# HOW ANTHROPOGENIC MODIFICATIONS INFLUENCE THE CYCLING OF NITROGEN IN INDIAN BEND WASH, AN URBAN DESERT STREAM

by

W. John Roach

A Dissertation Presented in Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

ARIZONA STATE UNIVERSITY

December 2005

HOW ANTHROPOGENIC MODIFICATIONS INFLUENCE THE CYCLING OF

NITROGEN IN INDIAN BEND WASH, AN URBAN DESERT STREAM

by

W. John Roach

has been approved

November 2005

APPROVED:

______________________________, Chair

______________________________

______________________________

______________________________

______________________________

Supervisory Committee

ACCEPTED:

______________________________

Director of the School

______________________________

Dean, Division of Graduate Studies

ABSTRACT

Cities have expanded in conjunction with rapid population growth, often at the expense of agricultural lands. Simultaneously, Earth's biogeochemical cycles have been altered by human activity. Concentrations of fixed nitrogen (e.g, nitrate, ammonium, and $NO_x$,) have been intentionally and unintentionally increased by human practices including synthetic fertilizer application and fossil-fuel combustion. Yet ecosystem services of nitrogen retention are threatened as ecosystem structure is altered by human activities. The research presented here addresses the question: *how do the hydrologic and geomorphic structure of a stream affect patterns of nitrogen availability and retention?* Research was conducted in Indian Bend Wash (IBW), a rapidly urbanizing watershed of Scottsdale, AZ.

Patterns of urbanization over the past half century were quantified using aerial photography. Changes in the mainstem of IBW were particularly marked. A series of artificial lakes was constructed in the low-flow channel, and adjacent floodplain sediments were stabilized with turf grass. Canals and groundwater pumping allowed the creation of a perennial reach in what was historically a dry wash. Fluctuations in proportion of groundwater and floodwater entering the lake series drove variations in the concentrations of nitrogen and phosphorus, causing phytoplankton growth to alternate between phosphorus and nitrogen limitation. A mass balance of the flux of nitrogen through the lake chain and its adjacent floodplain indicated that a significant proportion of the nitrogen was not exported. Experiments demonstrated that denitrification was the primary retention mechanism in floodplain soils while storage, presumably in sediments, was more important in lakes.

This study demonstrates that urbanization, by creating novel linkages between patches, can unintentionally increase nitrogen concentrations, disrupting fundamental processes like primary production. Although they are human-designed to serve other functions (e.g., flood management), artificial lakes and turf floodplains can act as important sites of denitrification, suggesting a possible means for managers to control nitrogen loading to recipient ecosystems. However, this potential is limited, and whereas the proportion of nitrogen retained by the stream-floodplain complex was large, the massive influx of nitrogen overwhelmed the ecosystem's nitrogen removal capacity and its ability to prevent export of significant quantities of nitrogen.

DEDICATION

For C. Lisa Dent, a brilliant ecologist, generous colleague and wonderful friend.

Her time with us was too short. She is missed.

## ACKNOWLEDGEMENTS

This research was made possible by generous contributions and tireless efforts of a large number of people in whose debt I will forever remain. First and foremost, I thank my advisor Dr. Nancy Grimm who provided intellectual guidance, moral support, and criticism, as needed. My gratitude is inestimable, for without her this work would have foundered. Drs. Ramon Arrowsmith, Jim Elser, Stuart Fisher, Ann Kinzig and Diane Hope through their insights, critiques and encouragement have substantially improved this work. To the many undergraduate and graduate students, not to mention post-docs, who lent strong backs, good ideas, and emotional release throughout, thanks. I also thank the IGERT program and its multifaceted students for pushing me to think differently about science. Although it is impossible to thank all who contributed, I thank Jennifer Edmonds, Jim Heffernan, Darrel Jenerette, Nicole Garber, Phil Tarrant, John Schade, David Lewis, Rich Sheibley, Libby Larson, Tamara Harms, Jennifer Zachary, Jill Welter, Harriet Van Vleck, Amy DiIorio, Julia Henry, Steve Swanson, Jill Koehler, Tracy Johns, Wayne Porter, Lela Preshad, Hillery Oberle, Roy Erickson, Matt Lord, Noah Dillard, Christine McLaughlin, Cathryn Meegan, Diane Miller, Emily Prud'homme, Darek Stauffer, John Schampel, Tracy Johns, Susan Goldsmith, Wontae Lee and the entire canal sampling team, in no particular order. I also thank Cathy Kochert, Marcia Kyle, and Tom Colella for invaluable assistance with analyses and Paul Westerhoff for laboratory access. I thank my brother, David Roach, for his continued encouragement and perspective. I thank my Mom and Dad, who have show shown unwavering faith in me and my grandmother, Mary Thompson, who expanded my horizons and gave me the courage to fail. And finally, thanks to Lisa Eby for, well, everything.

TABLE OF CONTENTS

LIST OF TABLES

Page

LIST OF FIGURES

# 1. INTRODUCTION

Humans are responsible for modifying between one third and one half of the Earth's surface (Vitousek et al. 1986, Vitousek et al. 1997a, Vitousek et al. 1997b), dramatically altering global biogeochemical cycles (Vitousek et al. 1997b, Falkowski et al. 1999). Anthropogenic alterations of biogeochemical cycles are particularly marked in and around cities, with dramatic effects on nutrient availability in recipient systems (Aber et al. 1989, Padgett et al. 1999, Baker et al. 2001). Widespread application of synthetic fertilizers has intentionally increased N availability in many human-dominated ecosystems (e.g., agricultural fields), while unintentionally increasing N availability downstream. Simultaneously, practices such as fossil-fuel combustion and livestock domestication have led to further unintended increases in N availability. For example, in Phoenix, farming and urbanization have increased inorganic soil N 2-10 fold (Zhu et al. in press). Much of this anthropogenic N does not remain in place, but is exported to recipient ecosystems via rivers (Goolsby and Battaglin 2001) or air currents (Padgett et al. 1999), where it contributes to eutrophication of water bodies (Carpenter and Pace 1997, Carpenter et al. 1998b), reduction of drinking-water quality (Neilsen and Lee 1987, Mosier et al. 2001), and N saturation of forests (Aber et al. 1989).

Biogeochemists are increasingly aware that as materials move across a landscape there are patches—'hot spots'—that are responsible for a disproportionate amount of nutrient processing (Peterjohn and Correll 1984, McClain et al. 2003). The identification of hot spots may be scale-dependent. Denitrification hot spots may be as small as individual earthworm casts (Svensson et al. 1986) and plant roots (Schade et al. 2001) and as large as entire riparian zones (Groffman et al. 1992, Pinay et al. 1993). At even larger scales, cities act as hot spots of N processing because they are largely heterotrophic, importing the majority of the materials and energy they consume from other regions (Luck et al. 2001, Kaye et al. in press). For example, the Central-Arizona Phoenix (CAP) ecosystem retains between 17 and 21 Gg N $yr^{-1}$, or between 17 and 21% of inputs, and thus is a net sink for fixed N as less is exported than imported from the ecosystem (Baker et al. 2001). Nevertheless, because fossil fuel combustion produces airborne $NO_x$, the city is simultaneously an important source of N to the surrounding Sonoran Desert.

Spatial arrangement of hot spots influences how materials move between patches, relative availability of materials to different patches, and export of materials to adjacent ecosystems. Geomorphology and hydrology are important drivers influencing origin, development, and persistence of patches as well as their interactions (McAuliffe 1994, Cirmo and McDonnell 1997, Fisher et al. 1998, Kling et al. 2000, Webster et al. 2000, Stanley and Doyle 2002). Thus, explicit consideration of hydrologic flowpaths and geomorphic templates can provide new insights into nutrient cycling.

American ecologists traditionally have sought 'pristine' ecosystems to answer ecological questions (Collins et al. 2000); however, truly 'pristine' ecosystems are rare and researchers are increasingly aware of the need to understand human-dominated ecosystems (Pickett et al. 1997, Vitousek et al. 1997b, Carpenter and Turner 1998). Although much of this research is motivated by the desire to develop solutions to environmental problems (Soranno et al. 1996, Carpenter et al. 1998a, Kates et al. 2001, Turner et al. 2003), researchers working in urban systems also hope to contribute more generally to ecological theory (Pickett et al. 1997, Collins et al. 2000, Grimm et al. 2000). The beauty of urban research is that both are possible. The research reported here takes advantage of changes made in Indian Bend Wash (IBW), an extensively modified urban stream (Fig. 1), to addresses the following question: *how do the hydrologic and geomorphic structure of a stream affect patterns of N availability and retention?* The specific objectives of this work were to (1) describe how urbanization has proceeded through the IBW watershed, and explore potential implications for N cycling of resulting hydrologic and geomorphic changes; (2) characterize spatial and temporal patterns of nutrient variability and net nutrient removal (input-output) along a string of eight lakes in the lower portion of the watershed; (3) determine how changes in nutrient concentration caused by management decisions and floods interact to affect primary production in these lakes; and (4) determine the ability of the lower reach to remove N through denitrification. Below, I present brief descriptions of research projects designed to meet each of these objectives, which correspond to the chapters reporting findings from these projects. Each chapter is presented as an independent manuscript. The final chapter of the dissertation is a synthesis of this body of work.

*Chapter 2: Anthropogenic modifications to hydrology and geomorphology of an urban desert stream: implications for nitrogen cycling*

This chapter describes direct and indirect effects of land-use change in Indian Bend Wash on watershed structure and function. We present a case study of changes in hydrology and geomorphology that accompany urbanization of a watershed, and explore potential implications of these changes for N cycling. Historic aerial photography spanning the years 1949 to 2003 was used to document urban development in the watershed. Specifically, we quantify change in the percentage of land in desert, agricultural and urban land over this period. Additionally, aerial photography allowed us to describe major geomorphic changes made to the stream's main channel as part of an extensive flood control project. On balance, urbanization has reduced coarse sediment availability while retention structures have reduced maximum discharge. Canals and groundwater pumping have created novel linkages between patches that both increase spatial extent of their interactions and introduce large temporal lags between human activities (e.g., fertilizer application) and impacts of those activities on ecosystem function (e.g., eutrophication).

This chapter was the product of an interdisciplinary workshop conducted under the auspices of Arizona State University's Integrative Graduate Education and Research Training (IGERT) in urban ecology, and fulfills the requirement of a collaborative portion of the dissertation for that program. The study was conducted and paper written in collaboration with workshop participants Ramón Arrowsmith, Chris Eisinger, Nancy Grimm, Jim Heffernan, and Tyler Rychener.

*Chapter 3: Nutrient dynamics in Indian Bend Wash: synchronous behavior in a highly variable stream*

This chapter focuses on spatial and temporal patterns of nutrient concentrations along a series of eight lakes constructed in the greenbelt of the lower portion of the IBW watershed. Research objectives were to determine (1) ability of the study reach to retain nutrients ($NH_4^+$, $NO_3^-$, SRP and DOC) and whether or not lake and stream segments differed in their capacity for nutrient retention; and (2) whether or not nine physical and chemical variables varied synchronously along the wash. On balance, the reach was a sink for SRP and a source for $NH_4^+$ and DOC. The processing of $NO_3^-$ was less predictable, with the wash alternately acting as a source and a sink for this nutrient. Of the variables measured, temperature displayed the highest degree of synchrony, indicating strong effects of climate. Synchrony in nutrient chemistry was attributed to strong effects of management decisions; specifically, relative amounts of different water sources used to maintain flow through the study reach. Synchrony of all variables declined with distance separating sampling points, but this decline was most rapid for $NO_3^-$, suggesting that $NO_3^-$ dynamics were most strongly affected by internal processing.

*Chapter 4: Anthropogenic and climatic drivers interact to determine nutrient limitation along an urban lake chain*

This chapter examines implications for ecosystem function of changes in nutrient concentration caused by temporal shifts in groundwater pumping rates and flash floods. Historic fertilizer use has elevated concentrations of $NO_3^-$ in the aquifer underlying IBW.

When groundwater was used to supplement flow and maintain lake levels, $NO_3^-$ was abundant and phytoplankton production was hypothesized to be P-limited. Conversely, floodwaters exhibited elevated P concentration and relatively low inorganic N concentrations. Thus, floods were hypothesized to cause a shift in nutrient limitation from N to P. This chapter reports the results of a nutrient limitation experiment designed to test these hypotheses. Results show that, while the wash tends to be P-limited most of the time, when groundwater pumping rates are low, floods are indeed capable of producing shifts from P to N limitation.

*Chapter 5: Denitrification in the stream-floodplain complex of a desert city: importance of natural and anthropogenic cross-system linkages*

This chapter concerns denitrification as a N removal mechanism in the stream-floodplain complex of lower Indian Bend Wash. Objectives were (1) to evaluate whether and which patch types (i.e., lakes, channelized stream segments, or turf-dominated floodplain) were important sites of denitrification; (2) to learn what factors controlled potential denitrification rates; (3) to examine how linkages between patches affected overall rates of denitrification; and (4) to quantify the importance of denitrification to overall N retention by the stream-floodplain complex. Both turf floodplain and lakes were important sites of denitrification, but controls on rates in the two patches were distinct: denitrification in lake sediments was $NO_3^-$-limited, whereas floodplain denitrification was limited by soil moisture. Although annual denitrification rates were highest in the lakes (nearly 111 kg N $ha^{-1}$ $y^{-1}$), because flux of N through lakes was so large this loss represented just 6% of hydrologic input. Conversely, nearly all the N applied to the floodplain was either stored or denitrified, with denitrification removing 74% of inputs or approximately 55 kg N $ha^{-1}$ $y^{-1}$. Because floodplain denitrification was limited by soil moisture and the most important source of water was irrigation water drawn from lakes, frequency of irrigation events ultimately determined annual N removal via denitrification in the floodplain.

The work presented in this dissertation demonstrates that stream biogeochemistry changes in response to changes in hydrology and geomorphology of watersheds during urbanization. I show how novel linkages between groundwater and surface water or between surface water and floodplains affect fundamental ecosystem processes like primary production and denitrification. The research also has important management implications, shedding light on how management decisions, such as those about where water is drawn from and how stream channel configuration is modified, affect N retention and thus the impact of cities on downstream ecosystems.

## LITERATURE CITED

Aber, J. D., K. J. Nadelhofer, P. Steudler, and J. M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience **39**:378-386.

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

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

Carpenter, S. R., N. F. Caraco, D. L. Correll, R. W. Howarth, A. N. Sharpley, and V. H. Smith. 1998b. Nonpoint pollution of surface waters with phosphorus and nitrogen. Ecological Applications **8**:559-569.

Carpenter, S. R., and M. L. Pace. 1997. Dystropy and eutrophy in lake ecosystems: implications of fluctuating inputs. Oikos **78**:3-14.

Carpenter, S. R., and M. G. Turner. 1998. At last: a journal devoted to ecosystem science. Ecosystems **1**:1-5.

Cirmo, C., and J. McDonnell. 1997. Linking the hydrologic and biogeochemical controls of nitrogen transport in near-stream zones of temperate-forested catchments: a review. Journal of Hydrology **199**:88-120.

Collins, J. P., A. Kinzig, N. B. Grimm, W. F. Fagan, D. Hope, J. Wu, and E. T. Borer. 2000. A new urban ecology. American Scientist **88**:416-425.

Falkowski, P. G., R. T. Barber, and V. Smetacek. 1999. Biological controls and feedbacks on ocean primary productivity. Science **281**:200-206.

Fisher, S. G., N. B. Grimm, E. Marti, R. M. Holmes, and J. B. Jones, Jr. 1998. Material spiraling in stream corridors: a telescoping ecosystem model. Ecosystems **1**:19-34.

Goolsby, D. A., and W. A. Battaglin. 2001. Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. Hydrological Processes **15**:1209-1226.

Grimm, N. B., J. M. Grove, S. T. A. Pickett, and C. L. Redman. 2000. Integrated approaches to long-term studies of urban ecological systems. BioScience **50**:571-583.

Groffman, P. M., A. J. Gold, and R. C. Simmons. 1992. Nitrate dynamics in riparian forests. Journal of Environmental Quality **21**:666-671.

Kates, R. W., W. C. Clark, R. Corell, J. M. Hall, C. C. Jaeger, I. Lowe, J. J. McCarthy, H. J. Schellnhuber, B. Bolin, N. M. Dickson, S. Faucheux, G. C. Gallopin, A. Grubler, B. Huntley, J. Jager, N. S. Jodha, R. E. Kasperson, A. Mabogunje, P. Matson, H. Mooney, B. Moore III, T. O'Riordan, and U. Svedlin. 2001. Environment and Development: Sustainability Science. Science **292**:641-642.

Kaye, J., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. in press. A distinct urban biogeochemistry? Trends in Ecology and Evolution.

Kling, G. W., G. W. Kipphut, M. M. Miller, and W. J. O'Brien. 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. Freshwater Biology **43**:477-497.

Luck, M. A., G. D. Jenerette, J. Wu, and N. B. Grimm. 2001. The urban funnel model and spatially heterogeneous footprint. Ecosystems **4**:782-796.

McAuliffe, J. R. 1994. Landscape evolution, soil formation, and ecological patterns and processes in Sonoran Desert bajadas. Ecological Monographs **54**:111-148.

McClain, M. E., B. E. W., C. L. Dent, C. 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 aquatic and terrestrial ecosystems. Ecosystems **6**:301-312.

Mosier, A. R., M. A. Bleken, P. Chaiwanakupt, E. C. Ellis, J. R. Freney, R. B. Howarth, P. A. Matson, K. Minami, R. Naylor, K. N. Weeks, and Z.-L. Zhu. 2001. Policy implications of human-accelerated nitrogen cycling. Biogeochemistry **52**:281-320.

Neilsen, E. G., and L. K. Lee. 1987. The magnitude and cost of groundwater contamination from agricultural contamination: a national perspective. AGES870318, Natural Resources Economics Division, U.S. Department of Agriculture, Washington, D.C.

Padgett, P. E., E. B. Allen, A. Bytnerowicz, and R. A. Minich. 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. Atmospheric Environment **33**:769-781.

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.

Pickett, S. T. A., J. Burch, WR, S. E. Dalton, T. W. Foresman, J. M. Grove, and R. Rowntree. 1997. A conceptual framework for the study of human ecosystems in urban areas. Urban Ecosystems **1**:185-199.

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

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

Soranno, P. A., S. L. Hubler, and S. R. Carpenter. 1996. Phosphorus loads to surface waters: a simple model to account for spatial pattern of land use. Ecological Applications **6**:865-878.

Stanley, E. H., and M. W. Doyle. 2002. A geomorphic perspective on nutrient retention following dam removal. BioScience **52**:693-701.

Svensson, B. H., U. Bostrum, and L. Klemedtsson. 1986. Potential for higher rates of denitrification in earthworm casts than in the surrounding soil. Biology and Fertility of Soils **2**:147-149.

Turner, B. L., P. A. Matson, J. J. McCarthy, R. W. Corelf, L. Christensen, N. Eckley, G. K. Hovelsrud-Broda, J. X. Kapsperson, R. E. Kasperson, A. Luers, M. L. Martello, S. Mathiesen, R. Naylor, C. Polsky, A. Pulsipher, A. Schiller, H. Selin, and N. Tyler. 2003. Illustrating the coupled human-environment system for vulnerability analysis: three case studies. Proceedings of the National Academy of Sciences **100**:8080-8085.

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

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, and W. H. Schlesinger. 1997b. Human alteration of the global nitrogen cycle: causes and consequences. Issues in Ecology **1**:1-14.

Vitousek, P. M., P. R. Ehrlich, A. H. Ehrlich, and P. A. Matson. 1986. Human appropriation of the products of photosynthesis. BioScience **36**:368-373.

Webster, K. E., P. A. Soranno, S. B. Baines, T. K. Kratz, C. J. Bowser, P. J. Dillon, P. Campbell, E. J. Fee, and R. E. Hecky. 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. Freshwater Biology **43**:499-515.

Zhu, W.-X., D. Hope, C. Gries, and N. Grimm. in press. Soil characteristics and the storage of inorganic nitrogen under different land uses in an arid urban ecosystem. Ecosystems.

Figure 1. 1. Oblique aerial photograph of Indian Bend Wash greenbelt looking north from near the mainstem's confluence with the Salt River.

# 2. ANTHROPOGENIC MODIFICATIONS TO HYDROLOGY AND GEOMORPHOLOGY OF AN URBAN DESERT STREAM: IMPLICATIONS FOR NITROGEN CYCLING

## ABSTRACT

Human manipulation is increasingly recognized as an important component, rather than an external disturbance, of ecological systems. Anthropogenic modifications influence the physical, chemical and biological structure of ecological systems, and may have both direct and indirect effects on ecological processes. In turn, the physical and biological template of ecosystems influences patterns of anthropogenic modification. We used Indian Bend Wash, an urbanizing watershed in the Central Arizona-Phoenix Long-Term Ecological Research (CAP LTER) study area, as a case study to investigate how human decisions interact to affect ecosystem structure and function, primarily by altering how water flows through the ecosystem. We used historic aerial photography spanning the years 1949 to 2003 to document urban development in the watershed, specifically focusing on canals and flood-control structures that dramatically altered geomorphology and hydrology of the watershed. Geomorphic modifications interacted with catchment-wide land-use changes to alter sediment transport and deposition. In particular, urbanization has reduced coarse sediment availability while water retention structures have reduced maximum discharges. Some 167 new, artificial lakes built in the watershed were likely sinks for fine sediments and were potential hot spots for nitrogen (N) processing. Hydrologic manipulations, such as groundwater pumping, have linked the

canal network to the ecosystem's aquifer and created perennial aquatic ecosystems where ephemeral ones existed before. We hypothesize that geomorphic and hydrologic changes are creating novel spatial and temporal patterns of N availability.

## INTRODUCTION

The world is becoming increasingly urban. While only 14% of the world's population lived in cities in 1900, by 1999 50% did (United Nations 1999). In the United States alone, metropolitan areas nearly tripled in area between 1950 and 1999, growing from 538,720 $km^2$ to 1,515,150 $km^2$ (Ewing 1994). Urbanization fragments natural habitats, alters hydrological systems, and modifies biogeochemical cycles and energy flows (Grimm et al. 2000, Alberti et al. 2003). Flux of materials and energy through urban ecosystems is much greater than that of undeveloped ecosystems (Baker et al 2001), as cities appropriate resources from ecosystems well beyond their physical boundary, producing large ecological 'footprints' (Folke et al. 1997, Luck et al. 2001, Jenerette et al. in press). Simultaneously, as cities export wastes they often increase nutrient availability in recipient ecosystems (e.g., Aber et al. 1989, Vitousek et al. 1997, Padgett et al. 1999). Effects of urbanization are not limited to interactions of cities with neighboring and distant ecosystems, but also include changes in ecological function within them. Although land-use change is an important driver of biogeochemical cycles (Carpenter et al. 1998, Bennett et al. 1999, Groffman and Crawford 2003, Meyer et al. 2005), few studies examine how spatial patterns of urban development affect ecosystem function (Alberti 1999, 2005).

We propose that urbanization proceeds, changes in land use and resulting changes in geomorphic structure and fluvial processes have both direct and indirect effects on biogeochemical cycles. Direct effects of land-use change are obvious. As cities grow, land is often re-contoured, vegetation is planted or removed, networks of paved roads are built, and, of course, various buildings in which people live and work are erected. These actions directly influence ecosystem conditions by creating novel vegetation patterns, shifting water and nutrient availability, and altering geomorphic structure. As important as these direct effects of urbanization are, some of the most profound effects may be indirect, resulting from changes in processes responsible for maintaining ecological structure and function. For example, urbanization often alters temporal and spatial availability of water and reduces channel complexity of stream ecosystems, disrupting processes responsible for generating and maintaining patterns of nutrient availability (Grimm et al. 2004, Grimm et al. 2005).

Geomorphology and hydrology are important drivers that influence the origin, development, and persistence of landscape patches as well as their interactions (McAuliffe 1994, Hupp and Osterkamp 1996). Biogeochemists are increasingly aware that, as materials move across a landscape, certain locations—'hot spots'—are responsible for a disproportionate amount of nutrient removal or processing (Peterjohn and Correll 1984, McClain et al. 2003). In turn, spatial arrangement of and connections between hot spots influence how materials move between patches, relative availability of materials to different patches, and export of materials to adjacent ecosystems. For example, recent work on lake districts (Webster et al. 2000) and lake chains (Kling et al.

2000) has demonstrated that lake solute chemistry is affected by both the degree to which lakes are hydrologically linked and by the flow paths between lakes, i.e., whether hydrologic linkages are predominantly through surficial streams or subsurface flows. Humans alter fluvial ecosystems by changing the spatial arrangement of and connections between impounded water bodies and thus the rate at which nutrients are exported to recipient ecosystems (Stanley and Doyle 2002). If we can understand how urbanization affects arrangement of and connection between hot spots, we can begin to answer the question: how do changes in land use produced by urbanization affect movement of nutrients through and within a city?

We address this question using a case-study approach that focuses on Indian Bend Wash (IBW), an urbanizing watershed in central Arizona located within the study area of the Central Arizona-Phoenix Long-Term Ecological Research (CAP LTER) program; hereafter, the CAP ecosystem (Grimm and Redman 2004). Because urbanization is a spatially explicit process, supplementing aggregate measures of land-use change with a more detailed description of the pattern of urban growth may yield new insights into the effects of urbanization on ecosystem function (Alberti et al. 2003, Alberti 2005). This paper presents (1) a spatially explicit description of how urban development has proceeded in the IBW watershed; (2) a narrative description of the important direct effects on geomorphology and hydrology of IBW resulting from this development; and (3) two examples of how these direct effects translate to indirect effects on biogeochemical cycling in aquatic systems within the watershed. In the first example, we argue that creation of artificial lakes influences distribution of hot spots of nitrogen (N) processing on the landscape. In the second example, we document how changes in hydrology influence spatial and temporal patterns of N availability in canals, and by analogy, in the larger CAP ecosystem.

## STUDY SITE

### *Climate and Geology*

Phoenix and contiguous municipalities of the CAP ecosystem are Sonoran Desert cities established near the confluence of the Salt and Gila Rivers (Fig. 2.1) in Arizona's Basin and Range Lowlands hydrogeologic province (Montgomery and Harshbarger 1989, Anderson 1995). The Sonoran Desert experiences hot summers and mild winters and two distinct rainy seasons. About half of precipitation falls during spatially extensive, low-intensity winter storms that span one or more days. In July and August, upper-level winds bring moisture from the Gulf of Mexico, resulting in a summer 'monsoon' season characterized by brief, intense, localized thunderstorms. Annual precipitation is exceeded by evapotranspiration, which averaged 16 cm/y and 195 cm/y, respectively, in the Phoenix area over the past five years (Arizona Meteorological Network 2004).

The Basin and Range Province is characterized by large, gently sloping basins filled with alluvial material eroded from the surrounding mountains (Arrowsmith and Pewe 1999). Deep sedimentary basins formed during regional continental extension when their keystone-like fault blocks subsided relative to adjacent blocks. During these periods of basin subsidence, sediments derived from adjacent mountain ranges were deposited in the basins. With time, the drainage network coalesced into the Colorado River system, establishing a connection between central Arizona and the Gulf of Mexico with flows from the Salt River feeding the Gila River and, in turn, the Colorado River. As the Salt River sub-basins filled with sediment, they also filled with water and these saturated sediments now comprise the principal regional aquifer system, storing an estimated 200,000 $m^3$ of water in the top 360 m of the Salt River Valley (Montgomery and Harshbarger 1989). Groundwater has been an important but declining source of water in the region, dropping from 56% of water use in 1990 to 25% of water consumed in 1999 (Arizona Department of Water Resources 1999), although a recent 5-year drought has increased reliance on groundwater.

Indian Bend Wash (IBW) is an ephemeral tributary of the Salt River (Fig. 2.1) that runs through the relatively young cities of Scottsdale (founded in 1888, incorporated in 1951) and Paradise Valley (incorporated in 1961) as well as a corner of the Salt River Pima Maricopa Indian Community (SRPMIC; established 1879). In the late 1800's, the watershed drained approximately 520 $km^2$ of desert and agricultural lands. Most of the watershed lies atop loose unconsolidated sediments derived from the McDowell Mountains on its northeast border. Prior to extensive urbanization, storm runoff flowed from the McDowell Mountains in subparallel channels southwestward towards the Phoenix Mountains (Fig 2.1). These small channels emptied into the mainstem of the wash, which flowed to the southeast until it passed Camelback Mountain, where the channel turned south and continued to its confluence with the Salt River (Fig. 2.1). Historically, the sediments of the low-gradient valley floor were reworked during episodic floods, producing relatively narrow low-flow channels subsumed within a broader active channels, a configuration typical of southwestern streams (e.g., Fisher 1986, Graf 1988, Grimm and Fisher 1992). Hydrologic exchange between surface and subsurface would likely have been rapid and frequent, though the fact that north of IBW's confluence with the Salt River the water table was well below the ground surface (Lee 1905, Arizona Department of Water Resources 1999) suggests IBW tended to be a losing stream that only flowed during floods.

### *Urban Development of the CAP Ecosystem and Indian Bend Wash*

The first irrigation canals in the CAP ecosystem were built by the Hohokam who inhabited the region for nearly 1800 years, beginning around 300 BC (Hayden 1970, Bayman 2001). Between about 600 A.D. and 1450 A.D. they constructed extensive canal systems on several rivers in Arizona, including the Salt and Gila Rivers (Fig. 2.1) before, for reasons that are not entirely clear, they disappeared, leaving remnants of their canals behind (Masse 1981, Bayman 2001).

Like the Hohokam before them, modern Phoenicians chose the area because its rivers promised a reliable source of irrigation water (Luckingham 1989), its flat, rock-free land hinted at easy plowing, and its warm climate suggested the possibility of harvesting two crops a year (Gammage 1999). Farming returned to the valley in the 1860's with construction of Swilling's ditch (Luckingham 1989). More canals soon followed, many of them re-excavated from old Hohokam structures, including the Arizona Canal in 1883. By 1910, approximately 101,000 ha were under irrigation (Luckingham 1989). Six dams were constructed along the hydrologically variable Salt and Verde Rivers between 1911 and 1946 in an effort to provide a reliable supply of irrigation water. As growth continued and additional water was sought, residents turned to groundwater to supplement surface flows. Extensive pumping in IBW dropped the water table by approximately 90 m between 1900 and 1990 in some areas (Arizona Department of Water Resources 1999). The Central Arizona Project canal, completed between 1973 and 1993, diverted an additional 1.7 x $10^9$ $m^3$ $y^{-1}$ of surface water to the region (U.S. Bureau of Reclamation 2005). In addition to diverting large quantities of water for irrigation, farmers relied heavily on fertilizer use. Fertilizer applications increased nutrient availability (Baker et al. 2001), elevating $NO_3^-$ concentrations both in soils (Hope et al. in press, Zhu et al. in press) and in underlying aquifer (Xu 2002).

As urban development continued, so did the region's mercurial relationship with water. Although nearly dry most of the year, IBW remained prone to periodic flash floods and many residents suffered severe economic damage during these rare events (Association of State Flood Plain Managers Inc. 2002). The city of Scottsdale, in conjunction with the Army Corp of Engineers, responded by building the IBW flood control project, which was designed to safely convey a 100-year storm discharge of 850 $m^3$/s through Scottsdale to the Salt River (U.S. Army Corps of Engineers 1975). Acquiescing to the desires of a citizenry hoping to avoid blemishing their city, engineers designed a solution that relied on protecting the existing floodplain by establishing a 12-km greenbelt with flows and artificial lakes rather than a cement-lined chute. Although initial planning for the project began in 1961, key components were not completed until 1985 (Matthews 1985).

## METHODS

The changes in land use, geomorphology, and hydrology resulting from urban expansion in IBW were hypothesized to affect biogeochemical processes. We used abundant historical data to describe how urbanization has altered the hydrology and geomorphology of the watershed. We then argue, largely by analogy, that these changes in hydrology and geomorphology have altered biogeochemical cycles.

### *Land-use change in Indian Bend Wash*

We used a geographic information system and aerial photographs from 1949 through 2003 to track watershed-scale changes in land use. We created data layers for 1949, 1962, 1971, 1978, 1987, 1997 and 2003 from images collected from a variety of digital and print sources (Table 2.1) using ArcGIS. Print images were first digitized and cropped. They were then georectified in ArcGIS using the 1997 digital orthophoto quarter quadrangles (DOQQs) as a base layer. With the exception of the 1949 data layers, which only covered the southern two thirds of the watershed, each layer covered almost all of the watershed (>95%). Because of the large number of photos involved in creation of the 1962 layer, individual georectified images were stitched together into one seamless image using ERDAS Imagine 8.6. Aerial photography was chosen over satellite images because of their higher spatial resolution and longer time coverage.

The resulting georectified data layers were used to assess changes in land use from desert to agricultural or urban uses. We accomplished this by overlaying a grid of 1.6 km x 1.6 km cells on the watershed. The choice of grid size was informed by the observation that development has largely followed the one mile-square grid pattern, and grid cells were generally aligned with the main roads. The entire grid was clipped to the watershed's extent (see below). Land cover in each cell for each year was then visually examined and designated as desert, agriculture, or urban, according to the land cover with the greatest areal extent in the cell. Desert areas were those areas that showed no sign of modern development. Agricultural areas were those comprised of cultivated or fallow fields and associated buildings. Urban areas were those lots containing any of the following: residential developments, commercial properties, irrigated urban parks, golf courses, and other built structures including roads. We assumed that if a cell was predominantly desert in one year than it was also desert in all previous years. Likewise, once a cell was converted to urban land covers, it was assumed to remain urban. Using this logic, because the entire unphotographed portion of the 1949 data layer was still desert in 1962, were able to classify the all cells in this unphotographed region as desert. We were also able to accurately classify the few unphotographed cells from 1971 and 1978 data layers based on photos of those cells from 1962 and 1987. We validated these assumptions using the remainder of the data set by looking for examples of any cells that reverted to desert or agriculture after being converted to urban land use; none was found.

Corresponding changes in population were tracked using U.S. Census data for the city of Scottsdale as reported by the U.S. Census Bureau (1995, 2003) for the final two dates and as reprinted by Luckingham (1989) for the earlier dates. Although the watershed includes much of the agrarian SRPMIC and portions of other cities in the greater Phoenix metropolitan area, virtually the entire city of Scottsdale lies within its boundaries and most people living in the watershed are residents of this city.

### *Changes in geomorphology and hydrology*

We focused on two distinct scales of change: the watershed (10s to 100s $km^2$) and the stream reach (100s to 1000s $m^2$). At the watershed scale, we were interested in broad changes in land use as well as large-scale modifications of hydrology. We used 7.5-minute digital-elevation models (DEMs), obtained from the USGS National Elevation Dataset, to calculate the watershed boundary and delineate major water flow paths. DEM analysis relied on a computational plug-in tool, TauDEM, created for ArcGIS by D. Tarboton at Utah State University (Tarboton 2004). Both 10-m and 30-m DEMs were used for the terrain analysis, with the finer-resolution DEM producing a more accurate watershed boundary and the coarser-resolution DEM being useful for identifying the major flow paths. Computational steps included filling pits (low spots in the DEM), calculating flow directions for each grid cell using steepest descent paths, and determining contributing area based on summation of upslope cells. Stream networks were ordered using an algorithm based on the Strahler ordering system (i.e., the immediate order of a stream at any given segment of its length; Strahler 1952), and the stream raster grid was converted to a vector network with the topological connectivity and other attributes recorded (Tarboton 2004). Finally, an IBW watershed polygon and sub-watershed polygons were generated using the flow direction grid and stream grid attributes as algorithm inputs. Because the entire watershed has been artificially truncated by the Arizona canal and CAP canal, we also used spatial vector data in ArcGIS to calculate the dimensions of the resulting three sub-basins. This allowed us to explore how canal construction might change the area contributing to surface flows (and thus stream power) as well as the movement of sediments.

We assessed reach-scale changes in geomorphology by comparing the georectified aerial photographs from different years and identifying important hydrologic and geomorphic modifications. We focused on the southern portion of the watershed where flooding has historically been most acute and documented changes in channel form, including the construction of artificial lakes, as well as changes in land use, paying particular attention to encroachment of farms and subdivisions onto the floodplain. Documents, particularly those produced by the Army Corp of Engineers, the Salt River Project, the Central Arizona Project, and the city of Scottsdale, helped identify timing of changes resulting from urbanization of the IBW watershed. Construction, modification and removal of artificial lakes proved to be one of the most striking modifications to the wash. Using ArcGIS, we manually digitized each lake built in the watershed, redigitizing them when they were re-contoured by developers. We were thus able to track each lake through the history of the wash and to calculate both the number of lakes and the total surface area of this standing water for each year in our dataset.

### *Patterns of surface-water nitrate concentration*

Canals supply a mix of surface and subsurface waters to the residents of central Arizona. One of the most pervasive changes in surface water-groundwater interactions in

IBW is linkage of the extensive Salt River aquifer with surface flows via groundwater pumping into these canals. We examined how this modification affects nitrate ($NO_3^-$) concentration in surface flows by conducting an extensive longitudinal survey along a 20-km section of the Southern/Tempe canal (Fig. 2.1). During a 3-h period on June 21, 1999, 803 water samples were collected at 50-m intervals by 13 sampling teams, each of which sampled a 1.5-km reach of the canal. Samples were safely collected from below the water surface approximately 2-3 m from the canal's edge using a 1-L bottle attached to an extendable painter's pole. Additional grab samples were taken from outflows of 11 groundwater wells that were actively pumping water into the canal on this date. Additional smaller-scale surveys were conducted one week later to test whether the longitudinal declines in $NO_3^-$ concentrations below well inputs could be explained by horizontal mixing of well inputs with the main flow. Samples were transferred to acid-washed pre-rinsed 60-ml bottles and placed on ice for transport back to the laboratory, where they were immediately filtered through Whatman GF/F filters. Within 24 h of collection, samples were analyzed for $NO_3^-$-N by colorimetric analysis after reduction to nitrite (Wood et al. 1967) on a Bran-Luebbe TrAAcs 800 autoanalyzer. Results were analyzed graphically.

## RESULTS

### *Land-use change in Indian Bend Wash*

Although Scottsdale was founded in 1888, urban development in the Indian Bend Wash watershed proceeded slowly during the first half of the 20$^{th}$ century. As of 1949, most of land remained undeveloped desert with some farming in the southern-most portion of the watershed below the Arizona canal (Fig. 2.2). However, beginning in the early 1970's, a rapid increase of new subdivisions occurred between the Arizona and Central Arizona Project canals. New subdivisions were built on an extension of the Phoenix's original 1.6 km x 1.6 km grid. Farms west of the SRPMIC were quickly converted to urban land use, resulting in a sharp edge between the dense housing developments of Scottsdale and the agricultural fields of the SRPMIC, which remains to this day (Fig. 2.2). Urban land use migrated east along the northern border of the Indian community land and north to the Central Arizona Project canal. Then, in the late 1980's, urbanization extended beyond the canal and moved rapidly north through the watershed, sometimes in a leap-frog pattern. By 1997, urban land use was the dominant cover type in the IBW watershed, and by 2003 65% of the watershed's area was considered urban (Fig. 2.3). There is a close correspondence between the observed increase in urban area and changes in the population of the city of Scottsdale (Fig. 2.3).

### *Watershed-scale changes in geomorphology and hydrology*

As urban land use expanded through the wash, many of the geomorphologic features that characterized the watershed disappeared, as can be seen by comparing the aerial photos from 1962 and 2003 (Fig. 2.2). In 1962, with the exception of two golf courses and the remains of the failed Old Verde canal (arrow a, Fig. 2.2) near the site of the yet-to-be-built Central Arizona Project canal, the watershed north of the Arizona Canal was dominated by desert land cover. The mainstem of IBW remained visible as a thin strip of vegetation (arrow b). By 2003, urban development not only had migrated all the way to the Central Arizona Project canal (arrow d), but also had extended beyond the canal into the northern portion of the watershed (arrow f); the IBW flood-control greenbelt encased the main channel of the wash (arrow e); and the subparallel channels of the upper portion of the wash, which were so conspicuous in 1962 (arrow c), were restricted to the narrow strip of desert along the southeastern edge of the watershed just north of the SRPMIC (arrow g).

An extensive network of canals provided a reliable supply of irrigation water in the CAP ecosystem. Unlike the rivers that feed them, flows through canals parallel the valley's contour lines rather than cutting across them. Because of this, canals disrupt historic flowpaths, effectively severing surface flows. Completion of the Arizona canal in 1878 cut the lower 48 km$^2$ of the IBW watershed from the northern 471 km$^2$ (Figs. 2.1, 2.2), restricting the majority of flows into the southern basin to where the IBW mainstem crossed the Arizona canal. The Central Arizona Project canal further divided the watershed when the portion crossing IBW was completed in 1980. In part to ensure integrity of the canal and in part to provide further flood control for the city of Scottsdale, designers of the Central Arizona Project canal engineered it so that floods from upslope areas collect in large retention basins (Matthews 1985). Sitting atop a large berm, the canal flows steadily eastward as floods collect against its northern bank. Thus, this canal effectively severs the northern 241 km$^2$ from remainder of the watershed (Fig. 2.1).

*Reach-scale changes in geomorphology and hydrology*

As deserts and farms of the IBW watershed were replaced by suburban subdivisions, new construction began to encroach on the floodplain (Fig. 2.4). In 1949, a large meander was a prominent feature downstream from the Salt River confluence (dotted line in Fig. 2.4a). Riparian trees lined the channel and dotted the broad, braided floodplain of the Salt River (arrows in Fig. 2.4a, g). The lower portion of the mainstem of IBW flowed in a relatively broad floodplain bounded by steep risers, which graded into the adjacent agricultural fields (arrows in Fig. 2.4g). By 1962, conversion of farmland into subdivisions had begun (arrows in Fig. 2.4b). Some of the new housing developments encroached well into the floodplains of both IBW and the Salt River, further reducing IBW's mesquite bosque to a narrow ribbon of riparian vegetation (arrows in Fig. 2.4b, h). Efforts to provide flood protection began with the city of Scottsdale's passage of Ordinance 181 in 1964 which prevented further subdivision of floodplain land (Matthews 1985), although many people already lived on the floodplain (arrows in Fig. 2.4c, 2.5i). Although no official plan had been approved, Scottsdale began working toward a greenbelt-based flood control project with construction of El Dorado Park in 1966 (Matthews 1985). The park included two of the greenbelt's first artificial lakes, which are visible in 1970 (arrows in Fig. 2.4i). Scottsdale continued its piecemeal approach to constructing a greenbelt when, in 1971, it constructed four lakes on recently purchased land that was soon to become Vista del Camino Park (arrows in Fig. 2.4j). Although the city began removing the homes most at risk of flooding as part of this project, in 1972 three floods caused \$3.5 million in damages and displaced many floodplain residents. After these floods, Maricopa Country Flood Control District joined the city of Scottsdale's efforts to develop a greenbelt as a flood-control measure. One year later, the Army Corps of Engineers joined the project (Matthews 1985). The remaining homes directly in the floodplain were subsequently demolished and replaced by lakes (arrows in Fig. 2.4k-l).

During the next few years, engineers created a wide, deep greenbelt that was protected from further encroachment by development and capable of handling the 100-y flood. In 1977, the wash's lower 3.2 km was reworked to create an outlet channel (Fig. 2.4e), and in 1978, a siphon shunting the Arizona canal under the greenbelt was completed (Matthews 1985). Four bridges over the wash were completed between 1974 and 1977 (e.g., arrows in Fig. 2.4l, m), easing traffic congestion during floods. Sediments were stabilized by planting grass and irrigating the resulting turf. Stream power was reduced through a variety of energy-dissipation structures, including riprap and gabion drop structures as well as artificial lakes (arrows in Fig. 2.4m). In addition to slowing floodwaters, artificial lakes of the IBW greenbelt serve as small reservoirs of irrigation water for the surrounding floodplain and enhance the recreational value of the wash. Since its completion in 1980, the 12-km greenbelt has remained largely unchanged, though one small lake was removed (Fig. 2.4f, arrow in Fig. 2.4n). The only recent, notable change loosely associated with the project was the addition of Tempe Town Lake, a large artificial water body constructed in 1999 in the Salt River bed at the IBW confluence (arrow in Fig. 2.4f) and Tempe's 'restoration project' just north of this new lake.

Historically, flow through IBW was intermittent and there was little to no standing water. The residents of Scottsdale, however, appear to value open water and numerous lakes were built throughout the watershed as amenities to urban parks for anglers and boaters, as hazards on golf courses, as energy-dissipating structures in the floodplain, and as accent features for residents of new subdivisions desiring 'lakefront property'. The result has been a dramatic increase in the number of lakes in the watershed (Fig. 2.5). By 2003 there were more than 180 lakes in watershed with a combined surface area of more than 1.4 $km^2$. Depending on the lake, water levels are maintained with canal water, groundwater, or reclaimed wastewater (City of Scottsdale, *personal communication*). For example, the Salt River Project diverts a mix of surface water from the Arizona canal and groundwater through a series of canal laterals (Fig. 2.6) to maintain lake levels in the lower IBW greenbelt Figs (2.4, 2.6 inset).

### *Canal nitrogen availability*

Relative proportions of Salt River water, Verde River water, Central Arizona Project water, and groundwater flowing through the CAP ecosystem's network of canals changes on both a seasonal and annual basis, producing spatial and temporal variation in concentration of solutes monitored by managers of the canals (Sullivan 1996, 1998). In the Southern/Tempe canal, we found that $NO_3^-$ increased overall as water flowed downstream (Fig. 2.7). The increase in $NO_3^-$ concentration was not linear; instead, it occurred in a series of abrupt spikes associated with the input of $NO_3^-$-rich ground water followed by gradual declines until the next groundwater input (Fig. 2.7). An additional survey suggested that declines between wells primarily resulted from the gradual lateral dispersion and mixing of groundwater into canal water (Fig 2.8). Below the well, $NO_3^-$ concentrations in samples collected from the same bank the well discharged from decreased with distance downstream while $NO_3^-$ in samples collected from the opposite bank increased.

