Coupled Hydrology and Biogeochemistry

in

Social-Ecological Watersheds

by

Rebecca Leslie Hale

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

Approved May 2013 by the
Graduate Supervisory Committee:

Nancy Grimm, Chair
Enrique Vivoni
Abigail York
Jianguo Wu
Daniel Childers

ARIZONA STATE UNIVERSITY

August 2013

ABSTRACT

Hydrology and biogeochemistry are coupled in all systems. However, human decision-making regarding hydrology and biogeochemistry are often separate, even though decisions about hydrologic systems may have substantial impacts on biogeochemical patterns and processes. The overarching question of this dissertation was: How does hydrologic engineering interact with the effects of nutrient loading and climate to drive watershed nutrient yields? I conducted research in two study systems with contrasting spatial and temporal scales. Using a combination of data-mining and modeling approaches, I reconstructed nitrogen and phosphorus budgets for the northeastern US over the 20th century, including anthropogenic nutrient inputs and riverine fluxes, for ~200 watersheds at 5 year time intervals. Infrastructure systems, such as sewers, wastewater treatment plants, and reservoirs, strongly affected the spatial and temporal patterns of nutrient fluxes from northeastern watersheds. At a smaller scale, I investigated the effects of urban stormwater drainage infrastructure on water and nutrient delivery from urban watersheds in Phoenix, AZ. Using a combination of field monitoring and statistical modeling, I tested hypotheses about the importance of hydrologic and biogeochemical control of nutrient delivery. My research suggests that hydrology is the major driver of differences in nutrient fluxes from urban watersheds at the event scale, and that consideration of altered hydrologic networks is critical for understanding anthropogenic impacts on biogeochemical cycles. Overall, I found that human activities affect nutrient transport via multiple pathways. Anthropogenic nutrient additions increase the supply of nutrients available for transport, whereas hydrologic infrastructure controls the delivery of nutrients from watersheds. Incorporating the effects of hydrologic

infrastructure is critical for understanding anthropogenic effects on biogeochemical fluxes across spatial and temporal scales.

ACKNOWLEDGMENTS

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Chapter 1

INTRODUCTION

Human modifications of the environment are both pervasive and diverse, ranging from altered atmospheric chemistry and biogeochemical cycles to dramatic modifications of the landscape for agriculture and urban uses (Vitousek et al. 1997, Kareiva et al. 2007). Environmental changes are often presented independently (Vitousek et al. 1997, Rockstrom et al. 2009), but one of the major challenges in understanding the consequences of human actions is that these changes are not independent. Land use change, for example, is intimately connected to the use of nutrients and water (e.g., Foley et al. 2005). Understanding these interactions is key to understanding the potential for nonlinear changes and unintended consequences and critical for evaluating major thresholds of change (e.g., Rockstrom et al. 2009). This complexity requires the development of frameworks for understanding multiple drivers of environmental change, not only for scientific understanding, but also so that decision-makers have information about the full suite of policy options to effect positive change.

This dissertation addressed interactions between engineered hydrologic systems and the delivery of nutrients, nitrogen (N) and phosphorus (P), from social-ecological watersheds. Human alterations of N and P cycles have been tremendous. Availability of N has increased by 200% and P by 400% since before the industrial revolution (Vitousek et al. 1997, Smil 2000, Falkowski et al. 2000, Galloway et al. 2004, Cordell et al. 2009). Increased nutrient availability has been accompanied by increases in agricultural yields that have undoubtedly benefitted society. However, nutrient use has also led to costly water quality problems, including eutrophication, that have detrimental effects on human

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health, environmental quality, and industries that depend on the environment (Carpenter et al. 1998, Hagy et al. 2004, Caccia and Boyer 2005, Elser et al. 2009, Grizzetti et al. 2012, Howarth et al. 2012).

Human use of N and P has increased exponentially (Smil 2000, Galloway et al. 2004, Cordell et al. 2009), and an ongoing challenge is how society can harness the benefits of nutrients while minimizing the negative effects on downstream ecosystems. To do this we must understand what controls the delivery of anthropogenic nutrients from land to downstream systems.

The watershed approach, pioneered by Bormann and Likens (1967), has traditionally been used by terrestrial ecologists to integrate ecological processes over large areas. A major criticism of the watershed approach has been that it uses the stream as an integrator of terrestrial processes and thus assumes that in-stream processes are insignificant. Despite extensive research demonstrating the importance of the hydrologic network (i.e., streams and rivers) for nutrient uptake and retention (Peterson et al. 2001, Mulholland 2004, Wollheim et al. 2008, Harrison et al. 2009, Helton et al. 2011), the "black box" watershed approach is frequently used to understand how land use and associated anthropogenic nutrient use affect nutrient delivery from watersheds (Howarth et al. 1996, Boyer et al. 2002, Sobota et al. 2009, Broussard and Turner 2009).

An integrated approach, combining terrestrial and aquatic approaches to watershed biogeochemistry, is further required because aquatic systems have also been subject to anthropogenic modifications. Parallel to land-use changes, humans have extensively engineered hydrologic systems at local to global scales (e.g., Graf 1999, Vorosmarty et al. 2003, Elmore and Kaushal 2008, Kaushal and Belt 2012), building, for

example, reservoirs, levees, storm sewer systems, water supply infrastructure, and wastewater infrastructure. These systems must be included in our models of nutrient transport because they directly affect the transport of water and nutrients through watersheds (Hatt et al. 2004, Alexander et al. 2008, Seitzinger et al. 2010). Furthermore, engineered hydrologic infrastructure is not uniformly distributed across space or time. A good example is dam building in the United States over the 19th and 20th centuries. Today the distribution of dams and the size of dams are not uniform across the U.S. There are many more and smaller dams in the northeastern US and fewer but larger dams in the western US (Graf 1999). Equally important is that the temporal patterns of dam building were also heterogeneous across the US.

Finally, any understanding of nutrient transport through watersheds must take into account the role of climate (Kaushal et al. 2008, Sobota et al. 2009, Howarth et al. 2012, Wu et al. 2012). Climate variability is important for understanding variation in nutrient transport across temporal scales (Sobota et al. 2009, Howarth et al. 2012, Alam and Goodall 2012). Previous research has found that nutrient delivery is related to interactions between land use and climate (Kaushal et al. 2008, Sobota et al. 2009, Howarth et al. 2012, Wu et al. 2012). What is unknown is how anthropogenic changes to hydrologic networks interact with land use and climate to generate patterns of nutrient delivery.

The overarching question for this dissertation is: How does hydrologic engineering interact with the effects of nutrient loading and climate to drive watershed nutrient yields? I use yield (mass / area time^{-1}) as a primary response variable because it enables comparisons across watersheds and within watersheds over time, as well as the

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calculation of nutrient budgets at the watershed scale. In this dissertation, I evaluate the role of hydrologic engineering in two systems that vary in both climate and spatial and temporal scale. One system is the northeastern region of the United States (NE) over the 20th century, and the other is arid urban watersheds in the Phoenix metropolitan area of Arizona. Despite their differences, both study areas contain spatial and temporal heterogeneity in hydrologic infrastructure: dams and sewers in the NE and stormwater drainage infrastructure in Phoenix. The objective of this dissertation is to evaluate how infrastructure heterogeneity, in combination with variation in nutrient inputs and climate, structures spatial and temporal patterns of nutrient delivery from social-ecological watersheds.

The conceptual framework for this dissertation is presented in Figure 1.1. In it, hydrology (Box C) and biogeochemistry (Box G) are represented as coupled biophysical systems. Hydrology is strongly linked to biogeochemistry, as a transport vector (Hatt et al. 2004, Kaye et al. 2006, Lewis and Grimm 2007, Walsh et al. 2009) and through the effects of water on the physical and chemical conditions of the environment and therefore rates of biogeochemical transformations (Paul and Meyer 2001, Groffman et al. 2002, Grimm et al. 2005, Walsh et al. 2005, Kaye et al. 2006). In this model, hydrology is driven by climate as well as by anthropogenic infrastructure and behaviors, which are in turn driven by policy. Biogeochemistry is also driven by anthropogenic infrastructure and behavior, as well as hydrology and climate. Climate affects biogeochemistry both indirectly via hydrology and directly due to temperature via effects on enzymatic activity and reaction rates. Dashed arrows between hydrology policy and nutrient management policy indicate that these systems are likely decoupled. That is, decision-making

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regarding hydrology (e.g., reservoir design) is usually not coordinated with decision-making regarding nutrient management. The dashed arrows between hydrology and policy and between biogeochemistry and policy indicate potential feedback loops from the functioning of the system (e.g., in terms of flood frequency, nutrient delivery, or water quality) and the management of those systems. Proposed feedback mechanisms include disturbances, changes in risk or risk perception, or the provisioning of ecosystem services (e.g., water supply). While these dashed arrows are not explicitly addressed in this dissertation, they are included in the conceptual figure to illustrate that these systems are dynamic and that possible drivers of change may be internal.

STRUCTURE OF THIS DISSERTATION

In chapters 2 and 3 I ask how anthropogenic N and P cycling have changed in the northeastern United States (NE) from 1930 to 2000. The NE includes 13 states and the District of Columbia. The region is dominated by temperate forest and in 1930 supported substantial agriculture and several major urban areas. Over the 70 year study period, the area of agricultural land declined by half, while the population doubled. The suburbanization of the region was accompanied by major changes in infrastructure – particularly wastewater sewers and wastewater treatment plants. The NE also has the highest density of dams in the United States (Graf 1999). This research was a collaborative effort with Charles Vörösmarty, Wil Wollheim, Balazs Fekete, and Joseph Hoover that emerged from a summer synthesis institute organized by Charles Vörösmarty in 2009 as part of the NSF-funded Northeast Consortium for Hydrologic Synthesis. The goal of the larger project was to synthesize disciplinary perspectives on hydrology to

understand how humans and water systems have changed over time. I was particularly interested in understanding how climate change, land use change, and widespread hydrologic engineering (e.g., dam building) have interacted to change water quality in the NE over the 20th century.

In Chapter 2, I reconstructed N and P budgets for the 437 counties of the NE, accounting for all anthropogenic inputs (e.g., fertilizers, food, livestock feed, atmospheric deposition) every five years from 1930-2000. This chapter addressed Arrow 1 and Box F in the conceptual figure (Fig. 1.1). I used the constructed budgets to assess temporal and spatial changes in human nutrient use (Fig. 1.1, Box F) and used these patterns in combination with the literature to generate hypotheses about the drivers of these changes. Although my conceptual framework only includes policy drivers (Fig. 1.1, Box E), my analysis was much broader in its inclusion of economics, technology, and scientific understanding. The manuscript resulting from this work (Hale et al. in revision) is currently in revision for resubmission to *Global Biogeochemical Cycles*.

In Chapter 3 I combined the data generated in Chapter 2 with hydrology data modeled by Balazs Fekete and data I compiled on dams, sewers, and wastewater treatment technology in a statistical water-quality transport model developed by Green et al. (2004). I used this model to develop scenarios to test hypotheses about the importance of anthropogenic nutrient inputs (Fig. 1.1, Box F and Arrow 2), hydrology as it is affected by climate (Fig. 1.1, Arrows 3 and 4), and hydrology as it is affected by hydrologic engineering (Fig. 1.1, Arrow 5) in determining N and P yields from watersheds (Fig. 1.1, Box G). This manuscript is currently under review by my co-authors (Hale et al. in preparation).

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In chapters 4 and 5, I ask similar questions about interactions between hydrologic engineering and biogeochemistry with regard to urban stormwater management in Phoenix, AZ. The Phoenix metropolitan area is a rapidly growing urban area in the Sonoran Desert. The climate is hot and dry, with rainfall averaging 200 mm annually. Despite low annual rainfall, urban flooding occurs frequently during storms. Although urban density in Phoenix is even across the city, there is substantial heterogeneity in stormwater drainage strategies. Older areas are drained by storm sewers, whereas newer areas are drained by retention basins and engineered channels. I monitored stormwater hydrology and chemistry for 10 watersheds that were drained by different stormwater infrastructure types and ranged in area from 5 to 17,000 ha. This research is part of a NSF-funded project to understand N sources and delivery in Phoenix and Tucson, AZ. Collaborators include Laura Turnbull, Stevan Earl, Nancy Grimm, Dan Childers, Kitty Lohse, Greg Michalski, Krystin Riha, Paul Brooks, and Tom Meixner.

In chapter 4 I reconstructed temporal changes in stormwater infrastructure design from 1955 to 2010 in Scottsdale, AZ (Fig. 1.1, Box B). As part of the stormwater N project, we instrumented 10 watersheds in Scottsdale and Tempe, AZ to collect data on stormwater hydrology and chemistry over two years. I used these data in structural equation models to test hypotheses about the importance of stormwater infrastructure design (Fig. 1.1, Box B, Arrows 4 and 5), watershed land cover, and storm characteristics (Fig. 1.1, Box B, Arrows 3 and 4) for solute delivery (N species, dissolved organic carbon, P, and chloride).

In Chapter 5, I address the mechanisms linking hydrology and biogeochemistry in urban watersheds. As mentioned above, hydrology can be important as a transport vector,

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but may also affect biogeochemistry by altering the physical and chemical conditions of the environment. Other research has also suggested that there may be a direct link between Boxes B and G in Figure 1.1. That is, infrastructure designed to alter hydrology may affect biogeochemistry directly. In Phoenix, for example, stormwater retention basins are designed to reduce peak stormwater flows, but also may support high rates of denitrification (Zhu et al. 2004, Larson 2010, Larson and Grimm 2012). My objective in Chapter 5 was to examine the balance of hydrological and biogeochemical control on N delivery in stormwater and to evaluate whether N sources varied across urban watersheds with different stormwater infrastructure designs. This research took advantage of NO_3^- isotopic data analysis by collaborators Krystin Riha and Greg Michalski at Purdue University. Triple isotopes of NO_3^- ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) were used to identify potential sources and transformations of NO_3^- in urban watersheds.

In the final chapter of the dissertation I return to this conceptual framework to synthesize the findings from Chapters 2 through 5. Despite differences in scale and climate, these two study systems share temporal and spatial heterogeneity in hydrologic infrastructure. I develop a second more mechanistic framework to parse the effects of land use, climate, and hydrologic infrastructure on nutrient delivery from these two systems and discuss the implications of this research for other systems and decision-makers.

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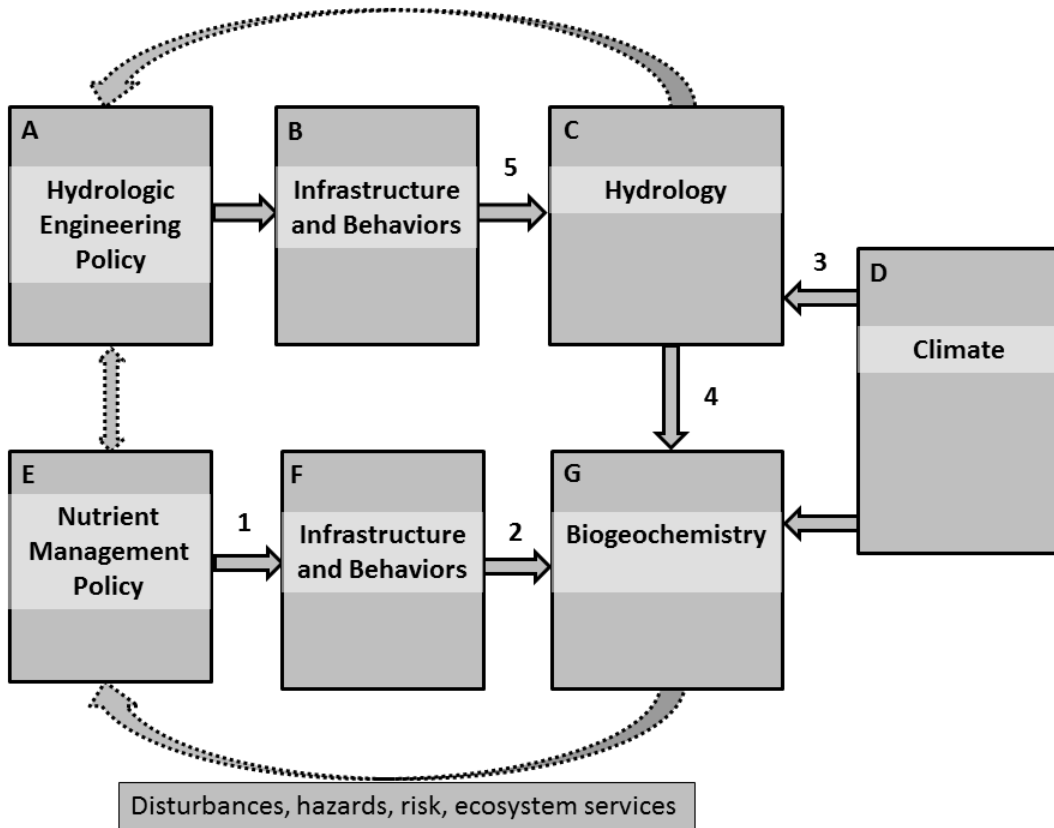
Figure 1.1. Conceptual framework for this dissertation. Labeled boxes and arrows are discussed in the text.

Chapter 2
A HISTORY OF NUTRIENT LOADING TO THE NORTHEASTERN UNITED

STATES

ABSTRACT

Humans have dramatically altered nutrient cycles at local to global scales. We examined changes in anthropogenic nutrient fluxes to the northeastern United States (NE) from 1930 to 2000. We created a comprehensive time series of anthropogenic N and P inputs to 437 counties in the NE at five-year intervals. Inputs included atmospheric N deposition, biological N_2 fixation, fertilizer, detergent P, livestock feed, and human food. Exports included exports of feed and food and volatilization of ammonia. N inputs to the NE increased throughout the study period, primarily due to increases in atmospheric deposition and fertilizer. P inputs increased until 1970 and then declined due to decreased fertilizer and detergent inputs. Livestock consistently consumed the majority of nutrient inputs over time and space. The area of crop agriculture declined during the study period but consumed more nutrients as fertilizer. We found that stoichiometry (N:P) of inputs and absolute amounts of N matched nutritional needs (livestock, humans, crops) when atmospheric components (N deposition, N_2-fixation) were not included. Differences between N and P led to major changes in N:P stoichiometry over time, consistent with global trends. N:P decreased from 1930 to 1970 due to increased inputs of P, and increased from 1970 to 2000 due to increased N deposition and fertilizer and decreases in P fertilizer and detergent use. We found that nutrient use is a dynamic product of social, economic, political, and environmental interactions. Therefore, future nutrient

management must take into account these factors to design successful and effective nutrient reduction measures.

INTRODUCTION

Globally, humans have increased the availability of the often-limiting nutrients nitrogen (N) and phosphorus (P) (Vitousek et al. 1997b, Falkowski et al. 2000, Galloway et al. 2008). Increased nutrient availability has had many positive effects on human well-being globally, primarily by increasing crop yields and therefore human food supply. However, it has also led to ecologically damaging and economically costly eutrophication problems (Carpenter et al. 1998). Humans have changed N and P cycles differently; whereas global N availability has doubled, P availability has quadrupled since the pre-industrial age (Falkowski et al. 2000). At the same time, regulatory controls for P have been more widespread and more successful than those for N (e.g., P detergent bans, Litke 1999, and P turf fertilizer bans, Lehman et al. 2009). However, human nutrient use does not respond to regulations alone. Although there have been no regulations directly controlling the use of agricultural fertilizer, inputs of fertilizer P have declined in the United States since 1980 (Alexander and Smith 1990). Global nutrient cycles are frequently depicted as systems spiraling out of control (Vitousek et al. 1997a, Childers et al. 2011); yet declines in P inputs from agricultural fertilizer, in the absence of direct regulation, suggest that anthropogenic nutrient cycles may respond to a diversity of drivers and thus may be subject to additional socio-ecological feedbacks (*sensu* Liu et al. 2007).

Because of the long-term legacy effects of human environmental management (McGuire et al. 2001, Pastore et al. 2010, Bain et al. 2012, MacDonald et al. 2012), a historical approach is critical for understanding how absolute quantities and geographic patterns of nutrient use emerge over time (Barles 2007, Billen et al. 2007) and provides a context for understanding the state of modern socio-ecosystems (Foster et al. 2003, Billen et al. 2007). Importantly, Barles (2007) notes that changes in human-nutrient systems are "not necessarily...continuous, systematic and deliberate." Human nutrient use is intricately tied to how we produce food and how we deal with waste (Jordan and Weller 1996, Barles 2007, Billen et al. 2007, Cordell et al. 2009). It is therefore also tied to the technologies that society has available for these two activities (e.g., fertilizer, water treatment), human perceptions regarding waste (e.g., Barles 2007), and the political and economic conditions within which these activities take place (e.g., U.S. food policy, global grain markets).

Historical approaches are also useful for understanding ecological consequences of nutrient inputs and the development of scientific knowledge regarding the pollution resulting from those inputs (Howarth and Marino 2006). Recent research suggests that increases in anthropogenic N inputs relative to P is a global phenomenon (Peñuelas et al. 2012) that may be causing shifts in nutrient limitation as well as species composition in both fresh (Elser et al. 2009) and marine waters (Justić et al. 1995, Turner et al. 2003, Billen et al. 2007, Grizzetti et al. 2012). Understanding the mechanisms underlying historic and ongoing changes in nutrient inputs is critical to designing effective solutions to current and future nutrient pollution (Foster et al. 2003) and improving the current

watershed management emphasis on problem remediation rather than prevention (Vörösmarty et al. 2010).

Nutrient use by humans is variable not only temporally but also spatially. Differences in the absolute quantities, drivers, and stoichiometry of nutrient use vary across regional and global scales (Jordan and Weller 1996, Boyer et al. 2002, Vitousek et al. 2009) as a result of differences in land use (Jordan and Weller 1996, Boyer et al. 2002) and economic development (Vitousek et al. 2009). Many recent assessments of anthropogenic nutrient inputs to the United States have focused on areas dominated by row-crop agriculture, especially the Mississippi River basin (David and Gentry 2000, Donner et al. 2004, Alexander et al. 2008, Broussard and Turner 2009). Relatively little research has focused on the historical nutrient patterns of the northeastern United States (NE, Fig. 2.1) from 1930 to 2000. The NE is one of the most densely populated regions of the US, and over the 20th century it experienced a significant reduction in cropland concurrent with a near doubling of the human population. However, the NE is also a major meat-producing region for the US, and so livestock agriculture is major driver of nutrient cycling (Boyer et al. 2002). Furthermore, the NE has vast areas of forested land that is subject to high rates of atmospheric N deposition (Boyer et al. 2002).

The objectives of this paper are to: (i) describe changes in the geographic patterns of nutrient inputs to the NE region over a near-century timeframe (1930-2000), (ii) assess how nutrient inputs have responded to changing demography, land use, technology, and legislation during this period, and (iii) identify potential ecological consequences of changes in nutrient inputs over time.

METHODS

We used a mass balance approach (Green et al. 2004) to estimate net anthropogenic fluxes of N and P to the NE during the 20th C. We created nutrient budgets for the 437 NE counties at five-year time steps from 1930 to 2000. For the present study, we measured the net inputs of nutrients to or from each county as fertilizer, atmospheric deposition (N only), biological N_2 fixation, livestock feed, human food, and detergent phosphates. To avoid double counting, the total net inputs of N and P took into account transfers within the county (e.g., crops consumed as human food). Where local production of food and feed exceeded local consumption, the balance was negative and was defined as a net export from the county. Exports included only excess agricultural production and ammonia volatilization. We use "net inputs" to refer to inputs associated with a single source of nutrients and "total net inputs" to refer to inputs from all sources. We made the simplifying assumption that P inputs from geologic weathering were unchanging and did not include them here. Manure and human sewage were calculated but were not considered additional inputs as they result from internal recycling of nutrients from fertilizer, food, and feed imports. Our budgets estimated the net inputs or exports of nutrients to or from each county and to watersheds, but we did not track nutrient transport or processing in receiving waters downstream. We also did not account for management strategies, such as riparian buffers or wastewater treatment, which may reduce the pathways and fluxes of nutrients in aquatic ecosystems.

Atmospheric Deposition

Data on N deposition rates are limited in time and space. To describe temporal changes in atmospheric deposition, we estimated atmospheric deposition of N to the

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whole region using relationships between gaseous N emissions (as nitrogen oxides [NO_x],

and ammonia [NH_3]) and N deposition. State-level NO_x emissions data for 1930 through

2000 came from Gschwandtner et al. (1985) and the EPA National Emissions Inventory

(NEI, http://www.epa.gov/ttn/chief/trends/index.html). Although state-level NH_3

emissions were available for 2000 from the EPA, they were not available for early parts

of the century. We therefore calculated historic NH_3 emissions using manure and

fertilizer data from our dataset (see below for manure and fertilizer methods) and NH_3

volatilization coefficients from Battye et al. (1994) and Boyer et al.(2002). Our calculated

NH_3 emissions were well correlated with EPA emissions data for the year 2000 ($r =$

0.998, $p < 0.001$). We obtained atmospheric deposition rates for the year 2000 from the

National Atmospheric Deposition Network (NADP, http://nadp.sws.uiuc.edu/). The

NADP collects data on annual wet deposition rates for nitrate (NO_3^-) and ammonium

(NH_4^+) from 41 sites throughout the NE. We estimated total deposition (wet + dry) by

assuming that dry deposition of NH_4^+ is 18% of wet deposition, and dry deposition of

NO_3^- is 48% of wet deposition (Bowen and Valiela 2001). These data were then spatially

interpolated in ArcGIS (ESRI, Redlands CA) using inverse distance weighting (following

NADP protocols) to create a continuous loading surface and calculate average state-level

deposition. We regressed state-level emissions against state-level deposition data for year

2000 independently for NO_3^- ($R^2 = 0.769$, $p < 0.001$) and NH_4^+ ($R^2 = 0.729$, $p < 0.001$).

These relationships were then applied to historic NO_x and NH_3 emissions data to estimate

past N deposition levels at the state level, which were added to estimate total N

deposition to the region.

To describe changes in the spatial pattern of N deposition, we used point-scale deposition data from the NADP and earlier literature (Eriksson 1952, Fisher 1968, Pearson and Fisher 1971, Cogbill and Likens 1974) to estimate atmospheric deposition based on latitude, longitude, and year. Deposition data extended from 1920 (4 sites) through 2000 (41 sites). We developed separate regression equations for the wet deposition of NO_3^- and NH_4^+. These regression equations (Eq. 1, 2) were then used to create a grid (7 km resolution) of N deposition rates for each study year in ArcGIS. Mean N deposition rates were then calculated for each county and each year in ArcGIS.

$NO_3^- = -489.9 - 1.01 *$ Longitude $+ 0.97 *$ Latitude $+ 0.19 *$ Year

$(R^2 = 0.24, p < 0.0001)$ (1)

$NH_4^+ = -50.68 - 0.21 *$ Longitude $+ 0.20 *$ Latitude $+ 0.01 *$ Year

$(R^2 = 0.27, p < 0.0001)$ (2)

Fertilizer Application

Fertilizer application rates (kg N or P ha^{-1} y^{-1}) for 1945 to 2002 were obtained at the county level from two USGS reports (for years 1945-1985: Alexander and Smith 1990, and for years 1982-2001: Ruddy et al. 2006). To estimate fertilizer application rates for earlier decades, we used state-level fertilizer sales and nutrient content from fertilizer use surveys (Smalley 1929, 1939) to calculate inputs of nutrients to each state (Eq. 3). State-level data were then disaggregated to county level using county harvested cropland (1930 and 1940) as a proportion of total state cropland data from the Census of

Agriculture (USCB, 1932; 1942). All inputs were calculated as kg N or P county^{-1} y^{-1} and then divided by county area to obtain inputs rates in units of kg N or P ha^{-1} y^{-1}.

$$F_{ik} = F_i * N_i * C_{ik}/C_i \hspace{5cm} (3)$$

where,

F_{ik}	inputs of fertilizer N or P for the *k*th county in the *i*th state (kg)
F_i	fertilizer sales for the *i*th state (kg)
N_i	nutrient content of fertilizer in the *i*th state (%)
C_{ik}	area of harvested cropland for the *k*th county in the *i*th state (ha)
C*i*	area of harvested cropland for the *i*th state (ha).

Biological Nitrogen Fixation

Biological N$_2$ fixation was calculated by multiplying crop and pasture areas (USCB 1932, 1942, USDA 1980, 1990, 1993, 1999, 2004) by rates of N$_2$ fixation obtained from Jordan and Weller (1996) and sources cited therein (Table 2.1). Because land-use data for our study period was unavailable and rates of N$_2$ fixation in non-agricultural lands are usually low (Jordan and Weller 1996), we assumed non-agricultural land had negligible N$_2$ fixation rates.

Crop-Livestock Balance

For each county at each time step, we calculated N and P in crops harvested, feed imported for livestock, and manure production to calculate the net flux of N and P as feed and food to or from the county (Eq. 4-6). All inputs were calculated in units of

kg county^{-1} y^{-1} and then divided by county area (in ha) to obtain net inputs as kg N or P

ha^{-1} y^{-1}. We used a spoilage rate of 10% for all food and feed, following Jordan and

Weller (1996).

For livestock feed:

$$LF_k = LD_k - LS_k *S \tag{4}$$

where,

      LF_k net inputs of nutrients in livestock feed for the kth county (kg)

      LD_k demand for nutrients by livestock in the kth county (kg)

      LS_k supply of nutrients for livestock feed by local crop production in

                      the kth county (kg)

      S   rate of spoilage (%).

For consumption of N and P by humans:

$$HF_k = HCD_k - HCS_k*S + HLD_k - HLS_k*S \tag{5}$$

where,

      HF_k net inputs of nutrients in human food for the kth county (kg)

      HCD_k demand for nutrients from crops by humans in the kth county (kg)

      HCS_k supply of nutrients for human food by local crop production in the

                      kth county (kg)

      HLD_k demand for nutrients from livestock by humans (e.g., meat, milk,

                      and eggs) in the kth county (kg)

      HLS_k supply of nutrients for human food from local livestock production

                      in the kth county (kg).

The local livestock production is defined as:

$$\mathrm{HLS}_k = (\mathrm{LD}_k - \mathrm{LM}_k) \hspace{5cm} (6)$$

where,

LM_k production of manure by livestock in the kth county (kg).

Total nutrients in crop harvest were estimated by multiplying county-level crop production data (USCB 1932, 1942, USDA 1980, 1990, 1993, 1999, 2004) by crop-specific nutrient content (Lander and Moffitt 1996) for the following crops: corn for grain, wheat, oats, barley, rye, soybeans, potatoes, sorghum, alfalfa hay, and non-alfalfa hay (Boyer et al. 2002). We ssumed that the nutrient content of each crop was constant over time. We assumed that the net input of food and feed was the difference between county-level supply and county-level demand. Therefore, if livestock feed supply was less than livestock feed demand, we assumed a net input of feed to make up the difference. Conversely, if supply was greater than demand, the balance was negative and the excess was assumed to be exported. Boyer et al. (2002) used this approach to estimate anthropogenic N inputs to the NE for a single year and found a strong correlation between feed imports calculated using this method and imports estimated from feed expenditure data. Local crop production is consumed by either livestock or humans or is exported. After subtracting a 10% spoilage rate (Jordan and Weller 1996), we made the following proportions of crops available for human consumption (i.e., HCS_k) : 100% of potatoes, 61% of wheat, 17% of rye, 4% of corn, 6% of oats, and 3% of barley (Jordan and Weller 1996). The remaining crops were made available for livestock consumption

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(i.e., LS_k) (Jordan and Weller 1996). Any crops not consumed by humans or livestock were exported.

Livestock nutrient demand (LD_k) was calculated from county-level inventories of livestock (cattle, chickens, turkeys, hogs and pigs) from the Census of Agriculture (USCB 1932, 1942, USDA 1980, 1990, 1993, 1999, 2004) and published nutrient consumption rates (Van Horn et al. 1996). Nutrient loss as manure (LM_k) was calculated using livestock inventories and published manure production rates per animal (Van Horn et al. 1996). The difference between feed inputs and manure losses, minus a spoilage rate of 10% (Jordan and Weller 1996) was assumed to go to human food products (HLS_k). Any production in excess of local demand was exported.

Human Food and Waste

To calculate net inputs of food nutrients consumed by humans, we calculated dietary demand for N and P using county-level population (USCB 1995, 2002) and estimates of per-capita N and P consumption rates. Based on the average protein consumption in the United States (80 g d^{-1})(Geissler and Powers 2005), we estimated N intake to be 4.7 kg cap^{-1} y^{-1}. This is similar to other values used in the literature (Boyer et al. 2002, Han and Allan 2012). The USDA recommended daily allowance of P is 0.256 kg cap^{-1} y^{-1}(Geissler and Powers 2005), and available P in the food supply averaged 0.55 kg cap^{-1} y^{-1} during our study period (Gerrior et al. 2004). Assuming that P consumption is higher than recommended values but lower than that available in food supply, we averaged these values to obtain a per capita P consumption rate of 0.4 kg P yr^{-1}. This value is similar to other estimates in the literature (Meybeck and Chapman 1990, David and Gentry 2000). We assumed no net accumulation of individuals for a given year; that

is, demand for food nutrients was assumed to be equal to nutrients in human waste. We assumed that human protein (and therefore nutrient) demand from animal and crop sources was 70 and 30%, respectively (FAO 2012). Net nutrient input or export to each county as food was calculated as the difference between human food demand and local supply. This was calculated separately for animal and crop sources (Eq. 5).

Detergent Phosphates

Phosphate-containing detergents were not used until 1945, but by 1970 inputs from detergents had reached 0.8 kg P cap^{-1} y^{-1} (Chapra 1980). We assumed a linear increase in per-capita phosphate use from 1945 to 1970. The first bans on detergent phosphates emerged in 1971. We used data from Litke (1999) on detergent bans (ban dates and phosphate limits for each state) to estimate state-level per-capita inputs for each decade. To convert the Litke data, given as detergent phosphate concentrations, to per-capita inputs, we assumed a pre-ban detergent P content of 12% for calculations (Litke 1999).

Temporal and Spatial Statistics

To determine the significance of trends in nutrient inputs to the region over time, we performed a linear regression using year as the predictor variable for annual net inputs to the region (total and for individual sources).

We investigated the degree to which nutrient inputs were distributed or concentrated across the NE throughout the 20th century by spatial autocorrelation. Spatial autocorrelation measures the degree to which data from locations close to each other are more similar than from remote locations (O'Sullivan and Unwin 2010). Positive spatial autocorrelation, the most commonly observed type, indicates that the data values for

spatial entities located near each other (e.g., contiguous counties) are similar. Global

spatial autocorrelation details the degree to which statistically significant spatial

clustering of high or low data values occurs throughout the study area. We used Moran's

I (Chang 2008) to measure the global spatial autocorrelation for the NE for five-year

periods between 1930 and 2000. Moran's I does not provide detail on where within the

study area nutrient inputs were concentrated. Therefore, we also used a local spatial

autocorrelation metric, Local Indicators of Spatial Association (LISA, Anselin 1995,

Franczyk and Chang 2009), to identify the locations of statistically significant spatial

clustering within the study area.

RESULTS AND DISCUSSION

Patterns in Nutrient Inputs to the NE over Time

Total net N inputs over the entire region increased steadily and significantly over

the study period (Fig 2.2A; $R^2 = 0.70$, $p < 0.001$). Farm-fertilizer inputs of N to the

landscape increased significantly ($R^2 = 0.91$, $p < 0.001$), despite a decline in cropland

area, reflecting agricultural intensification. Food N was exported most years, but exports

decreased significantly over the study period ($R^2 = 0.91$, $p < 0.001$; Fig 2.2A). As the

population nearly doubled (from 35 to 67.6 million) crop production for human food

declined (12% to 7% of total crop production). Although human food N was exported

throughout most of the century, the food system as a whole was an importer of N via

fertilizer and livestock feed (Fig 2.2A).

Atmospheric N deposition increased significantly over the study period ($R^2 =$

0.88, $p < 0.0001$) and contributed as much as 47% of net N inputs to the NE by the end of

the century. Since the mid-1990's, however, N deposition has decreased slightly due to reduced NO_x emissions (EPA NEI, http://www.epa.gov/ttn/chief/trends/index.html). Inputs of N as livestock feed ($R^2 = 0.39$, $p < 0.05$) and N_2 fixation ($R^2 = 0.36$, $p < 0.05$) decreased throughout the study period; however, these remained large contributors to total inputs, 23% and 15% respectively, as of 2002.

In contrast to N, there was no consistent linear trend in total net P inputs across the entire study period (Fig. 2.2B). Instead, total net P inputs increased nearly 4 fold from 1940 to 1969, from 0.08 Tg P y^{-1} to 0.29 Tg P y^{-1}, followed by a significant decline in the 1970's ($R^2 = 0.79$, $p < 0.01$). Human food P was exported throughout the study period, but exports declined significantly over time ($R^2 = 0.71$, $p < 0.001$), tracking the pattern of food N. Both detergent and fertilizer P inputs peaked around 1970 and thereafter declined significantly (detergent: $R^2 = 0.75$, $p < 0.05$; fertilizer: $R^2 = 0.90$, $p < 0.01$). Inputs of livestock feed P did not demonstrate any significant trend over the study period.

Since temporal patterns of net N and P inputs differed over the study period, the N:P of nutrient inputs also changed over time (Fig. 2.2C). The N:P of total net inputs increased from 1930 to 1940 as a result of several smaller changes in livestock populations and crop production. From 1940 to the mid-1960s the trend reversed as inputs of P fertilizer and detergents increased more rapidly than fertilizer N. The N:P of total inputs steadily increased from 1965 to 2002 due to concurrently increasing N inputs and declining P inputs. Across the study period the N:P of total net inputs was consistently greater than the N:P requirements of humans. When we excluded atmospheric deposition of N from the total (i.e., "Total direct inputs," Fig. 2.2C) as an indicator of food system N:P, the N:P of inputs was high from 1930 to 1940, largely due

to very low inputs of P fertilizer and high inputs of N via biological N_2 fixation. From 1940 onward, the N:P of total direct inputs was bounded between the livestock requirement of ~11 and the human requirement of ~26. This not only suggests that the major drivers of nutrient requirements were demands for human food and livestock feed, but also indicates that P and N inputs were well-matched with regard to demands. Excluding detergent P and nonfarm fertilizer inputs of N and P does not substantially change this pattern: N:P remains bounded within 11 and 26 (data not shown).

Two other important trends of note are the increases in N:P of farm fertilizer since 1950 (Fig 2.2C) and nonfarm fertilizer since the mid 1980's (data not shown). The N:P of farm fertilizer was much lower than that of harvested crops throughout much of the study period, but the two lines converged at the end of the century, indicating that fertilizer additions more closely matched crop needs. Of course, N is also added to croplands via N_2 fixation. The stoichiometry of all agricultural inputs (N_2 fixation and N fertilizer, P fertilizer) is much above that of crop removal throughout the study period, which indicates an oversupply of N to crop systems. Although the stoichiometry of inputs was at most 6.5 times higher than crop uptake, the N:P of inputs moved towards the N:P of crop removal over time, i.e., nutrient additions were more in balance with crop removal. One final consideration with regard to nutrient additions to agricultural soils is that P is much more likely to accumulate in soils, whereas N is more likely to leach from the soil column. That is, the average residence time of N and P may be different, and therefore annual inputs of fertilizers may not reflect the N:P of plant-available nutrients in agricultural soils.

Spatial patterns of nutrient inputs

The overriding trend for the 20th century NE has been a major reorganization of the landscape, as agriculture shifted southward, human population density increased, and livestock populations became more concentrated. The major pattern was a spatial separation of food production from food consumption. At the end of the 20th century, agricultural inputs (livestock feed, fertilizer, and N_2 fixation) remained the largest inputs of nutrients at the regional scale and were the largest source of nutrients for most counties. However, the decline in agricultural inputs for most counties (N: 71%, P: 64% of counties) mirrored an increase in urban N and P inputs (human food, nonfarm fertilizer, and detergent P, 72% of counties). The key feature of these trends was their spatial pattern: declines in agricultural inputs were collocated with increases in urban inputs (Fig 2.4; N: r = -0.22, P: r = -0.32), suggesting a specialization of the landscape into separate urban and agricultural subregions (Fig 2.4).

Spatially, N and P inputs became more clustered throughout the region, as measured by Moran's I (N:R^2 = 0.33, p = 0.02; P: R^2 = 0.73, p <0.0001). Differences in the changes in clustering between N and P are likely due to fertilizer-use patterns (less widespread for P than N) and N deposition (higher rates in forested areas of the NE). Moran's I was also consistently higher for P than for N throughout the study period. Hotspots of nutrient inputs — clusters of counties with statistically high nutrient inputs as identified by LISA (Anselin 1995, Franczyk and Chang 2009) — were similar for N and P (Fig 2.3). The spatial statistical analysis revealed persistent hotspots of N and P inputs around the New York metropolitan area (Fig 2.3). Since 1970, hotspots emerged around the Chesapeake Bay in Virginia, Pennsylvania, Maryland, and Delaware.

Nutrient inputs shifted southward over the study period (Fig 2.4). Changes in nutrient inputs from 1930-2000 were significantly negatively correlated with latitude for both N ($R^2 = 0.09$, $p < 0.0001$) and P ($R^2 = 0.07$, $p < 0.0001$). These shifts were related to significant southward shifts in agricultural inputs. Changes in livestock nutrient demand from 1930 to 2002 were significantly negatively correlated with latitude (N and P: $R^2 = 0.11$, $p < 0.0001$), as were changes in fertilizer (N: $R^2 = 0.05$, $p < 0.0001$; P: $R^2 = 0.11$, $p < 0.0001$) and N_2 fixation ($R^2 = 0.33$, $p < 0.0001$) from 1930-2002 (Fig 2.4). Changes in human population density over the study period were not significantly related to latitude.

Drivers of Changes over Space and Time.

Major changes in N and P inputs are apparent at the regional scale over space and time (Figs. 2.2, 2.3, 2.4). These changes resulted from changes in land use, technology, fertilizer and food production, and nutrient emission control legislation.

Role of Livestock Agriculture

Previous work on the theory of ecological stoichiometry suggests that human activities disproportionately affect P cycling in order to bring nutrient ratios towards the N:P of the human body (Sterner and Elser 2002). Our stoichiometry results suggest that livestock and human nutritional requirements are key drivers of nutrient inputs to the NE (Fig 2.2C). This pattern is in stark contrast to nutrient inputs in the central part of the US, which are driven by row-crop agriculture (Alexander et al. 2008, Broussard and Turner 2009).

Livestock husbandry was a defining feature of the NE nutrient landscape during the 20th century. The majority of the inputs of nutrients to the region were used to support livestock agriculture, either directly as livestock feed, or indirectly as fertilizer, most of

which was used on feed crops. Despite declines in cropland, crop production increased during the 20th century, peaking in 1992. Much of this production was for livestock feed crops, and production of food crops for human consumption did not change significantly since 1930 (Fig 2.5A,B). Despite massive inputs of fertilizer to produce feed crops, the crop system only provided 12 to 50% (33% on average) of the nutrients required by livestock. The remaining nutrient demand was met with imported feed (Fig 2.5C,D). This system was highly inefficient in terms of nutrient use. The greater part of feed nutrients was converted to manure, and only 6-24% of the nutrient inputs to the regional livestock system were consumed by humans locally (Fig 2.5C,D).

Spatial patterns also demonstrate the importance of livestock to NE nutrient inputs. To understand how the drivers of nutrient inputs varied between counties, we categorized counties as human-, livestock-, or crop-driven based on which had the largest demand for nutrients. We then regressed total net N and P inputs (kg N or P ha^{-1} y^{-1}) against human population density, total livestock nutrient requirements (a proxy for livestock population density), and crop uptake. Across all counties, human population density was the best predictor of total net nutrient inputs ha^{-1}y^{-1} across time (correlation coefficients ranged from 0.88 to 0.98), and the highest nutrient inputs were in counties with the highest population density (> 5 people ha^{-1}, N = 25 counties in 1930 and 63 counties in 2002; Fig 2.6). However, for counties with low population density (< 5 people ha^{-1}, N = 412 counties in 1930 and 374 counties in 2002), livestock nutrient requirements ha^{-1} (an integrative proxy for livestock population density that incorporates ranges in livestock body mass and nutrient demand) was the best predictor of total net N and P inputs ha^{-1} (Fig 2.6). Furthermore, although human population densities were the best

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predictor of nutrient inputs overall, livestock were the best predictor of nutrient inputs for the majority of counties. However, there was a decrease in livestock-driven counties over time, from 84 to 61%, and an increase in human-driven counties, from 15 to 31%, and crop-driven counties, from 0.5 to 9%.

Although the number of livestock-driven counties decreased over the study period, average nutrient inputs to livestock-driven counties increased from 35 to 58 kg N ha^{-1} and 2.7 to 3.7 kg P ha^{-1}. Median livestock densities (as measured by total livestock nutrient demand) declined over the study period ($R^2 = 0.61$, $p = 0.0002$), yet maximum densities increased ($R^2 = 0.94$, $p < 0.0001$), reflecting the rise of concentrated industrial animal agriculture. Importantly, total livestock populations for the region have not changed significantly over the study period. Rather, it is the shifting spatial distribution of these populations into smaller areas that is driving changes in nutrient inputs and possibly increasing the clustering of nutrient inputs as measured by Moran's I. Meanwhile, human population densities demonstrated the opposite pattern, where median human population density increased ($R^2 = 0.98$, $p < 0.0001$), and the maximum human population density decreased ($R^2 = 0.73$, $p < 0.0001$), suggesting declining urban populations and increased suburbanization or exurbanization, a trend shared with much of the Midwest and Eastern US (Brown et al. 2005).

Crop Agriculture and Fertilizers

The largest nutrient inputs to the NE during the 20th century were to support agriculture – fertilizers, N_2 fixation, and livestock feed (Fig 2.5). Figure 2.5 illustrates that accumulation and/or losses accounted for a large portion of nutrients added to agricultural crop systems as fertilizer and N_2 fixation. Although total N inputs to the crop

system did not change over time, fertilizer replaced N_2 fixation as the dominant input to the crop system. The majority of N inputs to the crop system either accumulated in soils or was lost to runoff, leaching, or denitrification (Fig 2.5A). Inputs of P to crop systems were less than crop uptake from 1930 through 1940, meaning that farmers were mining soils for P. Because crop uptake of P did not change significantly over the study period, changes in P fertilizer use primarily affected the amount of P accumulating in soils and lost downstream as eroding soils (Fig 2.5B).

