 4

NITRATE REDUCTION CAPACITY AND PATHWAYS OF URBAN ACCIDENTAL WETLANDS IN PHOENIX, ARIZONA

Abstract

Due to nitrate pollution, much research has focused on denitrification, a microbial transformation of nitrate to nitrogenous gas that effectively removes nitrogen from the ecosystem. However, there are other microbial processes that transform nitrate, including dissimilatory nitrate reduction to ammonium (DNRA), a process that conserves nitrogen in a biologically reactive form. In this study, I investigated rates of denitrification and DNRA at two sites in the Salt River accidental wetlands near downtown Phoenix, Arizona. I conducted an *ex-situ* soil microcosm incubation and an *in-situ* push-pull experiment in the three main patch types in the wetlands: dominant cover of *Typha domingensis*, dominant cover of *Ludwidgia peploides*, and open, unvegetated patches. DNRA accounted for between 0 and 38% of nitrate reduction while denitrification accounted for between 62 and 100%. The *L. peploides* patches had significantly elevated process rates compared to open patches and *T. domingensis* patches across experiments, indicating that this patch type promoted nitrate reduction. Interestingly, this pattern was not driven by dissolved organic carbon (DOC), which was significantly higher in the 7th Avenue bridge site that also had lower DNRA rates, leading to a negative correlation. Higher NO_3^- concentrations were associated with higher denitrification rates; high NO_3^- was unrelated to DNRA rates. I propose that as NO_3^- concentration increases during floods, denitrification increases while DNRA rates remain relatively stable. As NO_3^-

concentration falls, DNRA begins to account for proportionally more of the NO_3^- reduction. This research indicates that DNRA may serve as an important nitrogen conservation mechanism during low NO_3^- supply periods in urban wetlands.

Introduction

Nitrogen is an essential, often limiting, element for biological growth that can also be a pollutant if present in excess. Urban aquatic systems are particularly vulnerable to nitrogen pollution because of high nitrogen inputs, limited infiltration in uplands, and stormwater infrastructure designed to quickly transport runoff to recipient aquatic systems (Baker et al. 2001, Kaye et al. 2006). As a result, much research has been dedicated to understanding nitrogen transport and transformation in urban ecosystems with a particular focus on denitrification (Groffman et al. 2006). Denitrifying microbes transform biologically reactive nitrate (NO_3^-) to biologically less-reactive nitrogenous gases (N_2 and N_2O), effectively removing nitrogen from ecosystems. However, denitrification is just one of many potential transformation pathways for NO_3^- (Burgin and Hamilton 2007). Dissimilatory nitrate reduction to ammonium (DNRA) also consumes nitrate but produces biologically reactive ammonium (NH_4^+). The resulting NH_4^+ is available for plant uptake, assimilation by organisms, and nitrification, thereby conserving the element within the ecosystem (An and Gardner 2002). Denitrification and DNRA occur in locations with high organic carbon availability and low oxygen conditions. These conditions are common in wetland ecosystems where water-saturated soils and abundant plant growth and litter inputs fuel reducing conditions. This study investigates the relative rates of denitrification and DNRA in an urban accidental wetland ecosystem (sensu Palta et al. 2017) and how plant patches and NO_3^- concentration affect the rate of each process.

Relatively few studies have examined DNRA compared to the number of studies on denitrification. Many DNRA studies have taken place in coastal ecosystems (see Giblin et al. 2013 for a review) but the process has also been measured in streams (Kelso et al. 1997, Storey et al. 2004), lakes (Brunet and Garcia-Gil 1996), constructed freshwater wetlands (Scott et al. 2008), hot springs (Dodsworth et al. 2011), and soils (Silver et al. 2001, Rütting et al. 2011). To our knowledge, DNRA has not been measured in urban ecosystems. Nitrate can enter urban aquatic ecosystems through stormwater transport of applied fertilizer and atmospheric deposition, as well as through treated wastewater discharge and leaky septic systems (Paul and Meyer 2001). Therefore, understanding the relative proportion of denitrification and DNRA is crucial to understanding when nitrogen is removed and when nitrogen is conserved in urban ecosystems.

Plant cover and type can regulate nitrogen cycle transformations, including denitrification and DNRA, by providing a source of organic carbon to the heterotrophic organisms carrying out these processes (Alldred and Baines 2016). Plant litter quality, as measured by labile and structural carbon content, can directly affect carbon availability to microbial communities (Hume et al. 2002). Plants that have more structural carbon compounds, such as lignin, produce litter that is less bioavailable than plants with lower structural carbon content. Therefore, as the type and lability of carbon changes from patch to patch, so too will the magnitude of NO_3^- reduction processes.

Like denitrification, DNRA is controlled by the amount of available oxygen, NO_3^-, and carbon. However, the relative amounts of NO_3^- and carbon could affect which process dominates NO_3^- transformations. Tiedje (1988) proposed that DNRA is favored under low NO_3^-, high organic carbon conditions due to a higher electron transfer efficiency; in contrast, denitrification is favored under high NO_3^-, high organic carbon conditions. While studies in freshwater ecosystems have found evidence of higher denitrification rates compared to DNRA under high carbon, high NO_3^- conditions (Scott et al. 2008, Nizzoli et al. 2010), few studies have examined DNRA and denitrification rates under low NO_3^-, high carbon conditions (but see Storey et al. 2004). Some studies have found the highest NH_4^+ accumulation under low NO_3^-, high organic carbon conditions (Kelso et al. 1997, Scott et al. 2008, Crenshaw et al. 2010). Understanding which NO_3^- transformation dominates and when it dominates is particularly salient in urban aquatic ecosystems that experience frequent fluctuations in NO_3^- concentration, and potentially corresponding changes in the relative rates of DNRA and denitrification. Denitrification may dominate under high NO_3^- conditions such as during high-flow periods and DNRA may become a proportionally more important larger process only under lower NO_3^- conditions, such as between periods of high flow.

The objective of our research was twofold: (1) To quantify DNRA and denitrification activity in urban wetlands across patch types I hypothesized to have different carbon quantities, and (2) to test if NO_3^- concentration affected DNRA rates relative to denitrification rates. This research took place in the Salt River accidental wetlands (Palta et al. 2017) near Phoenix, AZ that receive fluctuating NO_3^- inputs depending on stormwater flow. I measured water chemistry in the wetlands to determine the degree of hydrologic connectivity between surface and subsurface water and connectivity across patch types. I used two approaches to measure DNRA and denitrification: (1) a laboratory microcosm experiment with soil from the field site incubated with two different levels of NO_3^- and (2) a push-pull method, incubating a plume of enriched water *in-situ*.

Methods

Site information

The Salt River is a tributary of the Gila River and part of the larger Lower Colorado River Basin. The river has been heavily modified by dams and diversion canals to support agricultural and municipal water demand (Fitzhugh and Richter 2004, Larson et al. 2005). All flow is diverted into canals upstream of Phoenix and, as a result, the stretch of river in the city lacks baseflow except during floods when water is released from the six upstream dams. However, portions of the Salt River channel in Phoenix receive water from irrigation and storm runoff (Makings et al. 2011, Bateman et al. 2015). These water sources support riparian and wetland vegetation, creating “accidental” wetland habitats that are not actively managed (Bateman et al. 2015, Palta et al. 2017). Dissolved inorganic nitrogen (DIN) concentration increases dramatically during storm flow (Palta et al. 2017), but microbial activity in the soil is nitrogen-limited during base flow (Suchy 2016). Where surface water is present, the wetlands are characterized by three main patch types: 1) dominant cover of *Typha domingensis* (TYDO), 2) dominant cover of *Ludwigia peploides* (LUPE), and 3) and open, non-vegetated areas with gravel-dominated substrate (OPEN). I conducted our investigations at two wetland sites in the

Salt River as is part of the Central Arizona-Phoenix Long Term Ecological Research program study area: one near Central Avenue (CEN) and one near 7th Avenue (7A), in Phoenix, Arizona (Figure 4.1).

Background water chemistry

I collected baseflow water-chemistry samples at the two sites in October, 2014 to determine the degree of hydrologic connectivity in the wetlands. At each wetland site, I identified two locations, one near a storm drain and one downstream from the drain location. At each location I identified three patches (LUPE, TYDO, and OPEN) and two sampling points within each patch. At each sampling point, I collected subsurface water with a porewater sampler (PushPoint Sampler, MHC Products, East Tawas, MI) attached to a GeoPump (Geotech Environmental Equipment, Inc. Denver, CO). I also collected surface water samples adjacent to the subsurface sampling point. Samples were transported on ice and filtered with a pre-combusted (4 hr at 490°C) 0.45 µm glass fiber filter (Whatman GF/F, Pittsburg, PA) in the laboratory. Samples were stored at –20°C for four weeks until analysis. I analyzed each sample for chloride (Cl^-), bromide (Br^-), NO_3^-, NH_4^+, phosphate (PO_4^{3-}), dissolved organic carbon (DOC), and total dissolved nitrogen (TDN) concentration.

Lab incubation experiment

To compare denitrification and DNRA rates under different NO_3^- concentrations, I conducted a paired-microcosm incubation of wetland soil. In December 2015, I collected approximately 5 kg of soil from one TYDO, one LUPE, and one OPEN patch at the 7A site on the day prior to the incubation. I also collected 8 L of surface water from a location adjacent to the soil collection site. Samples were stored on ice and immediately returned to the lab where I homogenized soil samples by patch type and removed particles >2 cm diameter. Each microcosm contained 500 g of the patch-specific homogenized soil in 1 L glass bottles. The bottles were covered with gas-tight caps and stored at 4°C until 4 h prior to the experiment for equilibration to room temperature. I added 500 mL of NO_3^--amended surface water to the soil at concentrations of 1 mg N/L (low treatment) or 7 mg N/L (high treatment) at 1 atom percent (at%) ^{15}N. There were 5 replicates for each patch and treatment level, for a total of 30 paired microcosms. I sparged the water overlying the sediments with N_2 gas for one minute to minimize dissolved oxygen (DO) and then capped the bottles. The initial microcosm was sampled 1 h following capping and the paired final microcosm was sampled 8 h later. I collected the dissolved N_2 gas sample by uncapping the microcosm and slowly drawing water into a 60 mL syringe. I filled 12-mL Exetainers (Labco Lampeter, Wales, United Kingdom) from the bottom up, overfilling approximately twice before poisoning with 20 µL saturated $ZnCl_2$ solution to prevent further microbial activity and then capping. I decanted and filtered any remaining water in the microcosm through a pre-combusted (4 hr at 490°C) 0.45 µm glass fiber filter (Whatman GF/F, Pittsburg, PA) and stored at –30°C for 4-8 weeks prior to analysis for NO_3^-, NH_4^+, $^{15}NO_3^-$, $^{15}NH_4^+$, and DOC concentrations.

In-situ push-pull incubation

To compare denitrification and DNRA rates in the field, I conducted an *in-situ* push-pull experiment (modified from Addy et al. 2002). The push-pull method involves enriching field-collected water with the biologically reactive tracer (NO_3^-) and an unreactive tracer to account for dilution (Br^-), injecting the water into the subsurface (“push”), and sampling from the plume after an incubation period (“pull”). I used bromide rather than chloride as a tracer because the background chloride concentration was high in the wetland and would have required large additions to raise the concentration to a level usable in the experiment, levels which may have been toxic to the organisms exposed to the water. I conducted experiments over four days in June 2016. On each date, I conducted two push-pull tests in each of the three dominant patch types for a total of six tests per date. I used 2.5 mm inner-diameter wells inserted to a depth of 7 cm. The wells had radial perforations around the bottom 1 cm and were capped at the base. I placed a 5 cm^2 rubber cap that sat flush with the soil surface on each well to prevent drawdown of surface water along the sides of the well. I collected a background dissolved N_2 gas sample by attaching a 60 mL syringe directly to the well and transferring to an Exetainer using the method described above. I then collected an additional 340 mL of porewater, to which I added a 20 mL dosing solution that enriched the field water by 7 mg N/L at 20 at% ^{15}N and 20 mg/L bromide (Br^-). Care was taken to minimize introduction of bubbles into the solution. I collected initial samples from this solution for analysis of NO_3^-, NH_4^+, $^{15}NH_4^+$, Br^-, and DOC. The remaining 190 mL of tracer-enriched solution was injected ("pushed") into the well. After a 30-minute incubation period I collected ("pulled") samples. The dissolved N_2 sample was collected first, followed by samples for analysis of NO_3^-, NH_4^+, $^{15}NH_4^+$, and Br^- (I assumed DOC concentration would not change substantially over a 30-minute period). All aqueous samples were field filtered using 0.45 µm mixed cellulose ester syringe filters (Fisher Scientific, Waltham, MA) and stored on ice until returned to the lab. Samples were stored at –30°C for 4-12 weeks until analysis.

Soil properties

To determine soil physical properties, I collected saturated soil cores of known volume from the same locations used for the push-pull experiment or the nearest saturated soil to the experiment location on June 15, 2017. I recorded the saturated core mass, then dried the cores at 60°C to constant mass and reweighed. I assumed a 1 g per 1 mL mass-volume relationship for the water mass lost to calculate the porosity as mass H_2O lost divided by the mass of bulk soil core.

Chemical analyses

I analyzed bromide ($Br^–$) using ion chromatography (Dionex ICS 1000, Thermo Scientific, Waltham, MA); $NO_3^–$, NH_4^+, $PO_4^{3–}$, and $Cl^–$ using a Lachat QC 8000 flow injection analyzer (Lachat Instruments, Loveland, CO); and dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a Shimadzu TOC-V (Shimadzu, Columbia, Maryland). Any concentration below the range of the instrument standard curve were assigned a value of one-half of the lowest concentration on the standard curve. I measured $^{15}N-NH_4^+$ by headspace diffusion of filtered water samples (Holmes et al. 1998). I measured $^{15}N-NO_3^–$ using reduction with Devarda's alloy followed by headspace diffusion on filtered water samples (Sigman et al. 1997). All aqueous ^{15}N samples were analyzed by an Elementar Vario EL Cube or Micro Cube elemental analyzer (Elementar Analysensysteme GmbH, Hanau, Germany) interfaced to a PDZ Europa 20-20 isotope ratio mass spectrometer (Sercon Ltd., Cheshire, UK) at the Stable Isotope Laboratory of the University of California, Davis. I determined N_2 gas concentration and isotopic composition using a membrane inlet mass spectrometer (MIMS; Bay Instruments, Easton, MD, USA; Kana et al. 1994, An et al. 2001).

Calculations and Analysis

I calculated NO_3^- consumption and NH_4^+ production rates as the change in N concentration in the respective N pool during the incubation period normalized to the mass of dry soil per hour. I calculated the denitrification rate based on the excess $^{29}N_2$ and $^{30}N_2$ signals in the N_2 pool after Nielson (Nielson 1991):

$$D_{15} = 2p_{30} + p_{29}, \qquad \text{Eq 4.1}$$

where p_{30} and p_{29} are the net production rates of $^{30}N_2$ and $^{29}N_2$, respectively. DNRA was calculated as the net production rate of $^{15}NH_4^+$ (Koop-Jakobsen and Giblin 2010). I performed multiple linear regressions of flux rates (NO_3^- flux, NH_4^+ flux, denitrification, DNRA) with explanatory variables including for patch, site, sample date, initial NO_3^- concentration, and initial DOC concentration. Response variables were evaluated for normality by testing whether the skewness and kurtosis of the distribution of each variable was significantly different from that of a normal distribution. I log-transformed variables if necessary to achieve a distribution sufficiently close to normal. Categorical variables including the site, patch cover, or sampling date were included as dummy codes in the models. All initial models included the variables for patch, site, sample date, initial NO_3^- concentration, and initial DOC concentration. Models were selected based AIC values that helps to identify models that explain the greatest amount of variation in the response variable while maintaining parsimony. All calculations and analyses were performed in R Studio (Version 1.1, r-project.org).