## Discussion

Despite its central position in the modern Phoenix metropolis, Indian Bend Wash remained dominated by desert (>75%) through 1970, until the explosive population growth of the latter half of the century. Urbanization of the watershed was characterized by a rapidly moving edge, with relatively uniform subdivisions at first replacing agricultural fields, and later replacing pristine desert as the fringe migrated northward.

### *Direct effects: Hydrology and geomorphology*

Effects of urbanization were manifest at both catchment and reach scales. At the catchment scale, construction of canals to serve water-supply needs of metropolitan Phoenix has had the greatest influence on hydrology and geomorphology. Unlike river networks, which continually concentrate flows into higher-order channels, canals produce hydrologic systems that resemble trees. Water is collected from the uplands through the dendritic river network (roots), is diverted to where it is needed via the arterial canals (trunk) and finally is broadly distributed across the landscape via dendritic lateral canals (branches). As a result, the rivers of central Arizona no longer deliver their dissolved and suspend loads to the Colorado River, but instead deliver them to the farms, parks, lakes and homes of the CAP ecosystem. This has important ramifications for nutrient cycling. Because the surface area to volume ratio of large rivers is small, processing rates are relatively low and N retention is limited (Alexander et al. 2000). By redistributing surface flows over broad areas, irrigation systems increase the contact between river water and sediment (and soils) and thus, in all likelihood, increase nutrient processing rates. This contrasts markedly with typical desert streams in which terrestrial-aquatic interactions, while particularly important for determining stream water chemistry, tend to be episodic and largely restricted to storm events (Grimm et al. 2004, Belnap et al. 2005, Grimm et al. 2005).

Second, construction of the Central Arizona Project and Arizona canals subdivided the watershed into three distinct basins, reducing the contributing areas and thereby peak flows. The Army Corp of Engineers estimated that the Central Arizona Project canal reduced peak flood discharges flowing through the IBW greenbelt by 37% (Lee 1988). This represents a substantial loss of stream power, and has reduced the ability of flood waters to transport and rework channel sediments (Graf 1988). Additionally, the Arizona Canal greatly restricts, and the Central Arizona Project canal virtually eliminates fluxes of materials (i.e., sediments and dissolved nutrients) between upper and lower sub-basins.

Flux of sediments into the mainstem of IBW likely has further reduced by increased impervious area resulting from construction of roofs and roads (Wolman 1967, Graf 1975) and establishment of irrigated turf. This reduction in sediment load may have important consequences for reach-scale geomorphology because streams starved of sediments tend to have increased channel erosion and incision (Trimble 1997, 2003). Our observations of the IBW mainstem suggest that reduced supply of coarse sediments has resulted in down-cutting along stream segments; vertically cut stream banks up to 1.0 m in height are prevalent in the lower reaches. Engineered features of the flood-control project exacerbate the geomorphologic changes resulting from this reduction in coarse sediment. Because irrigated turf has stabilized coarse sediments of the greenbelt, the low-flow channel no longer is able to migrate back and forth across the broader active channel. Instead, the low flow channel has become entrenched by down-cutting and punctuated with a series of artificial lakes, many of which are lined with clay and all of which are slowly filling with fine organic sediments (to a depth of >50 cm in some lakes; W.J. Roach, *personal observation*). The clay liners and deep fine sediments reduce hydrologic exchange between surface and subsurface compartments.

Since Leopold (1968), we have known that urbanization increases the imperviousness of mesic ecosystems, creating flashier hydrographs and increasing discharge. In the arid West, effects of urbanization are not always so predictable. Although construction of roofs, parking lots and roads represent increases in imperviousness and is expected to increase runoff and to stabilize underlying sediments in IBW, other changes resulting from urbanization may not increase imperviousness. Increased vegetation associated with irrigated crops, lawns, urban parks and retention basins may actually increase permeability of soils (Abrahams et al. 1995) when compared to hard-pan desert soils. Consequently, we are unable to infer whether the urbanization of

IBW has increased average imperviousness of the watershed or simply increased spatial variation in imperviousness by establishing new patches with altered perviousness.

*Indirect effects: Geomorphologic modification and hot spot distribution*

Urbanization of IBW has introduced of novel geomorphic features including golf courses, retention and detention basins, and artificial lakes. At the same time, low- and middle-order stream channels have been lost, via direct conversion of small rills and tributaries to turf or impervious surfaces (see also Fig .2.2, arrows c and g). Because geomorphology is a major determinant of the location of biogeochemical hot spots (i.e., patches with disproportionately high reaction rates compared with the surrounding landscape) (McClain et al. 2003), these changes may have a profound effect on the availability and cycling of nutrients like N.

Aquatic habitats (Seitzinger 1988, Jensen et al. 1991) and their interfaces with terrestrial habitats (Peterjohn and Correll 1984, Hedin et al. 1998, Dent and Grimm 1999) are frequently hot spots for N transformations. Shallow lakes, in particular, may remove large quantities of N from the water column because their characteristics frequently favor denitrification (Seitzinger 1988, Jensen et al. 1991, Jensen et al. 1992, Hilbricht-Ilkowska 1999), the microbially-mediated, anaerobic conversion of $NO_3^-$ to $N_2$. Research conducted over the past four years in IBW lakes (Fig. 2.6) indicates that these urban lakes may be hot spots as well (Chapter 5). Because the water is warm and shallow, rates of both primary production and community respiration are often high (GPP > 4 g C $m^{-2}d^{-1}$ and R > 3 g C $m^{-2}d^{-1}$; Roach, *unpublished data*). These high rates of primary production correspond to high $NO_3^-$ uptake rates (more than 0.5 g $NO_3^-$-N $m^{-2}d^{-1}$; Roach, *unpublished data*). Mean mass-specific estimates of potential denitrification rates in lake sediments are also high: up to 4.5 mg N $kg^{-1}h^{-1}$ (Chapter 5). The mean mass-specific potential denitrification rates observed in the surrounding floodplain soils, 1.7 mg $N_2O$-N $kg^{-1}$ $h^{-1}$ (Chapter 5), although significantly less than those observed in the lakes, are still high when compared to values from other studies of urban soils (Zhu et al. 2004) and stream sediments (Holmes et al. 1996), suggesting they may be seasonally important N sinks.

*Indirect Effects: Urbanization and scales of hydrologic exchange and N availability*

Channel modification associated with urbanization alters stream functioning by reducing the interactions between surface and subsurface water (Grimm et al. 2004, Grimm et al. 2005). Because IBW was a historically intermittent stream, surface-subsurface exchanges were likely limited to episodic discharge events. However, the relatively broad floodplain visible in 1945 suggests that when the wash flowed, surface-subsurface exchange was extensive. Although portions of IBW are now perennial, the clay liners and deep, fine sediments of the lakes serve reduce hydraulic conductivity and limit hydraulic exchange. In order to understand how this may affect N availability, we contrast the processes responsible for determining N availability in IBW with those of Sycamore Creek, a well-studied Sonoran Desert stream with a similar watershed area (505 $km^2$).

In Sycamore Creek (Fig. 2.9A), nutrient cycling is strongly affected by interactions between surface and subsurface patches, which is largely a function of geomorphology (Dent and Grimm 1999). Sediments of variable thickness (i.e., the hyporheic zone) are underlain by a bedrock layer. Recharge zones occur where sediments are relatively deep while discharge zones occur where shallow sediments force subsurface water into the surface channel. When surface waters enter the subsurface they bring with them high concentrations of dissolved oxygen and dissolved organic matter derived from primary production in the surface stream, creating ideal conditions for coupled mineralization and nitrification reactions (Holmes et al. 1994, Jones et al. 1995). When this $NO_3^-$-rich water returns to the surface in upwelling zones, primary producers use it to fuel further growth (Valett et al. 1994, Henry and Fisher 2003). Thus, although $NO_3^-$ concentrations are often high in upwelling zones, algal uptake causes a longitudinal decline in surface water $NO_3^-$ concentration as the water flows downstream (Valett et al. 1994, Dent et al. 2001; Fig. 2.7A).

We argue that N cycling in the Indian Bend Wash is analogous to that in Sycamore Creek (Fig. 2.9B). Nitrate concentrations in the groundwater below IBW, like those below the Southern/Tempe canal, have been substantially elevated (Chapter 4, Xu 2002) by leaching from fertilized agricultural fields (Baker, personal communication). When this groundwater is used to supplement canal flows or to maintain urban lake levels, $NO_3^-$ concentration is increased. For example, research on the lakes in Fig. 2.4m has shown that $NO_3^-$ concentrations vary from < 0.01 mg $NO_3$-N/L to >6.6 mg $NO_3^-$-N/L, depending upon the amount of groundwater feeding the lakes (Chapter 4). Although the effect of hydrologic exchange between groundwater and surface water in IBW is analogous to the exchanges between parafluvial and surface flows in Sycamore Creek, the spatial and temporal scales at which the interactions occur are much larger. Parafluvial sediments of Sycamore Creek are shallow (~1-2m) compared to depth to groundwater under IBW (~20-100m). Additionally, hydrologic exchange is relatively rapid in Sycamore Creek, with hyporheic residence times estimated to be on the order of hours to weeks (Valett et al. 1990). This contrasts sharply with the temporal scale of the interaction between surface flows and groundwater in the IBW ecosystem. Even ignoring the time it took to originally fill the Salt River aquifers, time required for irrigation water to percolate down to the water table and be returned to the surface via groundwater pumping is considerable (years to decades). The time required to complete this cycle implies a lag between shifts in agricultural management practices and changes in groundwater chemistry, reducing the ability of managers to limit the flux of N into IBW. Finally, the mechanisms producing groundwater-surface water exchange in Sycamore Creek are physical (e.g., positive vertical hydraulic gradients), whereas in IBW mixing of groundwater and surface streams can only occur by human action.

## CONCLUSIONS

Integrating humans into the study of ecological systems remains one of the central challenges of ecology (Pickett et al. 1997, Collins et al. 2000, Grimm et al. 2000, Redman et al. 2004). The evidence from IBW supports the thesis that effects of urbanization on ecological systems are often produced by land-use change and propagated by changes in hydrology. Effects of urbanization on some variables, like stream geomorphology, are direct, with human decisions capable of producing engineered systems that differ radically from their pristine predecessors. Other effects are indirect and result from changes made to underlying structure of the system; i.e., its habitat template (Poff et al. 1997, Tooth 2000). In IBW, excavation of artificial lakes and creation of irrigated floodplains introduced new potential hot spots. Water required for maintenance of these anthropogenic features was provided by an irrigation system that directly and indirectly altered the flow of water across the landscape; and groundwater pumping established a novel linkage between groundwater and surface flows dependent upon human action. Together, these alterations of IBW and its watershed have changed the spatial and temporal availability of N.

Patterns of development in the Phoenix area broadly, and Scottsdale specifically, resulted from a series of human decisions, both by individual developers choosing where to build and by larger institutions deciding how to provide flood control (e.g, the City of Scottsdale) and how to deliver water (e.g., the Salt River Project and the Army Corps of Engineers). Many of these decisions were guided by the conflicting needs to find a reliable water supply and to limit the effects of floods. Settlers built in the Phoenix region because of the promise of irrigation suggested by Hohokam canals and booster claims of 'greening the desert' (Reisner 1986). Efforts to establish reliable water supplies were largely successful. An elaborate canal network and extensive field of groundwater wells have succeeded in creating the illusion that water does not limit this desert ecosystem (Gammage 1999). The increased spatially and temporal availability of water has increased primary production, while the canal infrastructure has altered the flux of water and sediments through the ecosystem. Previous researchers have noted that the consequences of decisions about how and where a city develops are often ‘phase-lagged’ by a decade or more (Alberti 2005). In IBW the consequences of past fertilizer use just now are being realized as groundwater pumping increases surface $NO_3^-$ concentrations. Although N is an important constituent of all ecosystems, when in excess, it is problematic. This is because excess N tends not to remain in place, but rather to be exported to recipient ecosystems via surface transport (Goolsby and Battaglin 2001) or leaching, where it can contribute to the eutrophication of recipient ecosystems (Carpenter and Pace 1997, Carpenter et al. 1998a) and the reduction of drinking water quality (Neilsen and Lee 1987, Mosier et al. 2001). Clearly, understanding how urbanization alters the availability of important nutrients like N will be crucial if we hope to minimize impacts of an increasingly urban population.

## ACKNOWLEDGEMENTS

This manuscript was produced with support from the Urban Ecology IGERT and CAP LTER programs at Arizona State University, NSF Grants DGE-9987612 and DEB-9714833 and -0423704, respectively. Additional support was provided by the Arizona State University’s Center for Environmental Studies. The authors thank Wayne Porter and Lela Preshad for GIS assistance, Hillary Oberle with help with the acquisition of aerial photos, Cathy Kochert for laboratory assistance, and the canal sampling team for help in the field. This manuscript benefited from the comments of Lisa Eby.

## LITERATURE CITED

Aber, J. D., K. J. Nadelhofer, P. Steudler, and J. M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience **39**:378-386.

Abrahams, A. D., A. J. Parsons, and J. Wainwright. 1995. Effects of vegetation change on interrill runoff and erosion, Walnut Gulch, southern Arizona. Geomorphology **13**.

Alberti, M. 1999. Modeling the urban ecosystem: a conceptual framework. Environmental Planning **B 26**:605-630.

Alberti, M. 2005. The effects of urban patterns on ecosystem function. International Regional Science Review **28**:168-192.

Alberti, M., Z. Marzluff, E. Shulenberger, G. Bradley, C. Ryan, and C. Zumbrunnen. 2003. Integrating humans into ecology: opportunities and challenges for studying urban ecosystems. BioScience **53**:1169-1179.

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**:758-761.

Anderson, T. W. 1995. Summary of the Southwest Alluvial Basins, Regional Aquifer-System Analysis, South-Central Arizona and Parts of Adjacent States. U.S. Geological Survey Professional Paper 1406-A, USGS, Washington, DC.

Arizona Department of Water Resources. 1999. Third Management Plan 2000-2010: Phoenix Active Management Area. Phoenix, AZ.

Arizona Meteorological Network. 2004. Weather Data http:\\ag.arizona.edu\azmet. Tucson, AZ.

Arrowsmith, R., and T. L. Pewe. 1999. Geological overview of the McDowell Mountains. Pages 1-10 *in* K. J. Schroeder, editor. McDowell Mountains Archaeological Symposium. Roadrunner Publications in Anthropology, Scottsdale, AZ.

Association of State Flood Plain Managers Inc. 2002. Mitigation success stories in the United States. Pages 100 *in*, Madison, WI.

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

Bayman, J. M. 2001. The Hohokam of southwest North America. Journal of World Prehistory **15**:257-311.

Belnap, J., R. 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.

Bennett, E. M., T. Reed-Andersen, J. N. Houser, J. R. Gabriel, and S. R. Carpenter. 1999. A phosphorus budget for the lake Mendota watershed. Ecosystems **2**:69-75.

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, J. P., A. Kinzig, N. B. Grimm, W. F. Fagan, D. Hope, J. Wu, and E. T. Borer. 2000. A new urban ecology. American Scientist **88**:416-425.

Dent, C. L., and N. B. Grimm. 1999. Spatial heterogeneity of stream water nutrient concentrations over successional time. Ecology **80**:2283-2298.

Ewing, R. 1994. Characteristics, causes, and effects of sprawl: a literature review. Environmental and Urban Issues **21**:1-15.

Fisher, S. G. 1986. Structure and dynamics of desert streams. Pages 119-139 *in* W. G. Whitford, editor. Pattern and process in Desert ecosystems. University of New Mexico Press, Albuquerque.

Folke, C., A. Jansson, J. Larsson, and R. Costanza. 1997. Ecosystem appropriation by cities. Ambio **26**:167-172.

Gammage, G., Jr. 1999. Phoenix in perspective. Herberger Center for Design Excellence. Arizona State University College of Architecture and Environmental Design, Tempe, AZ.

Graf, W. L. 1975. The impact of surburbanization on fluvial hydrology. Water Resources Research **11**:690-692.

Graf, W. L. 1988. Fluvial Processes in Dryland Rivers. Springer-Verlag, New York.

Grimm, N., R. Arrowsmith, C. Eisinger, J. Heffernan, D. B. Lewis, A. MacLeod, L. Preshad, W. J. Roach, T. Rychener, and R. W. Sheibley. 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. *in* G. Asner and R. Houghton, editors. Ecosystems and Land Use Change. American Geophysical Union.

Grimm, N., and S. G. Fisher. 1992. Responses of arid land streams to changing climate. Pages 211-233 *in* P. Firth and S. G. Fisher, editors. Climate Change and Freshwater Ecosystems. Springer-Verlag, New York, NY.

Grimm, N. B., J. M. Grove, S. T. A. Pickett, and C. L. Redman. 2000. Integrated approaches to long-term studies of urban ecological systems. BioScience **50**:571-583.

Grimm, N. B., and C. L. Redman. 2004. Approaches to the study of urban ecosystems: the case of central Arizona-Phoenix. Urban Ecosystems **7**:199-213.

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

Groffman, P. M., and M. K. Crawford. 2003. Denitrification potential in urban riparian zones. Journal of Environmental Quality **32**:1144-1149.

Hayden, J. D. 1970. Of Hohokam origins and other materials. American Antiquity **35**:87-93.

Hedin, L. O., J. C. von Fischer, M. G. Brown, N. E. Ostrom, B. P. Kennedy, and G. P. Robertson. 1998. Thermodynamic constraints on nitrogen transformations and other biogeochemical processes at soil-stream interfaces. Ecology **79**:684-703.

Henry, J. C., and S. G. Fisher. 2003. Spatial segregation of periphyton communities in a desert stream: causes and consequences for N cycling. Journal of the North American Benthological Society **22**:511-527.

Hilbricht-Ilkowska, A. 1999. Shallow lakes in lowland river systems: role in transport and transformations of nutrients and biological diversity. Hydrobiologia **408/409**:349-358.

Holmes, R. M., S. G. Fisher, and N. 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, Jr., S. G. Fisher, and N. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry **33**:125-146.

Hope, D., W.-X. Zhu, C. Gries, J. Oleson, J. Kaye, N. B. Grimm, and L. A. Baker. in press. Spatial variation in soil inorganic nitrogen across an arid urban ecosystem. Urban Ecosystems.

Hupp, C. R., and W. R. Osterkamp. 1996. Riparian vegetation and fluvial geomorphic processes. Geomorphology **14**:277-295.

Jenerette, G. D., W. Wu, S. Goldsmith, W. A. Marussich, and W. J. Roach. in press. Contrasting water footprints of cities in China and the United States. Ecological Economics.

Jensen, J. P., E. Jeppesen, P. Kristensen, P. B. Christensen, and M. Søndergaard. 1992. Nitrogen loss and denitrification as studied in relation to reductions in nitrogen loading in a shallow, hypertrophic lake (Lake Søbygård, Denmark). Internationale Revue gesamten Hydrobiologie **77**:29-42.

Jensen, J. P., P. Kristensen, and E. Jeppesen. 1991. Relationships between nitrogen loading and in-lake nitrogen concentrations in shallow Danish lakes. Vereinigung fuer Theoretische und Angewandte Limnologie **24**:201-204.

Jones, J. B., Jr., S. G. Fisher, and N. B. Grimm. 1995. Vertical hydrologic exchange and ecosystem metabolism in a Sonoran Desert stream. Ecology **76**:942-962.

Kling, G. W., G. W. Kipphut, M. M. Miller, and W. J. O'Brien. 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. Freshwater Biology **43**:477-497.

Lee, S. E. 1988. Indian Bend Wash. *in* W. L. Graf, editor. The Salt and Gila Rivers in Central Arizona: A Geographic Field Guide. Arizona State University, Tempe, AZ.

Lee, W. T. 1905. Underground Waters of Salt River Valley, Arizona. Water-Supply and Irrigation Paper No. 136 U.S. Geological Survey, Washington, D.C.

Leopold, L. B. 1968. Hydrology for Urban Land Planning - A Guidebook on the Hydrologic Effects of Urban Land Use. Geological Survey Circular 554, U.S. Geological Survey, Washington, DC.

Luck, M. A., G. D. Jenerette, J. Wu, and N. B. Grimm. 2001. The urban funnel model and spatially heterogeneous footprint. Ecosystems **4**:782-796.

Luckingham, B. 1989. Phoenix: the history of a southwestern metropolis. The University of Arizona Press, Tucson.

Masse, W. B. 1981. Prehistoric irrigation systems in the Salt River Valley, Arizona. Science **214**:408-415.

Matthews, D. 1985. Indian Bend Wash. The City of Scottsdale Communications and Public Affairs, Scottsdale, AZ.

McAuliffe, J. R. 1994. Landscape evolution, soil formation, and ecological patterns and processes in Sonoran Desert bajadas. Ecological Monographs **54**:111-148.

McClain, M. E., B. E. W., C. L. Dent, C. 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 aquatic and terrestrial ecosystems. Ecosystems **6**:301-312.

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society **24**:602-612.

Montgomery, E. L., and J. W. Harshbarger. 1989. Arizona hydrogeology and water supply. Pages 827-840 *in* J. P. Jenney and S. J. Reynolds, editors. Geologic Evolution of Arizona. Arizona Geological Society Digest, Tucson, AZ.

Padgett, P. E., E. B. Allen, A. Bytnerowicz, and R. A. Minich. 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. Atmospheric Environment **33**:769-781.

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.

Pickett, S. T. A., J. Burch, WR, S. E. Dalton, T. W. Foresman, J. M. Grove, and R. Rowntree. 1997. A conceptual framework for the study of human ecosystems in urban areas. Urban Ecosystems **1**:185-199.

Poff, N. L., J. D. Allan, M. B. Bain, J. R. Karr, K. L. Prestegaard, B. D. Richter, R. E. Sparks, and J. C. Stromberg. 1997. The Natural Flow Regime. BioScience **47**:769-784.

Redman, C. L., J. M. Grove, and L. H. Kuby. 2004. Integrating social science into the Long-Term Ecological Research (LTER) Network: social dimensions of ecological change and ecological dimensions of social change. Ecosystems **7**:161-171.

Reisner, m. 1986. Cadillac desert: the American West and its disappearing water. Viking, New York, NY.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnology and Oceanography **33**:702-724.

Stanley, E. H., and M. W. Doyle. 2002. A geomorphic perspective on nutrient retention following dam removal. BioScience **52**:693-701.

Strahler, A. N. 1952. Dynamic basis of geomorphology. Geological Society of America Bulletin **63**:923-938.

Sullivan, J. F. 1996. 1995 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Sullivan, J. F. 1998. 1997 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Tarboton, D. G. 2004. Terrain Analysis Using Digital Elevation Models (TauDEM). http://hydrology.neng.usu.edu/taudem/, Utah State University.

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

Trimble, S. W. 1997. Contribution of stream channel erosion to sediment yield from an urbanizing watershed. Science **278**:1442-1444.

Trimble, S. W. 2003. Historical hydrographic and hydrologic changes in the San Diego creek watershed, Newport Bay, California. Journal of Historical Geography **29**:422-444.

U.S. Army Corps of Engineers. 1975. Gila River Basin, Arizona, Indian Bend Wash, Design Memorandum No. 1, General Design Memorandum, Phase II, Project Design for Indian Bend Wash. Los Angeles.

U.S. Bureau of Reclamation. 2005. Colorado River Basin Project: Central Arizona Project http://www.usbr.gov/dataweb/html/crbpcap.html.

U.S. Census Bureau. 1995. 1980 and 1990 Census counts for cities with 1990 population greater than 100,000 http://www.census.gov/population/censusdata/c1008090.txt.

U.S. Census Bureau. 2003. Census 2000 Data for the State of Arizona http://www.census.gov/census2000/states/az.html.

United Nations. 1999. The State of World Populations 1999 -- 6 Billion: A Time for Choices. United Nations Population Fund, New York.

Valett, H. M., S. G. Fisher, N. B. Grimm, and P. Camill. 1994. Vertical hydrologic exchange and ecological stability of a desert stream ecosystem. Ecology **75**:548-560.

Valett, H. M., S. G. Fisher, and E. H. Stanley. 1990. Physical and chemical characteristics of the hyporheic zone of a Sonoran Desert stream. Journal of the North American Benthological Society **9**:201-215.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, and W. H. Schlesinger. 1997. Human alteration of the global nitrogen cycle: causes and consequences. Issues in Ecology **1**:1-14.

Webster, K. E., P. A. Soranno, S. B. Baines, T. K. Kratz, C. J. Bowser, P. J. Dillon, P. Campbell, E. J. Fee, and R. E. Hecky. 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. Freshwater Biology **43**:499-515.

Wolman, M. G. 1967. A cycle of sedimentation and erosion in urban river channels. Geografiska Annaler **49A**:385-395.

Wood, E. D., F. A. J. Armstrong, and F. A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. Journal of the Marine Biology Association of the United Kingdom **46**:23-31.

Xu, Y. 2002. Assessment and prediction of groundwater nitrate contamination trends in the Salt River Project Area, Arizona. Dissertation. Arizona State University, Tempe, AZ.

Zhu, W.-X., N. D. Dillard, and N. B. Grimm. 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. Biogeochemistry **71**:177-196.

Zhu, W.-X., D. Hope, C. Gries, and N. Grimm. in press. Soil characteristics and the storage of inorganic nitrogen under different land uses in an arid urban ecosystem. Ecosystems.

Table 2.1. Description of aerial data.

| Year | Data Source | Format | Color/B&W | Description |
|---|---|---|---|---|
| 1949 | Flood Control District of Maricopa County | Digital | B&W | Georeferenced arial image |
| 1962 | U.S. Forest Service | Print | B&W | Original unrectified aerial photos |
| 1971 | U.S. Geological Survey | Print | B&W | Orthophoto quarter quadrangles |
| 1978 | Landis Corporation | Print | B&W | Black and white aerial images |
| 1987 | Landis Corporation | Print | B&W | Black and white aerial images |
| 1997 | U.S. Geological Survey | Digital | B&W | Orthophoto quarter quadrangles |
| 2003 | Landis Corporation | Digital | Color | Seamless, high-resolution, true-color orthorectified image |

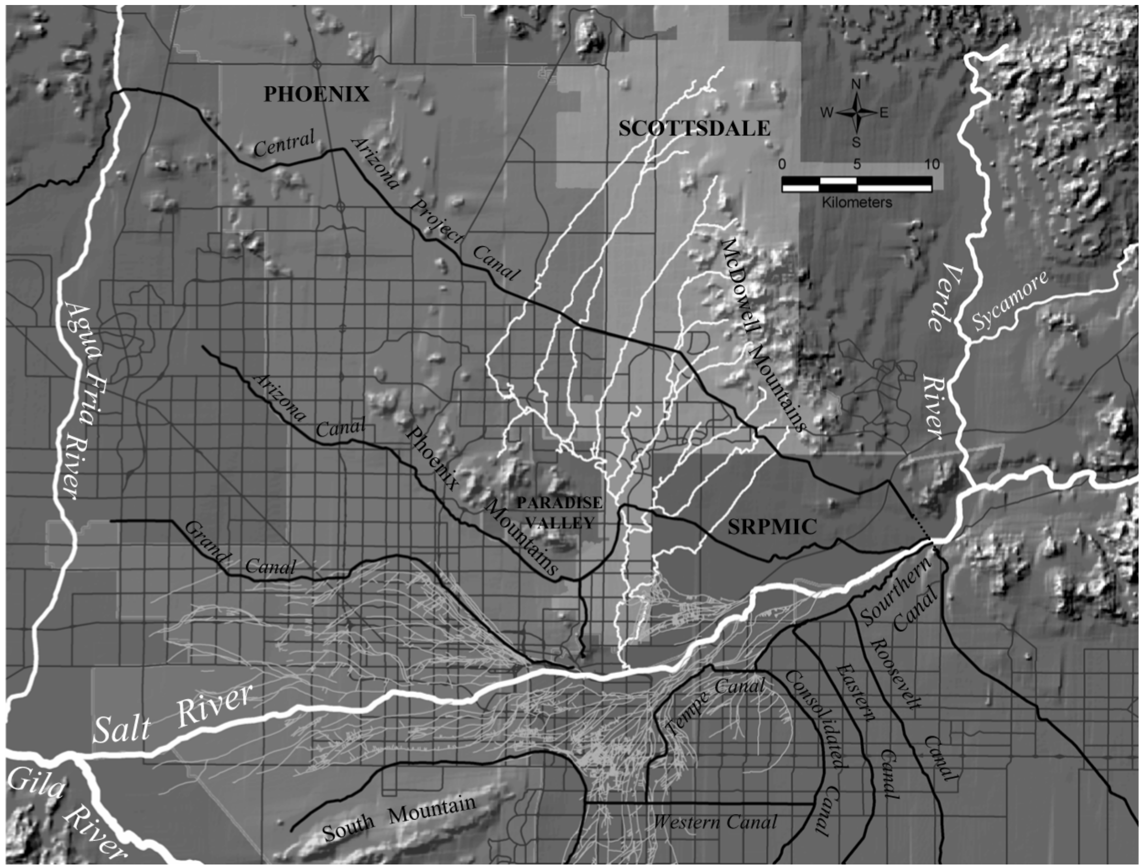


Figure 2.1. Shaded relief map of the Central-Arizona Phoenix ecosystem and its key hydrologic features. Major municipalities are indicated by slightly different shades of gray and are labeled accordingly. The rectilinear gray lines are the principal streets and indicate the current extent of the urban area. The main channels of the major rivers in the area are indicated by the white lines and labeled accordingly. The historic channel network of Indian Bend Wash Watershed is indicated by the fine white lines running through Scottsdale. Thick black lines indicate the major canals the Salt River Project as well as the Central Arizona Project canal. The fine light gray lines branching out from the Salt River indicate the location of the ancient but extensive Hohokam canal network.

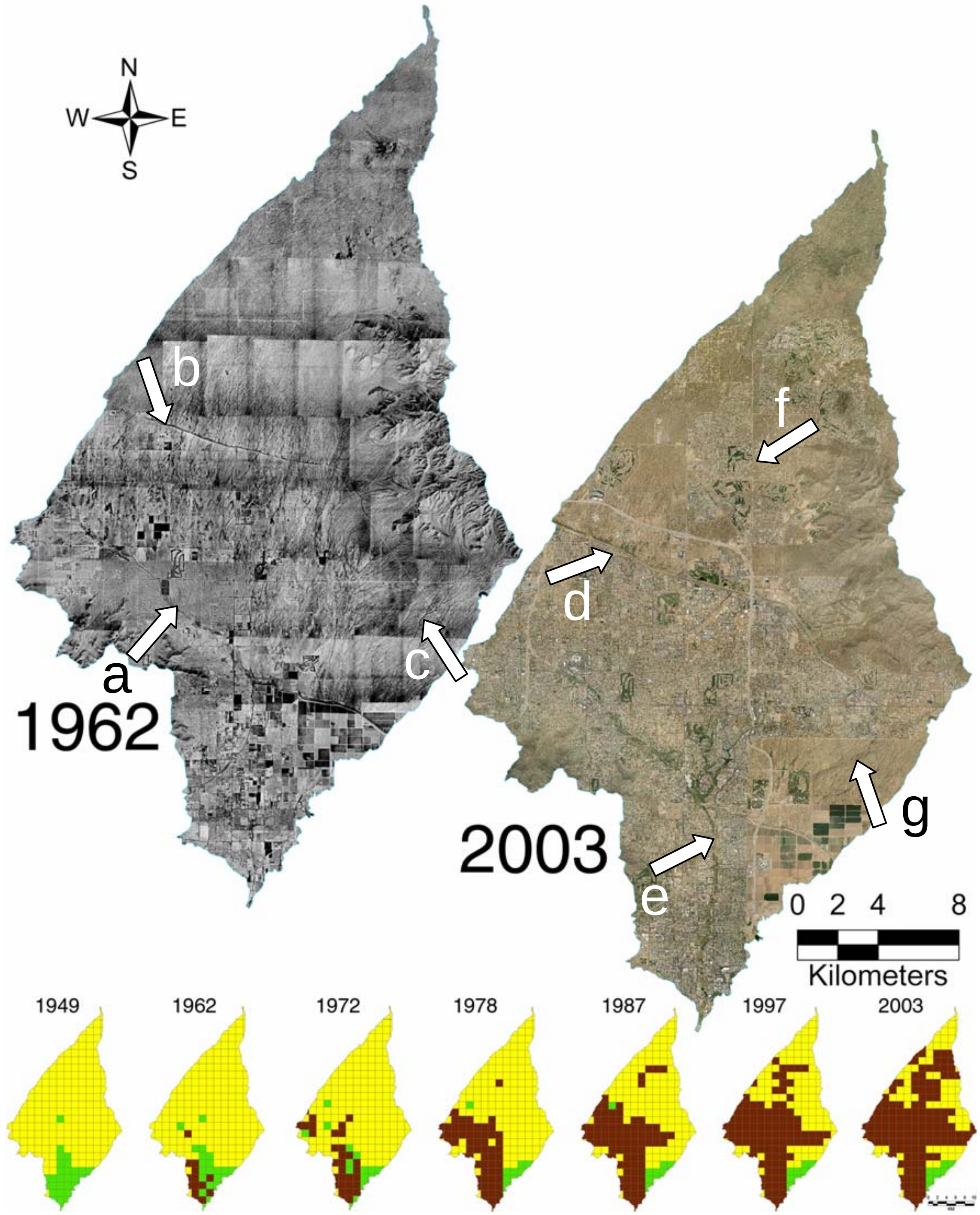


Figure 2. 2. Watershed scale land use change in Indian Bend Wash. Cartoons show land use patterns from 1949 through 2003. Each cell is one 1.6-km$^2$ and the dominant land cover type in each cell is indicated by the cell's hue. Desert (yellow), agricultural fields (green), and urban land use (brown) are indicated. Aerial image on left is a composite photograph of the wash in 1962. Dark bands running north-south and east-west are artifacts of the original photographs. Aerial image on right is from 2003. Arrows indicate important features. See text for explanation.

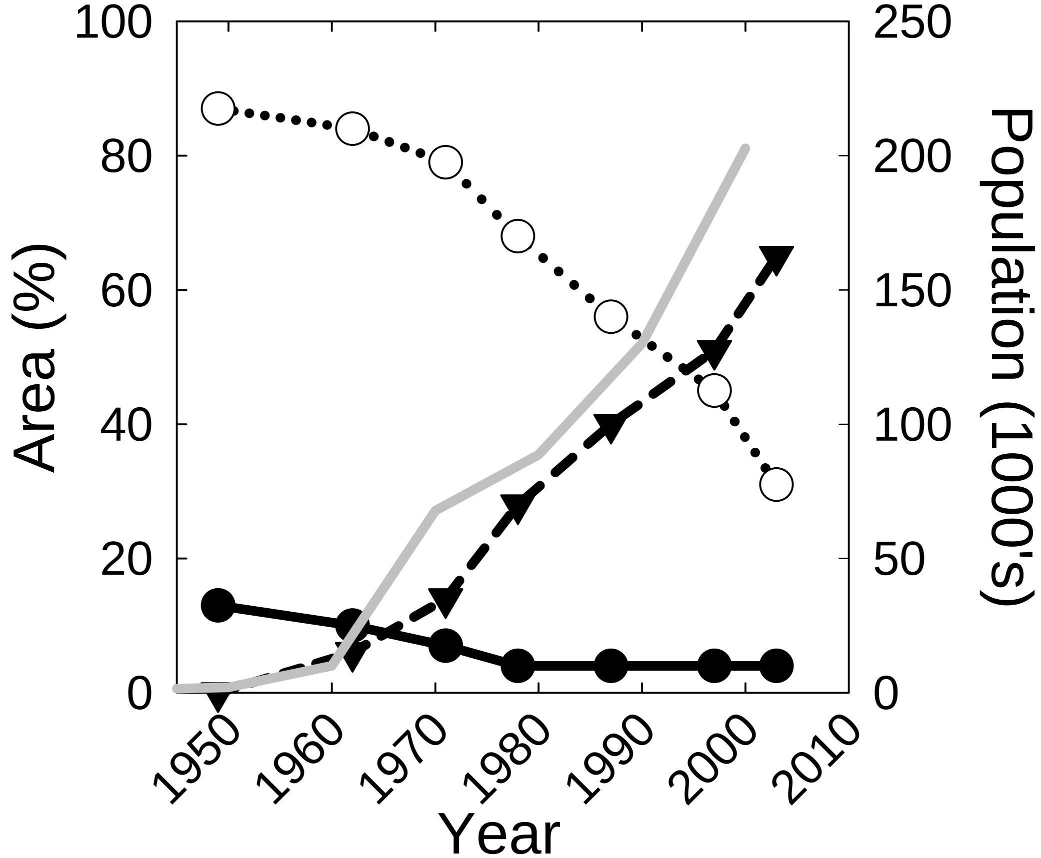

Figure 2.3. Change in the percentage of land in the Indian Bend Wash watershed classified as agriculture (solid circles, solid line), desert (open circles, dotted line), or urban (solid triangles, dashed line) over the past 55 years as well as changes in the population (solid gray line) of the city of Scottsdale.

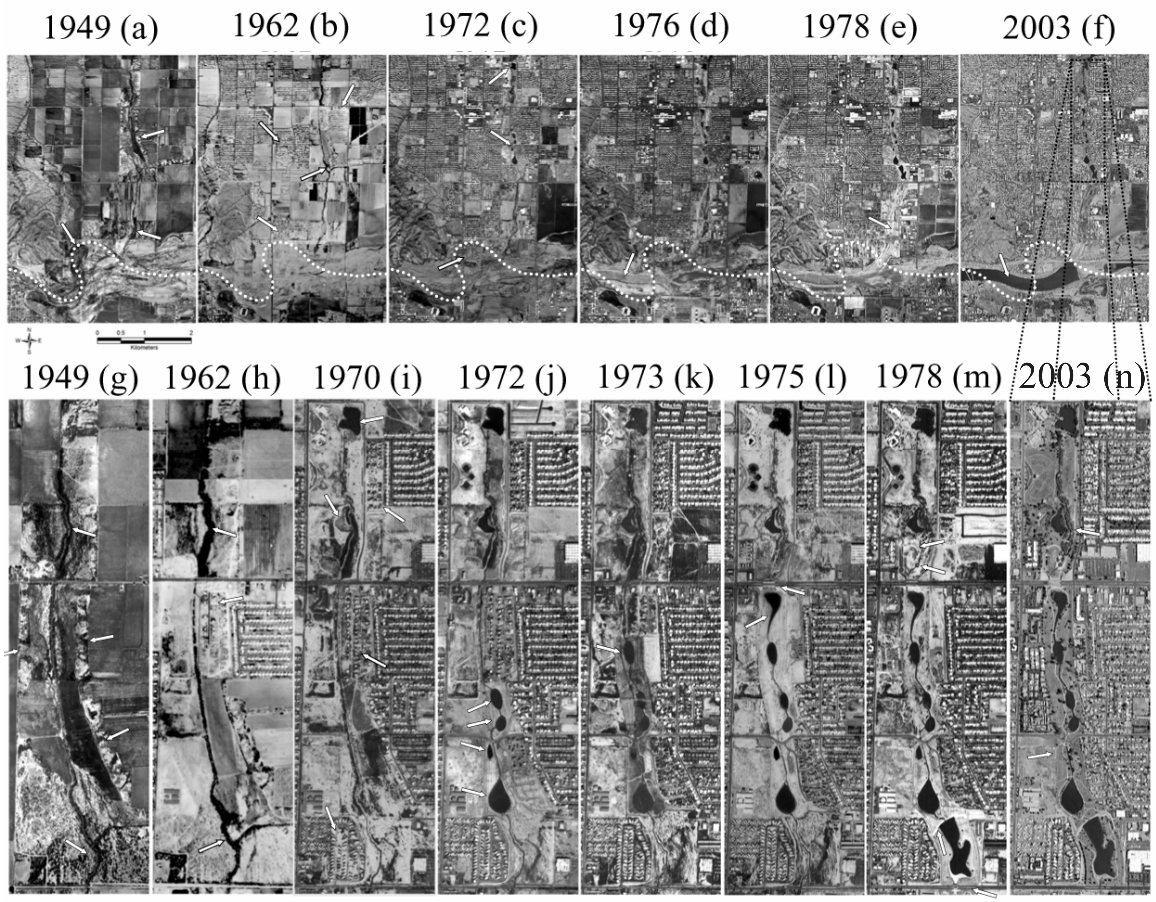


Figure 2.4. Aerial photographs documenting reach-scale changes in the lower portion of Indian Bend Wash and at its confluence with the Salt River over the study period (panels a-f). Dotted white line indicates position, in 1949, of a large meander in the Salt River located just downstream of river's confluence with IBW. Arrows indicate important features discussed more fully in the text, including original IBW floodplain and riparian vegetation (a); encroachment of new developments on floodplain (b); construction of artificial lakes in low flow channel (c); extensive modification of Salt River channel (d) and IBW outflow channel (e); and filling of Tempe Town Lake (f). Lower panels (g-h) provide more detailed view of modifications made to lower portion of IBW. Box indicated by the dotted black line in panel f shows location of reach. Arrows accent important changes that have occurred to broad, unconstrained floodplain, steep risers, and extensive mesquite bosques that characterized the reach in 1949 (g). Changes include encroachment and subsequent removal of subdivisions on the low flow channel (h-j); construction of various lakes (i-m) and other flood control structures (m); removal of one lake (n); and reduction of the mesquite bosque (m). Dates above each panel refer to the year the photograph was taken.

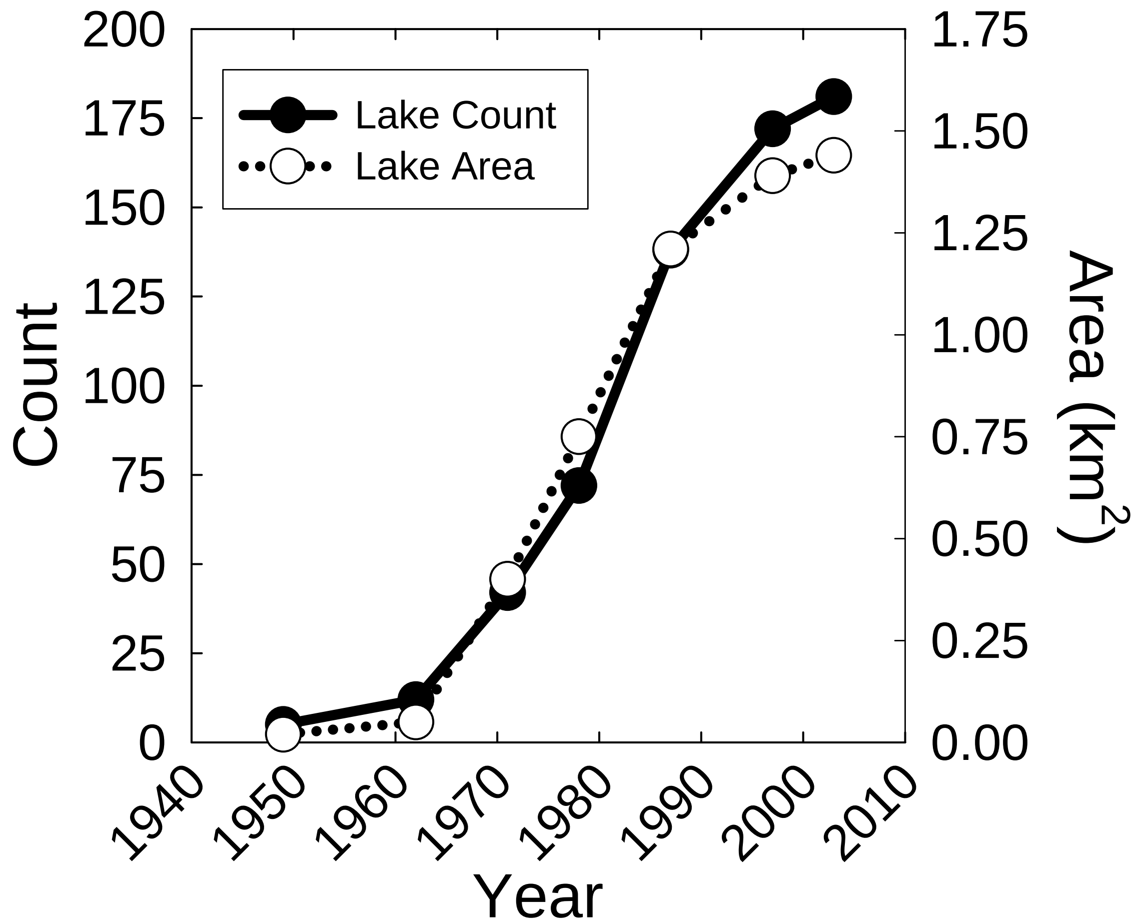


Figure 2.5. Increases in both the number of lakes (solid line; filled circles) in the Indian Bend Wash watershed as well as their aerial extent (dashed line; open circles) over the course of urban expansion. Although many of these artificial lakes were constructed in association with the IBW greenbelt (Fig. 2.4), others were built as water hazards in golf courses, as recreational amenities in urban parks, or as central features in new subdivisions.