Over the study period, N and P fertilizer use followed very different patterns (Fig 2.2A, 2.2B). We can understand the differences between N and P fertilizer use by comparing the absolute amount and stoichiometry of fertilizer nutrients to that removed from soils by crops. The ratio of fertilizer P inputs to P removed by harvested crops has moved towards one since 1970, indicating more efficient use of fertilizers (Fig 2.7). This pattern was not apparent for agricultural N inputs. N fertilizer inputs increased throughout the century, although until the mid-1990's inputs were lower than N removed by crops (Fig 2.7). Including biological N_2 fixation pushed agricultural N inputs far above crop removal, and declines in N inputs during the second half of the century were directly related to reductions in cropland area rather than reductions in N fertilizer use (Fig 2.7). Another way of understanding fertilizer use efficiency is to compare the stoichiometry of nutrients (i.e., N:P) added as fertilizer to the stoichiometry of nutrients removed as crops. Ideally, these would be equal, otherwise the nutrient added in excess would be unused and therefore vulnerable to downstream loss or, in the case of N, denitrification. In the NE, the N:P of fertilizer application was much lower than that of crop harvest during much of the study period (Fig 2.2C), indicating an over-application

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of P relative to N. The N:P of fertilizer and crop harvest converge by the end of the century, indicating a more efficient application of fertilizer at the regional scale. When N_2 fixation is included, however, the N:P of inputs was far in excess of that removed by crops, a possible contributor to N pollution in rivers—for example, throughout New England (Moore et al. 2004).

The increasing efficiency of P fertilizer use was driven by a confluence of factors: better science allowed farmers to calculate optimal rates of fertilization (e.g., Bray 1945), and the availability of individual nutrient fertilizers rather than multi-element fertilizers allowed farmers to apply fertilizers in ratios appropriate to their crops, soil, and climate. Previous over-fertilization meant that many soils had high levels of P that crops could mine (Parker 1950, MacDonald and Bennett 2009), and a major spike in the cost of fertilizer in the early 1970's acted as an incentive for farmers to use fertilizers judiciously (ERS 2011). Fertilizer N was not unaffected by these changes, but the effects were less dramatic. Rather than a drop in fertilizer N use, we see a slight leveling off. One potential reason for continued use of N fertilizers is that N is prone to leaching and denitrification and therefore less likely to accumulate in soils, regardless of over-fertilization. Continued use of N despite increased concern for N pollution compared to P with regard to water quality (Kurtz 1970) suggests that changes in society's environmental ethic were not important drivers of the changes in P fertilizer use during the 1970's.

Nutrient Legislation

Although agricultural fertilizer use was never directly regulated, detergent P and nonfarm P fertilizers have been subject to restrictive legislative controls. Most nutrient legislation during the latter part of the century focused on P reduction strategies and was

to some degree successful at reducing P concentrations in streams and rivers (Lettenmaier et al. 1991, Litke 1999, Lehman et al. 2009). The legislative focus on P during the 1970's, to the exclusion of N, was an important reason for several of the divergent patterns of N and P inputs and was in part due to the scientific understanding of nutrient limitation at the time (Howarth and Marino 2006). The science of the limnological tradition held that productivity in freshwater and marine systems was P-limited, and therefore the most effective strategy to reduce eutrophication was to reduce inputs of P. Although there was research demonstrating that many marine receiving waters were N-limited (Ryther and Dunstan 1971), water managers doubted the results and mistrusted the bioassay methods used in marine studies (Lee 1973, Cloern 2001, Howarth and Marino 2006). As a result, the contemporary knowledge of ecosystem function at the time had a strong influence on which pollution management strategies were pursued, with a long-term legacy effect on pollution patterns regionally.

Point sources of pollution were addressed in legislation before nonpoint sources because they were relatively easy to manage and their management had an identifiable impact on water resources (Carpenter et al. 1998, Litke 1999). However, the NE hosts a remarkable example of effective nonpoint source pollution legislation in the regulation of nonfarm fertilizers. Nonfarm fertilizer was one of the most rapidly increasing inputs of N and P to the NE. Although still a small percentage of total N (2%) and of P (4%) inputs by 2002, nonfarm fertilizer increased substantially from 4% of total fertilizer P inputs in 1987 (when records began) to 10% in 2002 (and from 5% to 18% for N). Spatially, areas with concentrated nonfarm fertilizer inputs (e.g., suburban and urban areas) were distinct from areas with high fertilizer use for agriculture (data not shown). Although agricultural

P fertilizer use is not regulated (Environmental Protection Agency 1999, The Fertilizer Institute 2003), there has been a recent emergence of P fertilizer bans for urban and suburban lawns due to eutrophication of local water bodies (e.g.,Lehman et al. 2009). Legislation has emerged across spatial and political scales at the municipal, county, and state level. At this time, eleven states in the US, five of which are in the NE (Maine, Maryland, New York, New Jersey, and Virginia), have passed laws banning the use of P fertilizers for turf grass.

Atmospheric N

Some variations between trends in N and P are due to differences in their biogeochemical cycling potential. The N cycle has a large inert atmospheric component while the P cycle is geologic. These differences have major consequences for the stoichiometry of NE nutrient inputs. There are three major pathways by which humans convert inert N_2 gas into reactive N species: 1) biological N_2 fixation, 2) industrial N_2 fixation (fertilizer production), and 3) NO_x production as a by-product of the combustion of fossil fuels. These types of human activities influence the N cycle without affecting P inputs. While industrial N_2 fixation for fertilizer manufacture is tightly controlled, N deposition is an inadvertent result of human activity, and biological N_2 fixation is indirectly controlled by farmers are a result of crop choices.

We found a consistent pattern when considering only total direct inputs of N (i.e., no atmospheric sources): the stoichiometry (N:P) of inputs and absolute amounts of N matched nutritional needs (livestock and human requirements, crop uptake). The N:P of total inputs to crop systems was substantially higher than the N:P of crop uptake and the N:P of the total nutrient inputs for the region was higher than the N:P of any of the major

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consumers in the system (humans, livestock, crops; Fig. 2.2C). This is evidence that the atmospheric component of N cycle in the NE has been poorly managed and that inputs of N from N deposition and N_2 fixation have not been adequately accounted for by nutrient users. The lack of attention to atmospheric inputs of N has led to increased N:P of nutrient inputs at the regional scale. The excess N entering the system is then especially vulnerable to downstream losses because it is not needed by the systems to which it is applied, with severe consequences for downstream ecosystems.

Potential Ecological Consequences

Accounting for anthropogenic nutrient inputs is easiest within human boundaries, such as municipalities and counties, but nutrient inputs are transported by water downstream, and thus ecological effects must consider ecological boundaries, in this case watersheds. We calculated the N:P of nutrient inputs to 256 watersheds draining to the NE coast (Fig. 2.8). These estimates do not account for processing (by ecosystems or technology such as waste water treatment) or transport processes that occur within the watershed and therefore ignore the large percentage of nutrient inputs that may be retained by watersheds (e.g., Seitzinger et al. 2002, Hong et al. 2012). An additional caveat is the potential for land use legacies to have a strong effect on downstream loading (Foster et al. 2003). P cycles much more slowly than N due to binding with soils and sediments, and therefore watersheds may be more retentive of P than of N (e.g., Hong et al. 2012). As a result, the N:P of inputs for a year may not be a good predictor of the N:P of nutrients delivered downstream. P inputs from fertilizer to agricultural soils are likely to build up over time (Dobermann and Cassman 2002, MacDonald and Bennett 2009, MacDonald et al. 2012). Since soil P content is the best predictor of P transport

downstream (Carpenter et al. 1998), it is likely that in agricultural areas cumulative P inputs could be a better predictor of downstream P export than annual inputs. Finally, we calculated nutrient inputs on an annual basis, but riverine exports are likely to vary seasonally (Carpenter et al. 1998) due to seasonal use of nutrients by humans as well as variability due to runoff patterns. Previous research has shown significant seasonal fluctuations in nutrient limitation of aquatic systems (Howarth 1988). However, these estimates do provide a qualitative spatial and temporal assessment of the stoichiometry of nutrient inputs to coastal areas.

The absolute amounts of nutrients entering coastal areas are critical for determining ecological effects. However, due to nutrient limitation, the ratios of elements are often just as, if not more important than, the total amounts. The ratios of nutrients entering estuaries and coastal areas can determine whether or not pollution will cause eutrophication and may cause significant shifts in phytoplankton community structure (Justić et al. 1995, Smith 2003). Although a comprehensive evaluation of the ecological consequences of coastal nutrient loading over time is beyond the scope of this work, we show that the N:P of nutrient inputs have changed dramatically over time, with potentially important ecological consequences. Figure 2.8 illustrates changes in watershed stoichiometry from 1930 to 1970 to 2000 relative to the Redfield ratio (16:1), the theoretical ratio of N:P in marine phytoplankton and ocean waters (Redfield 1958). In 1930, there was a distinct pattern where larger, more inland watersheds had N:P greater than 16, and smaller coastal watersheds had N:P less than 16. There was also a latitudinal pattern, where coastal watersheds along Maine were great than 16, whereas watersheds along the coast from Massachusetts southward had inputs with an N:P of less than 16.

The ratio of N:P decreased dramatically by 1970 due to increased P inputs as fertilizer and detergent. The N:P of nutrient inputs decreased for most watersheds, with the exception of northern watersheds in Maine and Cape Cod. More watersheds in 1970 experienced inputs with N:P less than the Redfield ratio compared to 1930. By 2002, however, there was a shift again in the opposite direction as P inputs decreased and atmospheric deposition of N increased. The ratios by the end of the century and for much of the northern part of the region reached an order of magnitude higher than the Redfield ratio. These findings are consistent with global trends (Peñuelas et al. 2012). Although in general marine systems are currently considered N-limited, this ratio of nutrient loading could shift receiving systems from N- to P-limitation, depending on loading relative to water volumes and flows as well as cycling rates in receiving waters. This is not unprecedented. Billen et al. (2007) found that legislative P controls and uncontrolled increases in N loading to the Seine River in France led to a shift from N- to P-limitation in the marine system. N inputs from atmospheric deposition have also been found to shift freshwater systems from N- to P-limitation (Elser et al. 2009). Shifts in nutrient limitation of NE coastal and freshwaters over time and space not only have implications for ecosystems and the economies that depend on them, but must also be taken into account when designing effective nutrient legislation.

Sources of Uncertainty and Limitations

Due to the scope of our work, particularly its historical nature, we relied entirely on publically available datasets for our data sources and for calculating nutrient inputs associated with each. Here we discuss the sources of uncertainty and the resulting limitations of our research. The two main sources of uncertainty are those associated with

the data themselves, including their spatial and temporal resolution, and the coefficients used to calculate the nutrient budgets.

Uncertainty in data sources

The majority of our data were obtained from the US Census of Agriculture reported at the county scale. These data are self-reported, and therefore there is a certain level of error that can be expected in these data. However, due to the large number of counties (437), we have confidence in the general spatial and temporal patterns generated by this resolution.

There is also uncertainty associated with our N deposition estimates. We have the most confidence in our estimates based on NADP data, for which there were 41 data points available since 1978. Interpolating regional N deposition from this many points certainly ignored smaller scale variation in deposition rates. Jaworski et al. (1997) demonstrated that riverine N export from watersheds with minimal agricultural or urban inputs was strongly predicted by N deposition estimated from NADP data, suggesting that this resolution of data is appropriate for regional-scale studies. Uncertainty increases for earlier years, where data were limited or nonexistent. County-level deposition rates were estimated using multiple regressions (Eq. 1 and 2), whereas total regional deposition rates were estimated from emissions data. These two methods yielded similar deposition estimates for the whole region from 1974 to 2002, but estimates increasingly diverged back in time, so that in 1930 our emissions-based deposition for the region was 0.82 Tg and our regression-based estimate was 0.23 Tg.

A second source of uncertainty in our N deposition data was the calculation of dry deposition and organic N deposition. Estimates of dry deposition as a proportion of total

deposition in the eastern U.S. range from 25-70% for NO_3^- and 2-33% for NH_4^+

deposition (Bowen and Valiela 2001) and are likely to be variable over space and time.

However, since there is little data on how dry deposition varies over space, we used a

consistent coefficient from the literature (Bowen and Valiela 2001). Spatial and temporal

variation in dry deposition might have either damped or strengthened the patterns that we

observed.

Uncertainty in data generated

Nutrient demand, consumption, and production by crops, livestock and humans

likely varied over time and space during our study period as agricultural practices and

human diets changed (Gerrior et al. 2004, Metson et al. 2012). Because of data

limitations and the scope of our research, we made the simplifying assumption that

coefficients used to calculate input rates did not vary.

Biological N_2 fixation rates range widely in the literature, though our estimates

fall in the middle (Smil 1999). We calculated N_2 fixation based on the area of cropland

planted in various crops. This is consistent with other nutrient inputs studies (e.g., Jordan

and Weller 1996, Boyer et al. 2002, Howarth et al. 2012, Hong et al. 2012). However,

other research has suggested that N_2 fixation varies with crop yield (Herridge et al. 2008),

and therefore it is possible that N_2 fixation rates per area increased as yields increased

over our study period. Similarly, we assumed that the nutrient content of crops remained

constant over the study period. Fertilizer use typically increases not only the yield but

also the nutrient content of crop plants (e.g., Lawlor 2002), thus nutrient uptake per crop

yield has likely increased over time. Since we used contemporary values of crop nutrient

content, estimates of nutrient accumulation in agricultural soils are possibly

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underestimates during the early part of our study period, though the magnitude of this uncertainty is unknown. .

Livestock nutrient demand was estimated based on inventories and published coefficients for livestock nutrient requirements. However, livestock nutrient demand per animal likely increased over time due to changing agricultural practices, which would strengthen the spatial and temporal trends that we described. Similarly, human nutrient demand likely increased over the study period as protein consumption increased in the United States (Gerrior et al. 2004). Thus our estimates of livestock and human nutrient demand are likely liberal in terms of inputs during the early part of our study period, but conservative in terms of changes in inputs over time, particularly the last few decades.

We assumed constant spoilage rates across food and feed types and over space and time. This assumption is consistent with previous anthropogenic nutrient budgeting literature (e.g., Boyer et al. 2002, Hong et al. 2012). The FAO publishes spoilage rates for various feed and food types that are higher and more variable than the rate we used (e.g., 20-60%, Gustavsson et al. 2011). However, given that spoilage rates likely vary over time and space, especially in response to changing agricultural, transport, and consumer practices, we think that a consistent value facilitates interpretation.

CONCLUSIONS

Anthropogenic nutrient use is highly dynamic both spatially and temporally and responds to scientific understanding, policy changes, technology, and land-use and demographic changes. Over the 20th century, we found that agriculture, and livestock agriculture in particular, was the major driver of spatial patterns of nutrient use.

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Livestock consumed the majority of nutrient inputs to the NE, and the spatial concentration of livestock populations over time drove changes in the spatial patterns of nutrient inputs. As result, spatial and temporal changes in nutrient inputs mirror the history of agricultural policies which have shifted the locations of U.S. agriculture, particularly the movement of row crop agriculture to the west and the development of concentrated livestock agriculture in the NE. Similarly, human demographic trends – suburbanization in particular – led to increases in human food nutrient inputs across the region.

Future nutrient management strategies will need to take into account the multiple pathways through which humans affect nutrient inputs. Our study period included major developments in environmental legislation, including the pioneering Clean Air and Water Acts. Our results show that environmental regulations that regulate direct emissions have been successful in reducing some inputs of P, namely detergents and nonfarm fertilizers. Agricultural fertilizers remain a major contributor to nutrient inputs in the NE and are a difficult management issue due to the distributed nature of the inputs, the lability and multi-phase nature of N and P, and the difficulty of enforcement. Although direct management of fertilizer use is challenging, we found that P fertilizer use responded strongly to economic drivers, suggesting that indirect economic mechanisms may be a viable option for fertilizer use management. Management of N remains more difficult than of P due to the atmospheric component of the N cycle, highlighting the importance of including the atmospheric component in managing N inputs. Of strategic importance to regional nutrient management is the fact that N uptake by agricultural crops is much higher than N fertilizer additions, suggesting the critical importance of both managed

applications (i.e., fertilizer) and N_2 fixation which today are equivalent to double crop needs. Nonetheless, there are continued water quality management challenges associated with fertilizer application. A complete accounting may facilitate fertilizer use management.

Optimizing nutrient management to co-balance agricultural protection and environmental protection remains a difficult task in the NE. Additional challenges will also be associated in refining the debate on carbon management, the use of cropland for biofuels and preparing the region for future climate change. The variety of drivers of nutrient use presents a challenge for decision-makers who must take in account the interactions between economics, biogeochemistry, technology, and policy. However, the diversity of drivers presents an opportunity as well – policy makers have many levers at their disposal beyond directly managing nutrient use. A historical approach can illustrate when and where different approaches may or may not succeed and facilitate a multi-faceted approach to nutrient management that takes advantage of the multiple social, political, economic and environmental drivers of human nutrient use.

ACKNOWLEDGEMENTS

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Table 2.1. N_2 fixation rates for various crops with references.

Crop	N_2 Fixation Rate (kg N ha^{-1} yr^{-1})	Reference
Soybeans	78	Barry et al. 1993; Messer and Brezonik 1983
Peanuts	86	Barry et al. 1993; Messer and Brezonik 1983
Nonlegume Crops	5	Barry et al. 1993; Messer and Brezonik 1983
Alfalfa Hay	218	Keeney 1979
Non-alfalfa Hay	116	Keeney 1979
Dry Edible Beans	40	Keeney 1979; Stevenson 1982
Nonwooded Pasture	15	Keeney 1979
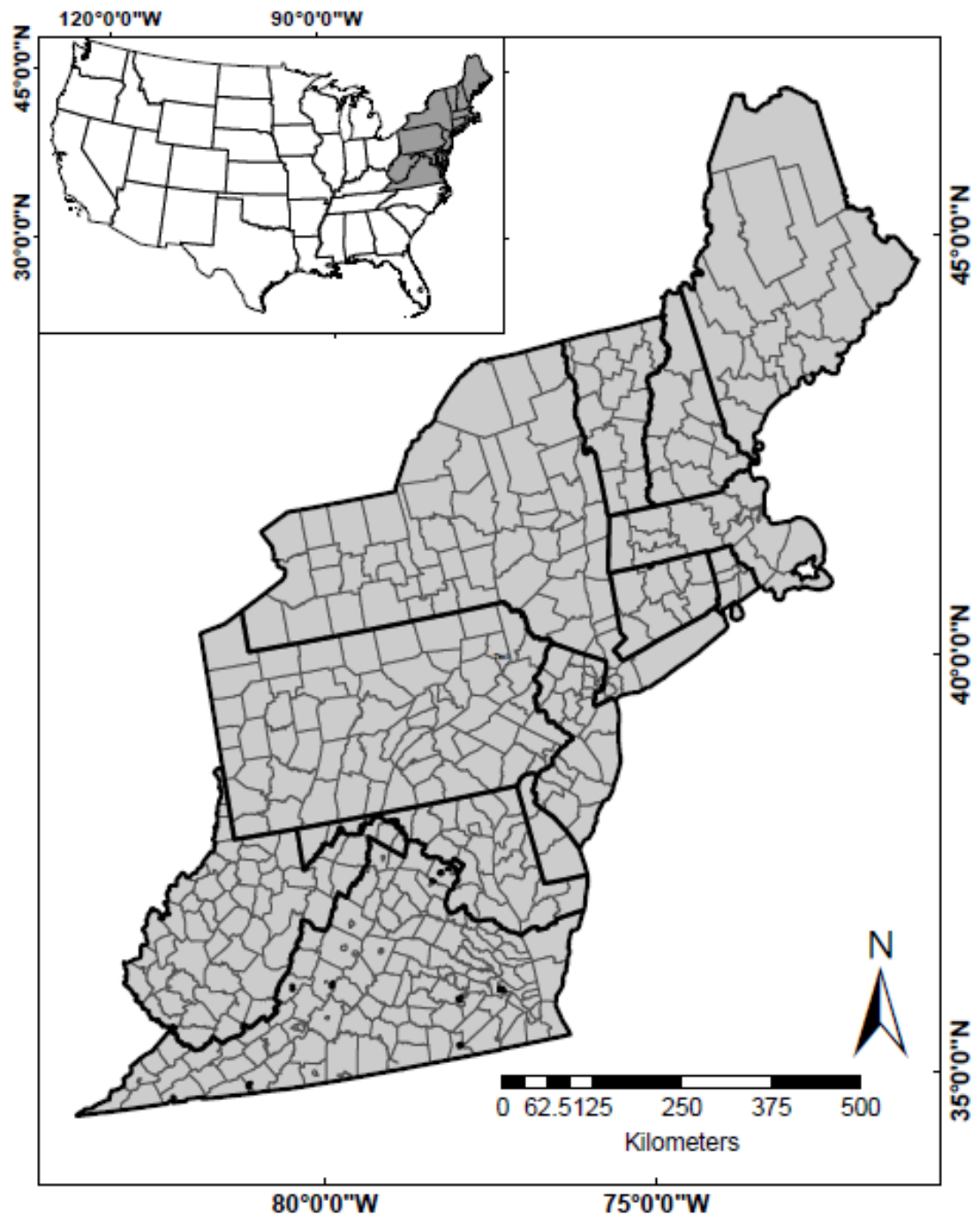
Figure 2.1. Study area includes the thirteen northeastern states and 437 counties.
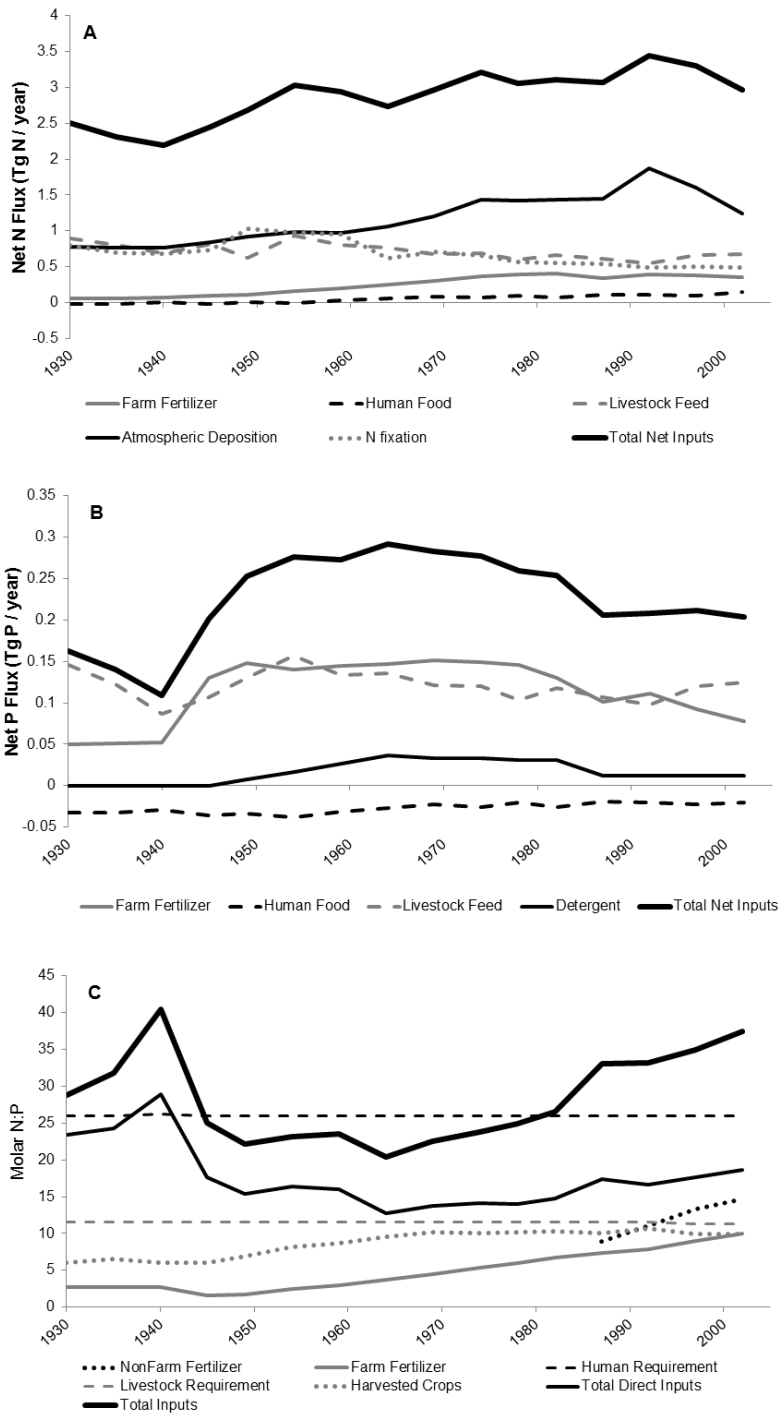
Figure 2.2 Temporal trends in net regional inputs of A) nitrogen, B) phosphorus and C) the molar stoichiometry of nutrient inputs.
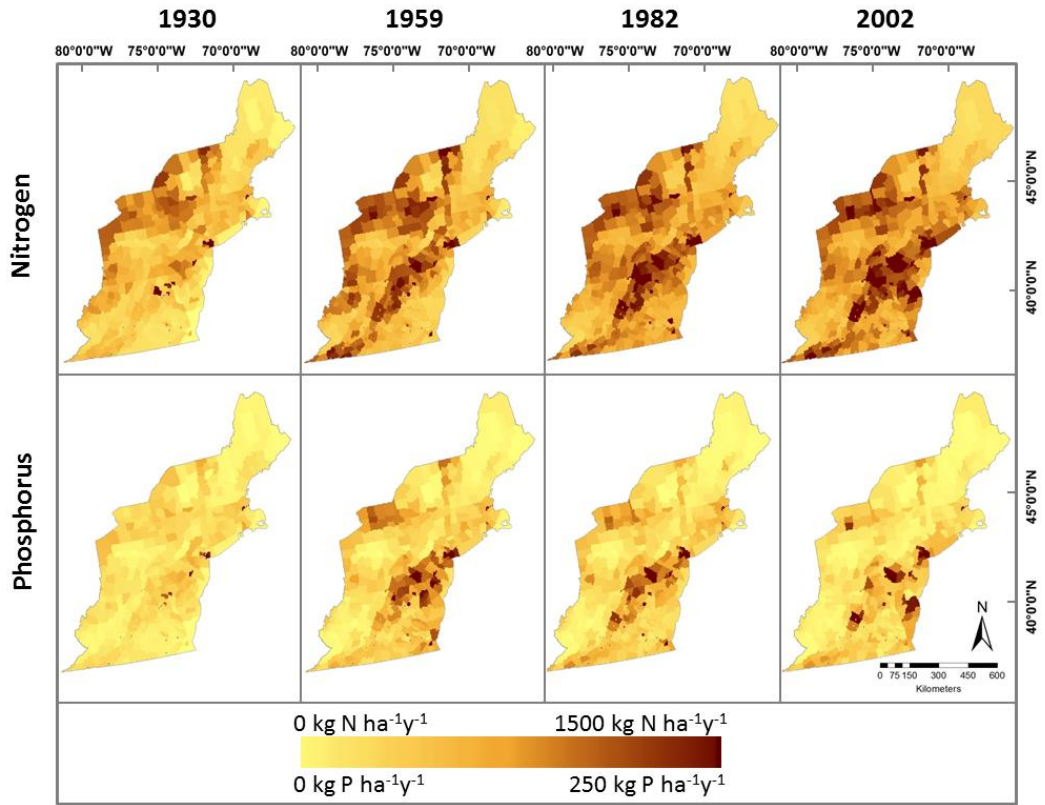
Figure 2.3. Net N and P inputs (kg / ha y) for 1930, 1960, 1982, and 2002.
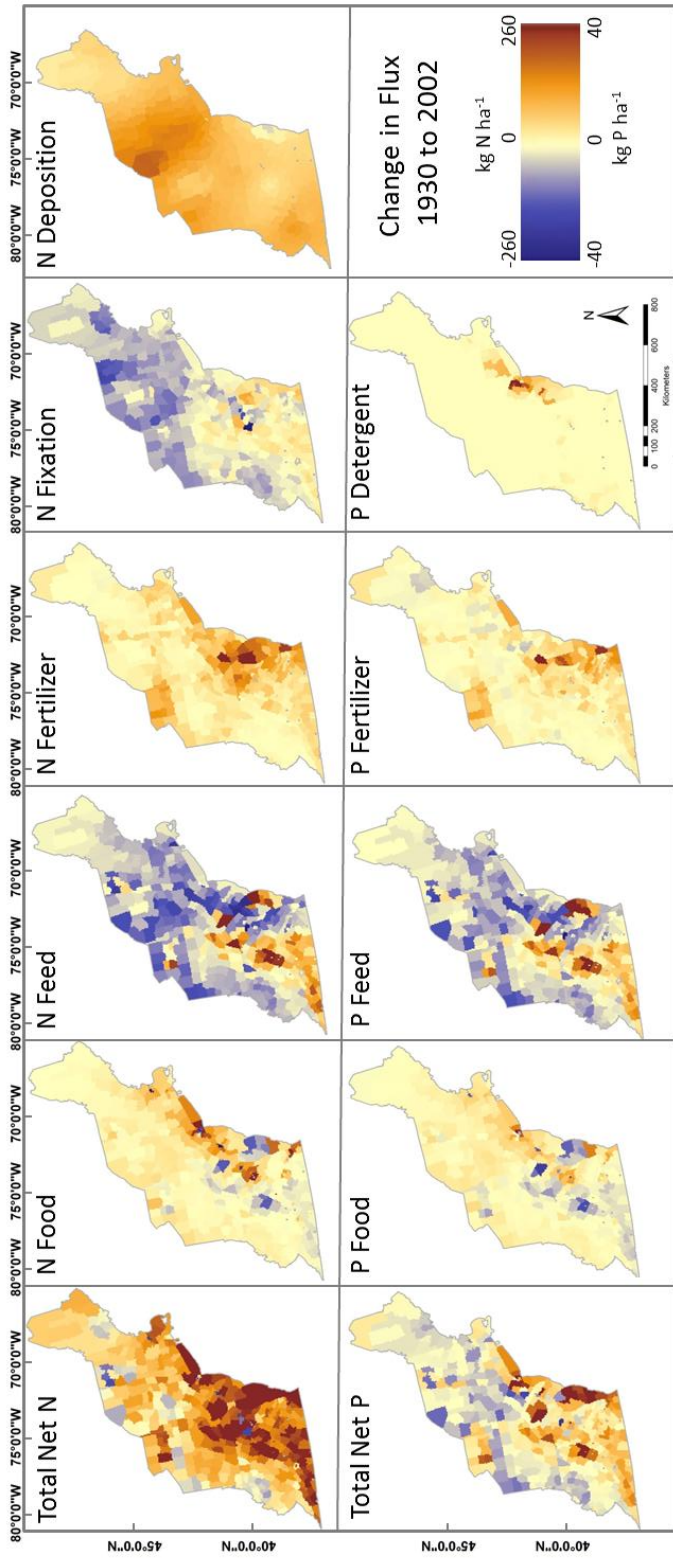
Figure 2.4. Change in N and P inputs from 1930 to 2002 for total net N and P inputs and individual nutrient sources. Data are presented as kg P (or N) ha^{-1}. Blue colors indicate a decrease in nutrient inputs from 1930 to 2002, orange colors indicate an overall increase in nutrient inputs from 1930 to 2002, and tan colors indicate no net change from 1930 to 2002.
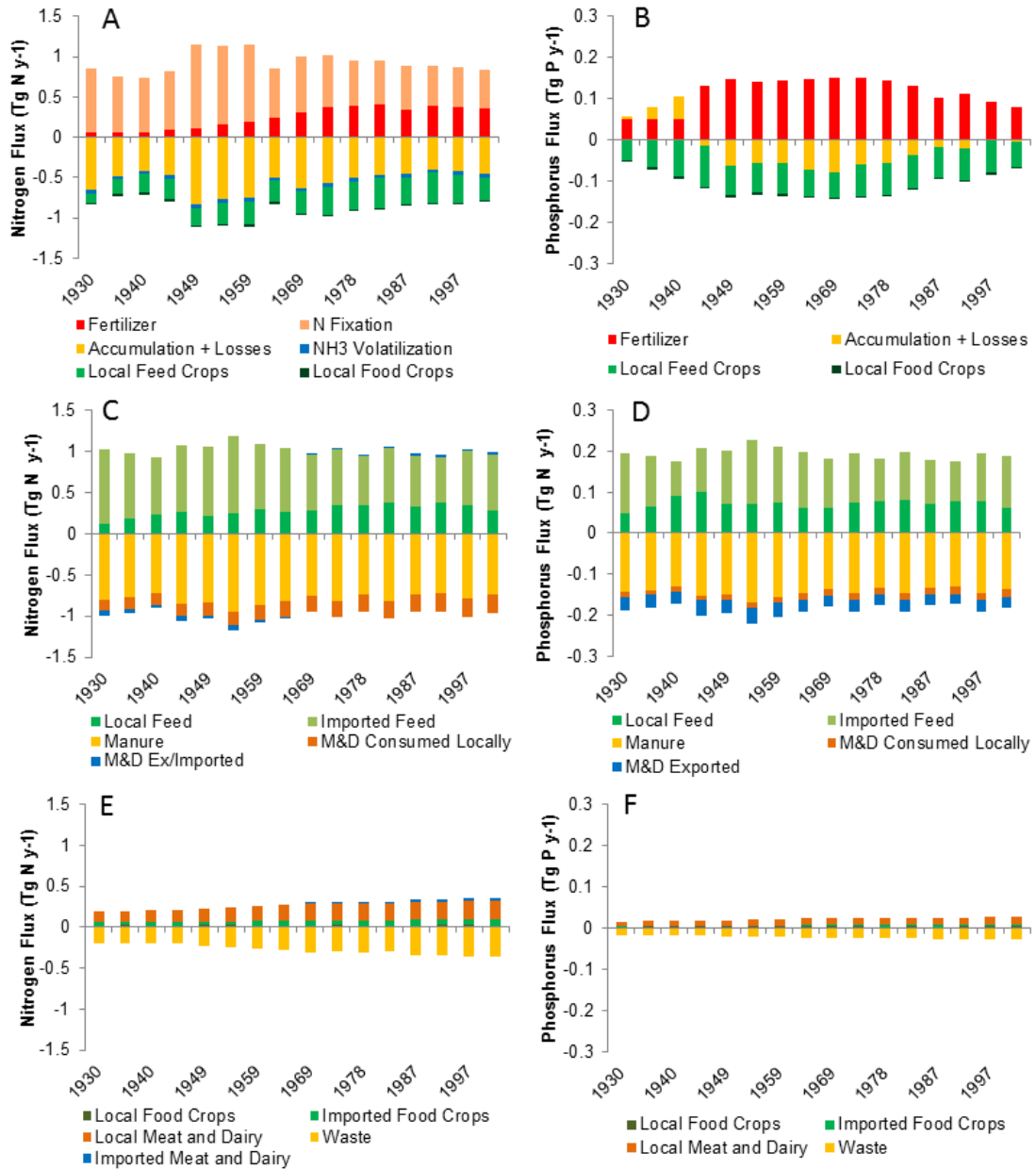
Figure 2.5. Detailed nutrient balances for crop, livestock, and human subsystems over time: A) N inputs to and exports from crop system. "Accumulation" in crop subsystem includes: accumulation in soils (change in storage), or denitrification, leaching and runoff losses (export from system); B) P inputs to and exports from crop system; C) N inputs to and exports from livestock system; D) P inputs to and exports from livestock system; E) N inputs to and exports from human subsystem; F) P inputs to and exports from human subsystem. Note that scales are the same for each element.
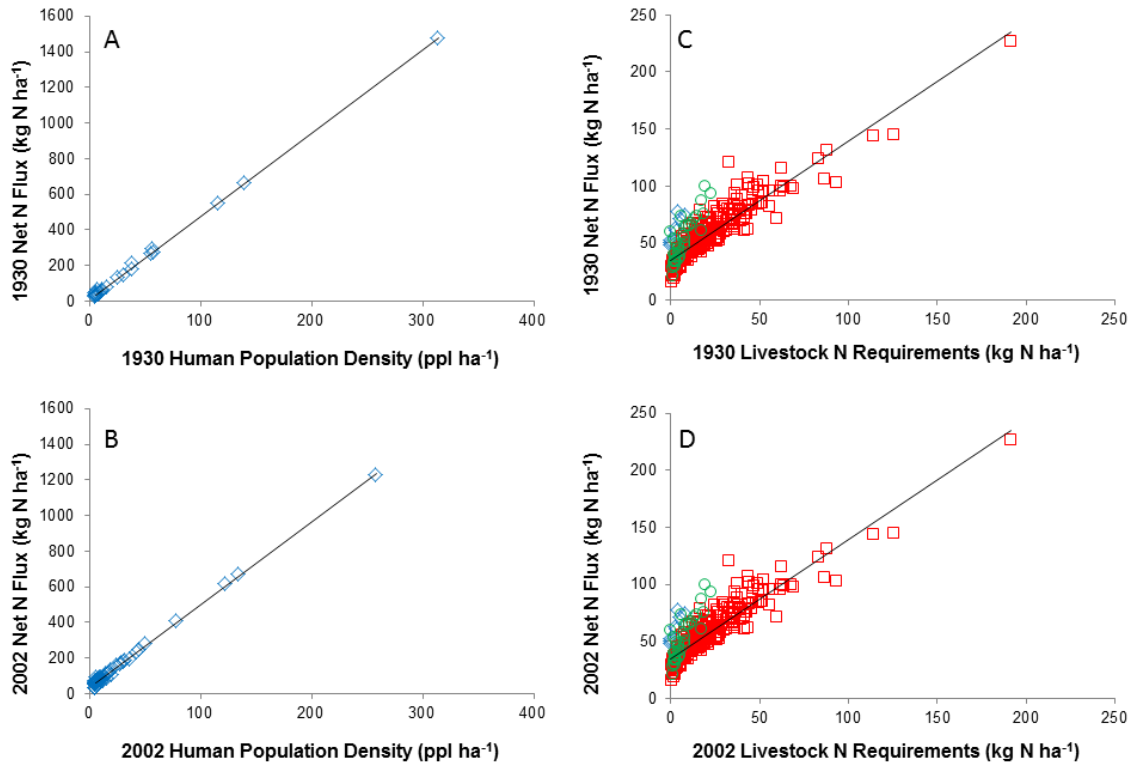
Figure 2.6. A and B) Total net N flux at the county-level is strongly correlated with human population density for counties with population densities > 5 ppl ha^{-1}. C and D) For counties with < 5 ppl ha^{-1}, livestock N demand is the best predictor of net N flux. Blue colors indicate counties where net N inputs are dominated by human food and nonfarm fertilizer. Red colors indicate counties where net N inputs are dominated by livestock feed. Green colors indicate counties where net N inputs are dominated by fertilizer and N$_2$ fixation.
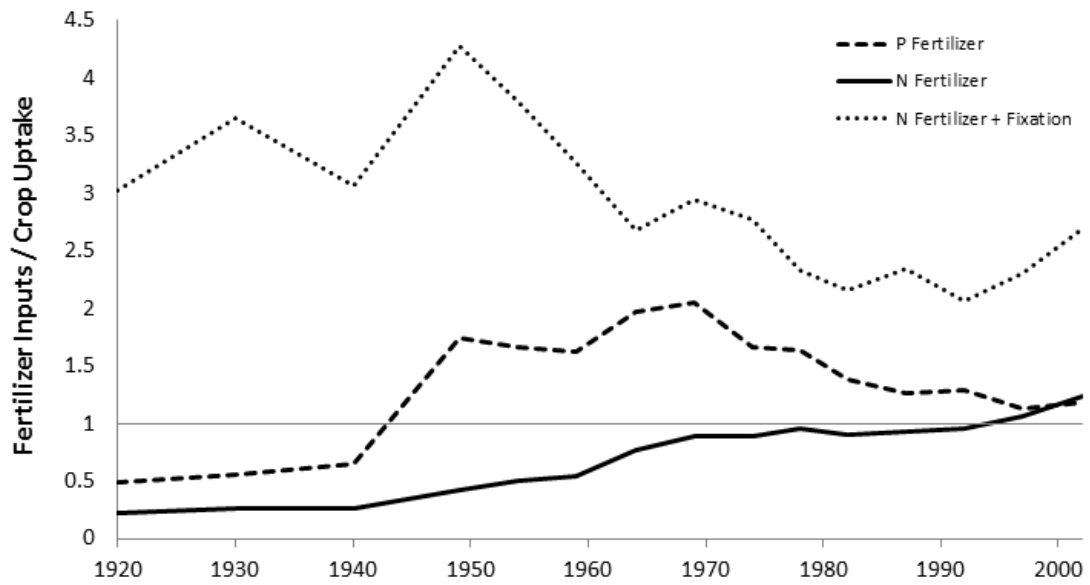
Figure 2.7. Ratio of fertilizer inputs to nutrients removed in crop harvest for the NE over time. Points above the 1:1 line indicate over-application of fertilizer (and N fixation); points below the line indicate under-application of agricultural inputs.

N:P

0 - 7   7 - 12   12 - 16   16 - 20   20 - 50   > 50

← N limitation   P limitation →
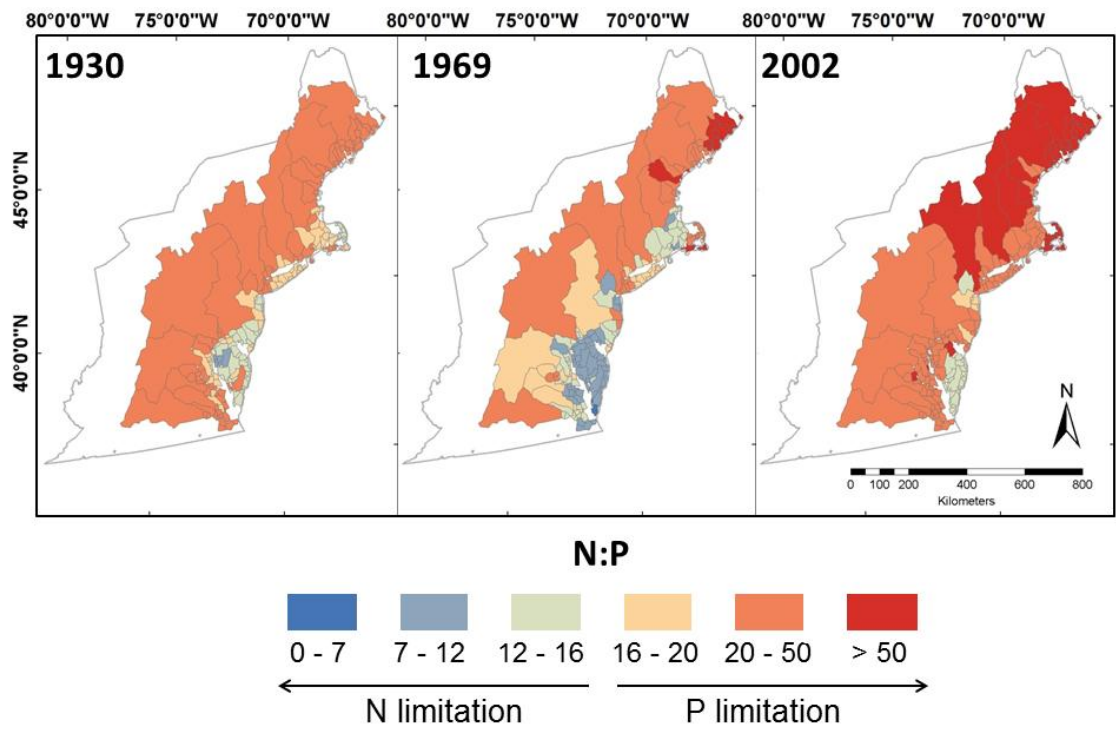
Figure 2.8. Molar N:P of nutrient inputs for watersheds draining into the Atlantic Ocean in 1930, 1970, and 2000. Ratios are displayed relative to the Redfield ratio.

Chapter 3

NITROGEN AND PHOSPHORUS FLUXES FROM WATERSHEDS OF THE

NORTHEASTERN U.S. FROM 1930-2000: ROLE OF ANTHROPOGENIC

NUTRIENT INPUTS, INFRASTRUCTURE, AND CLIMATE

Abstract:

Nutrient yields from watersheds are affected by anthropogenic nutrient inputs, climate, and human alterations of hydrology. The impacts of anthropogenic activities on nutrient fluxes from watersheds are dynamic over time and space. We used models that incorporate nutrient inputs, hydrology, and infrastructure (sewers, wastewater treatment plants, and reservoirs) to reconstruct historic nutrient yields for the northeastern U.S. from 1930 to 2002. While many studies have developed models to describe the effects of anthropogenic inputs, hydrology, and infrastructure on watershed nutrient fluxes, ours is the first to apply these models to historical datasets to reconstruct spatiotemporal patterns of nutrient loading and to explore how the importance of each of these factors changes over space and time. At the regional scale, increases in nutrient inputs were paralleled by an increase in fractional retention over time. As a result of increasing retention, there was no significant increase in N and P loading to the coast. At the regional scale, we found that temporal variation was strongly determined by infrastructure for both N and P. For a single point in time, however, nutrient inputs were the best predictor of the spatial pattern of nutrient yields. Our results demonstrate that historical changes in infrastructure were a key driver of temporal changes in nutrient yields and spatial patterns of TP yields, but not an important factor determining the spatial pattern of TN yields. Different spatial and temporal patterns of N and P yields created a dynamic spatial pattern of nutrient-yield

stoichiometry. Throughout the study period, most of the region had a molar N:P yield great than 16:1, indicating potential for P limitation. Understanding the spatiotemporal dynamics of the drivers of nutrient export is important for reconstructing historical ecosystem changes due to altered water quality. This research can be used to answer questions regarding historical changes in nutrient limitation and the ecological consequences of human nutrient use.