Results

Background water chemistry

Background water chemistry differed among patches, between surface and subsurface waters, and between sites (Figure 4.2). The only difference in water chemistry between patches was that DOC concentration was significantly higher in the TYDO patches compared to the open patches (mean ± SE: 6.73 ± 0.40 vs. 5.68 ± 0.17 mg/L). The DOC concentration in the LUPE patches was statistically indistinct from both the TYDO and open patches. Nitrate and NO_2^- concentrations were significantly higher in the surface water compared to the porewater (0.23 ± 0.05 vs. 0.02 ± 0.01 mg/L & 0.05 ± 0.01 vs. 0.006 ± 0.002 mg N/L for NO_3^- and NO_2^-, respectively); NH_4^+ concentration showed the opposite pattern with higher concentrations in the porewater compared to the surface (0.12 ± 0.01 vs. 0.47 ± 0.09 mg N/L). Chloride was higher in the surface compared to the porewater (51.4 ± 3.8 vs. 43.5 ± 2.8 mg/L) and PO_4^{3-} had the opposite pattern with higher concentration in the porewater compared to the surface (21.3 ± 2.3 vs. 46.7 ± 13.7 µg P/L). Nitrate, NO_2^-, Cl^-, and DON were significantly higher at CEN compared to 7A, while DOC concentration was higher at 7A.

Microcosm incubation experiment

Mean NH_4^+ production was 0.023 ± 0.041 µg N g dry soil^{-1} h^{-1} (Figure 4.3). Two observations were more than three standard deviations from the mean, leading to the high variation. When these points were removed, the NH_4^+ production ranged from -0.041 to 0.097 µg N g dry soil^{-1} h^{-1} and LUPE patches had significantly higher rates compared to open patches (Table 4.1) but did not significantly differ based on the NO_3^- amendment level. The NH_4^+ flux in the TYDO patches was statistically similar to the rates measured in both the LUPE and TYDO patches. Net NO_3^- consumption occurred in all microcosms with one exception. A higher starting NO_3^- concentration was significantly positively correlated with NO_3^- consumption. Changes in the isotope pools for NH_4^+ and N_2 were small for some microcosms, such that I could not be confident that the changes were signals from the added $^{15}NO_3^-$. I selected microcosms with >30‰ increase in the $\delta^{15}N$ of the NH_4^+ pool as a threshold for calculating DNRA; 16 of the 29 microcosms met the threshold. Our rationale for this selection was that naturally fractionating nitrogen transformations could have been responsible for a change below the threshold (Sharp 2017). For this subset of rates of DNRA ranged from 0.004 to 0.052 ng N g dry soil^{-1} h^{-1}; rates were significantly higher in the LUPE and TYDO patches compared to the open patches. For denitrification, I selected microcosms for which I measured any positive increase in the $^{29}N_2$ or $^{30}N_2$ pools as a threshold for calculating denitrification; 16 of the 26 microcosms met the threshold. For this subset, denitrification ranged from 0 to 0.65 µg N g dry soil^{-1} h^{-1} and was significantly positively correlated with NO_3^- concentration.

In-situ push-pull experiment

Ammonium production ranged from 0.04 to 3.4 µg N g dry soil^{-1} h^{-1} and was significantly higher in the LUPE patches compared to the OPEN patches and significantly negatively correlated with DOC concentration (Figure 4.4; Table 4.1). Four wells from OPEN patches had net NO_3^- production over the incubation period while all other 18 wells had net NO_3^- consumption. The NO_3^- flux ranged from -10.5 to 1.4 µg N g dry soil^{-1} h^{-1}. Nitrate consumption was significantly positively correlated with starting NO_3^- concentration and was significantly higher in the LUPE patches compared to the open patches. Rates of DNRA ranged from 0.03 to 2.0 µg N g dry soil^{-1} h^{-1} and were significantly higher in the LUPE patches compared to the OPEN patches; DNRA decreased significantly with increasing DOC concentration. Denitrification rates ranged from 0.20 to 11.6 µg N g dry soil^{-1} h^{-1} and were significantly higher in the LUPE and TYDO patches compared to the open patches. The ratio of denitrification to DNRA ranged from 1.4 to 42.8 with a median value of 8.2. Between 51 and 97% of the Br^- was lost due to advection during the incubation period. Accounting for dilution, I recovered between 3 and 95% of the ^{15}N-NO_3^- tracer as either N_2 or NH_4^+. From 27 to 79% of the tracer remained in the NO_3^- pool. Between 4 and 69% of the ^{15}N-NO_3^- tracer was not recovered in either the NO_3^-, NH_4^+, or N_2 pools.

Discussion

Our research objectives were to (1) quantify DNRA activity in urban wetlands across patches that I hypothesized to have different carbon quantities and (2) to test if NO_3^- concentration affected DNRA activity relative to denitrification. I found that DNRA accounted for a substantial portion of NO_3^- reduction in the Salt River Wetlands. The highest DNRA rate was associated with the vegetated patches in the microcosm experiment. For the *in situ* push-pull experiment, the highest rate occurred in the LUPE patches; the OPEN and TYDO patches had similar rates. Nitrate concentration had no relationship with DNRA rate, indicating that this process is controlled by other local factors.

The differences in surface water and porewater chemistry of the wetlands illustrate two specific redox zones common in wetlands: (1) oxic conditions in the surface water that allow nitrification and (2) anoxic or hypoxic subsurface conditions that support anaerobic processes of NO_3^- and NO_2^- reduction (Mitsch and Gosselink 2015). Supply of NO_3^- and NO_2^- is likely limited by diffusion from the surface water, where nitrification is taking place (Golterman 2000). Ammonium likely accumulates in the subsurface as mineralization of organic matter exceeds nitrification, given low oxygen availability (Mitsch and Gosselink 2015). Except for DOC, all analytes measured had similar concentration among the patch types, indicating either that patches do not have a significant effect on concentration or that lateral hydrologic mixing makes these signals undetectable. Interestingly, NO_3^-, NO_2^-, Cl^-, and DOC significantly differed between the CEN and 7A sites. These wetlands are fed by separate outlet pipes that drain different urban catchments and results suggest that water chemistry may reflect different characteristics or activities within the two catchments (Walsh et al. 2005, Palta et al. *unpublished data*). Studies in urban catchments in Phoenix (Lewis and Grimm 2007, Hale et al. 2014a) and Baltimore (Kaushal et al. 2011) found dissolved inorganic nitrogen (DIN) export varied significantly based on different land-use cover and stormwater infrastructure type. Lewis and Grimm (2007) found evidence that DIN export was related to accumulation of potentially mobile nitrogen on impervious surfaces that is quickly transported and exported from catchments during floods with little time for retention. Newcomer et al. (2012) found that urban streams differed in DOC quantity and composition based on the DOC sources within the drainage. The sites in this study have different characteristics. The 7th Ave site (7A) drains a portion of the urban core of downtown Phoenix while the Central Ave (CEN) site drains a much larger area with more residential cover. These differences may be driving differences in water chemistry between the sites.

Both the laboratory microcosm incubation and the push-pull experiments demonstrate that accidental wetlands in the Salt River channel have the capacity for NO_3^- consumption through both denitrification and DNRA. In the microcosm experiment, denitrification accounted for less than 1% and up to 38% of the NO_3^- flux; DNRA always accounted for less than 0.1% of the NO_3^- consumption (but see section on methodological considerations). In the push-pull experiment, denitrification accounted for between 2% and 49% of the ^{15}N mass balance and DNRA accounted for between 0.2% and 10%. Even though DNRA consumed a smaller amount of nitrate relative to denitrification, DNRA conserves nitrogen in the wetland rather than removing it. This nitrogen may further exacerbate elevated dissolved inorganic nitrogen concentrations in the wetlands, but may also serve as a sustained source of nitrogen during periods of nitrogen limitation (An and Gardner 2002).

Denitrification was dependent on NO_3^- concentration in the microcosm experiment, but not in the push-pull experiment. Since the NO_3^- concentration remained high throughout the push-pull experiment, with a mean NO_3^- concentration of 0.8 mg/L at the end of the incubation period, it is likely that NO_3^- was not limiting. Many studies have demonstrated that denitrification exhibits first-order dependence on NO_3^- concentration (Weier et al. 1993, Mulholland et al. 2008). However, DNRA was not related to NO_3^- concentration in either experiment, nor was it related to the DOC/NO_3^- ratio as hypothesized by Tiedje (1988). Several studies have found support for the Tiedje hypothesis in freshwater wetlands (Matheson et al. 2002, Scott et al. 2008), streams (Storey et al. 2004, Crenshaw et al. 2010), salt marshes (King and Nedwell 1985), and agricultural soils (Fazzolari et al. 1990). However, Matheson et al. (2002) argued that the relationship between high C:NO_3^- ratios and DNRA is one where an increase in carbon increases oxygen demand and creates more strongly reducing conditions that are more favorable for DNRA than denitrification. Several studies have also found that DNRA is unrelated to NO_3^- concentration (Sotta et al. 2008, Koop-Jakobsen and Giblin 2010, Nizzoli et al. 2010, Nogaro and Burgin 2014), which is consistent with our findings.

Complicating the picture is that DNRA is carried out via two primary pathways—fermentative and coupled to sulfur oxidation—that may be favored under different conditions (Burgin and Hamilton 2007). Fermentative DNRA is thought to require low oxygen and high organic carbon conditions, similar to denitrification. Many of the fermentative DNRA bacteria are obligate anaerobic organisms, whereas denitrifying bacteria are facultatively anaerobic (Burgin and Hamilton 2007). Thus, environments with aerobic microsites may favor denitrification through locations that support nitrification and maintain a nitrate supply for the reaction (Palta et al. 2014) and because denitrifiers can tolerate exposure to oxic conditions (Matheson et al. 2002). The second DNRA pathway, which is coupled to sulfur oxidation, is not dependent on availability of organic carbon. The sulfur oxidation pathway may be favored for NO_3^- consumption because free sulfide inhibits some of the reducing enzymes used in denitrification (Brunet and Garcia-Gil 1996). However, metal-bound sulfides such as iron sulfide can be abundant in wetland ecosystems (Haaijer et al. 2007), and do not inhibit denitrification to the same extent as free sulfide (Brunet and Garcia-Gil 1996). Lu et al. (2013) found evidence that fermentative and sulfur-coupled DNRA can compete for NO_3^- based on availability of labile organic carbon and free sulfide. Therefore, any relationship between

DNRA, NO_3^- concentration, and availability of organic carbon will depend on the community of organisms carrying out the process.

I propose that while denitrification is a NO_3^- concentration-dependent process, DNRA is determined by other local factors and is insensitive to changes in NO_3^- concentration. Whereas the role of denitrification in removing NO_3^- fluctuates based on the available NO_3^- and organic carbon sources, the amount of DNRA remains the same; only the relative proportion of NO_3^- consumed through DNRA increases relative to denitrification when NO_3^- is limiting.

Vegetated patches had a large effect on nitrogen cycling in the wetlands. Across both experiments, the LUPE patches had significantly higher process rates compared to the open patches and several process rates were higher in the TYDO patches as well. Plants are a source of organic carbon to soil through litter production (McClaugherty et al. 1982, Gift et al. 2010) and root exudation or decomposition (Schade et al. 2001). The composition of litter with respect to structural versus more labile forms of carbon can affect the supply of microbially available forms of carbon (Manzoni et al. 2008). LUPE has a lower tissue C/N ratio compared to TYDO (Suchy 2016). A lower C/N ratio increases potential denitrification by increasing the soil organic matter pool (Suchy 2016). The presence of plants can increase denitrification rates (Alldred and Baines 2016), but studies differ on whether denitrification rates differ for specific species (Hume et al. 2002, Alldred and Baines 2016). Our study indicates that vegetation type can significantly affect the magnitude and type of NO_3^- reduction process.

I calculated the proportion of NO_3^- consumed that was not accounted for by either denitrification or DNRA in the push-pull experiment. OPEN and LUPE patches had almost identical NO_3^- consumption patterns, with 32% consumed through denitrification, 6% through DNRA, and 60% consumption by some other process. I note that while the proportion of NO_3^- consumed by each process was similar, the overall magnitude of NO_3^- consumption in the OPEN patches was lower than in either the TYDO or the LUPE patches. In contrast, the TYDO patches had more consumption through denitrification (56%) with less DNRA (2%) and other consumption (40%). Plants may compete with microbial consumers of NO_3^-, especially during the growing season (Groffman et al. 1992, Pinay et al. 1993). The OPEN patches had a similar pattern of NO_3^- consumption, despite not having any vegetation cover. Other consumption of NO_3^- may be associated more broadly with microbial immobilization or plant assimilation (Groffman et al. 1992, Pinay et al. 1993, Hall et al. 2009a, Mulholland et al. 2009). Assimilation by plants is usually higher during the growing season (Groffman et al. 1992, Pinay et al. 1993) and during the daylight hours (Hall et al. 2009a), and can account for the majority of NO_3^- consumption (Mulholland et al. 2009). While the OPEN patches did not have any vegetation cover, there were often extensive biofilms present that may have included microbial and algal communities with a high capacity for NO_3^- assimilation.

Process rates measured by the push-pull experiment were at least one order of magnitude higher than those measured in the microcosm experiment. This is likely an artifact of the experimental design for the microcosm experiment, including: (1) not including the 1-h period between dosing the microcosms with the NO_3^- solution and when the first sample was collected in the analysis and (2) a long incubation period (8 h), that allowed complete consumption of NO_3^-. At the time that the first samples were collected from the microcosms, a mean of 78% of the added NO_3^- had been consumed.

Although I did not collect background samples, assuming the starting $^{29}N_2$ and $^{30}N_2$ signals were air-equilibrated, the denitrification rate during the first hour after the microcosms were closed was between 2 and more than 350 times greater than the rate measured during the incubation period considered in the experiment. The initial NH_4^+ isotope samples had a mean value of 0.42 at% ^{15}N or a $\delta^{15}N$ of 159‰. Nitrogen cycling transformations such as nitrification of NH_4^+ can fractionate as much as –29‰, leaving the NH_4^+ pool enriched in ^{15}N (Sharp 2017); therefore, the enriched $^{15}NH_4^+$ signal at the start of the experiment likely originates from the added $^{15}N\text{-}NO_3^-$ rather than from a fractionating processes. This indicates that enrichment through DNRA had already taken place prior to the incubation period considered in the experiment. In addition, more than half of the final samples had NO_3^- concentrations below instrument detection limits, indicating complete consumption of NO_3^-. This likely lead to an underestimate of NO_3^- consumption rates. While the microcosm experiments demonstrate that denitrification and DNRA are both occurring in the Salt River Wetlands, the flux estimates from this experiment are likely not representative of potential or maximum rates.

The rates of DNRA observed in the push-pull experiment (9.9 ± 2.8 μg N g dry soil^{-1} d^{-1}) were higher than other estimates from other terrestrial ecosystems that range from <0.01 to nearly 3 μg N g dry soil^{-1} d^{-1} (Rütting et al. 2011). The NO_3^- amendment in this study was in the lower range of those reported in Rütting et al. (2011; <1 to 70 μg N/g soil). If I convert the fluxes I measured to areal units by integrating over the well depth of 7 cm, the DNRA rates ranged from 0.84 to 5.0 mmol m^{-2} h^{-1}. These rates were substantially higher than many studies in coastal (Rysgaard et al. 1996, Tobias et al. 2001, An and Gardner 2002, Gardner et al. 2006, Koop-Jakobsen and Giblin 2010, Bernard et al. 2015) and freshwater ecosystems (Storey et al. 2004, Scott et al. 2008, Nizzoli et al. 2010, Nogaro and Burgin 2014); however, the NO_3^- amendment in the current study also exceeded that in most aquatic studies. Although the level of NO_3^- addition was high relative to other studies in aquatic ecosystems, the addition was necessary in order to recover sufficient NO_3^- to calculate the process rates and is probably reasonable for an urban ecosystem, especially one fed by stormwater runoff.