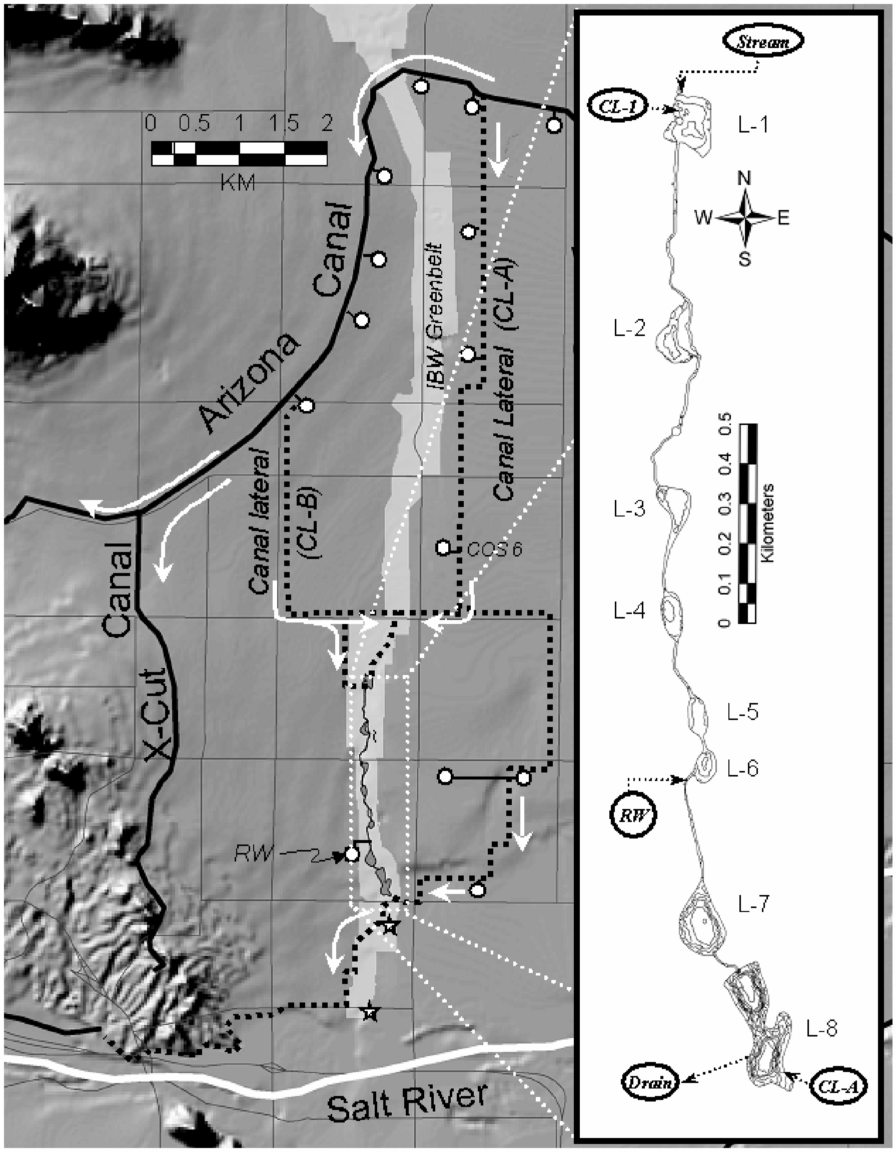


Figure 2.6. Map of canals (thick black lines), canal laterals (dashed black lines), and groundwater wells (circles) feeding eight lakes in lower watershed (inset). Surface water diverted from the Salt, Verde, and Colorado Rivers flows through the Arizona canal. During peak demand, flows are supplemented with groundwater from the wells along its southern edge. Two canal laterals (*CL-A* and *CL-B*) deliver water to the stream above the reach. *CL-1* and *CL-2* also deliver water directly to lakes L-1 and L-8, respectively, through subsurface pipes. Some of the water entering from the stream above L-1 is diverted around the lake through a bypass pipe (dashed gray line). The Roosevelt well discharges directly to the stream. During baseflow, water is returned to the canal system through a drain in lake L-8. Bathymetry of the lakes is indicated by 0.5 m contour lines. White arrows indicate dominant flowpaths. Stars indicate location of two permanent stream gauges.

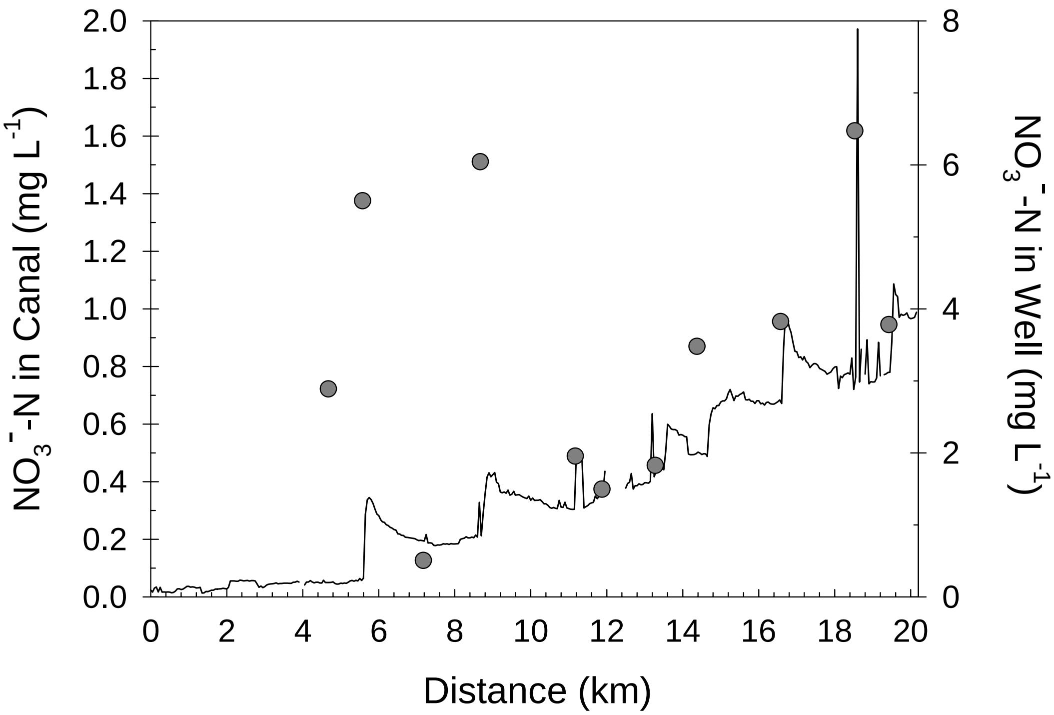


Figure 2.7. Downstream changes in $NO_3^-$ of canal water collected from Southern and Tempe canals during a synoptic survey June 21, 1999. A 20-km reach beginning just west of the Salt River on the Southern Canal and extending to a point on the Tempe Canal just north of the Western Canal was sampled. Solid line represents the $NO_3^-$ concentration in canal water collected every 50 m. Circles indicate concentration of $NO_3^-$ in groundwater well inputs. Note that groundwater and canal water N-concentrations are plotted on different axes. Not all wells were pumping during sampling, thus not all wells along the reach were sampled.

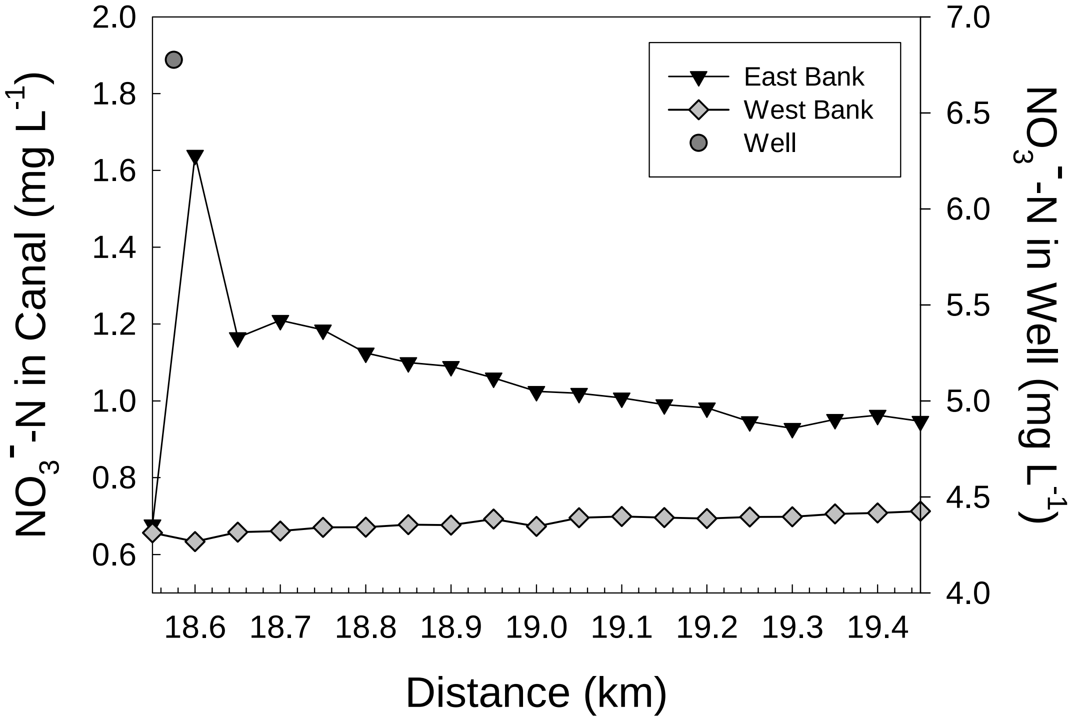


Figure 2.8. Contrasting changes in $NO_3^-$ of canal water collected from opposite banks of the Tempe canal at 50 m intervals below a groundwater well during a survey June 28, 1999. Circle indicates the concentration of $NO_3^-$ in groundwater well. Note that groundwater and canal water N-concentrations are plotted on different axes.

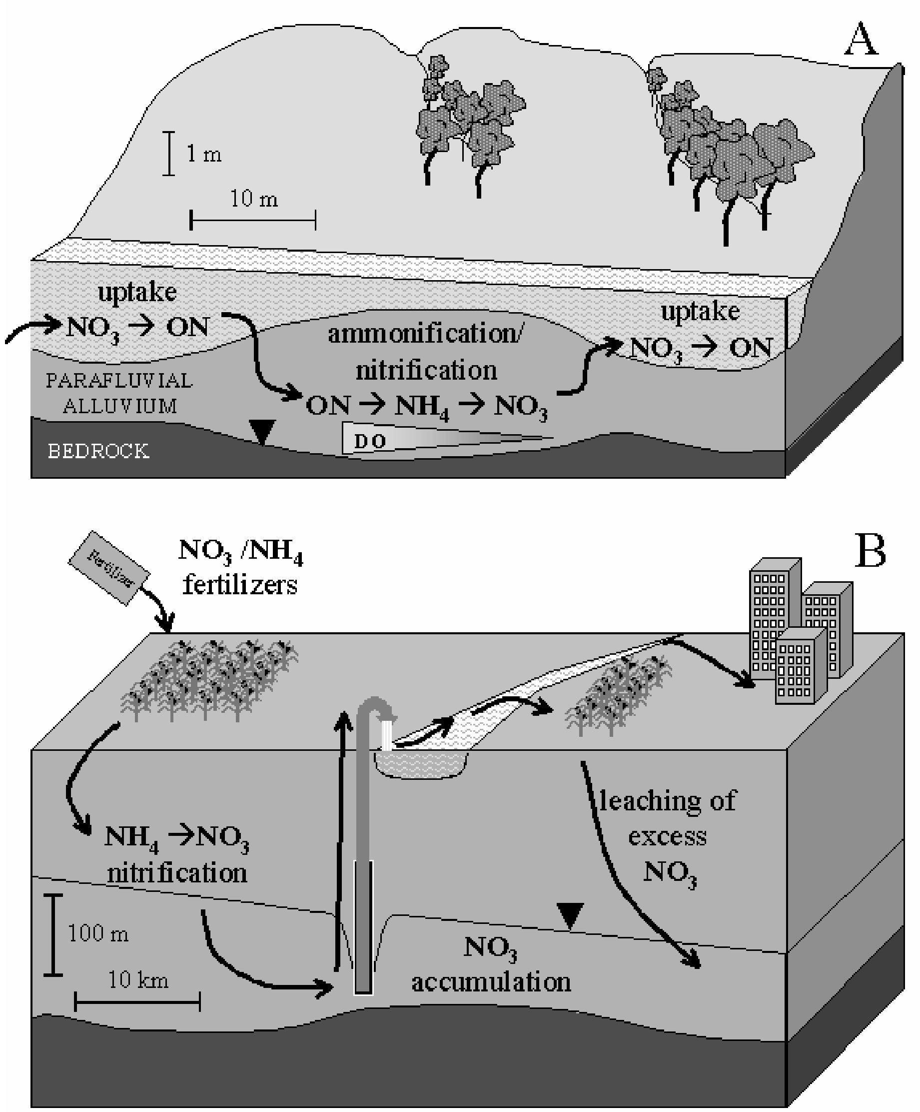


Figure 2.9. Conceptual model of how surface-subsurface interactions determine nitrate availability in Sycamore Creek (A) and the IBW ecosystem (B). The processes of assimilation, ammonification-nitrification, and hydrologic exchange determine N dynamics in both systems, but the scales at which these processes operate differ markedly. Cycling of N in Sycamore Creek tends to be rapid, is tightly coupled to biotic drivers, and occurs over short spatial scales. Conversely N cycling tends to be slow in IBW, is dominated by human inputs, and is characterized by long lag times between the leaching of N into the groundwater and its return to surface ecosystems. Further, groundwater pumping and canals establish novel spatial connections between distant, formerly isolated patches in IBW. Finally, drivers of hydrologic exchange in the two ecosystems are different, with physical processes forcing movement of water between surface and subsurface systems in Sycamore Creek while human actions connect groundwater with surface flows in IBW.

# 3. SYNCHRONOUS NUTRIENT DYNAMICS IN AN URBAN STREAM


## ABSTRACT

Indian Bend Wash is an extensively modified desert stream. The historically dry mainstem has been converted into a perennial lake chain maintained by diversion of surface flows from other streams and groundwater pumping. The ability of both the lake chain as a whole and the individual lake and stream segments to process nutrients (estimated as inlet – outlet concentrations) and thus limit their impact on recipient ecosystems was examined. Individual lakes processed statistically significant quantities of nitrate ($NO_3^-$) and soluble reactive phosphorus (SRP) while releasing ammonium ($NH_4^+$) and dissolved organic carbon (DOC). However, coefficients of variation of lake and stream processing were very large and median processing was approximately zero for all solutes. We conclude that individual lakes and stream segments do not behave consistently over time, but instead alternate between sources and sinks for a wide variety of limnological variables. On a given date, however, patterns were more spatially consistent and when the lake string was examined as a whole net processing of $NH_4^+$, $NO_3^-$, SRP and DOC was frequently observed. On balance, the lake chain tended to be a sink for SRP and a source for $NH_4^+$ and DOC, while processing of $NO_3^-$ was less predictable.

The degree to which a variable's dynamics over time are synchronized with other points in space is an indication of the scale of the driver producing observed variability. Synchrony of nine limnological variables measured at inlets and outlets of the lake chain

was used to evaluate relative importance of broad-scale climatic drivers versus lake specific-factors in IBW. All variables displayed a remarkable degree of synchrony that declined as distance between sampling points increased. Temperature dynamics, which are strongly driven by climatic factors, were most synchronous. Nutrient dynamics were also highly synchronous. Synchrony appeared strongly linked to management decisions, predominantly those regarding the mix of water sources used to maintain flows. As the relative proportion of different water sources varied, so did water chemistry. As a result, $NH_4^+$, $NO_3^-$, SRP, and $Cl^-$ dynamics were highly synchronous. Linear regression was used to examine effects of distance, area, and volume between sampling points on synchrony. Synchrony of all variables declined with different metrics of distance, but this decline was most rapid for $NO_3^-$, suggesting that $NO_3^-$ dynamics were strongly affected by lake-specific factors. Water volume was the best predictor of declines in synchrony of conductivity, $NO_3^-$, DOC and SRP, suggesting water column processes were the most important small-scale drivers for these variables. Water surface area was a better predictor of changes in synchrony of $Cl^-$, $NH_4^+$, and pH, suggesting either sediment processes or exchanges between the water surface and the atmosphere were driving small-scale variations in these variables. Thalweg distance separating sampling points best explained declines in synchrony of temperature and DO.

## INTRODUCTION

Urbanization, the increase in size, density, and heterogeneity of cities (Vlahov and Galea 2002), has had profound impacts on aquatic ecosystems generally (Booth and

Jackson 1997, Carpenter et al. 1998, Boesch et al. 2001, Nilsson et al. 2003) and on streams specifically (Paul and Meyer 2001, Grimm et al. 2004, Grimm et al. 2005, Meyer et al. 2005, Walsh et al. 2005b). Development often changes watershed hydrology and geomorphology and alters biogeochemical cycles. For example, N and P concentrations tend to be elevated in urban streams (Paul and Meyer 2001, Meyer et al. 2005), which can reduce nutrient limitation (Chapter 4, Grimm et al. 2005). The ability to process nutrients, an important function of stream ecosystems (Peterson et al. 2001), may also be compromised. Nutrient spiraling techniques, developed to describe nutrient transport and processing in pristine stream ecosystems (Stream Solute Workshop 1990), have been used recently to examine the effects of inputs from wastewater treatment plants (Martí et al. 2004, Haggard et al. 2005, Merseburger et al. 2005) and agricultural fields (Alexander et al. 2000, Merseburger et al. 2005) on nutrient processing. However, the ability of urban streams to process nutrients and limit their export to recipient ecosystems largely remains an open question (but see Grimm et al. 2005, Groffman et al. 2005, Meyer et al. 2005).

Simplification of stream channels and rerouting of flowpaths often accompany urban development (Grimm et al. 2005, Walsh et al. 2005a). In addition, desire for recreational opportunities or flood control resulted in the proliferation of new, artificial lakes in urban ecosystems, some of which require extensive modifications of watershed hydrology for their maintenance (Chapter 2, Gulati and van Donk 2002). In the Central-Arizona Phoenix (CAP) ecosystem, some new lakes are hydrologically connected, creating analogues to natural lake districts and lake chains (Chapter 2). Previous research on lake districts (Magnuson et al. 1990, Riera et al. 2000, Webster et al. 2000) and lake chains (Soranno et al. 1999, Kling et al. 2000) has demonstrated that landscape position and the extent and nature of the hydrologic connections between lakes can explain much observed variation. In lake districts of Wisconsin, for example, water chemistry of high-elevation lakes tends to more closely resemble that of precipitation whereas chemistry of lower-elevation lakes reflects the addition of weathering products that enter solution along groundwater flowpaths (Riera et al. 2000). Lake and stream segments along a chain of lakes flowing into Toolik Lake, Alaska were shown to exhibit distinct behavior (Kling et al. 2000); lakes tended to consume a number of solutes, including $NO_3^-$, while stream segments tended to produce similar quantities of those solutes. A chain of artificial lakes created along an urban stream channel in urban central Arizona provides an opportunity to explore the degree to which urbanization can recreate such patch-specific differences in biogeochemical processing.

Ecosystem dynamics are affected by both small-scale patch-specific processes and broader-scale extrinsic forces (Baines et al. 2000). Sometimes referred to as temporal coherence, synchrony describes the degree to which two points in space exhibit similar dynamics through time and is typically estimated as Pearson's correlation coefficient. Synchrony is a good indicator of the relative importance of broad-scale forcing (e.g., climatic variables) versus small-scale local factors (e.g., biotic uptake of N, physical weathering of $Ca^+$) as drivers of variability in physical (Magnuson et al. 1990, Baines et al. 2000, Järvinen et al. 2002), biogeochemical (Magnuson et al. 1990, Soranno et al.

1999, Baines et al. 2000, Webster et al. 2000, Pace and Cole 2002) and biotic variables (Magnuson et al. 1990, Rusaak et al. 1999, Soranno et al. 1999).

Synchrony depends upon the spatial extent of the dominant drivers and the degree to which upstream conditions affect variation downstream. Logically, immediately adjacent points experiencing identical conditions should display perfect synchrony. As distance between sampling points increases, the likelihood that two points will experience different conditions (e.g., slight variations in solar radiation or nutrient recycling rates) increases and their correlation declines. Thus, synchrony should decline with distance separating sampling points, and rate of decline should be proportional to the importance of internal patch-specific drivers. When small-scale processes (e.g., biotic uptake, denitrification) dominate, synchrony will decline rapidly with distance. Conversely, when regional (e.g., climate) or basin wide (e.g., lithology) factors drive variation, synchrony should remain relatively constant over broad distances. The relationship between distance and synchrony can be examined using linear regression.

Central to a regression-based approach to analyzing synchrony is an appropriate estimate of distance. Ideally, a good distance metric estimates both the spatial and temporal separation (i.e., the time needed for a force acting at one point in space to affect a point some distance away) of sampling points. In terrestrial ecosystems, the linear distance between sampling points may be the best metric. Indeed, geostatistics, which models the spatial dependence of a set of observations, relies on the linear distance between data points (Rossi et al. 1992). For limnological variables driven by large-scale processes, linear distance between two points may remain the best indicator of their separation. However, because water flows downhill, downstream points are explicitly linked to upstream points through the movement of water. Thus distance is a function of both flowpath length separating points *and* time required for water to travel between them. Because water volume is correlated with both the physical and temporal distance between two points (and relatively insensitive to changes in discharge, large floods notwithstanding), it may be a good metric of distance. Thus, volume should provide an index of the degree of internal processing (e.g., phytoplankton nutrient uptake, bacterial N mineralization) that occurs between two points on a lake chain. Similarly, some variables will be driven by interactions with adjacent patches that occur as water flows between two points (changes in water chemistry driven by exchanges with the atmosphere or with sediments, for example). In these cases, the area between two points may be a better indicator of the distance separating two points.

Synchrony in chemical parameters can also be affected by inputs of water from a source whose chemistry varies independently of the main stem, such as tributaries or groundwater. These point sources add an additional source of variation to stream reaches below the input (confluence, spring or well). This additional source of variation will decrease synchrony of points spanning the confluence if the drivers of variation are different; however, synchrony of pairs of points wholly upstream from the confluence should be unaffected.

Here, we explore how anthropogenic modifications made to an urban desert stream, Indian Bend Wash (IBW), affect patterns of nutrient cycling and processing. We take advantage of the creation of a perennial reach characterized by an artificial lake chain to explore how urbanization affects biogeochemical processes. We asked four questions: (1) Do lake and stream segments in IBW differ in their ability to process $NO_3^-$, $NH_4^+$, SRP, or DOC? (2) Is IBW a source or a sink for $NO_3^-$, $NH_4^+$, SRP, and DOC? (3) Do physical and chemical variables vary synchronously along IBW? and (4) What does the relationship between distance and synchrony suggest about the dominant drivers of variability along IBW?

## STUDY SITE

Prior to urban development, the Indian Bend Wash (IBW) drained ~520 km$^2$ of desert, agricultural, and suburban lands in Scottsdale, AZ (Fig. 3.1). However, the Central Arizona Project Canal now hydrologically severs the northern half of the watershed from the southern (Chapter 2) and the Arizona Canal limits surface flows through the lowermost 48 km$^2$ to the stream's main stem (Fig. 3.1). As a part of a flood-control project, a greenbelt was constructed in the main channel of the wash. Designed to accommodate the 100-year storm (U.S. Army Corps of Engineers 1975), the greenbelt's most striking feature is a series of shallow, permanent lakes (L-1 through L-8) in the larger floodplain (Fig. 3.1, inset). These lakes differ in surface area, depth and volume, as do the streams connecting them (Table 3.1). Between floods, lake levels are artificially maintained with mixed canal and groundwater. Canal water is diverted into the reach through the stream above L-1 or directly through a subsurface input to this lake. Periodically, the Roosevelt groundwater well pumps water into the stream between L-6 and L-7. Additional water is added via subsurface pumping to lake L-8. Canal water is a mix of surface water diverted from the Salt, Verde, and Colorado (via the Central Arizona Project Canal) Rivers and groundwater is used to supplement flows during periods of peak demand (Chapters 2, 4). $NO_3^-$ concentrations in the aquifer underlying IBW have been elevated as a result of historic fertilizer use (Xu 2002). As a result, when groundwater is used to supplement surface flows, $NO_3^-$ concentration in canal water increase (Chapters 2, 4).

## METHODS

### *Field sampling and laboratory analysis*

Complete surveys of the study reach were conducted on 23 dates in 2002 and 19 dates in 2003. Surveys were approximately monthly during winter and more frequent during summer, with survey frequency increasing directly after floods. In addition to complete surveys, a subset of points was also sampled during 6 flood events. Sample locations included inlets and outlets of all lakes between the outlet of L-1 and the outlet of L-8, plus additional inlet and outlet sites for other hydrologic inputs and off-channel components of the system (Fig., 1 inset). On each sampling date, stage height was measured and discharge estimated from an empirically derived relationship between stage height and discharge. Triplicate water samples were collected into new polyethylene centrifuge tubes and duplicate water samples were collected into acid-washed, polyethylene bottles. Samples were stored at 4 $^{o}$C until processed at the Goldwater Environmental Laboratory (GEL) of Arizona State University. With the exception of dissolved organic carbon (DOC), within 72 h of collection all three triplicates were analyzed colorimetrically on a Lachat QC8000 autoanalyzer for nitrite-N + nitrate-N (hereafter $NO_3^-$-N), ammonium-N ($NH_4^+$-N), soluble reactive phosphorus (SRP), and chloride ($Cl^-$). Prior to analyses, water was centrifuged at $10^4$ RPM for 10 minutes, which removes particles as effectively as a 0.45–µm membrane filter (Thomas Colella, GEL Director, *unpublished data*) without risking $NH_3$ volatilization (*personal observation*). Colorimetric analysis methods were the phenol-hypochlorite method for $NH_4^+$-N (Solorzano 1969), the cadmium-copper reduction method for $NO_3^-$-N (Wood et al. 1967); the ascorbic-acid reduction method for SRP (Henriksen 1966), and the mercuric thiocyanate method for $Cl^-$ (Zall et al. 1956). Duplicate samples were filtered through a Whatman GF/F glass-fiber filter (nominal pore size 0.7 µm) upon returning from the field and acidified with HCl, and samples were analyzed for DOC within 30 d of collection using high-temperature combustion (Katz et al. 1954) on a Shimadzu TOC 5000. Solute concentrations for a site on a sampling date are reported as the mean of the replicate samples. On four dates in 2002, laboratory difficulties necessitated that samples be centrifuged, decanted and frozen prior to analysis for $NH_4^+$, $NO_3^-$, SRP, and $Cl^-$. On each sampling date, dissolved oxygen (DO) and water temperature were measured in the field with either a YSI Model 85 or Model 95 DO Meter. On most dates, conductivity and pH were measured either in the field with VWR Symphony Conductivity (SP 40 C) and pH (SP 30 I) meters, or in the laboratory on unfiltered water samples using a Corning 320 pH Meter and an Orion 150 Conductivity Meter.

*Calculations of lake- and stream-specific processing and net uptake of nutrients*

We took two different approaches to estimating nutrient processing in IBW. First, changes in chemical and physical variables caused by internal processing of lakes and streams were calculated by subtracting the lake outlet value from the inlet value or the downstream stream values from upstream values. This approach is identical to the one adopted by Kling et al. (2000) for a lake chain in arctic Alaska, USA. Because of the subsurface additions to L-1 and L-8, they were not included in this analysis. The hypothesis that net processing was a consistent function of patch type was tested by comparing the mean difference values for all lakes and all streams to zero with one-sample *t*-tests using Bonferroni-adjusted probabilities for multiple comparisons. Change in flux (discharge x concentration) was also estimated, but yielded qualitatively similar results, so only concentration data are reported in this paper and flux data are not shown.

Second, we used a technique modified from Martí et al. (1997) to estimate the net uptake length between the outlets of L-1 and L-6 using natural declines in concentration of four reactive solutes ($NO_3^-$-N, $NH_4^+$-N, SRP, DOC) (Martí et al. 1997, Haggard et al. 2005). Briefly, this technique uses changes in downstream nutrient concentrations to estimate $S_{net}$ from the following equations:

(1) $C_x = C_0 e^{kx}$

(2) $\ln(C_x/C_0) = kx$

(3) $S_{net} = -1/k$

where $C_x$ is nutrient concentration (mg/L) at distance $x$ (m) from the top of the reach, $C_0$ is nutrient concentration (mg/L) at the outlet of lake L-1, and $k$ is the nutrient change coefficient (1/m). For each solute and date, simple linear regression was used to determine if the relation between nutrient concentrations and distance downstream (i.e., $S_{net}$) was significant at $\alpha = 0.05$. A positive net $S_{net}$ indicated net uptake of the solute whereas a negative $S_{net}$ indicated net release. This approach assumes that nutrient additions to the top of the reach are continuous, that the reach is relatively homogeneous, and that dissolved nutrients are removed from and released into the water column continuously (Haggard et al. 2005). To ensure that these assumptions were at met, at least approximately, we restricted our analysis to the reach between the outlet of L-1 and the outlet of L-6. On four of 48 sampling dates, large abrupt changes in $Cl^-$ concentration indicated that that the reach should be treated as two segments. On those dates, only the results from the longer reach are reported. For each of the four solutes, chi-square tests were used to test two hypotheses: (1) that the reach was reactive (i.e., showed net uptake or release) more frequently than not, and (2) that when the reach was reactive, it tended to consistently act as either a source or a sink for that nutrient.

### *Analysis of synchrony*

Synchrony was measured by calculating the Pearson product-moment coefficient ($r$) for all possible pairs of sampling points ($n = 153$), with observations paired by sampling date, for the nine measured variables. Degree of synchrony of the different variables was compared using a non-parametric Kruskal-Wallis test, with multiple post-hoc comparisons made using the Nemenyi test (Zar 1996). This test is preferred to an ANOVA when sample variances are not equal.

The effect of distance on synchrony was tested for each variable using linear regression analysis. For each variable, correlation coefficients, $r_{i,j}$, for each pair of points, $i j$, were regressed against three different estimates of distance ($D_{i,j}$) calculated as the thalweg length ($L_{i,j}$), area ($A_{i,j}$), or the volume of water ($V_{i,j}$) separating the two sampling points. For each dependent variable, overall fits of the three models were assessed and, if all assumptions were met, the model with the highest $R^2$ was judged superior. Regression coefficients (slopes) of the fitted models for various limnological variables were compared using a Tukey test following an analysis of covariance (Zar 1996).

Regression models were evaluated to ensure that they conformed to assumptions of linear regression. Because the incremental effect of distance on $r$ tended to decline as the total distance increased, all three distance metrics were square root transformed prior to analysis. This produced a more linear relationship between the transformed correlation coefficients and the distance metric. Because correlation coefficients are drawn from a binomial population ranging from –1 to +1, they were transformed prior to analysis using one of the following equations:

$$(5)\ r' = \arcsin [(r + 1)/2]^{1/2}$$

$$(6)\ r'' = 0.5 * \ln [(r+1)/(r-1)]$$

Both transformations served to make the residuals more normal, though equation (6) tended to overcorrect and was only used when equation (5) proved insufficient.

Effects of groundwater additions from the Roosevelt well were evaluated by comparing estimates of synchrony when the well was running versus when it was off. Because well water was not expected to vary synchronously with the rest of the wash, its addition was expected to decrease the synchrony between pairs of points spanning the well. Conversely, pairs that were located entirely above the well or below the well were not expected to be affected. We compared the number of significant correlation coefficients ($p < 0.05$) estimated using dates the well was running (WELL ON) versus dates when it was not (WELL OFF) for three different groups of sample pairs (i.e., ABOVE, both points located above well, SPAN, points spanned well, or BELOW, both below well). By way of comparison, the identical analysis of the effect of position was conducted using correlation coefficients estimated from the pooled data (ALL DATES). A chi-square test was used to test the null hypothesis that the distribution of significant correlations was proportional to the number of pairs in each group (ABOVE, SPAN, BELOW) for each data set (WELL ON, WELL OFF). For each data set, if the null was rejected, the chi-square analysis was subdivided to test whether the correlations of points spanning the well produced nonconformity, or if other groups also deviated significantly from expectations. This comparison was made using a chi-square test with Yates correction for continuity (Zar 1996).

Statistical analyses were performed using SYSTAT (version 10, SPSS Inc., 2000), SPSS for Windows (version 10.0), or by hand using Microsoft Excel 2000.

## RESULTS

### *Solute variability and nutrient uptake*

All measured variables displayed a high degree of spatial and temporal variation, both conservative parameters like conductivity (an index of total dissolved ions) and $Cl^-$

as well as the more reactive solutes like $NO_3^-$ and SRP. This variability contrasts markedly with the relative constancy of solute chemistry, temperature, pH and DO concentrations of the Roosevelt well (Fig. 3.2). Although differences between inlets and outlets were frequent, neither lakes nor streams had consistent (i.e., consistently positive or negative), strong effects on chemical or physical variables (Table 3.2). The degree of processing in both lakes and stream was highly variable, as indicated by the large range and high per cent covariation of the differences between inlet and outlet values (Table 3.2). Although DO, DOC, $NH_4^+$, and temperature increased significantly in lakes while SRP and $NO_3^-$ decreased significantly, the changes were small in magnitude for most variables.

Results differed when the lake chain was considered as a whole. On some dates, there were strong downstream trends in nutrient ($NH_4^+$, $NO_3^-$, SRP and DOC) concentrations (e.g., Fig. 3.3; upper panel), though the direction of trends was neither consistent (e.g., Fig. 3.3; lower panel) nor were they significant for all dates or for all nutrients. Significant reach-scale changes in $NH_4^+$, $NO_3^-$ and DOC were observed more frequently than not, as indicated by nutrient spiraling metrics (Table 3.3). Processing of $NH_4^+$ and DOC was most consistent, with net release occurring much more frequently than net uptake. Although net processing of $NO_3^-$ was significantly more frequent than not, there was no significant difference in the number of days on which net uptake versus release was observed. Conversely, although net processing of SRP occurred on just over half of the dates, when processing did occur SRP was much more likely to be processed than released (Table 3.3).

*Synchrony of physical and chemical variables*

Synchrony was typically high, with the nine parameters falling into roughly three groups (Fig. 3.4). Synchrony was highest for temperature and conductivity and slightly lower for the more reactive SRP, DOC and $NO_3^-$, while $Cl^-$ fell in between these two groups. Synchrony was lowest for pH, $NH_4^+$ and DO.

Synchrony varied strongly with distance and was well predicted by all three distance metrics (Table 3.4). Synchrony of temperature and DO were best predicted by thalweg length while $NH_4^+$ was best predicted by surface area. Volume was the best predictor for the remaining six variables. All regressions were significant, however, the amount of variation explained varied. For example, a maximum of 18 % of the variation in DO synchrony was explained by any distance metric, whereas 89% of the variation $NO_3^-$ synchrony was explained by volume. In part, this is because magnitude of the effect of distance on synchrony differed from one variable to the next. A comparison of regressions of synchrony against volume indicated that slopes were shallowest for temperature and DO and steepest for $NO_3^-$. Multiple comparisons were used to rank the nine variables according to the regression coefficients (Figure 3.5).

Synchrony was disrupted by discharge of well water into the reach. Regardless of solute, most correlation coefficients (97%) were significant when estimated using the entire data set or using just those dates on which the well was not flowing (Table 3.5). However, when synchrony was estimated from observations made only when the well was flowing, the number of correlations that were significant dropped dramatically, largely because of $NO_3^-$ and SRP. When the well was flowing the number of significant correlations between points that spanned the well dropped from 42 to 0 and from 56 to 2 for $NO_3^-$ and SRP, respectively. Surprisingly, average synchrony of $NO_3^-$, as indicated by the number of significant correlations, also dropped significantly for pairs above the well (Table 3.5). However, the reduction in significant correlations was comparatively small and likely due to season. Well pumping was more common during the summer when rates of primary production were highest (W.J. Roach, *unpublished data*).

## DISCUSSION

### *Patch and reach-scale nutrient uptake*

Nutrient (i.e. $NH_4^+$, $NO_3^-$, SRP and DOC) processing was frequently substantial when measured at the scale of the individual patch (i.e., individual lakes or stream segment) scale or reach between L-1 and L-6. Patch-specific nutrient processing rates, as indicated by the large range of processing values, was highly variable. Conversely, processing of conservative solutes tended to be less variable, though large differences between the up- and down-stream estimates of $Cl^-$ concentration and conductivity were occasionally observed. Some care should be taken when evaluating extreme differences between inflows and outflows, however, as they are most likely the result of two slugs of water with radically different water chemistry moving into and out of a lake or stream segment. This is particularly true for the conservative solute $Cl^-$ and for conductivity, neither of which were particularly sensitive to internal drivers.

On average, lakes were a source of DO, DOC, $NH_4^+$, and heat (temperature) and a sink for SRP and, to a lesser degree, $NO_3^-$. This is similar to the findings of Kling et al. (2000), who found consistent differences between lakes and streams in their processing of $NO_3^-$, $NH_4^+$, pH and conductivity, with $NO_3^-$ and conductivity tending to increase in lakes while $NH_4^+$ and pH decreased. The variation in processing observed in IBW, however, was higher than reported for many of the solutes in the Toolik Lake chain.

Patterns of lake- and stream-specific processing were temporally inconsistent, nevertheless, significant reach-scale processing was frequently observed, indicating that that broad-scale drivers were likely responsible for determining reach-scale dynamics. The reach-scale uptake rates of the four nutrients were not correlated, suggesting that they were not controlled by the same factors. The wash tended to be a source for $NH_4^+$ and DOC. Production of $NH_4^+$ is hypothesized to be a result of the mineralization of N in the sediments and the diffusion of this N species into the overlying waters. This is supported by the observation that $NH_4^+$ concentrations are high in the lake sediments of IBW (Chapter 5). Like $NH_4^+$, DOC increases could result from decomposition of organic matter. However, increases in DOC concentration could also be driven by exudates from the abundant algal and macrophyte growth in the wash (W.J. Roach, *personal observation*). Unfortunately, our data is insufficient to discriminate between these two alternatives.

While net changes in SRP only occurred on approximately half of the sampling dates, net uptake was much more common than net release. This is consistent with the observation that the lakes are often P limited (Chapter 4). We hypothesize that uptake by primary producers is responsible for observed declines in SRP.

Processing of $NO_3^-$ by the reach was least consistent. On 16 days the wash was a strong sink for $NO_3^-$, on 9 days it was a source of $NO_3^-$, and on 17 it was neither a source nor a sink (Table 3.3.). There are a variety of possible explanations for this inconsistent pattern. First, because the flux of $NO_3^-$ into the wash was highly variable, changes in concentration gradients may have affected uptake rates. For example, the efficiency with which photosynthesizing algae and macrophytes take up nitrate from the water column increases with concentration (Dodds et al. 2002) until uptake saturates, at which point further increases are not accompanied by increased processing rates (Bernot and Dodds 2005). Similarly, a reduced concentration gradient may have reduced the rate at which $NO_3^-$ diffused into lake sediments where denitrification may have removed nitrate (Mengis et al. 1997, Tomaszek and Czerwieniec 2003, Chapter 4). Unfortunately, uptake lengths were not well predicted by upstream nutrient concentrations, indicating that concentration gradients alone were not sufficient to explain the variation in uptake rates.

Management decisions also may affect the ability of the wash to process nutrients. During periods of maximum productivity, lakes are frequently treated with algaecides and herbicides in an effort to limit algae and macrophyte growth (City of Scottsdale, *personal communication*). As a result of these additions, there can be substantial die off of the standing crop of primary producers (W.J. Roach, *personal observation*). A significant pulse in DOC and nutrients as well as a substantial reduction in nutrient uptake by primary producers may accompany algal decay, and may persist until algal and macrophyte communities recover. The hypothesis that artificially reducing the standing crop of primary producers will reduce rates of nutrient uptake is supported by the findings of other researchers. Hall and Tank (2003) demonstrated that the uptake of $NH_4^+$ in 11 Wyoming streams was positively related to rates of both gross primary production and community respiration while the uptake of $NO_3^-$ was positively correlated with rates of gross primary production. In a study of two New Zealand streams, chlorophyll *a* explained a large proportion of the seasonal variation in the uptake of $NO_3^-$ and SRP in one stream but not in the other (Simon et al. 2005). Unfortunately, our data on timing of herbicide and algaecide treatments are insufficient to test this hypothesis.

In some ways, point-source inputs to L-1 at the top of the study reach are analogous to wastewater treatment plants (WWTP) outflows. Previous research on nutrient uptake in streams where WWTP are significant sources of $NH_4^+$, $NO_3^-$, or SRP has shown that these inputs can alter cycling rates. Haggard et al. (2005) found that a WWTP input to an Arkansas stream elevated SRP concentrations and increased processing lengths. Nevertheless, the stream remained a net sink for SRP on most dates. In contrast, they found that addition of inorganic $NH_4^+$ from the WWTP resulted in increased nitrification, but little net processing. Martí et al. (2004) examined nutrient uptake below WWTP located on 15 streams in Catalonia, Spain. Responses to the increased availability of inorganic N and P varied, with some streams acting as sources and other as sinks for $NH_4^+$, $NO_3^-$, and SRP. As in the Arkansas stream described by Haggard et al. (2005), Martí et al. (2004) found that declines in $NH_4^+$ were frequently associated with increases in $NO_3^-$. As these studies demonstrate, the response of streams to elevated nutrients can be highly variable, though increased processing rates is a common theme (Merseburger et al. 2005). However, these studies do not demonstrate as extensive a range of nutrient processing rates as that observed in IBW over the course of this study, especially with regard to $NO_3^-$. Unlike the above-mentioned studies, there was no close coupling between $NH_4^+$ declines and $NO_3^-$ production. In fact, the scales of change for the two solutes differed by an order of magnitude. Thus, nitrification is not a significant process in IBW.

*Synchronous dynamics in IBW*

Although net processing rates were temporally variable in IBW, the measured variables tended to vary synchronously. This was not surprising; since the relatively small spatial extent of the study reach ensured that all lakes and streams experienced substantially similar climatic drivers. The high degree of connectivity between lakes also contributed to their synchronous dynamics. Järvinen et al. (2002) found that lake pairs with a direct surface water channel connection exhibited higher degrees of synchrony than those that were not connected by surface flows. More interesting than the high degree of synchrony characterizing the dynamics of IBW were sharp declines in synchrony of some variables as distance between points increased. Sharp declines indicate that despite the strong effects of broad-scale drivers on the dynamics of IBW, small-scale factors remained important determinants of spatial patterns of variation.

Not surprisingly, the addition of well water disrupted patterns of synchrony by supplying water with characteristics that varied independently of the mainstem. In general, well water displayed very little variation in any of the measured variables. Because Roosevelt well water $NO_3^-$ concentration was typically higher than surface water concentration (Fig. 3.2), well water additions markedly reduced synchrony of $NO_3^-$. Abrupt changes in synchrony may be useful indicators of unknown, discrete subsurface inputs such as from springs or upwelling zones.

Numerous other researchers have shown that physical variables like temperature, which are tightly linked to climatic drivers, are highly synchronous across relatively large spatial scales (Kratz et al. 1998, Baines et al. 2000, Benson et al. 2000, Järvinen et al. 2002). Synchronous variation in lake water temperature has even been correlated with the North Atlantic Oscillation (George et al. 2000), suggesting that the spatial extent of climatic drivers can be quite large. Temperature, along with conductivity and $Cl^-$, displayed the highest degree of synchrony of any variable in IBW and the least variation. At the same time, synchrony of temperature was less affected by distance than any other variable other than DO, which had consistently low synchrony. Together, the relatively high synchrony and low sensitivity to distance suggests that climatic drivers of temperature change were operating at a scale larger than the reach. This is not surprising given the relatively short distance (< 3 km) between the upper and lower sampling points along the reach and the relative lack of shading of all but stream segments L-1 to L-2 and L-2 Bypass. Although there was little variation in synchrony of temperature along the reach, there was a significant decline in synchrony as the distance between points increased. This decline was most tightly coupled to thalweg length, which may be attributed more to time of sampling than to differences in the drivers of temperature variation (i.e, because sites were sampled in linear sequence, the top of the reach was consistently sampled later in the day and typically was warmer).

Mean synchrony of conductivity and $Cl^-$ were statistically indistinguishable from that of temperature, though they both exhibited more variation. This was largely because the synchrony of both conductivity and $Cl^-$ decreased more rapidly with distance than temperature, with $Cl^-$ having one of the steepest declines in synchrony with distance, as measured by volume, of the variables measured. Both $Cl^-$ and conductivity were expected to be relatively conservative solutes as their increase is driven by the weathering of minerals and by evaporative concentration. Indeed, previous research has attributed increased conductivity in lake water to the increased input of weathering products via groundwater flows of seepage versus drainage lakes (Riera et al. 2000). However, the relatively short length of the study reach coupled with the fact that the lakes are perched above the water table and groundwater inputs are likely low, argue against this hypothesis. Additionally, $Cl^-$ concentrations did not show consistent longitudinal patterns. The chemical characteristics of the water entering the wash did vary over time, however. This was largely because the water diverted into the stream channel from the Arizona Canal was a mix of water from three surface sources (the Colorado, Salt and Verde Rivers) and, to a varying degree, groundwater. These sources all differ in their chemical composition and the relative contribution of each source varied over time depending upon demand and management decisions (Sullivan 1998). Periodic flooding also contributed water with a slightly different chemical makeup than either canal water or groundwater. Thus, at any given time, water at two points could be composed of water from different sources and, as such, would be expected to differ accordingly. The volume of water between two points should be the best indicator of likelihood that water came from different sources. This was true for conductivity but less so for $Cl^-$, synchrony of which was better predicted by the area between two points, perhaps reflecting the contribution of evaporative concentration to changes in $Cl^-$ concentration.

Next to synchrony of conductivity and $Cl^-$, mean synchrony of SRP, DOC, and $NO_3^-$ were highest, even though synchrony of these solutes was highly dependent upon the water volume between sampling points. Lakes and streams of IBW were capable of significant processing these three solutes, based on frequent observation of significant net uptake lengths in the upper portion of the reach. The high degree of synchrony lends support to the hypothesis that broad-scale drivers determined whether or not the wash acted as a source or sink for each solute on any given date. Nevertheless, these three solutes showed three of the four steepest declines in synchrony with distance, suggesting internal, small-scale processes were also important in producing observed spatial variation.