INTRODUCTION

The global alteration of biogeochemical cycles is a major ecological change caused by human activities (Vitousek et al. 1997, Falkowski et al. 2000, Peñuelas et al. 2012). Of global environmental changes (e.g., Vitousek et al. 1997), three have significant, direct consequences for biogeochemical cycles. Humans have increased the availability of the biologically reactive nutrients nitrogen (N) and phosphorus (P) several fold, directly affecting global biogeochemical cycles of these elements (Falkowski et al. 2000, Gruber and Galloway 2008, Peñuelas et al. 2012). Land use and land cover change drives demand for nutrients and affects the spatial pattern of nutrient inputs and use (Boyer et al. 2002). Finally, humans have substantially altered hydrologic cycles via the construction of dams, water withdrawals, and interbasin transfers (Graf 1999, Vorosmarty et al. 2000), and these changes affect biogeochemical cycles by altering rates of material transport, retention, and transformation. Excess nutrient loading due to human activities has well documented ecological and social effects, such as altered water quality (Howarth et al. 2002, Caccia and Boyer 2005), eutrophication (Carpenter et al. 1998),

hypoxia (Hagy et al. 2004), and altered ecological communities (Turner et al. 2003, Billen et al. 2007, Elser et al. 2009, Grizzetti et al. 2012).

The impacts of anthropogenic activities on nutrient fluxes from watersheds are dynamic over time (Billen et al. 2007, Seitzinger et al. 2010) and space (Boyer et al. 2002, Green et al. 2004, Han and Allan 2012, Hong et al. 2012). Watershed nutrient yields are a function of anthropogenic nutrient inputs (Howarth et al. 1996, 2012, Boyer et al. 2002), which are variable over time and space (Boyer et al. 2002, Russell et al. 2008, Hale et al. in review). Nutrient export is mediated by the water cycle, thus spatial and temporal variability in climate may also contribute to the spatiotemporal patterns of nutrient yields (Howarth et al. 2012, Alam and Goodall 2012). Furthermore, human modifications of hydrology – in particular, the construction of infrastructure sewers and dams – also affect nutrient delivery (Alexander et al. 2008, Harrison et al. 2009, Seitzinger et al. 2010) and have variable distributions over time and space (e.g., Graf 1999). Therefore, we can also expect that water infrastructure may determine the spatiotemporal patterns of nutrient delivery.

Despite large number of studies on watershed nutrient fluxes and the effects of anthropogenic activities on those fluxes, many studies are limited in either spatial or temporal extent or resolution. These studies identified the important drivers of nutrient fluxes over space for a particular snapshot in time, or over time for a small number of watersheds. There is little research on how the importance of these drivers changes over time and space, or on how dynamic spatiotemporal patterns of anthropogenic nutrient inputs, infrastructure, and hydrology interact to determine the spatiotemporal patterns of watershed nutrient fluxes. Broussard and Turner (2009) demonstrated that the effects of

land cover on water quality are not static over time. Similarly, we can expect that the relationships between anthropogenic nutrient inputs, hydrology and infrastructure and watershed nutrient yields may also be dynamic over time. Our long study period allow us to incorporate major changes in anthropogenic uses of nutrients and alterations of the water cycle. Regional spatial extent and relatively fine scale resolution allow us to identify sources of spatial variation in nutrient fluxes

We used models that incorporate nutrient inputs, hydrology, and infrastructure (sewers, WWTPs, and reservoirs) to reconstruct historic nutrient yields for the northeastern U.S. over the 20th century. While many studies have developed models to describe the effects of anthropogenic inputs, hydrology, and infrastructure on watershed nutrient fluxes, ours is the first to apply these models to historical datasets to reconstruct spatiotemporal patterns of nutrient loading and to explore how the importance of each of these factors changes over space and time. N and P are nutrients of especial concern, given their role in limiting primary productivity in aquatic ecosystems, thus we focus our research on these two elements.

Objective, Research Questions, and Hypotheses:

Our overarching objective for this research was to determine the relative importance of nutrient inputs, infrastructure development, and climate in driving watershed nutrient fluxes over space and time at the regional scale. We developed the following research questions and hypotheses:

Q1: What were the most important drivers of nutrient (N and P) yields from watersheds in the northeastern U.S. (NE)?

H1a: Nutrient supply rates from anthropogenic inputs,

H1b: Transport due to variation in anthropogenic infrastructure (such as sewers, dams, and wastewater treatment plants),

H1c: Transport driven by climate variability.

Q2: How did nutrient fluxes to the Atlantic coast from the NE change over time?

H2a: Regional nutrient fluxes followed temporal trends in anthropogenic nutrient inputs,

H2b: Regional nutrient fluxes followed trends in infrastructure construction,

H2c: Inter-annual variation in regional nutrient fluxes was driven by regional runoff.

Q3: How did the spatial patterns of nutrient fluxes within the NE change over time?

H3a: Spatial patterns in nutrient fluxes were driven by spatial patterns of nutrient inputs,

H3b: Spatial patterns in nutrient fluxes were driven by spatial patterns of infrastructure,

H3c: Spatial patterns in nutrient fluxes were driven by spatial patterns of hydrology (runoff coefficient).

Q4: How did the importance of different drivers of nutrient yields change over space and time?

H4a: The importance of infrastructure as a driver of nutrient inputs increased over time as construction continued and the total amount of infrastructure increased.

METHODS

Study system and general approach

We estimated nutrient yields for watersheds in the northeastern United States (NE) from 1930 to 2002. Over this time period, the NE experienced major shifts in land use as cropland declined, and forested, urban, and suburban land uses increased (Brown et al. 2005). As the NE urbanized, there was a concurrent increase in waste-disposal infrastructure (e.g., sewers) and water storage and flood-control infrastructure (e.g., dams and reservoirs).

We used data on nutrient inputs to the NE (Hale et al. in review), hydrology (Fekete et al. 2002), and infrastructure (reservoirs, sewers, and WWTPs) to calibrate models of nutrient yield for N and P. We applied these models to estimate nutrient yields for two sets of watersheds. To address Q2, we estimated yields for the region as a whole with 42 watersheds ($>1000km^2$) that drained to the coast. These watersheds were delineated from a 3-minute stream network (Fekete et al. 2002). To describe temporal and spatial patterns of nutrient yield across the entire NE (Q3), we estimated yields for the 199 HUC-8 watersheds that fall within the region.

Data Sources

<u>Nutrient inputs</u>

We estimated inputs of N and P to NE counties (N = 437) at 5-year time steps from 1930 to 2002 following the approach of Green et al. (2004). Inputs included fertilizer, livestock manure, human waste, atmospheric deposition (N only), biological N_2 fixation (N only), and detergent P. See Hale et al. (in review) for details on data sources, calculations and assumptions. Nutrient inputs were categorized as point sources, organic

nonpoint sources, and inorganic nonpoint sources following Green et al. (2004). Point sources included sewered human waste and detergent sources of P. Organic nonpoint sources included unsewered human waste, livestock manure, and inputs from N_2 fixation. Inorganic nonpoint sources included fertilizer and atmospheric deposition.

Sewerage rates and wastewater treatment

Sewerage rates were estimated for each county at each time period. Data on the sewered population of each county were available from the U.S. Census of Population and housing for the years 1960, 1970, 1980, and 1990. Sewered populations for 1930 and 1940 were obtained at the national level from Tarr (1996). We assumed that sewered populations were primarily urban and calculated the % urban population with sewers for 1930 and 1940. We assumed that the sewerage rates for urban populations did not change from 1940 to 1960 (94%). These rates were applied to the urban population of each county (urban population from the Census) for 1930, 1940 and 1950. For the sewered population in 2000, we linearly extrapolated sewerage rates for each county from 1970 to 1990 and applied the extrapolated rate to the 2000 county population data from the US Census.

Wastewater treatment data were readily available only at the national scale. We used data on the proportion of the sewered U.S. population served by different levels of wastewater treatment (untreated, less than secondary, secondary, advanced, and no discharge) for 1940 through 2000 (EPA 2000). We used data from Metcalf and Eddy (1928) on wastewater treatment for 1924. N and P removal rates during wastewater treatment are highly variable, and therefore our estimates of removal are very coarse. However, we wanted to account for the potentially large effect of wastewater treatment

on watershed nutrient fluxes. We used estimates of N and P removal by primary, secondary, and tertiary treatment from Morse et al. (1993) to estimate average N and P removal rates for all sewered waste at the national scale. Because few of these data coincided with our study years, we used linear regression to model N and P removal rates as a function of time, and then used that model to estimate N and P removal rates for each study year (Fig 3.1).

Hydrology

We used hydrologic residence time (τ, in units of years), temperature (°C), and runoff coefficient (precipitation/discharge, unitless) to estimate transport of N and P from watersheds. Previous research has demonstrated that nutrient retention is related to hydrologic residence time at the watershed scale (Green et al. 2004). Annual precipitation (total), discharge (total), and soil moisture (average) were derived from a global-scale water-balance model (Fekete et al. 2002) and summed for each watershed in ArcGIS (ESRI 2011). Runoff coefficients were calculated for each watershed by dividing total precipitation by total discharge. Hydrologic residence time in soils (τ_{soil}) was calculated by dividing the total volume of water stored in soil for each watershed by discharge from the watershed. We calculated hydrologic residence time in rivers (τ_{riv}) by dividing total river volume by total watershed discharge. River volume was calculated by multiplying river length by average river cross-sectional area for the watershed. Total river length for each watershed was calculated from the Hydrosheds stream layer (Lehner et al. 2006). We estimated river cross-section (width x depth) by dividing mean discharge over the whole watershed (m^3/s) by velocity (m/s). We assumed a uniform channel velocity of 0.5 m/s after Vörösmarty et al. (2000). We estimated a regional residence time in rivers of

3.6 days, a bit below published global estimates which range from 16 to 26 days (Green

et al. 2004), which is consistent with the smaller area of NE watersheds compared to

many global watersheds. Hydrologic residence time in reservoirs (τ_{res}) was calculated by

dividing total storage in reservoirs for each watershed by total watershed discharge.

Reservoir storage was obtained from the National Inventory of Dams

(http://nid.usace.army.mil). Our estimate of τ_{res} for the region averaged 67 days over the

study period. Our estimate was much higher than Green et al. (2004)'s global estimate of

31 days, which is reasonable given the high density of dams in the NE (Graf 1999).

Residence time in lakes (τ_{lake}) was calculated by dividing the total lake volume for each

watershed by watershed discharge. Lake volume was estimated from lake areas in the

National Hydrography Dataset (Simley and Carswell 2009). Mean lake depth was

estimated from lake surface area, following Green et al. (2004), and volume was

calculated by multiplying lake area by mean depth. We calculated the mean regional τ_{lake}

for the region to be 164 days. Our estimate of τ_{lake} is lower than global estimates (0.45

years vs. 1.2 years, respectively; Green et al. 2004), again a reasonable estimate given the

absence large lakes within the NE.

Model Calibration

We used data on total nitrogen (TN) and total phosphorus (TP) concentrations and

discharge from the U.S. Geological Survey National Water Information System database

to calibrate our nutrient transport models. Selected watersheds were $> 1000 km^2$ in area,

had > 10 measurements of total unfiltered N or P, and had measurements for at least one

of the study years (N = 52 for TN and 22 for TP; Fig 3.2). Annual loads were calculated

by multiplying monthly average concentrations by total monthly discharge and summing

over the year. Monthly concentrations were estimated with discharge-concentration models:

$$Ln(C) = \lambda_0 + \lambda_1 \sin(month) + \lambda_2 \cos(month) + \lambda_3 d \ln(Q) + \lambda_4 [\ln(Q)]^2 \qquad [Eq.1]$$

where C is the concentration of TP or TN (mg/L), Q is discharge (L/s), and λ_0 through λ_4 are regression coefficients. Where monthly discharge measurements were not available from the USGS, we used monthly discharge estimates from the water balance model (Fekete et al. 2002). ArcGIS was used to aggregate nutrient input and hydrology data to scale of calibration watersheds.

We fitted and compared a nonlinear regression model (Green et al. 2004) and linear multiple-regression models to predict TN and TP yields. Green et al. (2004) developed a nonlinear regression model that estimates N yields based hydrologic residence time in rivers (τ_{riv}), lakes (τ_{lake}), reservoirs (τ_{res}), and soils (τ_{soil}), temperature, and inputs of nutrients as point sources (PtS), organic nonpoint sources (NonPtS$_{org}$), and inorganic nonpoint sources (NonPtS$_{inorg}$). N yields from the watershed are determined by the types of nutrient inputs and a set of delivery coefficients ranging from 0 to 1 that describe the fraction of N delivered through soils, lakes, reservoirs, and rivers.

$$\text{Yield}_N = E_{riv}E_{res}E_{lake}(\text{PtS} + \text{NonPtS}_{org}E_{soil\text{-}org} + \text{NonPtS}_{inorg}E_{soil\text{-}inorg}) \qquad [Eq. 2]$$

Where:

Yield$_N$ = watershed N yield in kg N ha^{-1}y^{-1}

Pts = Inputs from sewered human waste – removal from WWTPs

NonPts$_{org}$ = (Inputs from N$_2$ fixation + livestock manure + unsewered human

waste)(runoff/precipitation)

NonPtS$_{inorg}$ = (Inputs from atmospheric N deposition +

fertilizer)(runoff/precipitation)   [Eq. 3]

All inputs are in units of kg ha^{-1} y^{-1} and runoff and precipitation are in units of

mm y^{-1}.

Delivery coefficients were defined as:

$$E_{riv} = e^{(-\tau_{riv}T_{adj}\alpha_{riv})}, \qquad E_{res} = e^{(-\tau_{res}T_{adj}\alpha_{res})}, \qquad E_{lake} = e^{(-\tau_{lake}T_{adj}\alpha_{lake})},$$

$$E_{soil-org} = e^{(-\tau_{soil}T_{adj}\alpha_{soil-org})}, \quad E_{soil-inorg} = e^{(-\tau_{soil}T_{adj}\alpha_{soil-inorg})} \qquad \text{[Eq. 4]}$$

Where τ_{riv}, τ_{res}, τ_{lake}, τ_{soil} are the hydrologic residence times in each pool, T_{adj} is

the mean annual air temperature for each watershed, and α_{riv}, α_{res}, α_{lake}, $\alpha_{soil-org}$, $\alpha_{soil-inorg}$

are tunable parameters that define the shape of the delivery-coefficient response to

hydrologic residence time and temperature. These tunable parameters were estimated

using nonlinear least-squares estimation in SPSS (SPSS Inc., Chicago, IL) (Table 3.1).

Due to the small sample size of TP calibration watersheds, we were not able to fit this

model for TP yields.

We also fit linear multiple-regression models for both TN and TP yields. We

selected the models having the best fit and least bias that were ecologically meaningful.

Our best-fit model for TN yield (kg ha^{-1} y^{-1}) was:

$$Log_{10}(TN) = a + b*log_{10}(\tau_{res}) + c*log_{10}(\tau_{riv}) + d*log_{10}((NonPtS_{inorg} + NonPtS_{org}))$$

$$+ e*log(PtS) \hspace{4cm} [Eq. 5]$$

And our best-fit model for TP yield (kg ha^{-1} y^{-1}) was:

$$TP = a + b*log_{10}(\tau_{res}) + c*log_{10}(NonPtS_{org}) + d*log(PtS) \hspace{2cm} [Eq. 6]$$

Because the nonlinear and linear models for TN were biased in different directions, we averaged model results to minimize bias and improve model fit (Table 3.2). We used our fitted models to estimate mean annual TN and TP fluxes (kg ha^{-1} y^{-1}) for two sets of watersheds draining the NE. The first set of 42 watersheds that drained to the coast addressed our research question 2 regarding the temporal patterns of nutrient delivery to the Atlantic coastal ecosystem from the entire NE region. To address Q3, we also applied models to the 199 NE HUC-8 watersheds.

Sensitivity analysis

To evaluate how the relative importance of the three nutrient-yield drivers changes over time and space (Q3), we conducted simple sensitivity analyses, focusing on infrastructure and climate, to calculate a "scenario yield" for each variable. We then used the results from the sensitivity analyses to calculate an effect size (ES): ES = (Yield$_{Actual}$ − Yield$_{Scenario}$)/Yield$_{Actual}$, where a positive ES indicates that the variable had a positive effect on nutrient yields, and a negative ES indicates that the variable had a negative

effect on nutrient yields. Because ES is normalized by the magnitude of the modeled yield, it can be used to compare the importance of a variable for nutrient yields over time and space and across nutrients. These analyses assume that all other terms of the model stay constant.

For reservoirs, we simply evaluated the model without the τ_{res} term. For sewers, we added point source inputs to the $NonPtS_{org}$ inputs. To estimate the effect of sewers alone, rather than sewers and associated treatment infrastructure, we subtracted the ES of WWTPs. For WWTPs, we simply removed the WWTP removal term from the model. For climate, we calculated a temporal and a spatial effect size for runoff coefficient (RC). For the temporal RC effect size, we set the RC for each watershed equal to the study-period mean RC for each watershed (e.g., RC varies spatially but not temporally). For spatial RC effect size, we set the RC for each year equal to the mean RC for the region (e.g., RC varies temporally but not spatially).

RESULTS

What are the most important drivers of nutrient fluxes from watersheds?

For TN, the nonlinear and linear regression models both explained the majority of variation in observed TN fluxes (predicted vs observed $R^2 = 0.60$ and 0.69, respectively). The two models had similar fit and error, but were biased in opposite directions (Table 3.2); therefore, we averaged model results to reduce model bias and error and to improve fit (Table 3.2). The best linear-regression model for TN included τ_{riv}, τ_{res}, $NonPtS_{org}$, $NonPtS_{inorg}$ and treated Pts. For TP the best linear-regression model included τres,

NonPtS$_{org}$, and Pts. The model explained 74% of the variation in observed TP fluxes, and model error and bias were lower than those for TN models (Table 3.2).

Nutrient inputs, infrastructure, and hydrology were all important drivers of nutrient yields. NonPtS$_{org}$ and Pts inputs were consistently significant variables in TN and TP models. NonPtS$_{inorg}$ was important in some TN models but in none of the TP models. Sewer and WWTP infrastructure did not change model fit or significance for TN or TP, though treated point-source waste was a significant predictor in all models. Including τ_{res} improved model fits for both TN and TP, but there is some degree of uncertainty about direction of effect. The coefficient for τ_{res} was negative in all regression models but not significant (TN, $p = 0.10$; TP, $p = 0.10$). The estimate of α_{res} for the Green model was negative, indicating that reservoirs were a source of TN from watersheds. However, α_{res} was not significantly different from zero (Table 3.1). Runoff coefficient is a significant variable for both TN and TP. Models with inputs and runoff coefficients explained most (TN: 46% [improved 13% over inputs alone], TP: 61% [improved 25% over inputs alone]) of the variation in fluxes. Although runoff coefficient explains more variability for TP than TN, the slope of the relationship is stronger for TN than TP.

How do nutrient fluxes to the Atlantic coast from the NE change over time?

NE watersheds retained the vast majority of nutrients added by humans (73-90%). Although TN inputs increased significantly from 1930 to 2002 ($R^2 = 0.87$, $p < 0.00001$), there was no significant increase in total N fluxes from the NE to the Atlantic coast ($R^2 = 0.12$, $p = 0.196$; Fig 3.3A). Net inputs of TN ranged from 1.05 to 1.78 Tg N y^{-1} and TN exports to the coast ranged from 0.28 to 0.41 Tg N y^{-1}. TN retention exhibited high year-

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to-year variability, but increased overall over the study period ($R^2 = 0.56$, $p = 0.0008$) ranging from 73 to 86% (Fig 3.3A). TP inputs and watershed fluxes were best described by a cubic function ($R^2 = 0.673$, $p = 0.001$), increasing through the 1970s and then declining (Fig 3.3B). TP inputs to the region ranged from 0.12 to 0.22 Tg P y^{-1}, and TP exports to the coast ranged from 0.02 to 0.03 Tg y^{-1}. TP retention was higher than TN retention on average and less variable among years. TP retention also increased significantly over the study period ($R^2 = 0.57$, $p = 0.0007$) from 85 to just over 90% (Fig 3.3B).

As a result of differential retention of N and P, the flux of nutrients to the NE Atlantic coast had a much higher molar N:P than the nutrient inputs (Fig 3.3C). The molar N:P of nutrient inputs to the NE ranged from 14.9 to 24.3, whereas the N:P of fluxes to the coast ranged from 27.5 to 42.9. Thus, P accumulated (was retained) in the NE at a faster rate than N, relative to inputs (Fig 3.3C).

Inter-annual climate variability had much stronger effects on N transport than on P transport. The regional runoff coefficient explained most of the year-to-year variability for TN (regression, $R^2 = 0.71$, $p < 0.0001$), but only 10% of the variability in TP yield (regression, $R^2 = 0.10$, $p = 0.232$). We identified temporal trends in nutrient fluxes by curve fitting; the trend for TP explained 67% of variability in year to year fluxes, whereas the TN trend explained 12%.

How did the spatial patterns of nutrient fluxes within the NE change over time?

We applied our models to HUC-8 watersheds in order to assess spatial patterns of changes in nutrient yields from the NE. TN yields from HUC-8 watersheds decreased on

average 0.88 (+/- 4.21) kg TN / ha from 1930 to 2002. Changes in TN yields ranged from -12.15 to 17.28 kg / ha. TP yields from HUC-8 watersheds also declined on average, decreasing 0.12 (+/- 0.15) kg TP / ha. Changes in TP yields ranged from -3.25 to 0.47 kg TP / ha.

We found similarities and differences between spatial patterns for N and P. Over the study period, both N and P yields increased for the Delmarva Peninsula, greater NY metro area, and along the arc of northern Virginia (Fig 3.4). Outside of those areas, P yields decreased strongly across the region. N yields also increased from many watersheds in Maine and New Hampshire (Fig 3.4).

Hot- and coldspots of N and P yields displayed very different spatial patterns over time (Fig 3.5). P yields were highest from watersheds along the coast, and for the most part, high P yields were constrained to these areas. The pattern of P yields did not change much over time, besides expanding in 1978 and contracting in 2002. N yields displayed a very different spatiotemporal pattern, with three major hotspots of N yields: the greater New York City metropolitan region, the Lake Ontario coast, and northern Vermont. These three hotspots were persistent through the beginning of the study period, but by 2002, the Lake Ontario and Vermont clusters were smaller and yields had decreased (Fig 3.5).

Retention hotspots were overlapping but different for N and P (Fig 3.6). Retention of both nutrients was highest in the southern portion of the region. For TN, retention was highest in West Virginia and Virginia throughout the study period. For TP, there were two retention hotspots: one around the northern part of the Chesapeake Bay, and another in northwestern New York. The hotspot around the Bay expanded over time to include

most of Virginia and the Delmarva Peninsula, whereas the hotspot in NY shifted west from 1930 to 1969, had nearly disappeared by 2002 (Fig 3.6).

How does the importance of different drivers on nutrient yields change over space and time?

<u>Infrastructure</u>

In general, the effect of individual types of infrastructure (e.g., WWTPs, sewers, dams) on N and P yields increased over the study period as more infrastructure was constructed (Fig 3.7). However, the net effect of infrastructure on yields did not change significantly over time, and was positive overall (e.g., infrastructure increased yields; Fig 3.7). Sewers had the largest effect size at the regional scale, ranging from 0.214 to 0.424 for TN and 0.204 to 0.519 for TP. Both dams and WWTPs had a negative effect size, not large enough to counterbalance the effects of sewers. The effect size of dams was in general much smaller than effect size of other infrastructure, ranging from -0.004 to -0.015 for TN and -0.019 to -0.087 for TP. WWTP ES ranged from -0.010 to -0.201 for TN and -0.015 to -0.331 for TP (Fig 3.7).

The spatial patterns of dam effects were related to the distribution of large dams in the NE. In contrast, the effects of sewers and WWTPs were clustered around densely settled areas along the coast (Fig. 3.8). In general, infrastructure became increasingly important over time for both N and P, and the spatial patterns became stronger, consistent with the temporal changes in effect size at the regional scale (Fig 3.8). Patterns were similar for N and P (data for P are not shown). Net infrastructure effects were strongest in coastal watersheds with high population densities for both N and P (Fig 3.9). Net infrastructure effect did not change as much over time for N, in part due to the

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counteracting effects of sewers and WWTPs. Infrastructure effects on P yields did change over time, with the strongest effects in 1969. By the end of the century, the effect of infrastructure on P yields was negative for many watersheds (Fig 3.9).

Climate

The effect of runoff coefficient on nutrient yields were consistent over space for extremely wet and extremely dry years (Fig 3.10), where yields were positively affected by hydrology in wet years and negatively affected during dry years (Fig 3.10).

We also asked whether there was an effect of spatial variability in runoff on nutrient yields. The spatial effect of runoff coefficient (calculated relative to the regional mean) was much stronger for N than it was for P (Fig 3.11). A distinct north-south gradient in runoff coefficient created a parallel gradient in its effect size. This spatial pattern was consistent across time and similar for N and P. Greater than average runoff coefficient in the north yielded a positive effect size, whereas a lower than average value in the southern part of the region yielded a negative runoff-coefficient effect size. The stronger effect on N yields is consistent with higher sensitivity of N yield to hydrologic variation relative to P yield. The spatial pattern of the effect size for runoff coefficient was largely opposite of the spatial distribution of nutrient yields and infrastructure effect sizes; therefore, spatial patterns of hydrology dampened spatial variation in nutrient yields in the NE.

DISCUSSION

We hypothesized that nutrient yields are controlled by 1) nutrient supply rates from anthropogenic inputs, 2) variation in nutrient transport due to variation in

anthropogenic infrastructure, and 3) variation in transport driven by climate variability. Furthermore, we expected that the relative importance of these factors would vary over time. We predicted that directional trends in nutrient yields over time could be best explained by trends in nutrient inputs and infrastructure, such as sewers and wastewater treatment plants (WWTPs), whereas year-to-year variation in nutrient yields was driven by climate. Finally, we expected that infrastructure would have a greater effect on nutrient export over time as construction continued and the total amount of infrastructure increased.

What were the most important drivers of nutrient (N and P) yields from watersheds in the northeastern U.S. (NE)?

We found that nutrient yields from the NE were driven by the interactions between the supply of nutrients (anthropogenic inputs) and factors affecting their transport through the landscape (infrastructure and climate/hydrology). Our research supports the results of previous models that have found that nutrient inputs (Howarth et al. 1996, 2012, Boyer et al. 2002, Seitzinger et al. 2010), infrastructure (Alexander et al. 2008, Harrison et al. 2009, Seitzinger et al. 2010), and climate (Sobota et al. 2009, Howarth et al. 2012, Alam and Goodall 2012) are important drivers of watershed nutrient yields. Our work expands upon previous research by combining these three factors in a single model and using these models to explore how nutrient yields and the drivers of nutrient yields have changed over space and time at the regional scale.

How did nutrient fluxes to the Atlantic coast change over time?

Over our study period, inputs of N increased linearly and inputs of P followed a cubic function. Increases in inputs were paralleled by an increase in fractional retention over time. As a result of increasing retention, there was no significant increase in N and P loading to the coast from the NE as a whole. Overall, we found higher retention of P than N, in general agreement with the literature (e.g., Han et al. 2010, Alexander et al. 2008), that led to an increase in the molar N:P of nutrients delivered to the NE coast.

With regard to our hypotheses, we found that the important drivers of regional nutrient yields differed for N and P. For N, annual regional fluxes were best predicted by runoff coefficient (H2c, $R^2 = 0.55$, $p < 0.001$) and the net effect of infrastructure (H2b, R2 = 0.48, p = 0.003). Regional N fluxes were not significantly related to anthropogenic N inputs (H2a). Regional P yields, on the other hand, were most strongly predicted by the net effect of infrastructure (H2b, $R^2 = 0.83$, $p < 0.0001$) and anthropogenic P inputs (H2a, $R^2 = 0.59$, p = 0.005). P yields were unrelated to runoff coefficient.

While N retention increased significantly over the study period ($R^2 = 0.56$, p < 0.001), retention was most significantly related to runoff coefficient ($R^2 = 0.49$, p = 0.002), but was not significantly related to net infrastructure effect ($R^2 = 0.12$, p = 0.195). We found no significant relationships between P retention and infrastructure effects or runoff coefficient for the study period. However, P retention from 1945-2002 was significantly related to net infrastructure effect ($R^2 = 0.44$, p = 0.014) and weakly related to runoff coefficient ($R^2 = 0.30$, p = 0.055).

At the regional scale, we find that infrastructure effect was a significant predictor of both N and P yields over time. Hydrology was an important predictor of regional N, but not P, yields, and inputs were an important predictor of P, but not N, yields. Our results show that including infrastructure effects are key to reconstructing historical N and P yields. Previous work by Broussard and Turner (2009) demonstrated that the effects of land use on nitrate yields were not static over time, as a result of changing agricultural practices. Similarly, we have shown that historical nutrient yields cannot be predicted based on anthropogenic nutrient inputs alone. Hydrology is also important for determining N yields, as has been shown in previous studies (Sobota et al. 2009, Howarth et al. 2012, Alam and Goodall 2012), and changes in infrastructure over time – sewers, WWTPs, and dams – are essential for reconstructing regional nutrient yields over time and for understanding the drivers of those yields.

How did the spatial patterns of nutrient fluxes within the NE change over time?

N and P yields were dynamic over time and space. Many of the changes in yields over the study period could be explained by changes in inputs. Yields of N and P increased in the Delmarva Peninsula, greater NY metro area, and northern Virginia (Fig 3.4), where increases in livestock agriculture were strongest during the 20th century (see Hale et al.in review). Outside of those areas, P yields decreased strongly across the region, paralleling decreases in P inputs (Hale et al. in review). Increases in N yields from watersheds in Maine and New Hampshire were associated with increases in N deposition for those regions (Fig 3.4). The change in nutrient inputs for each watershed was the best

predictor of changes in yield over the study period, explaining ~30% of the variation (TN: $R^2 = 0.30$, $p < 0.0001$; TP: $R^2 = 0.27$, $p < 0.0001$).

Hotspots of yields and retention were different for N and P, although there was some overlap. For each year, yields from HUC-8 watersheds were best explained by nutrient inputs to each watershed. TN yields were highly correlated with TN inputs ($\rho = 0.60$ to 0.85), and TP yields were highly correlated with TP inputs ($\rho = 0.60$ to 0.84). In contrast with temporal trends at the regional scale, infrastructure had strong effects on TP yields ($\rho = 0.43$ to 0.83), but weaker and more variable effects on TN yields ($\rho = -0.13$ to 0.55). Consistent with regional temporal patterns, runoff coefficient significantly affected TN yields over space ($\rho = 0.12$ to 0.46), but had only a weak relationship with TP yields ($\rho = -0.19$ to 0.12).

The importance of different drivers in predicting the spatial and temporal patterns of TN and TP yields highlights importance of studies with large spatial and temporal extents and high resolution. At the regional scale, we found that temporal variation was strongly determined by infrastructure for both N and P. For a single point in time, however, nutrient inputs were the best predictor of the spatial pattern of nutrient yields. Our results demonstrate that historical changes in infrastructure were a key driver of temporal changes in nutrient yields and spatial patterns of TP yields, but not an important factor determining the spatial pattern of TN yields.

How did the importance of different drivers of nutrient yields change over space and time?

At the regional scale, the effect size of sewers, WWTPs and dams individually on TN and TP yields increased significantly over the study period. However, we found that the net effect of infrastructure did not change over time, contrary to our expectations. Although WWTPs did reduce yields over time, the positive effect of sewers on nutrient yields outweighed these reductions. Sewers had the largest effect on yields compared to WWTPs and reservoirs, because they bypass the ecological nutrient-removal capacity of soils. As would be expected, the effects of infrastructure were co-located spatially with the infrastructure itself. Infrastructure for human waste was concentrated in areas with high population density, whereas infrastructure for water supply/flood control was not clustered in any way.

At the HUC-8 scale, we did find that the drivers of spatial patterns of TN yields did change significantly over the study period. TN yields were significantly and strongly correlated with TN inputs throughout the study period, but the relationship between inputs and yields weakened significantly over time ($R^2 = 0.57$, $p < 0.001$). TN yields were significantly, but less strongly correlated with runoff coefficient. However, the relationship between TN yields and runoff coefficient strengthened significantly over time ($R^2 = 0.34$, $p = 0.02$), despite no significant trends in runoff coefficients over time. The relationship between TN yields and net infrastructure effect was the most variable, and there was a significant decline in the strength of the relationship between infrastructure effect and TN yields over time ($R^2 = 0.50$, $p = 0.002$). In contrast with TN yields, the correlations between the three drivers and TP yields did not change

significantly over time. Spatial patterns of TP yields were consistently well predicted by TP inputs and infrastructure.

Although previous literature has demonstrated the importance of nutrient inputs (Howarth et al. 1996, 2012, Boyer et al. 2002), hydrology (Smith et al. 2003, Donner et al. 2004, Green and Wang 2008, Sobota et al. 2009, Howarth et al. 2012, Hong et al. 2012, Alam and Goodall 2012), and infrastructure (Alexander et al. 2008, Harrison et al. 2009, Seitzinger et al. 2010) in determining nutrient exports from watersheds, we are the first to demonstrate that the importance of these three factors varies over time and space and between nutrients.

Implications

Different spatial and temporal patterns of N and P yields created a dynamic spatial pattern of nutrient-yield stoichiometry (Fig 3.12). Throughout the study period, most of the region had a molar N:P yield great than 16:1, indicating potential for P limitation. A north-south trend was also common throughout time, where the lower N:P in the southern part of the region may have been due to concentrated livestock agriculture, which is associated with lower N:P demands than anthropogenic inputs as a whole (Hale et al.), in combination with lower rates of N deposition than the northern portion of the region. Areas with N:P less than 16 expanded from 1930 to 1969, concurrent with increases in P inputs as fertilizer and detergent, and then contracted from 1969 to 2002 as N inputs continued to increase but P inputs decreased (Fig 3.12).

These patterns in the stoichiometry of yields may generate parallel patterns in the nutrient limitation of freshwater ecosystems. Previous research has found that increases

in N from atmospheric deposition can shift freshwater ecosystems from N to P limitation (Elser et al. 2009). Understanding how nutrient limitation of primary productivity varies over space and time is critical for designing effective nutrient management policies (Conley et al. 2009), as changing nutrient stoichiometry can alter the controls on eutrophication. Furthermore, increases in N:P in aquatic systems could cause changes in the community composition and structure (Justić et al. 1995, Turner et al. 2003).

Our results also support previous findings that nutrient loading, especially of N, has increased to the Chesapeake Bay since the 1950s (Boynton et al. 1995, Hagy et al. 2004). Boynton et al. (1995) found that N loading was strongly correlated with primary production in the Chesapeake Bay, and Hagy et al. (2004) found that the hypoxic volume of the Bay was significantly related to nitrate loading. In similar studies in Massachusetts, anthropogenic N loading was linked with eutrophication and loss of eelgrass habitat (Valiela et al. 1992, Hauxwell et al. 2003). The spatial specificity of our results should help pinpoint areas where additional management of nutrient loading is required to mitigate these ecosystem impacts and the associated losses of revenue from coastal marine fisheries and recreation.

CONCLUSIONS

We have conducted the most comprehensive reconstruction of nutrient yields to date in terms of spatial and temporal extent and resolution. Despite the aggregate nature of these models, we were able to limit some of the assumptions that need to be made in back-casting, particularly the assumption that the relationship between land use and nutrient export is static. We used a model developed by Green et al. (2004) to estimate

nutrient yields based on the sources of inputs and delivery efficiencies based on hydrology, bypassing the need to make assumptions about land use. The ecologically realistic structure of the models allowed us to conduct scenarios to explore the role of infrastructure and climate as drivers of nutrient yields and describe how those effects varied over time and space. We find that the influence of different drivers on watershed nutrient yields, as measured by effect size, vary over time and space and differ between N and P. Furthermore, the best predictors of nutrient yields over time differed from the best predictors of nutrient yields over space. Understanding the spatiotemporal dynamics of the drivers of nutrient export is important for reconstructing historical ecosystem changes due to altered water quality. This research can be used to answer questions regarding historical changes in nutrient limitation and the ecological consequences of human nutrient use.

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Table 3.1. Model results for nonlinear regression.

Parameter	Estimate	Std. Error	95% Confidence Interval	
			Lower Bound	Upper Bound
α_{res}	-9.433E-5	.004	-.007	.007
α_{lake}	.001	.003	-.005	.006
α_{riv}	1.604	.493	.611	2.596
α_{soili}	.239	.129	-.021	.498
α_{soilo}	.001	.002	-.003	.005

Table 3.2. Error analysis of TN and TP models.