Conclusion

I propose that denitrification and nitrogen removal increases when floods increase NO_3^- supply to the wetlands. When NO_3^- supply is low between floods, DNRA accounts for a higher proportion of the NO_3^- reduction, but the overall magnitude of DNRA remains low. Our data show that denitrification was positively correlated with NO_3^- concentration up until approximately 3 mg N/L, then it was limited by other factors. Regardless of NO_3^- concentration, DNRA rates were generally an order of magnitude less than denitrification and were driven by spatial factors such as plant patch cover and DOC concentration rather than NO_3^- concentration. Still, when NO_3^- concentration was low, denitrification rates were also lower and DNRA accounted for a larger proportion of NO_3^- reduction. DNRA can conserve NO_3^- during periods of low nitrogen supply, retaining the element in the less mobile NH_4^+ form that may then be assimilated by plants and microorganisms or nitrified. Regardless, approximately half of NO_3^- consumption occurred through processes other than denitrification and DNRA, presumably due to plant and microbial uptake. Therefore, biological assimilation is an important sink for NO_3^- in this wetland ecosystem, even in the absence of vegetation cover. Nitrate pollution is common in urban aquatic ecosystems; however, fluctuating NO_3^- supply can mean that the system oscillates between excessive and limiting concentrations. Our study indicates that this oscillation in NO_3^- concentration can have consequences for the proportion of NO_3^- removed through denitrification versus conserved through DNRA.

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Tables and Figures

Table 4.1. Standardized β coefficients with standard error in parentheses for the variables included in best fit general linear models of fluxes from the microcosm experiment and the push-pull experiment. All response variables were transformed to z-scores to show the relative importance of variables across models. The *L. peploides* (LUPE) and *T. dominigensis* (TYDO) coefficients are relative to the unvegetated open patches using a dummy code scheme. The NO_3^- and DOC variables are the standardized and zero-centered concentration at the start of the incubation. All response variables are in units of µg N g dry soil^{-1} hr^{-1}. A (-) denotes that the explanatory variable was not included in the final model. Significance levels: $p<0.05$ (*), $p<0.01$ (**), $p<0.001$ (***).

Response Variable	LUPE	TYDO	$[NO_3^-]$	DOC	R2
Microcosm Experiment					
NH_4^+ Flux	0.98(0.45)*	0.22(0.42)	-	-	17.0
DNRA	1.45(0.47)**	1.23(0.47)*	-	-	48.5
NO_3^- Flux	0.99(0.23)***	1.09(0.23)***	0.82(0.09)***	-	77.2
Log(DNIT)	-	-	0.61(0.20)**	-	42.7
Push-Pull Experiment					
Log(NH_4^+ Flux)	1.18(0.38)**	0.56(0.37)	-	-0.44(0.16)*	55.8
Log(DNRA)	1.22(0.36)**	0.58(0.36)	-	-0.45(0.16)**	59.6
NO_3^- Flux	1.51(0.26)***	0.44(0.26)	0.56(0.11)***	-	78.5
Log(DNIT)	1.35(0.46)**	0.92(0.44)	-	-	33.9

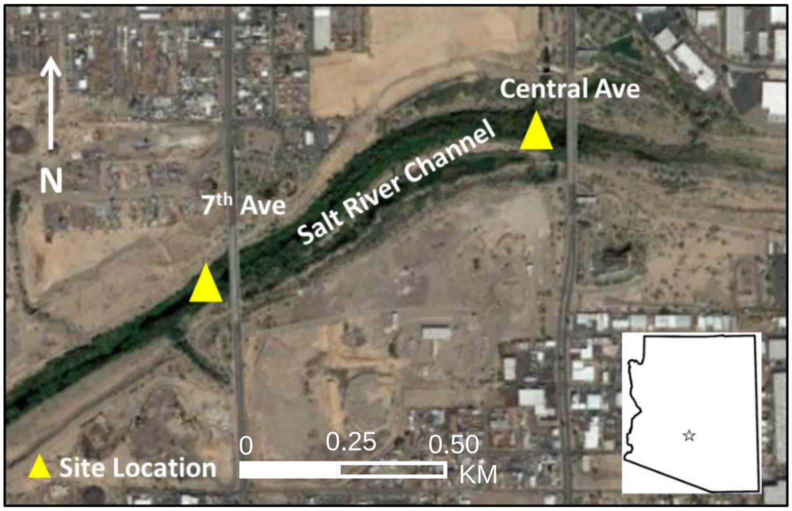

Figure 4.1: Map of field sites were located within the Central Arizona-Phoenix Long Term Ecological Research study area at two locations, 7th and Central Avenue, in the Salt River channel near downtown Phoenix, Arizona.

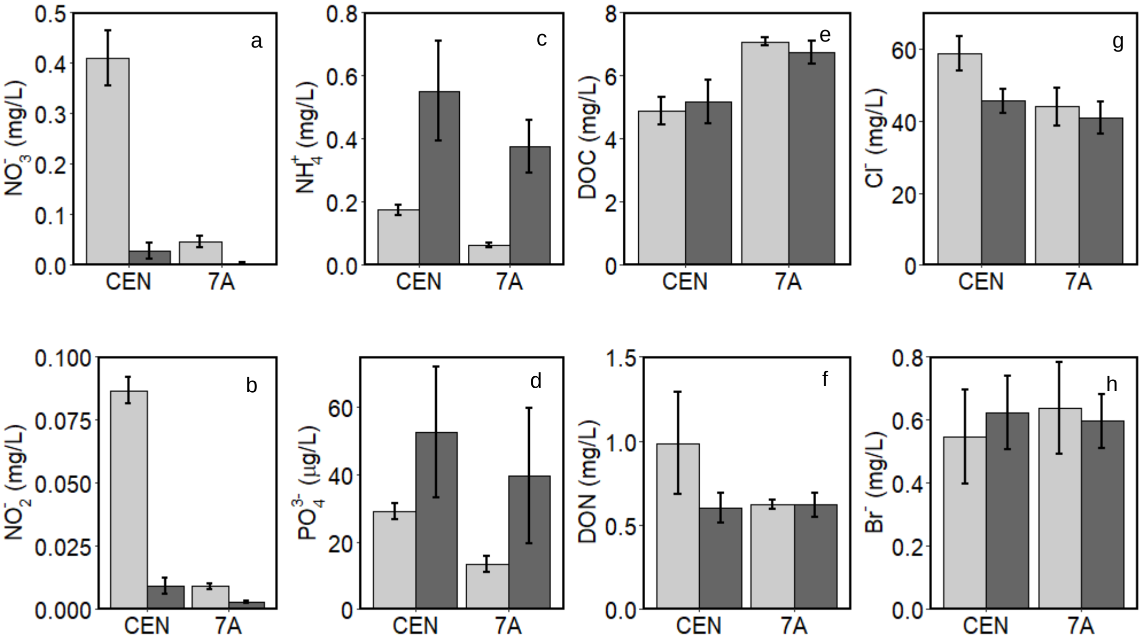

Figure 4.2: Mean background water concentration ± standard error for NO_3^- (a), NO_2^- (b), NH_4^+ (c), PO_4^{3-} (d), DOC (e), DON (f), Cl^- (g), and Br^- (h) in the Central Ave (CEN) and 7th Ave (7A) sites in the Salt River channel for surface water (light grey) or subsurface porewater (dark grey).

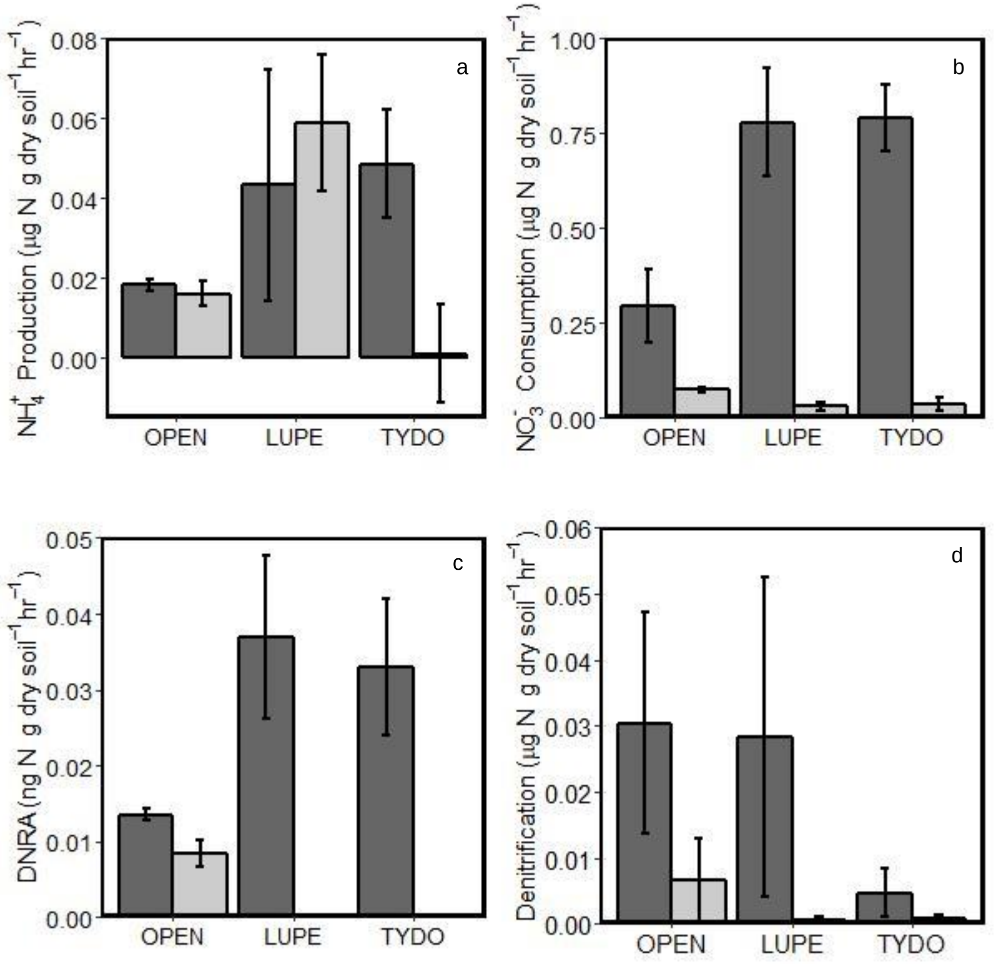

Figure 4.3. Mean fluxes for the microcosm experiment where soils were incubated in the lab under two different NO_3^- concentrations. Bars are mean fluxes ± standard error for NH_4^+ (a), NO_3^- (b), DNRA (c), and denitrification (d) for the unvegetated (OPEN), *L. peploides* (LUPE), and *T. domingensis* (TYDO) patches, for the high 7 ppm N-NO_3^- (dark bars) and low 1 ppm N-NO_3^- (light bars) treatments. Only data included in the general linear model analysis are plotted, extreme outliers and microcosms that had no detectable change in the isotope pool are omitted (likely due to methodological limitations, see text).

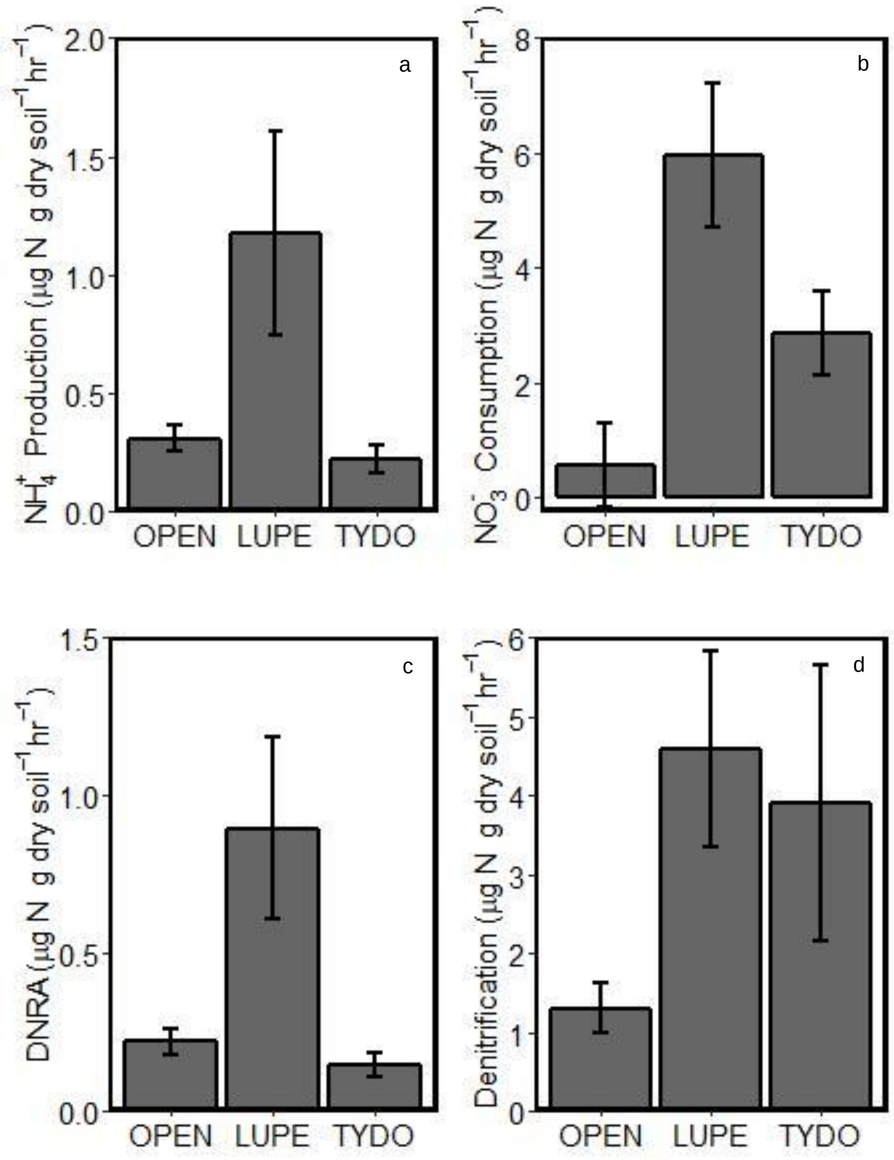

Figure 4.4. Mean process rates for the push-pull experiment. Bars are mean fluxes ± standard error for NH_4^+ (a), NO_3^- (b), DNRA (c), and denitrification (d) for the unvegetated (OPEN), *L. peploides* (LUPE), and *T. domingensis* (TYDO) patches. All incubations received a starting NO_3^- concentration of 7 ppm.

Literature Cited

Addy, K., D. Q. Kellogg, A. J. Gold, P. M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push–pull method to determine ground water denitrification in riparian zones. Journal of Environmental Quality 31:1017–1024.

Alldred, M., and S. B. Baines. 2016. Effects of wetland plants on denitrification rates: A meta-analysis. Ecological Applications 26:676–685.

An, S., and W. S. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Marine Ecology Progress Series 237:41–50.

An, S., W. S. Gardner, and T. Kana. 2001. Simultaneous measurement of denitrification and nitrogen fixation using isotope pairing with membrane inlet mass spectrometry analysis. Applied and environmental microbiology 67:1171–1178.

Baker, L. A., D. Hope, Y. Xu, J. Edmonds, and L. Lauver. 2001. Nitrogen balance for the Central Arizona-Phoenix (CAP) ecosystem. Ecosystems 4:582–602.

Bateman, H. L., J. C. Stromberg, M. J. Banville, E. Makings, B. D. Scott, A. Suchy, and D. Wolkis. 2015. Novel water sources restore plant and animal communities along an urban river. Ecohydrology 8:792–811.

Bernard, R. J., B. Mortazavi, and A. A. Kleinhuizen. 2015. Dissimilatory nitrate reduction to ammonium (DNRA) seasonally dominates NO3– reduction pathways in an anthropogenically impacted sub-tropical coastal lagoon. Biogeochemistry 125:47–64.

Brunet, R. C., and L. J. Garcia-Gil. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. FEMS Microbiology Ecology 21:131–138.

Burgin, A. J., and S. K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and the Environment 5:89–96.

Crenshaw, C. L., N. B. Grimm, L. H. Zeglin, R. W. Sheibley, C. N. Dahm, and a. D. P. Ershall. 2010. Dissolved inorganic nitrogen dynamics in the hyporheic zone of reference and human-altered southwestern U. S. streams. Fundamental and Applied Limnology / Archiv für Hydrobiologie 176:391–405.