For all three of the most reactive solutes, volume was the best distance metric. This suggests that differences in concentration at any two points were likely driven by extent of water column-driven processing. Thus, as volume between two points increases, opportunities for processing by algae or macrophytes also increase. The $NO_3^-$ data best support this contention, for the decline in synchrony with volume was significantly steeper for $NO_3^-$ than for the more conservative variables conductivity and $Cl^-$. It seems likely that water-column processing produced some of the decline in synchrony of SRP and DOC as the water volume between sampling points increased, but the rate of their decline, while more rapid than conductivity, was statistically indistinguishable from that of $Cl^-$. Differences in chemical composition of the water entering the study reach may also be responsible for some reductions in synchrony.

Synchrony of pH, $NH_4^+$, and DO was significantly lower than that of the other variables (Fig. 3.4). Further, synchrony of DO and pH were relatively unaffected by distance. This is in part because the variation in synchrony displayed by these two variables was comparatively high. Thalweg length explained only 18% of the variation in DO, while area explained 45% of the variation in pH. Changes in DO are driven by the relative importance of primary production and respiration and by gas-exchange between atmosphere and water. Although rates of primary production increase during summer and decrease in winter, primary production can be patchy, especially in IBW where macrophyte beds were important, but seasonally variable, primary producers. In addition, small waterfalls and artificial aeration devices locally increase re-aeration rates along the stream. As such, the relationship between distance and the synchrony of DO was not expected to be high, and the relatively high degree of variability in synchrony was not surprising. Similarly, changes in pH are frequently driven by atmospheric gas exchange and could explain why surface area was the best predictor of synchrony of pH. The observation that synchrony of $NH_4^+$ was best explained by area and not volume or thalweg length leads credence to the aforementioned hypothesis that variation in $NH_4^+$ is driven largely by sediment processes.

As Soranno et al. (1999) noted, any measure of synchrony is strongly scale dependent, and more frequent sampling is required for faster flushing systems. Other studies, however, have estimated synchrony based on annual variation (Magnuson et al. 1990, Soranno et al. 1999, George et al. 2000, Webster et al. 2000, Järvinen et al. 2002, Arnot et al. 2003), though some studies have relied on more frequent sampling regimes (Baines et al. 2000, Benson et al. 2000, Kling et al. 2000, Pace and Cole 2002). By sampling at comparatively frequent intervals, this study was able to capture effects of variation produced by changes in the chemistry of the incoming water. This variation was, in part, a result of differences in floodwater chemistry and, in part, a result of management decisions about the mix of surface water and groundwater flowing through the Arizona Canal and into IBW (Chapters 2, 4). Change in water source represents an exogenous factor driving synchronous variations in the wash and is analogous to large scale variation in solar radiation that influence broad patterns of temperature variation (Magnuson et al. 1990, Baines et al. 2000). Because much of this variation is directly under human control, it constitutes a strong ‘urban signal’.

## CONCLUSIONS

Nutrient dynamics in Indian Bend Wash resembled its more pristine counterparts in that it frequently exhibited significant processing of $NO_3^-$, $NH_4^+$, SRP and DOC. The degree of synchrony exhibited by a wide range of limnological variables was surprisingly high. However, except for temperature, this synchrony was not simply a function of climatic drivers. In the desert surrounding Phoenix, studies of Sycamore Creek have shown the importance of floods and season as drivers of N dynamics (Grimm and Fisher 1992). In IBW, floods are not as important as management decisions for driving large-scale variation in both conservative and reactive solutes. The water entering IBW can be viewed as coming from a variety of faucets, each of which taps into a water source with unique chemical characteristics. As managers turn these faucets on and off, the chemical composition of the water used to maintain IBW fluctuates, producing synchronous dynamics throughout the wash. In addition, seeking to maintain clear blue lakes, managers rely on chemical control of aquatic primary production. As a result, rates of primary production, decomposition and nutrient uptake can vary independently of climatic drivers that control these processes in less intensively managed ecosystems. Nevertheless, the lake stream remained an active ecosystem that periodically processed significant $NO_3^-$ and SRP.

## ACKNOWLEDGEMENTS

Thanks to Tom Colella, M. Amy DiIorio, Noah Dillard, Lisa Eby, Jennifer Edmonds, Roy Erickson, Jill Koehler, Nikol Garber, Susan Goldsmith, Julia Henry, Tamara Harms, Jim Heffernan, Darrel Jenerette, Tracy Johns, Cathy Kochert, Libby Larson, David Lewis, Matt Lord, Christine McLaughlin, Wontae Lee, Cathryn Meegan, Diane Miller, Wayne Porter, Emily Prud'homme, John Schade, Rich Sheibley, Derek Stauffer, Steve Swanson, Phil Tarrant, Harriet Van Vleck, Jill Welter, and Paul Westerhoff for help in the field, with lab analysis, and with conceptual development. Thanks to the City of Scottsdale and Mike Bishop for data on the management and maintenance of Indian Bend Wash. This manuscript was produced with support from the Urban Ecology IGERT and CAP LTER programs at Arizona State University, NSF Grants DGE-9987612 and DEB-9714833 and -0423704, respectively. Additional support was provided by the Arizona State University's Global Institute of Sustainability.

## LITERATURE CITED

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**:758-761.

Arnot, S. E., B. Keller, P. J. Dillon, N. D. Yan, M. Paterson, and D. Findlay. 2003. Using temporal coherence to determine the response to climate change in boreal shield lakes. Environmental Monitoring and Assessment **88**:365-388.

Baines, S. B., K. E. Webster, T. K. Kratz, S. R. Carpenter, and J. J. Magnuson. 2000. Synchronous behavior of temperature, calcium, and chlorophyll in lakes of northern Wisconsin. Ecology **81**:815-825.

Benson, B. J., J. D. Lenters, J. J. Magnuson, M. Stubbs, T. K. Kratz, P. J. Dillon, R. E. Hecky, and R. C. Lathrop. 2000. Regional coherence of climatic and lake thermal variables of four lake districts in the Upper Great Lakes Region of North America. Freshwater Biology **43**:517-527.

Bernot, M. J., and W. K. Dodds. 2005. Nitrogen retention, removal and saturation in lotic ecosystems. Ecosystems **8**:442-453.

Boesch, D. F., Brinsfield, and R. E. Magnien. 2001. Chesapeake Bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. Journal of Environmental Quality **30**:303-320.

Booth, D. B., and C. R. Jackson. 1997. Urbanization of aquatic systems -- degradation thresholds, stormwater detention, and the limits of mitigation. Journal of the American Water Resources Association **22**:1-20.

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.

Dodds, W. K., A. J. Lopez, W. B. Bowden, S. V. Gregory, N. B. Grimm, S. K. Hamilton, A. E. Hershey, E. Marti, W. H. McDowell, J. L. Meyer, D. Morrall, P. J.

Mulholland, B. J. Peterson, J. L. Tank, H. M. Valett, J. R. Webster, and W. M. Wollheim. 2002. N uptake as a function of concentration in streams. Journal of the North American Benthological Society **21**:206-220.

George, D. G., S. C. Maberly, and D. P. Hewitt. 2000. The influence of the North Atlantic Oscillation on the physical, chemical and biological characteristics of four lakes in the English Lake District. Freshwater Biology **49**:760-774.

Grimm, N., R. Arrowsmith, C. Eisinger, J. Heffernan, D. B. Lewis, A. MacLeod, L. Preshad, W. J. Roach, T. Rychener, and R. W. Sheibley. 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. *in* G. Asner and R. Houghton, editors. Ecosystems and Land Use Change. American Geophysical Union.

Grimm, N., and S. G. Fisher. 1992. Responses of arid land streams to changing climate. Pages 211-233 *in* P. Firth and S. G. Fisher, editors. Climate Change and Freshwater Ecosystems. Springer-Verlag, New York, NY.

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

Groffman, P. M., A. M. Dorsey, and P. M. Mayer. 2005. N processing within geomorphic structures in urban streams. Journal of the North American Benthological Society **24**.

Gulati, R. D., and E. van Donk. 2002. Lakes in the Netherlands, their origin, eutrophication and restoration: state-of-the-art review. Hydrobiologia **478**:73-106.

Haggard, B. E., E. H. Stanley, and D. E. Storm. 2005. Nutrient retention in a point-source-enriched stream. Journal of the North American Benthological Society **24**:29-47.

Hall, R. O., and J. L. Tank. 2003. Ecosystem metabolism controls nitrogen uptake in streams in Grand Teton National Park, Wyoming. Limnology and Oceanography:1120-1128.

Henriksen, A. 1966. An automatic method for determining orthophosphate in sewage and highly polluted waters. Analyst **91**:652.

Järvinen, M., M. Rask, J. Ruuhijärvi, and L. Arvola. 2002. Temporal coherence in water temperature and chemistry under the ice of boreal lakes (Finland). Water Research **36**:3949-3956.

Katz, J., S. Abraham, and N. Baker. 1954. Analytical procedure using a combustion-diffusion vessel: improved method for combustion of organic compounds in aqueous solution. Analytical Chemistry **26**:1503.

Kling, G. W., G. W. Kipphut, M. M. Miller, and W. J. O'Brien. 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. Freshwater Biology **43**:477-497.

Kratz, K., P. A. Soranno, S. B. Baines, J. J. Magnuson, T. M. Frost, and R. C. Lathrop. 1998. Interannual synchronous dynamics in north temperate lakes in Wisconsin, USA. Pages 273-287 *in* D. G. George, J. G. Jones, P. Puncochar, C. S. Reynolds, and D. W. Sutcliffe, editors. Management of lakes and reservoirs during global climate change. Kluwer, Dordrecht, The Netherlands.

Magnuson, J. J., B. J. Benson, and T. K. Kratz. 1990. Temporal coherence in the limnology of a suite of lakes in Wisconsin, U.S.A. Freshwater Biology **23**:145-159.

Martí, E., J. Autmatell, L. Godé, M. Poch, and F. Sabater. 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. Journal of Environmental Quality **33**:285-293.

Martí, E., N. B. Grimm, and S. G. Fisher. 1997. Pre- and post-flood retention efficiency of nitrogen in a Sonoran Desert stream. Journal of the North American Benthological Society **16**:805-819.

Mengis, M., R. Gächter, B. Wehrli, and S. Bernasconi. 1997. Nitrogen elimination in two deep eutrophic lakes. Limnology and Oceanography **42**:1530-1543.

Merseburger, G. C., E. Martí, and F. Sabater. 2005. Net changes in nutrient concentrations below a point source input in two streams draining catchments with contrasting land uses. Science of the Total Environment **347**:217-229.

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society **24**:602-612.

Nilsson, C., J. E. Pizzuto, G. E. Moglen, M. A. Palmer, E. H. Stanley, N. E. Bockstael, and L. C. Thompson. 2003. Ecological forecasting and the urbanization of stream ecosystems: challenges for economists, hydrologists, geomophologists, and ecologists. Ecosystems **6**:659-674.

Pace, M. L., and J. J. Cole. 2002. Synchronous variation of dissolved organic carbon and color in lakes. Limnology and Oceanography **47**:333-342.

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. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. V. Gregory, and D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. Science **292**:86-90.

Riera, J. L., J. J. Magnuson, T. K. Kratz, and K. E. Webster. 2000. A geomorphic template for the analysis of lake districts applied to the Northern Highland Lake District, Wisconsin, U.S.A. Freshwater Biology **43**:301-318.

Rossi, R. E., D. J. Mulla, A. G. Gournel, and E. H. Franz. 1992. Geostatsitical tools for modeling and interpreting spatial dependence. Ecological Monographs **62**:277-314.

Rusaak, J. A., N. D. Yan, K. M. Somers, and D. J. McQueen. 1999. The temporal coherence of zooplankton population abundances in neighboring North-Temperate lakes. The American Naturalist **153**:46-58.

Simon, K. S., C. R. Townsend, B. J. F. Biggs, and W. B. Bowden. 2005. Temporal variation of N and P uptake in 2 New Zealand streams. Journal of the North American Benthological Society **24**:1-18.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnology and Oceanography **14**:799-801.

Soranno, P. A., K. E. Webster, J. L. Riera, T. K. Kratz, J. S. Baron, P. A. Bukaveckas, G. W. Kling, D. S. White, N. Caine, R. C. Lathrop, and P. R. Leavitt. 1999. Spatial variation among lakes within landscapes: ecological organization along lake chains. Ecosystems **2**:395-410.

Stream Solute Workshop. 1990. Concepts and methods for assessing solute dynamics in stream ecosystems. Journal of the North American Benthological Society **9**:95-119.

Sullivan, J. F. 1998. 1997 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Tomaszek, J. A., and E. Czerwieniec. 2003. Denitrification and oxygen consumption in bottom sediments: factors influencing rates of the process. Hydrobiologia **504**:59-65.

U.S. Army Corps of Engineers. 1975. Gila River Basin, Arizona, Indian Bend Wash, Design Memorandum No. 1, General Design Memorandum, Phase II, Project Design for Indian Bend Wash. Los Angeles.

Vlahov, D., and S. Galea. 2002. Urbanization, urbanicity, and health. Journal of Urban Health **79**:S1-S12.

Walsh, C. J., T. D. Fletcher, and A. R. Ladson. 2005a. Stream restoration in urban catchments through redesigning stormwater systems: looking to the catchment to save the stream. Journal of the North American Benthological Society **24**:690-705.

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

Webster, K. E., P. A. Soranno, S. B. Baines, T. K. Kratz, C. J. Bowser, P. J. Dillon, P. Campbell, E. J. Fee, and R. E. Hecky. 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. Freshwater Biology **43**:499-515.

Wood, E. D., F. A. J. Armstrong, and F. A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. Journal of the Marine Biology Association of the United Kingdom **47**:23-31.

Xu, Y. 2002. Assessment and prediction of groundwater nitrate contamination trends in the Salt River Project Area, Arizona. Dissertation. Arizona State University, Tempe, AZ.

Zall, D. M., D. Fisher, and M. Q. Garner. 1956. Photometric determination of chlorides in water. Analytical Chemistry **28**:1665-1668.

Zar, J. H. 1996. Biostatistical Analysis, 3rd edition. Prentice Hall, Upper Saddle River, NJ.

Table 3.1. Morphometric data for the lakes and streams of Indian Bend Wash. A small fountain interrupts the breaks the reach between lakes L-2 and L-3 into two segments. The bypass channel on the west side of lake L-2 (Fig 1.) is L-2 Bypass.

| Reach Name | Perimeter (m) | Thalweg Length (m) | Surface Area (m2) | Volume (m3) | Max Depth (m) |
|---|---|---|---|---|---|
| Lake | | | | | |
| L-1 | 552 | 186 | 12018 | 12909 | 1.72 |
| L-2 | 443 | 218 | 5947 | 4865 | 1.54 |
| L-3 | 455 | 182 | 6222 | 3460 | 0.96 |
| L-4 | 308 | 134 | 4899 | 3751 | 1.30 |
| L-5 | 318 | 141 | 3999 | 2256 | 1.12 |
| L-6 | 267 | 117 | 3546 | 3634 | 1.80 |
| L-7 | 490 | 209 | 13665 | 25286 | 3.08 |
| L-8 | 950 | 291 | 25719 | 64144 | 4.96 |
| Stream | | | | | |
| L-1 to L-2 | 842 | 404 | 2006 | 715 | 0.62 |
| L-2 Bypass | 336 | 161 | 748 | 143 | 0.27 |
| L-3 to Fountain | 392 | 172 | 1067 | 429 | 0.97 |
| Fountain to L-3 | 329 | 161 | 615 | 41 | 0.10 |
| L-3 to L-4 | 301 | 112 | 654 | 257 | 0.72 |
| L-4 to L-5 | 267 | 127 | 625 | 301 | 1.01 |
| L-6 to L-7 | 581 | 200 | 1037 | 516 | 0.87 |
| L-7 to L-8 | 156 | 73 | 242 | 89 | 0.77 |
| Other | | | | | |
| Foutain | 85 | 40 | 308 | 188 | 0.64 |

Table 3.2. Statistical description of effects of lake and stream processing on chemical and physical variables calculated by subtracting the outlet values from the inlet values for six lakes and the downstream value from the upstream value for eight stream segments. Positive values indicate that the segment processed the variable in question whereas negative values indicate production. *t*-tests, with Bonferroni corrections for multiple comparisons, were used to test which mean values were significantly different than zero.

| Variable | Reach Type | *N* | Median | Mean | Minimum | Maximum | Std. Error | %CV |
|---|---|---|---|---|---|---|---|---|
| $Cl^-$ (mg $L^-1$) | Lake | 300 | -1 | 0 | -125 | 204 | 1 | 5054 |
| | Stream | 342 | 0 | -1 | -97 | 146 | 1 | 2538 |
| Conductivity | Lake | 276 | -2 | 1 | -301 | 387 | 4 | 4726 |
| (mS cm-1) | Stream | 317 | 0 | 2 | -153 | 395 | 2 | 1495 |
| DO (mg $L^-1$) | Lake | 300 | 0.13 | $-0.04^{***}$ | -12.08 | 9.96 | 0.14 | 6200 |
| | Stream | 342 | -0.13 | -0.17 | -7.98 | 7.83 | 0.08 | 842 |
| DOC (mg $L^-1$) | Lake | 260 | -0.2 | $-0.3^{***}$ | -6.4 | 10.2 | 0.08 | 463 |
| | Stream | 302 | -0.1 | -0.1 | -12.9 | 3.1 | 0.05 | 1141 |
| $NH_4^+$ (mg $L^-1$) | Lake | 300 | 0.00 | $-0.01^{***}$ | -0.24 | 0.23 | 0.00 | 420 |
| | Stream | 342 | 0.00 | 0.00 | -0.24 | 0.20 | 0.00 | 4413 |
| $NO_3^-$ (mg $L^-1$) | Lake | 300 | 0.006 | $0.112^{*}$ | -7.21 | 2.901 | 0.043 | 668 |
| | Stream | 342 | 0.003 | 0.005 | -2.125 | 3.238 | 0.016 | 5839 |
| pH | Lake | 275 | 0.00 | -0.01 | -1.12 | 1.04 | 0.01 | 2577 |
| | Stream | 316 | -0.02 | -0.02 | -1.02 | 1.18 | 0.01 | 1041 |
| SRP (mg $L^-1$) | Lake | 294 | 1 | $1^{***}$ | -30 | 28 | 0.4 | 464 |
| | Stream | 334 | 0 | 0 | -13 | 34 | 0.2 | 5179 |
| Temp($^oC$) | Lake | 300 | -0.2 | $-0.3^{***}$ | -5.7 | 4.8 | 0.1 | 482 |
| | Stream | 342 | 0 | 0.0 | -3.4 | 4.2 | 0.0 | 13630 |

$^{*}$, $^{**}$, $^{***}$ Indicate Bonferroni adjusted probabilities of P < 0.10, P < 0.05, and P < 0.01, respectively.

Table 3.3 Summary of results of reach-scale analysis of net uptake between the outlet of lake L-1 and the outlet of L-6. The number of days the reach exhibited net uptake, release or neither is reported. A significant fit of the model (Cx/Co) = *k*x indicated net processing (uptake or release) of the nutrient, while non-significance ($p > 0.05$) indicated that the reach was neither a source nor a sink on a given date. Chi-square tests were used to test whether or not was reactive (i.e., showed net uptake or release) more frequently than not (bold test statistics). A second set of chi-square tests were used to test whether or not the reach tended to display net uptake versus net release on those days net processing was significant (italicized test statistics).

| | $NH_4^+$ | | | $NO_3^-$ | | | SRP | | | DOC | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Net Result | No. of Days | $\chi^2$ | $p$ | No. of Days | $\chi^2$ | $p$ | No. of Days | $\chi^2$ | $p$ | No. of Days | $\chi^2$ | $p$ |
| Uptake | 1 | *22.15* | *< 0.001* | 16 | *1.96* | *0.375* | 20 | *14.73* | *< 0.001* | 2 | *16.67* | *< 0.001* |
| Release | 25 | | | 9 | | | 2 | | | 22 | | |
| Neither | 16 | **13.69** | **0.001** | 17 | **8.76** | **0.013** | 19 | **1.23** | **0.5** | 13 | **16.76** | **< 0.001** |
| Total | 42 | | | 42 | | | 41 | | | 37 | | |

Table 3.4. Comparison of regression models examining the relationship between distance and synchrony when distance is estimated as either the thalweg length between points ($L_{i,j}$), the surface area of the water between two points ($A_{i,j}$) , or the volume of water between two points ($V_{i,j}$). Correlation coefficients of the dependent variables were transformed according to equation (5) or (6) prior to analysis. Distance measures were square-root transformed. Models were evaluated according to whether or not they met the assumptions of regression analysis and the amount of variability explained as estimated by the *Adj-*$R^2$. For each variable, at least one model fit the assumptions well. The preferred model for each variable is shown in bold.

| Model: *Solute* | $r_{i,j} = \beta_0 + \beta_L*(L_{i,j})^{1/2}$ | | | | |
|---|---|---|---|---|---|
| | $b_o$ | $b_L$ | $F$ | $p$ | *Adj-*$R^2$ |
| Temperature | **87.15** | **-0.142** | **109.9** | **< 0.001** | **0.410** |
| Conductivity | 92.40 | -0.381 | 129.5 | < 0.001 | 0.450 |
| $Cl^-$ | 94.02 | -0.529 | 133.9 | < 0.001 * | 0.460 |
| $NO_3^-$ | 96.68 | -0.796 | 145.8 | < 0.001 * | 0.480 |
| $NH_4^+$ | 80.32 | -0.479 | 137.6 | < 0.001 ** | 0.470 |
| DOC | 91.22 | -0.548 | 95.7 | < 0.001 | 0.380 |
| SRP | 91.53 | -0.513 | 154.2 | < 0.001 | 0.500 |
| pH | 78.69 | -0.376 | 77.3 | < 0.001 | 0.330 |
| DO | **72.56** | **-0.310** | **34.7** | **< 0.001** | **0.180** |

* Residuals slightly non-normal ( 0.03 < $P < 0.05$; *K-S test).*

** Residuals highly non-normal ( $P < 0.001$; *K-S test).*

Table 3.4 (Cont.).

| Model: *Solute* | $r_{i,j} = \beta_0 + \beta_A*(A_{i,j})^{1/2}$ | | | | |
|---|---|---|---|---|---|
| | $b_o$ | $b_A$ | $F$ | $p$ | $Adj\text{-}R^2$ |
| Temperature | 86.22 | -0.736 | 86.4 | < 0.001 | 0.360 |
| Conductivity | 92.94 | -2.728 | 468.8 | < 0.001 | 0.750 |
| $Cl^-$ | **94.24** | **-3.650** | **383.3** | **< 0.001** | **0.710** |
| $NO_3^-$ | 97.01 | -5.499 | 453.7 | < 0.001 | 0.740 |
| $NH_4^+$ | **79.21** | **-2.990** | **220.8** | **< 0.001** | **0.590** |
| DOC | 92.39 | -4.019 | 301.9 | < 0.001 | 0.660 |
| SRP | 91.05 | -3.371 | 351.3 | < 0.001 | 0.690 |
| pH | **78.20** | **-2.436** | **126.5** | **< 0.001** | **0.450** |
| DO | 70.83 | -1.688 | 32.5 | < 0.001 | 0.170 |

| Model: | $r_{i,j} = \beta_0 + \beta_V*(V_{i,j})^{1/2}$ | | | | |
|---|---|---|---|---|---|
| Solute | $b_o$ | $b_V$ | $F$ | $p$ | $Adj\text{-}R^2$ |
| Temperature | 84.91 | -1.332 | 47.8 | < 0.001 | 0.230 |
| Conductivity | **90.21** | **-6.606** | **1281.0** | **< 0.001** | **0.890** |
| $Cl^-$ | 90.56 | -8.822 | 823.5 | < 0.001 * | 0.840 |
| $NO_3^-$ | **91.28** | **-13.134** | **952.6** | **< 0.001** | **0.860** |
| $NH_4^+$ | 75.31 | -6.526 | 200.8 | < 0.001 | 0.560 |
| DOC | **88.69** | **-9.986** | **737.5** | **< 0.001** | **0.820** |
| SRP | **87.39** | **-7.941** | **543.6** | **< 0.001** | **0.780** |
| pH | 74.95 | -5.261 | 113.3 | < 0.001 | 0.420 |
| DO | 67.41 | -2.725 | 15.5 | < 0.001 | 0.080 |

* Residuals slightly non-normal ( 0.03 < *p < 0.05; K-S test).*

** Residuals highly non-normal ( *p < 0.001; K-S test).*

Table 3.5. Number of pairs of points with significant (p<0.05) correlations for each variable as a function of the portion of the reach spanned by the pair as well as the subset of the data set that was used to calculate the correlations. For reference, the total number of pairs in each reach (out of 153) is indicated. For each solute and each data set, chi-square tests were used to evaluate the null hypothesis that the number of significant correlations was proportional to the number of pairs in that reach. In the two cases for which the null was rejected ($p < 0.05$), the chi-square test was subdivided and each reach was evaluated to determine whether the discrepancy of the specific reach from its expected was significant.

| Data Set | Reach | Pairs in Reach | Temp | Cond | Cl | $NO_3^-$ | $NH_4^+$ | DOC | SRP | pH | DO |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | ABOVE | *91* | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 90 | 82 |
| ALL DATES | SPAN | *56* | 56 | 56 | 56 | 42 | 53 | 55 | 56 | 54 | 51 |
| | BELOW | *6* | 6 | 6 | 6 | 5 | 6 | 6 | 6 | 6 | 6 |
| | ABOVE | *91* | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 89 |
| WELL OFF | SPAN | *56* | 56 | 56 | 56 | 42 | 48 | 50 | 56 | 51 | 56 |
| | BELOW | *6* | 6 | 6 | 6 | 4 | 5 | 5 | 6 | 6 | 6 |
| | ABOVE | *91* | 88 | 91 | 91 | 72 * | 73 | 91 | 91 * | 55 | 40 |
| WELL ON | SPAN | *56* | 52 | 53 | 56 | 0 * | 34 | 42 | 2 * | 29 | 17 |
| | BELOW | *6* | 6 | 5 | 6 | 5 | 6 | 5 | 6 | 4 | 4 |

* Indicates P < 0.001.

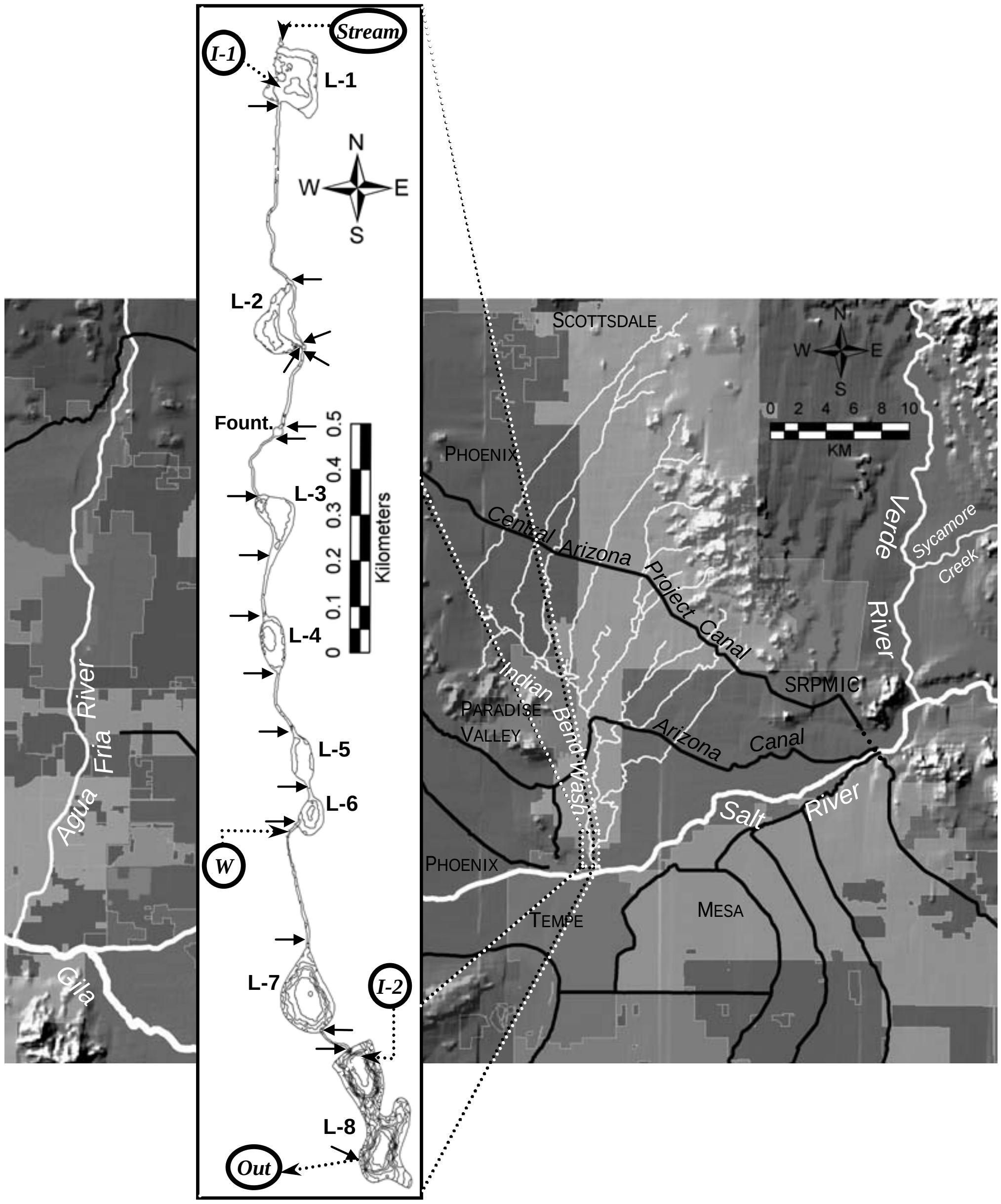


Figure 3.1. Map of Central-Arizona Phoenix ecosystem including modern arterial canals (black lines), major rivers (white lines), and main channels of the IBW watershed (thin white lines). Different municipalities are indicated by shades of gray, and occasionally labeled. Detail of study reach, including eight lakes (L-1 to L-8) and connecting streams (inset). Bathymetry is indicated by 0.5 m contour lines. A mix of surface water and groundwater originating from the Arizona canal enters the reach via stream above L-1 and exits via a drain in L-8. Additional canal water is delivered to L-1 through a subsurface pipe (*I-1*). The Roosevelt well (*W*), intermittently delivers groundwater the stream between L-6 and L-7. L-8 also receives a direct subsurface water input (*I-2*). Solid arrows indicate the location of sampling locations along the wash.

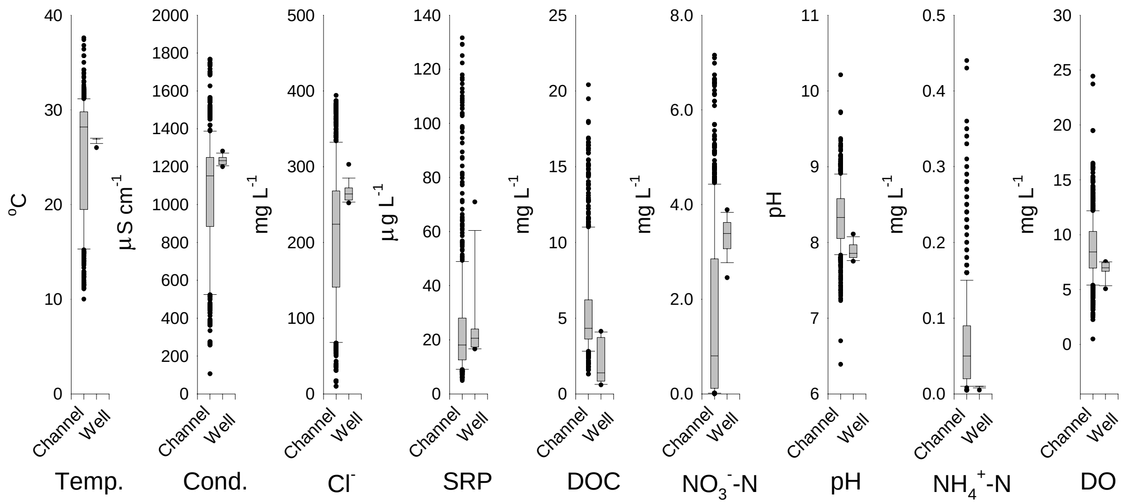


Figure 3.2. Box plots of chemical and physical variables across all sampling dates for the 18 channel sites vs. the Roosevelt well input. The lower boundary of the box is the 25th percentile, the upper boundary is the 75th percentile, and the horizontal line in the box is the median. Whiskers above and below the box indicate the 90th and 10th percentiles, respectively. Values beyond the whiskers are plotted.

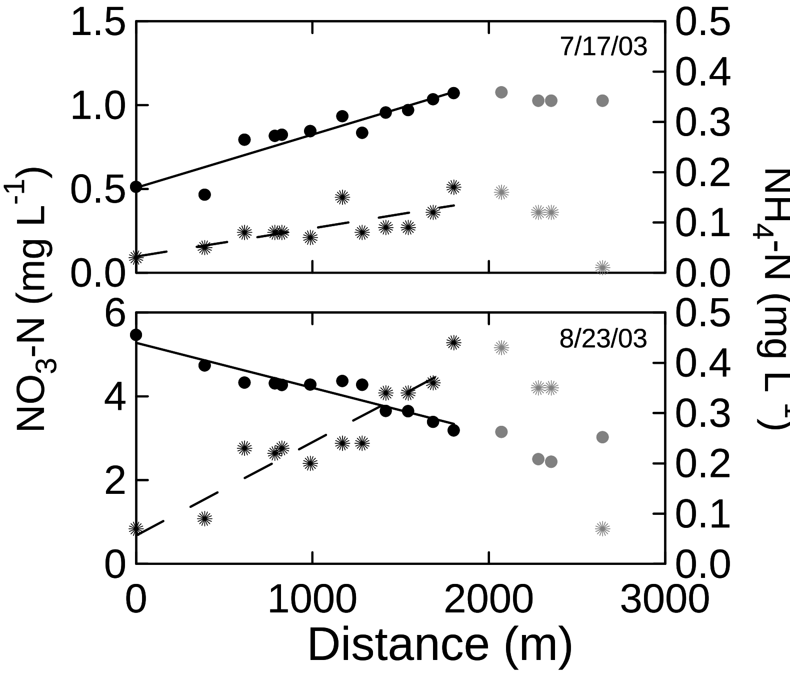


Figure 3.3. Variation in $NO_3^-$-N and $NH_4^+$-N as a function of the distance downstream of the outlet of lake H on two representative dates. Solid circles indicate $NO_3^-$-N values and stars indicate $NH_4^+$-N values. Black symbols indicate the sample point lay above the Roosevelt well and gray symbols indicate points below the well. Note the difference in scales for $NO_3^-$-N. The lines represent linear fits of nutrient concentration versus distance for the reach between the outlet of L-1 and the outlet of L-6. Note that $NO_3^-$ increased on July 17 whereas it decreased on August 23. Although $NH_4^+$ increased on both dates, it increased more slowly on the earlier date. Because flows diverge at the top of lake L-2, and flow through either the bypass channel or the lake, the samples collected from the outlet of lake L-2 and the bottom L-2 Bypass were not plotted. Instead, the sample collected from just below the confluence of these two reaches is plotted.

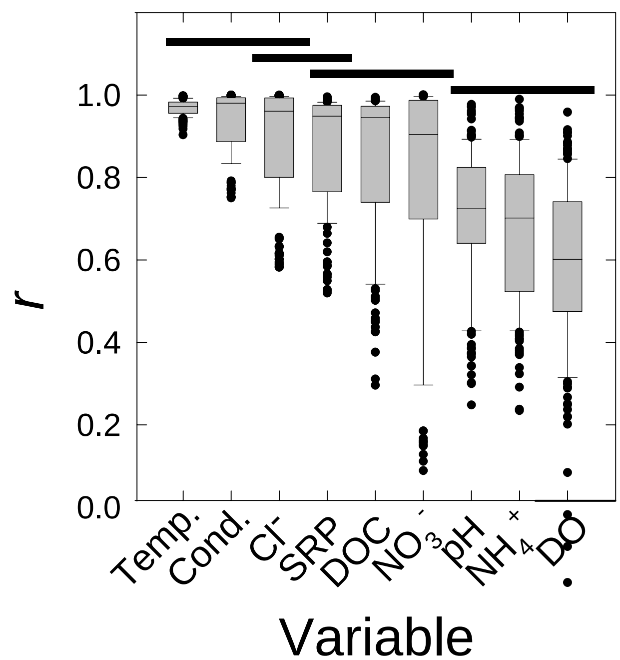


Figure 3.4. Box plots of the correlation coefficients of all pairs ($n$ = 153) for each of the nine variables. Thick lines at the top of the graph group variables not significantly different according to a Kruskal-Wallis test ($p < 0.05$). Box and whiskers as in Fig. 2.

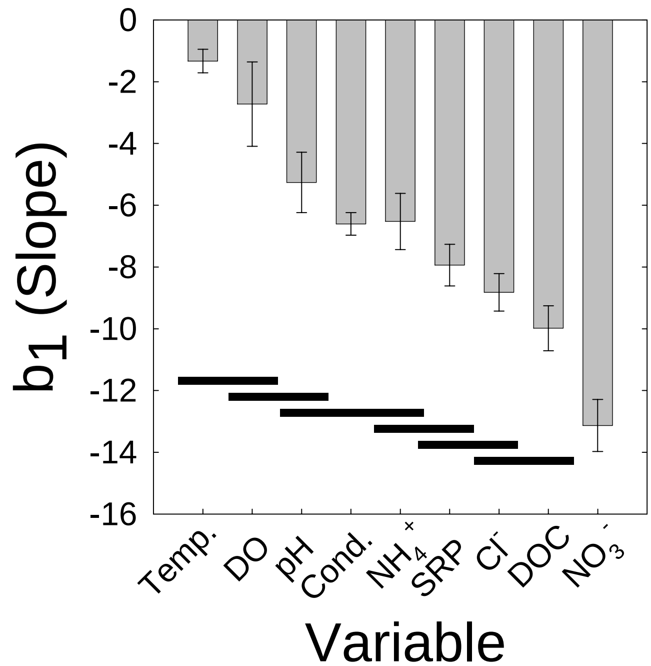


Figure 3.5. Plot regression coefficients estimated by fitting the model: $r_{i,j} = b_0 + b_1*(V_{i,j})^{1/2}$ for each solute. Error bars represent the 95 percent confidence interval. Thick lines at the bottom of the graph group variables with slopes that are not significantly different according to a Tukey test ($p < 0.05$).

# 4. ANTHROPOGENIC AND CLIMATIC DRIVERS INTERACT TO DETERMINE NUTRIENT LIMITATION ALONG AN URBAN LAKE CHAIN


## ABSTRACT

Indian Bend Wash, an urban desert stream, runs through historically agricultural lands in the lower portion of its watershed. A series of artificial lakes was constructed in the low-flow channel of the wash as part of a flood-control project. Lake water levels are maintained with a mix of canal and groundwater, which differ dramatically in their $NO_3^-$ content. Although $NO_3^-$ concentration in the canal reflects the low N content of the surrounding surface streams, groundwater has been substantially enriched in $NO_3^-$ as a result of prior agricultural practices. This legacy affects nutrient dynamics of the wash. $NO_3^-$ concentrations in lakes were best explained by groundwater pumping rates while SRP concentrations were more closely tied to the timing and magnitude of flash floods. On thirteen dates during 2003, we used bioassays to evaluate nutrient limitation in eight urban lakes in Scottsdale, AZ. During the summer, when groundwater-pumping rates were high, $NO_3^-$ was abundantly available and phytoplankton growth was strongly P limited. Although the system flooded repeatedly, floods did not dilute N concentration to the point where N became limiting. In November, however, groundwater contributions were reduced and $NO_3^-$ fell, producing secondary N limitation in two lakes and co-limitation in a third. This change in management placed the system on a tipping point that enabled the next flood to produce a switch from P to N limitation in three of the smaller

lakes while alleviating macronutrient limitation in three others. Water chemistry data from the previous year suggest that shifts between P and N limitation may be relatively common. These results highlight how management choices to meet urban water demand can unintentionally affect an ecosystem process like primary production.

## INTRODUCTION

Although Tansley (1935) argued for studies of anthropogenic ecosystems 70 years ago, American ecologists have only relatively begun to focus their research on urban ecosystems (Grove and Burch 1997, Pickett et al. 1997, Collins et al. 2000, Grimm et al. 2000, Grimm and Redman 2004). This shift was produced, in part, by the recognition of the pervasive effects of humans (Vitousek 1994, Chapin et al. 1997, Gallagher and Carpenter 1997, Vitousek et al. 1997a) and concerns about the ability of human-dominated ecosystems to continue to deliver ecosystem services (Costanza et al. 1997, Bolund and Hunhammar 1999). Particularly marked has been human appropriation of primary production (Vitousek et al. 1986) and renewable fresh water (Postel et al. 1996) and alteration of the global nitrogen cycle (Vitousek et al. 1997b). Population growth following the industrial revolution was accompanied by rapid increases in cultivated acreage (Matson et al. 1997) and in urbanization (UN, 1997).

Agricultural expansion required extensive infrastructural support. In particular, farmers increasingly relied on irrigation canals and artificial fertilizers to grow their crops (Postel et al. 1996). Globally, humans have appropriated more than half of the fresh water runoff that is reasonably accessible (Vitousek et al. 1997a), bringing 237 x $10^6$ hectares under irrigation worldwide, 19.6 x $10^6$ ha in North America alone (Naylor 1996). By impounding rivers and diverting their flows into irrigation systems, humans alter the spatial and temporal availability of water on both local and regional scales (Strange et al. 1999). Modern agriculture also relies on synthetic N and mined P to sustain yields (Matson et al. 1997, Schlesinger 1997). Fertilizer application and its subsequent mobilization from agricultural fields has greatly increased concentration of these nutrients in surface water (Howarth et al. 1996, Burkart and Stoner 2002), resulting in eutrophication downstream (Carpenter et al. 1998). For example, export of N from Midwestern agricultural catchments has been linked to intermittent zones of hypoxia in the Gulf of Mexico (Alexander et al. 2000). Likewise, excess phosphorus has led to the eutrophication of many lake ecosystems (Vollenweider 1968, Schindler et al. 1971, Bennett et al. 1999). Additionally, because of its high solubility $NO_3^-$ is readily transported from agricultural fields to aquifers (Hamilton and Helsel 1995, Casey et al. 2002) and groundwater $NO_3^-$-N concentration often exceeds the USEPA's maximum contaminant level of 10 mg $L^{-1}$ (Power and Schepers 1989, Spalding and Exner 1993, Nolan and Stoner 2000, Mitchell et al. 2003). In Wisconsin as much as 120 - 203 kg $NO_3^-$-N $ha^{-1}$ $y^{-1}$, representing nearly 70% of fertilizer N, leaches into shallow groundwater (Stites and Kraft 2001).

Nutrient loading to streams from urban land uses is similarly problematic. Meyer et al. (2005) coined the term 'urban stream syndrome' to refer to the characteristic changes in streams produced by urbanization, including elevated nutrient loads from point and non-point sources. Wastewater treatment plants, for example, can be an important point sources of N to urban streams (Martí et al. 2004, Haggard et al. 2005) while increased nutrient loading has been correlated with changes in imperviousness (Walsh et al. 2005). For example, dissolved organic carbon, soluble reactive phosphorus (SRP), total phosphorus (TP) and ammonium ($NH_4^+$) concentrations in small streams of Melbourne, Australia all increased with increasing watershed imperviousness (Hatt et al. 2004). In addition, because urban expansion often occurs through the conversion of agricultural lands to residential uses (Vesterby and Heimlich 1991, Reynolds 1993, Riebsame et al. 1996), urban ecosystems may have to deal with the legacies of past agriculture, including increased groundwater (Baresel and Destouni 2005) and soil (Compton and Boone 2000) nutrient concentrations.

Urbanization and agricultural legacies can alleviate historic N or P limitation in lakes and streams. For example, in urban Lake Mendota, Wisconsin, USA, external stream nutrient loading (Lathrop 1992), internal nutrient loading from sediments (Soranno et al. 1996), and internal regeneration through the food web all contribute to elevated P concentration that drives cultural eutrophication, complicating restoration efforts (Reed-Andersen et al. 2000). Management decisions can also affect nutrient status, even producing changes in the limiting nutrient. For example, Elser and Kimmel (1985) demonstrated that P limitation declined along a reservoir series due to discharge of nutrient-rich hypolimnetic waters from upstream impoundments.

This study examines how anthropogenic hydrologic alterations of an urban Sonoran Desert stream in a previously agricultural watershed affect (1) concentration of N and P and (2) spatial and temporal patterns of potential nutrient limitation along the stream. We show that the limiting nutrient changes over time and space, and attempt to establish which mechanism (management decisions or natural hydrologic variation) best explains these shifts.

## STUDY SITE

Indian Bend Wash (IBW) is a tributary of the Salt River that historically drained approximately 520 $km^2$ of desert, agricultural, and suburban lands, predominantly in Scottsdale, AZ. Water from the Arizona canal (Fig. 4.1) helped farmers bring nearly the entire lower 48 $km^2$ of the watershed under cultivation. As late as 1949 the entire southern portion of the watershed remained in agriculture. However, by 2003, urban expansion had converted all but ~20% of this cropland to urban uses (Chapter 2).