	Model	Predicted vs Observed R^2	Median Prediction Error (%)	Interquartile Range (IQR)	Prediction Errors (%)			
					min	25 Percentile	75 Percentile	max
TN	**Nonlinear Regression**							
	Calibration data (N=51)	0.6556	-6.29	43.59	-90.87	-31.15	12.44	168.47
	Validation data (N=145)	0.6081	-18.59	51.99	-92.34	-45.53	6.46	264.87
	Linear Regression							
	Calibration data	0.5967	21.25	60.45	-72.43	-15.13	45.32	114.48
	Validation data	0.6046	36.54	65.92	-72.43	-1.18	64.74	235.10
	Averaged Models							
	Calibration data	0.6772	5.65	47.42	-81.65	-16.82	30.60	108.82
	Validation data	0.6867	10.74	56.71	-71.79	-20.24	36.47	249.98
TP	**Linear Regression**							
	Calibration data (N=22)	0.7436	1.78	15.74	-48.01	-9.81	5.94	36.26
	Validation data (N=14)	0.6567	6.57	13.32	-12.90	0.09	13.41	15.95
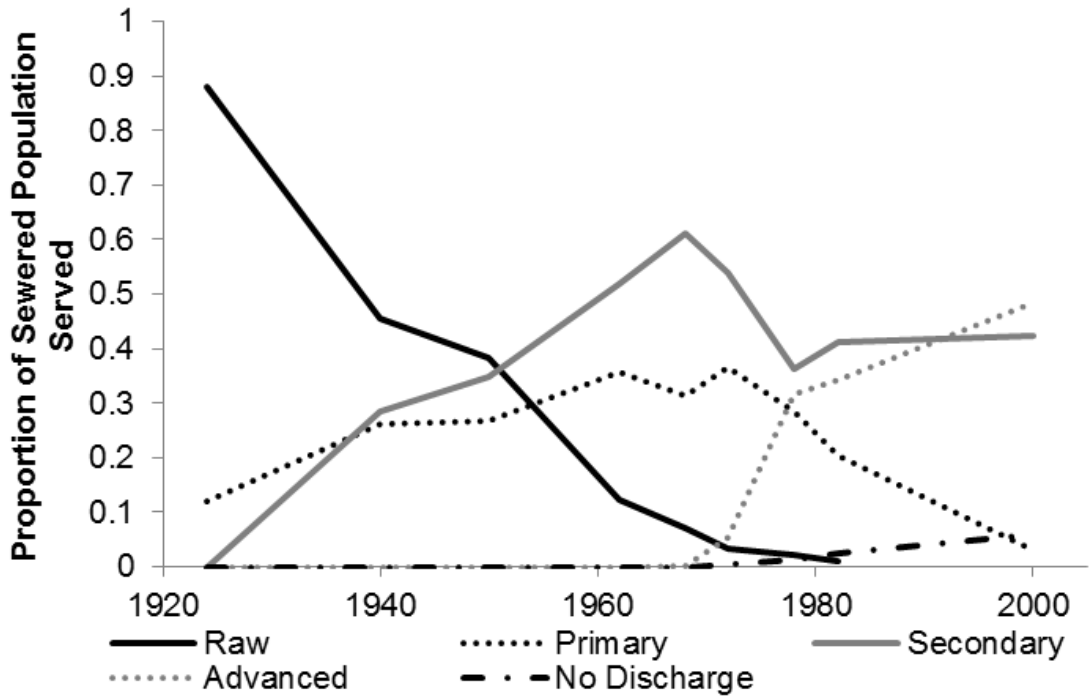
Figure 3.1. Proportion of sewered US population served by different levels of wastewater treatment over time.
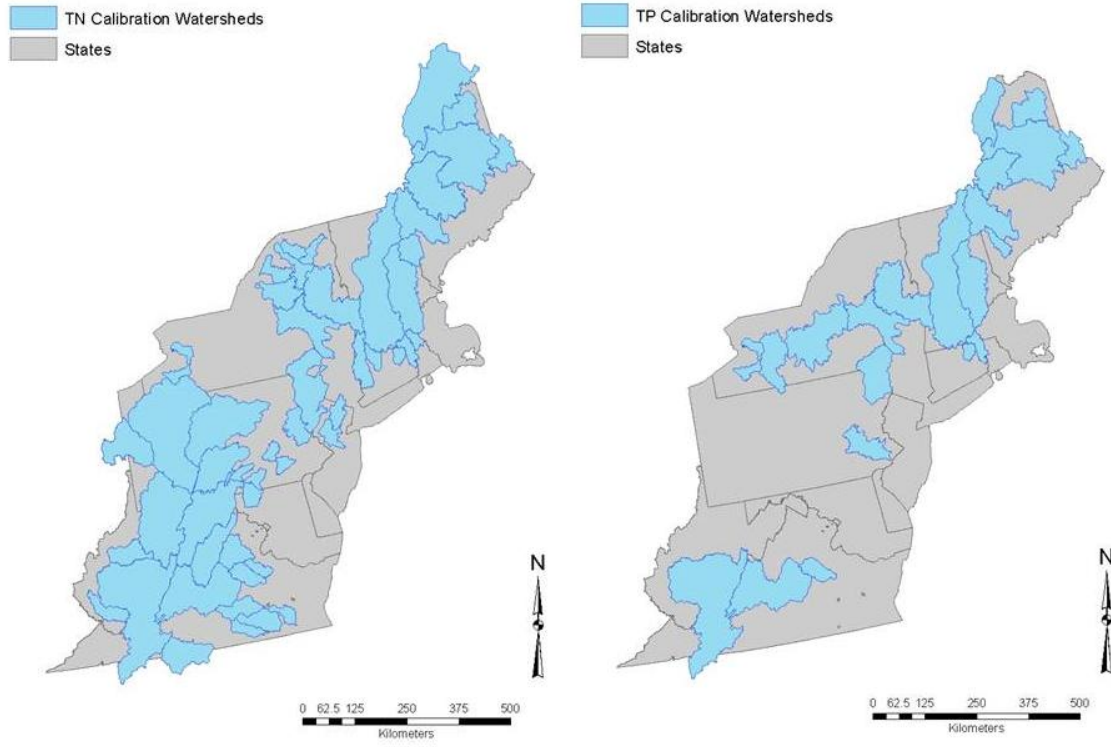
Figure 3.2. Watersheds used for calibration of nutrient load models for TN and TP.
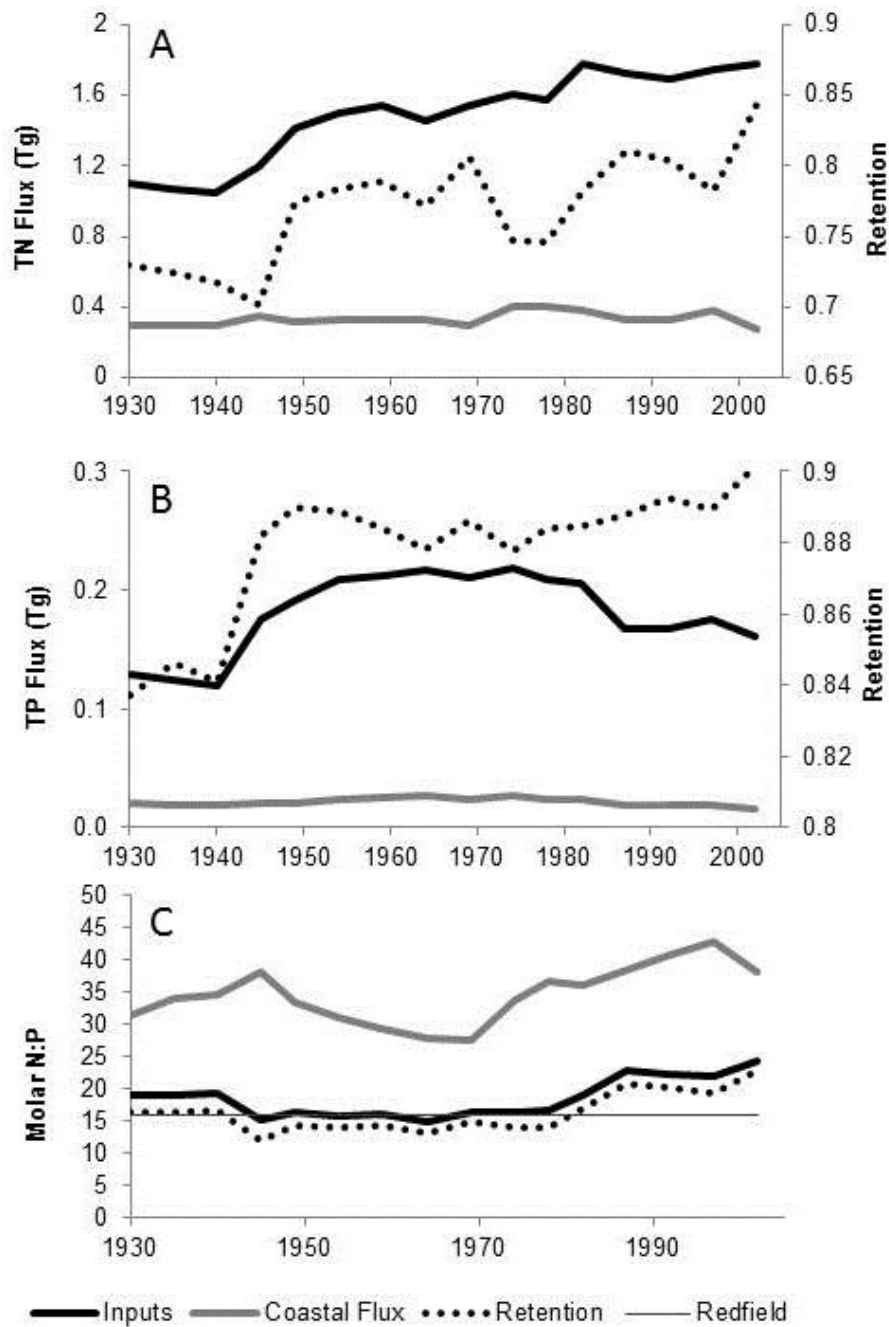
Figure 3.3. Nutrient fluxes (inputs and fluxes to the coast, Tg) and retention (proportion) of a) TN and b) TP for the NE from 1930-2002. c) molar N to P ratio of inputs, outputs, and retention, with the Redfield Ratio (Redfield 1958) plotted as a horizontal line.
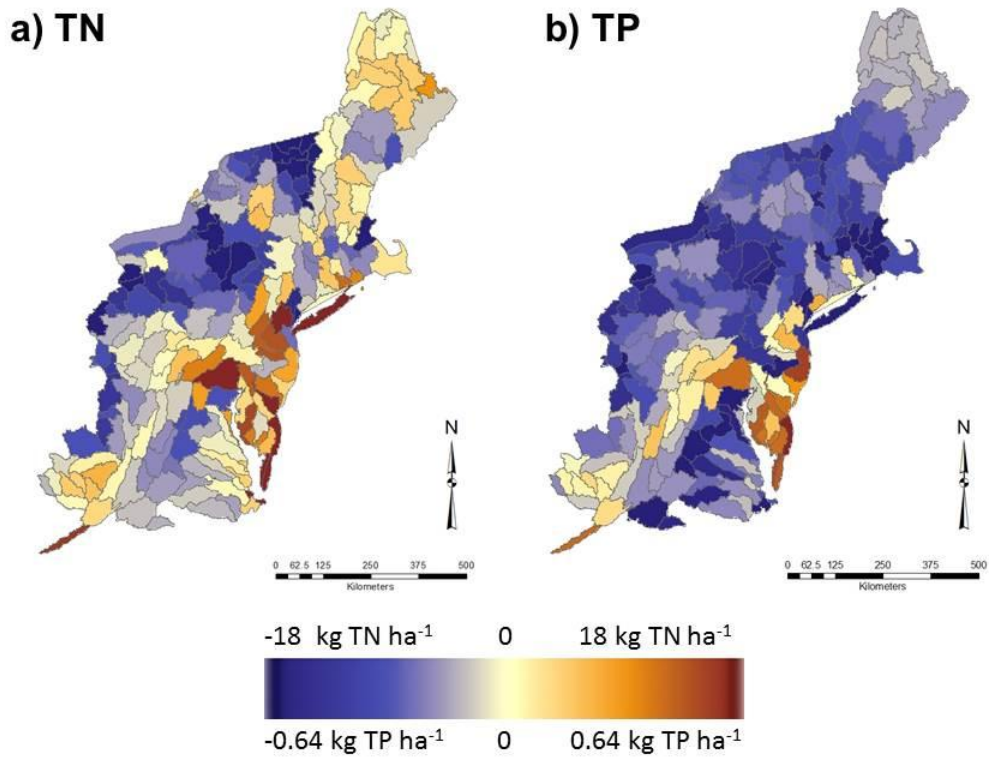
Figure 3.4. Map showing changes in A) TN and B) TP yields from NE HUC-8 watersheds from 1930 to 2002. Blue colors indicate that nutrient yields declined from 1930 to 2002, and brown colors indicate that nutrient yields increased from 1930 to 2002.
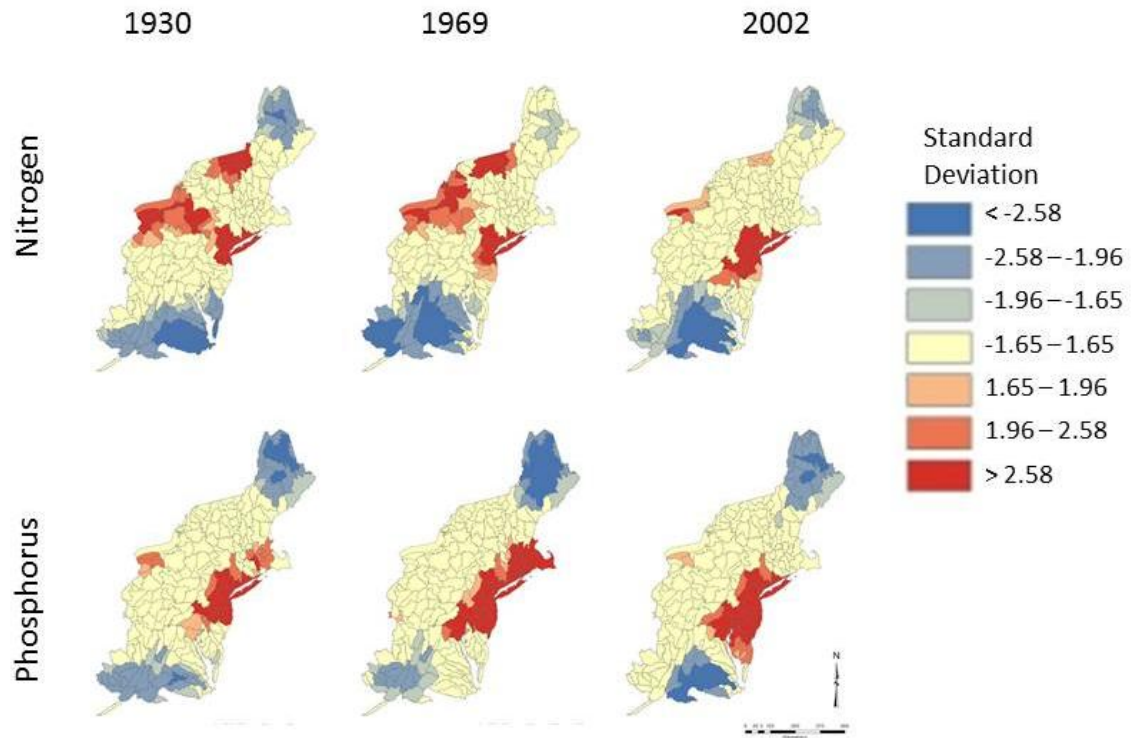
Figure 3.5. Hotspots and coldspots of nutrient yields for N and P in 1930, 1969, and 2002.
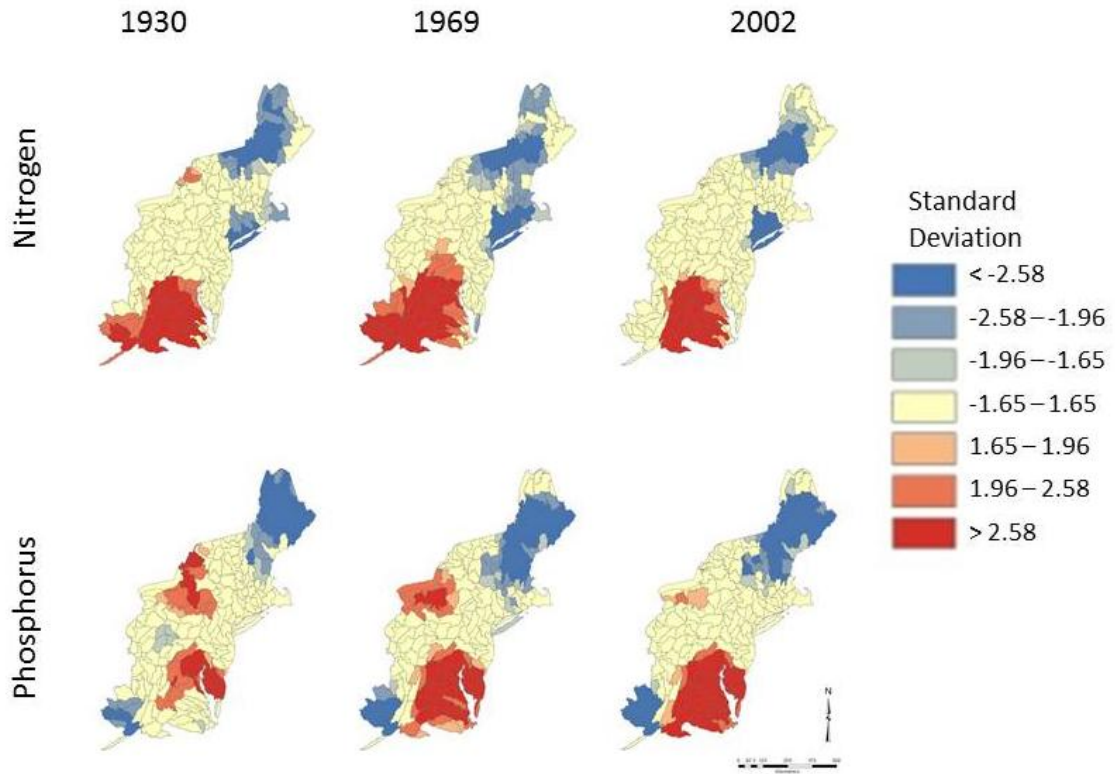
Figure 3.6. Hotspots and coldspots of nutrient retention (proportion) for N and P in 1930, 1969, and 2002.
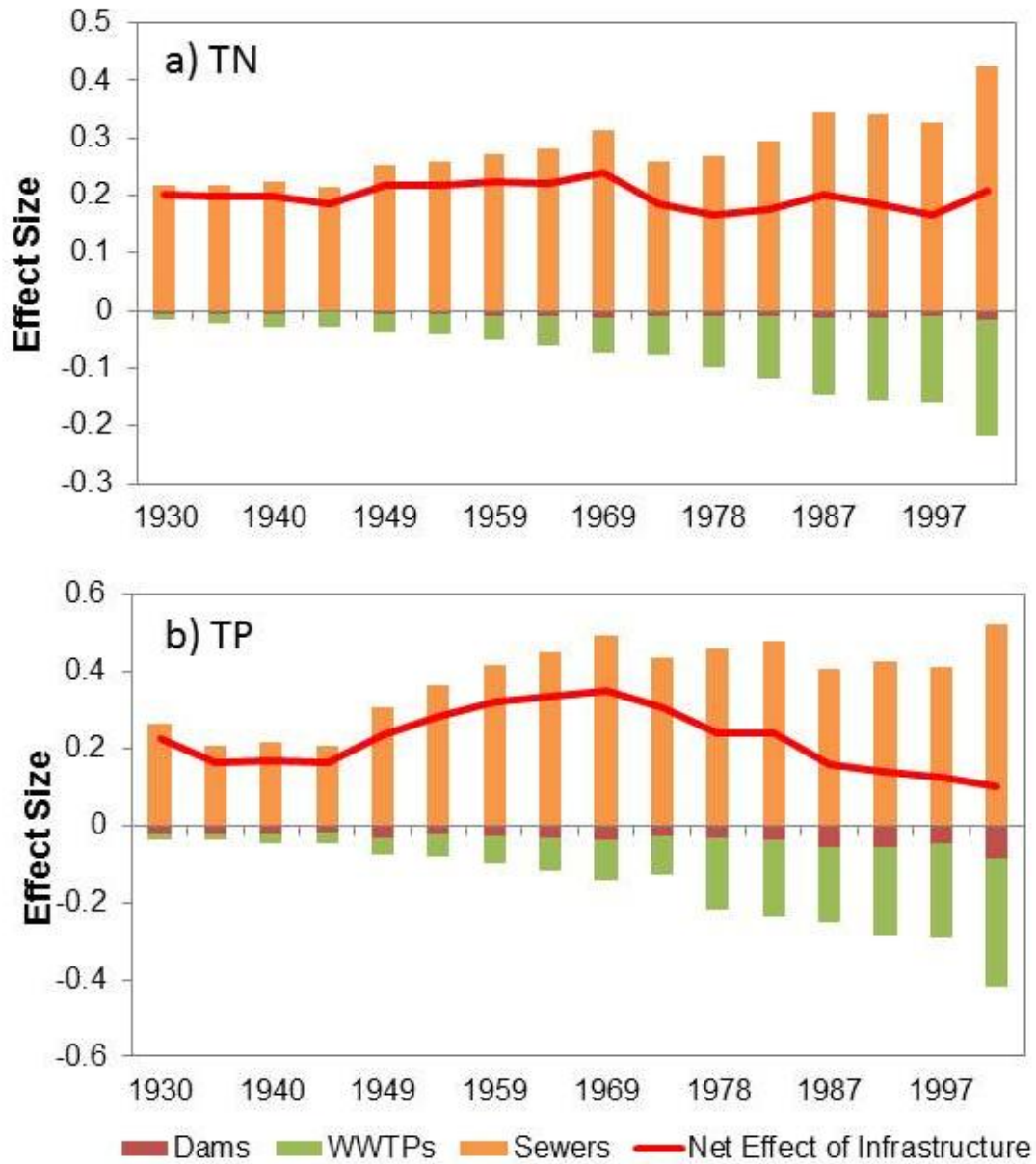
Figure 3.7. Effect size of infrastructure (reservoirs, sewers, and WWTPs) on A) TN and B) TP yields from the NE region.
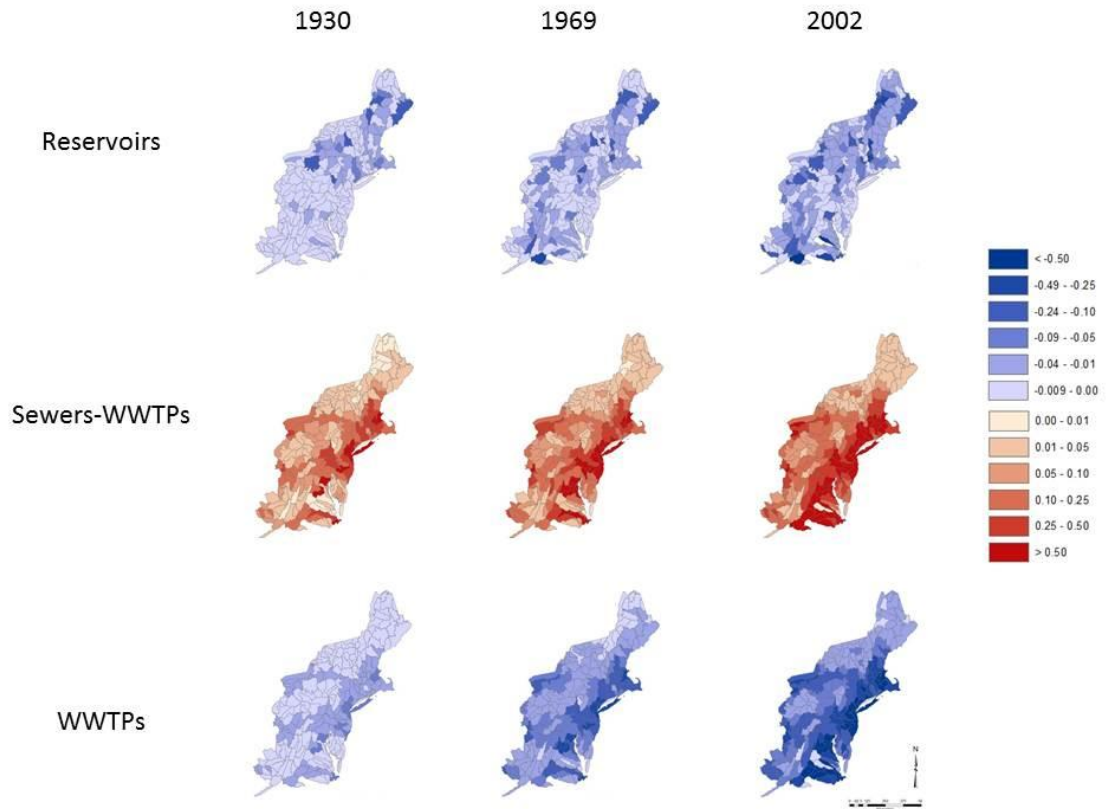
Figure 3.8. Effect size of infrastructure on TN yields in 1930, 1969, and 2002, where a negative effect size (blue colors) indicates that infrastructure reduced TN yields and a positive effect size (red colors) indicates that infrastructure increased TN yields. Patterns are similar for TP.
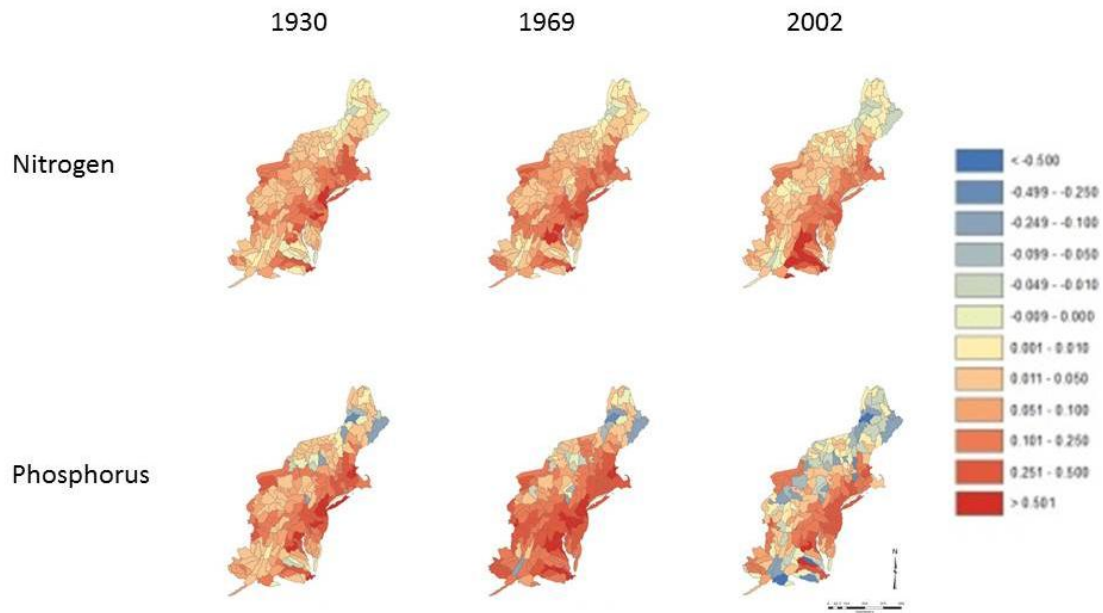
Figure 3.9. Net effect size of infrastructure on TN and TP yields in 1930, 1969, and 2002, where a negative effect size (blue colors) indicates that infrastructure reduced nutrient yields and a positive effect size (red colors) indicates that infrastructure increased nutrient yields.
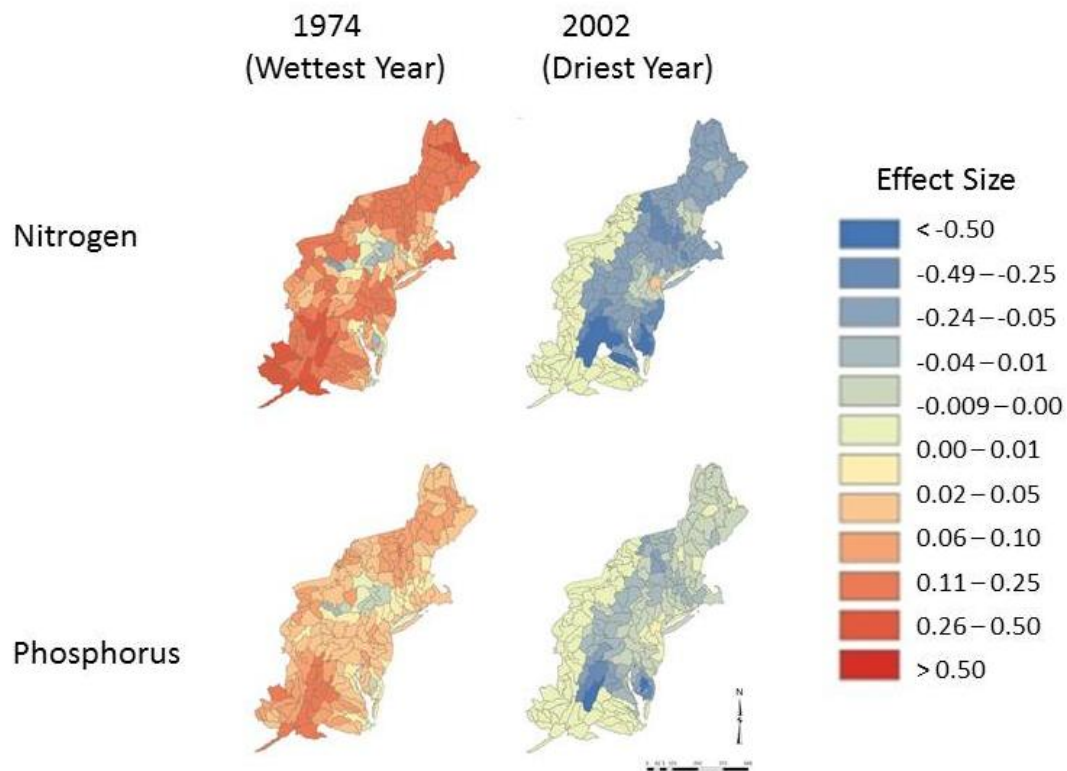
Figure 3.10. Spatial variation in the temporal effect size of runoff coefficients for N and P for the wettest year (1974), and the driest year (2002) in our study period. Effect size for each watershed is relative to the mean runoff coefficient for that watershed over the study period.
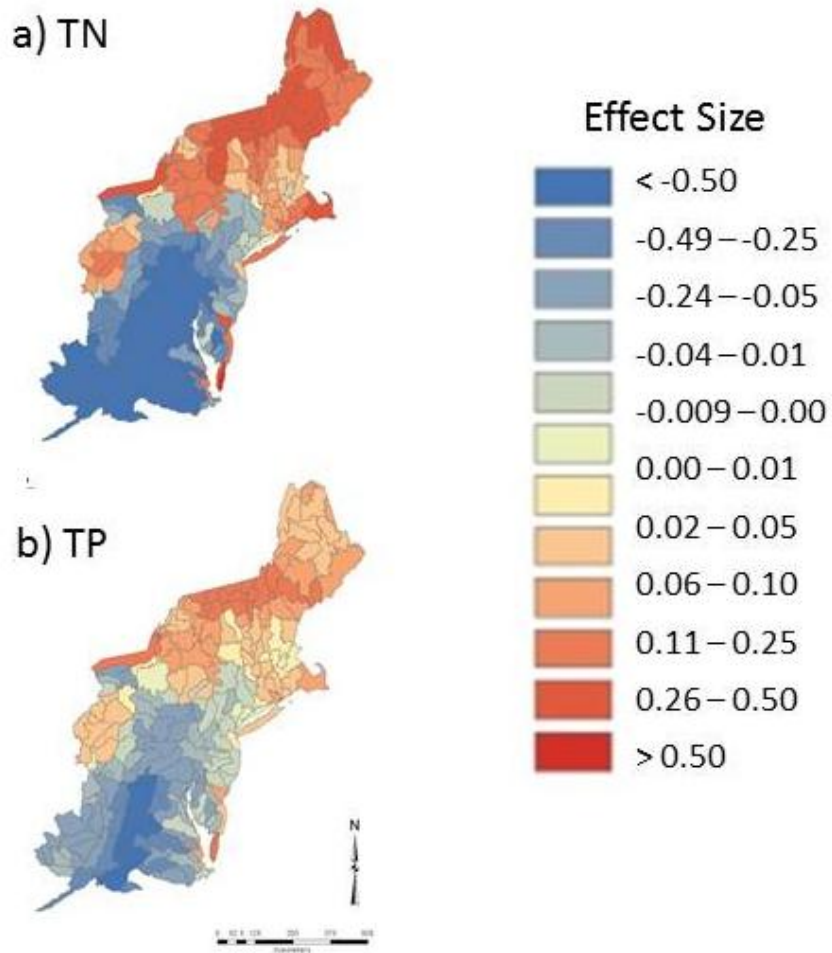
Figure 3.11. Spatial effect size of runoff coefficients on N and P yields in 1969. Spatial patterns are consistent across years. Effect size for each watershed is relative to the mean annual runoff coefficient for the region.
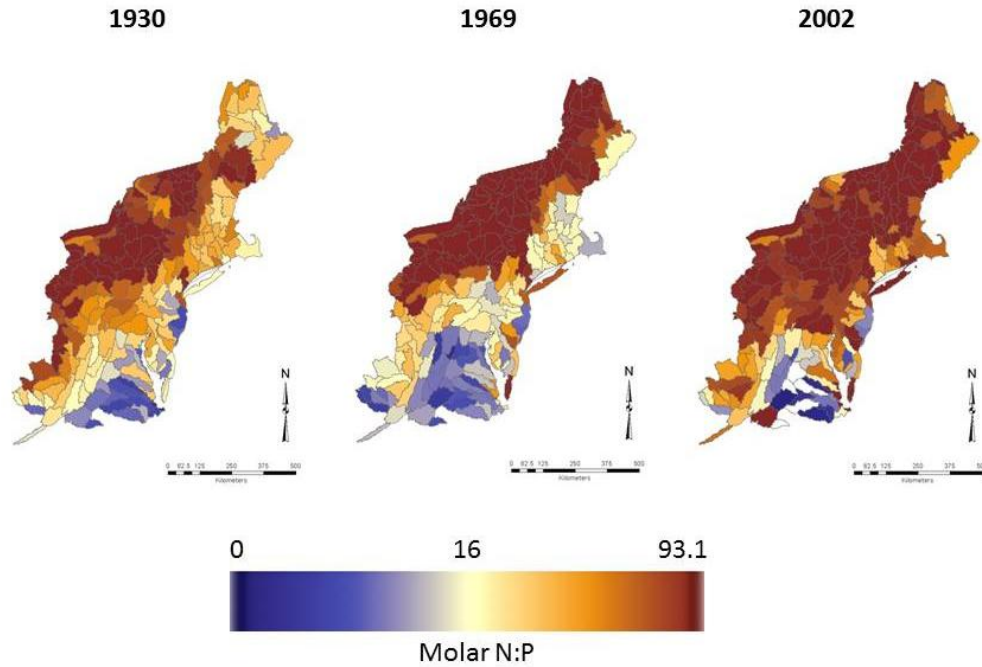
Figure 3.12. Stoichiometry of nutrient yield from NE watersheds over time. Molar ratio of N to P is displayed relative to the Redfield ratio (16:1), where blue colors indicate watersheds where aquatic ecosystems are likely to be N-limited, and brown colors indicate watersheds where aquatic ecosystems are likely to be P-limited.

Chapter 4

LAND COVER, STORMWATER INFRASTRUCTURE, AND STORM CONTROLS

ON STORMWATER SOLUTE DELIVER FROM ARID URBAN WATERSHEDS

ABSTRACT

Urbanization can have numerous detrimental effects on downstream systems, many of which are due to urbanizations effects on hydrology and water quality. A major challenge has been to understand what features of urban watersheds control the quantity and quality of stormwater runoff. Research has focused on land cover metrics to predict the effects of land use change, but metrics such as impervious cover are poor predictors of water quality. In Scottsdale, AZ, we found that stormwater infrastructure design varies substantially over time and space. Specifically, from 1955 to 2010, there was a major decline in the use of storm sewer pipes. The use of engineered channels and retention basins increased beginning in 1970, peaking in the late 1970s, when the use of un-engineered washes began to increase. To understand how spatial variation in stormwater infrastructure affects solute delivery, we monitored 10 watersheds ranging in size from 5 to 17,000 ha in the Indian Bend Wash watershed in Scottsdale, AZ. Small (< 200ha) watersheds had uniform land use (medium-density residential) but were drained by a variety of stormwater infrastructure types including surface runoff, pipes, engineered channels, and retention basins. We measured discharge and precipitation at the outflow of each subwatershed and collected stormwater samples for analyses of total dissolved nitrogen (TDN), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4), dissolved organic carbon (DOC), soluble reactive phosphorus (SRP), and chloride (Cl^-) for all events from

August 2010 to August 2012. We used structural equation modeling (SEM) to test

hypotheses about the relationships of infrastructure characteristics, land cover, and storm

variables on runoff, solute concentrations, and solute loads. Across these study

watersheds, solute delivery is better predicted by runoff than by solute concentrations.

Infrastructure and land cover affected solute delivery via effects on event runoff, but did

not affect solute concentrations. Event runoff decreased with engineered channel density

and increased with imperviousness and precipitation. Solute concentrations varied with

storm variables (rain-free days, season, precipitation), but were not affected by watershed

attributes. The lack of an effect of watershed attributes may be ascribed to the limited

range of land uses encompassed by our study (i.e., medium-density residential). Future

research should address interactions between infrastructure design and land use, which is

likely to have stronger impacts on solute concentrations compared to land cover. The

mechanisms linking watershed and storm characteristics with solute delivery found here

are likely region-specific. However, the spatial and temporal patterns of infrastructure

design in Scottsdale, AZ mirrored those described at the national scale. Infrastructure

design is likely to be an important watershed feature for understanding water and solute

delivery. Furthermore, spatial variation in infrastructure within and across cities may be

an important source of heterogeneity in urban ecosystem functioning, and thereby in the

benefits provided by these systems to society in terms of stormwater modulation.

INTRODUCTION

The effects of urbanization on stream ecosystems have been well-studied over the

past 40 years (Wolman and Schick 1967, Dunne and Leopold 1978, Paul and Meyer

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2001, Walsh et al. 2005) and have more recently been summarized as a general phenomenon known as the "urban stream syndrome" (Walsh et al. 2005). Many changes in ecosystems downstream of, or within urban areas, such as changes in ecological community composition and geomorphology, are caused by altered hydrology and elevated delivery of solutes (Paul and Meyer 2001, Walsh et al. 2005). A major challenge, therefore, has been to understand the controls on the delivery of water and solutes from urban watersheds.

An assessment of the controls on solute delivery must begin with the understanding that solute loads are controlled by both their supply – the availability of solutes in the watershed – and their transport – the ability of the watershed to convey those solutes downstream (Lewis and Grimm 2007). One focus in the literature has been on land-use change, particularly since additional solutes, such as nutrients, are introduced to a watershed as it urbanizes (Paul and Meyer 2001, Groffman et al. 2004, Walsh et al. 2005). Sources of additional solutes can include fertilizers, atmospheric deposition, leaky sewage systems, pesticides and herbicides, and road salt (Paul and Meyer 2001, Groffman et al. 2004, Walsh et al. 2005, Kaushal et al. 2005). Other research has focused on land cover change particularly the role of imperviousness (Arnold and Gibbons 1996, Paul and Meyer 2001, Brabec et al. 2002, Jacobson 2011). Impervious surfaces prevent rainfall from infiltrating, thereby increasing surface runoff (Arnold and Gibbons 1996). This change in the surface water balance can have significant effects on the hydrologic regime of the watershed – reducing baseflow, increasing peak flow and total runoff during storm events (Brabec et al. 2002, Schueler et al. 2009, Jacobson 2011). Although

imperviousness has been useful in describing some patterns of hydrology, it is generally a poor predictor of water quality (Cadenasso et al. 2007, Gallo et al. 2013).

Key in understanding solute delivery is climate. Many researchers have recognized that land-use effects on solute delivery are mediated by climate and storm characteristics. Kaushal et al. (2008) found that the difference between nitrogen (N) loads from urban and forested watersheds was great during wet years, but muted during dry years. In urban stormwater systems, interactions between land cover or land use and storm characteristics are important factors for understanding runoff and solute delivery (Lewis and Grimm 2007, Gallo et al. 2013).

An under-studied aspect of urbanization in this literature is the dynamic alterations to urban drainage systems. Early works noted that land-cover change during urbanization was accompanied by dramatic changes to the drainage system (Graf 1977). Increases in drainage density via the installation of extensive storm sewer networks underground can exacerbate the hydrologic impacts of impervious surfaces (Paul and Meyer 2001, Walsh et al. 2005, Kaushal and Belt 2012). However, urban stormwater management has not been static over time. Stormwater engineering and management have experienced several major paradigm shifts over the past 150 years, the earliest of which was the shift from combined to separate sewer systems (Burian et al. 2000, Delleur 2003). During the 1950's the primary objective of stormwater management was to remove stormwater as quickly and safely as possible from urban areas (Ellis and Marsalek 1996, Chocat et al. 2001, Delleur 2003). As researchers documented the adverse impacts of extensive storm sewer networks and impervious surfaces during the 1960s and 70s, the objectives and tools of stormwater management expanded to include

water quality and environmental protection as well (Ellis and Marsalek 1996, Chocat et al. 2001, Delleur 2003). These shifts suggest that possibility of a substantial temporal and spatial heterogeneity in stormwater management. Since stormwater management may substantially affect the transport of solutes from urban watersheds, an evaluation of their impacts is warranted, yet they have not been addressed previously in the literature.

The urban stream syndrome has become almost a paradigm with a tacit assumption that the effects of urbanization are consistent across regions, but regional contexts within which hypotheses have been developed and tested may be crucial (Grimm et al. 2008). In arid regions, such as the Phoenix, AZ metropolitan area (Fig. 4.1), many hydrologic aspects of the urban stream syndrome occur naturally, such as hydrograph flashiness (Grimm et al. 2004). This climatic context not only changes the baseline against which urbanization is compared, but may also affect stormwater management decisions, especially in comparison with more temperate cities where rainfall patterns are less extreme. One of the key features of urban watersheds in Phoenix is the use of several distinct infrastructure designs: storm sewers, engineered open channels, un-engineered washes, and retention basins.

Objectives and Hypotheses

The objectives of this research were to: 1) characterize spatial and temporal changes in urban drainage infrastructure for Scottsdale, AZ (part of the Phoenix metropolitan area); 2) characterize solute loads from watersheds with the same land use but different stormwater infrastructure designs, and 3) characterize relationships between infrastructure, land cover, storm characteristics and solute loads.

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We developed a set of hypotheses regarding the relationships between infrastructure, land cover, and storm characteristics on solute delivery (Fig. 4.2). We hypothesized that these three sets of variables would control solute delivery via control on runoff (solute transport) and solute concentration (supply of solutes within the watershed). Our overall expectation was that watershed features that increase stormwater conveyance (imperviousness and pipes) would have positive effects on solute delivery, whereas features that decreased conveyance (channels, retention basins, and % grass cover) would reduce solute delivery, via effects on runoff. We expected that solute concentrations would be controlled by variables that affected the supply of solute within the watershed, such as rain-free days (time over which solutes can accumulate; Welter et al. 2005, Lewis and Grimm 2007) and possible biogeochemical removal in channels, retention basins (Zhu et al. 2004, Larson and Grimm 2012), and grass (Hall et al. 2009).

For the purposes of this paper, we focus our analyses on several dissolved solutes: total dissolved nitrogen (TDN), nitrate (NO_3^-), nitrite (NO_2^-), ammonium (NH_4^+), soluble reactive phosphorus (SRP), dissolved organic carbon (DOC), and chloride (Cl^-). Both nitrogen (N) and phosphorus (P) may be limiting nutrients and concentrations are typically elevated in urban stormwater. The effects of urbanization on DOC concentrations and loads are not consistent in the literature. Cl^- is a conservative element, meaning that it is not biologically reactive, and therefore is included as a comparison with reactive carbon (C), N, and P. Furthermore, Cl^- concentrations have been found to be quite high in urban streams where road deicers are used (Kaushal et al. 2005). Although deicers are not used in Phoenix, Cl^- concentrations may be elevated due to high rates of irrigation and evaporation within urban watersheds.

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Site Description

The Phoenix, AZ metropolitan region (Fig. 4.1) is a rapidly growing urban area in the Sonoran Desert that includes 25 municipalities within Maricopa and Pinal Counties. With 4.3 million residents, the Phoenix metro area (hereafter, Phoenix) is the 12th most populous urban area in the United States. The Phoenix metropolitan region has developed and expanded throughout the alluvial plain of the Salt River above its confluence with the Gila River, from small agricultural communities in the late 1800's to today's 1700 km^2 urban-suburban agglomeration characterized by extensive hydrological modification (Larson et al. 2005, Keys et al. 2007, Roach et al. 2008). Although many older areas of the Phoenix metropolitan region are serviced with underground storm sewers, since the 1970's new developments have been required to retain a certain amount of runoff (for a 5 to 100 year storm), usually in retention basins. New development is explicitly prohibited from increasing the amount of runoff reaching stream channels.

Climate of the Sonoran Desert is hot and dry. Precipitation is highly variable within and between years, but averages 180mm annually. Within years, precipitation falls during the summer monsoon and winter rainy seasons (long-term average, ~50% in each season). Summer monsoon storms are convective events characterized by brief, intense, and highly localized rainfall, with moisture originating in the Gulfs of Mexico or California. Winter storms, in contrast, are Pacific frontal storm systems with lower-intensity, longer duration rainfall. Due to soil and vegetation characteristics of the Sonoran Desert, watersheds in this area experience higher flood peaks, flash-flood potentials, and runoff than wetter regions of the United States (Osterkamp and Friedman 2000).

METHODS

Objective 1: Infrastructure characterization

There are four primary stormwater infrastructure designs used in Phoenix: storm sewers, engineered channels, un-engineered washes, and retention basins. Storm sewers (hereafter "pipes") are simply pipes that drain urban land. This pipe system is separated from the sanitary sewer system. Engineered channels (hereafter "channels" are linear open channels, usually with a trapezoidal design. These channels are either concrete, gravel-lined, or planted with grass. Un-engineered washes are natural rather than designed features. These ephemeral stream features typically have gravel or sandy beds. Finally, retention basins are engineered depressions with xeric or grassy landscaping that are designed to retain water within the landscape. Some retention basins are connected to pipes or channels; others have drywells, intended to shunt water to the vadose zone. Retention basins range in size from ~40 m^2 to over 10 ha depending on the area being drained and the design objectives.

We obtained data from the City of Scottsdale on the locations of stormwater mains, engineered channels, and un-engineered washes. Retention basins were identified manually from a 0.6-m contour digital elevation model in GIS, and truthed using aerial photographs in GIS. Because data on construction years were not available for stormwater infrastructure, we assigned a year of construction to each individual infrastructure based the construction year of adjacent residential development. Development construction year was obtained from the Maricopa County Assessor subdivision dataset (http://mcassessor.maricopa.gov/assessor//).

To identify temporal changes in the use of different infrastructure designs, we normalized the length of each linear infrastructure feature type (pipes, channels, and washes) built each year by the total length of linear features built for that year to calculate a proportion of infrastructure that was pipes, channels, and washes. For example, the proportion of infrastructure design that was pipes was calculated as [length of pipes built in a year] / [length of pipes + channels + washes built in a year]. To identify changes in the use of retention basins, we calculated the total area of retention basins built in a year and normalized it by the total length of new linear infrastructure (pipes, channels, and un-engineered washes).

Objectives 2-3: Stormwater sampling

To understand the effects of stormwater infrastructure design on solute transport, we sampled 10 ephemeral watersheds that ranged in stormwater infrastructure and drainage area (Table 4.1). Nine of these watersheds were nested within the Indian Bend Wash (IBW) watershed that drains most of Scottsdale, AZ into the Salt River (Fig. 4.1; see also Roach et al. 2008). The 10th watershed (Kiwanis Park; KP) was located in Tempe, AZ, outside of the IBW watershed. Watersheds were selected to capture a range of stormwater infrastructure types, drainage areas, and land covers (Table 4.1). Seven watersheds <150 ha in drainage area contained only medium-density residential land use and were drained primarily by a single type of infrastructure. The 2 smallest of these (<10 ha) were drained only by surface runoff (ENC, PIE), and a mid-sized watershed (~100 ha) was drained by pipes (KP). Four watersheds were drained primarily by engineered channels (BV, MR), or retention basins (MS, SW). Three larger "integrator" watersheds

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(LA, SGC, IBW) drained areas with mixed land use and multiple forms of stormwater infrastructure, and provided a more comprehensive view of the stormwater and nutrient transport of the urban landscape.

<u>Sampling</u>

We used ISCO® automated samplers to collect up to 24 discrete stormwater samples during every storm event over two years, from August 2010 to August 2012. We measured stage height at all sites with an ISCO bubbler module. Stage height at all sites was measured in concrete channels or pipes to facilitate discharge calculations. Rating curves were developed using Manning's Equation to calculate discharge from stage height measurements (see Turnbull et al. in prep for details). For IBW and SGC, discharge data were obtained from USGS flow gauges near ISCO locations. Precipitation was measured using an ISCO 674 tipping-bucket rain gauge at 1-minute intervals. For PIE, LA, and SGC, 15-minute precipitation data were obtained from the Flood Control District of Maricopa County (http://fcd.maricopa.gov/Rainfall/Raininfo/raininfo.aspx). To account for the spatial variability of rainfall in the Phoenix area, we used rainfall data from our gauges, Flood Control District gauges, and the wunderground.com volunteer network of rain gauges to spatially interpolate rainfall depth across the study area for each event (see Turnbull et al. in prep for details). These interpolated rainfall surfaces were then used to estimate average precipitation over each watershed.

Stormwater samples were collected from the field within 12 hours of an event and transported back to the laboratory. Samples for ammonium (NH_4^+), nitrate-N (NO_3^-), nitrite-N (NO_2^-), soluble reactive phosphorus (SRP), and chloride (Cl^-) were either analyzed immediately or frozen for later analysis. Samples for TDN and DOC were

filtered through ashed GF/F filters and acidified to pH 2 with HCl. TDN samples were analyzed within 7 days by combustion on a Shimadzu TOC-VC/TN analyzer. Samples for Cl^- and SRP were filtered through ashed GF/F filters and analyzed on a Lachat Quick Chem 8000 Flow Injection Analyzer. NO_3^-/NH_4^+ samples were centrifuged to remove particulates and analyzed on a Lachat Quick Chem 8000 Flow Injection Analyzer.

Load Estimation

Event solute loads (L_e) were estimated as:

$$L_e = 60 \sum_{t=1}^{n} C_t \times Q_t$$

Where C_t is the solute concentration in mg / L, Q_t is the instantaneous discharge in L/s and 60 is a conversion factor to calculate load per minute. Concentrations were linearly interpolated between observed values. Event mean concentrations of each solute (EMC, in mg/L) were calculated as:

$$EMC = \frac{L_e}{Q_e} \times 10^6$$

Where Q_e is the total discharge in L and 10^6 is a conversion factor to obtain concentrations in units of mg/L.

Data analysis

All solute load data are expressed per unit watershed area (i.e., kg/ha). Precipitation and discharge are expressed as a depth (mm). Dissolved N loads are expressed in kg N/ha. Data were transformed if necessary to achieve normality and homoscedasticity. Unless stated otherwise, all analyses were conducted using R (version 12.15.1, http://cran.r-project.org/).

To test for differences in solute loads and concentrations from watersheds with different stormwater infrastructure designs, we used a 1-way analysis of variance (ANOVA) with site as the factor. We used Tukey's HSD post-hoc test to test for between-group differences. 17 events had runoff coefficients greater than 1, indicating error in our discharge measurements, precipitation measurements, or our watershed delineation. Twelve of these events were at the piped KP site, 4 events were at the channel-drained MR site, and 1 event was at the channel-drained BV site. These events were excluded from all analyses.

Watershed Characterization

Watersheds were delineated manually in ArcGIS using a 0.6-m digital elevation model (City of Scottsdale) and infrastructure data layers. We used a land-cover classification dataset created for the Central-Arizona Phoenix Long Term Research Site. Briefly, land cover was characterized from 4-band National Agriculture Imagery Program (NAIP) imagery using object-oriented classification. Land cover was classified as building, road, soil, shrub canopy, tree canopy, grass, lake, canal, pool, cropland, and fallowed cropland. For the purposes of understanding stormwater dynamics, only the surface cover was considered important, and we reclassified the original categories into the following cover classes: Impervious (roads + buildings), soil, grass, water (canal + pool + lake), and agricultural (cropland + fallow). We assumed that the surface cover below tree and shrub canopies was in the same proportion as the surface cover not below canopies. The proportion of each land cover class within each watershed was calculated in ArcGIS.

Infrastructure data were developed as described above. Each infrastructure file was clipped to watershed boundaries to calculate the total length of each infrastructure type and the total area of retention basins. Lengths and areas were then normalized by watershed area to obtain a measure of drainage density (m / m^2 or m^2 / m^2).

Path Analysis

We used path analysis, a type of structural equation modeling, to characterize relationships between infrastructure, storm characteristics, land cover, and loads of each solute (Objective 3). Separate models were constructed for each solute. We hypothesized that the effects of land cover, infrastructure, and storm characteristics on solute loads are mediated by their effects on runoff and concentration (Fig. 4.2). Path analysis allowed us to test hypotheses about the indirect effects of variables via their effects on runoff and concentration. This was particularly useful since some drivers were hypothesized to have a positive effect on loads via runoff and a negative effect via concentration (e.g., precipitation). We therefore constructed path models in which event scale load was directly affected by runoff and EMC, and indirectly affected by land cover, infrastructure, and storm variables via runoff and EMC. Land cover variables considered in the path analysis included imperviousness (%), grass (%) cover, and soil cover (%). Infrastructure variables included retention basin density (m^2 / m^2), pipe drainage density (m / m^2), and engineered channel density (m / m^2). Storm characteristics included rain-free days (days since the last rain event), flow-free days (days since the last discharge event), precipitation (mm), and season (binary: winter or summer). We also included watershed area (ha), since previous research has found relationships between solute loads and area

(Lewis and Grimm 2007). All variables were tested for normality and transformed as needed to achieve it.

We constructed a Pearson correlation matrix to assess relationships between all variables and used this to guide the selection of variables for the path models. We used a correlation matrix and our hypotheses to guide the selection of variables for each load model. All variables with significant correlations were included in our base model. The base model was fit to raw data using maximum likelihood estimation in Amos 20 (SPSS).We then removed any weak and insignificants paths (path coefficient < 0.1; α = 0.05) one at a time, re-evaluating the model between each removal until all path coefficients were > 0.1 and significant. Model fit was then evaluated using a variety of goodness-of-fit metrics. If model fit was unacceptable, additional paths were removed until an acceptable fit was reached. In the case of multiple acceptable models the model was selected with the most superior fit metrics. Once a best-fit model was selected, interaction terms between watershed characteristics (land cover and infrastructure) and storm characteristics were evaluated. Interaction terms were introduced to the model only if there was a direct effect of both a watershed and storm characteristic on an endogenous variable. Weak and insignificant paths were then removed from the model if necessary to achieve a final best-fit model. Model fit was evaluated using chi-square, root mean square error of approximation (RMSEA), Tucker-Lewis Index (TFI), and Normed Fit Index (NFI)(Hu and Bentler 1999, Kline 2010).

RESULTS

Changes in Infrastructure over Time and Space

The design of stormwater infrastructure in the City of Scottsdale varied substantially from 1955 to 2010. Pipes were the predominant design for linear stormwater infrastructure until the late 1970's (Fig. 4.3). Beginning in 1970, the use of engineered channels increased and peaked in 1980 when ~40% of new stormwater infrastructure was engineered channels. After 1980, the use of engineered channels declined. Un-engineered washes became a substantial contribution to linear stormwater infrastructure after 1980 and became the dominant linear design in the mid-1990's. By 2010, un-engineered washes made up ~70% of all new linear stormwater infrastructure. The use of retention basins in Scottsdale was also dynamic from 1955 to 2010. The highest density of retention basins was built in the early-1970s, after which the density of newly constructed retention basins sharply declined, returning to pre-1970 levels by the late 1980s (Fig. 4.3).

