Direct and Indirect Ecological Consequences of Human Activities in Urban and Native Ecosystems

by

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ABSTRACT

Though cities occupy only a small percentage of Earth’s terrestrial surface, humans concentrated in urban areas impact ecosystems at local, regional and global scales. I examined the direct and indirect ecological outcomes of human activities on both managed landscapes and protected native ecosystems in and around cities. First, I used highly managed residential yards, which compose nearly half of the heterogeneous urban land area, as a model system to examine the ecological effects of people’s management choices and the social drivers of those decisions. I found that a complex set of individual and institutional social characteristics drives people’s decisions, which in turn affect ecological structure and function across scales from yards to cities. This work demonstrates the link between individuals’ decision-making and ecosystem service provisioning in highly managed urban ecosystems.

Second, I examined the distribution of urban-generated air pollutants and their complex ecological outcomes in protected native ecosystems. Atmospheric carbon dioxide (CO₂), reactive nitrogen (N), and ozone (O₃) are elevated near human activities and act as both resources and stressors to primary producers, but little is known about their co-occurring distribution or combined impacts on ecosystems. I investigated the urban “ecological airshed,” including the spatial and temporal extent of N deposition, as well as CO₂ and O₃ concentrations in native preserves in Phoenix, Arizona and the outlying Sonoran Desert. I found elevated concentrations of ecologically relevant pollutants co-occur in both urban and remote native lands at levels that are likely to affect ecosystem structure and function. Finally, I tested the combined effects of CO₂, N, and
O$_3$ on the dominant native and non-native herbaceous desert species in a multi-factor dose-response greenhouse experiment. Under current and predicted future air quality conditions, the non-native species (*Schismus arabicus*) had net positive growth despite physiological stress under high O$_3$ concentrations. In contrast, the native species (*Pectocarya recurvata*) was more sensitive to O$_3$ and, unlike the non-native species, did not benefit from the protective role of CO$_2$. These results highlight the vulnerability of native ecosystems to current and future air pollution over the long term. Together, my research provides empirical evidence for future policies addressing multiple stressors in urban managed and native landscapes.
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CHAPTER 1
INTRODUCTION

Cities are interlinked social and ecological systems. The structure and function of the urban environment are inextricably connected with people and their actions (Grimm et al. 2000; Pickett et al. 2001). Urban ecosystems are currently home to more than half the world’s population, though they occupy only a small percentage of Earth’s terrestrial surface (United Nations 2012). Further, by 2030, urban land cover is expected to nearly triple, and by 2050, over 65% of the world’s population will be city dwellers (Seto, Güneralp, and Hutyra 2012; United Nations 2012). Humans concentrated in cities are the direct and indirect drivers of local and global change, altering ecosystem structure and function, and in turn, ecosystem services across multiple scales (Vitousek et al. 1997). Thus, understanding the functioning of these complex human-environment systems is of growing environmental, social, and economic concern.

Ecosystems are rarely exposed to a single stressor, particularly in and around cities. Yet, the ecological impacts in urban and near-urban areas from multiple environmental stressors and their interacting effects are largely unknown. In order to better protect and manage ecosystems in the face of global changes, there is an urgent need to develop a more complete understanding and generalizable theory of cities and their social-ecological feedbacks using comparative approaches within and among cities (Grimm, Faeth, et al. 2008; Grimm, Foster, et al. 2008; Boone et al. 2012; Bettencourt 2013). This understanding of urban social-ecological functioning must also incorporate the complex effects and interactions of chronic and multiple global change factors resulting from
human activities (Zavaleta et al. 2003; Grimm, Faeth, et al. 2008; M. D. Smith, Knapp, and Collins 2009; Hidy and Pennell 2010). Using urban and surrounding native ecosystems as a model system, I address these gaps by examining the complex drivers and direct and indirect ecological outcomes of human activities on both managed landscapes and protected native ecosystems in and around cities.

SCOPE AND STRUCTURE OF THIS DISSERTATION

In Chapter 2, in collaboration with social and natural scientists, I examine the ecological effects of people’s management choices in residential yards and the social-biophysical drivers of those decisions. Residential properties compose nearly half of heterogeneous urban land area and can be hotspots of nutrient inputs and non-point source pollution into urban and surrounding systems. Often highly managed ecosystems where people directly interact with their outdoor environment, residential properties are ideal model systems for examining complex human-environment feedbacks. With an interdisciplinary approach I synthesize the growing body of literature on residential landscapes, including the social drivers of management practices, the ecological outcomes, and the social-ecological feedbacks and tradeoffs. Through this synthesis, I develop a conceptual approach to guide future research and understanding of these complex social-ecological systems. This work was completed in close collaboration with Kelli Larson (Schools of Sustainability and Geography and Urban Planning, Arizona State University) and Sharon Hall (School of Life Sciences, Arizona State University).
In Chapters 3–5, I examine the urban “ecological airshed” and the indirect impacts of human activities via urban-generated air pollutants on protected native ecosystems within and outside of the urban boundary. Atmospheric reactive nitrogen (N), ozone (O₃) and carbon dioxide (CO₂) are elevated near human activities. Individually, elevated N and CO₂ act as a resource stimulating primary production, while O₃ is a stressor and inhibits production. Urban air quality is expected to have significant impacts on protected lands in urban and surrounding native ecosystems, yet the co-occurring distribution of N, O₃, and CO₂ in protected lands is unknown. Further, little is known about their combined impacts, and possible non-additive synergistic (amplifying or greater than the sum of the individual effects) or antagonistic (canceling or less than the sum of the individual effects) effects on ecosystem responses at realistic and predicted future concentrations in cities and more remote regions.