Numerous shallow lakes were constructed along a greenbelt in the lower portion of the watershed as part of a flood-control project (City of Scottsdale 1985). Between floods, lake levels are maintained with water delivered from an extensive series of lateral canals that originate with the Arizona canal (Fig. 4.1). The Arizona canal typically contains a mix of water from the Salt, Verde and, via the Central Arizona Project canal, Colorado rivers. During periods of peak demand, groundwater wells supplement flows in the Arizona canal, its laterals and, occasionally, IBW. This research focused on a string of eight lakes (L-1 through L-8; Fig. 4.1, inset) that differ in their morphometry (Table 4.1) and position relative to the major water inputs (Fig. 4.1).

## METHODS

### *Field sampling and laboratory analysis*

Lake nutrient concentrations were determined directly via complete surveys on 23 dates in 2002 and 19 dates in 2003; monthly during winter and more frequently in summer, with survey frequency increasing directly after flood events. Samples were collected from the outlet of each lake and, when it was pumping, from the Roosevelt well (Fig.2). Reduced surveys, during which samples were collected from a subset of sampling locations, were conducted during 6 mid-sized floods. On each sampling date, water temperature was measured in the field with either a YSI Model 85 or Model 95 DO Meter.

Triplicate samples were collected into new polyethylene centrifuge tubes and stored at 4 $^{o}$C until processed at the Goldwater Environmental Laboratory (GEL) of Arizona State University. All solute concentrations are reported as the mean of these triplicates. Within 72 h of collection, all three water-chemistry samples were analyzed colorimetrically on a Lachat QC8000 autoanalyzer for nitrite + nitrate (hereafter $NO_3^-$, ammonium ($NH_4^+$), soluble reactive phosphorus (SRP), and chloride ($Cl^-$). Prior to analyses, water was centrifuged at $10^4$ RPM for 10 minutes, which removes particles as effectively as a 0.45-μm membrane filter (Thomas Colella, GEL Director, *unpublished data*) without risking $NH_3$ volatilization (*personal observation*). Colorimetric methods for quantification were the phenol-hypochlorite method for $NH_4^+$ (Solorzano 1969), the cadmium-copper reduction method for $NO_3^-$ (Wood et al. 1967), the ascorbic acid reduction method for SRP (Henriksen 1966), and the mercuric thiocyanate method for $Cl^-$

(Zall et al. 1956). SRP was chosen to indicate P availability based on analysis of both SRP and total dissolved phosphorus (TDP) in samples from four different dates. Linear regression analysis indicated that the TDP pool was predominately SRP, with a slope approximately equal to 1 and an intercept not significantly different than zero ($F$ = 525; $df$ = 1,49; $P < 0.001$; $R^2 = 0.91$; $b_1 = 0.95$; $b_0$ = N.S.). On four dates in 2002, laboratory difficulties necessitated that samples be centrifuged, decanted and frozen prior to analysis for $NH_4^+$, $NO_3^-$, SRP, and $Cl^-$.

Discharge data for floods were obtained from a stream gauge maintained by the Flood Control District of Maricopa County, located approximately 400 m south of L-8 and from a USGS gauge approximately 1400 m further south (Fig.1). Water-chemistry data and monthly pumping totals for groundwater wells contributing water to the wash were taken from the Salt River Project's annual water quality reports (Sullivan 1996, 1998) and from reports prepared for the USEPA as part of a Superfund remediation project (NIBWPC 2002, NIBWPC 2003). Additional water chemistry data on the Arizona Canal and groundwater wells were provided directly by the Salt River Project.

### *Nutrient bioassays*

Nutrient addition, dilution bioassays were used to assess the potential for phytoplankton growth limitation by N and/or P. Briefly, these bioassays assess limitation by determining which nutrient or combination of nutrients stimulates phytoplankton growth. Unfiltered samples are diluted with filtered lake water to reduce effects of crowding and to minimizing consumption by microconsumer grazers, thereby improving the estimates of phytoplankton growth rates (Sommer 1989, Sterner and Grover 1998). To characterize how changes in chemical characteristics of water affected temporal and spatial variation in potential nutrient limitation, we conducted assays on samples collected 13 times between May 30 and December 3, 2003. Two liters of lake water were collected from the outlet of each lake and immediately returned to the lab, where incubations were initiated within 8 h. Experimental vials (acid-washed, clear 250-mL vials) were filled with ~130 mL lake water filtered through a Whatman GF/F glass fiber filter and inoculated with 20 ml unfiltered water. Experimental enrichment concentrations were approximately 500 μM $NO_3^-$ and/or 32 μM $PO_4^{3-}$ in a fully factorial set of treatments, except on May 30, when the 500 μM N was added as equal parts $NH_4^+$ and $NO_3^-$. Concentrations were chosen to reflect the frequently high nutrient concentrations observed in the lakes. Each treatment was executed in triplicate. After enrichment, vials were covered with petri dishes and incubated for 3 d in a growth chamber at light (PAR 120 - 150 μmol $s^{-1}$ $m^{-2}$) and temperature regimes that mimicked in situ conditions (14:10 light:dark and 27 $^oC$ for samples from May-Aug; 10.5: 13.5 light:dark and 25 $^oC$ for samples from Nov-Dec).

Bulbs located in the door supplied light within the chamber. As a result, irradiance experienced by the vials varied with distance from the door. Samples were staggered to limit shading and arrayed in random order (to avoid compounding effects of light and nutrient treatment) in three rows parallel to the door. Growth was assessed as change in *in vivo* fluorescence and measured on a Turner Design TD700 fluorometer, calibrated to a solid-state standard.

*Data analysis*

Linear regression analysis was used to assess the associations of various water sources (wells and floods) with variation in SRP and $NO_3^-$ concentrations entering the study reach. Where needed, data were transformed to ensure that assumptions of parametric analyses were met.

Phytoplankton growth was quantified by calculating exponential growth rate ($r$) in each vial:

$$r = (\ln(N_t/N_0))/t$$

where $N_t$ is the in-vivo fluorescence at the end of the incubation, $N_0$ is the initial in-vivo fluorescence, and $t$ is incubation duration. The resulting estimates of $r$ were analyzed using a general linear model:

$$r = b_0 + \text{Row} + \text{N} + \text{P} + \text{N*P})$$

where nutrient treatments (N and P) were considered fixed factors and Row was a blocking variable indicating the distance of the incubation bottles from the light source. Comparisons of cell means were made using Bonferroni tests. A hierarchal series of decision rules modified from Maberly et al. (2002) was used to distinguish between different types of nutrient limitation (Table 4.2). Statistical analyses were performed using SYSTAT (version 10, SPSS Inc., 2000).

## RESULTS

### *Nutrient influx*

SRP concentrations varied more than 15-fold over the course of the study (Table 4.2). This variation was driven largely by hydrologic regime: floodwaters delivered SRP, with SRP concentration increasing with size of flood (Fig. 4.2A) and decreasing with time since last flood (Fig. 4.2B). Together these two factors combined to explain just over 58% of the variation in SRP concentration (Table 4.3). Inorganic N concentrations were even more variable, although most of this variation was due to $NO_3^-$, which was much more variable than $NH_4^+$ (Table 4.3). Like SRP, $NH_4^+$ concentration was linked to floods (Table 4.4), with time since flood explaining 48% of the variation. Conversely, $NO_3^-$ did not vary with hydrologic variation, but was better explained by well pumping. Consistently low surface-inflow concentrations from the Arizona Canal (11.4 ± 4.5 µM; mean ± 1 SE of monthly samples collected by Salt River Project February, 2002 though December, 2003) did not explain variation in $NO_3^-$ concentration; rather, concentration was linked to well inputs. The monthly discharge of just one of groundwater well, COS 6, explained over 62% of the observed variation in $NO_3^-$ (Fig. 4.3; Table 4.4). These variations in water chemistry produced large changes in the dissolved N:P ratio of water flowing through IBW. In particular, lakes L-1 through L-6 displayed a high degree of temporal variation in their N:P ratio over the course of the study (Fig. 4.4). Conversely, the N:P ratio of L-8, and to a lesser degree L-7, did not vary as much (Fig. 4.4).

*Nutrient limitation*

Nutrient addition bioassays indicated that nutrient limitation of phytoplankton was spatially and temporally variable. Phytoplankton were P limited (e.g., Fig. 4.5A) during most of the summer. Between May 30 and August 28, the only exceptions were two cases of secondary N limitation observed on July 17 in L-1 and L-2. Changes in the concentration of N and P caused predictable changes in nutrient limitation towards the end of 2003 (Fig. 4.6). Between Aug 28 and Nov 5, the concentration of $NO_3^-$ and SRP in the wash declined in all lakes except lake L-8, and secondary N limitation was observed in 3 of the lakes. A moderate flood (24 h mean discharge = 57 $m^3$ $m^{-1}$) on November 13, was associated with elevated SRP concentrations, whereas dissolved inorganic N (DIN = $NH_4^+$ + $NO_3^-$) concentration remained relatively low. Bioassays conducted on samples from November 14 indicated that phytoplankton growth in L-2, L-4 and L-7 did not appear to be nutrient limited while lakes L-5, L-3, and L-1 were potentially N limited (e.g., Fig.5B). As time since flood increased, SRP concentrations in the incoming water declined. On November 21, the northern three lakes were either P limited, with two of them exhibiting secondary N limitation (i.e., P stimulated growth but response to combined addition of N and P was greater than P alone), while southern L-3 to L-7 were all co-limited (i.e., only combined addition of N and P stimulated growth). By December 3, the majority of the lakes were P limited with lake H exhibiting secondary N limitation. Only L-7, the largest of the lakes affected by the Nov 14th flood, was still exhibiting co-limitation (Fig. 4.6).

# DISCUSSION

## *Controls of nutrient availability*

Our data show clearly that concentrations of $NH_4^+$, $NO_3^-$ and SRP varied in both space and time, but drivers of that variation differed depending upon the nutrient in question. Floods explained much of the variation in both $NH_4^+$ and SRP, though the mechanisms were likely different. SRP increased directly after floods and in proportion to the size of the flood, suggesting that floodwaters were washing SRP that had accumulated in the surrounding watershed into the stream and that larger floods were able to mobilize more SRP. This is consistent with previous research in Sycamore Creek, a typical Sonoran desert stream, where floodwaters tended to increase the concentration of both $NO_3^-$ and SRP (Fisher et al. 1982) as well with urban streams in Melbourne, Australia (Hatt et al. 2004). In Sycamore Creek, P is derived from weathering of P-rich volcanic rocks (Grimm and Fisher 1986a). Indeed the source of SRP in runoff from parking lots in the CAP ecosystem has been hypothesized to be soil-derived dust from the surrounding desert (Hope et al. 2004). Geologic sources may also be important in IBW, but application of P-rich fertilizers to parks and golf courses is an additional potential source of P. Declining SRP concentrations following floods resulted from physical adsorption or biotic uptake of the nutrient and/or dilution floodwaters with canal water. Our data cannot discriminate between these two possibilities.

Even though $NH_4^+$ concentration declined with time since flood, like that of SRP, concentration was not affected by flood magnitude. We hypothesize that floodwaters are not a direct source of $NH_4^+$, but instead deliver water that either is poorly oxygenated or has a high biological oxygen demand (BOD), conditions that favor N mineralization but not nitrification (hence, accumulation of $NH_4^+$). In support of this hypothesis, we observed of declines in dissolved oxygen concentrations following floods (*data not shown*).

Floods did not increase concentration of $NO_3^-$ in IBW. Instead, $NO_3^-$ concentrations was a function of the groundwater contributed by COS 6. This is not surprising given the relatively low and constant $NO_3^-$ concentration in water entering the Arizona canal and the high nitrate concentration of wells, especially COS 6. Previous work on another canal in the Central-Arizona Phoenix ecosystem has shown that $NO_3^-$ concentration increased steadily as the number of groundwater wells contributing to the canal's discharge increased (Chapter 2). Lack of variation in the N:P ratio in L-8 is likely driven largely by a lack of variation in $NO_3^-$, which remained relatively high and constant, presumably because of substantial subsurface inputs, and by the lake's large size, which buffers its chemistry from short-term variation in inputs. When it was pumping, the Roosevelt well also increased the concentration of $NO_3^-$ and thus the N:P of L-6.

$NO_3^-$ leaching from agricultural systems has led directly to contaminated groundwater (Power and Schepers 1989, Spalding and Exner 1993) and surface waters (Howarth et al. 1996, Jordan et al. 1997), though riparian zones can ameliorate these effects (Peterjohn and Correll 1984). Although $NO_3^-$-contaminated groundwater has been recognized as a potential source of N for irrigated crops (Schepers and Mielke 1983), the effects of groundwater pumping on N cycling in streams remains largely unexplored.

Perhaps intentionally pumping groundwater into surface waters represents a relatively new phenomenon, resulting from the expansion of the urban fringe into cultivated lands and the appropriation of agricultural irrigation systems for urban uses. Now, instead of irrigating crops, the water is used to supply drinking water, irrigate parks, and maintain artificial lakes and streams. However, because newly urban groundwater wells tap aquifers that bear the legacy of past fertilization practices, using these waters to augment surface flows may result in the unintentional fertilization of the recipient ecosystem. This research demonstrates that these N inputs can be substantial and may strongly affect ecosystem function.

### *Nutrient limitation*

Our experiments demonstrate that nutrient limitation of phytoplankton varied depending upon the relative concentration of N and P in the lakes of IBW. During most of 2003, $NO_3^-$ concentration was high with atomic N:P ratio well in excess of 31:1—an empirically derived threshold for the switch between N and P limitation (Downing and McCauley 1992)—and growth was stimulated by P additions. N limitation was observed only when the combination of low groundwater and high floodwater inputs drove N:P towards and below 31:1 (Fig 4.4). Although these conditions were met only briefly during 2003 when the bioassays were conducted, the frequency with which atomic N:P ratio dropped below 31:1 in 2002 suggests that shifts in nutrient limitation may be a relatively common phenomenon. In fact, a survey of the atomic N:P ratio of 202 storm runoff events in several urban catchments of the Central-Arizona Ecosystem revealed that nearly half were below the Redfield ratio of 16:1 (Grimm et al. 2004).

Nutrient-addition bioassays have previously been used to show temporal and spatial variation in nutrient limitation in lakes (Morris and Lewis Jr. 1988, Goldman et al. 1993, Elser et al. 1995, Levine and Whalen 2001, Maberly et al. 2002). Nevertheless, they are not without their limitations (see Carrick et al. 1993). Perhaps most importantly for this experiment, they are unable to account for other potentially limiting factors, specifically light. Light can limit actual rates of photosynthesis in lakes even when nutrient limitation is indicated by a bioassay. In highly productive lakes like those of IBW, self-shading may limit phytoplankton growth before nutrient concentration does. Nevertheless, with proper statistical replication, bioassays can provide useful information about spatial and temporal variability in what is likely to be limiting (Elser et al. 1990). Because bioassays are conducted on grab samples they provide an estimate of the nutrient status of a lake at a specific point in time (but see Elser and Kimmel 1986). This is critical when shifts in water chemistry are abrupt, as is the case when a turn of a spigot or a flash flood can alter relative nutrient availability. This temporal variability may explain why previous research in IBW failed to demonstrate such dynamic responses. In this previous experiment nutrient-diffusing substrates, which provide a time-integrated measure of relative nutrient concentration (Fairchild et al. 1985), indicated P limitation in the summer only, when groundwater contributions are expected to be high, and no limitation during the rest of the year (A. Goettl and N. Grimm, *in preparation*).

The concentrations of N and P exert strong control on ecosystem function. Changes in nutrient concentration can influence a wide range of ecosystem processes including primary production (Schindler 1977a, Grimm and Fisher 1986a), decomposition (Elwood et al. 1981), denitrification (Groffman 1994), and nutrient retention (Peterson et al. 2001, Pregitzer et al. 2004). Cultural eutrophication, the frequent result of large additions of limiting nutrients, is often characterized by nuisance algal blooms and anoxia (Smith 1998) and may be accompanied by changes in species composition. For example, in P-limited systems, additions of P may drive the ecosystem towards N limitation, providing a competitive advantage to N-fixing cyanobacteria (Schindler 1977b, Howarth and Cole 1999). Myriad effects of altered biogeochemical cycles on ecosystem function necessitate a better understanding of how urbanization affects cycling of N and P (Kaye et al. in press).

Management decisions and hydrologic processes interact to determine nutrient concentration and potential nutrient limitation in this urban desert stream. Because there are multiple irrigation inputs to the lakes, changes in nutrient status do not always occur synchronously, but vary spatially along the wash. However, the hydrologic regime of IBW remains an important driver of water chemistry. As with non-urban desert streams, floods affected nutrient concentrations in IBW, but unlike more typical desert streams, which tend to be N limited (Grimm and Fisher 1986a, Grimm and Fisher 1986b), IBW is now characterized by long periods of P limitation punctuated by short-term shifts to co-limitation or N limitation.

These results argue for careful evaluation of the consequences of redistributing water and relying on groundwater to supplement surface flows. Because groundwater residence times can be very long, the legacies of previous management practices (e.g., fertilizer use) may persist in groundwater for decades and produce ecological surprises when water is returned to the surface. Explicit consideration of these legacies creates an additional challenge for water managers attempting to ensure a stable supply of potable water, but may help limit the magnitude of the resulting ecological surprises and enhance the ability of resource managers responsible for recipient systems (e.g., lakes and streams) to maintain desired ecological conditions.

## ACKNOWLEDGEMENTS

We thank Marcia Kyle, John Schampel and Jim Elser for assistance with the bioassays; Gregg Elliott, Dennis Shirley, the Salt River Project and Errol L. Montgomery and Associates, Inc. for providing data on ground water pumping rates, well water chemistry and the configuration of the irrigation laterals; and Phil Tarrant, Tamara Harms, Libby Larson, Rich Sheibley, and Harriet Van Vleck for help in the lab and in the field.

## LITERATURE CITED

[NIBWPC], N. I. B. W. P. C. 2002. Site Monitoring Report North Indian Bend Wash Superfund Site. Prepared for: U.S.E.P.A. Region IX.

[NIBWPC], N. I. B. W. P. C. 2003. Site Monitoring Report North Indian Bend Wash Superfund Site. Prepared for: U.S.E.P.A. Region IX.

[UN], U. N. P. D. 1997. Urban and Rural Areas, 1950-2030 (the 1996 revision). United Nations, New York.

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**:758-761.

Baresel, C., and G. Destouni. 2005. Novel quantification of coupled natural and cross-sectoral water and nutrient/pollutant flows for environmental management. Environmental Science and Technology **39**:6182-6190.

Bennett, E. M., T. Reed-Andersen, J. N. Houser, J. R. Gabriel, and S. R. Carpenter. 1999. A phosphorus budget for the lake Mendota watershed. Ecosystems **2**:69-75.

Bolund, P., and S. Hunhammar. 1999. Ecosystem services in urban areas. Ecological Economics **29**:293-301.

Burkart, M., and J. D. Stoner. 2002. Nitrate in aquifers beneath agricultural systems. Water Science and Technology **45**:19-28.

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.

Carrick, H. J., C. L. Schelske, F. J. Aldridge, and M. F. Coveney. 1993. Assessment of phytoplankton nutrient limitation in productive waters: application of dilution bioassays. Canadian Journal of Fisheries and Aquatic Sciences **50**:2208-2221.

Casey, F. X. M., N. Derby, R. E. Knighton, D. D. Steele, and E. C. Stegman. 2002. Initiation of irrigation effects on temporal nitrate leaching. Vadose Zone Journal **1**:300-309.

Chapin, F. S., III., B. H. Walker, R. J. Hobbs, D. U. Hooper, J. H. Lawton, O. E. Sala, and D. Tilman. 1997. Biotic control over the functioning of ecosystems. Science **277**.

City of Scottsdale. 1985. Indian Bend Wash. Communications and Public Affairs, Scottsdale, AZ.

Collins, J. P., A. Kinzig, N. B. Grimm, W. F. Fagan, D. Hope, J. Wu, and E. T. Borer. 2000. A new urban ecology. American Scientist **88**:416-425.

Compton, J. E., and R. D. Boone. 2000. Long-term impacts of agriculture on soil carbon and nitrogen in New England forests. Ecology **81**:2314-2330.

Costanza, R., R. d'Arge, R. de Groot, S. Farber, M. Grasso, B. Hannon, K. Limburg, S. Naeem, R. O'Neill, J. Paruelo, R. Raskin, P. Sutton, and M. van den Belt. 1997. The value of the world's ecosystem services and natural capital. Nature **15**:253-260.

Downing, J. A., and E. McCauley. 1992. The nitrogen: phosphorus relationship in lakes. Limnology and Oceanography **37**:936-945.

Elser, J. J., and B. L. Kimmel. 1985. Nutrient availability for phytoplankton production in a multiple-impoundment series. Canadian Journal of Fisheries and Aquatic Sciences **42**:1359-1370.

Elser, J. J., and B. L. Kimmel. 1986. Alteration of phytoplankton phosphorus status during enrichment experiments -- implications for interpreting nutrient enrichment bioassay results. Hydrobiologia **133**:217-222.

Elser, J. J., F. S. Lubnow, E. R. Marzolf, M. Brett, G. Dion, and C. R. Goldman. 1995. Factors associated with interannual and intrannual variation in nutrient limitation of phytoplankton growth in Castle Lake, California. Canadian Journal of Fisheries and Aquatic Sciences **52**:93-104.

Elser, J. J., E. R. Marzolf, and C. R. Goldman. 1990. Phosphorus and nitrogen limitation of phytoplankton growth in the freshwaters of North America: a review and critique of experimental enrichments. Canadian Journal of Fisheries and Aquatic Sciences **47**:1468-1477.

Elwood, J. W., J. D. Newbold, A. F. Trimble, and R. Stark. 1981. The limiting role of phosphorus in a woodland stream ecosystem: effects of P enrichment on leaf decomposition and primary producers. Ecology **62**:146-158.

Fairchild, G. W., R. L. Lowe, and W. B. Richardson. 1985. Algal periphyton growth on nutrient-diffusing substrates: an in situ bioassay. Ecology **66**:465-472.

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.

Gallagher, R., and B. Carpenter. 1997. Human-dominated ecosystems. Science **277**:485.

Goldman, C. R., A. D. Jassby, and S. H. Hackley. 1993. Decadal, interannual, and seasonal variability in enrichment bioassays at Lake Tahoe, California. Canadian Journal of Fisheries and Aquatic Sciences **50**:1489-1496.

Grimm, N., R. Arrowsmith, C. Eisinger, J. Heffernan, D. B. Lewis, A. MacLeod, L. Preshad, W. J. Roach, T. Rychener, and R. W. Sheibley. 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. *in* G. Asner and R. Houghton, editors. Ecosystems and Land Use Change. American Geophysical Union.

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

Grimm, N. B., and S. G. Fisher. 1986b. Nitrogen limitation potential of Arizona streams and rivers. Journal of the Arizona-Nevada Academy of Science **21**:31-43.

Grimm, N. B., J. M. Grove, S. T. A. Pickett, and C. L. Redman. 2000. Integrated approaches to long-term studies of urban ecological systems. BioScience **50**:571-583.

Grimm, N. B., and C. L. Redman. 2004. Approaches to the study of urban ecosystems: the case of central Arizona-Phoenix. Urban Ecosystems **7**:199-213.

Groffman, P. M. 1994. Denitrification in freshwater wetlands. Current Topics in Wetland Biogeochemistry **1**:15-35.

Grove, J. M., and J. R. Burch, WR. 1997. A social ecology approach and applications of urban ecosystem and landscape analyses: a case study of Baltimore, Maryland. Urban Ecosystems **1**:259-275.

Haggard, B. E., E. H. Stanley, and D. E. Storm. 2005. Nutrient retention in a point-source-enriched stream. Journal of the North American Benthological Society **24**:29-47.

Hamilton, P. A., and D. R. Helsel. 1995. Effects of agriculture on ground-water quality in five regions of the United States. Groundwater **33**:217-226.

Hatt, B. E., T. D. Fletcher, C. J. Walsh, and S. L. Taylor. 2004. The influence of urban density and drainage infrastructure on concentrations and loads of pollutants in small streams.

Henriksen, A. 1966. An automatic method for determining orthophosphate in sewage and highly polluted waters. Analyst **91**:652.

Hope, D., A. H. Chan, N. W. Naegeli, and N. B. Grimm. 2004. Nutrients on asphalt parking surfaces in an arid urban environment. Water Air and Soil Pollution: Focus **4**:371-390.

Howarth, R., B. G, D. Swaney, A. Townsend, N. Jaworski, K. Lajtha, J. A. Downing, R. Elmgren, N. F. Caraco, T. Jordan, F. Brerendse, J. R. Freney, V. Kudeyarov, P. Murdoch, and Z. L. Zhu. 1996. Regional nitrogen budgets and riverine N&P fluxes for the drainages to the North Atlantic Ocean: natural and human influences. Biogeochemistry **35**:75-139.

Howarth, R. W., and J. J. Cole. 1999. Do top-down and bottom-up controls interact to exclude nitrogen-fixing cyanobacteria from plankton of estuaries? An exploration with a simulation model. Biogeochemistry **46**:203-231.

Jordan, T. E., D. L. Correll, and D. E. Weller. 1997. Effects of agriculture on discharge from coastal plain watersheds on Chesapeake Bay. Journal of Environmental Quality **26**:836-848.

Kaye, J., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. in press. A distinct urban biogeochemistry? Trends in Ecology and Evolution.

Lathrop, R. C. 1992. Nutrient loadings, lake nutrients and water clarity. Pages 17-30 *in* J. F. Kitchell, editor. Food Web Management: a Case Study of Lake Mendota, Wisconsin. Springer-Verlag, New York.

Levine, M., and S. Whalen. 2001. Nutrient limitation of phytoplankton production in Alaskan Artic foothill lakes. Hydrobiologia **455**:189-201.

Maberly, S. C., L. King, M. M. Dent, R. I. Jones, and G. Gibson. 2002. Nutrient limitation of phytoplankton and periphyton growth in upland lakes. Freshwater Biology **47**:2136-2152.

Martí, E., J. Autmatell, L. Godé, M. Poch, and F. Sabater. 2004. Nutrient retention efficiency in streams receiving inputs from wastewater treatment plants. Journal of Environmental Quality **33**:285-293.

Matson, P. A., W. J. Parton, A. G. Power, and M. J. Swift. 1997. Agricultural intensification and ecosystem properties. Science **277**:504-509.

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society **24**:602-612.

Mitchell, R. J., R. S. Babcock, S. Gelinas, L. Nanus, and D. E. Stasney. 2003. Nitrate Distributions and Source Identification in the Abbotsford-Sumas Aquifer, Northwestern Washington State. Journal of Environmental Quality **32**:456-800.

Morris, D. P., and W. M. Lewis Jr. 1988. Phytoplankton nutrient limitation in Colorado mountain lakes. Freshwater Biology **20**:315-327.

Naylor, R. 1996. Energy and resource constraints on intensive agricultural production. Annual Review of Ecology and Systematics **21**:99-123.

Nolan, B. T., and J. D. Stoner. 2000. Nutrients in ground waters of the conterminous United States, 1992-1995. Environmental Science and Technology **34**:1156-1165.

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. Valett, A. E. Hershey, W. H. McDowell, W. K. Dodds, S. K. Hamilton, S. V. Gregory, and D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. Science **292**:86-90.

Pickett, S. T. A., J. Burch, WR, S. E. Dalton, T. W. Foresman, J. M. Grove, and R. Rowntree. 1997. A conceptual framework for the study of human ecosystems in urban areas. Urban Ecosystems **1**:185-199.

Postel, S. L., G. C. Daily, and P. R. Ehrlich. 1996. Human appropriation of renewable freshwater. Science **271**:785-788.

Power, J. F., and J. S. Schepers. 1989. Nitrate contamination of groundwater in North America. Agriculture, Ecosystems and Environment **26**:165-187.

Pregitzer, K. S., D. R. Zak, A. J. Burton, J. A. Ashby, and N. W. MacDonald. 2004. Chronic nitrate additions dramatically increase the export of carbon and nitrogen from northern hardwood ecosystems. Biogeochemistry **68**:179-197.

Reed-Andersen, T., S. R. Carpenter, and R. C. Lanthrop. 2000. Phosphorus flow in a watershed-lake ecosystem. Ecosystems **3**:561-573.

Reynolds, J. E. 1993. Urban land conversion in Florida -- Will agriculture survive? Soil and Crop Science Society of Florida Proceedings **52**:6-9.

Riebsame, W., H. Gosnell, and D. Theobald. 1996. Land use and landscape change in the Colorado Mountains. 1. Theory, scale, and pattern. Mountain Research and Development **16**:395-405.

Schepers, J. S., and L. N. Mielke. 1983. Nitrogen fertilization, mineralization, and leaching under irrigation in the Midwest. Pages 325-334 *in* R. R. Lowrance, R. L. Todd, L. E. Asmussen, and R. A. Leonard, editors. Nutrient Cycling in Agricultural Ecosystems. Univ. GA Coll. Agric. Spec. Pub No. 23, Athens, GA.

Schindler, D. W. 1977a. Evolution of phosphorus limitation in lakes. Science **195**:260-262.

Schindler, D. W. 1977b. Evolution of phosphorus limitation in lakes. Science:260-267.

Schindler, D. W., F. A. J. Armstrong, S. K. Holmgren, and G. J. Brunskill. 1971. Eutrophication of lake 227, Experimental Lakes Area, north-western Ontario, by addition of phosphate and nitrate. J. Fish Res Board Can **28**:2009-2036.

Schlesinger, W. H. 1997. Biogeochemistry, 2nd edition. Academic Press, San Diego, CA.

Smith, V. H. 1998. Cultural eutrophication of inland, estuarine, and coastal waters. Pages 7-49 *in* M. L. Pace and P. M. Groffman, editors. Successes, limitation, and frontiers in ecosystem science. Springer-Verlag, New York.

Solorzano, L. 1969. Determination of ammonia in natural waters by the phenolhypochlorite method. Limnology and Oceanography **14**:799-801.

Sommer, U. 1989. Nutrient status and nutrient competition of phytoplankton in a shallow, hypertrophic lake. Limnology and Oceanography **34**:1162-1173.

Soranno, P. A., S. R. Carpenter, and R. C. Lanthrop. 1996. Phosphorus loads to surface waters: a simple model to account for spatial pattern of land use. Ecological Applications **6**:865-878.

Spalding, R. F., and M. E. Exner. 1993. Occurrence of nitrate in groundwater - A review. Journal of Environmental Quality **22**:392-402.

Sterner, R. W., and J. P. Grover. 1998. Algal growth in warm temperate reservoirs: kinetic examination of nitrogen, temperature, light, and other nutrients. Water Research **32**:3539-3548.

Stites, W., and G. J. Kraft. 2001. Nitrate and chloride loading to groundwater from an irrigated North-Central U.S. sand-plain vegetable field. Journal of Environmental Quality **30**:1176-1184.

Strange, E. M., K. D. Fausch, and A. P. Covich. 1999. Sustaining ecosystem services in human-dominated watersheds: biohydrology and ecosystem processes in the South Platte river basin. Environmental Management **24**:39-54.

Sullivan, J. F. 1996. 1995 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Sullivan, J. F. 1998. 1997 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Tansley, A. G. 1935. The use and abuse of vegetational concepts and terms. Ecology **16**:284-307.

Vesterby, M., and R. E. Heimlich. 1991. Land use and demographic change: results from fast-growth counties. Land Economics **67**:279-291.

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

Vitousek, P. M. 1994. Beyond global warming: ecology and global change. Ecology **75**:1861-1876.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, and W. H. Schlesinger. 1997b. Human alteration of the global nitrogen cycle: causes and consequences. Issues in Ecology **1**:1-14.

Vitousek, P. M., P. R. Ehrlich, A. H. Ehrlich, and P. A. Matson. 1986. Human appropriation of the products of photosynthesis. BioScience **36**:368-373.

Vollenweider. 1968. The scientific basis of lake and stream eutrophication with particular reference to phosphorus and nitrogen as eutrophication factors. Technical Report DAS/C81/68, OECD, Paris.

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

Wood, E. D., F. A. J. Armstrong, and F. A. Richards. 1967. Determination of nitrate in seawater by cadmium-copper reduction to nitrite. Journal of the Marine Biology Association of the United Kingdom **47**:23-31.

Zall, D. M., D. Fisher, and M. Q. Garner. 1956. Photometric determination of chlorides in water. Analytical Chemistry **28**:1665-1668.

Table 4.1 Morphometric data for the lakes of Indian Bend Wash.

| Reach Name | Perimeter (m) | Thalweg Length (m) | Surface Area (m2) | Volume (m3) | Max Depth (m) |
|---|---|---|---|---|---|
| L-1 | 552 | 186 | 12018 | 12909 | 1.72 |
| L-2 | 443 | 218 | 5947 | 4865 | 1.54 |
| L-3 | 455 | 182 | 6222 | 3460 | 0.96 |
| L-4 | 308 | 134 | 4899 | 3751 | 1.3 |
| L-5 | 318 | 141 | 3999 | 2256 | 1.12 |
| L-6 | 267 | 117 | 3546 | 3634 | 1.8 |
| L-7 | 490 | 209 | 13665 | 25286 | 3.08 |
| L-8 | 950 | 291 | 25719 | 64144 | 4.96 |

Table 4.2. Hierarchical logic sequence to distinguish forms of nutrient limitation. Differences in growth rates, $r$, estimated under four different treatment combinations (control, +N, +P, + N and + P) were evaluated using the general linear model $r = b_0 +$ Row + N + P + N*P. Row was a blocking variable indicating an incubation bottle's distance from the light source in the growth chamber. Cell means were compared using Bonferroni tests.

| Effect | Logic | Decision |
|---|---|---|
| Sig. N*P interaction | If N ≤ C and P ≤ C and NP > C | Co-limitation |
| | If N ≤ C and P > C and NP > P | Primary P limitation; Secondary N limitation |
| | If P ≤ C and N > C and NP > N | Primary N limitation; Secondary P limitation |
| Sig. P and Sig. N | If P > C and N > C and NP > C | Both nutrients limiting |
| Sig P | If (NP ~ P) ≥ (N ~ C) | P limitation |
| Sig N | If (NP ~ N) ≥ (P ~ C) | N limitation |
| No significant effects | P ≤ C and N ≤C and NP≤ N and NP ≤ P | No limitation |

Table 4.3. Statistical description of nutrient concentrations at top of reach. Samples collected from riffle just below confluence of L-1. All concentrations are in µM.

| Nutrient | *N* | Median | Mean | Minimum | Maximum | SE |
|---|---|---|---|---|---|---|
| $NH_4^+$-N | 48 | 2.10 | 2.98 | 0.36 | 13.40 | 0.42 |
| $NO_3^-$-N | 48 | 22.93 | 107.50 | 0.61 | 474.42 | 20.52 |
| SRP | 48 | 0.66 | 1.25 | 0.27 | 4.25 | 0.14 |

Table 4.4 Results of multiple linear regression analysis showing effects of flood size and time since flood on the concentration of SRP (top) and the effect of well pumping by COS 6 on the concentration of $NO_3$ below L-1. Discharge, Days post flood and SRP were $\log_{10}$ transformed prior to analysis. Overall significance (ANOVA results and adjusted $R^2$ values) is reported.

| | | | | |
|---|---|---|---|---|
| SRP | | | Adj-$R^2$ | 0.559 |
| Effect | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | -0.253 | 0.110 | -2.31 | 0.026 |
| $Q_{max}$ | 0.325 | 0.077 | 4.21 | < 0.001 |
| Days post flood | -0.933 | 0.100 | -0.93 | 0.356 |
| $Q_{max}$*Days pot flood | -0.185 | 0.079 | -2.31 | 0.026 |
| ANOVA | df | MS | F | *p* |
| Regression | 3 | 0.94 | 20.8 | < 0.001 |
| Residual | 44 | 0.05 | | |
| Ammonium | | | Adj-$R^2$ | 0.467 |
| Effect | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | 0.700 | 0.082 | 8.67 | < 0.001 |
| Well Discharge | -0.492 | 0.076 | -6.49 | < 0.001 |
| ANOVA | df | MS | F | *p* |
| Regression | 1 | 4.44 | 42.2 | < 0.001 |
| Residual | 46 | 0.11 | | |
| Nitrate* | | | Adj-$R^2$ | 0.619 |
| Effect | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | 34.102 | 15.16 | 2.25 | 0.029 |
| Well Discharge | 0.023 | 0.00 | 8.80 | < 0.001 |
| ANOVA | df | MS | F | *p* |
| Regression | 1 | 596297 | 77.5 | < 0.001 |
| Residual | 46 | 7692 | | |

* Residuals were slightly non-normal due to presence of two outliers. When excluded from the analysis, the estimated intercept and slope were essentially identical (18.92 and 0.0235, respectively) while the adjusted $R^2$ was increased to 0.828.

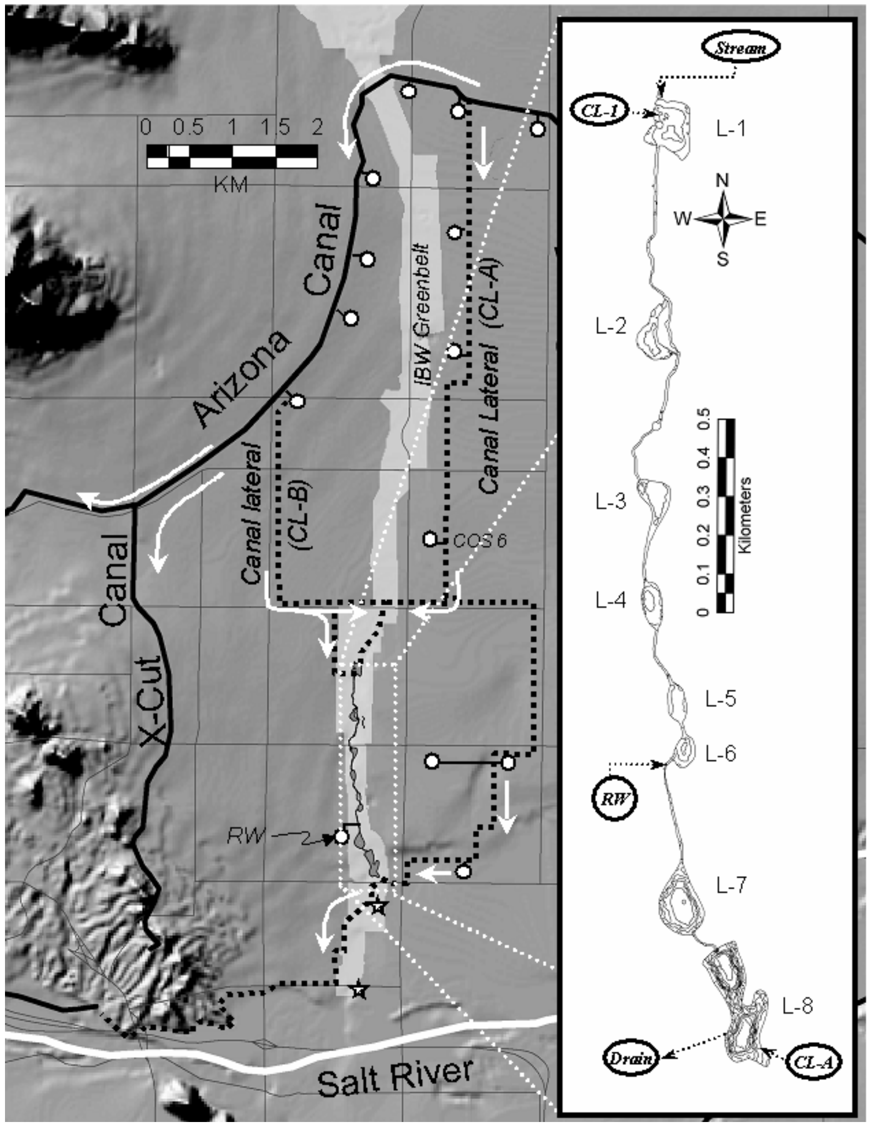


Figure 4.1. Map of canals (thick black lines), canal laterals (dashed black lines), and groundwater wells (circles) feeding the study reach (inset). Surface water diverted from the Salt, Verde, and Colorado Rivers flows through the Arizona canal. During peak demand, flows are supplemented with groundwater from the wells along its southern edge. Two canal laterals (*CL-A* and *CL-B*) deliver water to the stream above the study reach. *CL-1* and *CL-2* also deliver water directly to lakes L-1 and L-8, respectively, through subsurface pipes. Some of the water entering from the stream above L-1 is diverted around the lake through a bypass pipe (dashed gray line). The Roosevelt well (RW) discharges directly to the stream. During baseflow, water is returned to the canal system through a drain in lake L-8. Bathymetry of the lakes is indicated by 0.5-m contour lines (inset). White arrows indicate dominant flowpaths. Stars indicate location of two permanent stream gauges.

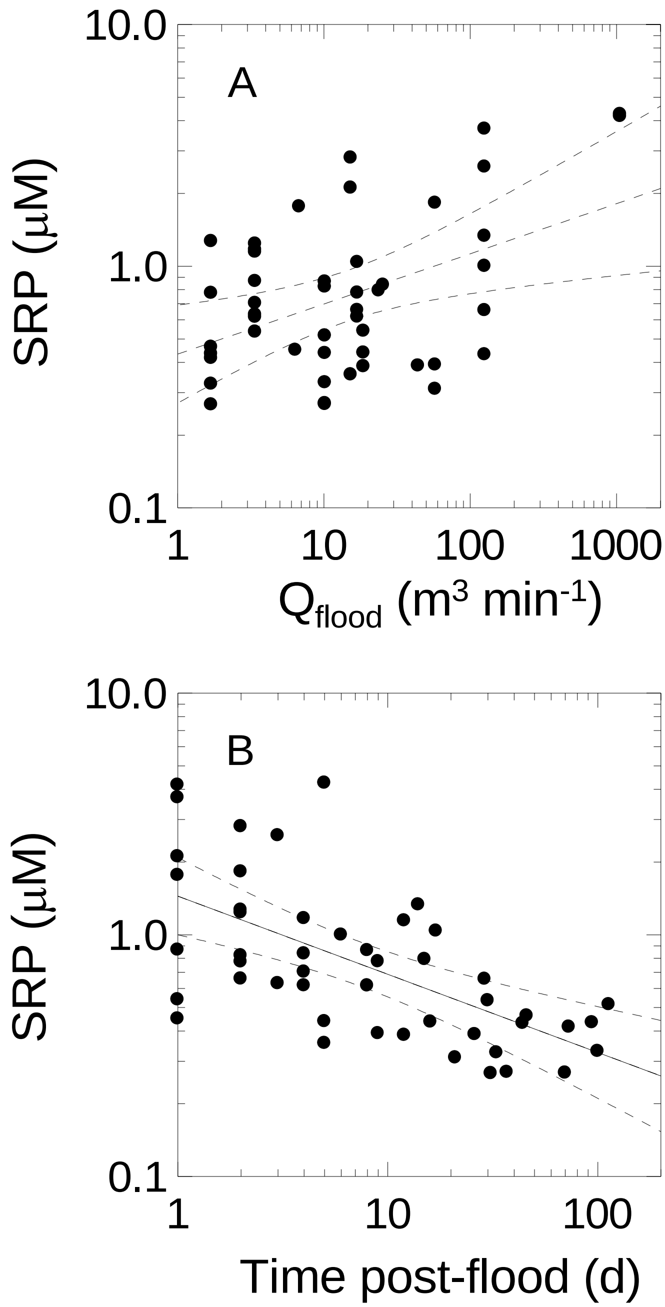


Figure 4.2. Relationship between average daily flood discharge (A) and time since flooding (B) and SRP concentration of water samples collected below L-1. Simple regression and 95% confidence intervals are plotted.

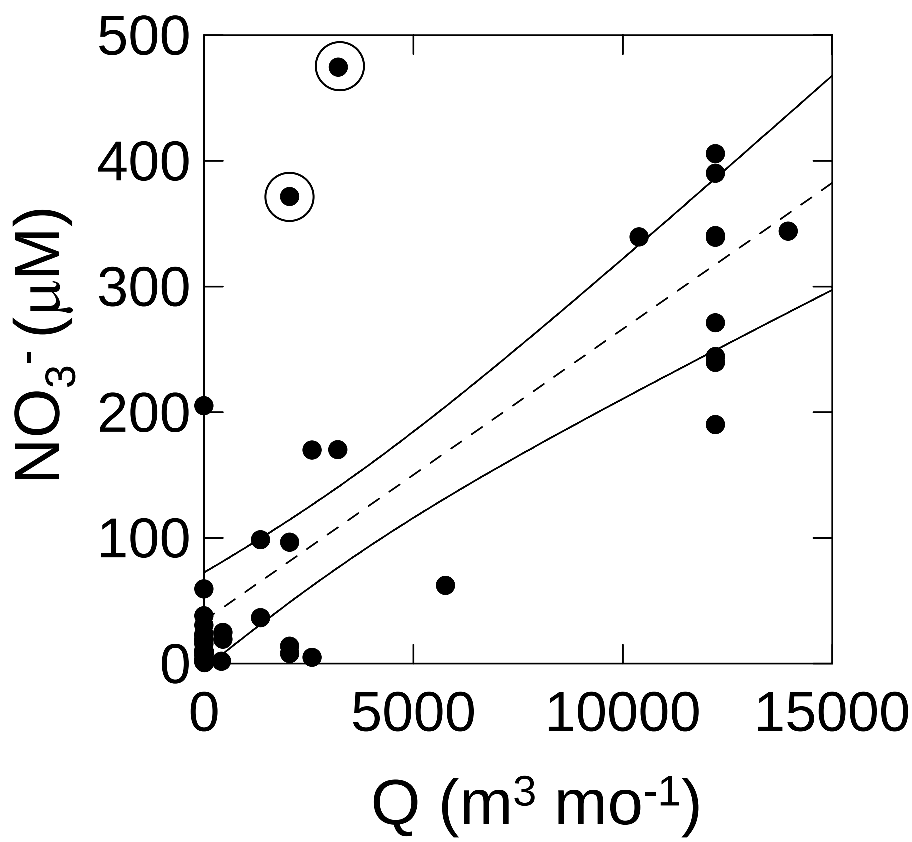


Figure 4.3. Relationship between monthly groundwater pumping of COS 6 and $NO_3^-$ concentration of water samples collected below L-1. Mean concentration of $NO_3^-$ in water samples collected from COS 6 was 889 ± 10 mM (Mean ± 1 SE of 2 samples collected in 1995 and 1997). Regression and 95% confidence interval is plotted. The two outliers (circled) are likely the result of $NO_3^-$ originating from other sources in the wash or temporarily stored in ponds upstream.