Dodsworth, J. A., B. A. Hungate, and B. P. Hedlund. 2011. Ammonia oxidation, denitrification and dissimilatory nitrate reduction to ammonium in two US Great Basin hot springs with abundant ammonia-oxidizing archaea. Environmental Microbiology 13:2371–2386.

Fazzolari, E., A. Mariotti, and J. C. Germon. 1990. Nitrate reduction to ammonia: a dissimilatory proces in Enterobacter amnigenus. Canadian Journal of Microbiology 36:779–1989.

Fitzhugh, T. W., and B. D. Richter. 2004. Quenching urban thrist: Growing cities and their impact on freshwater ecosystems. Bioscience 54:741–754.

Gardner, W. S., M. J. McCarthy, S. An, D. Sobolev, K. S. Sell, and D. Brock. 2006. Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries. Limnology and Oceanography 51:558–568.

Giblin, A. E., C. R. Tobias, B. Song, N. Weston, G. T. Banta, and W. H. Rivera-Monroy. 2013. The importance of dissimilatory nitrate reduction to ammonium (DNRA) in the nitrogen cycle of coastal ecosystems. Oceanography 26:124–131.

Gift, D. M., P. M. Groffman, S. S. Kaushal, and P. M. Mayer. 2010. Denitrification potential, root biomass, and organic matter in degraded and restored urban riparian zones. Restoration Ecology 18:113–124.

Golterman, H. L. 2000. Denitrification and a numerical modelling approach for shallow waters. Hydrobiologia 421:93–104.

Groffman, P. M., M. A. Altabet, J. K. Böhlke, K. Butterbach-bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, M. A. Voytek, P. M. Groffman, M. A. Altabet, J. K. Bohlke, K. Butterbach-bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, and M. A. Voytek. 2006. Methods for Measuring Denitrification : Diverse Approaches to a Difficult Problem. Ecological Applications 16:2091–2122.

Groffman, P. M., A. J. Gold, and R. C. Simmons. 1992. Nitrate dynamics in riparian forests: Microbial studies. Journal of Environment Quality 21:666–671.

Haaijer, S. C. M., L. P. M. Lamers, A. J. P. Smolders, M. S. M. Jetten, and H. J. M. Op de Camp. 2007. Iron sulfide and pyrite as potential electron donors for microbial nitrate reduction in freshwater wetlands. Geomicrobiology Journal 24:391–401.

Hale, R. L., L. Turnbull, S. Earl, N. Grimm, K. Riha, G. Michalski, K. A. Lohse, and D. Childers. 2014. Sources and transport of nitrogen in arid urban watersheds. Environmental Science and Technology 48:6211–6219.

Hall, R. O., J. L. Tank, D. J. Sobota, P. J. Mulholland, M. Jonathan, O. Brien, W. K. Dodds, J. R. Webster, H. M. Valett, G. C. Poole, J. Bruce, J. L. Meyer, W. H. Mcdowell, S. L. Johnson, S. K. Hamilton, B. Grimm, S. V Gregory, C. N. Dahm, L. W. Cooper, L. R. Ashkenas, M. Thomas, R. W. Sheibley, J. D. Potter, B. R. Niederlehner, L. T. Johnson, M. Helton, C. M. Crenshaw, A. J. Burgin, M. J. Bernot, J. J. Beaulieu, and C. P. Arango. 2009. Nitrate removal in stream ecosystems measured by Total uptake 15 N addition experiments : Limnology and

Oceanography 54:653–665.

Holmes, R. M., J. W. McClelland, D. M. Sigman, B. Fry, and B. J. Peterson. 1998. Measuring 15 N-NH 4 in marine, estuarine, and freshwaters: An adaptation of the ammonia diffusion method for samples with low ammonium concentrations. Marine Chemistry 60:235–243.

Hume, N. P., M. S. Fleming, and A. J. Horne. 2002. Denitrification potential and carbon quality of four aquatic plants in wetland microcosms. Soil Science Society of America Journal 66:1706–1712.

Kana, T. M., C. Darkangelo, M. D. Hunt, J. B. Oldham, G. E. Bennett, and J. C. Cornwell. 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N2, O2 , and Ar in environmental water samples. Anal. Chem 66:4166–4170.

Kaushal, S. S., P. M. Groffman, L. E. Band, E. M. Elliott, C. A. Shields, and C. Kendall. 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environmental Science and Technology 45:8225–8232.

Kaye, J. P., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. 2006. A distinct urban biogeochemistry? Trends in Ecology and Evolution 21:192–199.

Kelso, B. H. L., R. V. Smith, R. J. Laughlin, and S. D. Lennox. 1997. Dissimilatory nitrate reduction in anaerobic sediments leading to river nitrite accumulation. Applied and Environmental Microbiology 63:4679–4685.

King, D., and D. B. Nedwell. 1985. The influence of nitrate concentration upon the end-products of nitrate dissimilation by bacteria in anaerobic salt marsh sediment. FEMS Microbiology Letters 31:23–28.

Koop-Jakobsen, K., and A. E. Giblin. 2010. The effect of increased nitrate loading on nitrate reduction via denitirification and DNRA in salt marsh sediments. Limnology and Oceanography 55:789–802.

Larson, E. K., N. B. Grimm, P. Gober, and C. L. Redman. 2005. The paradoxical ecology and management of water in the Phoenix , USA metropolitan area. Ecohydrology & Hydrobiology 5:287–296.

Lewis, D. B., and N. B. Grimm. 2007. Hierarchical regulation of nitrogen export from urban catchments: Interactions of storms and landscapes. Ecological Applications 17:2347–2364.

Lu, W. W., H. L. Zhang, and W. M. Shi. 2013. Dissimilatory nitrate reduction to ammonium in an anaerobic agricultural soil as affected by glucose and free sulfide. European Journal of Soil Biology 58:98–104.

Makings, E., L. Butler, M. Chew, and J. C. Stromberg. 2011. Noteworthy collections from Tempe Town Lake riverbed. Desert Plants 27:3–10.

Manzoni, S., R. B. Jackson, J. A. Trofymow, and A. Porporato. 2008. The global stoichiometry of litter nitrogen mineralization. Science 321:684–686.

Matheson, F. E., M. L. Nguyen, A. B. Cooper, T. P. Burt, and D. C. Bull. 2002. Fate of 15N-nitrate in unplanted , planted and harvested riparian wetland soil microcosms. Ecological Engineering 19:249–264.

McClaugherty, C. A., J. D. Aber, and J. M. Melillo. 1982. The role of fine roots in the organic matter and nitrogen budgets of two forested ecosystems. Ecology 63:1481–1490.

Mitsch, W. J., and J. G. Gosselink. 2015. Wetlands. 5th edition. Wiley, Hoboken, NJ.

Mulholland, P. J., R. O. Hall, D. J. Sobota, W. K. Dodds, E. G. Stuart, N. B. Grimm, S. K. Hamilton, W. H. Mcdowell, J. M. O. Brien, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V Gregory, S. L. Johnson, J. L. Meyer, B. J. Peterson, G. C. Poole, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, A. M. Helton, L. T. Johnson, B. R. Niederlehner, J. D. Potter, R. W. Sheibley, and S. M. Thomas. 2009. Nitrate removal in stream ecosystems measured by 15N addition experiments: Denitrification. Limnology and Oceanography 54:666–680.

Mulholland, P. J., A. M. Helton, G. C. Poole, R. O. Hall, S. K. Hamilton, B. J. Peterson, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, W. K. Dodds, S. E. G. Findlay, S. V Gregory, N. B. Grimm, S. L. Johnson, W. H. McDowell, J. L. Meyer, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, L. T. Johnson, B. R. Niederlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, D. J. Sobota, and S. M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202–205.

Newcomer, T. A., S. S. Kaushal, P. M. Mayer, A. R. Shields, A. Elizabeth, P. M. Groffman, and A. J. Gold. 2012. Influence of natural and novel organic carbon sources on dentrification in forest, degraded urban, and restored streams. Ecological Monographs 82:449–466.

Nielson, L. P. 1991. Denitrification in sediment determined from nitrogen isotope pairing. FEMS Microbiology Ecology 9:357–361.

Nizzoli, D., E. Carraro, V. Nigro, and P. Viaroli. 2010. Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. Water Research 44:2715–2724.

Nogaro, G., and A. J. Burgin. 2014. Influence of bioturbation on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in freshwater sediments. Biogeochemistry 120:279–294.

Palta, M. M., J. G. Ehrenfeld, and P. M. Groffman. 2014. Hotspots and hot moments of denitrification in urban brownfield wetlands. Ecosystems 17:1121–1137.

Palta, M. M., N. B. Grimm, and P. M. Groffman. 2017. "Accidental" urban wetlands: Ecosystem functions in unexpected places. Frontiers in Ecology and the Environment 15:248–256.

Paul, M. J., and J. L. Meyer. 2001. Streams in the Urban Landscape. Annual Review of Ecology and Systematics 32:333–365.

Pinay, G., L. Roques, and A. Fabre. 1993. Spatial and temporal patterns of denitrification in a riparian forest. Journal of Applied Ecology 30:581–591.

Rütting, T., P. Boeckx, C. Müller, and L. Klemedtsson. 2011. Assessment of the importance of dissimilatory nitrate reduction to ammonium for the terrestrial nitrogen cycle. Biogeosciences 8:1779–1791.

Rysgaard, S., N. Risgaard-Petersen, and N. P. Sloth. 1996. Nitrification, denitrification, and nitrate ammonification in sediments of two coastal lagoons in Southern France. Hydrobiologia 329:133–141.

Schade, J. D., S. G. Fisher, N. B. Grimm, and J. Seddon. 2001. The influence of a riparian shrub on nitrogen cycling in a Sonoran Desert stream. Ecology 82:3363–3376.

Scott, J. T., M. J. McCarthy, W. S. Gardner, and R. D. Doyle. 2008. Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. Biogeochemistry 87:99–111.

Sharp, Z. 2017. Principles of stable isotope geochemistry. 2nd edition.

Sigman, D. M., M. a Altabet, R. Michener, D. C. McCorkle, B. Fry, and R. M. Holmes. 1997. Natural abundance-level measurements of the nitrogen isotopic composition of oceanic nitrate: an adaption of the ammonia diffusion method.

Silver, W. L., D. J. Herman, M. K. Firestone, S. Ecology, and N. Sep. 2001. Dissimilatory nitrate reduction to ammonium in upland tropical forest soils. Ecology 82:2410–2416.

Sotta, E. D., M. D. Corre, and E. Veldkamp. 2008. Differing N status and N retention processes of soils under old-growth lowland forest in Eastern Amazonia, Caxiuanã, Brazil. Soil Biology and Biochemistry 40:740–750.

Storey, R. G., D. D. Williams, and R. R. Fulthorpe. 2004. Nitrogen processing in the hyporheic zone of a pastoral stream. Biogeochemistry 69:285–313.

Suchy, A. K. 2016. Denitrification in accidental urban wetlands: Exploring the rolse of water flows and plant patches. Arizona State University.

Tiedje, J. M. 1988. Ecology of dentrification and dissimilatory nitrate reduction to ammonium. Pages 179–244 *in* A. J. B. Zehnder, editor. Environmental Microbiology of Anaerobes. John Wiley and Sons, New York.

Tobias, C. R., I. C. Anderson, and S. A. Macko. 2001. Nitrogen cycling through a fringing marsh- aquifer ecotone. Marine Ecology Progress Series 210:25–39.

Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan. 2005. The urban stream syndrome: Current knowledge and the search for a cure. Journal of the North American Benthological Society 24:706–723.

Weier, K. L., J. W. Doran, J. F. Power, and D. T. Walters. 1993. Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. Soil Science Society of America Journal 57:66.

CHAPTER 5

IMPORTANCE OF PLACE: HYDROLOGIC CONNECTIVITY AND DEVELOPMENT MEDIATE THE PRIMARY LOCATION OF NITROGEN RETENTION IN WATERSHEDS

Nitrogen is an essential, often limiting nutrient for organisms. Nitrogen has many different chemical forms, only a subset of which are biologically reactive. As a result, the form, transformation rate, and movement of nitrogen in ecosystems has consequences for ecosystem structure and function. Most autotrophs and microbes assimilate nitrogen as nitrate or ammonium, collectively referred to as dissolved inorganic nitrogen (DIN). Assimilated nitrogen becomes part of plant tissue or a microbe that once exuded, or dead, are subject to decomposition and mineralization to ammonium. Ammonium can be subject to nitrification to form nitrate or volatilization to form ammonia gas that is lost from the system. Nitrate is subject to dissimilatory nitrate reduction to ammonium (DNRA) or denitrification to nitrogenous gases that are lost from the system. Nitrification and DNRA can recycle nitrogen between different forms of DIN. In undeveloped ecosystems, the primary nitrogen inputs are nitrogen fixation and atmospheric deposition; however, in ecosystems with human activities, DIN inputs are drastically increased from fertilizer, food and feed imports, and higher atmospheric deposition from burning fossil fuels (Vitousek et al. 1997, Boyer et al. 2002). The result is that the amount of reactive nitrogen in the biosphere has more than doubled since the pre-industrial era, resulting in eutrophication in many aquatic ecosystems (Carpenter et al. 1998, Galloway et al. 2004, 2008).

Nitrogen movement through ecosystems is primarily mediated by water, but slowed by biological retention. The relative balance of nitrogen transport and retention is a function of the amount of nitrogen input to the landscape (Galloway et al. 2004, Howarth et al. 2012), the climate and hydrology of the system (Howarth et al. 2006, 2012), and the amount retained or transformed by the biological communities along flowpaths (Fisher et al. 2004). Much of the research on the relationship between these factors has been conducted in mesic ecosystems. Over the past several decades more studies have explored these variables in urban ecosystems that tend to have higher nitrogen inputs and altered hydrology (Paul and Meyer 2001). Less work has been done in the dryland ecosystems that cover two-fifths of terrestrial Earth (Bastin et al. 2017) and are expected to host a disproportionate amount of population growth in the future (Reynolds et al. 2007). Both urban and dryland ecosystems are characterized by high variability in hydrology due infrastructure in urban systems and precipitation variability in drylands. In addition, nitrogen inputs in urban systems vary due the to patchy distribution of development (Caraco and Cole 2001, Paul and Meyer 2001).

In this dissertation, I asked: What is the balance of nitrogen transformation, transport, and retention in dryland watersheds, and what is the fate of nitrogen export in urban ecosystems? I addressed the first part of my question through an investigation of the temporal—at seasonal and storm-level timescales—and spatial variables that affect nitrate and more broadly nutrient loading in dryland streams (Chapters 2 and 3). The second part of my question I addressed through an experimental investigation of the relative roles of denitrification and DNRA in nitrate attenuation in an urban wetland ecosystem (Chapter 4).

Each of the study systems used in this dissertation are situated in the combined Salt-Verde River Watersheds along flowpaths from uplands to the recipient ecosystems at the watershed outlet (Figure 5.1). They represent a gradient from the entirely undeveloped Sycamore Creek Watershed to the highly urban Salt River Wetlands. The flowpath from the uplands to temporary stream channels to perennial streams to the Salt River wetlands is indirect. Shortly after the confluence of the Verde and Salt Rivers and upstream of Phoenix, all surface water in the channel is diverted into canals for the municipal water supply. The river water is mixed with groundwater and water from the Colorado River via the Central Arizona Project aqueduct that together form most of Phoenix’s water supply (Guhathakurta and Gober 2007). Two thirds of residential water use in Phoenix is outside the home (Mayer et al. 1999) and some of this water forms runoff that enters the sewer system, eventually flowing into recipient water systems including wetlands and retention basins (Bateman et al. 2015, Palta et al. 2016, 2017). Residential wastewater is treated and either discharged to the Salt River Channel, injected into the groundwater, used for irrigation, or used for cooling generators at the Palo Verde nuclear facility (Lauver and Baker 2000). Thus, the water supplied from the Salt-Verde Rivers including Sycamore Creek and Oak Creek eventually reaches the Salt River Channel in urban Phoenix after flowing through the urban landscape.