In part because Scottsdale has been able to grow northwards over time, rather than via infill development (Fig. 4.4A), changes in stormwater infrastructure design over time are mirrored in the spatial patterns of infrastructure use. Retention basin density is highest in the middle part of Scottsdale, in the area developed between 1976 and 1995 (Fig. 4.4B). Similarly, there is a distinct north-south transition from the predominance of pipes in the southern-most part of the city, then a shift to engineered channels, and a sharp transition to washes in the northern half of the city (Fig. 4.4C).

Solute loads and EMCs from watersheds with different infrastructure types

We sampled TDN and DOC for 120 events, NO_3^-, NH_4^+, and NO_2^- for 106 events, and Cl^- and SRP for 111 events over our two-year study period (Table 4.5). We sampled 33 events from 3 integrator watersheds, 26 events from 2 retention basin-drained watersheds, 26 events from 2 channel-drained watersheds, 7 events from 1 pipe-drained watershed, and 38 events from 2 surface-drained watersheds (Table 4.1). Because of the difficulty of sampling very small events, our sampled events were larger than all observed events over the study period (N = 344 events). Precipitation for our sampled events averaged 11 mm ($\pm$ 8) and was significantly greater than precipitation for all events (6 $\pm$ 6; Fig. 4.5). Runoff coefficient was also larger for sampled events (0.33 +/- 0.28) than all observed events (0.20 $\pm$ 0.25). Mean runoff was greater for sampled events (3 $\pm$ 4) than all observed events (2 $\pm$ 4). However, antecedent dry days were similar for sampled (18 $\pm$ 22) and observed events (18 $\pm$ 22). Storm duration was also statistically the same from sampled and all events (Fig. 4.5). Solute concentrations and loads were similar to those observed by Lewis and Grimm (2007) for other watersheds in Phoenix (Table 4.2).

Loads were significantly different across watersheds (Fig. 4.6). Loads were consistently lowest from SW and SGC, and consistently highest from ENC, PIE, and KP across all solutes. With the exception of TDN and NH_4^+ loads, for which ENC and PIE were significantly different, loads were not statistically different between watersheds with similar infrastructure. However, within channel and retention basin categories, loads tended to be higher from larger watersheds (i.e., BV > MR and MS > SW), although these differences were not significant (Fig. 4.6).

Event mean concentrations of TDN, NH_4^+, DOC, and Cl^- varied across watersheds, but concentrations of NO_3^- and NO_2^- did not (Fig. 4.7). Concentrations of all solutes were lowest at IBW, except Cl^- which was highest at IBW. Concentrations of TDN were significantly lower from IBW than from ENC and PIE, and concentrations of NH_4^+ were lower from IBW than all other sites except KP and MS. DOC concentrations were lower from IBW than from PIE. SRP concentrations from IBW were lower than those from the surface and integrator sites, but similar to concentrations from all other sites. Patterns of Cl^- concentrations differed from other solutes in that concentrations were highest from IBW and lowest at channel and retention basin drained sites (Fig. 4.7).

Effects of land cover, infrastructure, and storm characteristics on solute loads and concentrations

Best-fit path models fit the data well according to a variety of metrics (Table 4.5). However, due to the limited number of observations, we were not able to validate the models with independent data. Models for all solutes included land cover, infrastructure, and storm characteristics (Table 4.6). Both runoff and EMC were significant covariates of solute loads in all models (Table 4.6). The total effects of concentration on loads were positive and moderate, while the effects of runoff on loads were positive and strong.

Watershed area was significantly correlated with runoff and solute loads across all sites (Table 4.3) but was not retained in any of the best fit path models. When correlations were conducted excluding large integrator and small surface sites, there were no relationships between area and hydrology or loads (Table 4.4), suggesting that any

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differences between these sites is not related to area. However, among these 5 sites, watershed area was strongly correlated with infrastructure metrics (Table 4.4).

Imperviousness was the most important land-cover variable; grass and soil cover did not covary strongly with solute concentrations or loads (Tables 4.3 and 4.6). Imperviousness was not retained as an independent variable in any of the best fit models, but there was a strong effect of the interaction term between imperviousness and precipitation. This was the strongest covariate with runoff across all models (Figs. 4.8 and 4.9).

Total infrastructure effects on loads were moderate (total effects ~ 0.3 to ~0.5; Table 4.6). Increased channel density was associated with decreased loads of Cl^-, NO_2^-, and NO_3^-, whereas for runoff, DOC, NH_4^+, SRP, and TDN, retention basins / channels was a stronger correlate. Channel density and retention basins / channels were the only infrastructure variables retained in the best-fit models (Table 4.4). The effects of infrastructure were almost exclusively via effects on hydrology, where reduced runoff associated with increased channel density and increased retention basins / channels led to reduced loads.

Precipitation was the only consistently significant storm characteristic in all models. Although it was not retained as an independent variable in most best-fit models, the interaction between imperviousness and precipitation was the strongest covariate with runoff, where increased precipitation increased runoff. Precipitation did have negative total effects on loads of TDN, NH_4^+, and DOC (Table 4.6), via negative effects on concentration, and direct negative effects on TDN loads (Table 4.4; Figs. 4.8 and 4.9).

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Solute concentrations were most strongly related to storm characteristics: rain-free days, flow-free days, season, and precipitation. Rain-free days had weak to moderate positive effects on concentrations of DOC, NH_4^+, NO_3^-, SRP, and TDN (Table 4.6). While rain-free days was important for most reactive solutes, flow-free days was a moderate covariate with Cl^- concentrations (Fig. 4.9). Season had weak effects on concentrations of Cl^-, DOC, NH_4^+, and NO_2^-, with higher concentrations during summer months than winter months. Precipitation was retained as an independent variable in models of DOC, NH_4^+, and TDN loads (Table 4.6), where it had weak negative effects on concentrations.

DISCUSSION

Changes in Infrastructure over Time and Space

We found evidence of clear spatial and temporal variation in stormwater infrastructure design. Overall, these patterns match those that have been described at the national scale (Ellis and Marsalek 1996, Burian et al. 2000, Chocat et al. 2001, Delleur 2003). Cities began using centralized infrastructure solutions for urban stormwater management in the mid-1800's (Burian et al. 2000). The original objective of centralized drainage infrastructure was to remove water as quickly and safely as possible from urban areas (Carter 1961, Ellis and Marsalek 1996, Chocat et al. 2001, Brabec et al. 2002, Delleur 2003). In the 1960s and 1970s, however, there was a shift in focus as engineers and planners recognized the environmental consequences of conveyance-oriented infrastructure (Wolman and Schick 1967, Dunne and Leopold 1978, Ellis and Marsalek 1996, Delleur 2003). This period also saw increased attention to issues of stormwater

quality, in addition to quantity (Delleur 2003). The timing of these changes align well with temporal patterns we documented in Scottsdale (Fig. 4.3), where the use of more retentive infrastructure such as engineered channels and retention basins began in the early 1970s. The introduction of sustainability concepts in 1980's to stormwater engineering has had an influence on stormwater infrastructure discussions in the literature (Delleur 2003, Echols 2008, Walsh et al. 2012). At present, stormwater infrastructure design is more focused on decentralized solutions such as retention and detention basins, swales, and rain barrels (Burian et al. 2000, Delleur 2003), and integrated management (Chocat et al. 2001). In Scottsdale, the use decentralized retention basins has strongly declined since the mid-1990s, but the use of un-engineered washes for stormwater drainage mirrors the national trend towards more sustainable solutions. Our study did not investigate the efficacy of these more recent stormwater management strategies, but un-engineered washes would continue the trend toward more absorptive substrates that can promote infiltration and prevent downstream losses, as in the engineered channels and retention basins.

That temporal pattern of infrastructure use translated into spatial patterns was a reflection of the high cost of retrofitting stormwater systems (Chocat et al. 2001). As a result, there is a spatial legacy of past design decisions. Persistence in urban form is common across urban systems (e.g., Redfearn 2009). The legacy of combined sewer systems in many older cities is a clear indication that stormwater infrastructure is no exception. The use of retention basins and channels in Phoenix, while effective, requires a good deal of space. In built up areas, there is rarely the space available to build a retention basin. Retrofits do occur on occasion, as illustrated by the development of the

Indian Bend Wash floodplain (Roach et al. 2008). More research is needed to understand when shifts in stormwater design paradigms lead to the retrofitting of the existing system or simply the use of new designs in future developments.

Although much urban watershed research has focused on increases in hydrological connectivity that accompany urbanization (McBride and Booth 2005, Elmore and Kaushal 2008, Kaushal and Belt 2012), there is some evidence that the patterns we found are not unique to Arizona. Although they only studied 3 watersheds, Meierdiercks et al. (2010) did find that stormwater infrastructure in Baltimore, MD was related to the time of development, where newer developments had a higher density of stormwater ponds. Comparisons across and within cities are needed to understand variation in how stormwater management paradigms shift and how those paradigms translate into infrastructure decisions on the ground. Transitions in stormwater infrastructure are not just based on technical decisions, but take place within a political, social, and economic context (Ellis and Marsalek 1996, Chocat et al. 2001, Dolowitz et al. 2012), and the policy goals of stormwater management may be broader than the range of approaches advocated by engineers (Ellis and Marsalek 1996). It has been noted that effective stormwater design must be done within the context of the local impacts on receiving waters (Pitt and Clark 2008). The complexity of stormwater management beyond the technical aspects highlights the importance of conclusions by Grimm et al. (2008) that cities need to be understood within their biophysical and social contexts.

Supply vs Transport Control of Solute Delivery

Loads from these watersheds were more strongly driven by variation in runoff than by variation in concentrations, though both effects were significant for all solutes. This may be partly due to the low variation in solute concentrations across sites (Table 4.2, Fig. 4.7). In contrast, Lewis and Grimm (2007) studied the controls on dissolved N delivery in stormwater across watersheds with different land uses and found that stormwater N loads in Phoenix were driven more by concentration than by discharge. However, they used total discharge volume (L) rather than runoff depth in their models. We reanalyzed their data and found that discharge explained more variance in dissolved loads of NO_3^-, NH_4^+, and TDN, but that concentration explained marginally more of the variance in DON load. Still, correlation coefficients between concentrations and loads for the Lewis and Grimm (2007) dataset were approximately double ($\rho = 0.42$ to 0.57) those from our study ($\rho = 0.18$ to 0.36). The likely reason for this difference is the wider variation in N sources, and thus concentrations, encompassed by the watersheds they studied (e.g., Table 4.2).

The choice of study locations and study design likely drives the relative importance of solute supply and solute transport in controlling solute loads. Across our study watersheds, land use and therefore solute supply and concentrations, did not vary widely, but there was very strong variation in infrastructure and runoff. The watersheds evaluated by Lewis and Grimm (2007) varied primarily by land use. This suggests that variation in land use may generate important differences in solute storage within watersheds that were not captured in our study due to our focus on a single residential type of land use. A comparison of our results with those of Lewis and Grimm (2007)

suggest that the supply of solutes may be primarily determined by land use, whereas the transport of solutes downstream is primarily determined by land cover and infrastructure design. More research is needed to understand potential interactions between land use and infrastructure design in controlling solute delivery from urban watersheds.

Effects of land cover on solute delivery

A major focus of the urban watershed literature is the role of imperviousness (Arnold and Gibbons 1996, Brabec et al. 2002, Schueler et al. 2009, Jacobson 2011). While imperviousness tends to be a good predictor of urban hydrology (Brabec et al. 2002, Jacobson 2011), previous research has found that imperviousness is a poor predictor of water quality (Brabec et al. 2002, Cadenasso et al. 2007, Schueler et al. 2009). In many studies, imperviousness is used as an indicator of the extent of urbanization, often without taking into account other factors that may be more directly related to solute supply such as land use (Brezonik and Stadelmann 2002, Lewis and Grimm 2007, Schueler et al. 2009) or factors that control solute delivery, such as storm characteristics (Brezonik and Stadelmann 2002, Lewis and Grimm 2007). Other studies have found that the configuration of land cover and the location of imperviousness is frequently a better predictor of water chemistry than land cover composition alone (Brabec et al. 2002, Cadenasso et al. 2007, Walsh and Kunapo 2009, Carey et al. 2013).

Our research supported the idea that impervious cover is an important land cover feature for understanding solute delivery, as imperviousness explained more variability in watershed runoff than grass or soil cover. Importantly, we found that imperviousness was an important predictor of solute loads, but not solute concentrations. This is consistent

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with the literature. The effects of imperviousness on urban hydrology are relatively consistent and strong in the literature (Schueler et al. 2009, Jacobson 2011), and imperviousness was a strong control on watershed runoff in our system. Via its effects on hydrology, imperviousness was an important predictor of solute loads, even though there was no relationship between imperviousness and water quality.

Effects of storm characteristics on solute concentrations and delivery
Precipitation

Storm characteristics were important drivers of solute loads via controls on both transport (runoff) and supply (concentrations). Precipitation increased solute loads via increases in runoff and had a negative effect on loads via dilution of solute concentrations. In addition to the dilution effects of precipitation, concentrations were most strongly controlled by antecedent dry days and season.

Runoff was most strongly controlled by the interaction between imperviousness and precipitation, such that the effects of precipitation were stronger where imperviousness was greater. These results are similar to those of Gallo et al. (2013) who found that runoff from urban watersheds in Tucson, AZ was most strongly predicted by the interaction between imperviousness and precipitation. In Baltimore, MD, Kaushal et al. (2008) found that the differences in solute loads between forested and urban watersheds was exacerbated during wet years, when more solutes were washed from urban surfaces, compared to dry years, when solute delivery was limited by transport.

<u>Season</u>

Solute concentrations were not correlated with any land cover or infrastructure variables (with the exception of the correlation of Cl$^-$ concentration with channel density), but they were correlated with storm characteristics. Concentrations of NO_2^-, NH_4^+, DOC, and Cl were higher during summer storms than during winter storms, but there was no seasonal effect on NO_3^-, SRP, or TDN. Lewis and Grimm (2007) also found that concentrations of NO_3^-, NH_4^+, DON, and TDN were higher during summer stormwater events in Phoenix than in winter. In a study of stormwater runoff from a Sonoran Desert watershed, Welter et al. (2005) found that rainfall intensity and the concentrations of both NO_3^- and NH_4^+ were higher during summer storms than during winter storms. Differences in both of rainfall intensity and concentration could contribute to seasonal differences in runoff concentrations. Because we do not have rainfall intensity data for all of our study sites, we were not able to evaluate the effects of rainfall intensity as a correlate of solute concentrations, but it is likely to be an important factor. Similarly, we collected rainfall chemistry for a limited number of storms. However, in a study of wet and dry deposition of a variety of solutes in the Phoenix metro area, Lohse et al. (2008) found that concentrations of DOC, NH_4^+, NO_3^-, and SRP (but not Cl$^-$) in rainfall were higher during summer storms than during winter storms. Thus, these seasonal patterns in precipitation chemistry are likely to account for much of difference in runoff chemistry.

<u>Antecedent Conditions</u>

The number of rain-free days before an event was the most common storm characteristic to appear as an explanatory variable in path models of solute

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concentrations, being retained in all models except that for NO_2^-. Direct effects of rain-free days on concentrations were moderate, ranging from 0.22 to 0.45. These findings are consistent with other arid urban stormwater studies. Gallo et al. (2013) found that the number of rain-free days preceding an event was positively related to concentrations of DOC, Cl^-, NH_4^+, DON, negatively related to NO_3^- and SRP, and unrelated to NO_2^- concentrations in Tucson, AZ stormwater. In Phoenix, AZ stormwater, Lewis and Grimm (2007) found that NH_4^+ concentrations increased with rain-free days, but that rain-free days had no significant effects on NO_3^-, DON, or TDN concentrations. Dry days are often important metrics of solute supply and predictors of concentrations in mesic urban systems (Brabec et al. 2002) and natural desert systems (Welter et al. 2005).

While rain-free days was an important correlate of DOC, NH_4^+, NO_3^-, TDN, and SRP concentrations, flow-free days was an important correlate of Cl^- concentrations. This suggests that storm events that do not generate runoff have no consequences for the supply of Cl^- in the watershed. That is, rainfall events that do not generate watershed discharge may redistribute Cl^- within the watershed, but they do not alter supply. In contrast, reactive solutes were more strongly controlled by rain-free days than flow-free days, indicating that storm events that do not generate flow are still affecting solute storage, possibly via biogeochemical mechanisms. The results suggest that biogeochemical losses are occurring between flow events, likely triggered by rainfall events that do not produce flow. This is in line with results from desert watershed studies that have found pulses of biogeochemical activity following wetting events (Austin et al. 2004, Belnap et al. 2005, Sponseller and Fisher 2008) and strong relationships between rain-free days and dissolved inorganic N concentrations in stormwater runoff (Welter et

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al. 2005). Although urban soils in Phoenix are highly managed and irrigated, Hall et al. (2009) found that N_2O fluxes from both lawns and xeriscaped yards responded to experimental wetting. Biogeochemical processes in desert soils are often C limited (Sponseller and Fisher 2008) in addition to being water limited (Austin et al. 2004, Belnap et al. 2005). In cities, however, high carbon stocks remove C limitation, so between-event solute reactions are likely to affect watershed nutrient storage. Hall et al. (2009) suggest that microbes in Phoenix lawns may be limited by N and P rather than by C. The absence of relationship between rain-free days and concentrations of conservative Cl^- further support these possibilities.

Effects of stormwater infrastructure on runoff and solute loads

Characteristics of the stormwater infrastructure system were correlated with loads of all solutes from our study watersheds. Retention basin density, channel density, and retention basins / channels were all strongly correlated with solute loads and runoff. Retention basins / channels were the strongest correlate with runoff and may be a useful index for retentive infrastructure as it includes both retention basins and pervious channels. Pipe density was not an important predictor or correlate for runoff or any loads (Table 4.3). With the exception of Cl^-, the effects of retention basins and channels on solute loads were via effects on runoff only and were not related to concentrations.

Some work to date has addressed the role of drainage density of storm sewers on urban hydrology, suggesting that increased pipe density exacerbates the hydrologic effects of imperviousness, increasing runoff volume and peak flows further (Paul and Meyer 2001, Shuster et al. 2005, Walsh et al. 2005, Ogden et al. 2011). One difficulty in

these studies is the frequent correlation between imperviousness and infrastructure density (Graf 1977, Walsh et al. 2012, Gallo et al. submitted). Although infrastructure density was significantly correlated with imperviousness in our study watersheds, the correlations between imperviousness and channel density were weak ($\rho < 0.3$), and the direction of their effects on hydrology were opposite, allowing us to separate their effects. While several researchers have investigated the effects of drainage density and best stormwater management practices (e.g., swales, stormwater ponds) on hydrology (Goff and Gentry 2006, Dietz and Clausen 2008, Meierdiercks et al. 2010, Ogden et al. 2011, Gallo et al. submitted) fewer have linked stormwater infrastructure design to solute delivery. Dietz and Clausen (2008) monitored a traditional and a low impact development (LID) over the construction period and found that LID measures (swales and infiltration basins) completely mitigated the effects of increasing imperviousness on runoff and loads of N and P over annual time scales, but they did not evaluate whether differences in loads were due to changes in concentration or runoff alone. In Tucson, AZ, Gallo et al. (submitted) found that pervious channel density was negatively correlated with runoff ratio and with concentrations of Cl^-, NO_2^-, and NH_4^+, but was unrelated to concentrations of TDN, NO_3^-, and SRP.

We have a better understanding of the functioning of stormwater infrastructure features individually than at the watershed scale. Zhu et al. (2004) and Larson and Grimm (2012) assessed the potential of retention basin soils in Phoenix to remove N via denitrification. These soils have some of the highest rates of potential denitrification recorded in the literature (Zhu et al. 2004). However, our research shows that retention basins do not have an appreciable effect on stormwater N concentrations at the watershed

scale. Gallo et al. (in press) evaluated solute retention in grassy, gravel, and concrete channels in Tucson, AZ, and found that gravel and concrete channels function as flow-through systems, with no sources or retention of solutes. Grassy channels had more variable sourcing and retention. Overall, results from the literature suggest that more retentive infrastructure such as retention basins and channels have the capacity to remove solutes via biogeochemical mechanisms. However, our results at the watershed scale suggest that infrastructure design does not have an appreciable effect on solute concentrations on event time scales. More research is needed to understand the effects of infrastructure design on biogeochemical transformations at annual time scales as it is likely that between-event processing may differ across watersheds.

Effects of land cover, infrastructure, and storm characteristics on solute loads and concentrations – Implications

We propose a conceptual model of urban stormwater solute delivery that describes the effects of land cover, land use, infrastructure, and storm characteristics based on our research and the literature (Fig. 4.14). In our model, solute delivery is controlled by both the supply of solutes in the watershed and the transport of those solutes from the watershed. The balance of supply- vs. transport-limitation will vary across watersheds and from event to event. Transport is determined by the combination of three factors: 1) the land cover of the watershed that controls surface water balances and therefore runoff generation; 2) event precipitation determines the availability of the transport vector – water; and 3) stormwater infrastructure controls the conveyance of runoff through the watershed. Watershed solute supply, on the other hand, is controlled

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by two main factors: 1) the land use determines the rate at which solutes enter the watershed, and 2) the time over which solute inputs occur. One of the benefits of this model is that it separates out the effects of land cover from land use that have been confounded in some earlier work. Land use is a description of kinds and intensities of human activities that take place on the land, and therefore will be strongly related to the rate at which solutes enter the watershed. Land cover, on the other hand, determines the physical properties of the land surface and therefore has more direct control on surface water balances, runoff generation, and any potential upland retention. This model hypothesizes these relationships within the particular geomorphic context of this arid urban environment. Future work will be needed to see if it can be applied across urban areas. Regional context is critical in evaluating and making recommendations for infrastructure design (Booth and Jackson 1997, Grimm et al. 2008, Pitt and Clark 2008), and it is likely that new patterns will emerge in other climates and in cities with variable stormwater management systems.

CONCLUSIONS

Our research highlights the importance of including dynamic stormwater infrastructure in assessments of the effects of urbanization on hydrology and solute loads. We documented major variation in urban stormwater infrastructure design and found that that variation led to variation in urban stormwater runoff and solute delivery. Urbanization is a dynamic social, economic, and political process, and we have shown that as a result the environmental effects of urbanization are dynamic as well. Our

research has shown that drainage infrastructure, in combination with land cover and climate, is critical to understanding patterns of solute delivery from urban watersheds.

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Table 4.1. Site characteristics of study watersheds.

Site Abbreviation	Watershed Name	Drainage Area (ha)	Predominant Infrastructure	% Impervious Surface Cover	% Grass Cover	% Soil Cover	Retention Basin Density (m^2/ha)	Pipe Density (m/ha)	Channel Density (m/ha)	Total Drainage Density (m/ha)
ENC	Encantada	6.08	Surface	48.35	46.48	4.30	0.00	6.00	0.00	6.00
PIE	Pierce	10.23	Surface	56.69	38.18	4.68	0.00	0.00	0.00	0.00
MR	Martin Residence	18.44	Wash	41.61	44.71	12.50	0.00	1.00	21.18	22.18
BV	Bella Vista	56.53	Wash	68.91	18.05	12.70	558.78	16.00	33.33	49.33
KP	Kiwanis Park	106.42	Pipes	*50.00*	*3.00*	*46.00*	0.00	24.00	0.00	24.00
SW	Sweetwater	117.64	etention Basin	48.61	39.20	11.55	531.05	15.00	9.20	24.20
MS	Montessori	140.55	etention Basin	48.80	38.81	11.77	454.75	14.00	41.12	55.12
LA	Lake Angel	1662.40	Integrator	57.15	33.43	8.98	169.51	12.00	24.72	36.72
SGC	Silverado Golf Course	15454.54	Integrator	46.19	42.17	10.47	45.81	4.00	5.33	9.33
IBW	Indian Bend Wash	20247.14	Integrator	48.65	39.31	10.57	48.08	7.00	4.38	11.38

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Table 4.2. Means, standard deviations, and ranges of observed event mean concentrations and loads from our study watersheds and those observed for other watersheds in Phoenix by Lewis and Grimm 2007.

| | This Study | | | | Lewis and Grimm 2007 | | | |
	Min	Max	Mean	SD	Min	Max	Mean	SD
-----Event Mean Concentrations (mg/L)-----								
Cl$^-$	1.60	463.88	23.79	56.94	-	-	-	-
DOC	0.87	143.95	19.64	23.07	-	-	-	-
NH$_4^+$	0.02	20.75	0.99	2.24	0.03	64.00	1.78	4.11
NO$_2^-$	<0.01	2.86	0.13	0.32	-	-	-	-
NO$_3^-$	0.03	23.58	1.16	2.37	0.03	8.60	1.19	0.98
TDN	0.10	71.88	3.53	7.19	0.70	120.96	5.41	7.64
PO$_4^{3-}$	0.01	2.15	0.19	0.23	-	-	-	-
-----Loads (kg/ha)-----								
Cl$^-$	<0.01	6.49	0.41	0.85	-	-	-	-
DOC	<0.01	2.36	0.38	0.50	-	-	-	-
NH$_4^+$	<0.01	0.76	0.02	0.07	0.00	2.77	0.06	0.18
NO$_2^-$	<0.01	0.02	0.00	0.00	-	-	-	-
NO$_3^-$	<0.01	0.21	0.02	0.04	0.00	0.66	0.04	0.06
TDN	<0.01	1.00	0.07	0.13	0.00	2.87	0.19	0.32
PO$_4^{3-}$	<0.01	0.06	0.00	0.01	-	-	-	-

Table 4.3. Pearson correlation matrix of variables considered in path analysis. Only significant (p < 0.05) correlations are shown.

	Land Cover				Infrastructure						Storm Characteristics				Hydrology		Event Mean Concentrations							Loads						
	Area	% Impervious	% Grass	% Soil	Retention Basin Density (m2/ha)	Pipe Density (m/ha)	Channel Density (m/ha)	Total Drainage Density (m/ha)	Retention Basin / Channel (m2/m)	Retention Basin / Total Drainage (m2/m)	Season	Rain-free Days	Flow-free Days	Precipitation	Runoff Coefficient	Runoff	Cl EMC (mg/L)	DOC EMC (mg/L)	NH4 EMC (mg/L)	NO2 EMC (mg/L)	NO3 EMC (mg/L)	TDN EMC (mg/L)	SRP EMC (mg/L)	Cl Load (kg/ha)	DOC Load (kg/ha)	NH4 Load (kg/ha)	NO2 Load (kg/ha)	NO3 Load (kg/ha)	TDN Load (kg/ha)	SRP Load (kg/ha)
% Impervious	-																													
% Grass	-	-0.56																												
% Soil	-	-	-0.78																											
Retention Basin Density (m2/ha)	-	0.48	-0.33	0.68																										
Pipe Density (m/ha)	0.22	0.31	-0.76	0.68	0.62																									
Channel Density (m/ha)	-	0.25	-0.19	-	0.69	0.37																								
Total Drainage Density (m/ha)	-	0.32	-0.45	0.30	0.78	0.68	0.93																							
Retention Basin / Channel (m2/m)	0.23	-	-	-	0.74	0.44	0.19	0.32																						
Retention Basin / Total Drainage (m2/m)	0.26	0.25	-	-	0.88	0.53	0.40	0.52	0.96																					
Season	-	-	-	-	-	-	-	-	-	-																				
Rain-free Days	-0.32	-	-	-	-	-	-	-	-	-	-0.22																			
Flow-free Days	0.19	-	-	-	-	-	-	-	-	-	-	0.25																		
Precipitation	-	-	-	-	-	-	-	0.19	-	-	-0.31	0.29	-																	
Runoff Coefficient	-0.64	0.25	-0.19	-	-0.29	-0.30	-0.23	-0.25	-0.47	-0.47	-	0.21	-	0.24																
Runoff	-0.38	0.21	-0.25	-	-0.25	-0.23	-	-0.41	-0.41	-0.41	-	-	0.35	0.30	0.78															
Cl EMC (mg/L)	0.24	-0.20	0.26	-	-0.39	-0.28	-0.40	-0.42	-	-0.25	0.20	-	-	-0.40	-	-														
DOC EMC (mg/L)	-0.26	-	-	-	-0.19	-0.26	-	-	-	-	0.34	0.47	-	-	-	-0.23	0.41													
NH4 EMC (mg/L)	-0.25	-	-	-	-	-	-	-	-	-	0.26	0.26	-	-	-	-0.19	0.20	0.52												
NO2 EMC (mg/L)	-0.24	-	-	-	-	-	-	-	-	-	0.34	0.26	-	-	-	-0.23	-	0.58	0.51											
NO3 EMC (mg/L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.28	0.42	0.76	0.41										
TDN EMC (mg/L)	-0.24	-	-	-	-0.24	-0.21	-	-	-	-	0.19	0.44	-	-	-	-0.22	0.37	0.77	0.68	0.52	0.51									
SRP EMC (mg/L)	-	-	-	-	-	-	-	-	-	-0.20	-	0.33	-	-	-	-	-	0.44	0.41	0.30	-	0.39								
Cl Load (kg/ha)	-0.40	-	-	-	-0.40	-0.39	-0.39	-0.38	-0.34	-0.40	-	-	-	-	0.44	0.53	0.69	-	-	-	-	-	-							
DOC Load (kg/ha)	-0.32	-	-	-	-0.23	-	-0.22	-0.18	-0.31	-0.33	-	-	-	-	0.55	0.61	0.41	0.26	-	-	-	-	-	0.50						
NH4 Load (kg/ha)	-0.51	-	-	-	-0.20	-	-0.34	-0.34	-0.34	-0.34	-	-	-	0.19	0.64	0.61	-	0.20	0.58	-	0.37	0.24	0.23	0.60	0.47					
NO2 Load (kg/ha)	-0.50	0.27	-	-	-	-	-	-0.32	-0.33	-0.28	-	-	-0.23	0.34	0.68	0.53	-	0.25	0.26	0.62	-	0.21	-	0.26	0.44	0.61				
NO3 Load (kg/ha)	-0.39	0.19	-	-	-0.19	-	-	-0.33	-0.33	-0.33	-	-	-	0.22	0.60	0.65	-	-	0.38	-	0.49	-	-	0.61	0.44	0.88	0.51			
TDN Load (kg/ha)	-0.55	0.23	-	-	-0.27	-	-0.23	-	-0.45	-0.45	-	-	-	0.21	0.84	0.88	-	-	-	-	-	-	-	0.62	0.95	0.76	0.66	0.68		
SRP Load (kg/ha)	-0.30	-	-	-	-0.27	-	-0.21	-0.19	-0.35	-0.36	-	-	-	-	0.58	0.64	0.36	-	-	-	-	-	0.24	0.87	0.52	0.74	0.38	0.72	0.73	

Table 4.4. Pearson correlation matrix of variables, excluding surface-drained and integrator sites. Only significant ($p < 0.05$) correlations are shown.

	Land Cover				Infrastructure					Storm Characteristics				Hydrology		Event Mean Concentrations							Loads						
	Area	% Impervious	% Grass	% Soil	Retention Basin Density (m2 / ha)	Pipe Density (m / ha)	Channel Density (m / ha)	Retention Basin / Channel (m2 / m)	Retention Basin / Total Drainage (m2 / m)	Season	Rain-free Days	Flow-free Days	Precipitation	Runoff Coefficient	Runoff	Cl EMC (mg / L)	DOC EMC (mg / L)	NH4 EMC (mg / L)	NO2 EMC (mg / L)	NO3 EMC (mg / L)	TDN EMC (mg / L)	SRP EMC (mg / L)	Cl Load (kg / ha)	DOC Load (kg / ha)	NH4 Load (kg / ha)	NO2 Load (kg / ha)	NO3 Load (kg / ha)	TDN Load (kg / ha)	SRP Load (kg / ha)
% Impervious	0.30																												
% Grass	-0.41	-0.62																											
% Soil	0.28	-	-0.77																										
Retention Basin Density (m2 / ha)	0.59	0.69	-	-0.43																									
Pipe Density (m / ha)	0.84	0.55	-0.83	0.61	0.44																								
Channel Density (m / ha)	-	0.36	-	-0.60	0.49	-																							
Retention Basin / Channel (m2 / m)	0.51	-	-	-0.31	0.70	0.30	-																						
Retention Basin / Total Drainage (m2 / m)	0.57	0.41	-	-0.38	0.87	0.38	-	0.96																					
Season	-	-	-	-	-	-	-	-	-																				
Rain-free Days	-	-	-	-	-	-	-	-	-	-																			
Flow-free Days	-	-	-	-	-	-	-	-	-	-	0.59																		
Precipitation	0.29	-	-	-	-	0.28	-	-	-	-0.32	-	-																	
Runoff Coefficient	-	0.32	-0.65	0.56	-0.30	0.33	-	-0.50	-0.46	-	-	-	0.54																
Runoff	-	-	-0.63	0.57	-	0.35	-	-0.48	-0.42	-	-	-	0.54	0.89															
Cl EMC (mg / L)	-	-0.30	-	-	-0.35	-	-0.30	-	-	-	0.30	-	-0.28	-	-														
DOC EMC (mg / L)	-	-	-	-	-	-	-	-	-	0.55	0.45	-	-0.52	-	-	0.56													
NH4 EMC (mg / L)	-	-	-	-	-	-	-	-	-	0.38	-	-	-	-0.31	-0.31	-	0.34												
NO2 EMC (mg / L)	-	-	-	-	-	-	-	-	-	0.46	-	-	-0.28	-	-0.31	-	0.46	0.51											
NO3 EMC (mg / L)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.93	0.97	0.41										
TDN EMC (mg / L)	-	-	-	-	-	-	-	-	-	0.62	0.36	-	-0.60	-	-	0.58	0.93	0.37	0.44	0.30									
SRP EMC (mg / L)	-	-	-	-	-	-	-	-	-	-	0.51	-	-	-	-	0.58	0.71	0.32	0.34	-	0.67								
Cl Load (kg / ha)	-	-	-	0.30	-0.35	-	-	-0.34	-0.37	0.29	-	-	-	0.51	0.46	0.77													
DOC Load (kg / ha)	-	-	-0.34	0.34	-	-	-	-0.35	-0.33	-	-	-	0.34	0.73	0.74	-	-	-	-	-	-	-	0.45						
NH4 Load (kg / ha)	-	-	-0.41	0.38	-	-	-	-0.33	-0.29	-	-	-	-	0.43	0.51	-	-	0.59	-	0.63	-	-	0.59	0.39					
NO2 Load (kg / ha)	-	0.33	-0.43	-	-	-	-0.31	-	-	-	-	-	-	0.55	0.60	-	-	-	0.46	-	-	-	-	0.41	0.41				
NO3 Load (kg / ha)	-	-	-0.39	0.35	-	-	-	-0.34	-0.29	-	-	-	0.29	0.44	0.54	-	-	0.53	-	0.61	-	-	0.61	0.41	0.99	0.39			
TDN Load (kg / ha)	-	0.31	-0.58	0.48	-	-	-	-0.55	-0.49	-	-	-	0.32	0.93	0.92	-	-	-	-	-	-	-	0.53	0.99	0.56	-	0.58		
SRP Load (kg / ha)	-	-	-	-	-	-	-	-0.34	-0.32	-	-	-	-	0.50	0.48	0.64	-	-	-	-	-	-	0.94	0.44	0.67	-	0.68	0.55	

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Table 4.5. Goodness of fit metrics for path models

Model Analyte	Chi-Square[1]			RMSEA (90% CI)[2]	PCLOSE[3]	NFI[4]	TLI[5]	Parameters Estimated	Observations
	X^2	df	P						
Runoff	1.832	1	0.176	0.084 (0.00-0.275)	0.238	0.976	0.928	8	120
Cl	29.515	19	0.058	0.073 (0.00-0.122)	0.214	0.945	0.960	25	104
DOC	28.494	20	0.098	0.063 (0.00-0.112)	0.312	0.953	0.973	24	107
NH_4	27.940	20	0.111	0.060 (0.00-0.109)	0.345	0.947	0.971	24	111
NO_2	16.844	9	0.051	0.092 (0.00-0.159)	0.142	0.951	0.943	18	104
NO_3	15.669	10	0.110	0.072 (0.00-0.137)	0.265	0.959	0.967	17	111
SRP	6.683	10	0.755	0.000 (0.00-0.076)	0.874	0.979	1.023	17	104
TDN	21.492	12	0.090	0.071 (0.00-0.128)	0.255	0.958	0.969	21	107

[1]Chi-square tests the null hypothesis that the data and the model are the same. P>0.05 indicates that the model is a reasonable fit for data.

[2]RMSEA <0.01 is excellent fit, <0.05 is good fit, <0.08 is mediocre fit.

[3]PCLOSE is the probability that RMSEA is equal to 0.05, P>0.05 indicates that model is a good fit to data

[4]NFI (Normed Fit Index): <0.90 poor fit, 0.90-0.95 marginal fit, >0.95 good fit

[5]TLI (Tucker Lewis Index): <0.90 poor fit, 0.90-0.95 marginal fit, >0.95 good fit

Table 4.6. Standardized total effects in all path models. Effects should be interpreted as the change in the endogenous variable (load) given an increase in of one standard deviation in the exogenous (driving) variable. Total effects are the net effect of the exogenous variable through all paths.