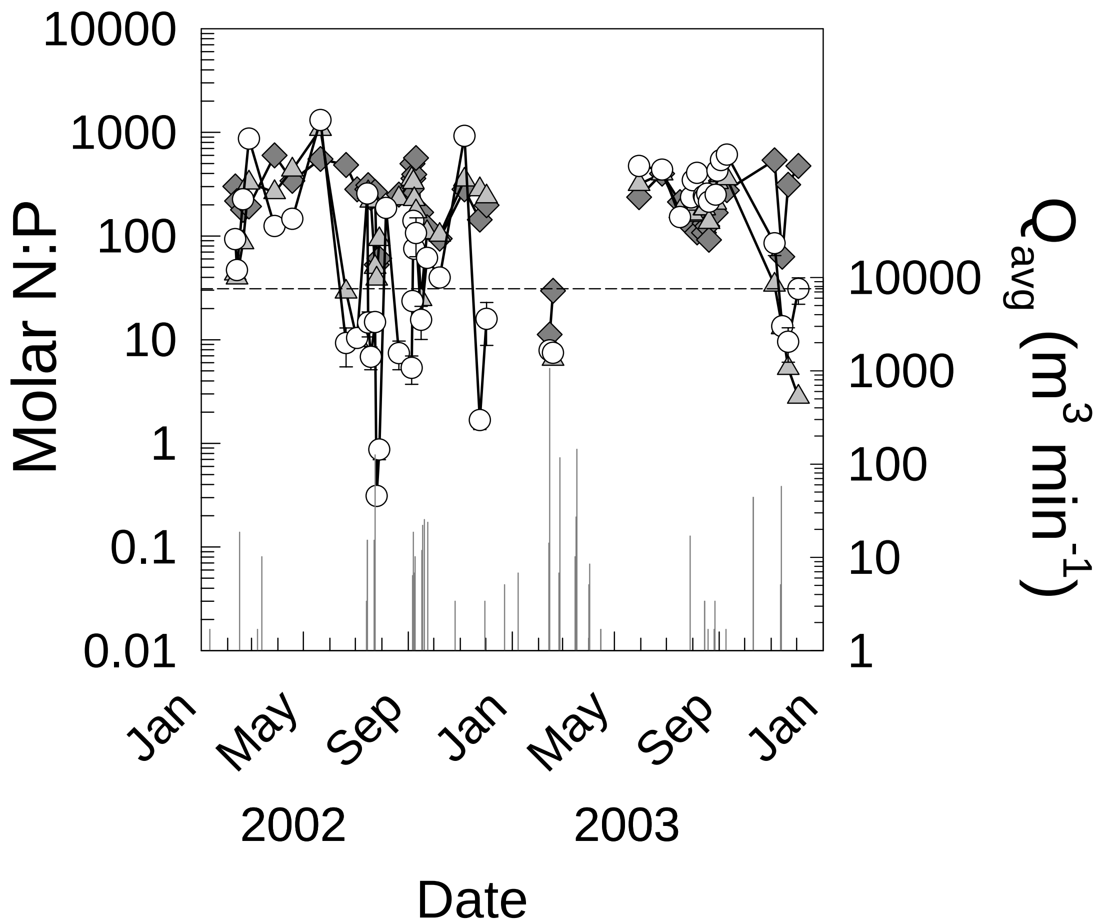


Figure 4.4. Variation in the mean ratio of TIN ($NO_3^-$ + NH4+) to SRP (atomic N:P) in water collected from the outlets lakes L-1 through L-6 (open circles) compared to the variation in N:P in water from the outlets of L-7 (closed triangles) and L-8 (closed diamonds) across 48 sampling dates in 2002 and 2003. Error bars represent ± 1 SE about the mean of replicate samples. The expected cutoff between N and P limitation (dashed line; N:P = 31:1) is plotted for reference. The average daily discharges of 39 floods during this period are plotted at the bottom of the panel.

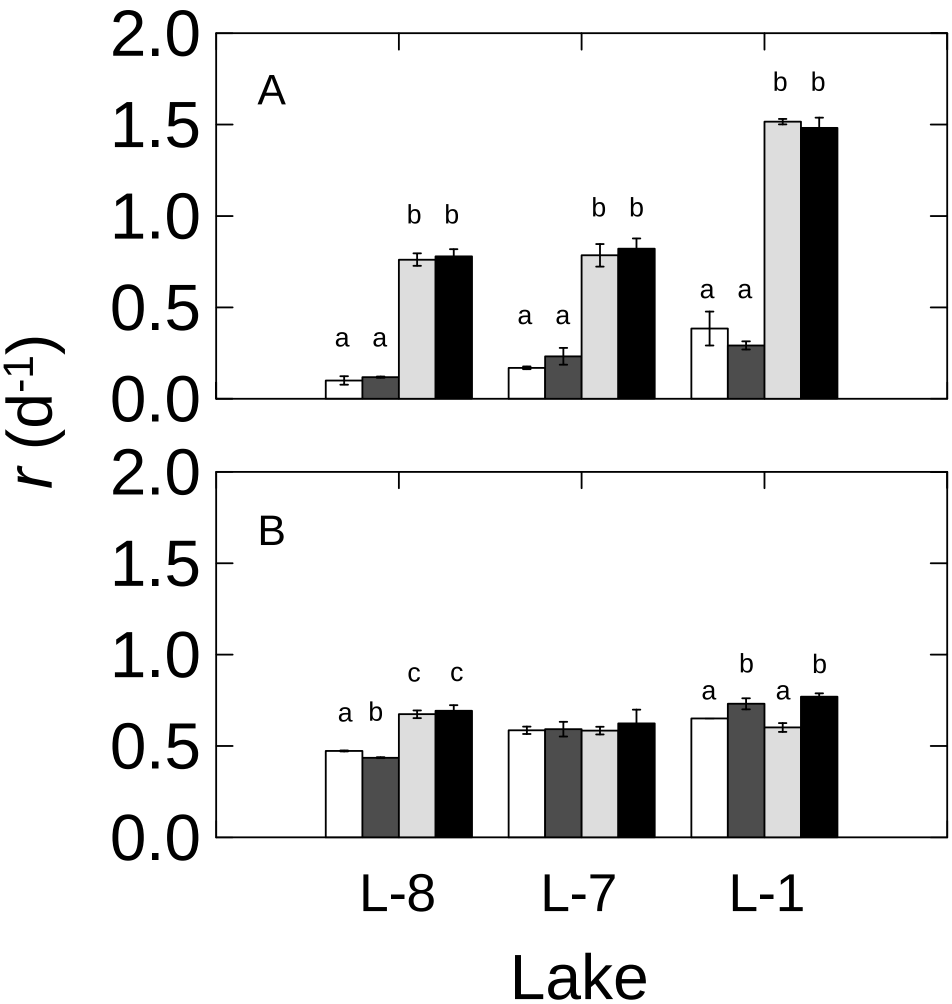


Figure 4.5. Intrinsic growth rates (Mean ± 1 SE) of algal samples incubated in filtered lake water without supplemental nutrients (open bars), with supplemental N (dark gray bars), P (light gray bars), or N and P (black bars) on August 14 (A) and November 14 (B). Data from three lakes are presented. Bars with different letters are significantly different ($P < 0.05$) as indicated by Bonferroni-adjusted pair-wise comparisons. August 14 was a typical summer day while both water management decisions and a flood the preceding day influenced November 14.

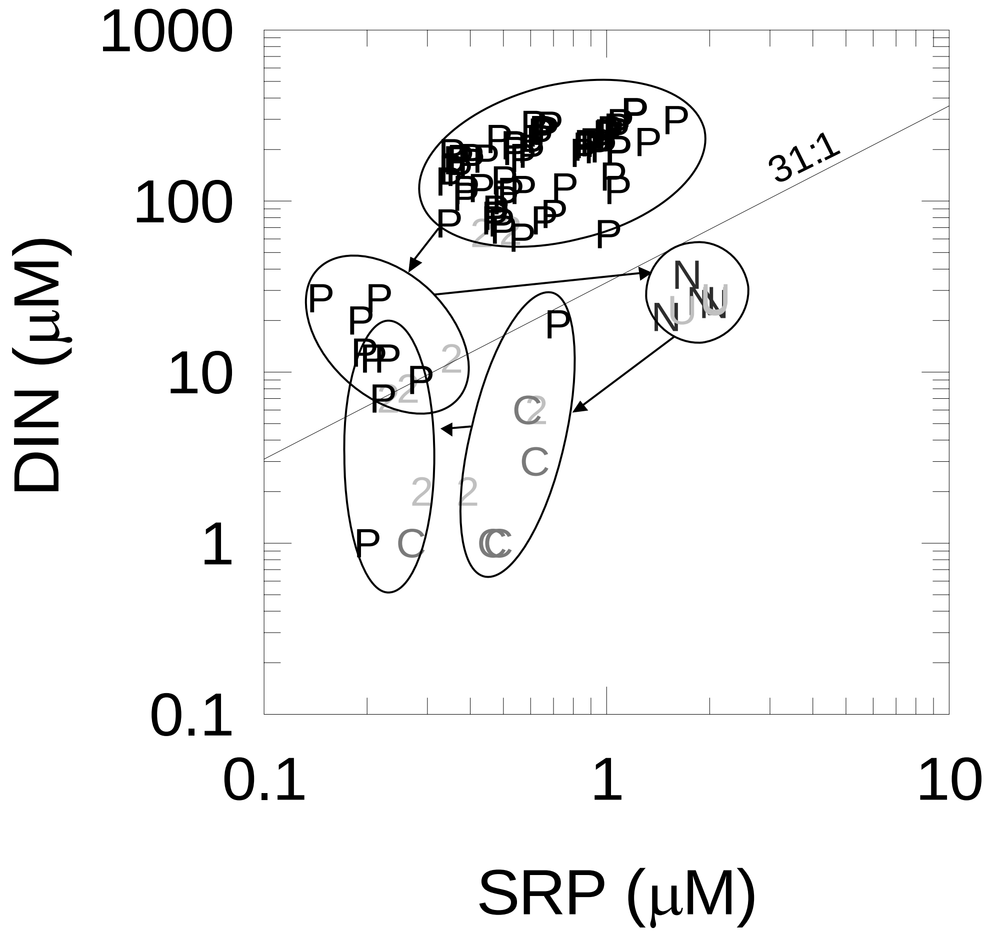


Figure 4.6. Results of nutrient bioassays from the 8 lakes on all sampling dates plotted as a function of the total dissolved inorganic nitrogen (DIN) and soluble reactive phosphorus (SRP) in outlet water of each lake. P indicates P-limitation, N indicates N-limitation, C indicates co-limitation, 2 indicates secondary N limitation, and U indicates no nutrient limitation. The theoretical cutoff (atomic N:P = 31:1) is plotted for reference. Circles and arrows indicate the trajectory of the system through the phase space. The lake chain begins with all lakes either P-limited or secondarily N-limited. A reduction in the input of $NO_3^-$ between September 10 and Nov 5 initiates the migration of L-1 through L-7 down and to the left. After a November 13 flood assays suggest all lakes except L-8 are either N-limited or not nutrient limited. On two subsequent sampling dates (November 21 and December 2, 2003), the system migrates towards its pre-flood condition..

# 5. DENITRIFICATION IN A STREAM-FLOODPLAIN COMPLEX OF A DESERT CITY: IMPORTANCE OF NATURAL AND ANTHROPOGENIC CROSS-SYSTEM LINKAGES


## ABSTRACT

The Indian Bend Wash flood-control project relies on a greenbelt to safely convey floods through Scottsdale, AZ. A chain of shallow artificially maintained lakes in a larger, undeveloped floodplain of irrigated turf grass characterizes the greenbelt. We conducted a series of experiments to evaluate whether and which of these novel patch types (i.e., lakes, channelized stream segments, and turf-dominated floodplain) were important sites of denitrification and to determine what factors controlled potential denitrification rates, using assays of denitrification enzyme activity (DEA). DEA analyses on sediments collected from eight lake and six stream segments as well as soil samples from eight floodplain transects demonstrated that mass-specific potential denitrification rates were significantly higher in lakes than in streams or floodplains. Nutrient limitation bioassays revealed that nitrogen (N) limited denitrification in lake sediments whereas in floodplain soils were limited by soil moisture. Although rain is rare in the desert, irrigation is common and we conclude that annual denitrification in the floodplain can be substantial. Because lake water nitrate concentrations often exceed 1 mg N $L^{-1}$, the finding of N-limited denitrification in lake sediments was surprising. However, further experiments using intact cores demonstrated that it was not so much the

concentration of nitrate in the overlying water as the rate at which it diffused into the sediments that limited denitrification in the lakes.

## INTRODUCTION

Changing patterns of land use and land cover across the globe have dramatically altered Earth's global biogeochemical cycles (Vitousek et al. 1997). Widespread application of synthetic fertilizers has intentionally increased nitrogen (N) concentrations in many ecosystems, while unintentionally fertilizing downstream ecosystems. Simultaneously, practices such as fossil-fuel combustion and livestock domestication have led to further unintended increases in N. In Phoenix, for example, farming and urbanization have increased inorganic soil N by 74 kg ha$^{-1}$ (Zhu et al. in press). Much of this anthropogenic N does not remain in place, but is exported to recipient ecosystems via rivers (Goolsby and Battaglin 2001) or air currents (Padgett et al. 1999) where it contributes to eutrophication of aquatic ecosystems (Carpenter and Pace 1997, Carpenter et al. 1998), degradation of drinking water (Neilsen and Lee 1987, Mosier et al. 2001), and N saturation of forests (Aber et al. 1989).

A variety of physical and biologic mechanisms may remove and/or retain inorganic N, reducing its flux across the landscape and thereby its impact on recipient ecosystems. Nitrogen incorporated into plant biomass (Moeller et al. 1988, Stephen et al. 1998) or by fungi and bacteria (Groffman et al. 1993) is at least temporarily retained in place. Sedimentation can lead to the burial and retention of organic N, and though permanent burial is rare in stream sediments or floodplain soils, it is a major retention mechanism in lakes and oceans (Essington and Carpenter 2000). Denitrification, the microbially mediated conversion of $NO_3^-$ to $N_2$ and $N_2O$, may be the most important mechanism as it results in permanent removal of biologically available N from the ecosystem. Unfortunately, although many urban ecosystems have elevated nutrient concentrations (Paul and Meyer 2001, Walsh et al. 2005b) , they frequently exhibit reduced nutrient retention. For example, increasing urbanization decreased the rates at which $NH_4^+$ and SRP were removed from the water column (as indicated by uptake velocity) of the Chattahoochee River (Meyer et al. 2005), while in southwestern desert streams $NO_3^-$ retention was lower in urban streams compared to their more pristine counterparts (Grimm et al. 2005).

Because denitrification greatly reduces the impact of excess N on recipient ecosystems, many researchers and managers focus on identifying conditions promoting denitrification (Boesch et al. 2001, Clément et al. 2002). For example, a riparian forest removed 89% of the inorganic nitrogen flux from groundwater passing beneath it, primarily through denitrification, thus buffering the adjacent stream from the impact of fertilizer running off a farm (Peterjohn and Correll 1984). Wetlands have proven important sinks for $NO_3^-$ on the landscape, with macrophyte beds being particularly active sites of denitrification (Weisner et al. 1994). Similarly, artificial ponds (Jansson et al. 1994) and floodplains can be also important sites of denitrification (Kern et al. 1996, Brettar and Höfle 2002, Kreibich and Kern 2003, Gergel et al. 2005). Much of this research has suggested that there are patches–'hot spots'–responsible for a disproportionate amount of denitrification (Peterjohn and Correll 1984, McClain et al.

2003). For example, floodplain hotspots are often associated with fine-textured soils, the location of which is a function of hydrology and geomorphology (Pinay et al. 2000), whereas in urban streams debris dams act as denitrification hot spots (Groffman et al. 2005).

The spatial arrangement of hot spots may influence which patches interact and thus can regulate the flux of N between patches, the relative availability of N to different patches, and the net export of materials to adjacent ecosystems. Recent evidence suggests that geomorphic and hydrologic drivers determine the origin, development, and persistence of patches as well as their interactions (McAuliffe 1994, Kling et al. 2000, Webster et al. 2000, Stanley and Doyle 2002). For example, in Sycamore Creek, AZ, hydrologic variability operating at two distinct temporal scales drives spatial patterns of denitrification. Over the short term, individual floods determine the location of downwelling zones, which deliver algal-derived organic matter to denitrifiers in the hyporheic zone (Holmes et al. 1996). On longer time scales droughts reduce the frequency of flooding, promoting the colonization of sand bars by seepwillow, the roots of which, in turn, stimulate denitrification by exuding dissolved organic C (Schade et al. 2001).

Conversely, patch location in urban ecosystems has less to do with hydrologic, geomorphic, and biologic processes and more to do with human actions and the frequently unintentional consequences of human decisions (Pickett et al. 1997, Grimm et al. 2000, Paul and Meyer 2001, Pickett et al. 2001, Kaye et al. in press). Urbanization produces marked changes in hydrology that not only alter fluvial geomorphic processes responsible for maintaining stream channel structure (Graf 1975, Schick 1995), but also dramatically alter the way in which patches are connected (Grimm et al. 2004, Walsh et al. 2005a). In arid-land cities, for example, surface flows are often shunted into canals that deliver water for irrigation and municipal use and out of naturally flowing rivers that, in turn, are channelized and simplified to facilitate flood control. Reduced channel complexity is hypothesized to reduce denitrification by limiting interactions between nutrient-rich surface flows and subsurface zones of high denitrification potential (Grimm et al. 2004). In many urban streams of the eastern U.S., channel incision has dropped the water table, hydrologically isolating riparian zones, and reducing their importance as denitrification hotspots (Groffman et al. 2002, Groffman et al. 2005).

This study sought to better understand how the altered hydrology and geomorphology of urban streams affects the location of denitrification hotspots and overall N retention. We used Indian Bend Wash (IBW), an extensively modified urban stream, to address the question: *how do modifications of the hydrology and geomorphic structure of an urban stream affect spatial and temporal patterns of nitrogen retention and denitrification in the stream-floodplain complex?* Objectives were (1) to determine if potential denitrification rates differed between three different patch types—lake sediments, stream sediments, and floodplain soils; (2) to determine what factors limited denitrification in the two most important patch types (lakes and floodplains); (3) to assess the relative effectiveness of lake and floodplain patches in overall N removal from the entire system; i.e., to determine whether either patch acted as a hotspot of denitrification; (4) to assess how cross-system linkages affected patterns of denitrification; and (5) to determine how annual denitrification contributed to overall N retention in the stream-floodplain complex.

## STUDY SITE

Historically, Indian Bend Wash (IBW), a tributary of the Salt River, drained 520 $km^2$ as it flowed over alluvial fans of the McDowell Mountains in northeast Scottsdale, AZ (Fig. 5.1). Although dry most of the year, IBW was prone to flash floods. Flood management was achieved with arrival of the Central Arizona Project Canal, which essentially severed flows from the northern portion of the watershed to the main stem, and construction of the IBW flood control project (City of Scottsdale 1985). The project's floodway is a greenbelt that has been protected from encroaching development and engineered to accommodate the 100-year flood (U.S. Army Corps of Engineers 1975).

The greenbelt's most striking feature is a series of shallow artificial lakes in the broader floodplain. This study was conducted in an eight-lake chain running through a 3-km reach of lower IBW (Fig. 5.1, inset). A mixture of surface and groundwater from the Arizona Canal enters the reach via a stream above L-1 and through a subsurface pipe discharging directly to L-1. Flows in the wash are periodically supplemented with groundwater pumped into the stream below L-6 and a mix of canal water and groundwater discharged into L-8 through a subsurface pipe. Except during floods, water flows out of L-8 through a drain and back into the canal system. Three urban parks dominated by irrigated turf form the floodplain of the reach. Irrigation water for El Dorado Park, Vista del Camino Park and the northern portion of McKellips Park is drawn directly from L-1 and L-6. A separate groundwater well provides irrigation water to the southern half of McKellips Park. Nitrogen fertilizer is applied to the parks at the rate of approximately 140 kg N $ha^{-1}$ $y^{-1}$ (City of Scottsdale*, personal communication*)

The concentration of $NO_3^-$ in the aquifer underlying IBW south of the Arizona Canal ranges from 1.48 to 15.40 mg $NO_3^-$-N $L^{-1}$ (Sullivan 1998) as a result of historic fertilizer use (Xu 2002). When groundwater is used to supplement surface flows in IBW, $NO_3^-$ concentrations are high. During a two-year study of this reach, $NO_3^-$-N concentration at the top of the reach ranged from 0.01 mg $L^{-1}$ to in > 6.6 mg $L^{-1}$ (Chapter 3). Observed natural declines in $NO_3^-$ concentrations indicated that the reach oscillated between being a net sink and a net source of inorganic N (Chapter 3).

Based on these anthropogenic modifications made to IBW, we hypothesized that the fine-textured sediments of lake sediments would stimulate denitrification and would lead to higher mass-specific rates of denitrification in lake sediments versus stream sediments and floodplain soils. We hypothesized that because lake-sediments were saturated and likely anoxic, their denitrification rates would be limited by supply of organic carbon or $NO_3^-$. Further, because of the high $NO_3^-$ content of the lake water, we hypothesized that organic carbon was more likely to limit denitrification than $NO_3^-$. Conversely, because floodplain soils are frequently dry, we hypothesized that denitrification events were likely episodic, occurring primarily in response to wetting events. Further, because of the application of synthetic fertilizers and the abundant turf grass, we hypothesized that organic carbon and $NO_3^-$ may accumulate in the soil and that only water or anoxia would stimulate denitrification.

## METHODS

### *Denitrification enzyme activity*

*Potential denitrification in lakes, streams and floodplains (experiment 1).* — Potential denitrification rates in the three patches were compared using denitrification enzyme activity (DEA) assays based on methods originally developed by Yoshinari et al. (1976) and Smith et al. (1978) and later refined by Groffman et al. (1999). Five 10-cm deep cores were collected from eight lakes, six streams, and eight floodplain transects on April 22-23, 2004.

Standard DEA assays measure potential denitrification and require that both C and N be provided in excess. Thus, ~ 50 g of sample were incubated in 50 ml of media amended with $NO_3^-$ (13 mg $NO_3^-$-N kg$^{-1}$, all additions were calculated on the basis of soil or sediment fresh weight) and dextrose (100 mg kg$^{-1}$). .

*N vs. C limitation of denitrification (experiment 2).* —Nutrient limitation bioassays were conducted on lake sediment cores collected from L-1 ($n$ = 8) and L-8 ($n$ = 11) on October 7, 2003 and soil cores collected from adjacent floodplain transects ($n$ = 8 and $n$ = 7, respectively) on September 24, 2003. As with the potential denitrification assay, rates were estimated using short-term assays in which $NO_3^-$ (100 mg $NO_3^-$-N kg$^{-1}$) and dextrose (100 mg kg$^{-1}$) were added to the incubation media in a factorial fashion to establish four treatments: $NO_3^-$ only ($DR_{+N}$), dextrose only ($DR_{+C}$), $NO_3^-$ and dextrose ($DR_{+N,+C}$), and a control in which only nanopure water was added ($DR_{Control}$).

*Threshold water limitation of floodplain denitrification (experiment 3).* —The hypothesis that denitrification was stimulated once soil moisture exceeded a threshold water content was tested using 5 soil cores collected on July 10, 2004 along a transect by L-7. Cores were subsampled and five treatment levels established by adding sufficient nanopure water to raise the soil moisture by the following proportions: 0.0, 0.05, 0.10, 0.15, 0.25, 0.50. Actual water content was calculated after the experiment based on the mass added and the initial water content of the sample. Denitrification rates were estimated as in the previous experiments.

*Water versus anoxia limitation of floodplain denitrification (experiment 4).*— The hypothesis that anoxia, not water content, stimulates floodplain denitrification was tested using soils collected on July 14, 2004 from floodplain transects by L-1 ($n$=8) and L-8 ($n$ = 6). Two experimental factors, anoxia (created by purging with $N_2$) and supplemental water (1 ml $H_2O$ $g^{-1}$ soil), were compared in a factorial experiment consisting of four treatments: anoxic only ($DR_{Anoxic}$), water only ($DR_{Water}$), anoxic water ($DR_{Anoxic\ Water}$), and a control to which no water was added and which was not purged ($DR_{Control}$).

Similar incubation protocols were followed in each experiment. Sediment cores were collected in acrylic tubes that were sealed remotely prior to retrieval. Core collection sites were longitudinally arrayed and evenly spaced along the centerline of each lake or stream segment. Soil cores were taken with a hammer corer along transects extending perpendicularly from the water's edge into the floodplain. All cores were kept at 4 $^{o}C$ from the time they were collected until the assay was initiated. Upon returning to the lab, each core was weighed, homogenized and subsampled. Initial subsampling occurred within 48 h of collection and assays were conducted within 96 h, usually sooner. For each assay, approximately 50 g of sediment or soil was incubated with the appropriate incubation medium (1 ml $g^{-1}$, except as noted) in 125 ml-Wheaton bottles equipped with rubber septa. Bottles were made anoxic by purging with $N_2$ (except as noted) and 10 ml acetylene was added to block the final step in the denitrification pathway, the reduction of $N_2O$ to $N_2$. Bottles were shaken to equilibrate acetylene between the aqueous and gas phases and the headspace pressure equilibrated with the atmosphere by briefly piercing septa with a hollow needle after collection of initial gas samples. Gas samples were collected in pre-evacuated Vacutainer vials at 15 min and after a 4-h incubation in the dark at a constant 25 $^{o}C$. Samples were analyzed for $N_2O$-N using a gas chromatograph equipped with an electron capture detector. Denitrification rates were calculated as the difference between the initial and final headspace $N_2O$-N content (corrected for $N_2O$-N dissolved in the aqueous phase, Bunsen coefficient = 0.49) divided by the time elapsed, and were expressed on either a unit area or unit dry mass basis.

Water content of each core was estimated by difference after drying a subsample to constant mass at 105 $^{o}C$. Soil organic matter (SOM) content was estimated as mass loss after ignition at 550 $^{o}C$ for 4 h. $NO_3^-$ content of the stream, lake and floodplain cores collected for potential denitrification rates (experiment 1) was estimated from subsamples by extraction with 2 M KCl. Similarly, $NH_4^+$ content of floodplain soils was estimated by

KCl extraction of soils collected for experiment 4. Concentrations of $NO_3^-$-N or $NH_4^+$-N in the extracts were estimated by colorimetric analysis with a Lachat 'Quick Chem 8000' flow-injection autoanalyzer.

*Actual denitrification rates*

Actual denitrification rates in lake sediments were estimated from intact cores collected from L-1, L-5, L-6, L-7, and L-8 on August 20, 2004. The technique used was a modification of the acetylene-block approach described by Sørensen (1978). Four pairs of 10-cm deep cores from each lake were collected in acrylic tubes (40-cm long and 4.4 cm in diameter) and returned to the laboratory where they were stored at 4 $^0$C overnight. The tubing contained 6 columns of 10 silicon-stoppered injection ports spaced at 1-cm intervals.

Immediately prior to incubations, overlying lake water was aspirated from each core and replaced with 150 ml acetylene-saturated lake water collected from the corresponding lake. Approximately 400 µL of acetylene-saturated nanopure water was injected through each port as the needle was slowly horizontally withdrawn through the sediment, ensuring as even a distribution of the acetylene as feasible without disrupting cores. Cores were stoppered and incubated in the dark at a constant temperature without stirring. One core from each pair was incubated for 0.5 h while the second core was incubated for 8.0 h. Prior to collecting gas samples from the headspace, each core was vigorously shaken to equilibrate $N_2O$ that had accumulated in sediment pore water, overlying lake water, and the headspace. The destructive nature of this sampling protocol necessitated use of two cores per incubation. Denitrification was calculated as the difference in Bunsen-corrected $N_2O$ accumulation in the two cores divided by the difference in incubation time, and was expressed on an areal basis.

Sediment $NH_4^+$ concentration was estimated on the aqueous solution extracted from the equilibrated core, which represented a mix of pore and lake water. Assuming that lake-water $NH_4^+$ concentration added was the same in all cases and that concentration did not change in either pore water or overlying lake water during the incubation, measured aqueous concentration can be taken as an index of $NH_4^+$ availability. Pore water volume was estimated as the difference between mass lost after drying the core to a constant weight at 105 °C following the experiment (i.e., the total water volume) and known lake-water volume added to initiate the experiment. The assumption of minimal concentration change was judged reasonable based on comparison of $NH_4^+$ concentration from cores incubated for 0.5 h versus 8 h (paired t-test; $t = -0.07$, $p = 0.94$, $df = 19$).

Actual denitrification rates in the floodplain were also estimated from intact 10-cm deep cores collected from floodplains adjacent to L-1, L-5, L-6, L-7, and L-8 on August 26, 2004. Cores were collected with a hammer corer fitted with a butyrate plastic liner. Each core was incubated twice. The first incubation was done without adding any supplemental water. The second incubation was done after a simulated irrigation event in which 0.7 cm of lake water (the same source used for irrigation in the parks) was added. The amount of water was based on average water depth collected in rain gauges ($n = 15$) deployed during three irrigation events.

al.

ce, and was mixed into the core by repeatedly pumping with a 60 mL syringe. Cores were incubated in the dark at a constant 25°C for 6 h. Gas samples were collected at 2 h and again at 6 h. Bunsen-corrected rates of $N_2O$-N production between the two sampling points, expressed on an areal basis, were taken as denitrification rates.

### *Statistical analyses*

Statistical analyses were performed using SYSTAT (version 10, SPSS Inc., 2000). Treatments were compared using analysis of variance (ANOVA) with specific comparisons made using Tukey's HSD. Multiple linear regressions were used to test effects of organic matter, moisture content, and $NO_3^-$ content on potential DEA, and to test whether these effects varied with patch type.

Piecewise linear regression analysis was used to evaluate results of experiment 3 and to test for a threshold percentage soil moisture content. The following model was fit to the data:

$$(1)\ DR = b_0 + b_1 * P_{H20} + b_2 * (P_{H20} - P_{thresh}) * (P_{H20} > P_{thresh})$$

where DR is denitrification rate, $P_{\mathrm{H20}}$ is percentage water content, and $P_{\mathrm{thresh}}$ is threshold water content required to stimulate denitrification. The term ($P_{H20} > P_{thresh}$) is a conditional that equals 0 or 1, depending upon whether $P_{thresh}$ has been exceeded. The term ($P_{H20} - P_{thresh}$) ensured the fitted model was a continuous line with a slope break at

$P_{thresh}$. The model was fit using a Gauss-Newton algorithm. Significance of each parameter was evaluated using Wald 95% confidence intervals.

For all analyses, residuals were examined to ensure they conformed to assumptions of the analysis. Where necessary, variables were transformed (natural log or square-root). In one case, assumptions of an ANOVA could not be met by transformation and data were analyzed using the Kruskal-Wallis test with specific comparisons made using Dunn's Q statistic (Zar 1996).

### *Mass-balance calculations*

Retention of inorganic N between the inlet of L-3 and the outlet of L-7 (Fig. 5.1) was estimated from the annual fluxes of $NH_4^+$ and $NO_3^-$ through the lakes, floodplain, and stream-floodplain complex using a mass-balance approach. The mass balance was restricted to this reach because reasonable estimates of hydrologic fluxes were not available for the remainder of the study reach. Annual denitrification was estimated from intact cores. The maximum amount of N stored in each patch was estimated as the difference between retention and denitrification. However, this estimate was almost certainly an overestimate, as a number of potentially important fluxes were not measured including flux of particulate and dissolved organic matter during baseflow, sediment export during floods, leaching to the aquifer, and the flux of trace gasses (e.g., $NO_{x)}$ in and out of the system.

Discharge and nutrient concentrations along the reach were measured periodically ($n$ = 51 sampling dates, see Chapter 3 for details of sampling methodology), with values between sampling dates estimated by interpolation. These data were used to estimate annual flux in of $NH_4^+$ and $NO_3^-$ via the inlet to L-3 and the Roosevelt well, and flux out of the wash via the outlet to L-7. Irrigation transferred a substantial quantity of water and N from L-6 to the floodplain. Fluxes of $NH_4^+$ and $NO_3^-$ from this lake were estimated from average monthly nutrient concentrations at the outlet and monthly irrigation rates provided by the City of Scottsdale (*personal communication*).

Fertilizer application rates were obtained from park managers (City of Scottsdale, *personal communication*). The total flux of fertilizer onto the floodplain was estimated from areal application rate, park area, and proportion of $NH_4^+$-N and $NO_3^-$-N in fertilizer. The areal extents of the wash's lakes and floodplain were determined from georectified aerial photos using ArcGIS.

Annual denitrification in lake sediments was estimated as average denitrification rate of intact cores multiplied by total lake sediment area in the reach. Because of their relatively small surface area and comparatively low mass-specific rates, denitrification in streams was ignored. Annual flux of N from the floodplain via denitrification was slightly more complex. Because denitrification was hypothesized to proceed more rapidly directly after irrigation events than when the soil was dry, annual denitrification was estimated as the sum of denitrification under dry floodplain conditions and denitrification on days when it was wet (i.e., days it was irrigated). Areal denitrification rates under these two conditions (wet and dry) were estimated from intact cores. The number of days irrigation occurred was estimated as total depth of irrigation water applied per year (1.52 m) divided by average depth per event, or irrigation rate (cm $d^{-1}$). Two approaches were taken to estimating irrigation rate. Rain gauges estimated irrigation rates of 0.7 cm $d^{-1}$ ($n$ = 15), suggesting 218 days were required to deliver 1.52 m. However, managers indicated that sprinklers ran every other day during the summer and less frequently during the rest of the year (*personal communication*), suggesting irrigation rates closer to 1.6 cm $d^{-1}$ and thus 95 days of irrigation. The average value of these estimates, 156 days, was taken as the best estimate of number of irrigation events and thus number of days on which denitrification was occurring at the higher rate.

Soil and sediment $NO_3^-$ pools were estimated from KCl extractions (experiment 1). Soil $NH_4^+$ pools were estimated from KCl extractions (experiment 4) while sediment $NH_4^+$ pools were estimated from intact cores.

## RESULTS

### *Denitrification enzyme activity analyses.*

Potential denitrification rates (Experiment 1), when expressed on a per unit mass basis, differed significantly between patch types ($F$ = 37.7, $p$ < 0.001, $df$ = 2,19; Fig. 5.2) with lake sediments exhibiting higher denitrification rates than stream sediments or floodplain soils. Because water content, organic matter content, and $NO_3^-$ content of cores were all highly correlated (Table 5.1), effects of each variable on DEA were analyzed separately. DEA was positively correlated with soil moisture, organic matter content, and $NO_3^-$ content (Fig. 5.3; Table 5.2). Effects of soil moisture did not vary as a function of patch type, however, effects of organic matter were more pronounced in lakes and streams than in floodplains (Fig. 5.3A; Table 5.2), whereas effects of $NO_3^-$ were stronger in lakes than in streams or floodplains (Fig. 5.3C; Table 5.2). Although each or these three variables, in conjunction with patch type, was capable of explaining > 79% of the variance in DEA, because they were highly correlated it is impossible to say definitively which variable actually drove the variation in DEA. Because average soil moisture was so much greater in lake sediments than floodplain soils, areal specific denitrification rates were much more similar (209 ± 14 mg $N_2O$-N $m^{-2}$ $h^{-1}$ and 197 ± 14 mg $N_2O$-N $m^{-2}$ $h^{-1}$, for lake sediment and floodplain soils, respectively).

The nutrient-limitation bioassay of lake sediments (experiment 2) indicated that denitrification rates in the lakes were limited by N (Kruskal-Wallis $H = 57.9$, $p < 0.001$, $df = 3$; Fig. 5.4a), whereas denitrification in floodplain sediments was limited neither N nor C ($F = 0.71$, $p = 0.55$, $df = 3, 44$; Fig. 4b). Soil and sediment nutrient content data were consistent with these results; there was significantly more $NO_3^-$ in floodplain soils than in lake or stream sediments ($F = 53.2$, $p < 0.001$, $df = 2, 19$; Fig. 5.5).

Denitrification in floodplain soils was stimulated by the addition of water (experiment 3), with DEA increasing markedly once soil moisture exceeded the threshold of 31% (Wald 95% C.I.: $22.0 \leq P_{thresh} \leq 39.6$; Fig. 5.6). As expected, below the threshold water content, denitrification rates were approximately zero (Wald 95% C.I.: $-122 \leq b_0 \leq 104$) and were unaffected by changes in water content (Wald 95% C.I.: $-4.0 \leq b_1 \leq 5.4$). Although both the addition of water and the creation of anoxic incubation conditions (Experiment 4) appeared to stimulate denitrification rates (Fig. 5.7), only the effect of water addition was statistically significant (Table 5.3).

*Intact cores*

Areal denitrification rates estimated from intact lake sediment cores and intact floodplain soil cores indicated that lake sediments and recently irrigated soils had similar denitrification rates ($3.0 \pm 1.2$ mg $m^{-2}$ $h^{-1}$ and $2.5 \pm 1.8$ mg $m^{-2}$ $h^{-1}$, respectively). Denitrification rates in fresh (i.e., unirrigated; $0.5 \pm 0.3$ mg $m^{-2}$ $h^{-1}$ ) soil cores were significantly lower than both irrigated soils and lake sediments ($F = 11.52$, $p = 0.001$, $df = 2, 12$; Fig. 5.8). Not surprisingly, these rates were orders of magnitude lower than the potential denitrification rates of lake sediments and floodplain soils expressed on a per unit area basis.

*Mass balance of reach L-3 to L-7*

The hydrologic flux of $NH_4^+$ and $NO_3^-$ into the lakes of was large (10.7 Mg N $y^{-1}$). Nevertheless, retention of inorganic N was substantial, with 26% (3.3 Mg N $y^{-1}$) less inorganic N flowing out of the lake chain than flowed in. Denitrification removed 0.9 Mg N $y^{-1}$ (24%) of this N. The remaining 2.6 Mg N $y^{-1}$ was either stored in sediments and standing biomass or exported through unmeasured fluxes (i.e., particulate and organic N fluxes, flood export, leaching to groundwater, or $NH_4^+$ or $NO_x$ volatilization) (Table 5.4).

Fertilizer application was the most important flux of inorganic N onto the floodplain, contributing 2.2 Mg N $y^{-1}$, while irrigation delivered another 0.4 Mg N $y^{-1}$. There was no measurable hydrologic flux of N from the floodplain, thus by definition, all of the N received by the floodplain was retained. Denitrification was far and away the most important retention mechanism, removing 2.0 Mg N $y^{-1}$ (74%) of the flux of inorganic N onto the floodplain (Table 5.4). An additional 0.7 Mg N $y^{-1}$ was either stored by the floodplain or lost via unmeasured fluxes (i.e., subsurface leaching, surface runoff, or $NH_4^+$ or $NO_x$ volatilization).

In total, the stream-floodplain complex appeared to retain or remove 36% (5.5 Mg N $y^{-1}$) of the flux of inorganic N into the ecosystem. Denitrification in lake sediments and floodplain soils accounted for 50% of this total (2.7 Mg N $y^{-1}$).

## Discussion

### *Factors influencing potential denitrification rates in lakes and streams*

Since its first development (Yoshinari and Knowles 1976, Smith et al. 1978), variations of the acetylene-block denitrification enzyme assay have been extensively used to provide estimates of the existing microbial community's capacity for denitrification (Table 5.5). Although the technique is not without its critics (Seitzinger et al. 1993, Svensson 1997) who note that it tends to underestimate denitrification rates, especially when coupled nitrification-denitrification is responsible for a large fraction of denitrification activity (Rudolph et al. 1991), because it responds well to longer-term variation in the factors that control denitrification, the acetylene-block technique has been widely adopted for comparison of soils, ecosystems and treatments (Groffman et al. 1999).

Potential denitrification rates (DEA) reported in this study are on the high end of those reported in mass-specific units, but are within ranges typical of other studies (Table

5.5). The DEA in IBW lake sediments (2.55 - 6.49 mg N $kg^{-1}$ $h^{-1}$) was higher than that reported from studies of other lakes, a result that most likely reflects the paucity of studies reporting mass-specific DEA in lake sediments. DEA rates in other aquatic ecosystems including streams (0.01 - 3.64 mg N $kg^{-1}$ $h^{-1}$) and estuaries (0.434 - 4.26 mg N $kg^{-1}$ $h^{-1}$) are of a similar magnitude (Table 5.5). DEA rates observed in IBW's floodplain soils were similar to rates from studies of other urban ecosystems (Groffman et al. 2002, Groffman and Crawford 2003, Zhu et al. 2004; Table 5.5)

Within IBW, DEA varied strongly as a function of patch type. Furthermore, controls on DEA also differed between patches. Although either organic matter content or $NO_3^-$ concentration could be used to predict DEA, these relationships varied with patch type. This suggests that while similar processes drive DEA in each patch type, the nature of denitrifier response is different in lakes, streams and floodplains, in agreement with work in other urban soils where DEA was found to be a function of organic matter content (Zhu et al. 2004) or both water and organic matter content (Groffman and Crawford 2003). Unfortunately, because of the high degree of multicollinearity between the independent variables in this study, it was impossible to tease out relative importance of different drivers, via this analysis.

Results of experiments 1 and 2 suggest that denitrification in IBW's lakes, though influenced by organic matter content, was limited by N. This N may be supplied either by diffusion from the overlying $NO_3^-$-rich lake water or by nitrification of the abundant $NH_4^+$ in the sediments. Because $C_2H_2$ inhibits nitrification, slurry assays shed little light on the importance of coupled nitrification-denitrification in lake sediments. Some studies have demonstrated that most of the $NO_3^-$ denitrified in lake sediments is produced in lake sediments (Klingensmith and Alexander 1983, Seitzinger 1988), while others have shown diffusion of $NO_3^-$ from the overlying water limits denitrification (Mengis et al. 1997, Tomaszek and Czerwieniec 2003). While coupled nitrification-denitrification is potentially important in IBW's lakes, the hypothesis that diffusion supplies much of the $NO_3^-$ denitrified in the sediments is supported by high denitrification rates observed in the intact core assay during which nitrification was blocked by the addition of $C_2H_2$.

Denitrification in floodplain soils was not limited by $NO_3^-$ or C availability, yet was still limited by environmental conditions, specifically, the availability of water (experiment 3). This is consistent with other research showing that denitrification rates increase with added water or reduced aeration (Bremner and Shaw 1958, Groffman and Tiedje 1989, Frank and Groffman 1998). The mechanism, however, is unclear. Water probably helps create anoxic microsites by limiting the diffusion of oxygen to these areas; however, the fact that anoxia alone only marginally stimulated denitrification rates (experiment 4) suggests that the water provided an additional benefit to denitrifiers. Rewetting soils has been shown to stimulate aerobic microbial processes like respiration, N mineralization and nitrification (Davidson et al. 1990, Fierer and Schimel 2002, Belnap et al. 2005) as well as anaerobic denitrification. We therefore hypothesize that the rewetting of floodplain soils stimulated denitrification both by creating favorable redox conditions and by directly stimulating microbial activity, either by rehydrating denitrifiers or by mobilizing substrates in the soil. Although denitrification in soil slurries was not stimulated until the soil water content exceeded 31%, the amount of water required to stimulate denitrification activity *in situ*, where soil structure is intact and pore space reduced, is probably much lower.

Although water alone stimulated denitrification in floodplain soils during experiments 3 and 4, denitrification rates did appear low when compared to potential soil denitrification rates. For example, potential denitrification, as estimated by DEA, was 1.5 ± 0.1 mg $N_2O$-N $kg^{-1}$ $h^{-1}$ whereas average denitrification rates of wet soils in experiment 4, regardless of the anoxia treatment, were 0.8 ± 0.1.mg $N_2O$-N $kg^{-1}$ $h^{-1}$. Although this may indicate a stimulatory effect of C and/or $NO_3^-$ additions, it more likely reflects temporal variability in denitrification rates.

*Actual denitrification rates*

Intact soil and sediment cores provided the best estimates of actual denitrification rates. Because denitrification rates were estimated from cores collected over a short time period, we were unable to estimate extent of seasonal variation in denitrification rates. Other authors have shown that denitrification rates often vary substantially across seasons both in lakes (Van Luijn et al. 1999, Hasegawa and Okino 2004) and in floodplains (Groffman and Tiedje 1989, Clément et al. 2002). In lakes, much of this variation has been attributed to seasonal changes in temperature and nutrient availability, whereas in soils, seasonal variation in denitrification rates is more frequently a function of changes in soil moisture content as well as temperature. Nevertheless, we remain confident that the estimates developed from intact-core assays represent good first approximations of patch-specific denitrification rates in IBW. This assertion is supported by the degree of concordance between rates of denitrification we report for lake sediments and floodplain soils and those reported in other studies (Table 5.6).