Based on my dissertation research, I propose that the primary location of nitrogen retention changes based on the hydrologic connectivity and type of human development in the watershed. For the ephemeral and intermittent streams that form the headwaters of larger watersheds, the primary site of nitrogen retention is the uplands, where rain pulses in biological activity process and retain nitrogen. For larger perennial streams that are connected to a regional groundwater system, some development occurs along the stream margins that increases both nitrogen loading and hydrologic connectivity between these sources and the stream. As a result, the primary location for nitrogen retention and removal in perennial systems is the stream network. Finally, in dryland, urban ecosystems with heavy development and increased nitrogen inputs, the water infrastructure shifts the primary site of nitrogen retention to downstream recipient ecosystems that store water, including wetlands and retention basins. In this way, water availability as a stimulator of biological activity and hydrologic connectivity combined with human development can alter the primary location of nitrogen retention in the watershed.

For drylands, nitrogen processing and retention in undeveloped intermittent and ephemeral watersheds is limited by water. Water limits both biological activity and hydrologic connectivity between landscape components. Full connection between uplands and the stream network may only occur during large floods. If undeveloped, most of the nitrogen inputs are due to nitrogen fixation and atmospheric deposition. Without substantial water to transport the element, most of the processing and retention of these inputs will occur in place during small to moderately sized storms. Hot moments of biological activity during and following precipitation inputs can mineralize, nitrify, and denitrify nitrogen, and also enable more biological nitrogen uptake (McClain et al. 2003, Belnap et al. 2005, Harms and Grimm 2008). As a result, smaller precipitation inputs that do not generate floods may encourage retention of nitrogen in the uplands, thus reducing the pool of potentially mobile nitrogen. When large floods occur, there is less nitrogen available for export. Sycamore Creek followed this pattern (Chapter 3) in that higher precipitation inputs in the season prior to a flood lowered the concentration and load of total dissolved nitrogen and dissolved organic carbon in flood water. This indicates that precipitation in the prior season stimulated biological retention and removal of these nutrients such that the pool that was available for export during floods was reduced. During floods, the transport rate exceeds the biological reaction rates, thus there is little retention occurring during floods (Oldham et al. 2013, Welter and Fisher 2016), although transformation between different forms of nitrogen may occur during transport (Welter et al. 2005, Harms and Grimm 2010). During seasonal flow or flow recession following a flood, temporary streams can have high nitrogen uptake rates (Fisher et al. 1982), though are still largely disconnected from upland sources of nutrients. As a result, the processing and retention of nitrogen that takes place in the uplands is the major control point for nitrogen in intermittent and ephemeral dryland watersheds.

Dryland perennial streams are connected to a groundwater system which maintains surface flow during extended dry periods. As a result of relative water security, perennial streams are also favored sites for human development. The primary source of nitrogen in these systems are the groundwater and human activities near the stream channel. As a result, the stream network is the primary control point for nitrogen processing and retention in these ecosystems. The source and transfer of nutrients between the land surface, groundwater, stream network, and downstream systems is highly dependent on the amount of precipitation and evapotranspiration variation across seasons and years in drylands. The strength of the connection between groundwater systems and the stream network can vary throughout the year (Brooks and Lemon 2007, Meixner et al. 2007). Human development alters the hydrology of landscapes such that hydrologic connectivity can increase or decrease between landscape sources of nutrients and aquatic systems. Agricultural activities may include diverting surface water (Larned et al. 2010) and pumping groundwater (Kustu et al. 2011) for irrigating residential or agricultural landscapes. Irrigation water can increase groundwater–surface water connections, especially during dry summer seasons (Kustu et al. 2011) and this water may entrain nitrate placed on the landscape. This was the case in Oak Creek (Chapter 2), where nitrate loading to the stream network remained high even during the summer season in the portion of the watershed with agricultural land cover adjacent to the stream. Despite the high nitrate loading in these sections of the watershed, the high capacity for biological nitrogen uptake in the stream ensured that the stream nitrogen load remained low. Thus, perennial streams are the primary reactive interface responsible for reducing nitrogen loads to downstream ecosystems in drylands.

In urban ecosystems, nitrogen inputs are higher, there is lower biological retention in the uplands due to the ubiquity of impervious surfaces, and infrastructure favors efficient runoff removal to recipient ecosystems rather than retention on the landscape. As a result, in urban ecosystems the primary sites of nitrogen retention are the recipient aquatic systems. Urban ecosystems have extensive impervious surfaces (Arnold and Gibbons 1996) with less area available for water infiltration. Many cities rely on infrastructure that diverts water through pipes and into stream channels, wetlands, and other recipient systems during storms (Hale et al. 2014b). As a result, any water in the system will tend to flow overland and even small precipitation events can generate flood conditions in these recipient systems (Walsh et al. 2005, Hale et al. 2014b). This is apparent in the Salt River Wetlands that experience regularly flooding associated with storms in Phoenix. The flooding is accompanied by high nutrient loading (Palta et al. 2016, 2017). In addition, these wetlands have perennial water supply from stormwater drains even during prolonged dry periods, indicating that runoff from lawn irrigation and groundwater pumping is diverted to this recipient system rather than infiltrating in the urban terrestrial sphere (Palta et al. 2016, 2017). Since the Salt River wetlands have highly urban drainages, the amount of nitrogen drained to these systems can accumulate over time and may exceed the assimilating biological demand. As a result, other transformations can become important sinks for nitrogen (Burgin and Hamilton 2007, Suchy 2016, Palta et al. 2017). My research in these wetlands demonstrates that denitrification rates increased with higher nitrate supply; in contrast, DNRA was insensitive to changes in nitrate supply (Chapter 4). This means that the wetlands are capable of mediating increased nitrogen inputs by removal through denitrification. Decades of research has demonstrated the nitrogen attenuation capacity of wetland ecosystems (Nichols 1983, Peterjohn and Correll 1984, Bowden 1987, Hill 1996, Saunders and Kalff 2001, Mayer et al. 2007, Racchetti et al. 2011). The Salt River wetlands are consistent with this research, removing nitrogen at the patch scale (Suchy 2016) and at the wetland scale (Palta et al. 2017). The denitrification capacity of wetlands has led to their widespread construction and to restoration projects in locations that have high nitrogen loading, such as treatment wetlands to remove nitrogen from municipal wastewater effluent or in locations with high nonpoint source nitrogen pollution, such as agricultural areas (Nichols 1983, Brix 1994, Vymazal 2007, Lee et al. 2009).

Rising temperatures due to climate change and increasing water extraction for human water consumption mean that intermittency in stream ecosystems is expected to increase (Larned et al. 2010). In addition, urban areas are expected to increase and with them the ecological footprint of cities (Grimm et al. 2008). As ecosystems become drier and more urban, there is a need to understand the consequences for nutrient cycling. Drier ecosystems may mean that a larger proportion of nitrogen processing and retention occurs surrounding rain pulses in biological activity. More development along perennial stream margins and in larger cities will likely increase nitrogen supplies and alter hydrology such that the new sources of nitrogen are more connected to aquatic ecosystems. Accumulating nitrogen in recipient ecosystems may also shift the types of nitrogen retention from more assimilative biological uptake to higher rates nitrogen removal by denitrification. Insight into the primary locations for nitrogen processing and removal in different ecosystem types is needed in order to prioritize areas for this ecosystem service.

Figures

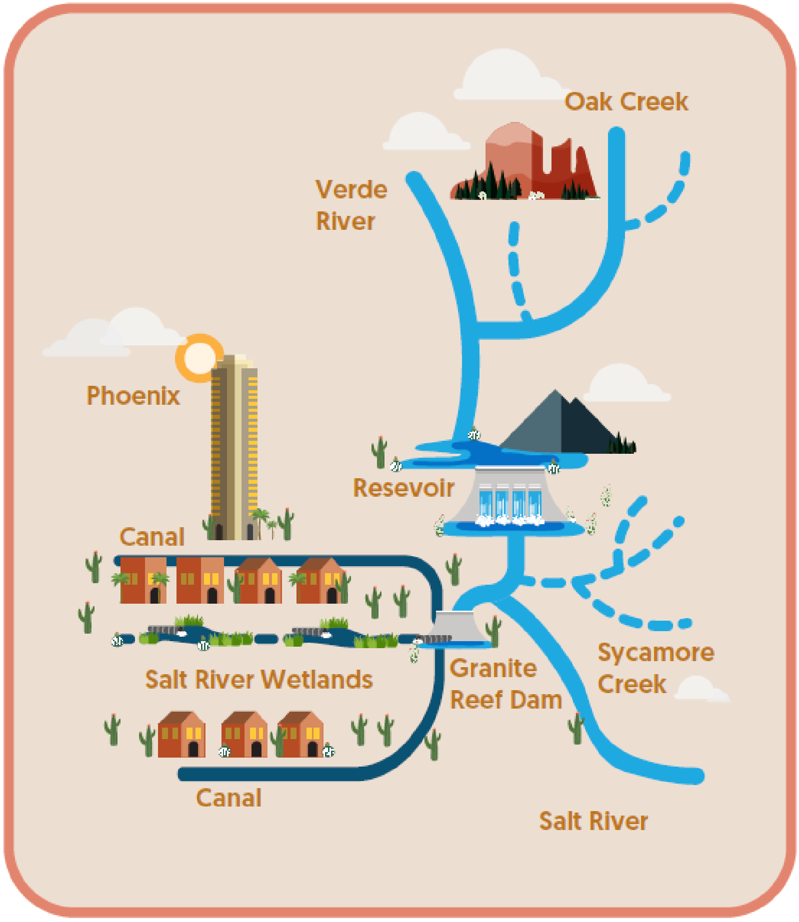

Figure 5.1. A schematic of study sites and relationship to Phoenix metropolitan area water supply. Oak Creek has both temporary and perennial sections with small urban and agricultural areas in the watershed. Sycamore Creek is spatially intermittent and has very little development within the watershed boundary. Both Sycamore Creek and Oak Creek flow into the Verde River that converges with the Salt River. Upstream of the city, all water in the Salt River is diverted into municipal canals and the river channel is dry through the city. The exception is the accidental wetlands (sensu Palta et al. 2017), which have developed near storm drains in the channel that deliver urban runoff to the channel.

Literature Cited

Arnold, C. L., and C. J. Gibbons. 1996. Impervious surface coverage: The emergence of a key environmental indicator. Journal of the American Planning Association 62:243–258.

Bastin, J., N. Berrahmouni, A. Grainger, D. Maniatis, D. Mollicone, R. Moore, C. Patriarca, N. Picard, B. Sparrow, E. M. Abraham, K. Aloui, A. Atesoglu, F. Attore, A. Bey, M. Garzuglia, L. G. García-montero, N. Groot, G. Guerin, L. Laestadius, A. J. Lowe, and B. Mamane. 2017. The extent of forest in dryland biomes. Science 638:635–638.

Bateman, H. L., J. C. Stromberg, M. J. Banville, E. Makings, B. D. Scott, A. Suchy, and D. Wolkis. 2015. Novel water sources restore plant and animal communities along an urban river. Ecohydrology 8:792–811.

Belnap, J., J. R. Welter, N. B. Grimm, N. Barger, and J. A. Ludwig. 2005. Linkages between microbial and hydrologic processes in arid and semiarid watersheds. Ecology 86:298–307.

Bowden, W. B. 1987. The biogeochemistry of nitrogen in freshwater wetlands. Biogeochemistry 4:313–348.

Boyer, E. W., C. L. . Goodale, N. A. . Jaworski, and R. W. Howarth. 2002. Anthropogenic Nitrogen Sources and Relationships to Riverine Nitrogen Export in the Northeastern U.S.A. Biogeochemistry 57–58:137–169.

Brix, H. 1994. Functions of macrophytes in constructezd wetlands. Water Science and Technology 29:71–78.

Brooks, P. D., and M. M. Lemon. 2007. Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Burgin, A. J., and S. K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and the Environment 5:89–96.

Caraco, N. F., and J. J. Cole. 2001. Human influence on nitrogen export: a comparison of mesic and xeric catchments. Marine and Freshwater Research 52:119–125.

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8:559–568.

Fisher, S. G., L. J. Gray, N. B. Grimm, and D. E. Busch. 1982. Temporal succession in a desert stream ecosystem following flash flooding. Ecological Monographs 52:93–

110.

Fisher, S. G., R. A. Sponseller, and J. B. Heffernan. 2004. Horizons in stream biogeochemistry: Flowpaths to progress. Ecology 85:2369–2379.

Galloway, J. N., F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vo. 2004. Nitrogen cycles: Past, present, and future. Biogeochemistry 70:153–226.

Galloway, J. N., A. R. Townsend, J. W. Erisman, M. Bekunda, Z. Cai, J. R. Freney, L. A. Martinelli, S. P. Seitzinger, and M. A. Sutton. 2008. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. Science 320:889–892.

Grimm, N. B., S. H. Faeth, N. E. Golubiewski, C. L. Redman, J. Wu, X. Bai, J. M. Briggs, N. B. Grimm, S. H. Faeth, N. E. Golubiewski, C. L. Redman, J. Wu, X. Bal, and J. M. Briggs. 2008. Global change and the ecology of cities. Science (New York, N.Y.) 319:756–760.

Guhathakurta, S., and P. Gober. 2007. The impact of the Phoenix urban heat island on residential water use. Journal of the American Planning Association 73:317–329.

Hale, R. L., L. Turnbull, S. R. Earl, D. L. Childers, and N. B. Grimm. 2014. Stormwater infrastructure controls runoff and dissolved material export from arid urban watersheds. Ecosystems 18:62–75.

Harms, T. K., and N. B. Grimm. 2008. Hot spots and hot moments of carbon and nitrogen dynamics in a semiarid riparian zone. Journal of Geophysical Research: Biogeosciences 113:1–14.

Harms, T. K., and N. B. Grimm. 2010. Influence of the hydrologic regime on resource availability in a semi-arid stream-riparian corridor. Ecohydrology 3:349–359.

Hill, A. R. 1996. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25:743–755.

Howarth, R., D. Swaney, G. Billen, J. Garnier, B. Hong, C. Humborg, P. Johnes, C. Mörth, and R. Marino. 2012. Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. Fronteiers in Ecology and Emvironment 10:37–43.

Howarth, R. W., D. P. Swaney, E. W. Boyer, R. Marino, N. Jaworski, and C. Goodale. 2006. The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Pages 163–186 *in* L. A. Martinelli and R. W. Howarth, editors. Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. Springer, Dordrecht.

Kustu, M. D., Y. Fan, and M. Rodell. 2011. Possible link between irrigation in the U.S. High Plains and increased summer streamflow in the Midwest. Water Resources Research 47:W03522.

Larned, S. T., T. Datry, D. B. Arscott, and K. Tockner. 2010. Emerging concepts in temporary-river ecology. Freshwater Biology 55:717–738.

Lauver, L., and L. A. Baker. 2000. Mass balance for wastewater nitrogen in the Central Arizona-Phoenix ecosystem. Water Research 34:2754–2760.

Lee, C. G., T. D. Fletcher, and G. Sun. 2009. Nitrogen removal in constructed wetland systems. Engineering in Life Sciences 9:11–22.

Mayer, P. M., W. B. DeOreo, E. M. Opitz, J. C. Kiefer, W. Y. Davis, B. Dziegielewski, and J. O. Nelson. 1999. Residential end uses of water. AWWA Research Foundation and American Water Works Association Rep.

Mayer, P. M., S. K. Reynolds, M. D. McCutchen, and T. J. Canfield. 2007. Meta-analysis of nitrogen removal in riparian buffers. Journal of Environment Quality 36:1172.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H. McDowell, and G. Pinay. 2003. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. Ecosystems 6:301–312.

Meixner, T., A. K. Huth, P. D. Brooks, M. H. Conklin, N. B. Grimm, R. C. Bales, P. A. Haas, and J. R. Petti. 2007. Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Nichols, D. S. 1983. Capacity of natural wetlands to remove nutrients from wastewater. Journal (Water Pollution Control Federation) 55:495–505.