| Analyte	Direct Drivers		Infrastructure		Storm Characteristics				Watershed X Storm Interactions	
	EMC	Runoff	Channel Density (m / ha)	Ret Basin / Channel (m² / m)	Season	Rain-free Days	Flow-free Days	Precip Depth	Imperviousness X Precip	Channel Density X Flow-free Days
Runoff	-	-	-	-0.479	-	-	-	-	0.535	-
Cl	0.483	0.791	-0.261	-	0.109	-	0.249	-	0.403	-0.231
DOC	0.430	0.965	-	-0.461	0.133	0.193	-	-0.179	0.512	-
NH₄	0.438	0.910	-	-0.443	0.113	0.129	-	-0.122	0.467	-
NO₂	0.565	0.843	-0.259	-	0.256	-	-	-	0.278	-
NO₃	0.287	0.935	-0.300	-	-	0.061	-	-	0.475	-
SRP	0.248	0.933	-	-0.448	-	0.056	-	-	0.460	-
TDN	0.360	0.956	-	-0.457	-	0.135	-	-0.132	0.507	-
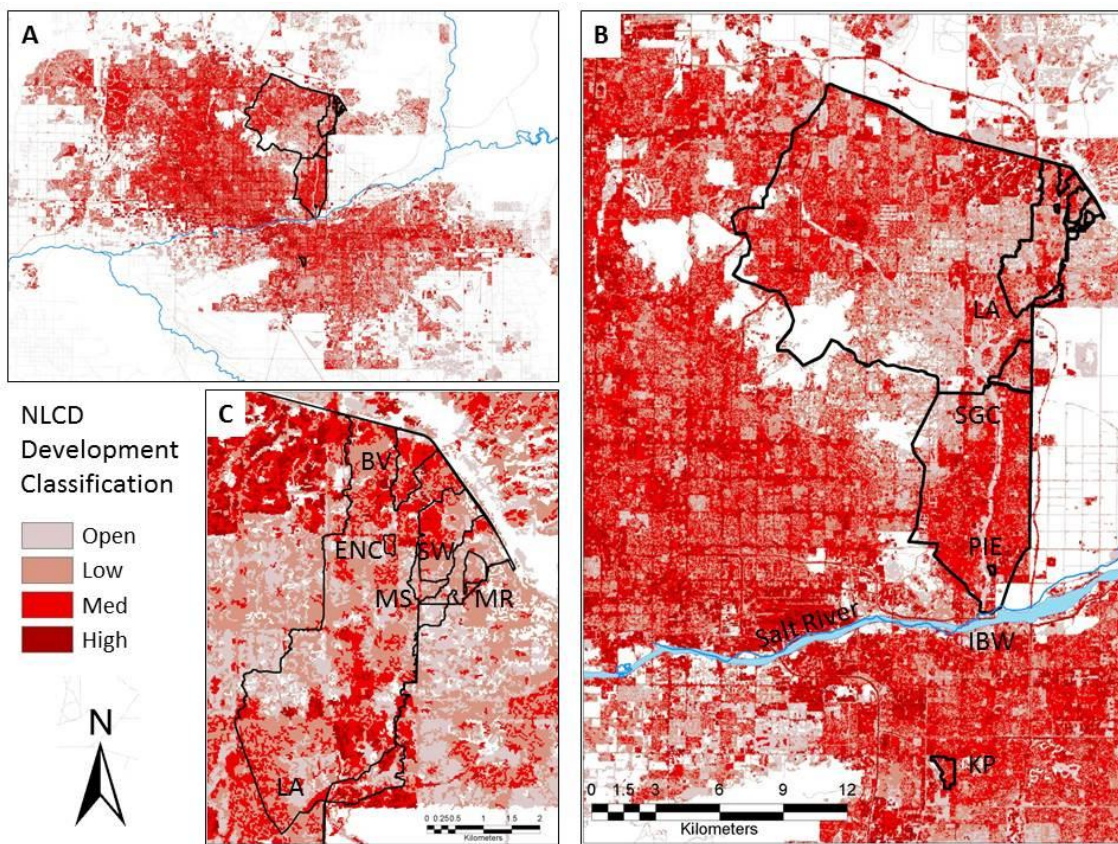
Figure 4.1. Location of study watersheds. A) Location of watersheds within the Phoenix metropolitan region; B) Location of watersheds within Indian Bend Wash Watershed; C) Location of small watersheds within Lake Angel watershed. Background indicates the intensity of development based on 2001 National Land Cover Database classification.
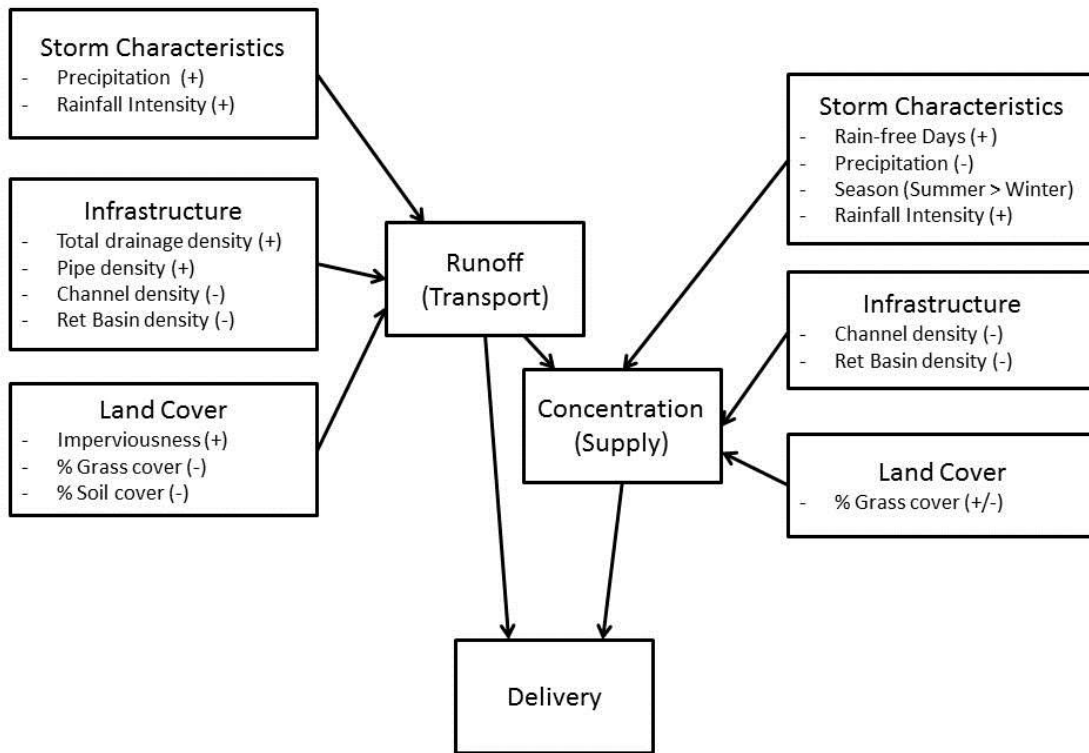
Figure 4.2. Hypothesized relationships between storm characteristics, infrastructure, and land cover on solute delivery, as mediated by control on runoff and solute concentrations.
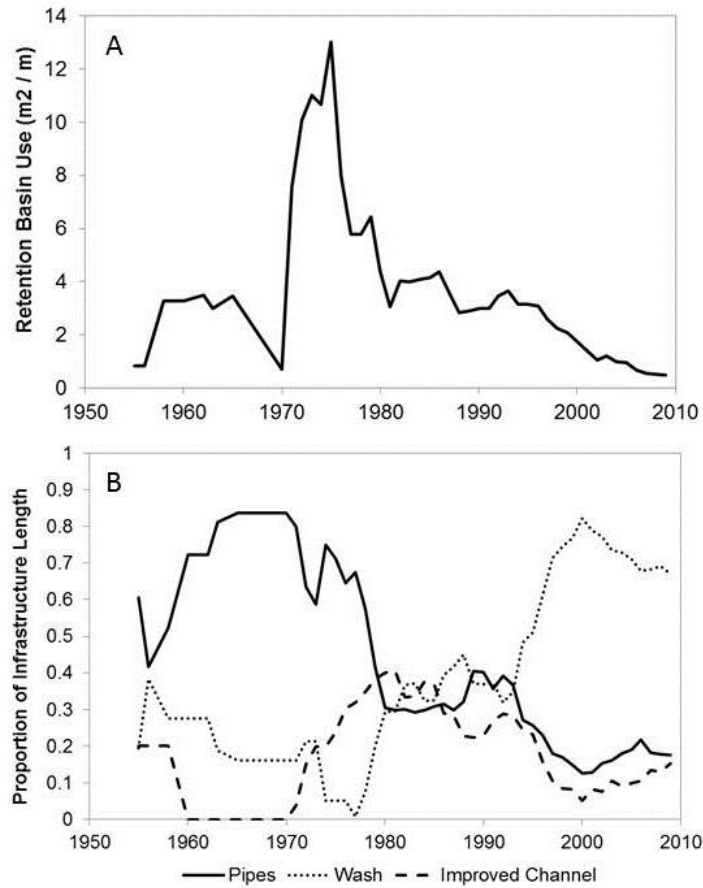
Figure 4.3. Temporal changes in stormwater infrastructure design for the City of Scottsdale, AZ. A) area of new retention basins per total new infrastructure length from 1955 to 2010, B) length of newly constructed pipes, washes, and improved channels as a proportion of total new infrastructure length.
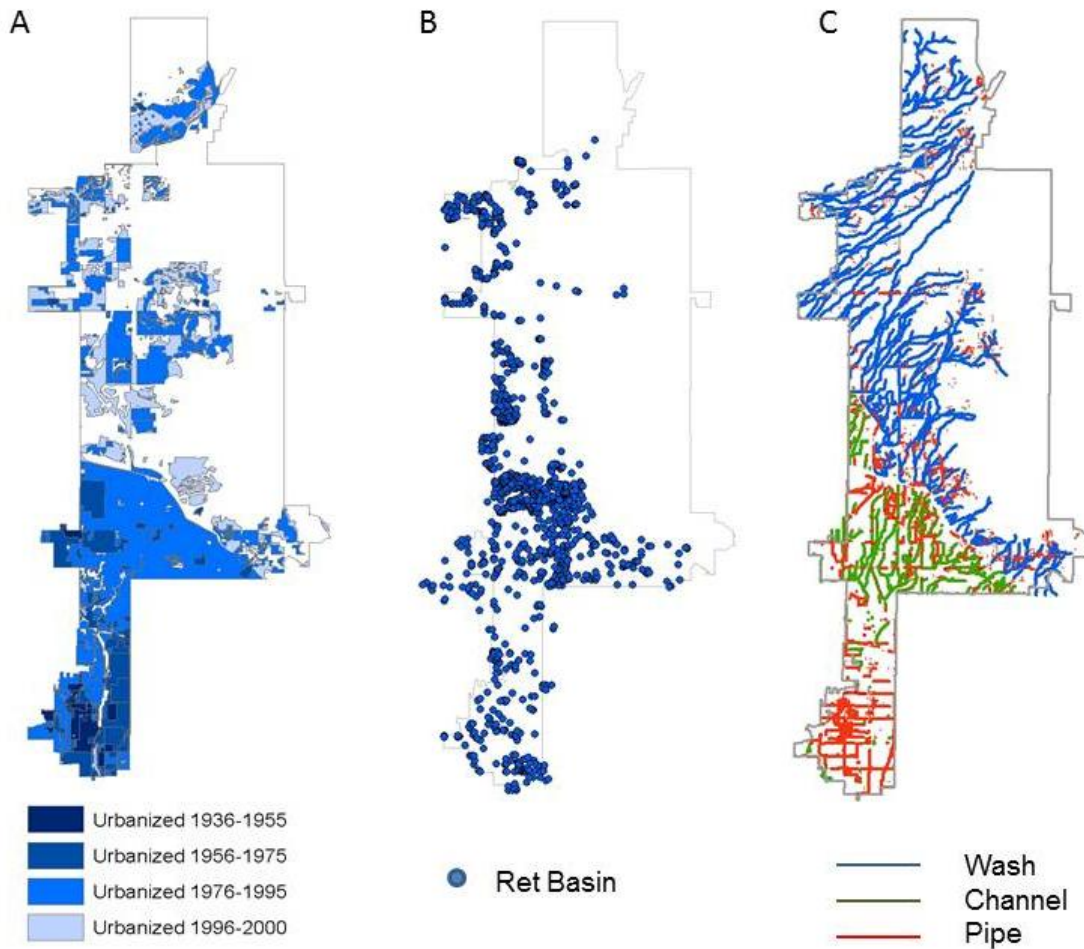
Figure 4.4. Date of urbanization and stormwater infrastructure design for the city of Scottsdale. A) Date of urbanization (data from CAP LTER, www.caplter.asu.edu); B) Retention basin density; C) Location of linear drainage features (data from City of Scottsdale).
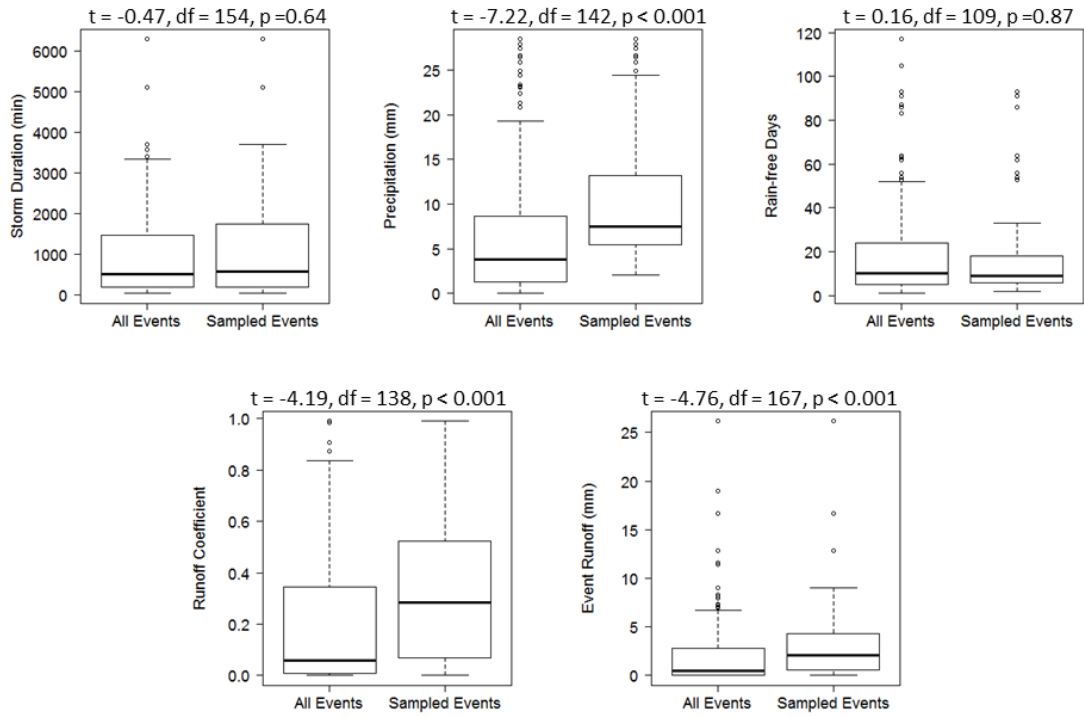
Figure 4.5. Comparison of storm characteristics for sampled events and all observed events.
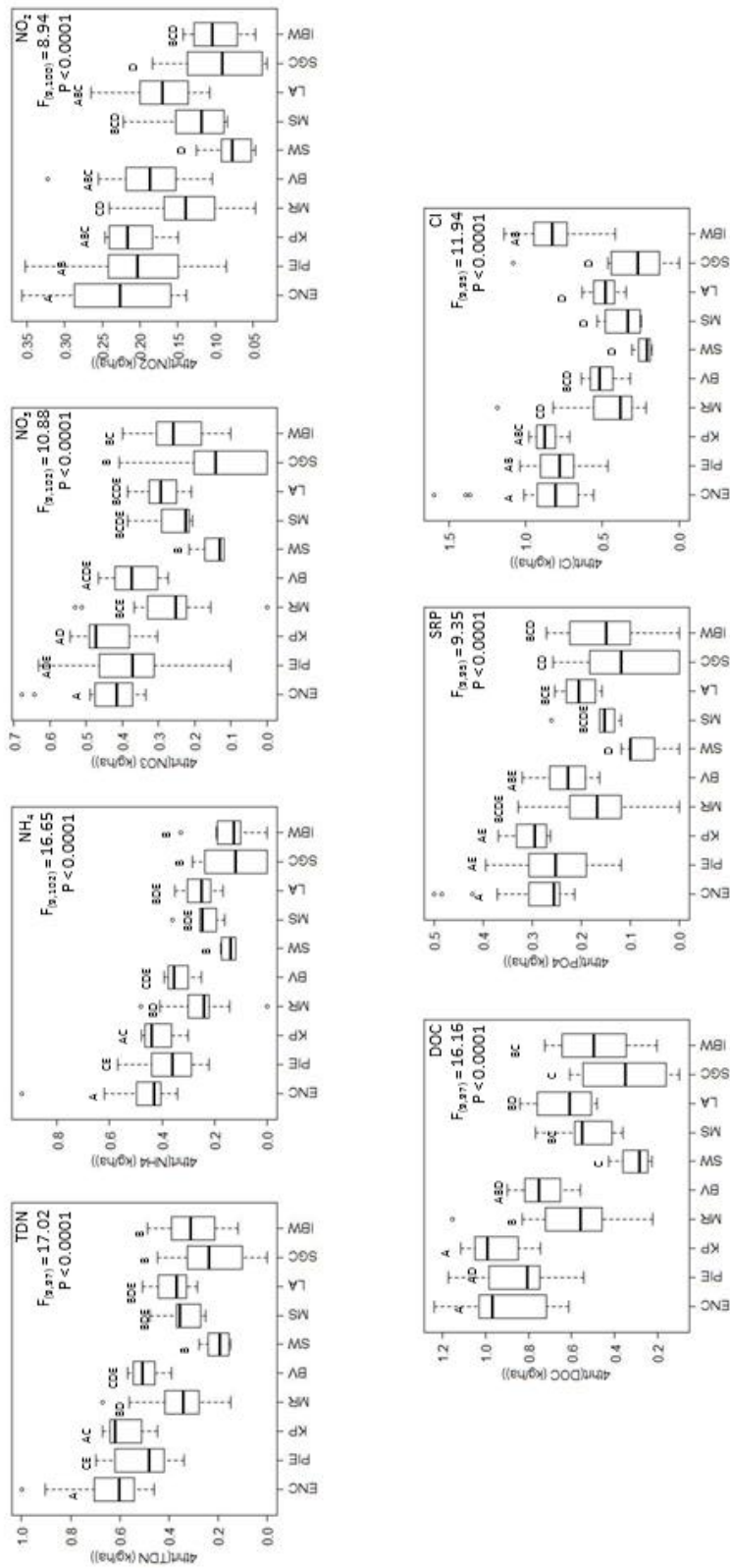
Figure 4.6. Mean event solute loads from each watershed across all events. Boxes with different letters indicate significant difference at alpha = 0.05, using Tukey's HSD.
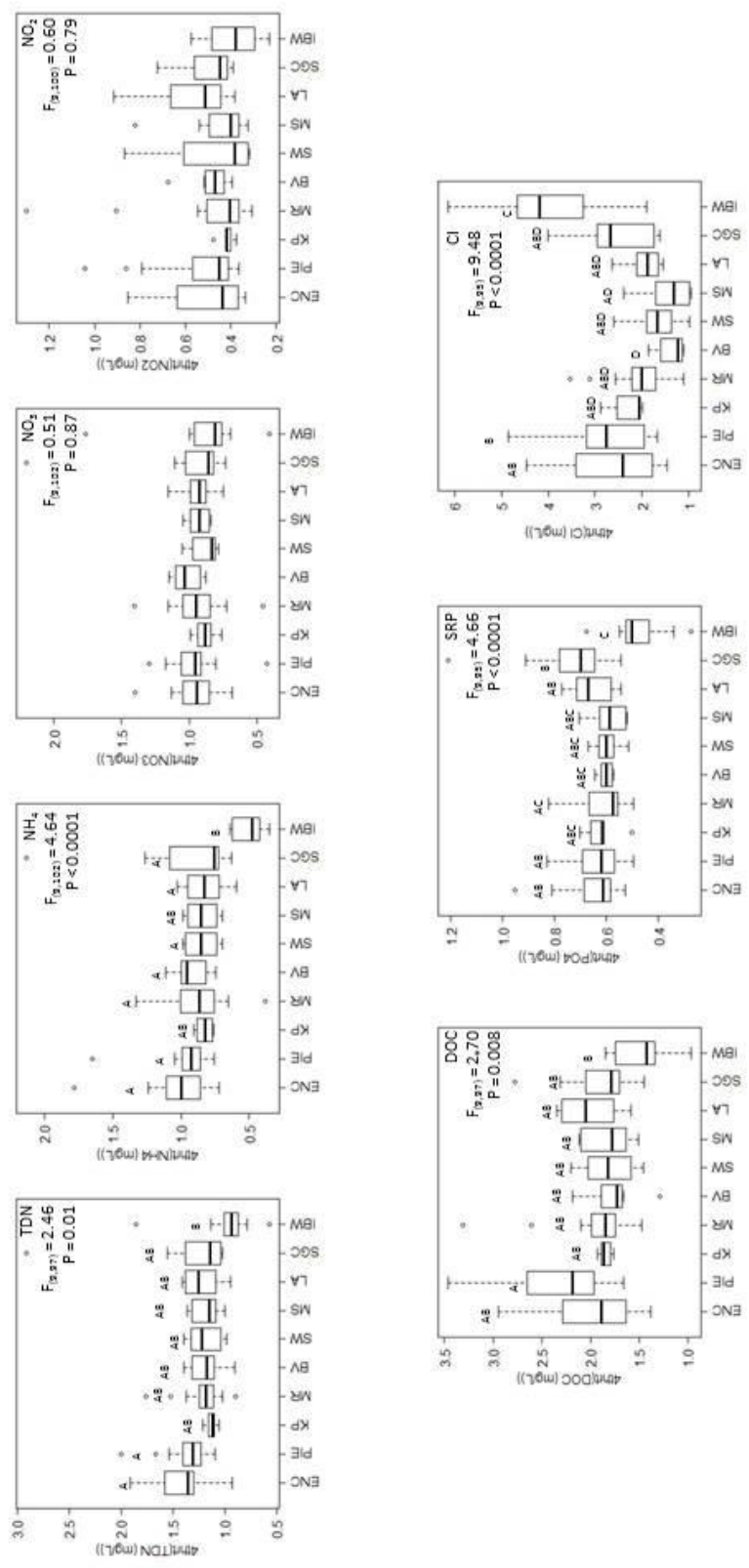
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Figure 4.7. Mean event mean concentrations from each watershed across all events. Boxes with different letters indicate significant difference at alpha = 0.05, using Tukey's HSD.
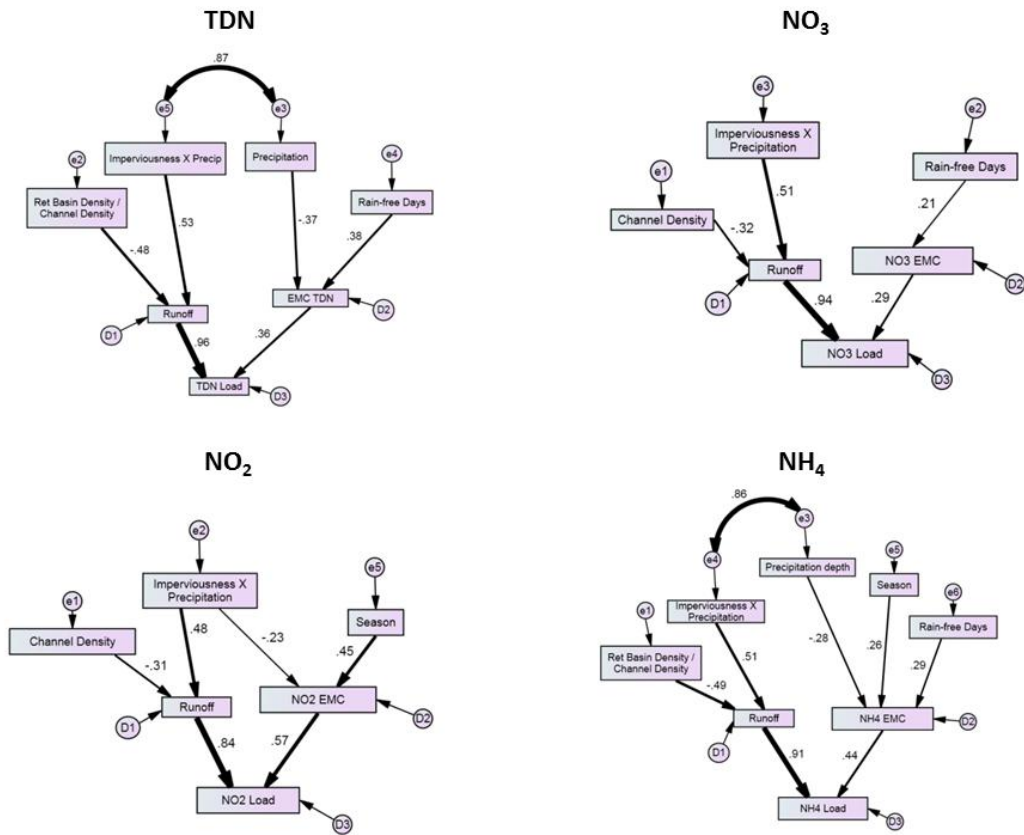
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Figure 4.8. Best fit path models for dissolved N loads.
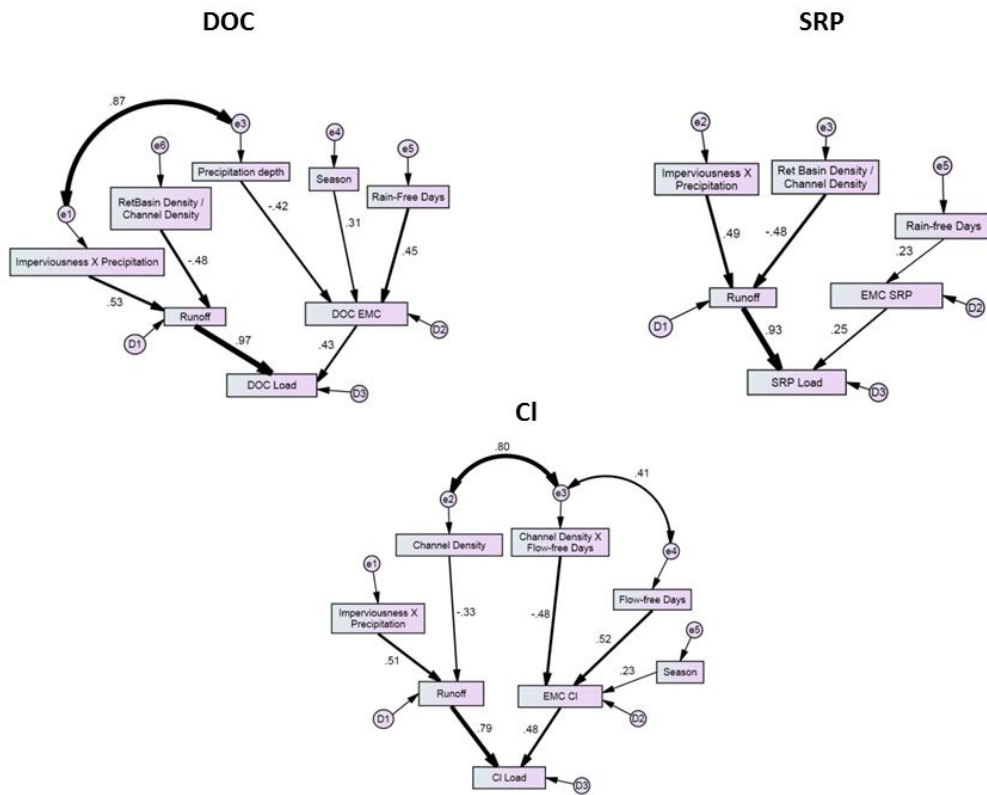
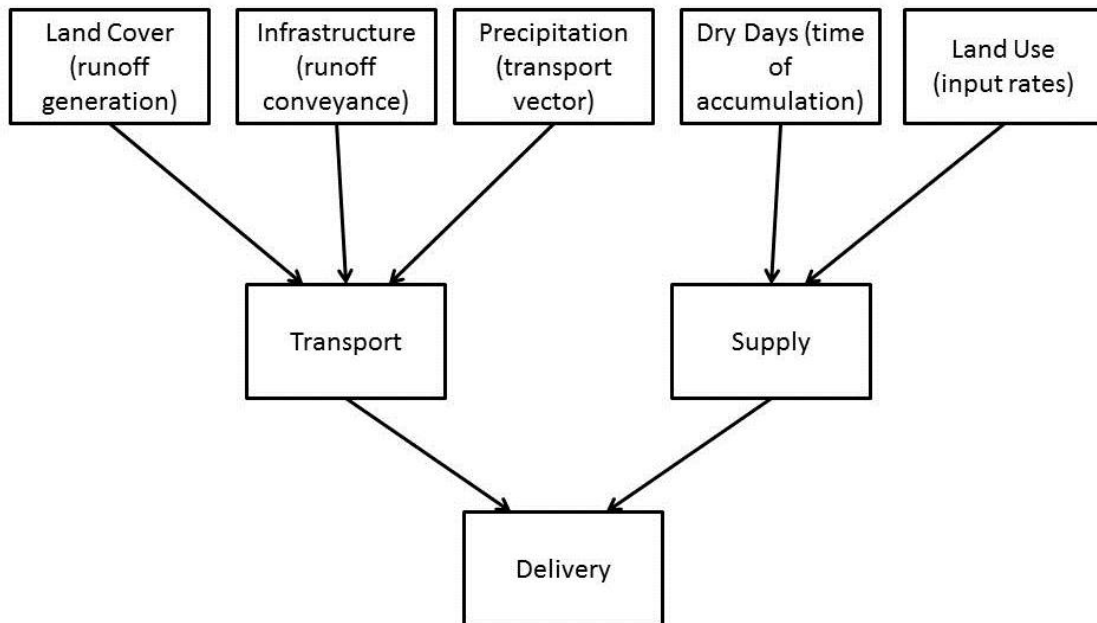Figure 4.9. Best fit path models for DOC, PO_4^{3-}, and Cl^- loads.

Figure 4.10. Conceptual model of the drivers of solute delivery in urban watersheds.

Chapter 5

SOURCES AND TRANSPORT OF NITROGENIN ARID URBAN WATERSHEDS

ABSTRACT

Urban watersheds are sources of nitrogen (N) to downstream systems, contributing to poor water quality. However, these watersheds also retain the majority of annual N inputs. Where and when N is retained in urban watersheds is unknown. Previous research has suggested that yards and stormwater retention features may be important sites of N retention, yet it is not clear how the functioning of these systems affects N retention and transport at the watershed scale or whether variation in watershed features (i.e., lawn cover, stormwater retention basins) leads to predictable differences in N retention. In Phoenix, AZ storm watersheds, event N loads are attributed to differences in stormwater infrastructure. In this study, we asked: Q1. Is N retention in urban watersheds controlled by hydrologic transport or biogeochemical retention mechanisms? Q2: Do the sources, isotopic chemistry, and speciation of N vary systematically between watersheds? And if so, what watershed features (e.g., land cover and stormwater infrastructure design) are important in determining source characteristics? We used triple isotopes of NO_3^- ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) to test hypotheses about sources and transformations of NO_3^- during three storm events from 10 urban watersheds that varied in stormwater infrastructure type and drainage area. We also sampled watershed soils, impervious surfaces, and rainfall to assess the chemistry and isotopic composition of potential sources to runoff.

The isotopic chemistry of NO_3^- differed significantly among sources including rain and different land covers (e.g., soil, impervious surfaces). Urban yards – mesic and xeric – are major sources of N to stormwater but are also sinks of N overall within urban watersheds. Patterns of N loads across many events suggest that hydrology is the dominant control on N delivery from urban watersheds. However, our results demonstrate that urban watersheds are not just passive conduits for N; rather, isotopic evidence suggests that all urban watersheds retain the majority of NO_3^- that enters watersheds as atmospheric deposition. It seems likely that most of this retention occurs in residential yards, rather than in stormwater infrastructure features, given the large area of yards and the high rates of biogeochemical processing within them. These findings contrast with earlier work that suggested that stormwater features may be hotspots of biogeochemical transformations at the watershed scale. Stormwater infrastructure features may indeed be hotspots of N removal, but our research suggests that the mechanisms are hydrologic rather than biogeochemical.

INTRODUCTION

Urban watersheds are sources of nitrogen (N) and other nutrients and pollutants to downstream systems, often contributing to problems of eutrophication and poor water quality (Paul and Meyer 2001, Groffman et al. 2004, Walsh et al. 2005, Kaushal et al. 2011). Both increased inputs of N that accompany urbanization and altered hydrology, which can affect N transport, contribute to N pollution from urban watersheds (Paul and Meyer 2001, Walsh et al. 2005). Inputs of N to urban systems include fertilizers, elevated atmospheric deposition, pet waste, and leaking septic and sewer systems (Paul and Meyer

2001, Baker et al. 2001, Groffman et al. 2004, Walsh et al. 2005). Hydrologic changes alter the transport of N from urban watersheds and include changes to urban land surfaces such as increased imperviousness (Arnold and Gibbons 1996, Brabec et al. 2002, Jacobson 2011) as well as changes to the hydrologic network (Hatt et al. 2004, Walsh et al. 2005, Meierdiercks et al. 2010).

Although urban watersheds do contribute N and other pollutants to downstream systems, researchers have found that they retain the majority of inputs (Baker et al. 2001, Groffman et al. 2004, Wollheim et al. 2005, Kaushal et al. 2008). As a result, there has been an effort to identify hotspots (McClain et al. 2003) of N removal in urban watersheds; i.e., places that have a disproportionate effect on N removal relative to their area. Terrestrial ecologists have largely focused on the role of residential landscapes – yards – as potential hotspots (Raciti et al. 2008, 2011, Hall et al. 2009), whereas aquatic ecologists have focused on the potential of aquatic features – streams and stormwater infrastructure features – to remove N (Groffman and Crawford 2003, Zhu et al. 2004, Grimm et al. 2005, Roach and Grimm 2011, Larson and Grimm 2012, Bettez and Groffman 2012). N may be retained in watersheds via denitrification, the conversion of nitrate (NO_3^-) to N gas, or via assimilation into plant or microbial biomass. Most research has focused on the potential for denitrification to remove N because as a gaseous pathway, removal is relatively permanent. Yards are expected to be important due to their wide extent and active management, such as irrigation and fertilization, that may maintain active microbial communities that can remove N inputs (Hall et al. 2009). Stormwater infrastructure features, such as retention basins or streams, in contrast, are expected to be hotspots because of their landscape position. Situated in low areas of the

landscape, stormwater features receive high inputs of N and organic carbon that are critical for denitrification (Zhu et al. 2004, Larson and Grimm 2012). To date, several studies have addressed the potential of these systems to remove N, either with potential denitrification assays or measurements of actual rates (Grimm et al. 2005, Hall et al. 2009, Roach and Grimm 2011, Larson and Grimm 2012, Bettez and Groffman 2012). Potential rates of denitrification in urban soils (Hall et al. 2009, Raciti et al. 2011) and retention basins (Zhu et al. 2004, Larson and Grimm 2012) are very high. However, it is not clear how the functioning of these systems affects N retention and transport at the watershed scale or whether variation in watershed features (i.e., lawn cover, stormwater retention basins) leads to predictable differences in N retention.

Previous findings from this study (Hale et al. in prep) suggest that some of the variation in N delivery can be attributed to differences in stormwater infrastructure (i.e., storm pipes, retention basins, engineered channels). However, N delivery was most strongly related to hydrology across events and sites. The aim of the present study was to determine whether the relationship between N delivery and hydrology is due to entirely to transport, or whether variation in hydrology causes variation in watershed biogeochemistry. We used a combination of chemistry, hydrology, and triple isotopes of NO_3^- to answer the following questions and evaluate the associated hypotheses:

Q1. Is N retention in urban watersheds controlled by hydrologic transport or biogeochemical retention mechanisms? We tested the two competing hypotheses that N delivery was controlled predominantly by hydrology (H1a) or biogeochemical transformations (H1b) using dual isotopes of NO_3^-. $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ are commonly used in watershed studies to determine the sources of NO_3^- in stream water or

runoff (Kendall et al. 2007). Dual isotopes can also be used to detect the occurrence of biogeochemical processes such as denitrification (Panno et al. 2006, Kendall et al. 2007, Burns et al. 2009). All biological processes fractionate stable isotopes (Kendall et al. 2007). That is, the lighter isotope is preferentially incorporated into the product, leading to predictable changes in the isotopic composition of the reactant and product (Kendall et al. 2007). This is true of biological processes such as assimilation, nitrification, and denitrification as well as physical processes such as volatilization. Denitrification preferentially consumes ^{14}N and ^{16}O, leading to an enrichment of both $\delta^{15}N$ and $\delta^{18}O$ in the remaining pool of NO_3^-. Although there is substantial variation, denitrification usually follows a 1:2 fractionation line (i.e., $\delta^{15}N$ and $\delta^{18}O$ of the remaining NO_3^- pool become enriched along a line with a slope of 0.5; Kendall et al. 2007).

Q2a: Do the sources, isotopic chemistry, and speciation of N vary systematically between watersheds? Q2b: If so, what watershed features (e.g., land cover and stormwater infrastructure design) are important in determining sources characteristics? We evaluated two hypotheses regarding watershed features that may control variation in NO_3^- sources among watersheds. First, based on reports of high potential denitrification rates in stormwater infrastructure features such as retention basins (Zhu et al. 2004, Larson and Grimm 2012, Bettez and Groffman 2012), we hypothesized that stormwater features are biogeochemical hotspots (H2a). That is, as these features represent a confluence of water, oC, and NO_3^-, they are likely to affect the sources and transformations of N within events. The competing hypothesis (H2b) was that urban yards (lawns and xeriscapes), as extensive and biogeochemically active land covers (Hall

et al. 2009), are likely to exert greater control on the sources and delivery of N within events.

In addition to comparisons of dual-isotope patterns, we also used $\Delta^{17}O$ to evaluate variation in NO_3^- sources among watersheds. Although $\delta^{15}N$ and $\delta^{18}O$ may be used to identify NO_3^- sources the method is semi-quantitative at best because of variation in the isotopic composition of sources and loss of source signals owing to fractionation processes (Kendall et al. 2007). $\Delta^{17}O$ is a relatively new tracer of atmospherically deposited NO_3^- that is not subject to many of the problems faced with $\delta^{18}O$. In biological processes, $\delta^{17}O$ fractionates along a characteristic line with $\delta^{18}O$ (described by relationship: $\delta^{17}O = 0.52(\delta^{18}O)$; Michalski et al. 2003, 2004). Because this relationship is based on the mass of $\delta^{17}O$ and $\delta^{18}O$, it is referred to as a mass-dependent fractionation. In contrast, atmospheric reactions that produce NO_3^- do not fractionate in a mass-dependent manner. The difference between $\delta^{17}O$ predicted by the mass-dependent fractionation line and the $\delta^{17}O$ of atmospheric NO_3^- is positive and is denoted $\Delta^{17}O$ (Michalski et al. 2003). Because $\Delta^{17}O$ is an anomaly, it is conserved even when fractionation occurs (i.e., during denitrification) and can be used as a tracer of atmospheric NO_3^- deposition. However, the signal can be overprinted by microbial nitrification (i.e., denitrification and subsequent nitrification will produce NO_3^- with $\Delta^{17}O$ of zero; Michalski et al. 2003, 2004, Dejwakh et al. 2012). $\Delta^{17}O$ can therefore be used to trace atmospheric NO_3^- through watersheds and to estimate the contribution of atmospheric relative to terrestrial (microbial) NO_3^- to runoff (Michalski et al. 2004, Dejwakh et al. 2012). We used $\Delta^{17}O$ -NO_3^- to evaluate hypotheses about variation in the processing and delivery of atmospheric N deposition from urban watersheds. We predicted that if stormwater infrastructure features were

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biogeochemical hotspots (H2a correct), the amount of atmospheric NO_3^- in stormwater runoff would decline as the density of stormwater features such as retention basins and channels increased. We also expected that there would be more evidence of denitrification and nitrification in watersheds with retention basins if these were biogeochemical hotspots of N retention. In contrast, if urban yards were primarily responsible for N processing (H2b correct), we predicted that we would find a strong relationship between % grass or % soil cover and the contribution of microbial NO_3^-, as well as more evidence of denitrification and nitrification in watersheds with more pervious cover.

METHODS

Sampling

Stormwater and Rain Sampling

We sampled 10 ephemeral watersheds that varied in stormwater infrastructure type and drainage area (Ch 4, Table 5.1). Seven watersheds contained residential land use, but varied in area and in stormwater infrastructure design. Three larger watersheds contained mixed land uses and mixed stormwater infrastructure (Table 5.1).

We used ISCO® automated samplers to collect up to 24 discrete stormwater samples during every storm event from August 2010 to August 2012. Stage height was measured at all sites with an ISCO bubbler module. We measured stage height in concrete channels or pipes to facilitate discharge calculations. Rating curves were developed using Manning's Equation to calculate discharge from stage height measurements (see Turnbull et al. in prep for details). For IBW and SGC, discharge data

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were obtained from USGS flow gauges near ISCO locations. Stormwater samples were collected from the field within 12 hours of an event and transported back to the laboratory. Samples for TDN were filtered through ashed GF/F filters and acidified to pH 2 with HCl. TDN samples were analyzed within 7 days by combustion on a Shimadzu TOC-VC/TN analyzer. Samples for ammonium (NH_4^+), nitrate-N (NO_3^-), nitrite-N (NO_2^-) were centrifuged to remove particulates and analyzed on a Lachat Quick Chem 8000 Flow Injection Analyzer. A subset of samples was selected for isotopic analysis of NO_3^-. Samples were selected from three storm events during which the majority of watersheds flowed: 5 Oct 2010, 7 Nov 2011, and 13 Dec 2011. Samples for isotopes of NO_3^- ($\delta^{18}O$, $\delta^{17}O$, and $\delta^{15}N$) were filtered through ashed GF/F filters and frozen immediately. Samples were shipped on ice to the Purdue Stable Isotope facility at Purdue University for isotopic analysis using the denitrifier method (Sigman et al. 2001, Casciotti et al. 2002, Kaiser et al. 2007). Briefly, NO_3^- was denitrified to N_2O by a pure culture of denitrifying bacteria. N_2O samples are then combusted to form N2 and O2, which are subsequently analyzed for $\delta^{15}N$, $\delta^{17}O$, and $\delta^{18}O$ on a Delta V Termo-Finnegan isotope mass spectrometer. We report $\delta^{15}N$ relative to air, and $\delta^{17}O$ and $\delta^{18}O$ relative to VSMOW.

For a subset of storm events we collected bulk rainfall samples for chemical analysis. Samplers were acid-washed, 1-L bottles fitted with a funnel and stopper that were co-located with ISCO locations, deployed before rains, and collected within 12 hours of the event. Rain samples were processed using the same protocol as for runoff.

Soil and Impervious Surface Sampling

We collected soils from a total of 60 residential yards to characterize the N chemistry of watershed soils in March and April 2011. Soils were sampled within 3 watersheds: Encantada (ENC), Sweetwater (SW), and Kiwanis Park (KP), to capture a range of development age. Within each watershed, 10 xeriscaped yards and 10 mesic (i.e., lawns with turf grass) yards were sampled. For each watershed 40 random addresses were selected from Maricopa County Assessor database (www.maricopa.gov/assessor/). Within that list, sampling was opportunistic, being dependent on resident permission to sample. Three 5-cm deep 5-cm diameter cores were collected from each yard and homogenized in the field. Samples were transported on ice back to the laboratory where they were sieved to 2mm. Extractions with 2M KCl were conducted within 24 hours of soil collection for analysis of NH_4^+, NO_3^-, and NO_2^-. Extractions with nanopure water were conducted within 24 hours of soil collection for analysis of N and O isotopes of NO_3^-. All samples were frozen until analysis. KCl extracts were analyzed on a Lachat Quick Chem 8000 Flow Injection Analyzer. A subset of samples (N=27) for triple NO_3^- isotopes were shipped on ice to Purdue University to be analyzed as described previously. Soil moisture was measured by mass difference before and after drying at 105°C for 24 hours. Concentrations of N in soil were converted to an areal density (g N/m^2) using the < 2mm bulk density of the soil sample. A subset of soils was also analyzed for $\delta^{15}N$ of total soil N. Soils were dried at 105°C, ground, and analyzed for $\delta^{15}N$ using a coupled Elemental Analyzer – Isotope Ratio Mass Spectrometer at the ASU Keck Lab.

Gravel samples were collected at a subset (N=4) of xeric yard sites. The top layer of gravel was collected from within a 470-cm^2 PVC ring. Gravel samples were shaken

with 1 L deionized water for 5 minutes. Water samples were then processed using the same protocols for stormwater and analyzed for all species of dissolved N and tripe isotopes of NO_3^-.

Impervious surfaces are major sources of nutrients and other materials to runoff (Hope et al. 2004). To characterize these sources of N, we conducted wash-off experiments of impervious surfaces in the same watersheds sampled for soils during May 2011. Within each watershed, we collected samples from 10 concrete surfaces (i.e., sidewalks) and 10 asphalt surfaces (i.e., roads). Rather than try to mimic rainfall-runoff processes, the purpose of these samples was to characterize the total material accumulated on urban surfaces. Small-diameter (470 cm^2) PVC rings fitted with foam tape to create a temporary seal with pavement were used as mini-catchments. We added 1L of deionized water, agitated the solution to ensure dissolution of accumulated material, and collected water using a peristaltic pump. Water samples were then transported on ice to the laboratory where they were processed using the same protocols as for stormwater runoff and analyzed for NO_3^-, NH_4^+, and NO_2^-. A subset (N=16) of samples were analyzed for triple isotopes of NO_3^-.

Data Analysis

For the purposes of calculating event mean concentrations (hereafter EMC or concentration), event solute load (L_e) was estimated as:

$$L_e = 60 \sum_{t=1}^{n} C_t \times Q_t$$

Where C_t is the solute concentration in mg / L, Q_t is the instantaneous discharge in L/s and 60 is a conversion factor to calculate load per minute. Concentration was linearly interpolated between observed values within each event. Event mean concentration of each solute (EMC, in mg/L) was calculated as:

$$EMC = \frac{L_e}{Q_e} \times 10^6$$

Where Q_e is the total discharge in L and 10^6 is a conversion factor to obtain concentrations in units of mg/L.

Temporal dynamics of N delivery

We used the relationship between N loads and discharge to characterize the temporal dynamics of N delivery. For each event with more than 5 observations of concentration, we fitted the following relationship:

$$NCL = NCQ^b$$

Where NCL is the normalized cumulative load, NCQ is the normalized cumulative discharge, and b is a fitted parameter that describes the shape of the curve (Bertrand-Krajewski et al. 1998, Hathaway et al. 2012; Fig. 5.1). This relationship is commonly used to determine if pollutant delivery is characterized by a first flush – that is, if loads are delivered disproportionately during the beginning of the storm event, rather than evenly distributed or delivered near the tail of the event (Bertrand-Krajewski et al. 1998, Hathaway et al. 2012). We used this relationship to characterize N delivery as transport limited ($b > 1$, load disproportionately near end of event) or supply limited ($b < 1$, load disproportionately at the beginning of the event; Fig. 5.1).

<u>Isotopic Analysis</u>

The $\Delta^{17}O$ of NO_3^- is a tracer of atmospherically derived NO_3^- and is calculated as follows:

$$\Delta^{17}O = \delta^{17}O - 0.52(\delta^{18}O)$$

Since $\Delta^{17}O$ of atmospheric NO_3^- (hereafter $NO_{3\ atm}^-$) is a positive number and NO_3^- produced via microbial nitrification (hereafter $NO_{3\ microb}^-$) has a $\Delta^{17}O$ value of zero, a simple mixing model can be used to determine the contribution of atmospheric NO_3^- (Michalski et al. 2003, 2004). We used the average $\Delta^{17}O$ over all rainfall samples as an approximation of average annual values of $\Delta^{17}O$ for NO_3^-. We did this because rainfall is not the only source of atmospheric NO_3^- to urban stormwater. Urban watersheds, especially in arid regions, contain large quantities of NO_3^- deposited as dryfall to the land surface (Hope et al. 2004, Lohse et al. 2008). We therefore wanted to use an average to recognize that the $\Delta^{17}O$ signal of atmospheric NO_3^- within the watershed is not only determined by event rainfall. The proportion of $NO_{3\ atm}^-$ was calculated for each sample as:

$$Proportion\ NO_{3-atm} = \frac{\Delta^{17}O - NO_{3-sample}^-}{\Delta^{17}O - NO_{3-atmosphere}^-}$$

To estimate differences in the delivery of $NO_{3\ atm}^-$ and $NO_{3\ microb}^-$, we linearly interpolated observed $\Delta^{17}O$ values within each event for events with at least 5 observations. These values were then used to calculate the proportion of the total NO_3^- load that was atmospherically derived. We also calculated normalized cumulative loads

of $NO_3^-{}_{atm}$ and $NO_3^-{}_{microb}$ separately, which were then used to estimate b for each source of NO_3^- for each event.

Dual-isotope plots ($\delta^{18}O$-NO_3^- vs $\delta^{15}N$-NO_3^-) were constructed for all samples and for each event individually. Plots were assessed visually for evidence of denitrification and mixing. The relationship between $\delta^{18}O$ and $\delta^{15}N$ for each event was assessed using linear regression and compared across sites.

Event-scale mass balance

We estimated inputs of dissolved inorganic N (DIN) in rainfall to all watersheds during the 13 Dec 2011 event to calculate DIN retention at the event scale. We spatially interpolated rainfall depth from our gages and gages operated by the Flood Control District of Maricopa County and a volunteer network (wunderground.com) to create a continuous raster file of total precipitation for the event (see Turnbull et al. in prep for details). We also spatially interpolated precipitation chemistry using an inverse distance weighting method in ArcGIS. These two datasets were then multiplied to get the spatial distribution of load for each analyte and total inputs were calculated by summing over the watershed area. Event scale N retention was then calculated as:

$$Retention_{DIN} = \frac{\left(DIN_{rainfall} - DIN_{runoff}\right)}{DIN_{rainfall}}$$

We also calculated the event scale retention of $NO_3^-{}_{atm}$ as:

$$Retention_{NO3-atm} = \frac{\left(NO_{3-atm-rainfall} - NO_{3-atm-runoff}\right)}{NO_{3-atm-rainfall}}$$

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Statistical Analysis

One-way analysis of variance (ANOVA) was used to test for differences in N density on different land surface types (mesic, xeric, concrete, asphalt, and gravel). To understand watershed controls on NO_3^- sources, we used linear regression to characterize relationships between land cover (% impervious, grass, and soil cover), stormwater infrastructure (density of retention basins, pipes, and channels) and the proportion of atmospheric NO_3^- in stormwater runoff. All statistical analyses were conducted in R.

RESULTS

Sources of N in urban watersheds

Soils and Impervious surfaces

The supply of N ranged widely across and within surface types. Average NO_3^- density was highest for gravel surfaces (9.0 ± 9.8 g/m^2), lowest for mesic soils (0.8 ± 1.7g/m^2), and intermediate for all other surfaces (Fig. 5.2). NH_4^+ density was also highest for gravel (17.2 ± 6.4 g/m^2), followed by asphalt and concrete. NH_4^+ density was very low for mesic (0.2 ± 0.6 g/m^2) and xeric soils (0.04 ± 0.07 g/m^2). NO_2^- density was low and similar for asphalt, concrete, xeric and mesic soils, but significantly higher on gravel surfaces (0.7 ± 0.8 g/m^2). N speciation also varied across sites. Gravel sites had significantly higher NO_2^-:NO_3^- ratios than all other sites (Fig. 5.2). NH_4^+:NO_3^- ratios were also higher for impervious surfaces and gravel than in soils.

The isotopic signatures of NO_3^- varied across surface types as well. Although there were no significant differences in δ^{15}N-NO_3^- across site types, δ^{15}N values were generally enriched, and all soil samples fell between 0 and 21‰ δ^{15}N. Pavement samples

were the most variable in terms of δ^{15}N, ranging from 0.82 to 148.88‰. Most values were between 0 and 29‰, but there were two samples with greater than 100‰ δ^{15}N. Gravel samples also varied in δ^{15}N, ranging from -8.22 to 14.90‰. The greatest difference between sites was in Δ^{17}O-NO_3^- (Fig. 5.2). Δ^{17}O was highest on impervious surfaces, ranging from 10.85 to 21.83‰. This translated into a range of 42 to 84% atmospheric NO_3^-. Soils had much lower Δ^{17}O-NO_3^-, ranging from 0 to 1.45‰ (equivalent to 0 to 6% atmospheric NO_3^-). Gravel was much more variable than pavement and soil samples, and Δ^{17}O ranged from 0 to 18.56‰ (Fig. 5.2).

δ^{15}N of NO_3^- in soils was positively correlated with δ^{15}N in total soil N (Fig. 5.3). In most samples, NO_3^- was more depleted in δ^{15}N than total soil N. In three samples, NO_3^- was more enriched than total N in δ^{15}N (Fig. 5.3).

Rainfall

Total N concentration in rainfall varied within and between events (Fig. 5.4), averaging 1.2 ± 1.3 mg N/L. NH_4^+ concentrations ranged from 0.2 to 2.5 mg NH_4^+-N / L, NO_3^- concentrations ranged from 0.1 to 0.8 mg NO_3^--N / and NO_2^- concentration was very low in all rain samples, ranging from below the detection limit (0.005 mg N / L) to 0.01 mg NO_2^--N / L. Speciation was also variable within and between events. NH_4^+:NO_3^- in rainfall samples averaged 2.3 ± 1.3, but ranged from 0.3 to 6.

Isotopes of NO_3^- in rainfall were variable between and within events. The largest variation was within δ^{15}N values, which ranged from -5.6 to 4.2‰ and averaged -0.5‰ across all samples. There were significant differences between the average δ^{15}N values for different events. δ^{15}N values were lowest for the event on 7 Nov 2011, mid-ranged for the event six days later, and highest during the event on 13 Dec 2011 (Fig. 5.4). Δ^{17}O

values were also variable across and within rain events, but averaged $25.5 \pm 3.1‰$ across all samples.

N delivery from arid urban watersheds

Concentration of N in runoff and rainfall

Concentration of TDN was uniformly higher in runoff than in rainfall (Fig. 5.5), although patterns were not consistent among sites. NO_3^- concentration in runoff from all sites was greater than that in rainfall during the 7 Nov 2011 event, but NO_3^- concentration in runoff during the 13 Dec 2011 event was more variable: some runoff samples had a higher concentration than rainfall, others had a lower concentration (Fig. 5.5). Concentration of NH_4^+ was higher in runoff than rainfall for some sites, but was lower for the integrator sites. During the 13 Dec 2011 event, NH_4^+ concentrations at three sites (MR, SW, and MS) were lower than that of rainfall, but the pattern was opposite during the 7 Nov 2011 event. We only have NO_2^- data for the 7 Nov 2011 event, but for that event, the concentration of NO_2^- was much higher in runoff than in rainfall. NO_2^- :NO_3^- ratios in runoff for the 7 Nov 2011 event were higher in runoff than in rainfall (Fig. 5.6), but the rainfall samples fall within the range of NO_2^-:NO_3^- in runoff samples for all three events. NH_4^+:NO_3^- was much higher in rainfall than in runoff during the 7 Nov 2011 event, but was similar during the 13 Dec 2011 event (Fig. 5.6).