Because rates measured by the acetylene-block technique do not include the contribution of coupled nitrification-denitrification, our estimates may, in fact, be low (Seitzinger et al. 1993). This is particularly true for estimates of denitrification in lake sediments, where $NO_3^-$ concentrations were low and $NH_4^+$ concentrations were high. High $NO_3^-$ concentrations in floodplain soils and lack of response of DEA activity to added $NO_3^-$ suggest that coupled nitrification-denitrification does not limit denitrification in this patch. However, $NH_4^+$ concentrations are approximately one tenth those of $NO_3^-$, even though $NO_3^-$ is supplied at only 1.2 x the rate of $NH_4^+$ (Table 5.4), suggesting that combined nitrification and $NH_4^+$ uptake is more rapid than combined denitrification and $NO_3^-$ uptake (Table 5.4).

Like other urban sites where fertilization is common and organic matter abundant (Groffman et al. 2002, Zhu et al. 2004), actual denitrification rates in floodplain soils were high and were stimulated by simulated irrigation. This is consistent with research in forest (Groffman and Tiedje 1989) and grassland (Frank and Groffman 1998) soils, where simulated irrigation stimulated denitrification, but not with an earlier study of turf soils in retention basins of the CAP LTER ecosystem in which simulated irrigation did not increase denitrification (Zhu et al. 2004). The lack of agreement between our study and the previous work on retention basin soils is perplexing at first glance, however, the discrepancy may reflect methodological differences. In the retention basin study, intact soil cores received a stimulated irrigation event in which 3 cm of $NO_3^-$ enriched water was added and allowed to drain though the soils for 24 h prior to the incubation. Given the high initial soil moisture content of these soils, this approach may not have produced a net increase in soil moisture, thus explaining the inability of the simulated irrigation to stimulate denitrification. In addition, some soil cores were so impervious that the water remained on top. In these cores, denitrification removed a majority of the $NO_3^-$ in the overlying water during the pre incubation period, reducing $NO_3^-$-N in the standing water by > 3 mg/L (Zhu et al. 2004), suggesting that surface denitrification in these soils could be stimulated by water.

*Mass Balance*

Although the IBW stream-floodplain complex retained 300 kg N $ha^{-1}$ $y^{-1}$, this represents only 36% of the flux of N into the ecosystem with denitrification accounting for 50% of the retained N. The other 50% was stored in the ecosystem (or exported in unmeasured fluxes), suggesting an N accumulation rate of 150 kg N $ha^{-1}$ $y^{-1}$. Though high, this accrual rate would be only slightly higher than the 107 kg N $ha^{-1}$ $y^{-1}$ that the urban portion of the CAP ecosystem is estimated to store annually (Baker et al. 2001). Denitrification explains much of the difference as Baker et al. (2001) estimate the average urban denitrification rate is 38 kg N $ha^{-1}$ $y^{-1}$ as compared to 150 kg N $ha^{-1}$ $y^{-1}$ for the IBW stream-floodplain complex. Thus maximum total retention rate ($\Delta$ storage + denitrification) of the IBW floodplain complex (300 kg N $ha^{-1}$ $y^{-1}$) is much higher than the average urban retention rate estimated for the CAP ecosystem (146 kg N $ha^{-1}$ $y^{-1}$; Baker et al 2001), strongly suggesting IBW is a hotspot of N retention.

Although lakes represent only 18% of the area in the stream-floodplain complex, they were responsible for 46% of the N retained by the ecosystem, suggesting they are indeed hot spots for N retention. Of the 1000 kg N $ha^{-1}$ $y^{-1}$ retained by lakes, 26% (260 kg N $ha^{-1}$ $y^{-1}$) was denitrified. The remaining N was stored in the lakes, exported to the aquifer, or exported downstream as particulate and organic N. Export of N to the aquifer is likely low, however, as clay liners in many of the lakes limit the vertical flux of water (Chapter 2). Storage of organic matter in the sediments, however, is a likely retention mechanism. High rates of primary production have been observed (GPP > 4 g C $m^{-2}d^{-1}$; Roach, *unpublished data*) and deep sediments (> 1m thick) have accumulated in many of the lakes (Roach, *personal observation*), lending support to this assertion. However, severe flash floods, though rare, may export a large proportion of the accumulated organic N if sediments are mobilized and swept downstream (Choen and Laronne 2005). Additionally, phytoplankton are responsible for much of the primary production in the wash and represent a potentially important unmeasured export of particulate organic N.

Concentration of $NO_3^-$-N in waters entering IBW varied dramatically over time, with concentrations at the top of the reach ranging from less than 0.01 mg $L^{-1}$ to in excess of 6.6 mg $L^{-1}$ (Chapter 3), owing to variations in the amount of groundwater entering into the wash. An additional source of variation is the Roosevelt well, which discharges water with an average of $NO_3^-$-N concentration of 3.35 ± 0.13 mg $L^{-1}$ on the 11 of 48 sampling dates that it was pumping (Chapter 3). As a result, actual retention is likely to vary substantially due to changes in the diffusion gradient produced by fluctuations in the $NO_3^-$ concentrations of the overlying lake water.

Areal retention rates were lower in the floodplain than in the lakes (170 kg N $ha^{-1}$ $y^{-1}$ and 1000 kg N $ha^{-1}$ $y^{-1}$, respectively) as were denitrification rates (120 kg N $ha^{-1}$ $y^{-1}$ and 260 kg N ha $y^{-1}$). Nevertheless, virtually the entire flux of N onto the floodplain was retained, with denitrification responsible for the majority (74%) of retention. Although most denitrification occurred when the floodplain was wet, estimates of annual floodplain denitrification were sensitive to both the number of days per annum that the floodplain was irrigated, as well as estimates of the wet and dry denitrification rates. Applying mean denitrification rates for the floodplain ($DR_{fp,dry}$ = 0.59 mg N $m^{-2}$ $h^{-1}$; $DR_{fp,wet}$ = 2.55 mg N $m^{-2}$ $h^{-1}$) and varying irrigation days ($d_{wet}$) between 95 and 218 per year, annual denitrification ranged from 1.5 to 2.4 Mg N $y^{-1}$. Holding $d_{wet}$ fixed at 156 and varying wet and dry denitrification rates by $\pm$ 1 SE (0.80 mg N $m^{-2}$ $h^{-1}$ and 0.11 mg N $m^{-2}$ $h^{-1}$, respectively) yielded a similar range in annual denitrification rates of 1.4 to 2.5 Mg N $y^{-1}$. Under all scenarios, 60 - 86% of N removal occurred when the floodplain was wet, suggesting that post-irrigation and post-rain periods could be considered hot moments (McClain et al. 2003) for denitrification.

### *Cross-system linkages and implications for urban ecology.*

Patch-specific characteristics are important determinants of microbial activity and ecosystem function. For example, denitrification rates in aquatic systems have been positively correlated with sediment characteristics like the proportion of fine particles (Flemer et al. 1998, García-Ruiz et al. 1998a, Pattinson et al. 1998). Similarly, denitrification rates in soil vary with water-filled pore space, soil texture, and soil organic matter (Groffman and Tiedje 1989, Pinay et al. 2000, Pinay et al. 2003). Differences between these patch types, not to mention the gross differences between lakes, streams and floodplains, are to a large extent a function of geomorphology and pedology. As such, fluvial geomorphic processes and hydrologic regimes are frequently responsible for maintaining patch-specific differences.

In desert ecosystems, hydrologic flows between patches deliver water and other resources that influence the timing and rates of microbial activities (Belnap et al. 2005). These cross-system linkages can be important determinants of landscape level fluxes because they link patches with different characteristics. Cross-system linkages also play critical roles in stimulating denitrification of recipient systems by supplying needed substrates to recipient patches (Edmonds and Grimm in review). For example, hydrologic flows have been shown to stimulate denitrification by transferring organic C from the surface stream to hyporheic (Holmes et al. 1996, Lefebvre et al. 2004) or $NO_3^-$ floodplain sediments (Baker and Vervier 2004, Richardson et al. 2004). In Indian Bend Wash, cross-system linkages occurring over a wide range of spatial and temporal scales play a key role in regulating annual denitrification. At small scales flux of irrigation water from lake L-6 to floodplains supplies N to the floodplain and stimulates denitrification by creating favorable environmental conditions. At larger spatial and temporal scales, the canal system maintains hydrologic characteristics of lake and stream patches by diverting water from adjacent watersheds through the lake chain (Chapter 2). At a similar spatial scale but a longer temporal scale, groundwater pumping connects the aquifer underlying the urban area to surface flows. Without this connection, $NO_3$ in groundwater, which has percolated from agricultural fields and slowly accumulated in the aquifers (Xu 2002) would not reach the surface. At the largest spatial scale, the production, transport, and application of fertilizers links the wash with remote ecosystems where $N_2$ is anthropogenically fixed. Thus, through canals and via importation of fertilizer, denitrification in IBW is linked to central Arizona's ever-growing ecological footprint (Luck et al. 2001).

In comparatively pristine ecosystems, cross-system linkages are, to a large extent, a function of ecosystem hydrology and geomorphology and connections between patches are made when water flows (Belnap et al. 2005). In urban ecosystems, fluvial geomorphic processes are short-circuited. Bulldozers, not floods, create geomorphic patches such as the lakes of IBW (Chapter 2). Naturally occurring linkages are severed as a result of stream channel simplification and channelization (Grimm et al. 2004). Although new, novel linkages are created as development proceeds, because managers' goals are often set by social institutions without regard to ecological ramifications (Grimm et al. 2000), these linkages may or may not maintain ecosystem function.

## ACKNOWLEDGEMENTS

Thanks to Tom Colella, M. Amy DiIorio, Noah Dillard, Lisa Eby, Jennifer Edmonds, Tamara Harms, Jim Heffernan, Tracy Johns, Cathy Kochert, Libby Larson, David Lewis, Wayne Porter, Phil Tarrant, Harriet Van Vleck, and Jill Welter for help in the field, lab analysis, and conceptual development. Thanks to the City of Scottsdale and Mike Bishop for data on the management and maintenance of Indian Bend Wash. This manuscript was produced with support from the Urban Ecology IGERT and CAP LTER programs at Arizona State University, NSF Grants DGE-9987612 and DEB-9714833 and -0423704, respectively. Additional support was provided by the Arizona State University's Center for Environmental Studies.

## LITERATURE CITED

Aber, J. D., K. J. Nadelhofer, P. Steudler, and J. M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience **39**:378-386.

Ahlgren, I., F. Sörensson, Waara, and K. Vrede. 1994. Nitrogen budgets in relation to microbial transformations in lakes. Ambio **23**:367-377.

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

Baker, m. A., and P. Vervier. 2004. Hydrologic variability, organic matter supply and denitrification in the Garonne River ecosystem. Freshwater Biology **49**:181-190.

Belnap, J., R. 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.

Boesch, D. F., Brinsfield, and R. E. Magnien. 2001. Chesapeake Bay eutrophication: scientific understanding, ecosystem restoration, and challenges for agriculture. Journal of Environmental Quality **30**:303-320.

Bremner, J. M., and K. Shaw. 1958. Denitrification in soil II. Journal of Agricultural Science **51**:40-52.

Brettar, I., and M. G. Höfle. 2002. Close correlation between the nitrate elimination rate by denitrification and the organic matter content in hardwood forest soils of the upper Rhine floodplain (France). Wetlands **22**:214-224.

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**:559-569.

Carpenter, S. R., and M. L. Pace. 1997. Dystropy and eutrophy in lake ecosystems: implications of fluctuating inputs. Oikos **78**:3-14.

Choen, H., and J. B. Laronne. 2005. High rates of sediment transport by flashfloods in the Southern Judean Desert, Israel. Hydrological Processes **19**:1687-1702.

City of Scottsdale. 1985. Indian Bend Wash. Communications and Public Affairs, Scottsdale, AZ.

Clément, J., G. Pinay, and P. Marmonier. 2002. Seasonal dynamics of denitrification along topohydrosequences in three different riparian wetlands. Journal of Environmental Quality **31**:1025-1037.

Cooper, A. B. 1990. Nitrate depletion in the riparian zone and stream channel of a small headwater catchment. Hydrobiologia **202**:13-26.

Davidson, E. A., J. M. Stark, and M. K. Firestone. 1990. Microbial production and consumption of nitrate in an annual grassland. Ecology **71**:1968-1975.

Edmonds, J., and N. B. Grimm. in review. Terrestrial-aquatic linkages in a desert stream ecosystem: influence of flowpath and antecedent conditions on dissolved organic carbon chemistry.

Essington, T. E., and S. R. Carpenter. 2000. Nutrient cycling in lakes and streams: insights from a comparative analysis. Ecosystems **3**:131-143.

Esteves, F. A., A. Enrich-Prast, and D. D. Biesboer. 2001. Potential denitrification in submerged natural and impacted sediments of Lake Batata, an Amazonian lake. Hydrobiologia **444: 111-117**.

Fierer, N., and J. P. Schimel. 2002. Effects of drying-rewetting frequency on soil carbon and nitrogen transformations. Soil Biology and Biochemistry **34**:777-787.

Flemer, D. A., E. M. Lores, and C. M. Bundrick. 1998. Potential sediment denitrification rates in estuaries of northern Gulf of Mexico. Journal of Environmental Quality **27**:859-868.

Frank, D. A., and P. M. Groffman. 1998. Denitrification in a semi-arid grazing ecosystem. Oecologia **117**:564-569.

García-Ruiz, R., S. N. Pattinson, and B. A. Whitton. 1998a. Denitrification in river sediments: relationship between process rate and properties of water and sediment. Freshwater Biology **39**:467-476.

García-Ruiz, R., S. N. Pattinson, and B. A. Whitton. 1998b. Denitrification in sediments of the freshwater tidal Yorkshire Ouse. The Science of the Total Environment **210/211**:321-327.

Gardner, W. S., T. F. Nalepa, and J. M. Malczyk. 1987. Nitrogen mineralization and denitrification in Lake Michigan sediments. Limnology and Oceanography **32**:1226-1248.

Gardner, W. S., L. Yang, J. B. Cotner, T. H. Hohengen, and P. J. Lavrentyev. 2001. Nitrogen dynamics in sandy freshwater sediments (Saginaw Bay, Lake Huron). Journal of Great Lakes Research **27**:84-97.

Gergel, S. E., S. R. Carpenter, and E. H. Stanley. 2005. Do dams and levees impact nitrogen cycling? Stimulating the effects of flood alterations on floodplain denitrification. Global Change Biology **11**:1352-1367.

Goolsby, D. A., and W. A. Battaglin. 2001. Long-term changes in concentrations and flux of nitrogen in the Mississippi River Basin, USA. Hydrological Processes **15**:1209-1226.

Graf, W. L. 1975. The impact of surburbanization on fluvial hydrology. Water Resources Research **11**:690-692.

Grimm, N., R. Arrowsmith, C. Eisinger, J. Heffernan, D. B. Lewis, A. MacLeod, L. Preshad, W. J. Roach, T. Rychener, and R. W. Sheibley. 2004. Effects of urbanization on nutrient biogeochemistry of aridland streams. *in* G. Asner and R. Houghton, editors. Ecosystems and Land Use Change. American Geophysical Union.

Grimm, N. B., J. M. Grove, S. T. A. Pickett, and C. L. Redman. 2000. Integrated approaches to long-term studies of urban ecological systems. BioScience **50**:571-583.

Grimm, N. B., R. W. Sheibley, C. L. Crenshaw, C. N. Dahm, and W. J. Roach. 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.

Groffman, P. M., and M. K. Crawford. 2003. Denitrification potential in urban riparian zones. Journal of Environmental Quality **32**:1144-1149.

Groffman, P. M., A. M. Dorsey, and P. M. Mayer. 2005. N processing within geomorphic structures in urban streams. Journal of the North American Benthological Society **24**.

Groffman, P. M., E. A. Holland, D. D. Myrold, G. P. Robertson, and X. Zou. 1999. Denitrification. Pages 272-290 *in* G. P. Robertson, D. C. Coleman, C. S. Bledsoe, and P. Sollins, editors. Standard Soil Methods for Long-Term Ecological Research. Oxford University Press, New York.

Groffman, P. M., and J. M. Tiedje. 1989. Denitrification in north temperate forest soils: spatial and temporal patterns at the landscape and seasonal scales. Soil Biology and Biochemistry **21**:613-620.

Groffman, P. M., D. R. Zak, S. Christensen, A. Mosier, and J. M. Tiedje. 1993. Early spring nitrogen dynamics in a temperate forest landscape. Ecology **74**:1579-1585.

Hasegawa, T., and T. Okino. 2004. Seasonal variation of denitrification rate in Lake Suwa sediment. Limnology **5**:33-39.

Holmes, R. M., J. B. Jones, Jr., S. G. Fisher, and N. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry **33**:125-146.

Inwood, S. E., J. L. Tank, and M. J. Bernot. 2005. Patterns of denitrification associated with land use in 9 midwestern streams. Journal of the North American Benthological Society **24**:227-245.

Jansson, M., L. Leonardson, and J. Fejes. 1994. Denitrification and nitrogen retention in a farmland stream in southern Sweden. Ambio **23**:326-331.

Kaye, J., P. M. Groffman, N. B. Grimm, L. A. Baker, and R. V. Pouyat. in press. A distinct urban biogeochemistry? Trends in Ecology and Evolution.

Kern, J., A. Darwich, K. Furch, and W. J. Junk. 1996. Seasonal denitrification in flooded and exposed sediments from the Amazon floodplain at Lago Camaleão. Microbial Ecology **32**:47-57.

Kling, G. W., G. W. Kipphut, M. M. Miller, and W. J. O'Brien. 2000. Integration of lakes and streams in a landscape perspective: the importance of material processing on spatial patterns and temporal coherence. Freshwater Biology **43**:477-497.

Klingensmith, K. M., and V. Alexander. 1983. Sediment nitrification, denitrification, and nitrous oxide production in a deep arctic lake. Applied and Environmental Microbiology **46**:1084-1092.

Kreibich, H., and J. Kern. 2003. Nitrogen fixation and denitrification in a floodplain forest near Manaus, Brazil. Hydrological Processes **17**:1431-1441.

Laursen, A. E., and S. Seitzinger. 2002. Measurement of denitrification in rivers: an integrated whole reach approach. Hydrobiologia **485**:67-81.

Lefebvre, S., P. Marmonier, and G. Pinay. 2004. Stream regulation and nitrogen dynamics in sediment interstices: comparison of natural and straightened sectors of a third-order stream. River Research and Applications **20**:499-512.

Luck, M. A., G. D. Jenerette, J. Wu, and N. B. Grimm. 2001. The urban funnel model and spatially heterogeneous footprint. Ecosystems **4**:782-796.

McAuliffe, J. R. 1994. Landscape evolution, soil formation, and ecological patterns and processes in Sonoran Desert bajadas. Ecological Monographs **54**:111-148.

McClain, M. E., B. E. W., C. L. Dent, C. 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 aquatic and terrestrial ecosystems. Ecosystems **6**:301-312.

Mengis, M., R. Gächter, B. Wehrli, and S. Bernasconi. 1997. Nitrogen elimination in two deep eutrophic lakes. Limnology and Oceanography **42**:1530-1543.

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society **24**:602-612.

Moeller, R. E., R. G. Wetzel, and C. W. Osenberg. 1988. Concordance of phosphorus limitation in lakes: Bacterioplankton, phytoplankton, epiphyte-snail consumers, and rooted macrophytes. Pages 318-325 *in* E. Jeppesen, M. Søndergaard, and K. Christoffersen, editors. The Structuring Role of Submerged Macrophytes. Springer-Verlag, New York.

Mosier, A. R., M. A. Bleken, P. Chaiwanakupt, E. C. Ellis, J. R. Freney, R. B. Howarth, P. A. Matson, K. Minami, R. Naylor, K. N. Weeks, and Z.-L. Zhu. 2001. Policy implications of human-accelerated nitrogen cycling. Biogeochemistry **52**:281-320.

Mulholland, P. J., H. M. Valett, J. R. Webster, S. A. Thomas, L. W. Cooper, S. K. Hamilton, and B. J. Peterson. 2004. Stream denitrification and total nitrate uptake rates measured using a field $^{15}N$ tracer addition approach. Limnology and Oceanography **49**:809-820.

Neilsen, E. G., and L. K. Lee. 1987. The magnitude and cost of groundwater contamination from agricultural contamination: a national perspective. AGES870318, Natural Resources Economics Division, U.S. Department of Agriculture, Washington, D.C.

Padgett, P. E., E. B. Allen, A. Bytnerowicz, and R. A. Minich. 1999. Changes in soil inorganic nitrogen as related to atmospheric nitrogenous pollutants in southern California. Atmospheric Environment **33**:769-781.

Pattinson, S. N., R. García-Ruiz, and B. A. Whitton. 1998. Spatial and seasonal variation in denitrification in the Swale-Ouse system, a river continuum. The Science of the Total Environment **210/211**:289-305.

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. 1991. Denitrification: enzyme content and activity in desert soils. Soil Biology and Biochemistry **23**:845-855.

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.

Pickett, S. T. A., J. Burch, WR, S. E. Dalton, T. W. Foresman, J. M. Grove, and R. Rowntree. 1997. A conceptual framework for the study of human ecosystems in urban areas. Urban Ecosystems **1**:185-199.

Pickett, S. T. A., M. L. Candenasso, J. M. Grove, C. H. Nilon, R. V. Pouyat, W. C. Zipperer, and R. Costanza. 2001. Urban ecological systems: linking terrestrial ecological, physical and socioeconomic components of metropolitan areas. Annual Review of Ecology and Systematics **32**:127-157.

Pinay, G., V. J. Black, A. M. Planty-Tabacchi, B. Gumiero, and H. Decamps. 2000. Geomorphic control of denitrification in large river floodplain soils. Biogeochemistry **50**:163-182.

Pinay, G., T. O'Keefe, R. Edwards, and R. J. Naiman. 2003. Potential denitrification activity in the landscape of a western Alaska drainage basin. Ecosystems **6**:336-343.

Richardson, W. B., E. A. Strauss, L. A. Bartsch, E. M. Monroe, J. C. Cavanaugh, L. Vingum, and D. M. Soballe. 2004. Denitrification in the upper Mississippi River: rates, controls, and contribution to nitrate flux. Canadian Journal of Fisheries and Aquatic Sciences **61**:1102-1112.

Royer, T. V., J. L. Tank, and M. B. David. 2004. Transport and fate of nitrate in headwater agricultural streams in Illinois. Journal of Environmental Quality **33**:1296-1304.

Rudolph, J. P., P. Frenzel, and N. Pfennig. 1991. Acetylene inhibition technique underestimates in situ denitrification rates in intact cores of freshwater sediments. FEMS Microbial Ecology **85**:101=106.

Saunders, D. L., and J. Kalff. 2001. Denitrification rates in the sediments of lake Memphremagog, Canada-USA. Water Research **35**:1897-1904.

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

Schaller, J. L., T. V. Royer, M. B. David, and J. L. Tank. 2004. Denitrification associated with plants and sediments in an agricultural stream. Journal of the North American Benthological Society **23**:667-676.

Schick, A. P. 1995. Fluvial processes on an urbanizing alluvial fan: Eilat, Israel. Pages 209-217 *in* Natural and Anthropogenic Influences in Fluvial Geomorphology. Geophysical Monograph.

Seitzinger, S. P. 1988. Denitrification in freshwater and coastal marine ecosystems: ecological and geochemical significance. Limnology and Oceanography **33**:702-724.

Seitzinger, S. P., R. V. Styles, E. W. Boyer, R. B. Alexander, G. Billen, R. W. Howarth, B. Mayer, and N. V. Van Breemen. 1993. Denitrification measurements in aquatic sediments: a comparison of three methods. Biogeochemistry **33**:702-724.

Šimek, M., D. Elhottová, F. Klimeš, and D. Hopkins. 2004. Emissions of $N_2O$ and $CO_2$, denitrification measurements and soil properties in red clover and ryegrass stands. Soil Biology and Biochemistry **36**:9-21.

Sjodin, A. L., W. M. Lewis Jr., and J. F. Saunders III. 1997. Denitrification as a component of the nitrogen budget for a large plains river. Biogeochemistry **39**:327-342.

Smith, M. S., M. K. Firestone, and J. M. Tiedje. 1978. The acetylene inhibition method for short-term measurement of soils denitrification and its evaluation using nitrogen-13. Soil Science Society of America Journal **42**:611-615.

Sørensen, J. 1978. Denitrification rates in a marine sediment as measured by the acetylene inhibition technique. Applied Environmental Microbiology **36**:139-143.

Stanley, E. H., and M. W. Doyle. 2002. A geomorphic perspective on nutrient retention following dam removal. BioScience **52**:693-701.

Stephen, D., B. Moss, and G. Phillips. 1998. The relative importance of top-down and bottom-up control of phytoplankton in a shallow macrophyte-dominated lake. Freshwater Biology **39**:699-713.

Sullivan, J. F. 1998. 1997 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Svensson, J. 1997. Influence of *Chironomus plumosus* larvae on ammonium flux and denitrification (measured by the acetylene blockage- and the isotope pairing-technique) in eutrophic lake sediment. Hydrobiologia **346**:157-168.

Tomaszek, J. A., and E. Czerwieniec. 2003. Denitrification and oxygen consumption in bottom sediments: factors influencing rates of the process. Hydrobiologia **504**:59-65.

U.S. Army Corps of Engineers. 1975. Gila River Basin, Arizona, Indian Bend Wash, Design Memorandum No. 1, General Design Memorandum, Phase II, Project Design for Indian Bend Wash. Los Angeles.

Van Luijn, F., P. C. M. Boers, L. Lijklema, and J. P. R. A. Sweerts. 1999. Nitrogen fluxes and processes in sandy and muddy sediments from a shallow eutrophic lake. Water Research **33**:33-42.

Vitousek, P. M., J. D. Aber, R. W. Howarth, G. E. Likens, P. A. Matson, D. W. Schindler, and W. H. Schlesinger. 1997. Human alteration of the global nitrogen cycle: causes and consequences. Issues in Ecology **1**:1-14.

Walsh, C. J., T. D. Fletcher, and A. R. Ladson. 2005a. Stream restoration in urban catchments through redesigning stormwater systems: looking to the catchment to save the stream. Journal of the North American Benthological Society **24**:690-705.

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

Watts, S. H., and S. Seitzinger. 2000. Denitrification rates in organic and mineral soils from riparian sites: a comparison of $N_2$ flux and acetylene inhibition methods. Soil Biology and Biochemistry **32**:1383-1392.

Webster, K. E., P. A. Soranno, S. B. Baines, T. K. Kratz, C. J. Bowser, P. J. Dillon, P. Campbell, E. J. Fee, and R. E. Hecky. 2000. Structuring features of lake districts: landscape controls on lake chemical responses to drought. Freshwater Biology **43**:499-515.

Weisner, S. E. B., P. G. Eriksson, W. Granéli, and L. Leonardson. 1994. Influence of macrophytes on nitrate removal in wetlands. Ambio **23**:363-366.

Welter, J. W. 1994. Nitrogen transport and processing in the intermittent drainage network: linking terrestrial and aquatic ecosystems. Arizona State University, Tempe, AZ.

Xu, Y. 2002. Assessment and prediction of groundwater nitrate contamination trends in the Salt River Project Area, Arizona. Dissertation. Arizona State University, Tempe, AZ.

Yoshinari, T., and R. Knowles. 1976. Acetylene inhibition of nitrous oxide reduction by denitrifying bacteria. Biochemical and Biophysical Research Communications **69**:705-710.

Zar, J. H. 1996. Biostatistical Analysis, 3rd edition. Prentice Hall, Upper Saddle River, NJ.

Zhu, W.-X., N. D. Dillard, and N. B. Grimm. 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. Biogeochemistry **71**:177-196.

Zhu, W.-X., D. Hope, C. Gries, and N. Grimm. in press. Soil characteristics and the storage of inorganic nitrogen under different land uses in an arid urban ecosystem. Ecosystems.

Table 5.1. Pearson correlation coefficients for correlations between proportion water ($pH_2O$), proportion organic matter (pOM) and log transformed $NO_3^-$ content ($log_{10}NO_3$) of samples used to estimate DEA.

| | | | |
|---|---|---|---|
| Lake | | | |
| | $pH_20$ | pOM | $log_{10}(NO_3\text{-}N)$ |
| $pH_20$ | 1 | | |
| pOM | 0.93*** | 1 | |
| $log_{10}(NO_3\text{-}N)$ | 0.61*** | 0.46*** | 1 |
| Floodplain | | | |
| | $pH_20$ | pOM | $log_{10}(NO_3\text{-}N)$ |
| $pH_20$ | 1 | | |
| pOM | 0.76*** | 1 | |
| $log_{10}(NO_3\text{-}N)$ | 0.40* | 0.51** | 1 |
| Stream | | | |
| | $pH_20$ | pOM | $log_{10}(NO_3\text{-}N)$ |
| $pH_20$ | 1 | | |
| pOM | 0.78*** | 1 | |
| $log_{10}(NO_3\text{-}N)$ | 0.40 | 0.61*** | 1 |

*, **, and *** indicate Bonferroni-adjuted probability that the

Table 5.2. Results of multiple linear regression analyses showing the effects of proportion organic matter (pOM), proportion water content ($pH_20$) or $NO_3^-$ concentration ($log_{10}NO_3$-N) on DEA, and how these effects vary with patch. $NO_3^-$ content was log-transformed prior to analysis. 'Lake' and 'Floodplain' are dummy variables that test whether the constant is different for either of these two patch types than it is for streams. Interactions of these two dummy variables with pOM, $pH_2O$ or $log_{10}NO_3$-N test whether slope of these relationships differs as a function of patch type. Overall significance (ANOVA result and adjusted $R^2$ value) is reported for each model.

| | | | | | |
|---|---|---|---|---|---|
| Proportion Organic Matter | | | | Adj-$R^2$ = | 0.864 |
| Effect | | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | | 0.0 | 0.3 | -0.02 | 0.980 |
| Lake | | 1.9 | 0.4 | 4.50 | < 0.001 |
| Floodplain | | 0.1 | 0.5 | 0.13 | 0.896 |
| pOM | | 64.5 | 13.0 | 4.98 | < 0.001 |
| pOM * Lake | | -11.5 | 14.1 | -0.82 | 0.414 |
| pOM * Floodplain | | -39.7 | 15.1 | -2.63 | 0.010 |
| ANOVA | SS | df | MS | F-ratio | *p* |
| Regression | 368.88 | 5 | 73.78 | 140.34 | < 0.001 |
| Error | 54.7 | 104 | 0.53 | | |
| Proportion Water | | | | Adj-$R^2$ = | 0.895 |
| Effect | | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | | -1.43 | 0.44 | -3.23 | 0.002 |
| Lake | | 1.20 | 0.62 | 1.95 | 0.053 |
| Floodplain | | 1.60 | 0.58 | 2.77 | 0.006 |
| $pH_20$ | | 11.46 | 1.96 | 5.84 | < 0.001 |
| $pH_20$ * Lake | | -2.97 | 2.09 | -1.42 | 0.156 |
| $pH_20$ * Floodplain | | -4.03 | 2.73 | -1.47 | 0.142 |
| ANOVA | SS | df | MS | F-ratio | *p* |
| Regression | 381.31 | 5 | 76.26 | 187.81 | < 0.001 |
| Error | 42.2 | 104 | 0.41 | | |
| Nitrate Content | | | | Adj-$R^2$ = | 0.797 |
| Effect | | Coefficient | Std. Error | t | *p* (2-tail) |
| Constant | | 5.41 | 1.23 | 4.38 | < 0.001 |
| Lake | | 7.56 | 1.83 | 4.13 | < 0.001 |
| Floodplain | | -3.24 | 1.52 | -2.13 | 0.035 |
| $log_{10}(NO_3$-N) | | 1.22 | 0.34 | 3.54 | < 0.001 |
| $log_{10}(NO_3$-N) * Lake | | 1.02 | 0.50 | 2.04 | 0.044 |
| $log_{10}(NO_3$-N) * Floodplain | | -0.92 | 0.54 | -1.69 | 0.093 |
| ANOVA | SS | df | MS | F-ratio | *p* |
| Regression | 341.9 | 5 | 68.38 | 87.10 | < 0.001 |
| Error | 81.7 | 104 | 0.79 | | |

Table 5.3. ANOVA table for Experiment 4 where effects of creating an anoxic environment and adding water is contrasted. The variable, CORE, is a blocking variable identifying the original core that each subsample was taken from. Each core was subsampled to establish the four treatments as detailed in the text.

| Effect | SS | df | MS | F-ratio | *p* |
|---|---|---|---|---|---|
| Core | 84.02 | 12 | 7.0 | 4.80 | <0.001 |
| Anoxia | 5.15 | 1 | 5.1 | 3.53 | 0.068 |
| Water | 89.30 | 1 | 89.3 | 61.28 | <0.001 |
| Anoxia*Water | 0.54 | 1 | 0.5 | 0.37 | 0.547 |
| Error | 52.46 | 36 | 1.5 | | |

Table 5.4. Mass balance of the annual flux of inorganic N, by species, into the lakes and onto the floodplains of Vista del Camino Park. Annual retention ($R_i$) of inorganic N and denitrification ($Denit_i$) are estimated for each subsystem (lake and floodplain) as well as for the stream-floodplain complex as a whole. The difference between $R_i$ and $Denit_i$ provides an estimate of the N stored in sediments or lost in unmeasured fluxes. Estimates of inorganic N stored in lake sediments and floodplain soils is also provided.

| Flux/Pool | | $NH_4^+$-N | $NO_3^-$-N | Total iN |
|---|---|---|---|---|
| Lakes (3.3 ha) | | | | |
| Hydrologic flux IN via F In ($Flux_{L-3,IN}$) | (Mg N $y^{-1}$) | 0.3 | 10.4 | 10.7 |
| Hydrologic flux IN via Roosevelt Well ($Flux_{Well,IN}$) | (Mg N $y^{-1}$) | 0.0 | 2.5 | 2.5 |
| Hydrologic flux OUT via B Out ($Flux_{L-7,OUT}$) | (Mg N $y^{-1}$) | -0.5 | -8.9 | -9.4 |
| Hydrologic flux OUT via Irrigation ($Flux_{Irr,OUT}$) | (Mg N $y^{-1}$) | 0.0 | -0.4 | -0.4 |
| **$R_{LAKE} = \Sigma\ Flux_{i,IN} + \Sigma\ Flux_{i,OUT}$** | **(Mg N $y^{-1}$)** | **-0.2** | **3.6** | **3.3** |
| Flux out via Denitrification ($Denit_{LAKE}$) | (Mg N $y^{-1}$) | | 0.9 | 0.9 |
| **$\Delta S_{LAKE}$ + Unaccounted for N = $R_{LAKE} - Denit_{LAKE}$** | **(Mg N $y^{-1}$)** | **-0.2** | **2.7** | **2.5** |
| *Sediment Pool (inorganic)* | *(Mg N)* | *0.0* | *0.0* | *0.0* |
| Floodplains (15.4 ha) | | | | |
| Fertilizer Inputs ($Flux_{fert,IN}$) | (Mg N $y^{-1}$) | 1.1 | 1.0 | 2.2 |
| Irrigation Inputs from lakes ($Flux_{Irr,IN}$) | (Mg N $y^{-1}$) | 0.0 | 0.4 | 0.4 |
| Hydrologic flux off floodplain ($Flux_{FP,OUT}$) | (Mg N $y^{-1}$) | 0.0 | 0.0 | 0.0 |
| **$R_{FP} = \Sigma\ Flux_{FP,IN} + Flux_{FP,OUT}$** | **(Mg N $y^{-1}$)** | **1.2** | **1.4** | **2.6** |
| Flux out via Denitrification$_{dry}$ ($Denit_{FP,dry}$) | (Mg N $y^{-1}$) | | 0.5 | 0.5 |
| Flux out via Denitrification$_{wet}$ ($Denit_{FP,wet}$) | (Mg N $y^{-1}$) | | 1.5 | 1.5 |
| **$\Delta S_{FP}$ + Unaccounted for N = $R_{FP} - Denit_{FP}$** | **(Mg N $y^{-1}$)** | **1.2** | **-0.5** | **0.7** |
| *Soil Pool (inorganic)* | *(Mg N)* | *0.0* | *0.2* | *0.2* |
| Totals ( 18.7 ha) | | | | |
| $Flux_{Total,IN} = Flux_{L-3,IN} + Flux_{Well,IN} + Flus_{Fert,IN}$ | (Mg N $y^{-1}$) | 1.5 | 13.9 | 15.4 |
| $Flux_{Total,OUT} = Flux_{L-7,Out} + Flux_{FP,Out}$ | (Mg N $y^{-1}$) | -0.5 | -9.3 | -9.9 |
| **$R_{Total} = Flux_{Total,IN} + Flux_{Total,OUT}$** | **(Mg N $y^{-1}$)** | **0.9** | **4.6** | **5.5** |
| $Denit_{Total = DenitLAKE} + Denit_{FP,dry} + Denit_{FP,wet}$ | (Mg N $y^{-1}$) | 0.0 | 2.8 | 2.8 |
| **$\Delta S$ + Unaccounted for N = $R_{Total} - Denit_{Total}$** | **(Mg N $y^{-1}$)** | **0.9** | **1.8** | **2.7** |
| *Pools (inorganic)* | *(Mg N)* | *0.1* | *0.2* | *0.3* |

Table 5.5 Literature values of mass-specific denitrification rates estimated using the acetylene block technique on soil or sediment slurries incubated under various treatment conditions. Studies ranked by patch type and maximum denitrification rate.

| Site | US. State /Country | Description | treatment /media§ | Denitrification Rate | Citation |
|---|---|---|---|---|---|
| Lake | | | | | |
| Lake Batata | Brazil | Tropical forest | +N,+C | 0.02 - 0.08 | Esteves et al. 2001 |
| CAP-LTER, IBW | AZ | Urban desert | +N,+C | 0.1 - 3.0 | Larson and Grimm, unpublished |
| CAP-LTER, IBW | AZ | Urban desert | +N,+C | 2.55 - 6.49 | This Study |
| Estuary | | | | | |
| Perdido & Pensicola | Florida | Tidal estuary | +N,+C | 0.43-4.26 | Flemer et al. 1998 |
| Stream | | | | | |
| Sycamore Creek | AZ | Sonoran desert | +N,+C | 0.01 - 0.02 | Holmes et al. 1996 |
| Yorkshire Ouse | England | Freshwater tidal river | +N,+C | 0.41 - 0.49 | Garcia-Ruiz et al. 1998b |
| Scotsman Valley | New Zealand | Headwater stream, pasture | +N | 0.08 - 0.52 | Cooper et al. 1990 |
| Kalamazoo Watershed | MI | Forest, agricultural and urban | Stream Water | 0.03 - 0.69 | Inwood et al. 2005 |
| CAP-LTER, IBW | AZ | Urban desert | +N,+C | 0.49 - 2.13 | This Study |
| English Streams | England | Multiple stream sites | Stream Water | bdl - 3.64 | Garcia-Ruiz et al. 1998a |
| Soil | | | | | |
| South Bohemia | Chech Republic | Fertilized pasture (red | +N,+C | 0.08 - 0.09 | Šimek et al. 2004 |
| Brittany | France | Mixed Forest and Grassland | +N,+C | 0.08 - 0.16 | Clément et al 2002 |
| Desert Southwest | NM,CA, NV | Desert bajadas and playas | +N,+C | 0.01 - 0.24 | Peterjohn 1991 |
| Garonne River | France | Floodplain | +N,+C | 0.01 - 0.53 | Pinay et al. 2000 |
| CAP-LTER | AZ | Retetention basins | +N,+C | 0.39 - 1.15 | Zhu et al. 2004 |
| Yellowstone Park | WY | Grassland soils | +N,+C | 0.02 - 1.25 | Frank and Groffman 1998 |
| Baltimore-LTER | MD | Forest, suburban and urban streams | +N,+C | 0.46 - 2.20 | Groffman et al. 2002 |
| Baltimore-LTER | MD | Urban and rural riparian streams | +N,+C | 0.23 - 7.59 | Groffman and Crawford, 2003 |
| Sycamore Creek | AZ | Sonoran Desert uplands | +N,+C | 0.0 - 2.0 | Welter 2004 |
| CAP-LTER, IBW | AZ | Urban floodplain | +N,+C | 1.03 - 2.07 | This Study |

§ +N, +C: potential denitrification rates (DEA) estimated under ideal conditions where $NO_3^-$ and a carbon source were added in excess; +N: denitrificaiton rates estimated under anaerobic conditions where only $NO_3^-$ was added in excess; Stream Water: incubation intiated with addition of stream water with variable nitrate concentrations, rates expected to be lower than potentials.

Table 5.6. Literature values of actual denitrification rates measured in lakes, streams and soils under different treatment conditions. Studies ranked by patch type and maximum denitrification rate.

| Site | US. State /Country | Description | Technique* | Core/Slurry /Other† | Incubation treatment /media§ | Denitrification Rate ($mg\ N*m^{-2}*h^{-1}$) | Citation |
|---|---|---|---|---|---|---|---|
| Lake | | | | | | | |
| Lakes Vallentuna & Norriviken | Sweden | Shallow polymictic, deeper dimictic | $^{15}N$ pairing | Intact Core | Lake Water | 0.03 - 0.05 | Ahlgren et al. 1994 |
| Lake Michigan | Michigan | Large deep | $N_2$ accum. | Intact Core | - | 0.01 - 0.05 | Gardner et al. 1987 |
| Lake Huron | Michigan | Large deep | $N_2$ accum. | Intact Core | - | 0.02 - 0.08 | Gardner et al. 2001 |
| Lakes Vallentuna & Norriviken | Sweden | Shallow polymictic, deeper dimictic | Mass balance | - | - | 0.07 - 0.10 | Ahlgren et al. 1994 |
| Lake Baldegg | Switzerland | Deep eutrophic | $C_2H_2$ | Intact Core | - | 0.52 - 0.70 | Mengis et al 1997 |
| Lake Suwa | Japan | Shallow eutrophic | $C_2H_2$ | Intact Core | Lake water | 0.0 - 1.11 | Hasegawa and Okino 2004 |
| Lake Sövdösjon | Sweeden | Eutrophic | $C_2H_2$ | Resettled core | Low/High $NO_3$; +/- chironomids | 0.11 - 1.67 | Svensson 1997 |
| Lake Baldegg | Switzerland | Deep eutrophic | $^{15}N$ pairing | Intact Core | - | 2.10 - 2.28 | Mengis et al 1997 |
| Lake Baldegg | Switzerland | Deep eutrophic | $^{15}N$ pairing | In situ Flux Chamber | - | 2.51 | Mengis et al 1997 |
| Lake Nuldernauw | Netherlands | Shallow eutrophic | $N_2$ accum. | Intact core | Nut-free water | 0 - 3.53 | Van Luijn et al. 1999 |
| Lake Baldegg | Switzerland | Deep eutrophic | Mass balance | | - | 3.56 | Mengis et al 1997 |
| CAP-LTER, IBW | Arizona | Urban desert | $C_2H_2$ | Intact Core | Lake water | 1.53 - 4.27 | This study |
| Lake Memphremagog | Quebec | Large oligotrophic | $N_2$ accum. | Intact Core | Lake water | 0.12 - 4.76 | Saunders and Kalff 2001 |
| Lake Sövdösjon | Sweeden | Eutrophic | $^{15}N$ pairing | Resettled core | Low/High $NO_3$; +/- chironomids | 0.31 - 5.41 | Svensson 1997 |
| Wilcza Wola, Rzeszów, Solina & Besko | Poland | Reservoir | $N_2$ accum. | *In situ* chambers | Lake Water | 0.36 - 15.41 | Tomaxzek and Czerwieniec 2003 |
| Stream | | | | | | | |
| Walker Branch | Tennessee | Deciduous Forest | $^{15}N$ injection | Whole stream | - | 0.16 | Mulholland et al. 2004 |
| Sycamore Creek | Arizona | Sonoran desert | $C_2H_2$ | Field Chamber | - | 0.04 - 0.19 | Holmes et al. 1996 |
| Sugar Creek | Illinois | Agricultural | $N_2$:Ar | Whole stream | - | 3.78 | Laursen and Seitzinger 2002 |
| Kalamazoo Watershed | Michigan | Forest, Ag, & Urban | $C_2H_2$ | Slurry | Stream water | 0.09 - 4.90 | Inwood et al. 2005 |
| Swale-Ouse River | England | Park & Ag. | $C_2H_2$ | Intact Core | Stream water | 0.28 - 12.36 | Pattinson et al. 1998 |
| Big Ditch | Illinois | Agricultural | $C_2H_2$ | Slurry | Stream water | 0 - 15.80 | Schaller, et al. 2004 |
| South Platte River | Colorado | Mixed agriculture, plains | Mass balance | Whole stream | - | 2 - 100 | Sjodin et al 1997 |
| Iroquois River | Indiana | Agricultural | $N_2$:Ar | Whole stream | - | 48 - 119 | Laursen and Seitzinger 2002 |
| Millstone River | New Jersey | Mixed suburban & agriculture | $N_2$:Ar | Whole stream | - | 27 - 221 | Laursen and Seitzinger 2002 |

Table 5.6. Continued

| Site | US. State /Country | Description | Technique* | Core/Slurry /Other† | Incubation treatment /media§ | Denitrification Rate (mg N*m$^{-2}$*h$^{-1}$) | Citation |
|---|---|---|---|---|---|---|---|
| Soil | | | | | | | |
| Yellowstone Park | Wyoming | Grassland soils | $C_2H_2$ | Intact Core | Irrigated | 0.00 - 1.07 | Frank and Groffman 1998 |
| Georgia Farm Preserve | Pennsylvania | Riparian forest | $C_2H_2$ | Intact Core | - | 0.00 - 0.14 | Watts and Seitzinger 2000 |
| Pinelands | New Jersey | Ceder swamps | $C_2H_2$ | Intact Core | - | 0.00 - 0.04 | Watts and Seitzinger 2000 |
| Yellowstone Park | Wyoming | Grassland soils | $C_2H_2$ | Intact Core | - | 0.00 - 0.29 | Frank and Groffman 1998 |
| CAP-LTER, IBW | Arizona | Urban floodplain | $C_2H_2$ | Intact Core | - | 0.07 - 0.72 | This Study |
| CAP-LTER | Arizona | Retention basins | $C_2H_2$ | Intact Core | - | 0.14 - 2.40 | Zhu, et al. 2004 |
| Pinelands | New Jersey | Ceder swamps | $N_2$ accum. | Intact Core | - | 0.14 - 3.43 | Watts and Seitzinger 2000 |
| Georgia Farm Preserve | Pennsylvania | Riparian forest | $N_2$ accum. | Intact Core | - | 0.45 - 1.82 | Watts and Seitzinger 2000 |
| East Lansing | Michigan | Forest | $C_2H_2$ | Intact Core | Irrigated | 0.67 - 1.42 | Groffman and Teidje 1989 |
| East Lansing | Michigan | Forest | $C_2H_2$ | Intact Core | - | 0.68 - 0.75 | Groffman and Teidje 1989 |
| CAP-LTER, IBW | Arizona | Urban floodplain | $C_2H_2$ | Intact Core | Irrigated | 1.11 - 5.46 | This Study |

* $C_2H_2$ inhibition: samples incubated in the presence of $C_2H_2$ and denitrification estimated as the accumulation of $N_2O$; 15N istotope pairing: sample incubated in the presence of $^{15}$N-NO3 anddentirification estimated based on the relative accumulation of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$; mass balance: whole system approach where denitrification is estimated based on the difference between fluxes in and out of the ecosystem; $N_2$ accumulation: samples incubated is air-tight chamber and denitrification estimated as the difference between $N_2$ produced by degassing and $N_2$ produced by degassing and denitrification; N2:Ar: improved method for directly measuring flux of N2 gas, can be used in whole-system studies; $^{15}$N injection: whole system approach that traces fate of $^{15}$N labeled $NO_3$ or $NH_4$ through stream and estimates denitrification based on accumulation of $^{28}N_2$, $^{29}N_2$ and $^{30}N_2$.