Oldham, C. E., D. E. Farrow, and S. Peiffer. 2013. A generalized Damkohler number for classifying material processing in hydrological systems Solid. Hydrology and Earth System Sciences 17:1133–1148.

Palta, M., M. V. du Bray, R. Stotts, A. Wolf, and A. Wutich. 2016. Ecosystem services and disservices for a vulnerable population: Findings from urban waterways and wetlands in an American desert city. Human Ecology 44:463–47816.

Palta, M. M., N. B. Grimm, and P. M. Groffman. 2017. “Accidental” urban wetlands: Ecosystem functions in unexpected places. Frontiers in Ecology and the Environment 15:248–256.

Paul, M. J., and J. L. Meyer. 2001. Streams in the Urban Landscape. Annual Review of Ecology and Systematics 32:333–365.

Peterjohn, W. T., and D. L. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. Ecology 65:1466–1475.

Racchetti, E., M. Bartoli, E. Soana, D. Longhi, R. R. Christian, M. Pinardi, and P. Viaroli. 2011. Influence of hydrological connectivity of riverine wetlands on nitrogen removal via denitrification. Biogeochemistry 103:335–354.

Reynolds, J. F., D. M. S. Smith, E. F. Lambin, B. L. Turner, M. Mortimore, S. P. J. Batterbury, T. E. Downing, H. Dowlatabadi, R. J. Fernández, J. E. Herrick, E. Huber-sannwald, H. Jiang, R. Leemans, T. Lynam, F. T. Maestre, M. Ayarza, and B. Walker. 2007. Global desertification: Building a science for dryland development. Science 316:847–852.

Saunders, D. L., and J. Kalff. 2001. Nitrogen rentention in wetlands, lakes and rivers. Hydrobiologia 443:205–212.

Suchy, A. K. 2016. Denitrification in accidental urban wetlands: Exploring the rolse of water flows and plant patches. Arizona State University.

Vitousek, P. M., H. a Mooney, J. Lubchenco, and J. M. Melillo. 1997. Human domination of Earth’s ecosystems. Science 277:494–499.

Vymazal, J. 2007. Removal of nutrients in various types of constructed wetlands. Science of the Total Environment 380:48–65.

Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan. 2005. The urban stream syndrome: Current knowledge and the search for a cure. Journal of the North American Benthological Society 24:706–723.

Welter, J. R., and S. G. Fisher. 2016. The influence of storm characteristics on hydrological connectivity in intermittent channel networks: Implications for nitrogen transport and denitrification. Freshwater Biology 61:1214–1227.

Welter, J. R., S. G. Fisher, and N. B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76:421–440.

REFERENCES

Addy, K., D. Q. Kellogg, A. J. Gold, P. M. Groffman, G. Ferendo, and C. Sawyer. 2002. In situ push–pull method to determine ground water denitrification in riparian zones. Journal of Environmental Quality 31:1017–1024.

Aguilera, R., R. Marcé, and S. Sabater. 2012. Linking in-stream nutrient flux to land use and inter-annual hydrological variability at the watershed scale. Science of the Total Environment 440:72–81.

Alexander, R. B., R. A. Smith, and G. E. Schwarz. 2000. Effect of stream channel size on the delivery of nitrogen to the Gulf of Mexico. Nature 403:758–762.

Alldred, M., and S. B. Baines. 2016. Effects of wetland plants on denitrification rates: A meta-analysis. Ecological Applications 26:676–685.

An, S., and W. S. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). Marine Ecology Progress Series 237:41–50.

An, S., W. S. Gardner, and T. Kana. 2001. Simultaneous measurement of denitrification and nitrogen fixation using isotope pairing with membrane inlet mass spectrometry analysis. Applied and environmental microbiology 67:1171–1178.

Arce, M. I., C. Mendoza-lera, M. Almagro, N. Catalán, A. M. Romaní, E. Martí, R. Gómez, S. Bernal, A. Foulquier, M. Mutz, R. Marcé, A. Zoppini, G. Gionchetta, G. Weigelhofer, C. T. Robinson, A. Gilmer, M. Rulik, B. Obrador, O. Shumilova, S. Zlatanović, S. Arnon, P. Baldrian, G. Singer, T. Datry, N. Skoulikidis, B. Tietjen, and D. Von Schiller. 2019. A conceptual framework for understanding the biogeochemistry of dry riverbeds through the lens of soil science. Earth-Science Reviews 188:441–453.

Arce, M. I., M. del M. Sánchez-Montoya, M. R. Vidal-Abarca, M. L. Suárez, and R. Gómez. 2014. Implications of flow intermittency on sediment nitrogen availability and processing rates in a Mediterranean headwater stream. Aquatic Sciences 76:173–186.

Arnold, C. L., and C. J. Gibbons. 1996. Impervious surface coverage: The emergence of a key environmental indicator. Journal of the American Planning Association 62:243–258.

Austin, A. T., L. Yahdjian, J. M. Stark, J. Belnap, A. Porporato, U. Norton, D. A. Ravetta, and S. M. Schaeffer. 2004. Water pulses and biogeochemical cycles in arid and semiarid ecosystems. Oecologia 141:221–235.

Austin, B. J., and E. A. Strauss. 2011. Nitrification and denitrification response to varying periods of desiccation and inundation in a western Kansas stream.

Hydrobiologia 658:183–195.

Baker, L. A., D. Hope, Y. Xu, J. Edmonds, and L. Lauver. 2001. Nitrogen balance for the Central Arizona-Phoenix (CAP) ecosystem. Ecosystems 4:582–602.

Baldwin, D. S., A. M. Mitchell, and G. N. Rees. 2000. The effects of in situ drying on sediment-phosphate interactions in sediments from an old wetland. Hydrobiologia 431:3–12.

Barnett, T. P., D. W. Pierce, H. G. Hidalgo, C. Bonfils, D. Benjamin, T. Das, G. Bala, A. W. Wood, T. Nozawa, A. A. Mirin, D. R. Cayan, and M. D. Dettinger. 2008. Human-induced changes United States in the hydrology of the western United States. Science 319:1080–1083.

Bastin, J., N. Berrahmouni, A. Grainger, D. Maniatis, D. Mollicone, R. Moore, C. Patriarca, N. Picard, B. Sparrow, E. M. Abraham, K. Aloui, A. Atesoglu, F. Attore, A. Bey, M. Garzuglia, L. G. García-montero, N. Groot, G. Guerin, L. Laestadius, A. J. Lowe, and B. Mamane. 2017. The extent of forest in dryland biomes. Science 638:635–638.

Bateman, H. L., J. C. Stromberg, M. J. Banville, E. Makings, B. D. Scott, A. Suchy, and D. Wolkis. 2015. Novel water sources restore plant and animal communities along an urban river. Ecohydrology 8:792–811.

Beaulieu, J. J., H. E. Golden, C. D. Knightes, P. M. Mayer, S. S. Kaushal, M. J. Pennino, C. P. Arango, D. A. Balz, C. M. Elonen, K. M. Fritz, and B. H. Hill. 2015. Urban stream burial increases watershed-scale nitrate export. PLoS ONE 10.

Belnap, J., J. R. Welter, N. B. Grimm, N. Barger, and J. A. Ludwig. 2005. Linkages between microbial and hydrologic processes in arid and semiarid watersheds. Ecology 86:298–307.

Bernard, R. J., B. Mortazavi, and A. A. Kleinhuizen. 2015. Dissimilatory nitrate reduction to ammonium (DNRA) seasonally dominates NO3– reduction pathways in an anthropogenically impacted sub-tropical coastal lagoon. Biogeochemistry 125:47–64.

Bernhardt, E. S., J. R. Blaszczak, C. D. Ficken, M. L. Fork, K. E. Kaiser, and E. C. Seybold. 2017. Control points in ecosystems: Moving beyond the hot spot hot moment concept. Ecosystems 20:665–682.

Birch, H. F. 1958. The effect of soil drying on humus decomposition and nitrogen availability. Plant and Soil 10:9–31.

Bowden, W. B. 1987. The biogeochemistry of nitrogen in freshwater wetlands. Biogeochemistry 4:313–348.

Boyer, E. W., C. L. . Goodale, N. A. . Jaworski, and R. W. Howarth. 2002. Anthropogenic Nitrogen Sources and Relationships to Riverine Nitrogen Export in the Northeastern U.S.A. Biogeochemistry 57–58:137–169.

Brix, H. 1994. Functions of macrophytes in constructezd wetlands. Water Science and Technology 29:71–78.

Brooks, P. D., and M. M. Lemon. 2007. Spatial variability in dissolved organic matter and inorganic nitrogen concentrations in a semiarid stream, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Brown, J. B., L. A. Sprague, and J. A. Dupree. 2011. Nutrient sources and transport in the Missouri River Basin with emphasis of the effect of irrigation and reservoirs. Journal of the American Water Resources Association 47:1034–1060.

Brunet, R. C., and L. J. Garcia-Gil. 1996. Sulfide-induced dissimilatory nitrate reduction to ammonia in anaerobic freshwater sediments. FEMS Microbiology Ecology 21:131–138.

Burgin, A. J., and S. K. Hamilton. 2007. Have we overemphasized the role of denitrification in aquatic ecosystems? A review of nitrate removal pathways. Frontiers in Ecology and the Environment 5:89–96.

Butman, D., and P. A. Raymond. 2011. Significant efflux of carbon dioxide from streams and rivers in the United States. Nature Geoscience 4:839–842.

Butman, D., R. Striegl, S. Stackpoole, P. del Giorgio, Y. Prairie, D. Pilcher, P. Raymond, and F. P. Pellat. 2018. Inland Waters. Pages 568–595 State of the Carbon Cycle 2.

Caraco, N. F., and J. J. Cole. 1999. Human impact on nitrate export: An analysis using major world rivers. Ambio 28:167–170.

Caraco, N. F., and J. J. Cole. 2001. Human influence on nitrogen export: a comparison of mesic and xeric catchments. Marine and Freshwater Research 52:119–125.

Carbone, M. S., G. C. Winston, and S. E. Trumbore. 2008. Soil respiration in perennial grass and shrub ecosystems: Linking environmental controls with plant and microbial sources on seasonal and diel timescales. Journal of Geophysical Research: Biogeosciences 113:1–14.

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications 8:559–568.

Collins, S. L., J. Belnap, N. B. Grimm, J. A. Rudgers, C. N. Dahm, P. D. Odorico, M. Litvak, D. O. Natvig, D. C. Peters, W. T. Pockman, R. L. Sinsabaugh, and B. O. Wolf. 2014. A multiscale, hierarchical model of pulse dynamics in arid-land ecosystems. Annual Review of Ecology, Evolution, and Systematics 45:397–419.

Collins, S. L., R. L. Sinsabaugh, C. Crenshaw, L. Green, A. Porras-Alfaro, M. Stursova, and L. H. Zeglin. 2008. Pulse dynamics and microbial processes in aridland ecosystems. Journal of Ecology 96:413–420.

Covino, T. P., B. L. McGlynn, and R. A. McNamara. 2010. Tracer additions for spiraling curve characterization (TASCC): Quantifying stream nutrient uptake kinetics from ambient to saturation. Limnology and Oceanography: Methods 8:484–498.

Crenshaw, C. L., N. B. Grimm, L. H. Zeglin, R. W. Sheibley, C. N. Dahm, and a. D. P. Ershall. 2010. Dissolved inorganic nitrogen dynamics in the hyporheic zone of reference and human-altered southwestern U. S. streams. Fundamental and Applied Limnology / Archiv für Hydrobiologie 176:391–405.

Datry, T., S. T. Larned, and K. Tockner. 2014. Intermittent rivers: A challenge for freshwater ecology. BioScience 64:229–235.

Davidson, E. A. 1992. Sources of nitric oxide and nitrous oxide following wetting of dry soil. Soil Science Society of America Journal 56:95–102.

Dent, C. L., N. B. Grimm, E. Martí, J. W. Edmonds, J. C. Henry, and J. R. Welter. 2007. Variability in surface-subsurface hydrologic interactions and implications for nutrient retention in an arid-land stream. Journal of Geophysical Research: Biogeosciences 112:1–13.

Dodsworth, J. A., B. A. Hungate, and B. P. Hedlund. 2011. Ammonia oxidation, denitrification and dissimilatory nitrate reduction to ammonium in two US Great Basin hot springs with abundant ammonia-oxidizing archaea. Environmental Microbiology 13:2371–2386.

Dong, X., N. B. Grimm, K. Ogle, and J. Franklin. 2016. Temporal variability in hydrology modifies the influence of geomorphology on wetland distribution along a desert stream. Journal of Ecology 104:18–30.

Fazzolari, E., A. Mariotti, and J. C. Germon. 1990. Nitrate reduction to ammonia: a dissimilatory proces in Enterobacter amnigenus. Canadian Journal of Microbiology 36:779–1989.

Fierer, N., and J. P. Schimel. 2003. A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil. Soil Science Society of America Journal 67:798–805.

Fisher, S. G., L. J. Gray, N. B. Grimm, and D. E. Busch. 1982. Temporal succession in a desert stream ecosystem following flash flooding. Ecological Monographs 52:93–110.

Fisher, S. G., N. B. Grimm, E. Martí, and R. Gómez. 1998. Hierarchy, spatial configuration, and nutrient cycling in a desert stream. Australian Journal of Ecology 23:41–52.

Fisher, S. G., R. A. Sponseller, and J. B. Heffernan. 2004. Horizons in stream biogeochemistry: Flowpaths to progress. Ecology 85:2369–2379.

Fitzhugh, T. W., and B. D. Richter. 2004. Quenching urban thrist: Growing cities and their impact on freshwater ecosystems. Bioscience 54:741–754.

Galloway, J. N., F. J. Dentener, D. G. Capone, E. W. Boyer, R. W. Howarth, S. P. Seitzinger, G. P. Asner, C. C. Cleveland, P. A. Green, E. A. Holland, D. M. Karl, A. F. Michaels, J. H. Porter, A. R. Townsend, and C. J. Vo. 2004. Nitrogen cycles: Past, present, and future. Biogeochemistry 70:153–226.

Galloway, J. N., A. R. Townsend, J. W. Erisman, M. Bekunda, Z. Cai, J. R. Freney, L. A. Martinelli, S. P. Seitzinger, and M. A. Sutton. 2008. Transformation of the nitrogen cycle: Recent trends, questions, and potential solutions. Science 320:889–892.

Gardner, K. K., and B. L. McGlynn. 2009. Seasonality in spatial variability and influence of land use/land cover and watershed characteristics on stream water nitrate concentrations in a developing watershed in the Rocky Mountain West. Water Resources Research 45:1–14.

Gardner, W. S., M. J. McCarthy, S. An, D. Sobolev, K. S. Sell, and D. Brock. 2006. Nitrogen fixation and dissimilatory nitrate reduction to ammonium (DNRA) support nitrogen dynamics in Texas estuaries. Limnology and Oceanography 51:558–568.

Gebauer, R. L. E., and J. R. Ehleringer. 2000. Water and nitrogen uptake patterns following moisture pulses in a cold desert community. Ecology 81:1415–1424.

Giblin, A. E., C. R. Tobias, B. Song, N. Weston, G. T. Banta, and W. H. Rivera-Monroy. 2013. The importance of dissimilatory nitrate reduction to ammonium (DNRA) in the nitrogen cycle of coastal ecosystems. Oceanography 26:124–131.

Gift, D. M., P. M. Groffman, S. S. Kaushal, and P. M. Mayer. 2010. Denitrification potential, root biomass, and organic matter in degraded and restored urban riparian zones. Restoration Ecology 18:113–124.

Golterman, H. L. 2000. Denitrification and a numerical modelling approach for shallow waters. Hydrobiologia 421:93–104.

Gómez, R., I. M. Arce, J. J. Sánchez, and M. del Mar Sánchez-Montoya. 2012. The effects of drying on sediment nitrogen content in a Mediterranean intermittent stream: A microcosms study. Hydrobiologia 679:43–59.

Grimm, N. B. 1987. Nitrogen dynamics during succession in a desert stream. Ecology

68:1157–1170.