Isotopes of NO_3^- in runoff across events

Most stormwater NO_3^- had $\delta^{15}N$ and $\delta^{18}O$ values that were between those of rainfall and soil NO_3^- (Fig. 5.7). NO_3^- in stormwater samples from the 13 Dec 2011 event did not have distinctive isotopic signatures across sites, with the exception of IBW, which

had NO_3^- that more closely matched the isotopic signature of soils, having more depleted $\delta^{18}O$ values and more enriched $\delta^{15}N$ values (Fig. 5.8). The proportion of NO_3^- from atmospheric sources based on $\Delta^{17}O$ values was very high in rainfall for both sampled events (Fig. 5. 6). The contribution of atmospheric NO_3^- to total NO_3^- load ranged from 5 to 53% and averaged 39% ($\pm$10%) over all observed events. Individual observations of $NO_3^-{}_{atm}$ within events ranged much more widely (0 to 84% over all samples) across and within sites and events (Fig. 5.9).

Across the three events for which we characterized isotopic values, between-site variation in the proportion of $NO_3^-{}_{atm}$ was not consistent (Fig. 5.9). For the 5 Oct 2010 event there were no watershed features that explained variation in $NO_3^-{}_{atm}$. Percent grass cover explained 74% of the variation in $NO_3^-{}_{atm}$ across sites for the 7 Nov 2011 event (Fig. 5.10), but was not a significant predictor for either of the other sampled events. For the 13 Dec 2011 event there were no significant predictors of $NO_3^-{}_{atm}$ across all sites, but retention basin density explained 47% of the variation in $NO_3^-{}_{atm}$ across sites when IBW was excluded (data not shown).

Event Scale N Retention

During the 13 Dec 2011 event, rainfall N inputs and N retention varied considerably across sites (Fig. 5.11A). Inputs of dissolved inorganic N ($NH_4^+ + NO_3^-$) ranged from 0.12 to 0.27 kg N/ha and fluxes of DIN in runoff ranged from 0.0006 to 0.24 kg N/ha. Thus, most watersheds were sinks for DIN, exporting less than entered the watershed as rainfall, but ENC and KP were sources of DIN downstream and PIE was a very small sink, exporting nearly all DIN that entered as rainfall. When only atmospherically derived NO_3^- is considered, spatial variation in runoff exports was much

lower and all sites were sinks for $NO_3^-{}_{atm}$ (Fig. 5.11B). The exception was KP, from which exports were similar to other sites, but to which rainfall NO_3^- inputs to this site were very low, and the site was a source of $NO_3^-{}_{atm}$ downstream.

DIN retention was strongly related to runoff coefficient (RC; Rainfall / Runoff) across sites for the 13 Dec 11 event (Fig. 5.12); watersheds were sources of DIN downstream when a high proportion of rainfall appeared in runoff. Watersheds with low RC values retained upwards of 90% of DIN inputs in rainfall. Retention of $NO_3^-{}_{atm}$ was also related to RC (Fig. 5.12), but all watersheds retained the majority of $NO_3^-{}_{atm}$ inputs even with very high runoff coefficients. Despite strong relationships between retention and RC, there was no relationship between RC and the proportion of $NO_3^-{}_{atm}$ delivered during the event (Fig. 5.13).

<u>Changes in isotopes and concentrations of N within storms</u>

Stormwater chemistry was dynamic across the course of a storm (e.g., Fig. 5.14). Over the course of the 13 Dec 2011 event, concentration of NH_4^+ declined significantly over time at all sites except SW, where it increased significantly over time (Table 5.2). NO_3^- concentration decreased significantly over time at all sites except IBW, MS, and SW, where concentration increased significantly over the course of the event. The ratio of NH_4^+ to NO_3^- also changed significantly over time at all sites: increasing for BV, KP, LA, and PIE, and decreasing for all other sites. $\Delta^{17}O$ (and therefore the proportion $NO_3^-{}_{atm}$) declined significantly through the event for ENC, LA, MS, and SW, but there were no significant patterns at the other sites.

Within the event, $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- were significantly and inversely correlated for ENC, MS, and PIE. LA and SGC both had 1-2 samples that were outliers

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in the dual isotope plots. When these were removed, these sites had significant and

negative relationships between $\delta^{15}N$ and $\delta^{18}O$. At some sites, the contribution of

atmospheric NO_3^- was significantly and positively related to $NH_4^+:NO_3^-$ (Table 5.2).

We observed a wide range of N delivery patterns from supply to transport

limitation both within and across sites (Fig. 5.15). Overall, there were more observations

of flushing ($b < 1$; supply limitation) than of transport limitation ($b > 1$) across all events

and N species, although patterns across sites were inconsistent. We calculated the ratio of

b_{NO3} to b_{NH4} to compare delivery of different N species within an event (Fig. 5.15). For

many events, $b_{NO3}:b_{NH4}$ was close to 1. However, integrator and retention basin sites

tended to flush NH_4^+ more than NO_3^-, and the opposite pattern was suggested – though

not consistently – for smaller sites, where NO_3^- flushed more than NH_4^+.

The temporal delivery of NO_3^- loads (e.g., flushing) from atmospheric and

microbial sources were significantly different across all observations and for the 13 Dec

2011 event (Fig. 5.16). Overall, $NO_3^-_{atm}$ was flushed from watersheds more than

microbial sources of NO_3^-. However, when this is expressed as a ratio ($b_{NO3-atm}:b_{NO3-microb}$, Fig. 5.16C), it is clear that there is a great deal of variation across and with sites.

Most observations suggest that $NO_3^-_{atm}$ flushes before microbial NO_3^-, yet the flushing of

microbial NO_3^- before $NO_3^-_{atm}$ was observed during 5 events (out of 21 total). Again,

patterns were not consistent across sites, with values of $b_{NO3-atm}:b_{NO3-microb}$ ranging widely

even within a single site (Fig. 5.16C).

DISCUSSION

Major differences in isotopic composition of NO_3^- pools in urban residential landscapes

The chemical and isotopic composition of N pools varied significantly within urban watersheds. Soils had very low NH_4^+ relative to impervious surfaces, and the near zero $\Delta^{17}O$ - NO_3^- of most soil samples suggested that atmospherically deposited NO_3^- was being rapidly consumed and that nitrification was actively occurring in these soils. The $\delta^{15}N$-NO_3^- was relatively enriched in all soil samples, falling in the range usually reported for manure and septic sources (Kendall et al. 2007). Since these watersheds are sewered and the groundwater table is quite deep, it is unlikely that these values represent inputs from human waste. Enriched $\delta^{15}N$ values may instead be traced to the use of organic N fertilizers. Although previous research has found high rates of denitrification in Phoenix residential soils (Hall et al. 2009), our data suggest that denitrification is also unlikely to be the dominant control of $\delta^{15}N$ values since it would enrich $\delta^{18}O$-NO_3^- as well (Kendall et al. 2007). Another possibility would be the volatilization of NH_4^+ and subsequent nitrification of enriched NH_4^+ to NO_3^-. The lighter N isotope ^{14}N preferentially volatilizes, leaving the remaining pool of NH_4^+ enriched (Kendall et al. 2007). Subsequent nitrification would incorporate enriched N with O from relatively depleted O_2 and water. Because nitrification preferentially incorporates lighter N, we would expect to find $\delta^{15}N$- NO_3^- to be depleted relative to $\delta^{15}N$-TN. This is a pattern we see at most sites (Fig. 5.3), however, our small sample size precludes us from drawing conclusions about the predominant N transformations occurring in residential soils. Previous work in Phoenix has found especially high rates of both nitrification and denitrification in urban lawns (Hall et al. 2009). The isotopic composition of urban soils

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likely reflects the balance of these two processes as well as the isotopic composition of new N inputs.

In contrast to soils, impervious surfaces effectively collect atmospheric NO_3^-, which is later flushed by stormwater runoff. We found that NO_3^- on impervious surfaces was predominantly atmospheric (mean 69% $NO_3^-{}_{atm}$), suggesting that these surfaces integrate dry deposition over longer time scales. The slightly lower percentage of $NO_3^-{}_{atm}$ compared to rainfall may be due to mixing with NO_3^- from yards or variation in the isotopic composition of $NO_3^-{}_{atm}$. Our samples also included two samples with highly enriched δ^{15}N- NO_3^-, above 100‰ δ^{15}N. These values are higher than anything reported in the literature. One possible explanation would be extreme enrichment due to volatilization. These samples were collected in May when surface temperatures were already reaching 38°C. Hope et al. (2004) measured material stored on parking lot surfaces in Phoenix, AZ. In measuring runoff from a storm 1 month later, they found that phosphorus and organic carbon export were similar to that predicted from surface pools and rainfall chemistry, but NO_3^- and NH_4^+ export were much lower than expected. N may have been retained or removed during the storm, or other loss pathways active between the time of surface sampling and the storm could have caused a reduction in the N stored in these watersheds. The contrast between patterns for N compared with carbon and phosphorus suggest that gaseous loss pathways such as volatilization may have been important in these watersheds as well. However, these two samples seem to be extreme cases especially since we did not observe δ^{15}N values greater than 22.5‰ in our runoff samples.

Variation in rainfall chemistry and composition of NO_3^- isotopes

We found variation in rainfall chemistry and isotopic composition, both spatially within events and temporally between events. Unfortunately, we did not sample enough events to test any hypotheses about the drivers of this variation. Previous work in natural and urban areas around Phoenix has reported that rainfall N chemistry is strongly related to storm characteristics and season (Welter et al. 2005, Lohse et al. 2008). Specifically, at both desert and urban sites, concentrations of NO_3^- and NH_4^+ are higher in summer than in winter and decrease with increasing storm size (Welter et al. 2005, Lohse et al. 2008).

Overall, the isotopic composition of NO_3^- in our rain samples was well matched to values found in previous studies (Michalski et al. 2004). However, we did have some rain samples with very low $\delta^{18}O$ and $\Delta^{17}O$, which fell outside the range expected for atmospheric deposition (e.g., <60‰ $\delta^{18}O$ and <20‰ $\Delta^{17}O$). Some variation is expected due to variation in the dominant chemical reactions producing NO_3^- in the atmosphere (Michalski et al. 2004). These very low values, however, suggest the presence of other sources of NO_3^- in rainwater beyond atmospherically produced NO_3^-. This is also suggested by the relatively high concentrations of NH_4^+ in rainfall. Other sources of NO_3^- could include soil emissions or volatilization of fertilizers and manure (Russell et al. 1998, Kendall et al. 2007). More work is needed to understand the spatial controls on rainfall chemistry and NO_3^- isotopes in arid urban environments to accurately account for redeposition of locally produced N compared to new atmospheric sources of NO_3^-. Furthermore, much less is known about the isotopic composition of NO_3^- in dry deposition and how this may compare with wet deposition values (Buda and DeWalle 2009). It is especially important to understand these sources of variation in arid urban

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watersheds where dry deposition can equal or exceed wet deposition (Baker et al. 2001, Lohse et al. 2008), and where impervious surfaces can integrate atmospheric deposition over long time periods, as demonstrated by our surface sampling results.

Urban watersheds process and retain most atmospheric NO_3^- deposition

Our results suggest that urban watersheds do not passively transport atmospheric N deposition; microbial NO_3^- makes up the majority of NO_3^- delivered in stormwater. Atmospheric NO_3^- made up a large fraction of some individual samples (up to 80%), but over the course of storm events, total loads were only 20-55% $NO_3^-{}_{atm}$ for most sites and <5% $NO_3^-{}_{atm}$ at IBW. Importantly, these proportions were similar for both a small (7 mm) and a large (26 mm) event.

There are two aspects of $NO_3^-{}_{atm}$ to consider: the proportion of NO_3^- in runoff from atmospheric sources, and the retention of $NO_3^-{}_{atm}$ during storm events. Our results suggest that the proportion of $NO_3^-{}_{atm}$ in runoff does not vary systematically between sites (Q2) and may be driven by between-event processes occurring within the landscape. In contrast, the retention of $NO_3^-{}_{atm}$ during an event is driven by event hydrology (H1a), which in turn is controlled by characteristics of the storm event, water land cover, and the stormwater infrastructure system (Ch 4).

The proportion of atmospheric NO_3^- did not vary systematically between sites (Q2), and relationships between sites were not consistent. We found some support for both our hypotheses regarding watershed controls on NO_3^- sources (H2a: stormwater features, and H2b: land cover). The only significant relationship between the proportion of $NO_3^-{}_{atm}$ and watershed characteristics was with % grass cover for the 7 Nov 2011

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event (H2a). This relationship, in combination with our soil results, suggests that mesic

yards could play a crucial role in mediating N delivery from urban watersheds. These

findings make sense given the high rates of denitrification and nitrification in urban

lawns in this ecosystem (Hall et al. 2009). However, this relationship did not emerge

from the 13 Dec 2011 or 5 Oct 2010 event data. In contrast, the density of retention

basins was a significant predictor of proportion $NO_3^-{}_{atm}$ for the 13 Dec 2011 event if the

largest integrator site, IBW, was excluded (H2b). Retention basins in the Phoenix area

have been found to have high rates of potential denitrification (Larson and Grimm 2012),

although those rates are substantially lower than those observed in both mesic and xeric

yards (Hall et al. 2009, Table 5.3). With the small number of events sampled for NO_3^-

isotopes, we are unable to draw any conclusions about the drivers of atmospheric NO_3^-

contributions to runoff within urban watersheds. Because we were comparing $NO_3^-{}_{atm}$

contributions to total event NO_3^- load, we could not conduct a statistical analysis of

differences between sites. However, the range of observed $NO_3^-{}_{atm}$ values within each

site was quite broad and overlapped for all sites.

These results contrast with findings from other studies that found significant

relationships between impervious surface cover or area developed and atmospheric NO_3^-

(Ging et al. 1996, Silva et al. 2002, Chang et al. 2002, Anisfeld et al. 2007). The key

difference is the range of land cover variation addressed in these studies. Chang et al.

(2002) and Anisfelt et al. (2007) were both addressing differences across and land use

gradient ranging from forested to agricultural to urban. Ging et al. (1996) and Silva et al.

(2002) evaluated differences in NO_3^- sources across a similarly wide range of

imperviousness, from ~10 to over 90%. Our study watersheds, in contrast, were all the

same land use (residential urban) and spanned a much narrower range of imperviousness, from 46 to 68%. This range of land cover variability may not be wide enough to overwhelm background variation in NO_3^- isotopes due to the spatial and temporal heterogeneity in management practices (Larson et al. 2009, Cook et al. 2012). Indeed, the variation in the proportion of $NO_3^-{}_{atm}$ in total event loads is likely noise resulting from landscape management variability, rather than a signal resulting from fundamental differences in N cycling across these watersheds.

In contrast, we did find systematic differences in $NO_3^-{}_{atm}$ retention across our study sites. During the 13 Dec 2011 event, all watersheds were sinks for $NO_3^-{}_{atm}$, retaining 60 to 99% of $NO_3^-{}_{atm}$ inputs in rainfall. Variation in $NO_3^-{}_{atm}$ retention was strongly related to hydrologic transport, as measured by the runoff coefficient. Previous research has found that the runoff coefficient in these watersheds is controlled by interactions between land cover, stormwater infrastructure, and storm characteristics (Ch 4). So although watershed characteristics did not control variation in the processing of atmospheric NO_3^- deposition, they did control the delivery of NO_3^-, atmospheric and microbial, downstream.

Within event variation in NO_3^- likely due to mixing of sources rather than biogeochemical processes

Patterns of N chemistry and NO_3^- isotopes suggest that processing of atmospheric NO_3^- to microbial NO_3^- occurs between rather than during events, lending support to H1a, that N delivery is controlled by hydrology rather than biogeochemical transformations. We did not find support for H1b, that biogeochemical processes are

responsible for retaining N during storms. Dual isotopes of NO_3^- ($\delta^{18}O$ and $\delta^{15}N$) are a commonly used tool to examine patterns and infer processes occurring within a watershed. Relationships between $\delta^{18}O$ and $\delta^{15}N$ within each site during the 13 Dec 2011 event were either negative or not significant. All biological processes that remove NO_3^- (e.g., denitrification and assimilation) will fractionate both N and O isotopes, leading to a positive relationship between $\delta^{15}N$ and $\delta^{18}O$ (Kendall et al. 2007). The absence of this pattern at our sites is strong evidence that denitrification and nitrification are not dominant processes affecting NO_3^- concentrations and yields during storm events. The only significant relationships between $\delta^{15}N$ and $\delta^{18}O$ were negative and were at the two small surface-drained sites and MS, a retention basin site. The negative slope indicates mixing of two distinct sources of NO_3^-: one with an enriched $\delta^{18}O$ and depleted $\delta^{15}N$ and one with depleted $\delta^{18}O$ and enriched $\delta^{15}N$. These sources match the isotopic compositions of rainfall and soil NO_3^-. When plotted together, most stormwater runoff NO_3^- appeared to fall between soil and rainfall NO_3^- isotopic values. The lack of clear mixing signal at other sites could be due to variation in the isotopic signal on impervious surfaces (i.e., variation in sources). The isotopic signature of NO_3^- pools on impervious surfaces were highly variable compared to soil and rainfall values and could play a large role in driving the variability of NO_3^- isotopes in runoff. It is not clear why PIE, ENC, and MS had stronger mixing lines. At PIE and ENC variation in $\delta^{15}N$ explained ~90% of variation in $\delta^{18}O$. At MS, much less variance was explained by the relationship (32%). PIE and ENC are the smallest watersheds, and therefore we might expect less variation in NO_3^- sources within the watersheds and a stronger relationship between $\delta^{15}N$ and $\delta^{18}O$ than at larger watersheds.

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These results support findings from other studies that urban NO_3^- isotopes are primarily a result of mixing of sources rather than biogeochemical processing (Ging et al. 1996, Silva et al. 2002, Mayer et al. 2002, Burns et al. 2009, Buda and DeWalle 2009, Kaushal et al. 2011). Similar reports come from non-urban watersheds as well (e.g., Burns and Kendall 2002, Buda and DeWalle 2009). Across a range of land uses, isotopic evidence of denitrification is largely limited to agricultural watersheds (Panno et al. 2006, Chen et al. 2009). Furthermore, Panno et al. (2006) suggest that even in agricultural watersheds, a denitrification signal could be the result of mixing with a denitrified source. Across landscapes, most denitrification occurs within terrestrial ecosystems, rather than in rivers or lakes (Panno et al. 2006, Seitzinger et al. 2006). In the study watersheds, denitrification is likely occurring in residential soils between storm events. However, the wide variety in landscape management within watersheds would likely mask any isotopic signals of denitrification.

Indian Bend Wash

IBW was the only site that was substantially different from the others in terms of chemistry and isotopic composition of NO_3^-. There was very little atmospheric NO_3^- signal at IBW and the $\delta^{15}N-NO_3^-$ was also higher than other sites. It's not clear from the data whether these differences are due to the mixing of different sources or if biogeochemical processes are occurring during the storm. The sampling location for IBW is located below a large flood control project that includes a lake and stream system (filled with groundwater) and a large grassy floodplain (Roach et al. 2008). Previous

research has found that denitrification rates within the lakes and floodplain are both very high (Roach and Grimm 2011).

We found no isotopic evidence of denitrification at IBW based on dual isotopes of NO_3^-. However, several other studies have also found an absence of isotopic denitrification signal at the watershed scale despite reach-scale evidence of denitrification (Mayer et al. 2002, Chang et al. 2002, Lefebvre et al. 2007, Chen et al. 2009). Possible explanations offered by these authors include a dilution of the denitrification signal by other sources of NO_3^- or a weak fractionation signal from denitrification (Chang et al. 2002, Chen et al. 2009). Weak fractionation could occur if denitrification was NO_3^- - limited and therefore consumed most of the NO_3^- pool (Mayer et al. 2002, Kendall et al. 2007). This is unlikely in IBW, where the lake and stream waters have NO_3^- concentrations in up to 7 mg N / L (Roach and Grimm 2009). Fractionation could also be weak if denitrification is primarily occurring in benthic sediments and is diffusion limited. Diffusion limitation would create NO_3^- limitation for denitrification in the sediments, and fractionation would then be weak or nonexistent (Sebilo et al. 2003). Roach and Grimm (2011) did find that denitrification in lake sediments was diffusion limited, lending support to this hypothesis. However, they also found that floodplain soils, which were not diffusion-limited, contributed to more than two-thirds of denitrification in the system (Roach and Grimm 2011). Another hypothesis is that the groundwater filling the lakes and streams in the IBW flood control project are contributing to stormwater chemistry. This is supported by the very high concentrations of NO_3^- observed at IBW during the 13 Dec 2011 event compared to rainfall and runoff at all other sites. Unfortunately, we did not characterize the isotopic signal of

groundwater NO_3^- in this study, so we cannot be certain that groundwater inputs would lead to the isotopic composition of NO_3^- found at IBW.

CONCLUSIONS

The objective of this study was to use information on the concentrations, speciation, and isotope chemistry of potential N sources to stormwater across and within events to understand the controls on N sources and transformation during urban storm events. In particular, we were interested to understand more about the balance of hydrologic and biogeochemical control of N delivery from these watersheds (Q1) and how that may vary across sites with different watershed characteristics (Q2). We found major differences in the isotopic chemistry of NO_3^- across land cover N sources (e.g., soil, impervious surfaces). These differences highlight the spatial variation in biogeochemical processes within watersheds. Specifically, a key finding is that urban yards – mesic and xeric – are major sources of N to stormwater but are also sinks of N overall within urban watersheds. Patterns of N loads across many events suggest that hydrology is the dominant control on N delivery from urban watersheds (H1a). However, our results here demonstrate that urban watersheds are not just passive conduits for N; rather, isotopic evidence suggests that all urban watersheds retain the majority of NO_3^- that enters watersheds as atmospheric deposition. It seems likely that most of this retention occurs in residential yards, rather than in stormwater infrastructure features, given the large area of yards and the high rates of biogeochemical processing within them. However, we found inconsistent relationships between stormwater features (H2a), land cover (H2b) and NO_3^- sources. This research lends further support to the conceptual

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model developed in Hale et al. (in prep/Ch 4), in which land use and land cover drive concentrations via biogeochemical processing/transformations. Stormwater infrastructure in this system controls loads via transport/hydrology rather than via biogeochemistry. These findings contrast with earlier work that suggested that stormwater features may be hotspots of biogeochemical transformations at the watershed scale. Stormwater infrastructure features may indeed be hotspots of N removal, but our research suggests that the mechanisms are hydrologic rather than biogeochemical.

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Table 5.1. Characteristics of study watersheds.

Site Abbreviation	Watershed Name	Drainage Area (ha)	Predominant Infrastructure	% Impervious Surface Cover	% Grass Cover	% Soil Cover	Retention Basin Density (m²/ha)	Pipe Density (m/ha)	Channel Density (m/ha)	Total Drainage Density (m/ha)	Ret Basin / Channel (m²/m)	Storms Sampled (N)
ENC	Encantada	6.08	Surface	48.35	46.48	4.30	0.00	6.00	0.00	6.00	0.00	17
PIE	Pierce	10.23	Surface	56.69	38.18	4.68	0.00	0.00	0.00	0.00	0.00	21
MR	Martin Residence	18.44	Wash	41.61	44.71	12.50	0.00	1.00	21.18	22.18	0.00	15
BV	Bella Vista	56.53	Wash	68.91	18.05	12.70	558.78	16.00	33.33	49.33	16.76	11
KP	Kiwanis Park	106.42	Pipes	50.00	3.00	46.00	0.00	24.00	0.00	24.00	0.00	7
SW	Sweetwater	117.64	Retention Basins	48.61	39.20	11.55	531.05	15.00	9.20	24.20	57.73	8
MS	Montessori	140.55	Retention Basins	48.80	38.81	11.77	454.75	14.00	41.12	55.12	11.06	8
LA	Lake Angel	1662.40	Integrator	57.15	33.43	8.98	169.51	12.00	24.72	36.72	6.86	12
SGC	Silverado Golf Course	15454.54	Integrator	46.19	42.17	10.47	45.81	4.00	5.33	9.33	8.60	10
IBW	Indian Bend Wash	20247.14	Integrator	48.65	39.31	10.57	48.08	7.00	4.38	11.38	10.97	11

Table 5.2. Relationships between $\delta^{15}N$ and $\delta^{18}O$ and changes in N chemistry over time during 13 Dec 2011 event. *Indicates an outlier affected the direction and significance of the relationship.

Site	$\delta^{15}N$ vs $\delta^{18}O$	Changes over Time		
		$\Delta^{17}O$	[NH$_4$]	[NO$_3$]
BV	ns	ns	-	-
ENC	-	-	-	ns
IBW	ns	ns	-	ns
KP	ns	ns	-	-
LA	+*	-	ns	-
MR	ns	ns	-	-
MS	-	-	ns	ns
PIE	-	ns	ns	ns
SGC	ns*	ns	-	ns
SW	ns	-	+	+

Table 5.3. Potential denitrification rates in Phoenix land cover types. Rates are in units of μg N_2O-N/kg soil h^{-1}.

Ecosystem Type	Mean	Variability	Reference
Grassy Retention Basin	673	Range: 407-1251	Larson 2010
Xeric Retention Basin	285	Range: bdl - 1090	Larson 2010
Xeriscape yard, between plants	1503.4	Standard Error: 1392.2	Hall et al. 2009
Xeriscaped yard, under plants	1511.1	Standard Error: 717	Hall et al. 2009
Lawn	2676.6	Standard Error: 479.3	Hall et al. 2009
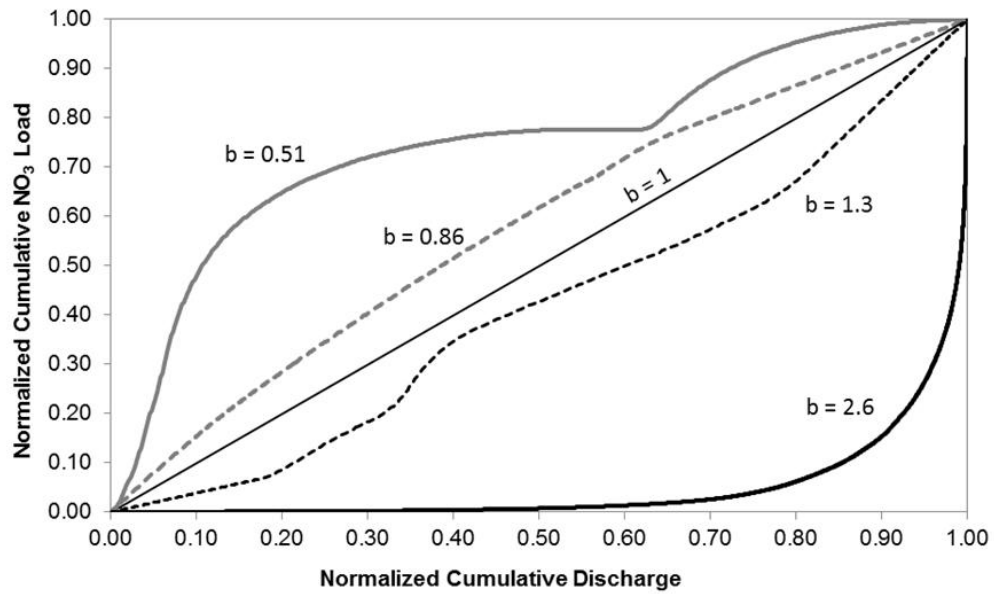
Figure 5.1. Illustration of characteristic relationships between normalized cumulative load (NCL) and normalized cumulative discharge (NCQ) for NO_3^-. Values for *b* listed next to each line indicate the b parameter for the relationship: $NCL = NCQ^b$. Values for *b* < 1 indicate flushing, whereas values of *b* > 1 indicate transport limitation.
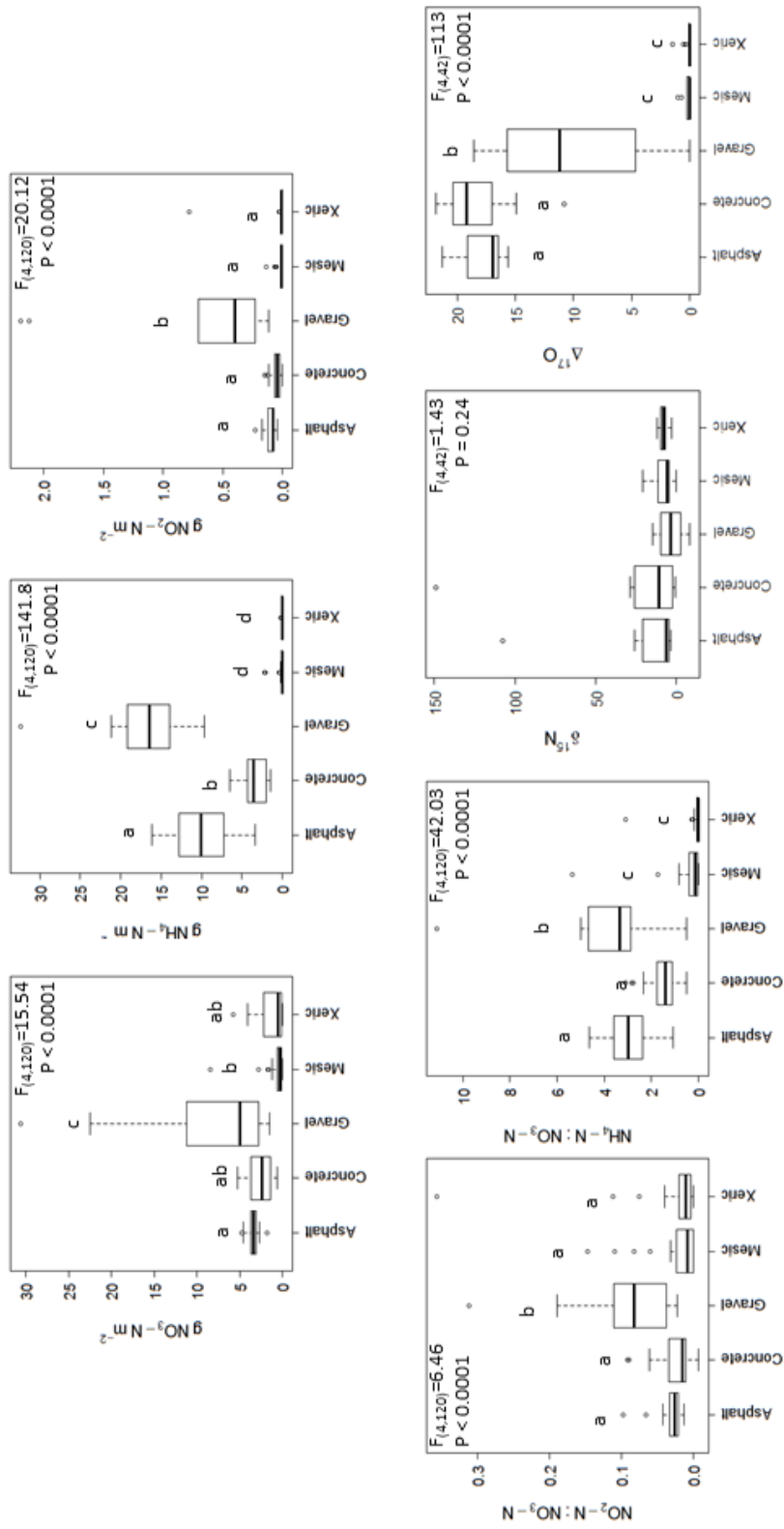
Figure 5.2. Density, speciation, and isotopic composition of N on five different surface types within urban watersheds.
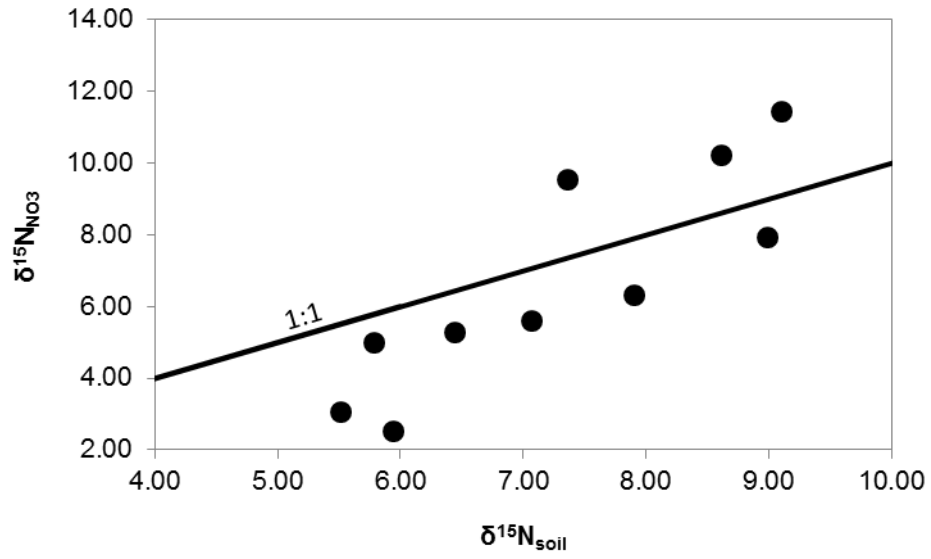
Figure 5.3. Relationship between $\delta^{15}N$ of NO_3^- and $\delta^{15}N$ of total soil N for a subset of soil samples.
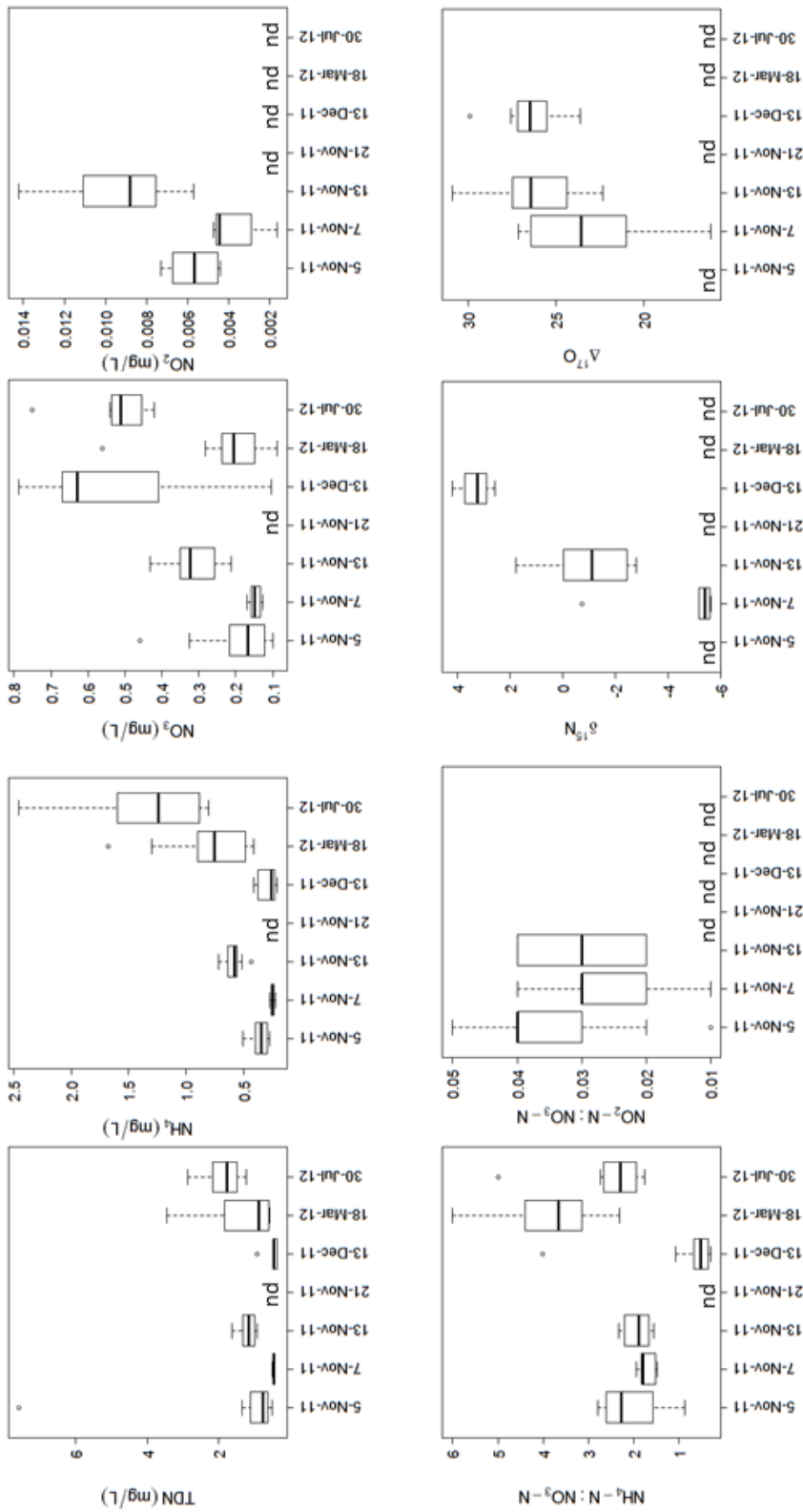
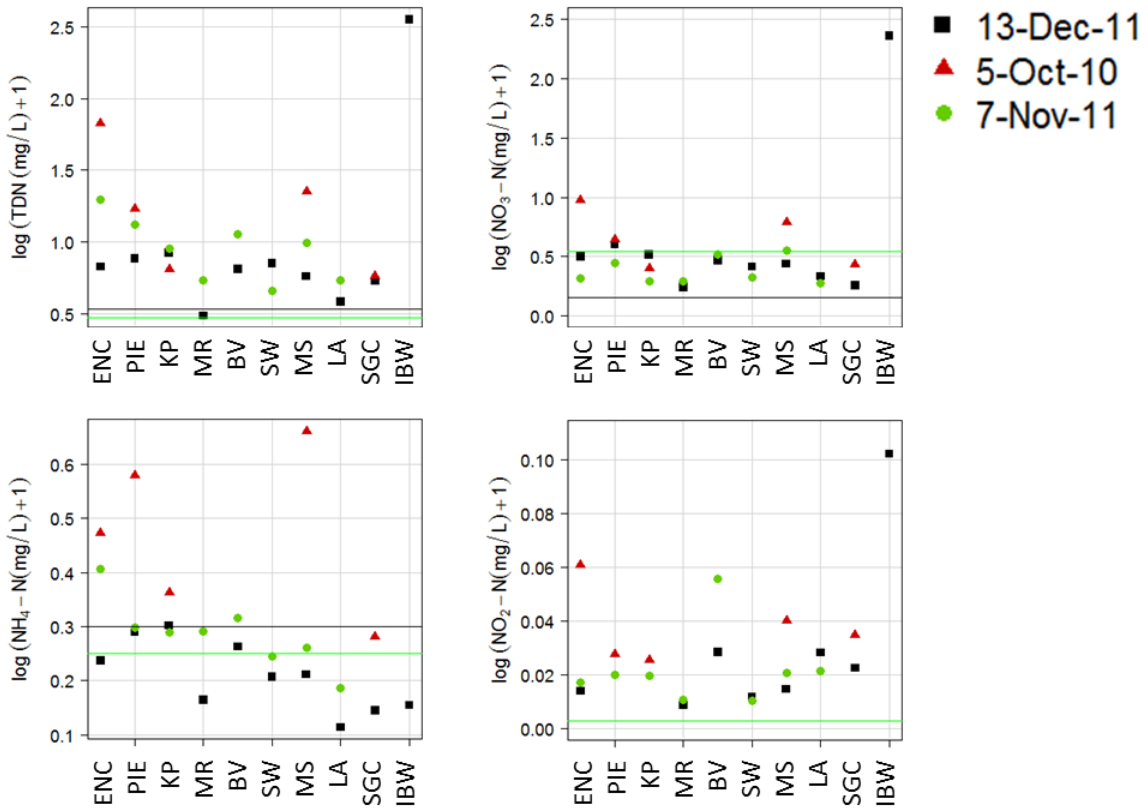Figure 5.4. Variation in rain chemistry, N speciation, and NO3- isotope chemistry across sampled events.