† Denitrification estimate conducted using intact cores, slurries of sediment or soil samples and incubation media, chambers placed on sediment surface or whole system approaches.

§ Intact core incubations of lake and stream sediments initiated with the introduction of either artificial media or water collected from the site. In addition to being used to introduce $^{15}$N to the sytem, the media may or may not contain elevated nutrients. In one case, cores were treated so as to control degree of bioturbation through the introduction or removal of Chironomids. Soil cores were either incubated under field conditions or after a simulated irrigation event.

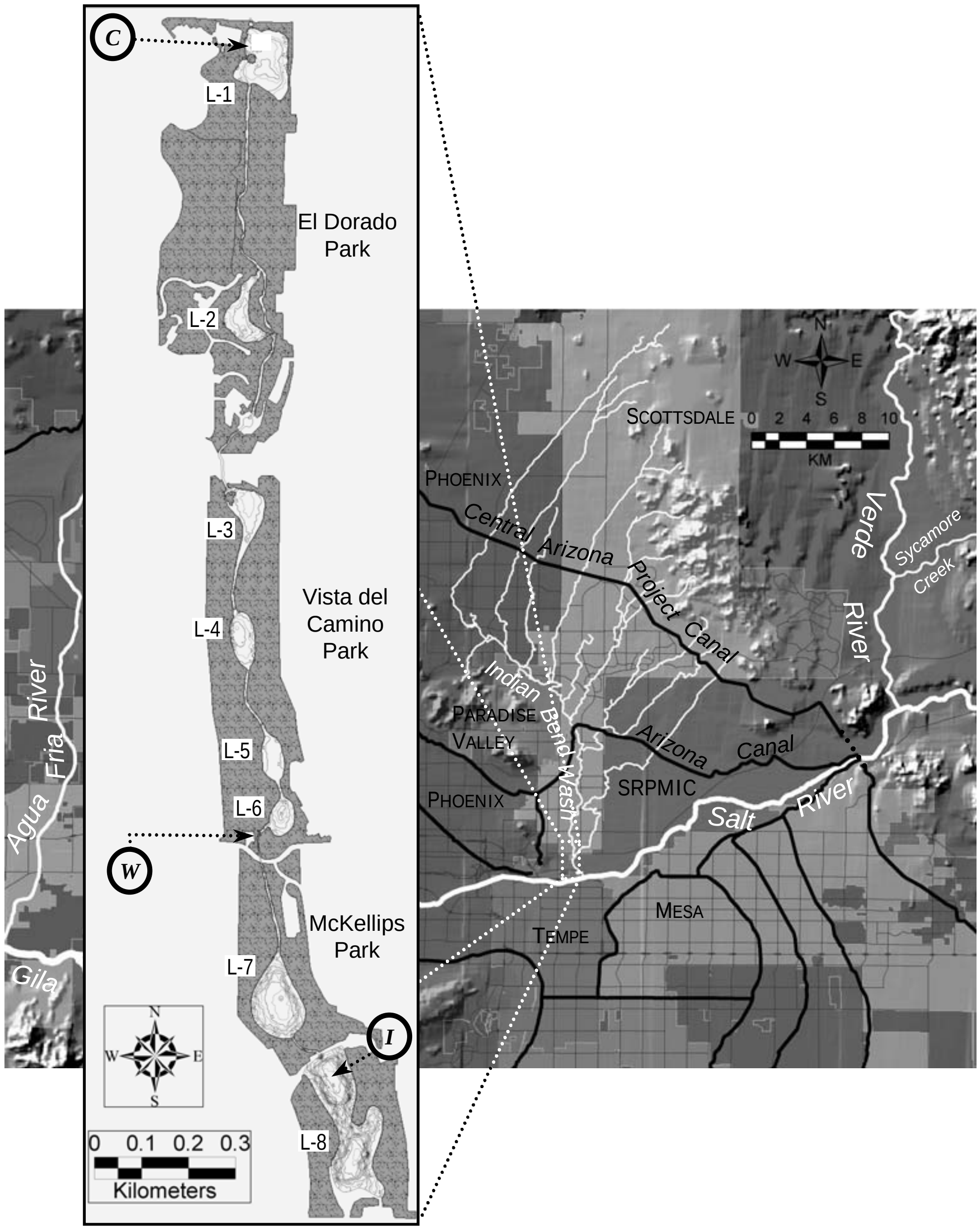


Figure 5.1. Map of Central-Arizona Phoenix LTER showing arterial canals (black lines), major rivers (thick white lines), and the main channels of the IBW watershed (thin white lines), though these only flow during floods. Major municipalities are indicated by different shades of gray and labeled accordingly. Inset map shows detail of study reach. Lake bathymetry is indicated by 0.5-m contour lines. A mix of canal and groundwater enters the wash at L-1 through a surface stream on its northern edge and via a subsurface pipe, *C*, as well as through a subsurface pipe, *I*, discharging into L-8. The Roosevelt Groundwater well, *W*, delivers water below L-6.

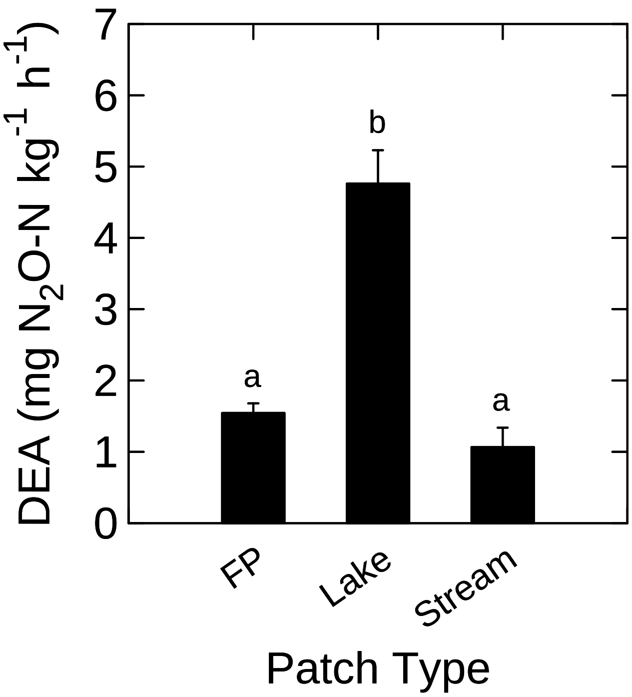


Figure 5.2. Mean (+1 SE) DEA from slurries of floodplain soils ($n$ = 8), lake sediments ($n$ = 8), or stream sediments ($n$ = 6) expressed per unit dry mass. Bars with the same letter are not significantly different.

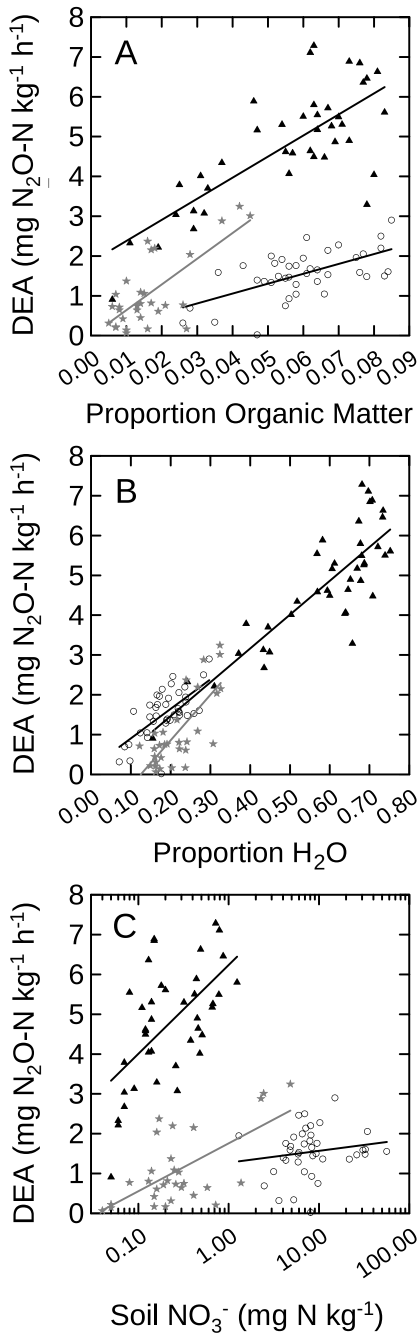


Figure 5.3. DEA of samples collected from floodplains (*n* = 40; open circles), lakes (*n* = 40; filled triangles) and streams (*n* = 30; filled stars) as a function of the proportion organic matter (Panel A), proportion water (Panel B), and soil $NO_3^-$ (Panel C). Denitrification rates from each core are reported. Regression lines for each patch type are shown.

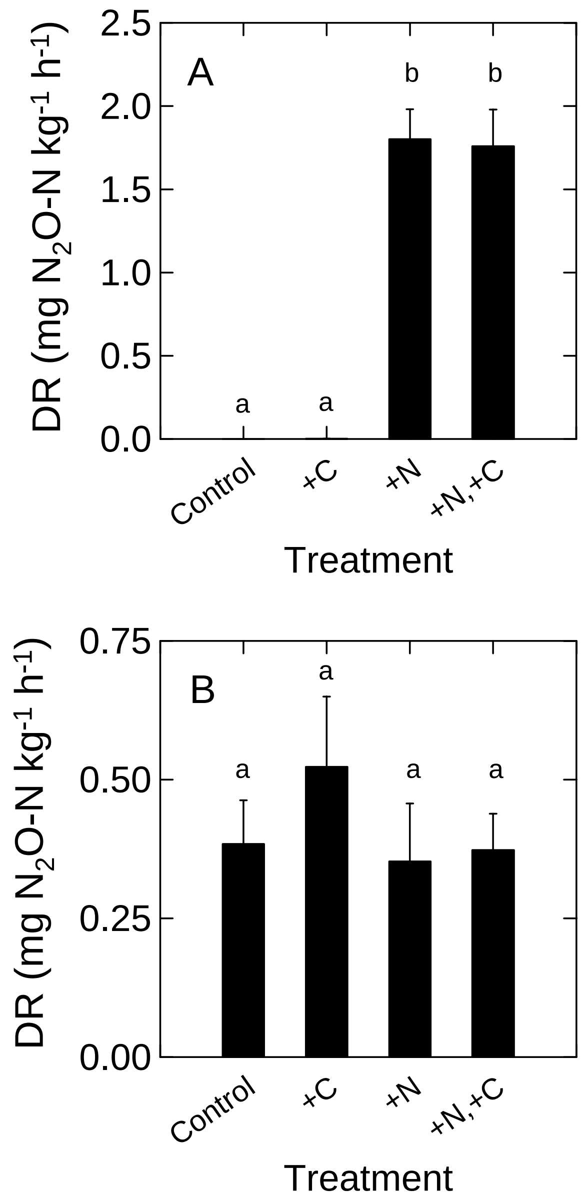


Figure 5.4. Mean (+1 SE) DEA from slurries of lake sediments (panel A) and floodplain soils (panel B) subjected to one of four different nutrient amendment treatments (Experiment 2). Bars with the same letter are not significantly different. Because the four lake treatments had unequal variances, the overall comparison of means was conducted using the nonparametric Kruskal-Wallis test with multiple comparisons for the lake sediments made using Dunn's Q statistic. The results of the floodplain nutrient addition experiment were analyzed using a standard one-way ANOVA after a square root transforming the data.

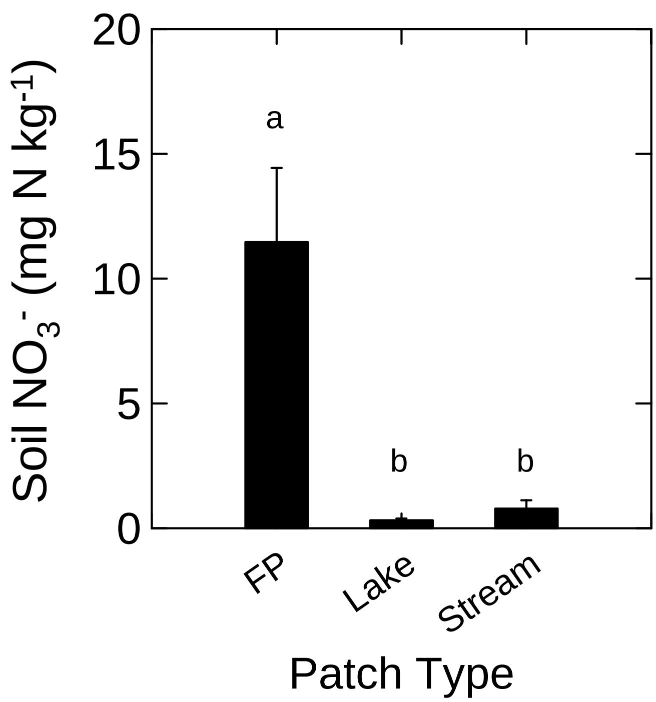


Figure 5.5. Mean (+1 SE) $\log_{10}NO_3^-$-N content of floodplain soils, lake sediments and stream sediments. Bars with the same letter are not significantly different.

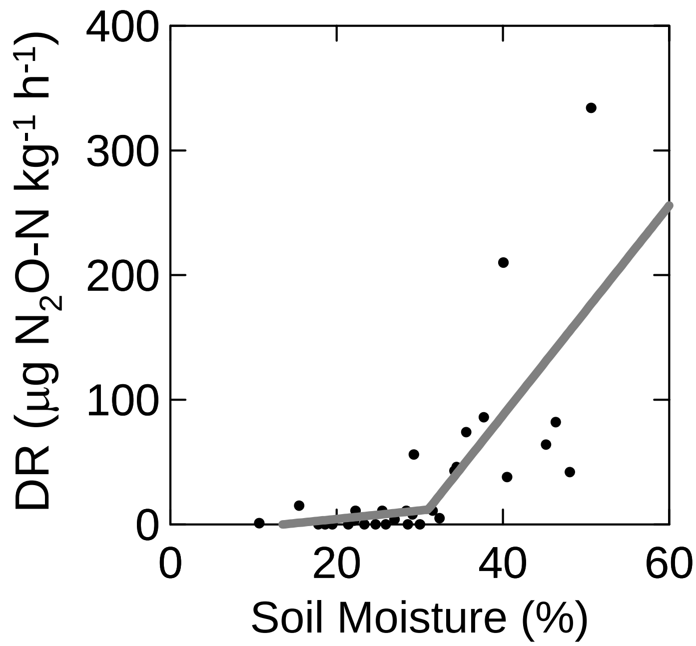


Figure 5.6. DEA in floodplain soil slurries as a function of percent soil water content. The solid line represents the best fit of nonlinear regression model: DEA = $b_0 + b_1{*}P_{H20} + b_2{*}(P_{H20} - P_{thresh}){*}(P_{H20} > P_{thresh})$.

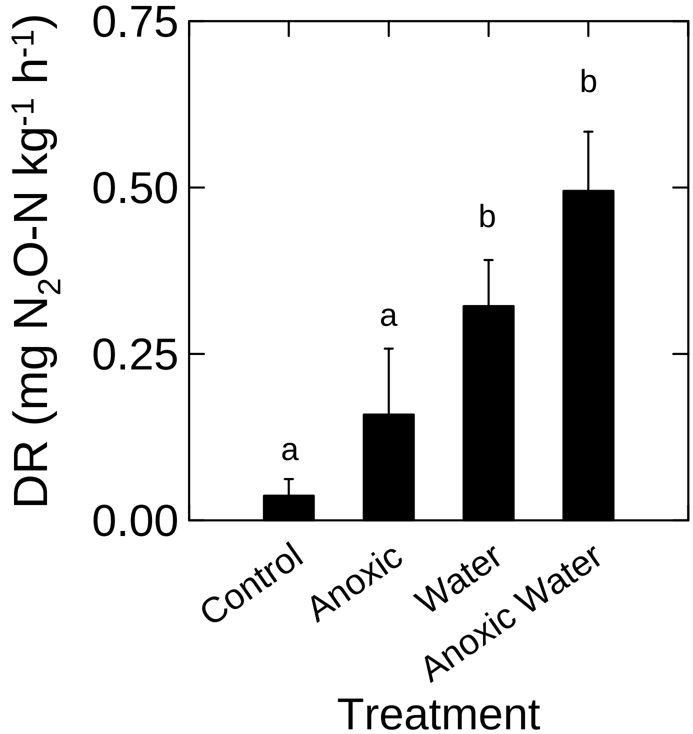


Figure 5.7. Mean (+1 SE) DEA of floodplain soils subjected to one of four different treatments (Experiment 4) in which incubation vials were either made anoxic or had water added or both or neither. Bars with the same letter are not significantly different.

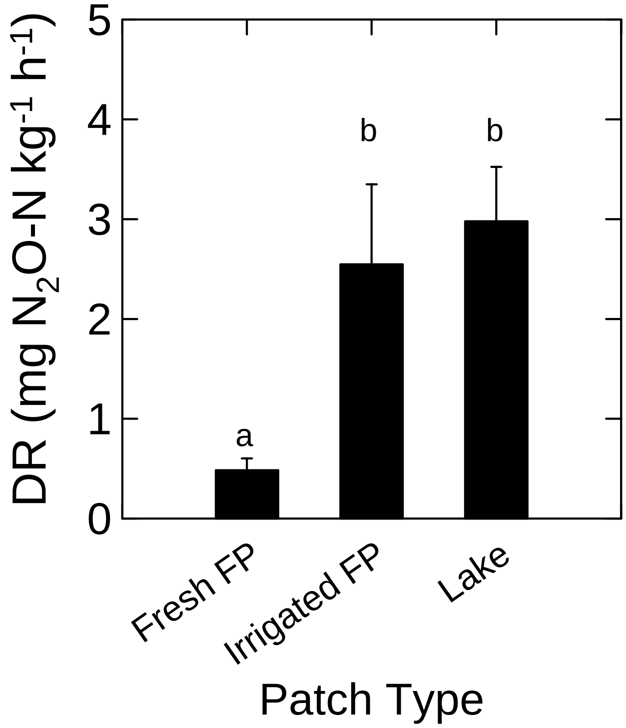


Figure 5.8. Mean (+1 SE) denitrification rate (DR) of intact floodplain soil cores and of intact lake cores. Floodplain cores were first incubated under field moisture conditions (Fresh) and than after a simulated irrigation event during which 0.7 cm of water was added to the core (Irrigated). Bars with the same letter are not significantly different.

# 6. SYNTHESIS

Ecologists' foray from the forest into the city represents recognition of the growing importance of urban ecosystems. Urbanization is essentially an unplanned experiment conducted on a massive scale (McDonnell and Pickett 1990). Current estimates place the human population at more than 6 billion and demographers predict a doubling of the number of people living in cites during the next 30-50 years (Stokstad 1995). Yet, while people continue to pack into cities, ecological characteristics of these metropolises remains largely unknown. Ecologists are now grappling with questions addressing the function of natural areas within urban ecosystems, including parks (e.g., Zhu et al. 2004), streams (e.g., Grimm et al. 2005, Meyer et al. 2005), and lakes (e.g., Bennett et al. 1999), as well as questions of how cities function as ecosystems in the broader landscape (e.g., Baker et al. 2001, Luck et al. 2001, Jenerette et al. in press).

## WHAT HAVE WE LEARNED?

The research reported in this dissertation sheds light on how changes in stream hydrology and geomorphology affect nutrient cycling in Indian Bend Wash (IBW) as compared to Sycamore Creek, a comparatively pristine desert stream of similar size. Previous research in Sycamore Creek (Fig. 6.1A) suggest that storm event wash nutrient off the uplands into the stream, where they fuel primary production in the mainstem (Fisher et al. 1982). Although P is mainly supplied by weathering of geologic material (Fisher et al. 1982), N in the uplands is supplied by atmospheric deposition and nitrogen fixation. During periods when $NO_3^-$ concentrations are low, nitrogen fixation in the stream channel may contribute additional inorganic N (Grimm and Petrone 1997). Uptake by primary producers tends to reduce the concentration of inorganic N in stream water (Grimm and Fisher 1986), whereas mineralization or organic N and nitrification in hyporheic sediments increase concentrations of $NO_3^-$ and $NH_4^+$ (Valett 1993, Jones et al. 1995). Together uptake and release processes create spatial and temporal variation in the concentration of inorganic N (Dent and Grimm 1999), which, along with variation in organic carbon concentration resulting from algal decay (Jones et al. 1996) and root exudates influence patterns of denitrification (Holmes et al. 1996, Schade et al. 2001). In addition to washing nutrients off the uplands, rain increases soil moisture, stimulating denitrification in upland patches (Welter 1994, Belnap et al. 2005).

Similar processes operate in Indian Bend Wash (Fig. 6.1B). Rain still washes nutrients off the surrounding upland into the stream; but here storms increase the concentrations of SRP and $NH_4^+$ while diluting $NO_3^-$ concentration in the main channel. Increased moisture still stimulates denitrification in soils, whereas denitrification in sediments is, to a large extent, a function of nutrient ($NO_3^-$) availability (Chapter 4). In short, the ecosystem responds to ecological drivers much as one would predict from existing ecological theory.

Although a new conceptualization of how ecosystems function is not required to understand what proximal factors drive ecological processes in IBW (e.g., the ratio of N:P still determines which nutrient limits primary production), a more holistic understanding of urban streams requires explicit consideration of the effects of human action (Fig. 6.1B). Radical manipulation of the watershed's hydrology, which ensures flows through this urban lake chain, has established linkages between IBW, the surface flows of other rivers, and the underlying aquifer that are entirely anthropogenic in origin and remain controlled by human decision makers. Because the chemical makeup of the water diverted through the wash varies depending upon which 'taps' are turned on, variation in water chemistry (i.e., conductivity, pH, $Cl^-$, $NH_4^+$, SRP, $NO_3^-$ ) tends to be highly synchronous (Chapter 3). More specifically, linkages between groundwater and surface flows are principal drivers of temporal patterns of $NO_3^-$ concentration within the wash (Chapters 2-4). Groundwater pumping does not simply link physically separated water sources, but also links past land-use practices (i.e., historic fertilizer use) to current water quality (Chapter 2). As a result, $NO_3^-$ concentration in IBW is tightly linked to groundwater pumping (Fig. 6.1B). This contrasts with surrounding desert streams where floods are the most important mechanism increasing surface-water $NO_3^-$ concentrations in surface flows (Fig. 6.1A).

In addition, people have initiated important geomorphic changes. Artificial lakes and irrigated-turf floodplains of IBW are novel geomorphic features that have no analogues in the surrounding desert. This highly engineered greenbelt has become the poster child for 'designer ecosystems'—ecosystems which are the product of human imagination and, though they may bear little resemblance to a past state, are nevertheless functioning ecosystems in their own right (Palmer et al. 2004). Baker (2001) estimated that average denitrification rates in the urban portion of the Central-Arizona Phoenix (CAP) ecosystem were 38.5 kg N $ha^{-1}$ $y^{-1}$. Since impervious surfaces (e.g. streets, parking lots and rooftops) are unlikely to retain N, other patches on the urban landscape must support correspondingly greater denitrification rates. The lakes and floodplains of IBW, which denitrify 258 and 124 kg N $y^{-1}$, respectively, are two such hotspots (Chapter 5). These rates are not only high when compared to the relatively inactive portions of the urban landscape, but also when compared to desert patches within the CAP where denitrification removes ~28 kg N $ha^{-1}$ $y^{-1}$ (Baker et al. 2001).

The geomorphic and pedological characteristics that make lake sediments and turf soils potential hotspots are largely anthropogenic in origin (Fig. 6.1B). Other research has demonstrated that denitrification is promoted by fine, organically rich material in soils (e.g., Groffman and Tiedje 1989, Brettar and Höfle 2002, Pinay et al. 2003) and sediments (e.g., García-Ruiz et al. 1998, Van Luijn et al. 1999). Deep, organically rich, fine materials did not accumulate in the channel of IBW until artificial lakes were constructed and act as large settling basins (Chapter 2). As with other urban soils (Zhu et al. in press), organic matter content of IBW's floodplain is much higher than that of the surrounding desert, probably reflecting effects of regular irrigation and fertilization. The high organic-matter content of the lake sediments and floodplain soils is partially responsible for the high denitrification rates observed in these patches (Chapter 5). In other words, by constructing artificial lakes and creating a turf floodplain, engineers created conditions that promoted denitrification (Chapter 2, Chapter 5). Use of lake water to irrigate turf further stimulated denitrification by increasing $NO_3^-$ availability and by creating conditions (i.e., wet soils) that stimulated denitrification (Chapter 5).

*Implications for ecology in cities*

These findings have important implications for efforts to develop a theoretical framework for studying ecology *in* cities (Grimm et al. 2000). Many of the key drivers (e.g., nutrient availability, redox conditions, pedology) that determine processing rates in more pristine ecosystems remain important in urban ecosystem; thus, we need not invoke new conceptualizations of controls on ecosystem function. However, it is equally clear that human agents play a critical role in determining ecosystem behavior. Some of the effects of these actions are intentional. People actively 'manage' ecosystems in an attempt to push them to a desired state. For example, creating and maintaining clear, aesthetically appealing lakes in the IBW floodplain required carving basins in the floodplain, diverting water into the channel to maintain water levels, stabilizing the surrounding sediments with irrigated turf, and controlling macrophyte and algal growth with herbicides and algaecides.

Other actions produce unintended consequences as a byproduct of decisions by managers of seemingly unrelated systems who may or may not be responsible for or even aware of the repercussions. For example, decisions about the exact mix of surface flows and groundwater pumping are largely made in an effort to produce a potable water supply with $NO_3^-$-N <10 mg L-1. Effects of still-elevated $NO_3^-$ concentrations on ecosystem processes may or may not be considered by managers when they decide which complement of wells to tap. As a result, managers responsible for the parks of IBW may be faced with additional challenges when trying to limit either effects of elevated N on their lakes or flux of $NO_3^-$ back into the canal system. Coordination between the two decision makers may allow for novel solutions satisfying the needs of both groups. For example, if a stable, predictable supply of $NO_3^-$-rich water is delivered to the lakes, park managers may be able to reduce fertilizer inputs by relying more on lake water to supply N to the floodplain. Similarly, by managing the flow of water through the system to promote denitrification, park managers may be able to help return water to the canals with substantially reduced $NO_3^-$ loads.

Finally, actions by individual decision makers may affect ecosystem function in unintended and often surprising ways. Certainly, farmers fertilizing their crops in the small agrarian community of Scottsdale 50 years ago did not envision that these nutrients would one day be returned to the surface to and negatively affect an artificial lake chain. Similarly, it is difficult for individuals to foresee how individual choices about landscaping practices affect sediment supply and geomorphic form in the stream channel of the larger watershed.

Clearly, human actions have strong, lasting effects on urban ecosystems. Thus, urban ecologists should not only seek to understand the consequences of these decisions on ecosystem function but also how these decisions come to be made.

### *Implications for the ecology of cities*

This research also has implications for the ecology *of* cities (Grimm et al. 2000). Virtually all water from the Salt and Verde rivers is diverted out of their channels and through the CAP ecosystem. As water flows through the city, some water is lost to evaporation, some leaches into groundwater, and the remainder is discharged to the Salt and Gila rivers via wastewater treatment plants or agricultural returns, or runs off the landscape during floods. The quality of water exported to recipient ecosystems depends on net processing that occurs within the city, which, in turn, is a function of aggregate effects of various patches that interact with water as it flows through the city. Baker et al (2001) report that while net import of N to the CAP ecosystem is approximately 21 Gg N $y^{-1}$, more than twice as much N is exported via surface flows (2.6 Gg N $y^{-1}$) than is imported via Central Arizona Project Canal and the Salt, Verde, and Gila rivers combined (1.2 Gg $y^{-1}$). The research reported here sheds light on one of the mechanisms responsible for this increase (groundwater pumping), and suggests two means by which the export of N could be further reduced by creating conditions that promote denitrification (Chapter 5). Specifically, artificial lakes are capable of removing large amounts of $NO_3^-$ from their overlying waters, while irrigated turf has the potential to be an important hot spot for denitrification, with the amount of $NO_3^-$ removed by floodplain soils depending on both the quantity of fertilizer they receive and the timing and quantity of irrigation. Clearly, 'designer ecosystems' like IBW perform an ecosystem service (Costanza et al. 1997) by removing a large fraction of the $NO_3^-$ flowing through them. Equally clear, more N enters these systems than they remove, suggesting that they are N-saturated (Aber et al. 1989).

WHAT ARE THE IMPLICATIONS FOR THE CENTRAL-ARIZONA PHOENIX ECOSYSTEM?

The greenbelt running through IBW is an unusual solution to flood control. Elsewhere in the CAP ecosystem managers have taken other, more drastic hard-engineered, approaches to flood control. Cave Creek, for example, now flows through a cement-lined channel; its banks replaced with vertical walls. Nevertheless, many of the greenbelt's components are proliferating throughout the CAP ecosystem. More than 160 lakes have been constructed in the IBW watershed (Chapter 2) and are potential denitrification hot spots. Turf-lined retention basins are increasingly relied on to receive stormwater from the urban landscape. The same characteristics that make IBW's floodplain a hot spot for denitrification also stimulate denitrification in retention basins (Zhu et al. 2004). In fact, because they are designed to prevent export of surface waters, most of the N retention basins receive is denitrified, stored in soil, or exported to the underlying aquifer.

It would be an oversimplification, however, to assume that all lakes and all irrigated turf soils behave exactly as those in IBW. This is primarily because the management of these features is likely to differ. $NO_3^-$ concentrations in the lake waters of IBW are primarily determined by origin of the water used to fill them, with lakes that receive more groundwater having higher $NO_3^-$ concentration. However, the spatial variation in groundwater $NO_3^-$ concentration is enormous (0.47-41 mg $L^{-1}$; Sullivan 1998). Much of this variation appears to be a result of differences in land-use practices; groundwater directly below current or historic agricultural fields tends to have higher $NO_3^-$ concentrations. As a result, lakes receiving groundwater (or surface water) of lower

$NO_3^-$ concentration may have much lower denitrification rates. In other words, historic legacies of past management practices may be important determinants of processing rates in these new lakes. Similarly, fertilizer inputs and irrigation water stimulated floodplain denitrification (Chapter 5), suggesting that management decisions about the timing and extent of irrigation and the application of fertilizers will strongly affect denitrification from other turf-dominated patches. Clearly, determining how the CAP ecosystem processes nitrogen will require a more complete understanding of these anthropogenic hot spots.

## FUTURE SCENARIOS

As cities grow, they will continue to face challenges associated with maintaining clean, reliable of water supplies while developing the ability to convey stormwater safely through the urban infrastructure and to limit the export of water-borne pollutants to recipient ecosystems. The legacies of past land-use practices will only complicate the solutions to these challenges. It is not hard to envision cities where nearly all surface flows are restricted to surface streets, storm drains, and cement-line channels; and where in-channel processing of nutrients is virtually zero. Such designs may efficiently shunt floodwaters from the city, but will perform few other ecosystem services. It is also possible to imagine cities that adopt a different approach, one where maintaining ecosystem functions in addition to flood control are prioritized. In this model, cities may choose greenbelts like that of IBW to provide a non-structural or ‘soft’ means of flood control. Such designer ecosystems may be specifically engineered to promote denitrification (Groffman et al. 2005) and thus treat groundwater or surface flows that have been contaminated by $NO_3^-$, alleviating the effects of past fertilizer use. However, addition of fertilizer N in conjunction with N from groundwater may overwhelm the ecosystem's ability to remove N through denitrification causing it to function as an N source versus sink. Further, decisions to limit in-stream primary production with algaecides and herbicides might warrant re-evaluation until the effects of these decisions on N export become better understood.

Managing urban streams for their ability to perform ecosystem services will also necessitate engaging the local citizenry. Visions of what urban streams, lakes, and floodplains should look like are usually influenced by values that are independent of their ecological function (McDonald et al. 2004). The potential exists, however, for urban streams and lakes to provide a multitude of ecological services in addition to nutrient retention, including regulating services (e.g, flood control, waste assimilation), cultural services (e.g, spiritual fulfillment, recreation and aesthetics), provisioning services (e.g., fresh drinking and irrigation water), and supporting services (i.e., those necessary for production of the service categories) (Millennium Ecosystem Assessment 2003). Maximizing the ability of urban streams to provide these services requires explicit consideration not only of the specific services a stream could provide but also their relative importance to the citizenry. The often-conflicting valuation of these services will make this challenging. Results of this study and others are encouraging, however, and suggest that urban streams in moderately developed catchments may retain much of their ecological function and continue to provide ecosystem services (e.g., Booth et al. 2002, King et al. 2005), though other urban stream studies suggest this may be difficult (Walsh et al. 2005). Nevertheless, the potential remains for urban streams to be engineered to provide multiple ecosystem services.

## CONCLUSIONS

Increasingly, existing ecosystems are intentionally and unintentionally altered to meet people's needs and desires. For stream ecosystems, changes can result from hydrologic modifications (e.g., introduction of novel flowpaths or the alteration of flow regimes) as well as changes in channel morphology (e.g., construction of novel patch types or reduction of channel complexity). In IBW both occurred. Surface flows were made perennial and supplemented with groundwater additions that elevated $NO_3^-$ concentrations in surface flows. Simultaneously, artificial lakes were built in a newly constructed turf-dominated floodplain. These lakes act as hot spots for N processing within the larger watershed. Although this research is essentially a case study describing how the biogeochemistry of one stream is altered by urbanization, many of the changes are common in the broader CAP ecosystem. Moreover, the redistribution of water (i.e., canals), the linkages of historically discrete subsystems (i.e., groundwater to surface water), and the creation of novel patch types (i.e., lakes and irrigated turf) are common features in many urban landscapes. This research provided a better understanding of the mechanisms by which urbanization can alter N availability and through which N retention can be promoted.

LITERATURE CITED

Aber, J. D., K. J. Nadelhofer, P. Steudler, and J. M. Melillo. 1989. Nitrogen saturation in northern forest ecosystems. BioScience **39**:378-386.

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

Belnap, J., R. 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.

Bennett, E. M., T. Reed-Andersen, J. N. Houser, J. R. Gabriel, and S. R. Carpenter. 1999. A phosphorus budget for the lake Mendota watershed. Ecosystems **2**:69-75.

Booth, D. B., D. Hartley, and R. Jackson. 2002. Forest cover, impervious-surface area, and the mitigation of stormwater impacts. Journal of the American Water Resources Association **38**:835-845.

Brettar, I., and M. G. Höfle. 2002. Close correlation between the nitrate elimination rate by denitrification and the organic matter content in hardwood forest soils of the upper Rhine floodplain (France). Wetlands **22**:214-224.

Costanza, R., R. d'Arge, R. de Groot, S. Farber, M. Grasso, B. Hannon, K. Limburg, S. Naeem, R. O'Neill, J. Paruelo, R. Raskin, P. Sutton, and M. van den Belt. 1997. The value of the world's ecosystem services and natural capital. Nature **15**:253-260.

Dent, C. L., and N. B. Grimm. 1999. Spatial heterogeneity of stream water nutrient concentrations over successional time. Ecology **80**:2283-2298.

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.

García-Ruiz, R., S. N. Pattinson, and B. A. Whitton. 1998. Denitrification in river sediments: relationship between process rate and properties of water and sediment. Freshwater Biology **39**:467-476.

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

Grimm, N. B., J. M. Grove, S. T. A. Pickett, and C. L. Redman. 2000. Integrated approaches to long-term studies of urban ecological systems. BioScience **50**:571-583.

Grimm, N. B., and K. C. Petrone. 1997. Nitrogen fixation in a desert stream ecosystem. Biogeochemistry **37**:33-61.

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

Groffman, P. M., A. M. Dorsey, and P. M. Mayer. 2005. N processing within geomorphic structures in urban streams. Journal of the North American Benthological Society **24**.

Groffman, P. M., and J. M. Tiedje. 1989. Denitrification in north temperate forest soils: spatial and temporal patterns at the landscape and seasonal scales. Soil Biology and Biochemistry **21**:613-620.

Holmes, R. M., J. B. Jones, Jr., S. G. Fisher, and N. Grimm. 1996. Denitrification in a nitrogen-limited stream ecosystem. Biogeochemistry **33**:125-146.

Jenerette, G. D., W. Wu, S. Goldsmith, W. A. Marussich, and W. J. Roach. in press. Contrasting water footprints of cities in China and the United States. Ecological Economics.

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

Jones, J. B., Jr., S. G. Fisher, and N. Grimm. 1996. A long term perspective of dissolved organic carbon transport in Sycamore Creek, Arizona, USA. Hydrobiologia **317**:183-188.

King, R. S., M. E. Baker, D. F. Whigham, D. E. Weller, T. E. Jordan, P. F. Kazyak, and M. K. Hurd. 2005. Spatial considerations for linking watershed land cover to ecological indicators in streams. Ecological Applications **15**:137-153.

Luck, M. A., G. D. Jenerette, J. Wu, and N. B. Grimm. 2001. The urban funnel model and spatially heterogeneous footprint. Ecosystems **4**:782-796.

McDonald, A., S. N. Lane, N. E. Hycock, and E. A. Chalk. 2004. Rivers of dreams: on the gulf between theoretical and practical aspects of an upland river restoration. Transactions of the Institute of British Geographers **29**:257-281.

McDonnel, M. J., and S. T. A. Pickett. 1990. Ecosystem structure and function along urban-rural gradients: an unexploited opportunity. Ecology **71**:1232-1237.

Meyer, J. L., M. J. Paul, and W. K. Taulbee. 2005. Stream ecosystem function in urbanizing landscapes. Journal of the North American Benthological Society **24**:602-612.

Millennium Ecosystem Assessment. 2003. Ecosystems and Human Well-being: A Framework for Assessment. Island Press, Washington, DC.

Palmer, M. A., E. Bernhardt, E. Chornesky, S. L. Collins, A. P. Dobson, C. Duke, B. Gold, R. Jacobson, S. Kingsland, K. R., M. Mappin, M. L. Marinez, F. Micheli, J. Morse, M. L. Pace, M. Pascual, S. Palumbi, O. J. Reichman, A. Simmons, A. Townsend, and M. Turner. 2004. Ecology for a crowded planet. Science **304**:1251-1252.

Pinay, G., T. O'Keefe, R. Edwards, and R. J. Naiman. 2003. Potential denitrification activity in the landscape of a western Alaska drainage basin. Ecosystems **6**:336-343.

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

Stokstad, E. 1995. Will Malthus continue to be wrong? Science **309**:102.

Sullivan, J. F. 1998. 1997 Annual Water Quality Report. Salt River Project, Phoenix, AZ.

Valett, H. M. 1993. Surface-hyporheic interactions in a Sonoran Desert stream: hydrologic exchange and diel periodicity. Hydrobiologia **259**:133-144.

Van Luijn, F., P. C. M. Boers, L. Lijklema, and J. P. R. A. Sweerts. 1999. Nitrogen fluxes and processes in sandy and muddy sediments from a shallow eutrophic lake. Water Research **33**:33-42.

Walsh, C. J., T. D. Fletcher, and A. R. Ladson. 2005. Stream restoration in urban catchments through redesigning stormwater systems: looking to the catchment to save the stream. Journal of the North American Benthological Society **24**:690-705.

Welter, J. W. 1994. Nitrogen transport and processing in the intermittent drainage network: linking terrestrial and aquatic ecosystems. Arizona State University, Tempe, AZ.

Zhu, W.-X., N. D. Dillard, and N. B. Grimm. 2004. Urban nitrogen biogeochemistry: status and processes in green retention basins. Biogeochemistry **71**:177-196.

Zhu, W.-X., D. Hope, C. Gries, and N. Grimm. in press. Soil characteristics and the storage of inorganic nitrogen under different land uses in an arid urban ecosystem. Ecosystems.

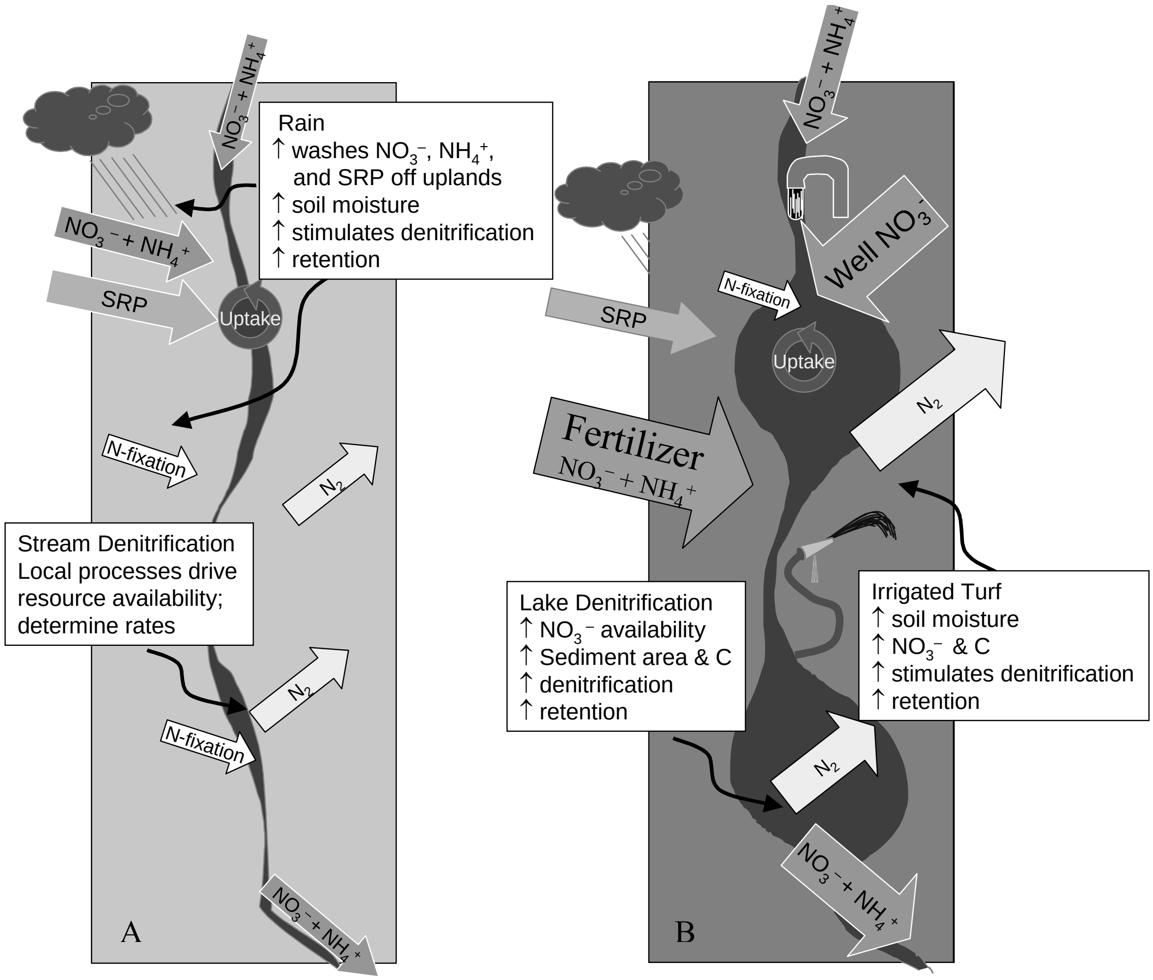


Figure 6.1. Schematic diagram contrast major drivers of N cycling in a pristine Sonoran desert stream (A) and IBW (B). Arrows indicate major fluxes into and out of the stream-floodplain complexes including the flux of nutrients from uplands, upstream reaches, fertilizers, and groundwater wells and out of the reach in surface flows ($NO_3^-$ and $NH_4^+$, SRP). Additional fluxes of N to the atmosphere via denitrification ($N_2$) and into the system via fixation (N-fixation) are also indicated. Boxes describe effects of key drivers in the two ecosystems. Note that the stream channel is narrower and vegetation is sparser (as indicated by lighter color) in the desert ecosystem than in the urban system where lakes have been sculpted into the floodplain and irrigation and fertilizer inputs support turf growth.