Grimm, N. B., S. H. Faeth, N. E. Golubiewski, C. L. Redman, J. Wu, X. Bai, J. M. Briggs, N. B. Grimm, S. H. Faeth, N. E. Golubiewski, C. L. Redman, J. Wu, X. Bal, and J. M. Briggs. 2008. Global change and the ecology of cities. Science (New York, N.Y.) 319:756–760.

Grimm, N. B., and S. G. Fisher. 1986a. Nitrogen limitation potential of Arizona streams and rivers. Journal of the Arizona-Nevada Academy of Sciences 21:31–44.

Grimm, N. B., R. W. Sheibley, C. L. M. Crenshaw, C. N. Dahm, W. J. Roach, and L. H. Zeglin. 2005. N retention and transformation in urban streams. Journal of the North American Benthological Society 24:626–642.

Grimm, N., and S. G. Fisher. 1986b. Nitrogen limitation in a Sonoran Desert stream. North American Benthological Society 5:2–15.

Groffman, P. M., M. A. Altabet, J. K. Böhlke, K. Butterbach-bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, M. A. Voytek, P. M. Groffman, M. A. Altabet, J. K. Bohlke, K. Butterbach-bahl, M. B. David, M. K. Firestone, A. E. Giblin, T. M. Kana, L. P. Nielsen, and M. A. Voytek. 2006. Methods for Measuring Denitrification : Diverse Approaches to a Difficult Problem. Ecological Applications 16:2091–2122.

Groffman, P. M., N. J. Boulware, W. C. Zipperer, R. V. Pouyat, L. E. Band, and M. F. Colosimo. 2002. Soil nitrogen cycle processes in urban riparian zones. Environmental Science and Technology 36:4547–4552.

Groffman, P. M., A. J. Gold, and R. C. Simmons. 1992. Nitrate dynamics in riparian forests: Microbial studies. Journal of Environment Quality 21:666–671.

Guhathakurta, S., and P. Gober. 2007. The impact of the Phoenix urban heat island on residential water use. Journal of the American Planning Association 73:317–329.

Haaijer, S. C. M., L. P. M. Lamers, A. J. P. Smolders, M. S. M. Jetten, and H. J. M. Op de Camp. 2007. Iron sulfide and pyrite as potential electron donors for microbial nitrate reduction in freshwater wetlands. Geomicrobiology Journal 24:391–401.

Hale, R. L., L. Turnbull, S. Earl, N. Grimm, K. Riha, G. Michalski, K. A. Lohse, and D. Childers. 2014a. Sources and transport of nitrogen in arid urban watersheds. Environmental Science and Technology 48:6211–6219.

Hale, R. L., L. Turnbull, S. R. Earl, D. L. Childers, and N. B. Grimm. 2014b. Stormwater infrastructure controls runoff and dissolved material export from arid urban watersheds. Ecosystems 18:62–75.

Hall, R. O., J. L. Tank, D. J. Sobota, P. J. Mulholland, M. Jonathan, O. Brien, W. K.

Dodds, J. R. Webster, H. M. Valett, G. C. Poole, J. Bruce, J. L. Meyer, W. H. Mcdowell, S. L. Johnson, S. K. Hamilton, B. Grimm, S. V Gregory, C. N. Dahm, L. W. Cooper, L. R. Ashkenas, M. Thomas, R. W. Sheibley, J. D. Potter, B. R. Niederlehner, L. T. Johnson, M. Helton, C. M. Crenshaw, A. J. Burgin, M. J. Bernot, J. J. Beaulieu, and C. P. Arango. 2009a. Nitrate removal in stream ecosystems measured by Total uptake 15 N addition experiments : Limnology and Oceanography 54:653–665.

Hall, R. O., J. L. Tank, D. J. Sobota, P. J. Mulholland, J. M. O'Brien, W. K. Dodds, J. R. Webster, H. M. Valett, G. C. Poole, B. J. Peterson, J. L. Meyer, W. H. McDowell, S. L. Johnson, S. K. Hamilton, N. B. Grimm, S. V Gregory, C. N. Dahm, L. W. Cooper, L. R. Ashkenas, S. M. Thomas, R. W. Sheibley, J. D. Potter, B. R. Niederlehner, L. T. Johnson, A. M. Helton, C. M. Crenshaw, A. J. Burgin, M. J. Bernot, J. J. Beaulieu, and C. P. Arango. 2009b. Nitrate removal in stream ecosystems measured by 15N addition experiments: Total uptake. Limnology and Oceanography 54:653–665.

Harms, T. K., and N. B. Grimm. 2008. Hot spots and hot moments of carbon and nitrogen dynamics in a semiarid riparian zone. Journal of Geophysical Research: Biogeosciences 113:1–14.

Harms, T. K., and N. B. Grimm. 2010. Influence of the hydrologic regime on resource availability in a semi-arid stream-riparian corridor. Ecohydrology 3:349–359.

Harms, T. K., and N. B. Grimm. 2012. Responses of trace gases to hydrologic pulses in desert floodplains. Journal of Geophysical Research: Biogeosciences 117:1–14.

Hatt, B. E., T. D. Fletcher, C. J. Walsh, and S. L. Taylor. 2004. The influence of urban density and drainage infrastructure on the concentrations and loads of pollutants in small streams. Environmental Management 34:112–124.

Helton, A. M., G. C. Poole, J. L. Meyer, W. M. Wollheim, B. J. Peterson, P. J. Mulholland, E. S. Bernhardt, J. A. Stanford, C. Arango, L. R. Ashkenas, L. W. Cooper, W. K. Dodds, S. V. Gregory, R. O. Hall, S. K. Hamilton, S. L. Johnson, W. H. McDowell, J. D. Potter, J. L. Tank, S. M. Thomas, H. M. Valett, J. R. Webster, and L. Zeglin. 2011. Thinking outside the channel: Modeling nitrogen cycling in networked river ecosystems. Frontiers in Ecology and the Environment 9:229–238.

Hill, A. R. 1996. Nitrate removal in stream riparian zones. Journal of Environmental Quality 25:743–755.

Holloway, J. M., R. A. Dahlgren, B. Hansen, and W. H. Casey. 1998. Contribution of bedrock nitrogen to high nitrate concentrations in stream water. Nature 395:785–788.

Holmes, R. M., S. G. Fisher, and N. B. Grimm. 1994. Parafluvial nitrogen dynamics in a desert stream ecosystem. Journal of the North American Benthological Society

13:468–478.

Holmes, R. M., J. B. Jones, S. G. Fisher, and N. B. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry 33:125146.

Holmes, R. M., J. W. McClelland, D. M. Sigman, B. Fry, and B. J. Peterson. 1998. Measuring 15 N-NH 4 in marine, estuarine, and freshwaters: An adaptation of the ammonia diffusion method for samples with low ammonium concentrations. Marine Chemistry 60:235–243.

Hoos, A. B., and G. McMahon. 2009. Spatial analysis of instream nitrogen loads and factors controlling nitrogen delivery to streams in the southeastern United States using spatially referenced regression on watershed attributes (SPARROW) and regional classification framworks. Hydrological Processes 23:2275–2294.

Howarth, R., D. Swaney, G. Billen, J. Garnier, B. Hong, C. Humborg, P. Johnes, C. Mörth, and R. Marino. 2012. Nitrogen fluxes from the landscape are controlled by net anthropogenic nitrogen inputs and by climate. Fronteiers in Ecology and Emvironment 10:37–43.

Howarth, R. W., D. P. Swaney, E. W. Boyer, R. Marino, N. Jaworski, and C. Goodale. 2006. The influence of climate on average nitrogen export from large watersheds in the Northeastern United States. Pages 163–186 *in* L. A. Martinelli and R. W. Howarth, editors. Nitrogen Cycling in the Americas: Natural and Anthropogenic Influences and Controls. Springer, Dordrecht.

Hume, N. P., M. S. Fleming, and A. J. Horne. 2002. Denitrification potential and carbon quality of four aquatic plants in wetland microcosms. Soil Science Society of America Journal 66:1706–1712.

Huxman, T. E., K. A. Snyder, D. Tissue, A. J. Leffler, K. Ogle, W. T. Pockman, D. R. Sandquist, D. L. Potts, and S. Schwinning. 2004. Precipitation pulses and carbon fluxes in semiarid and arid ecosystems. Oecologia 141:254–268.

Jarvis, P., A. Rey, C. Petsikos, L. Wingate, J. Pereira, J. Banza, J. David, F. Miglietta, M. Borghetti, G. Manca, and R. Valentini. 2007. Drying and wetting of Mediterranean soils stimulates decomposition and carbon dioxide emission: The “Birch effect.” Tree Physiology 27:929–940.

Jencso, K. G., B. L. McGlynn, M. N. Gooseff, S. M. Wondzell, K. E. Bencala, and L. A. Marshall. 2009. Hydrologic connectivity between landscapes and streams: Transferring reach- and plot-scale understanding to the catchment scale. Water Resources Research 45:1–16.

Jones, J. B., S. G. Fisher, and N. B. Grimm. 1995. Nitrification in the hyporheic zone of a desert stream ecosystem. Journal of the North American Benthological Society 14:249–258.

Kana, T. M., C. Darkangelo, M. D. Hunt, J. B. Oldham, G. E. Bennett, and J. C. Cornwell. 1994. Membrane inlet mass spectrometer for rapid high-precision determination of N2, O2 , and Ar in environmental water samples. Anal. Chem 66:4166–4170.

Kaushal, S. S., P. M. Groffman, L. E. Band, E. M. Elliott, C. A. Shields, and C. Kendall. 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. Environmental Science and Technology 45:8225–8232.

Kaye, J. P., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. 2006. A distinct urban biogeochemistry? Trends in Ecology and Evolution 21:192–199.

Kelso, B. H. L., R. V. Smith, R. J. Laughlin, and S. D. Lennox. 1997. Dissimilatory nitrate reduction in anaerobic sediments leading to river nitrite accumulation. Applied and Environmental Microbiology 63:4679–4685.

King, D., and D. B. Nedwell. 1985. The influence of nitrate concentration upon the end-products of nitrate dissimilation by bacteria in anaerobic salt marsh sediment. FEMS Microbiology Letters 31:23–28.

Koop-Jakobsen, K., and A. E. Giblin. 2010. The effect of increased nitrate loading on nitrate reduction via denitirification and DNRA in salt marsh sediments. Limnology and Oceanography 55:789–802.

Kurc, S. A., and E. E. Small. 2007. Soil moisture variations and ecosystem-scale fluxes of water and carbon in semiarid grassland and shrubland. Water Resources Research 43:1–13.

Kustu, M. D., Y. Fan, and M. Rodell. 2011. Possible link between irrigation in the U.S. High Plains and increased summer streamflow in the Midwest. Water Resources Research 47:W03522.

Larned, S. T., T. Datry, D. B. Arscott, and K. Tockner. 2010. Emerging concepts in temporary-river ecology. Freshwater Biology 55:717–738.

Larson, E. K., N. B. Grimm, P. Gober, and C. L. Redman. 2005. The paradoxical ecology and management of water in the Phoenix , USA metropolitan area. Ecohydrology & Hydrobiology 5:287–296.

Lauver, L., and L. A. Baker. 2000. Mass balance for wastewater nitrogen in the Central Arizona-Phoenix ecosystem. Water Research 34:2754–2760.

Lee, C. G., T. D. Fletcher, and G. Sun. 2009. Nitrogen removal in constructed wetland systems. Engineering in Life Sciences 9:11–22.

Leopold, L. B., and T. Maddock. 1953. The hydraulic geometry of stream channels and some physiograhpic implications. Page Geological Survey Profession Paper.

Lewis, D. B., and N. B. Grimm. 2007. Hierarchical regulation of nitrogen export from urban catchments: Interactions of storms and landscapes. Ecological Applications 17:2347–2364.

Lillebø, A. I., M. Morais, P. Guilherme, R. Fonseca, A. Serafim, and R. Neves. 2007. Nutrient dynamics in Mediterranean temporary streams: A case study in Pardiela catchment (Degebe River, Portugal). Limnologica 37:337–348.

Lowrance, R. R., R. A. Leonard, L. E. Asmussen, and R. L. Todd. 1985. Nutrient budgets for agricultural watersheds in the southeastern coastal plain. Ecology 66:287–296.

Lu, W. W., H. L. Zhang, and W. M. Shi. 2013. Dissimilatory nitrate reduction to ammonium in an anaerobic agricultural soil as affected by glucose and free sulfide. European Journal of Soil Biology 58:98–104.

Ludwig, J. A., and D. J. Tongway. 1997. A landscape approach to rangeland ecology. Pages 1–12 *in* J. Ludwig, D. Tongway, D. Freudenberger, J. Noble, and K. Hodgkinson, editors. Landscape ecology: Function and management. CSIRO Publishing, Collingwood, Victoria, Australia.

Makings, E., L. Butler, M. Chew, and J. C. Stromberg. 2011. Noteworthy collections from Tempe Town Lake riverbed. Desert Plants 27:3–10.

Manzoni, S., R. B. Jackson, J. A. Trofymow, and A. Porporato. 2008. The global stoichiometry of litter nitrogen mineralization. Science 321:684–686.

Marcé, R., B. Obrador, L. Gómez-Gener, N. Catalán, M. Koschorreck, M. I. Arce, G. Singer, and D. von Schiller. 2018. Emissions from dry inland waters are a blind spot in the global carbon cycle. Earth-Science Reviews 188:240–248.

Matheson, F. E., M. L. Nguyen, A. B. Cooper, T. P. Burt, and D. C. Bull. 2002. Fate of 15N-nitrate in unplanted , planted and harvested riparian wetland soil microcosms. Ecological Engineering 19:249–264.

Mayer, P. M., W. B. DeOreo, E. M. Opitz, J. C. Kiefer, W. Y. Davis, B. Dziegielewski, and J. O. Nelson. 1999. Residential end uses of water. AWWA Research Foundation and American Water Works Association Rep.

Mayer, P. M., S. K. Reynolds, M. D. McCutchen, and T. J. Canfield. 2007. Meta-analysis of nitrogen removal in riparian buffers. Journal of Environment Quality 36:1172.

McCalley, C. K., and J. P. Sparks. 2008. Controls over nitric oxide and ammonia emissions from Mojave Desert soils. Oecologia 156:871–881.

McClain, M. E., E. W. Boyer, C. L. Dent, S. E. Gergel, N. B. Grimm, P. M. Groffman, S. C. Hart, J. W. Harvey, C. A. Johnston, E. Mayorga, W. H. McDowell, and G. Pinay. 2003. Biogeochemical Hot Spots and Hot Moments at the Interface of Terrestrial and Aquatic Ecosystems. Ecosystems 6:301–312.

McClaugherty, C. A., J. D. Aber, and J. M. Melillo. 1982. The role of fine roots in the organic matter and nitrogen budgets of two forested ecosystems. Ecology 63:1481–1490.

McDonald, R. I., I. Douglas, C. Revenga, R. Hale, B. Fekete, N. Grimm, and J. Gro. 2011. Global urban growth and the geography of water availability, quality, and delivery. Ambio 40:437–446.

McIntyre, R. E. S., M. A. Adams, and P. F. Grierson. 2009. Nitrogen mineralization potential in rewetted soils from a semi-arid stream landscape, north-west Australia. Journal of Arid Environments 73:48–54.

McKee, L., B. Eyre, and S. Hossain. 2000. Intra- and interannual export of nitrogen and phosphor us in the subtropical Richmond River catchment, Australia. Hydrological Processes 14:1787–1809.

McLaughlin, C. 2008. Evaporation as a nutrient retention mechanism at Sycamore Creek, Arizona. Hydrobiologia 603:241–252.

Meixner, T., A. K. Huth, P. D. Brooks, M. H. Conklin, N. B. Grimm, R. C. Bales, P. A. Haas, and J. R. Petti. 2007. Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona. Journal of Geophysical Research: Biogeosciences 112:1–11.