Figure 5.5. Concentrations of N species in rainfall and runoff from urban watersheds across three sampling dates. Note that there is no rain chemistry for 5 Oct 2010. Rainfall chemistry for each event is indicated by a horizontal line.
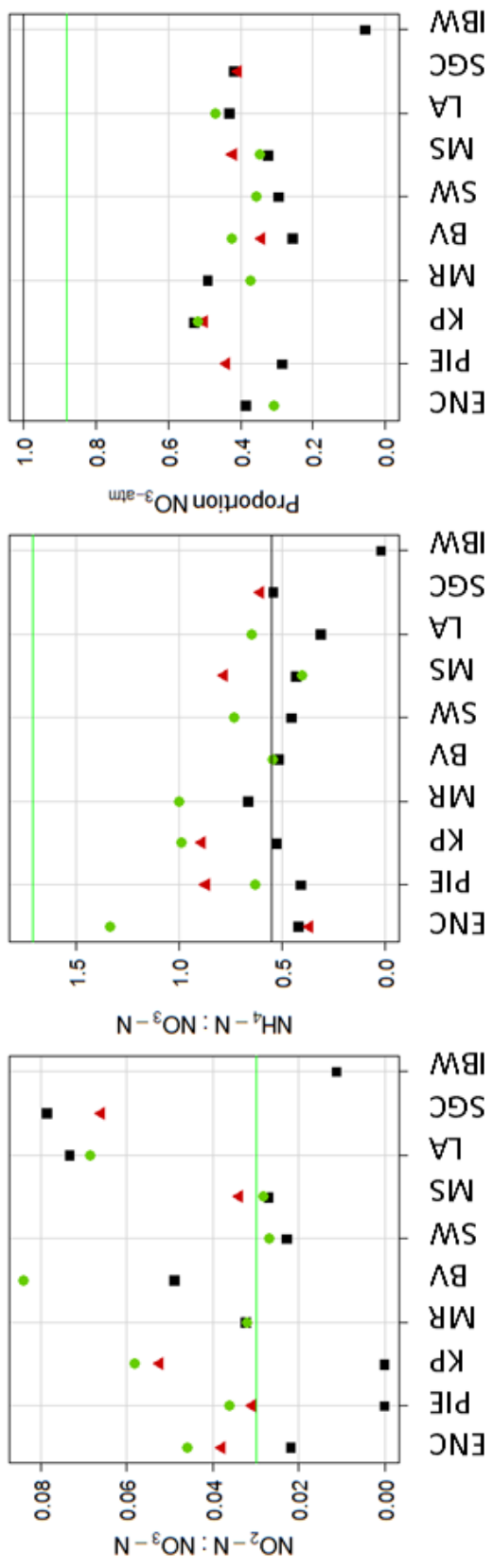
Figure 5.6. Speciation of N in rainfall samples and stormwater runoff from urban watersheds across three storm dates. Symbols are as in Fig. 5.5. Rainfall chemistry for each event is indicated by a horizontal line.
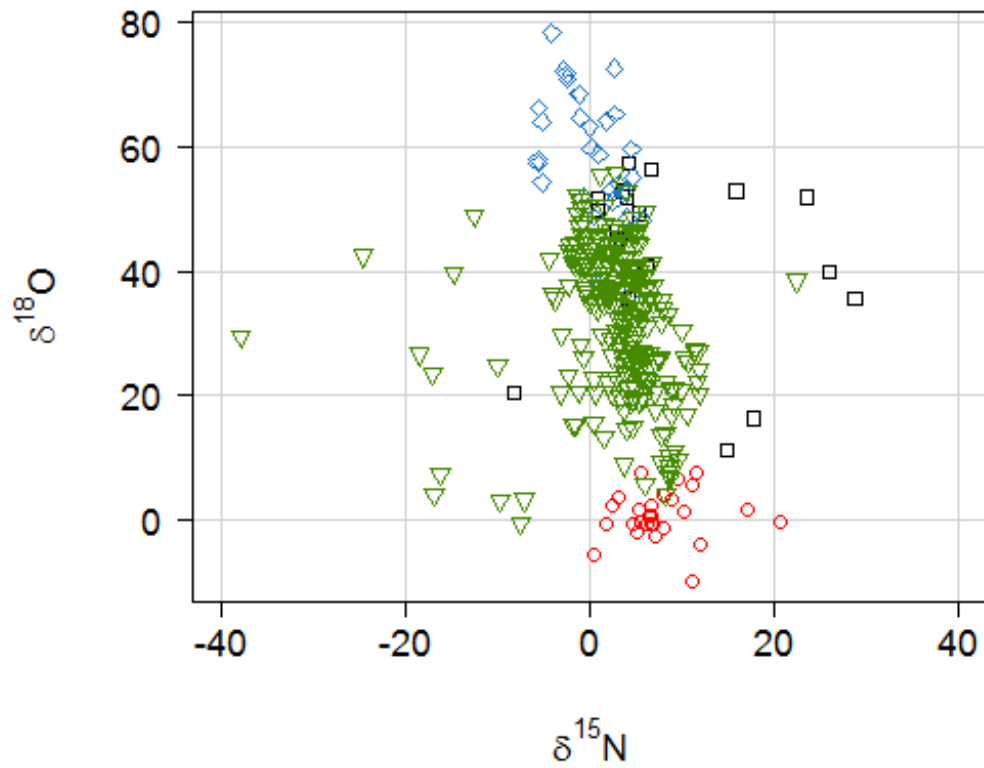
Figure 5.7. Dual isotope plot of all samples. Blue diamonds indicate rainfall samples, red dots indicate soil samples, black squares indicate impervious surface samples, and green triangles indicate stormwater runoff samples.
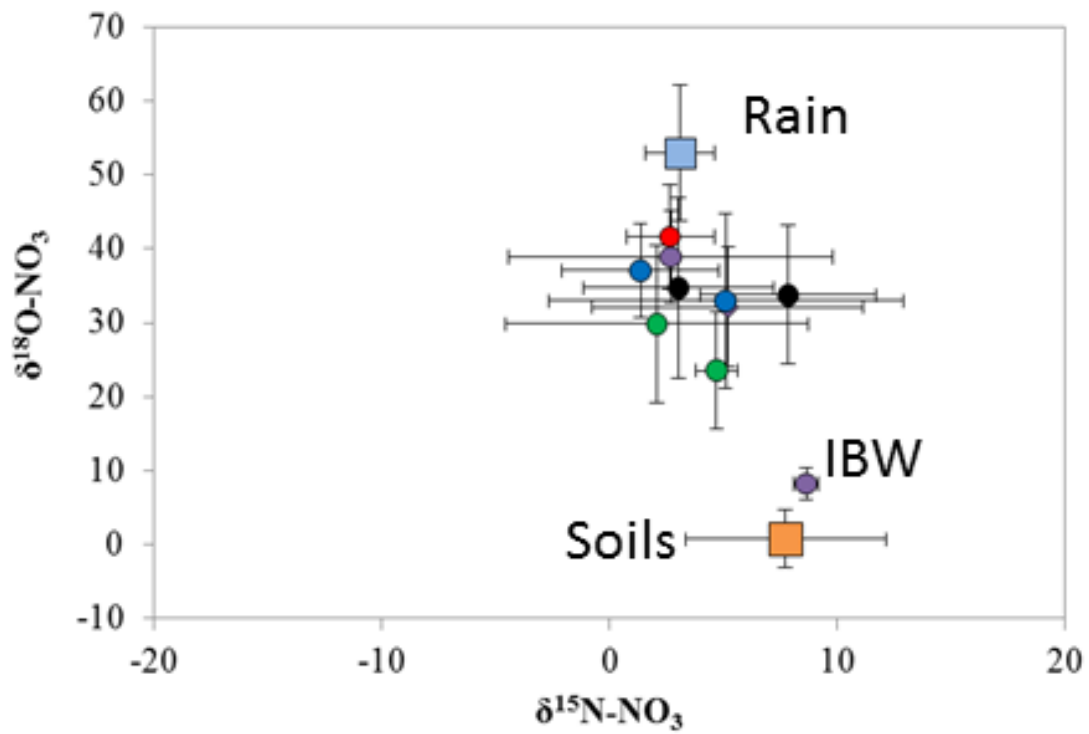
Figure 5.8. Dual isotope plot of means and standard deviations across all soil samples, 13 Dec 2011 rainfall samples, and runoff samples from each site during the 13 Dec 2011 event.
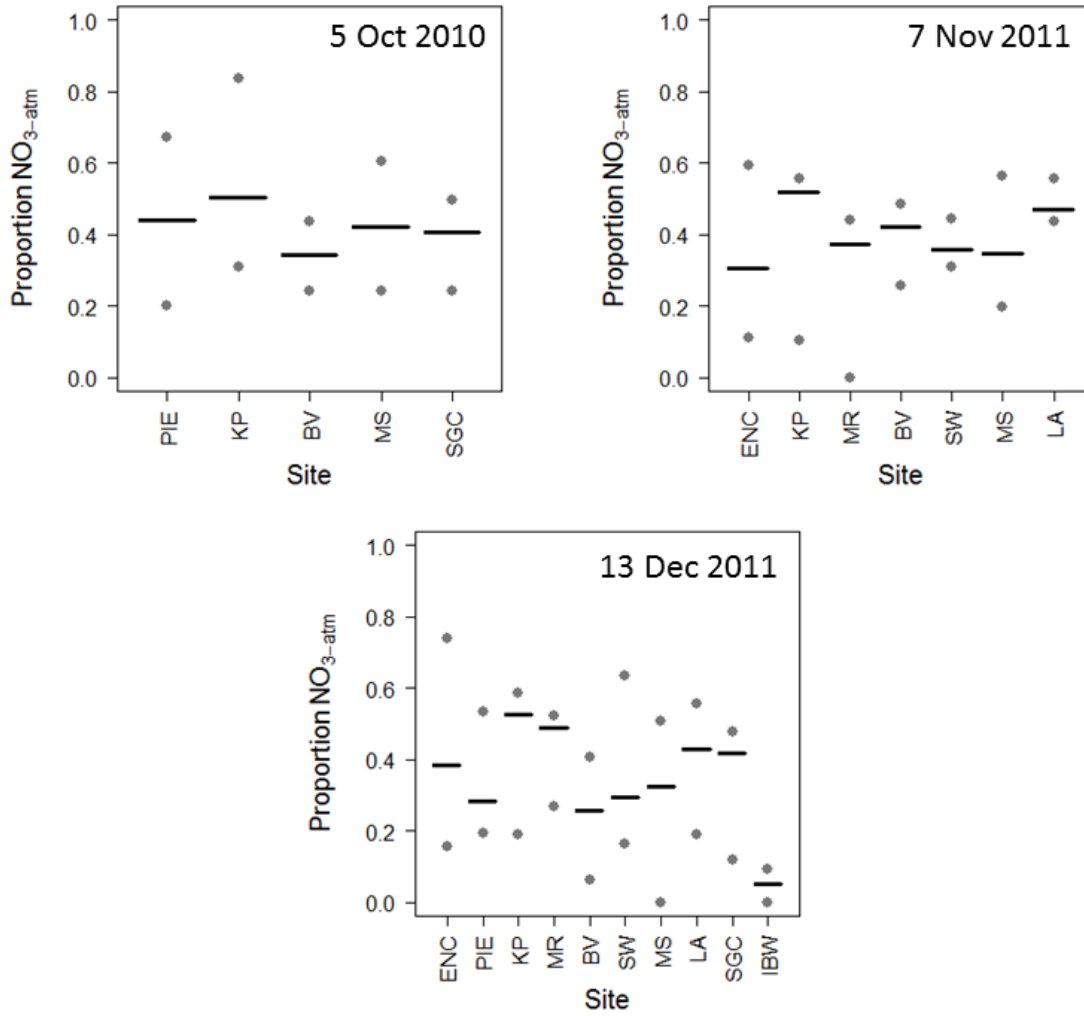
Figure 5.9. Proportion of total atmospheric NO_3^- load (black bars), and minimum and maximum $NO_3^-{}_{atm}$ observations (gray dots) at each site across three events.
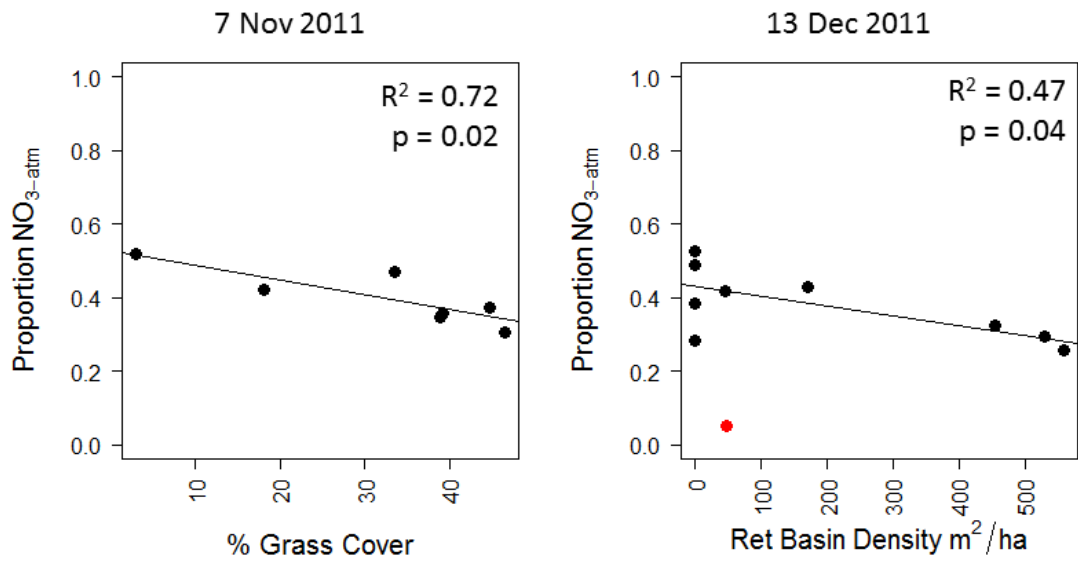
Figure 5.10. Significant relationships between total atmospheric proportion of NO_3^- and watershed characteristics for three storm events (there were no significant relationships for 5 Oct 2010). Regression statistics for 13 Dec 2011 exclude data from IBW (red point in figure).
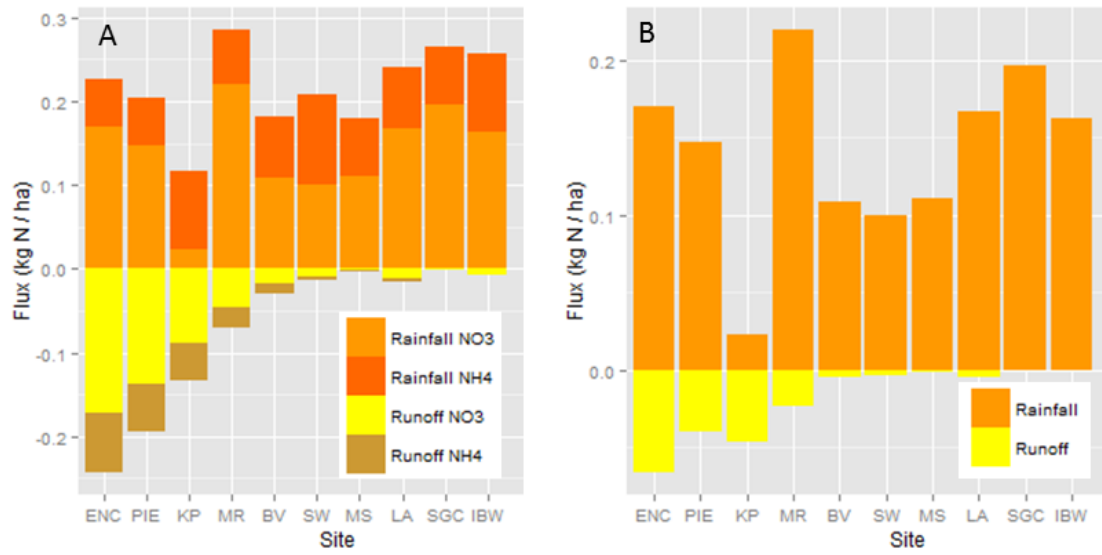
Figure 5.11. Inputs in rainfall and outputs in runoff for each site during the 13 Dec 2011 event of A) dissolved inorganic N, and B) atmospheric NO_3^-.
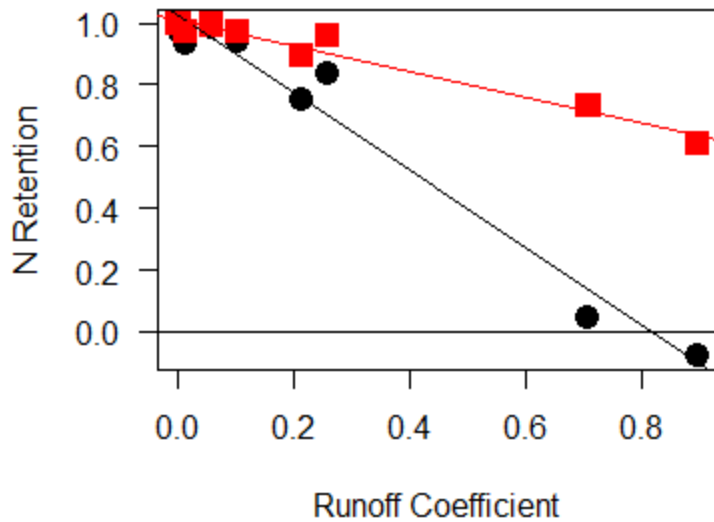
Figure 5.12. Relationship between event N retention and runoff coefficient across watersheds during the 13 Dec 2011 event. Black points indicate retention of DIN (linear regression: $R^2 = 0.97$, df = 7, p < 0.0001), red squares indicate retention of atmospheric NO_3^- (linear regression: $R^2 = 0.95$, df = 7, p < 0.0001). Note that KP is excluded from figure. When KP is included in the analysis, there is not a significant relationship between $NO_3^-_{atm}$ retention and RC, but there is a significant relationship between DIN retention and RC ($R^2 = 0.90$, df = 8, p < 0.0001).

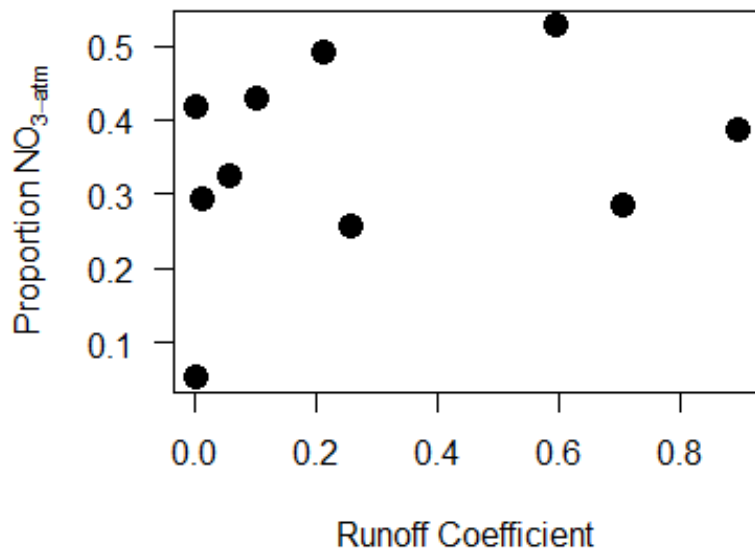Figure 5.13. Relationship between the proportion of atmospheric NO_3^- in stormwater runoff and the runoff coefficient for watersheds during the 13 Dec 2011 event. Relationship is not statistically significant ($R^2 = 0.08$, df=8, p = 0.43).
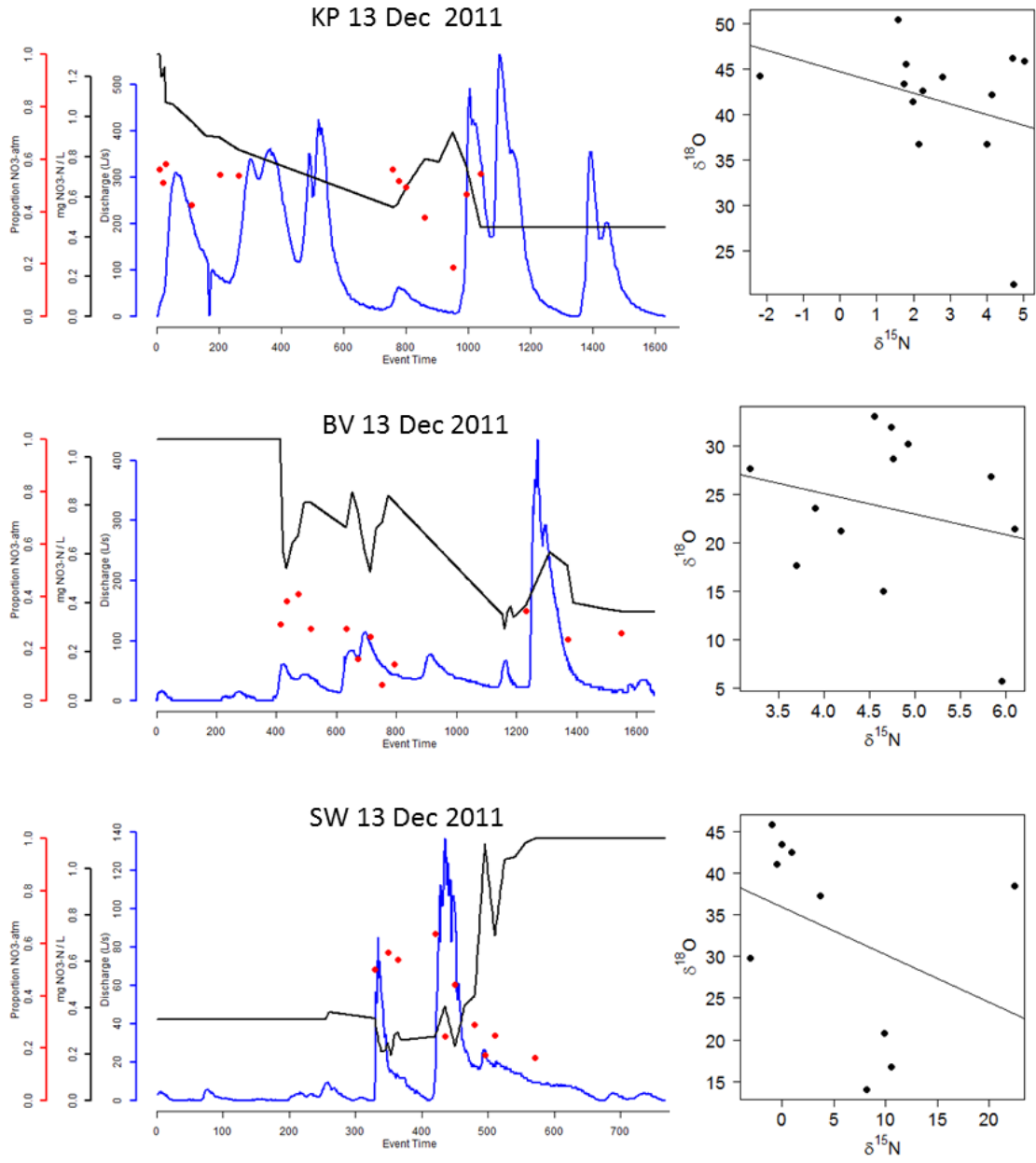
Figure 5.14. Hydrographs (blue line), NO_3^- concentration (black line), proportion $NO_3^-{}_{atm}$ (red dots), and dual-isotope plots for three sites during the 13 Dec 2011 event.
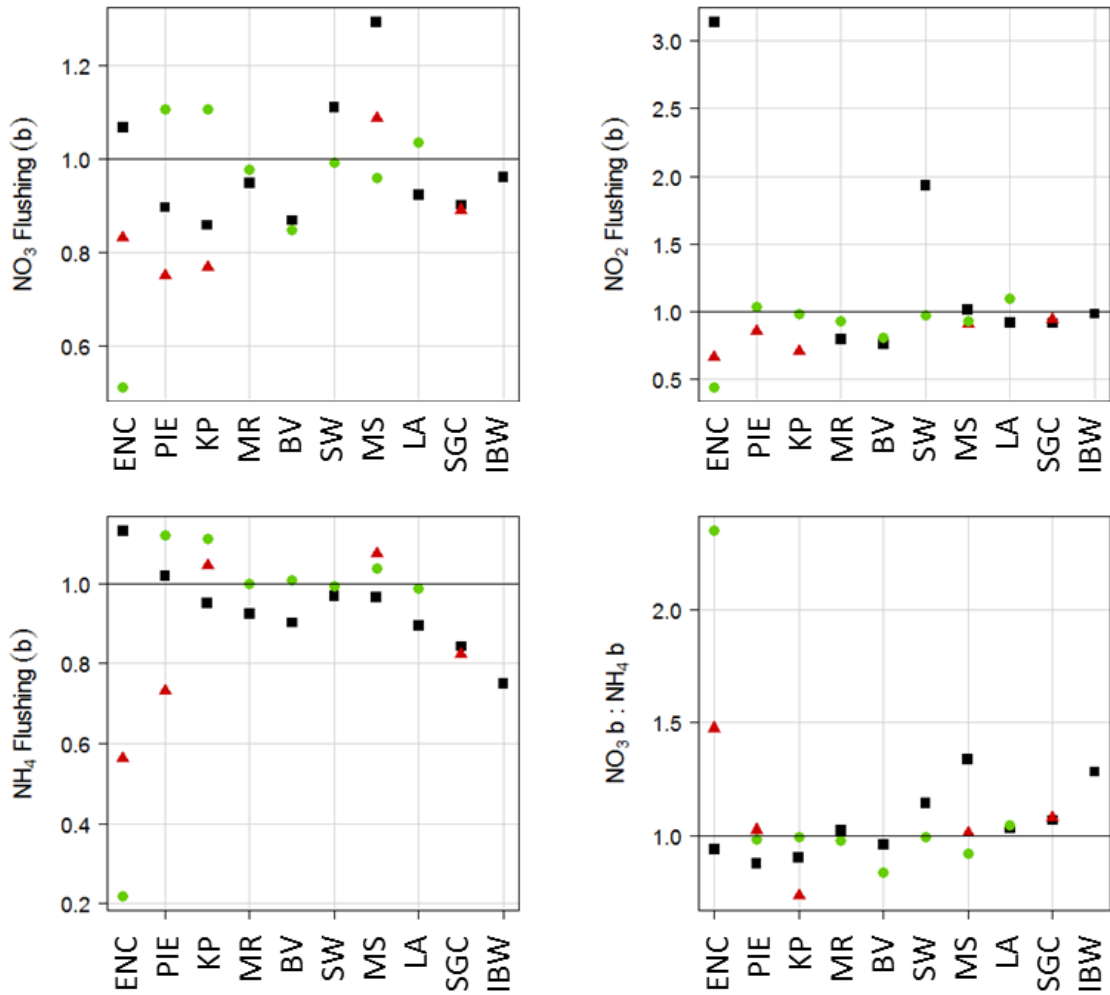
Figure 5.15. Delivery of N species relative to discharge across three events as measured by *b* parameter (see text for calculation). Horizontal line indicates b = 1. Points above the line indicate transport limitation, and points below the line indicate flushing (supply limitation). Symbols are as in Fig. 5.5.
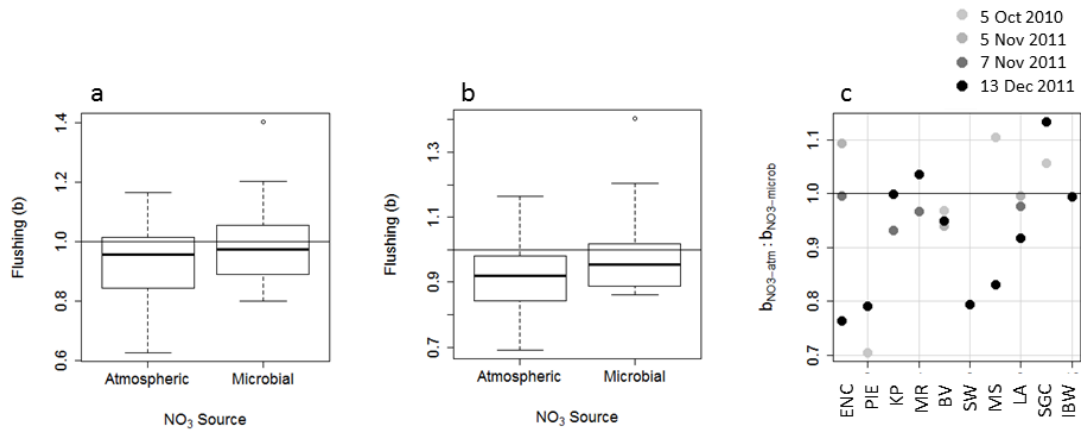
Figure 5.16. Flushing characteristics of NO$_3^-$ by source A) across all observed events (one-tailed paired t-test, t=-2.06, df=20, p = 0.03), B) during the 13 Dec 2011 event (one-tailed paired t-test, t=-2.17, df=9, p = 0.03), and C) ratio of atmospheric NO$_3^-$ flushing to microbial NO$_3^-$ flushing across sites and events.

Chapter 6

SYNTHESIS: DISENTANGLING MULTIPLE ANTHROPOGENIC DRIVERS OF

WATERSHED NUTRIENT YIELDS FROM SOCIAL-ECOLOGICAL WATERSHEDS

Human activities are driving global environmental change via multiple pathways:

land-cover change, climate change and resultant effects on hydrology, and altered global

biogeochemical cycles (Vitousek et al. 1997b, 1997a, Foley et al. 2005, Rockstrom et al.

2009). Nutrient cycles have been dramatically affected at local to global scales,

accelerating rates of biogeochemical cycling and threatening the sustainability of the

ecosystems upon which our economies and well-being depend (Carpenter et al. 1998,

Foley et al. 2005). Researchers have made great strides in understanding the patterns and

drivers of altered nutrient cycles and the hydrologic effects of extensive hydrologic

engineering. However, scholars in these fields have not yet adequately addressed the

interactions between hydrology and biogeochemistry within the context of global

environmental change. Without an understanding of the indirect effects of hydrologic

alterations on biogeochemical changes, policy solutions to nutrient pollution may not

consider the full suite of drivers that need to be addressed or may unnecessarily limit

possible policy options for the management of nutrient pollution.

This dissertation addresses this gap by explicitly considering the role of climate,

anthropogenic nutrient inputs, and hydrologic alterations in controlling nutrient transport.

I evaluated the importance of these drivers in two systems that contrasted in spatial and

temporal scale as well as in climate. In this synthesis, I first summarize the key findings

from these two systems. I then return to the broad conceptual framework introduced in

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Chapter 1 (Fig. 6.1) and introduce and discuss a more mechanistic framework based on the results of this dissertation. I end with a brief discussion of the implications of this research for nutrient management.

Drivers of nutrient delivery are diverse

In the northeastern United States (NE) over the 20th century, human use of nutrients was dynamic (Fig. 6.1, Box F), responding to changing technology, land use, demographics, regulations, and the economy. Hydrologic infrastructure was spatially and temporally heterogeneous across the NE as well. Underlying heterogeneity in human activities was interannual climate variability. Nutrient inputs to the NE became spatially segregated over time by type. That is, land use and associated nutrient inputs became more distinct, with urban areas becoming more urban and agricultural areas becoming dominated by agricultural inputs. Although the types and amounts of nutrient inputs were strongly related to land use (Chapter 2), the relationship between land use and nutrient inputs was not static over time and space (Chapter 2; Broussard and Turner 2011). Nutrient management policy did directly affect two specific types of nutrient use: P in detergents and in lawn fertilizers. However, most changes in nutrient use in the NE over time were not related to direct nutrient management policies. Rather, agricultural P fertilizer use responded to changes in agricultural policy and the resulting fluctuations in P fertilizer prices. The spatial and temporal patterns of human food nutrient use were driven by larger-scale social trends, such as suburbanization and the movement westward of crop agriculture. All types of nutrient use were constrained by the technology to

produce and use nutrients, and direct nutrient management policy was constrained by current scientific understanding of how nutrient pollution affects ecosystems.

The relationships between nutrient inputs and nutrient exports from NE watersheds changed over time (Chapter 3). Watershed retention of N and P inputs increased over the 70-year study period. Interestingly, the strongest correlates of spatial and temporal variation in loads differed. At the regional scale, changes in N and P loads over time were related to changes in infrastructure. Within the region, variation in load over space was correlated with patterns of nutrient inputs. Furthermore, N and P responded differently to infrastructure and climate due to their different mobility in soils. N and P were also subject to different trends in inputs. These differences combined to create spatial and temporal variation in the stoichiometry (i.e., elemental ratios) of nutrient yields and therefore to generate the potential for heterogeneity in ecosystem nutrient limitation and ecosystem response to nutrient loading.

Although occurring on different time scales, N yields from Phoenix, AZ watersheds were related to a similar set of characteristics: land use, land cover, infrastructure, and climate (storm characteristics). I used a path analysis to assess how land cover, infrastructure, and storm characteristics affected solute delivery indirectly through effects on runoff and concentration (Chapter 4). Delivery of solutes (N species, P, dissolved organic carbon, and chloride) was correlated with both runoff (transport) and solute concentration (supply), but runoff was more important than concentration for all solutes. Runoff, in turn, varied with land cover, storm characteristics, and infrastructure. Impervious surfaces were associated with increased runoff generation, as was the amount of precipitation. The type of stormwater infrastructure in the watershed affected how

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runoff was conveyed through the watershed. Infrastructure that was designed to retain (retention basins) or slow (engineered channels) runoff was effective at reducing event runoff and solute delivery. Comparison of my results, where land use was controlled for, with results from previous stormwater research in Phoenix that included a range of land uses, suggested that land use was an important watershed control on solute concentrations. This comparison highlights an important difference between land cover and land use with respect to their effects on nutrient transport.

Although I did not find significant relationships between land cover and nutrient concentrations in Chapter 4, isotopic analysis presented in Chapter 5 suggests that land cover did affect rates of biogeochemical cycling. The absence of atmospheric nitrate (NO_3^-) in residential yards suggests a rapid processing of N deposited from the atmosphere. However, variation in biogeochemical processing rates across land-cover types did not translate into effects on the amount of N (or NO_3^-) in the watershed or in stormwater runoff. I found no isotopic evidence of biogeochemical cycling during storms and no differences in the sources of NO_3^- across watersheds with different stormwater infrastructure. However, N retention during an event was strongly related to runoff coefficient. These results suggest that the mechanisms linking stormwater infrastructure and nutrient delivery were hydrological rather than biogeochemical.

A framework for disentangling multiple anthropogenic drivers of nutrient delivery

The objective of this dissertation was to address the implications of coupled biophysical systems that are managed by separate and decoupled decision-making. Figure 6.1 describes the scope and context of this research. Specifically, I assessed sources of

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variability in watershed nutrient loads (Fig. 6.1, Box G) from climate (Box D), hydrology and anthropogenic modifications of the water cycle (Boxes B and C), and anthropogenic nutrient use (Box F). My dissertation highlighted the strong coupling of hydrology and nutrient delivery in social-ecological watersheds within two very different contexts. My results and this conceptual framework highlight the need to integrate scientific research and decision-making processes across coupled biophysical systems. From the scientific research perspective, models need to consider the many possible indirect effects of human activities on the system of interest. Nutrient delivery may be more strongly affected by flood control engineering than by any human behaviors directly related to nutrient use. As a result, dynamic changes in the system may result from feedbacks unrelated to nutrient biogeochemistry. For example, in Phoenix watersheds, nutrient delivery was strongly related to infrastructure design (Chapter 4). Yet temporal changes in design were driven by urban flooding objectives and were unrelated to nutrient management. From the decision-making perspective, this framework illustrates two key points. First, management of coupled biophysical systems can have unintended consequences if couplings are not taken into consideration. A dramatic example is the Mississippi River system, which has been drastically modified with the intention of altering hydrologic patterns, but which has also had the unintended consequences of severely degrading the river delta due to changes in sediment loads (Blum and Roberts 2009). The second consideration for decision-makers is that coupled biophysical systems can expand the potential realm of policy options. In the case of nutrient management, this means that beyond nutrient use management exist options within the realm of hydrology and hydrologic engineering.

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Within this broad framework, my dissertation addresses the mechanistic linkages between climate, altered hydrology, nutrient use, and nutrient delivery. Based on my findings, I developed a more circumscribed and mechanistic conceptual model for describing the multiple pathways through which human activities affect nutrient delivery (Fig. 6.2).

Supply and Transport

As a first step in disentangling anthropogenic drivers of nutrient delivery, I categorized variables in terms of the mechanisms linking them with nutrient delivery. Specifically, I have identified two key intermediate variables – the supply of nutrients in the watershed and the transport of those nutrients downstream. This distinction has the benefit of conceptually isolating human activities that directly affect biogeochemistry (corresponding to Fig. 6.1 Box F and Arrow 2) and those that affect biogeochemistry via hydrology (corresponding to Fig. 6.1 Arrow 4). A second benefit is that the importance of nutrient supply can now be compared with that of transport. This could be strategically important for decision-makers (i.e., Is it more important to manage inputs or hydrologic systems?). It also parallels the concept of supply- and transport-limitation which has been developed in the literature on sediment transport (e.g., Worrall and Burt 1999, Nistor and Church 2005, Blum and Roberts 2009) to describe the delivery of sediment (or solutes) from watersheds. Human activities affect both supply and transport, but they do so in different ways that are often not coordinated.

The balance of transport and supply depends on the solute and the system in question. Previous researchers have suggested that the delivery of some solutes is consistently transport-limited, others supply-limited, and still others chemostatic (Worrall

and Burt 1999, Nistor and Church 2005, Godsey et al. 2009, Thompson et al. 2011, Gallo et al. 2013). My research also suggests that behavior varies from element to element. For example, some differences between N and P delivery in the NE were driven by their different mobility in soils. Year-to-year climate variation was more important in driving annual N yields, suggesting transport limitation, whereas P was more strongly affected by variability in inputs, suggesting supply limitation. The balance of supply and transport limitation also depends on the study system in question, what has been controlled for in the study design, and what is most variable across study units. In the NE, I found that transport (infrastructure) was the strongest correlate with temporal variation in N and P yields from the region, but that supply (inputs) were the strongest correlate with spatial variation within the region (Chapter 3). Similarly, the fact that I controlled for land use in the selection of stormwater monitoring sites meant that transport-limitation was the dominant behavior observed (Chapter 4).

Controls on supply

I did not explicitly test the effects of land use in either of these studies, yet it emerged in both as an important control on nutrient supply in watersheds (Fig. 6.1; Chapters 2 and 4). Land use is a metric to describe human behavior. As a description of the types of activities are taking place on the landscape, land use is therefore linked to the use of nutrients. Importantly, the relationship between land use and nutrient use is not static, but dynamic over space and time (Chapter 2). How land use translates into nutrient use depends on the regulatory, technological, and economic context of the system.

In contrast to land use, which is more of a measure of human behavior, land cover describes the physical aspects of land surface (Cadenasso et al. 2007). As a result, land

cover is likely to be more closely connected to runoff-generation processes and biogeochemical process rates. Across these two studies, land cover was not a good predictor of nutrient supply within watersheds. However, stable isotope work in Phoenix (Chapter 5) suggested that even though land-cover type did not affect the supply of N, biogeochemical processing was occurring at different rates across the landscape according to land cover. While this does not indicate a strong relationship between land cover and supply, and is therefore represented with a dashed line in Figure 6.1, it does indicate a potential relationship between land cover and the sources and speciation of N.

Finally, time is likely to be an important variable in many systems. In this case, I use time to describe the time over which nutrient inputs are occurring. Time emerged as an important variable in the urban stormwater system, where the number of rain-free days was a good predictor of most solute concentrations (Chapter 4). Time did not emerge in the nutrient transport models for the NE, but other researchers have suggested that this is could be an important variable to consider, especially in areas where nutrient inputs, such as fertilizer, are likely to accumulate over time (e.g., Park 1950).

Controls on transport

In both study systems, nutrient transport was strongly affected by climate, land cover, and infrastructure. Climate is fundamental to understanding transport because precipitation provides the transport vector of interest – water. However, transport also requires consideration of energy balances, as runoff depends not only on inputs, but also losses via evaporation and transpiration. This was built into the NE study as part of the water balance model (Fekete 2002). We did not consider evaporative losses in the stormwater research, due to the technical challenges and data requirements for modeling

evapotranspiration in urban areas. However, precipitation was an important control on transport in urban watersheds.

As mentioned above, land cover can be an important control on runoff generation processes. Runoff generation is determined by point-scale water balance: inputs as precipitation, and losses to soil water storage, infiltration, evapotranspiration, and runoff. Both natural and built land cover affects surface properties and local water balance. Impervious surfaces, for example, reduce infiltration and increase runoff (Chapter 4, Arnold and Gibbons 1996, Brabec et al. 2002). Runoff generation is also determined by vegetation cover and soil type, variables that were incorporated into the NE work via the water balance model (Fekete et al. 2002). It is important to note here that runoff generation is a point-scale process and does not necessarily correlate with the amount of runoff that is conveyed to the base of the watershed. Land cover may also be important for understanding conveyance, but variables such as configuration are likely to be more important than composition (Hatt et al. 2004, Walsh et al. 2005, Cadenasso et al. 2007, Alberti et al. 2007). I did not evaluate the role of land cover configuration in either of these studies. However, in Phoenix, land cover composition (% imperviousness) was correlated with stormwater runoff at the watershed scale.

Finally, the objective of this dissertation was to evaluate the importance of hydrologic infrastructure. I conclude from the two study systems, encompassing different spatial and temporal scales, that the impacts of hydrologic infrastructure are expressed predominantly via transport. Hydrologic infrastructure directly impacts the transport of water and whatever materials it is carrying. This pattern was found across a range of infrastructure types including stormwater drainage, wastewater removal, and reservoirs

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that were used for either or both water supply and flood control. The effects of infrastructure may be solely via transport, or infrastructure may moderate opportunities for biogeochemical cycling and retention. Researchers have long noted that changes in hydrology, flow paths or the velocity of flow, for example, can provide opportunities for biogeochemical processes (Groffman et al. 2002, McClain et al. 2003, Grimm et al. 2003, Dent et al. 2007). Research on coupled hydrology and biogeochemistry of riparian zones and the hyporheic areas of streams are emblematic examples (Groffman et al. 2002, McClain et al. 2003, Grimm et al. 2003, Dent et al. 2007). Previous research in urban ecosystems has suggested that the lack of hydrologic connection and decreases in transient storage have contributed to increased nutrient delivery from urban watersheds (Groffman et al. 2002, Grimm et al. 2005). Reservoirs have also been found to increase opportunities for nutrient removal via biogeochemical mechanisms (Alexander et al. 2008, Harrison et al. 2009, Miller 2012). The hydrologic or biogeochemical mechanisms linking infrastructure and nutrient transport in the NE were not identifiable from the modeling approach used. However, it was clear that reservoirs reduced nutrient delivery from watersheds and that sanitary sewers increased nutrient delivery by bypassing the removal capacity of watershed soils. In the urban watersheds, evidence from the path analysis and isotopic results suggest that stormwater infrastructure did not affect biogeochemical cycling at the event scale. Rather, nutrient delivery was related to changes in hydrology associated with different infrastructure types. The general patterns across sites were similar and intuitive: infrastructure that sped water and material delivery (i.e., sanitary sewers, storm sewers) increased yields, whereas infrastructure that increased hydrologic residence time and contact with soils and sediments (i.e., retention

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basins, reservoirs) reduced watershed nutrient yields. These clear patterns suggest that hydrologic infrastructure is a critical watershed feature to include in models of nutrient delivery, regardless of scale.

<u>Benefits of this model</u>

This model explicitly breaks down human activities and the mechanisms linking those activities to changes in nutrient transport, specifically, effects on supply and transport limitation. The selection of these variables and the mechanisms linking them with solute delivery were derived from research in these two systems. Less important than the specific linkages presented in Figure 6.2 is the approach. Human-driven environmental change can be enormously complex, but simple frameworks such as this can be tools for simplifying problems. Complexity can then be added into conceptual and mathematical models as needed to explain patterns within or across sites. Disentangling multiple drivers is necessary due to frequent co-variation between variables within the model. For example, urban land use is often associated with changes in land cover (increased imperviousness) and infrastructure (stormwater, wastewater). However, these associations are not consistent enough to limit focus on a narrow range of variables. In fact, variation in land cover within land use, or variation in infrastructure within land cover is likely why many models to date have had limited explanatory power.

<u>Understanding social-ecological watersheds as dynamic systems</u>

Returning to the broader conceptual model (Fig. 6.1), this dissertation has demonstrated that the linkages between hydrology, nutrient delivery, and climate are strong (Arrows 2, 3, and 4). However, it is important to understand social-ecological watersheds as dynamic systems. Climate change is an important exogenous source of

variability in all ecosystems, and one that is rapidly changing (Milly et al. 2008).

Hydrology and nutrient transport are strongly related to infrastructure and human

behaviors (Fig. 6.1). A key finding from both studies was the temporal and spatial

heterogeneity in hydrologic infrastructure and human behaviors (Chapters 2, 3, and 4).

Nutrient inputs to the NE (Fig. 6.1, Box F) were dynamic and varied with economics,

technology, and land use (Chapter 2). Hydrologic infrastructure in both studies varied

over time and space (Chapters 3 and 4). This variation at times reflected the expansion of

a particular type of infrastructure – such as sanitary sewers. However, urban stormwater

infrastructure variation entailed not only spreading use of storm pipes, but also temporal

variation in design that fundamentally altered how water moved through urban

watersheds. These findings suggest that hydrologic infrastructure may be a major source

of spatial and temporal variability in watershed functioning.

Implications for Nutrient Management Policy

It is my hope that this research will help elucidate the suite of policy options

available to decision makers with regard to nutrient management at the watershed scale.

With regard to decision-making, a main conclusion from this research is that

management must consider multiple biophysical domains. Nutrient delivery is controlled

by two biophysical domains: hydrology and biogeochemistry, and multiple management

domains: agricultural policy, economics, technology, and others.

This dissertation highlights the importance of hydrology for nutrient management.

Hydrologic infrastructure directly affects the transport of nutrients downstream and can

be managed to increase opportunities for biogeochemical removal. Management may also

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focus on controlling the supply of nutrients in the landscape. A key finding is that

nutrient inputs and supply are not strictly determined by use. There are many gains to be

made in terms of efficiency. History illustrates both the dynamics of nutrient use and

instances of increased efficiency, such as with agricultural N and P fertilizer use. A

second finding with regard to nutrient use is that not all inputs have clear beneficial uses

and not all inputs are intentional. Atmospheric N deposition was a major input in both

studies. Urban watersheds processed a remarkable amount of N deposition, but

atmospherically derived NO_3^- was still more than 20% of NO_3^- load in most watersheds.

Similarly, atmospheric deposition made up ~50% of N inputs to the NE by the end of the

20th century.

Finally, the research in Chapter 2 illustrates that there are multiple pathways to

influence nutrient use. Direct regulations do have a history of effective nutrient use

reduction, but these have only been applied in specific cases: detergent P and lawn P

fertilizers. Direct regulations are less likely to emerge or be effective with regard to other

types of nutrient use. However, policies not directly aimed at driving nutrient use have

had substantial impacts. Agricultural policy contributed to the price fluctuations that

drove changes in P fertilizer use during the 1970s. Other drivers of nutrient use may be

less manageable to manipulate, but could be included in the suite of policy options.

Urban planning, for example, can be used to affect the amount and spatial patterns of

land use and land cover, indirectly affecting nutrient inputs and transport.

Overall, my research shows that human activities affect nutrient delivery via

multiple pathways. This multiplicity presents decision-makers with many opportunities to

manage nutrient delivery from watersheds. Yet this diversity also challenges our

understanding of how these systems work. A conceptual framework that applies to different temporal and spatial scales and situations is a step towards disentangling these multiple human drivers of change.

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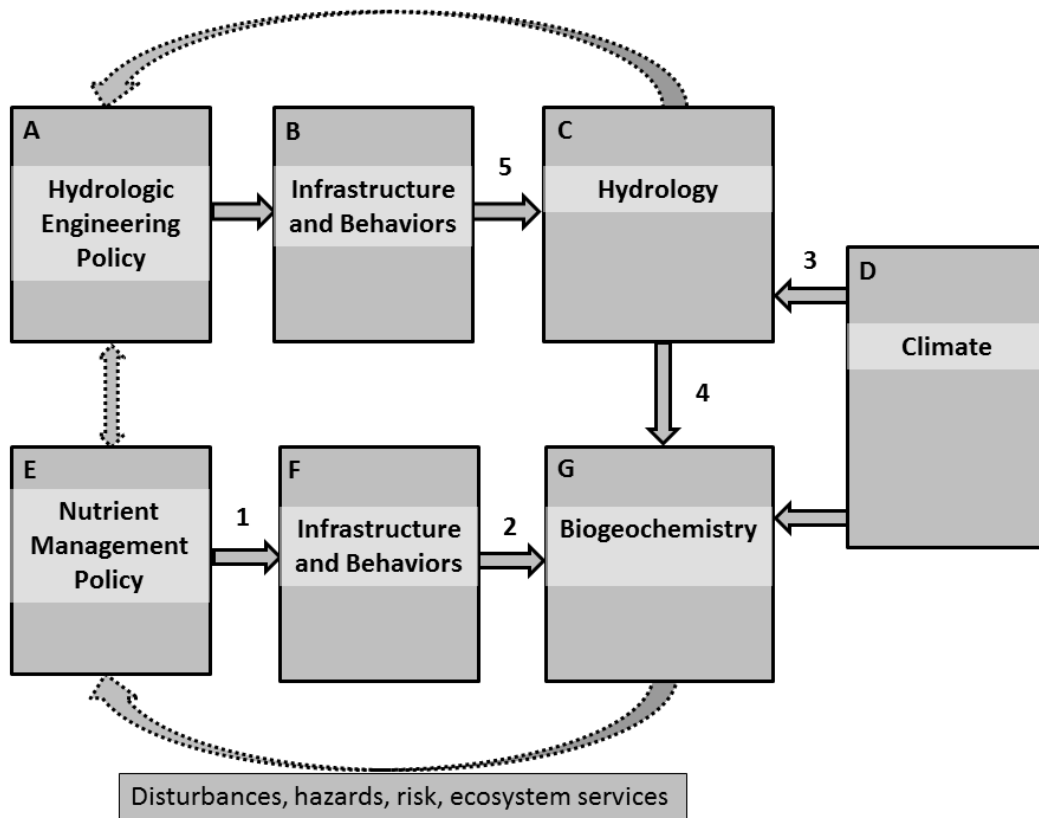
Figure 6.1. Conceptual framework for this dissertation. Labeled boxes and arrows are discussed in the text.
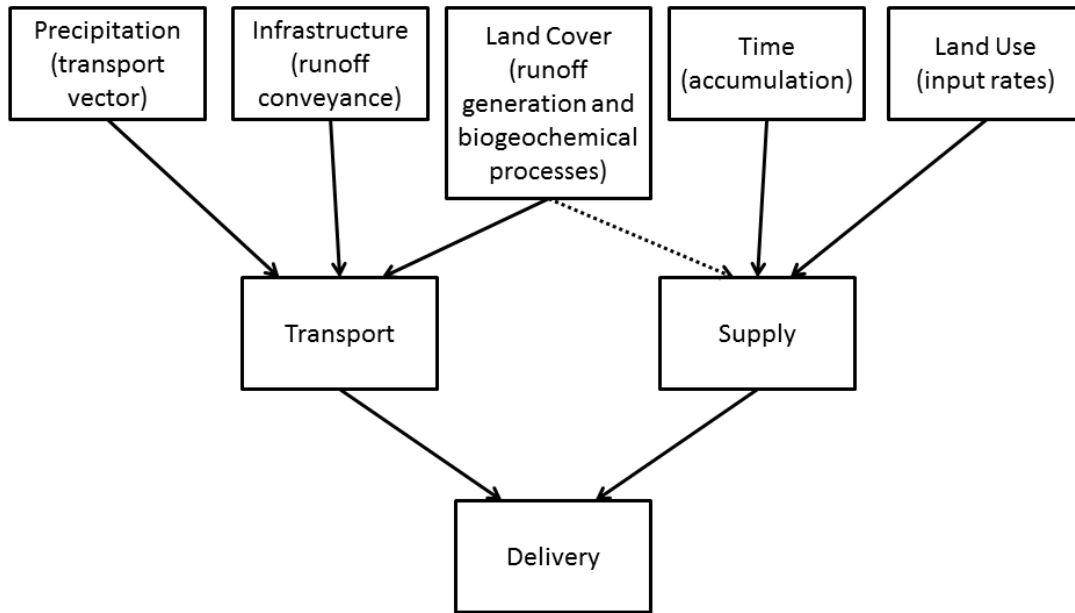
Figure 6.2 Conceptual framework for disentangling multiple anthropogenic drivers of watershed nutrient yields from social-ecological watersheds.