Merbt, S. N., L. Proia, J. I. Prosser, E. Marti, E. O. Casamayor, and D. Von Schiller. 2016. Stream drying drives microbial ammonia oxidation and first-flush nitrate export. Ecology 97:2192–2198.

Van Meter, K. J., and N. B. Basu. 2015. Catchment legacies and time lags: A parsimonious watershed model to predict the effects of legacy storage on nitrogen export. PLoS ONE 10:1–22.

Meybeck, M., H. H. Dürr, and C. J. Vörösmarty. 2006. Global coastal segmentation and its river catchment contributors: A new look at land-ocean linkage. Global Biogeochemical Cycles 20:1–15.

Meyer, J. L., and G. E. Likens. 1979. Transport and transformation of phosphorus in a forest stream ecosystem. Ecology 60:1255–1269.

Mitsch, W. J., and J. G. Gosselink. 2015. Wetlands. 5th edition. Wiley, Hoboken, NJ.

Moore, R. B., C. M. Johnston, R. A. Smith, and B. Milstead. 2011. Sources and delivery of nutrients to the receiving water in the Northeastern and Mid-Atlantic regions of the United States. Journal of the American Water Resources Association 47:965–990.

Mulholland, P. J., R. O. Hall, D. J. Sobota, W. K. Dodds, E. G. Stuart, N. B. Grimm, S. K. Hamilton, W. H. Mcdowell, J. M. O. Brien, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, S. V Gregory, S. L. Johnson, J. L. Meyer, B. J. Peterson, G. C. Poole, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, A. M. Helton, L. T. Johnson, B. R. Niederlehner, J. D. Potter, R. W. Sheibley, and S. M. Thomas. 2009. Nitrate removal in stream ecosystems measured by 15N addition experiments: Denitrification. Limnology and Oceanography 54:666–680.

Mulholland, P. J., A. M. Helton, G. C. Poole, R. O. Hall, S. K. Hamilton, B. J. Peterson, J. L. Tank, L. R. Ashkenas, L. W. Cooper, C. N. Dahm, W. K. Dodds, S. E. G. Findlay, S. V Gregory, N. B. Grimm, S. L. Johnson, W. H. McDowell, J. L. Meyer, H. M. Valett, J. R. Webster, C. P. Arango, J. J. Beaulieu, M. J. Bernot, A. J. Burgin, C. L. Crenshaw, L. T. Johnson, B. R. Niederlehner, J. M. O'Brien, J. D. Potter, R. W. Sheibley, D. J. Sobota, and S. M. Thomas. 2008. Stream denitrification across biomes and its response to anthropogenic nitrate loading. Nature 452:202–205.

Newbold, J. D., J. W. Elwood, R. V. O'Neill, and W. Van Winkle. 1981. Measuring nutrient spiralling in streams. Canadian Journal of Fisheries and Aquatic Sciences 38:860–863.

Newcomer, T. A., S. S. Kaushal, P. M. Mayer, A. R. Shields, A. Elizabeth, P. M. Groffman, and A. J. Gold. 2012. Influence of natural and novel organic carbon sources on dentrification in forest, degraded urban, and restored streams. Ecological Monographs 82:449–466.

Nichols, D. S. 1983. Capacity of natural wetlands to remove nutrients from wastewater. Journal (Water Pollution Control Federation) 55:495–505.

Nielson, L. P. 1991. Denitrification in sediment determined from nitrogen isotope pairing. FEMS Microbiology Ecology 9:357–361.

Nizzoli, D., E. Carraro, V. Nigro, and P. Viaroli. 2010. Effect of organic enrichment and thermal regime on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in hypolimnetic sediments of two lowland lakes. Water Research 44:2715–2724.

NOAA National Centers for Environmental Information. 2018. State of the Climate: National Climate Report for Annual 2017.

Nogaro, G., and A. J. Burgin. 2014. Influence of bioturbation on denitrification and dissimilatory nitrate reduction to ammonium (DNRA) in freshwater sediments. Biogeochemistry 120:279–294.

Noy-Meir, I. 1973. Desert ecosystems: Environment and producers. Annual Review of Ecology and Systematics 4:25–51.

Oak Creek Watershed Council. 2012. Improvement plan for the Oak Creek Watershed, Arizona.

Ogle, K., and J. F. Reynolds. 2004. Plant responses to precipitation in desert ecosystems: Integrating functional types, pulses, thresholds, and delays. Oecologia 141:282–294.

Oldham, C. E., D. E. Farrow, and S. Peiffer. 2013. A generalized Damkohler number for classifying material processing in hydrological systems Solid. Hydrology and Earth System Sciences 17:1133–1148.

Palta, M., M. V. du Bray, R. Stotts, A. Wolf, and A. Wutich. 2016. Ecosystem services and disservices for a vulnerable population: Findings from urban waterways and wetlands in an American desert city. Human Ecology 44:463–47816.

Palta, M. M., J. G. Ehrenfeld, and P. M. Groffman. 2014. Hotspots and hot moments of denitrification in urban brownfield wetlands. Ecosystems 17:1121–1137.

Palta, M. M., N. B. Grimm, and P. M. Groffman. 2017. "Accidental" urban wetlands: Ecosystem functions in unexpected places. Frontiers in Ecology and the Environment 15:248–256.

Paul, M. J., and J. L. Meyer. 2001. Streams in the Urban Landscape. Annual Review of Ecology and Systematics 32:333–365.

Peterjohn, W. T., and D. L. Correll. 1984. Nutrient dynamics in an agricultural watershed: Observations on the role of a riparian forest. Ecology 65:1466–1475.

Peterson, B. J., W. M. Wollheim, P. J. Mulholland, J. R. Webster, J. L. Meyer, J. L. Tank, E. Marti, W. B. Bowden, H. M. Vallett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. Gregory, and D. D. Morrall. 2001. Control of nitrogen export from headwaters by headwater streams. Science 292:86–90.

Pinay, G., L. Roques, and A. Fabre. 1993. Spatial and temporal patterns of denitrification in a riparian forest. Journal of Applied Ecology 30:581–591.

R Core Team. 2018. R: A language and environment for statistical computing. R Foundation for Statistical Computing, Vienna, Austria.

Racchetti, E., M. Bartoli, E. Soana, D. Longhi, R. R. Christian, M. Pinardi, and P. Viaroli. 2011. Influence of hydrological connectivity of riverine wetlands on nitrogen removal via denitrification. Biogeochemistry 103:335–354.

Raymond, P. A., J. E. Saiers, and W. V. Sobczak. 2016. Hydrological and biogeochemical controls on watershed dissolved organic matter transport: Pulse-shunt concept. Ecology 97:5–16.

Rebich, R. A., N. A. Houston, S. V Mize, D. K. Pearson, P. B. Ging, and C. E. Hornig.

2011. Sources and delivery of nutrient to the Northwestern Gulf of Mexico from stream in the South-Central United States. 2011 47:1061–1086.

Reynolds, J. F., P. R. Kemp, K. Ogle, and R. J. Fernández. 2004. Modifying the "pulse-reserve" paradigm for deserts of North America: Precipitation pulses, soil water, and plant responses. Oecologia 141:194–210.

Reynolds, J. F., D. M. S. Smith, E. F. Lambin, B. L. Turner, M. Mortimore, S. P. J. Batterbury, T. E. Downing, H. Dowlatabadi, R. J. Fernández, J. E. Herrick, E. Huber-sannwald, H. Jiang, R. Leemans, T. Lynam, F. T. Maestre, M. Ayarza, and B. Walker. 2007. Global desertification: Building a science for dryland development. Science 316:847–852.

Robertson, D. M., and D. A. Saad. 2013. Nutrient inputs to the Laurentian Great Lakes by source and watershed estimated using SPARROW watershed models. Journal of the American Water Resources Association 49:725–734.

Rütting, T., P. Boeckx, C. Müller, and L. Klemedtsson. 2011. Assessment of the importance of dissimilatory nitrate reduction to ammonium for the terrestrial nitrogen cycle. Biogeosciences 8:1779–1791.

Rysgaard, S., N. Risgaard-Petersen, and N. P. Sloth. 1996. Nitrification, denitrification, and nitrate ammonification in sediments of two coastal lagoons in Southern France. Hydrobiologia 329:133–141.

Saleh, D., and J. Domagalski. 2015. SPARROW modeling of nitrogen sources and transport in rivers and stream of California and adjacent states, U. S. Journal of the American Water Resources Association 51:1483–1507.

Saunders, D. L., and J. Kalff. 2001. Nitrogen rentention in wetlands, lakes and rivers. Hydrobiologia 443:205–212.

Schade, J. D., S. G. Fisher, N. B. Grimm, and J. Seddon. 2001. The influence of a riparian shrub on nitrogen cycling in a Sonoran Desert stream. Ecology 82:3363–3376.

von Schiller, D., V. Acuña, D. Graeber, E. Martí, M. Ribot, S. Sabater, X. Timoner, and K. Tockner. 2011. Contraction, fragmentation and expansion dynamics determine nutrient availability in a Mediterranean forest stream. Aquatic Sciences 73:485–497.

von Schiller, D., S. Bernal, C. N. Dahm, and E. Martí. 2017. Nutrient and oganic matter dynamics in intermittent rivers and ephemeral streams. Pages 135–160 Intermittent Rivers and Ephemeral Streams. Elsevier Inc.

von Schiller, D., R. Marcé, B. Obrador, L. Gómez-Gener, J. P. Casas-Ruiz, V. Acuña, and M. Koschorreck. 2014. Carbon dioxide emissions from dry watercourses. Inland Waters 4:377–382.

Schlesinger, W. H., and W. T. Peterjohn. 1991. Processes controlling ammonia volatilization from Chihuahuan desert soils. Soil Biology and Biochemistry 23:637–642.

Schlesinger, W. H., J. F. Reynolds, G. L. Cunningham, F. Laura, W. M. Jarrell, R. A. Virginia, W. G. Whitford, S. Science, N. Series, N. Mar, W. H. Schlesinger, G. L. Cunningham, R. A. Virginia, W. G. Whitford, L. F. Huenneke, and W. M. Jarrell. 1990. Biological feedbacks in global desertification. Science 247:1043–1048.

Schwinning, S., and O. E. Sala. 2004. Hierarchy of responses to resource pulses in arid and semi-arid ecosystems. Oecologia 141:211–220.

Scott, J. T., M. J. McCarthy, W. S. Gardner, and R. D. Doyle. 2008. Denitrification, dissimilatory nitrate reduction to ammonium, and nitrogen fixation along a nitrate concentration gradient in a created freshwater wetland. Biogeochemistry 87:99–111.

Seitzinger, S. P., R. V Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. Breemen. 2002. Nitrogen retention in rivers: model development and application to watersheds in the northeastern U.S.A. Biogeochemistry 57/58:199–237.

Sharp, Z. 2017. Principles of stable isotope geochemistry. 2nd edition.

Sigman, D. M., M. a Altabet, R. Michener, D. C. McCorkle, B. Fry, and R. M. Holmes. 1997. Natural abundance-level measurements of the nitrogen isotopic composition of oceanic nitrate: an adaption of the ammonia diffusion method.

Silver, W. L., D. J. Herman, M. K. Firestone, S. Ecology, and N. Sep. 2001. Dissimilatory nitrate reduction to ammonium in upland tropical forest soils. Ecology 82:2410–2416.

Sotta, E. D., M. D. Corre, and E. Veldkamp. 2008. Differing N status and N retention processes of soils under old-growth lowland forest in Eastern Amazonia, Caxiuanã, Brazil. Soil Biology and Biochemistry 40:740–750.

Southam, G., P. Keim, and C. Keys. 2000. The Oak Creek Canyon Escherichia coli genotyping project. Flagstaff, AZ.

Sponseller, R. A. 2007. Precipitation pulses and soil CO2 flux in a Sonoran Desert ecosystem. Global Change Biology 13:426–436.

Sponseller, R. A., and S. G. Fisher. 2008. The Influence of Drainage Networks on Patterns of Soil Respiration in a Desert Catchment. Ecology 89:1089–1100.

Stanley, E. H., S. G. Fisher, and N. B. Grimm. 1997. Ecosystem expansion and contraction in streams. Bioscience 47:427–435.

Stieglitz, M., J. Shaman, J. P. McNamara, V. Engel, J. Shanley, and G. W. Kling. 2003. An approach to understanding hydrologic connectivity on the hillslope and the implications for nutrient transport. Global Biogeochemical Cycles 17:1–15.

Storey, R. G., D. D. Williams, and R. R. Fulthorpe. 2004. Nitrogen processing in the hyporheic zone of a pastoral stream. Biogeochemistry 69:285–313.

Suchy, A. K. 2016. Denitrification in accidental urban wetlands: Exploring the rolse of water flows and plant patches. Arizona State University.

Thomsen, B. W., and H. H. Schumann. 1968. Water resources of the Sycamore Creek watershed, Maricopa County, Arizona. Page United States Geological Survey Water-Supply Paper.

Tiedje, J. M. 1988. Ecology of dentrification and dissimilatory nitrate reduction to ammonium. Pages 179–244 *in* A. J. B. Zehnder, editor. Environmental Microbiology of Anaerobes. John Wiley and Sons, New York.

Tobias, C. R., I. C. Anderson, and S. A. Macko. 2001. Nitrogen cycling through a fringing marsh- aquifer ecotone. Marine Ecology Progress Series 210:25–39.

Tooth, S. 2000. Process, form and change in dryland rivers: A review of recent research. Earth Science Reviews 51:67–107.

USDA-NASS. 2017. USDA National Agricultural Statistics Service Cropland Data Layer. https://nassgeodata.gmu.edu/CropScape/.

Vitousek, P. M., H. a Mooney, J. Lubchenco, and J. M. Melillo. 1997. Human domination of Earth's ecosystems. Science 277:494–499.

Vymazal, J. 2007. Removal of nutrients in various types of constructed wetlands. Science of the Total Environment 380:48–65.

Walsh, C. J., T. D. Fletcher, and A. R. Ladson. 2009. Retention capacity: A metric to link stream ecology and storm-water management. Journal of Hydrologic Engineering 14:399–406.

Walsh, C. J., A. H. Roy, J. W. Feminella, P. D. Cottingham, P. M. Groffman, and R. P. Morgan. 2005. The urban stream syndrome: Current knowledge and the search for a cure. Journal of the North American Benthological Society 24:706–723.

Weier, K. L., J. W. Doran, J. F. Power, and D. T. Walters. 1993. Denitrification and the dinitrogen/nitrous oxide ratio as affected by soil water, available carbon, and nitrate. Soil Science Society of America Journal 57:66.

Welter, J. R., and S. G. Fisher. 2016. The influence of storm characteristics on hydrological connectivity in intermittent channel networks: Implications for nitrogen transport and denitrification. Freshwater Biology 61:1214–1227.

Welter, J. R., S. G. Fisher, and N. B. Grimm. 2005. Nitrogen transport and retention in an arid land watershed: Influence of storm characteristics on terrestrial-aquatic linkages. Biogeochemistry 76:421–440.

Wise, D. R., and H. M. Johnson. 2011. Surface-water nutrient conditions and sources in the United States Pacific Northwest. Journal of the American Water Resources Association 47:1110–1135.

Wollheim, W. M., G. K. Mulukutla, C. Cook, and R. O. Carey. 2017. Aquatic nitrate retention at river network scales across flow conditions determined using nested in situ sensors. Water Resources Research 53:9740–9756.

Wollheim, W. M., B. A. Pellerin, C. J. Vo, and C. S. Hopkinson. 2005. N Retention in Urbanizing Headwater Catchments. Ecosystems 8:871–884.

Xu, L., D. D. Baldocchi, and J. Tang. 2004. How soil moisture, rain pulses, and growth alter the response of ecosystem respiration to temperature. Global Biogeochemical Cycles 18:1–10.

Yahdjian, L., and O. E. Sala. 2010. Size of precipitation pulses controls nitrogen transformation and losses in an arid Patagonian ecosystem. Ecosystems 13:575–585.

Ye, L., and N. B. Grimm. 2013. Modelling potential impacts of climate change on water and nitrate export from a mid-sized, semiarid watershed in the US Southwest. Climatic Change 120:419–431.