For this research, I focus on Phoenix, Arizona and the surrounding Sonoran Desert as a case study and part of the Central Arizona-Phoenix Long-term Ecological Research (CAP LTER) project. Arid and semi-arid ecosystems cover over a third of the world’s terrestrial land and human population growth and urban expansion are occurring more rapidly in dryland ecosystems than other ecosystem types (MEA 2005; United Nations 2012). The Phoenix metropolitan area, situated in the northern Sonoran Desert, is home to over 4 million people who have significant impacts on ecosystems and air quality.

In addition, this research builds on previous unexpected findings from the Sonoran Desert that reveal limited responses by herbaceous vegetation to elevated urban N deposition, even in rainy years (Hall et al. 2011). Furthermore, Schmoker/Davis and colleagues (In prep) found that while herbivory accounted for 30% loss of winter
herbaceous biomass in dry years, the rates of herbivory are not significantly higher in the urban than outlying locations. Thus, herbivory in cities does not account for the unexpected findings reported by Hall and colleagues (2011). Together, these results suggest that other co-occurring factors related to urbanization and human activity (e.g., elevated CO$_2$, O$_3$, or temperature) may play a significant role in modulating annual plant production. I test this by examining the distribution of ecologically relevant pollutants and their combined impacts on the dominant Sonoran Desert herbaceous species.

In Chapter 3, I specifically investigate the spatial and temporal distribution of N deposition to an arid ecosystem. Anthropogenic activities have doubled the rate of atmospheric reactive N inputs to many ecosystems worldwide with potentially significant ecological implications for biogeochemical cycling and biological diversity in recipient ecosystems (Vitousek et al. 1997; Galloway et al. 2008; Bobbink et al. 2010). Yet, N deposition to dryland ecosystems is not well characterized due to challenges in quantifying dry deposition and inputs from spatially and temporally patchy precipitation (Fenn et al. 2009). Using multiple sampling approaches, I examine the spatial and temporal patterns and dominant drivers of total wet and dry N deposition in urban and more remote outlying desert locations. Accurately estimating the rate and distribution of N deposition in native ecosystems is essential for determining where ecosystems exceed the critical load, the level at which negative ecological effects occur.

In Chapter 4, I focus more broadly on the “ecological airshed” created by multiple urban pollutants. These ecologically important atmospheric compounds are often transported into native ecosystems beyond the urban political boundaries in which they are generated and regulated. Some urban air pollutants (e.g. O$_3$ and O$_3$ precursors) are
regulated in cities and routinely monitored in dense urban areas for their human health implications. However, the extent of other ecologically significant atmospheric compounds, such as ground-level CO₂ and reactive N, within and outside of urban areas is less well known. Identifying the land area affected by the co-distribution of these atmospheric compounds is an important step for setting effective management and conservation strategies to protect native ecosystems and the ecosystem services they provide. Specifically, I monitor local and regional patterns of CO₂, O₃, and reactive gaseous N concentrations and deposition in native protected desert ecosystems in the urban and outlying regions of the Phoenix metropolitan area. In addition, I examine the small-scale variability of N and O₃ concentrations along a transect from the exterior to interior of a large protected desert area within the city. I expect areas in the interior to more closely resemble outlying native ecosystems with decreasing pollutant concentrations farther from the source (i.e. exterior edge). This study is the first to identify the distinct spatial pattern of co-occurring, ecologically important urban pollutants within protected lands.

In Chapter 5, I examine the combined ecological effects of co-occurring CO₂, N, and O₃. Though the individual effects of CO₂, N, and O₃ are well understood, it is uncertain if their combined impacts will cause non-additive (i.e. synergistic or antagonistic) ecosystem responses, which are more difficult to predict and model. In a multi-factor dose-response greenhouse experiment, I investigate the net growth and physiological responses of dominant native and non-native desert species found ubiquitously throughout the native desert near Phoenix, Arizona. Specifically, I test the combined impact of CO₂, N, and O₃ at levels that are reflective of current air quality conditions in
Phoenix, as well as predicted future air quality under current rates of global change (IPCC 2014). With the full factorial experimental design, I compare the potential for synergistic or antagonistic responses in multi-factor treatments. Ultimately, this research will provide empirical evidence relevant for future management decisions for preserving native ecosystems within the “airshed” affected by co-occurring pollutants.

Finally, in Chapter 6, I briefly synthesize the overarching findings and main contributions from this research, as well as suggest some next steps and implications for future management.
REFERENCES


http://www.ipcc.ch/


CHAPTER 2

RESIDENTIAL LANDSCAPES AS SOCIAL-ECOLOGICAL SYSTEMS: SYNTHESIS OF MULTI-SCALAR INTERACTIONS BETWEEN PEOPLE AND THEIR HOME ENVIRONMENT

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ABSTRACT

Residential landscapes are a common setting of human-environment interactions. These ubiquitous ecosystems provide social and ecological services, and yard maintenance leads to intended and unintended ecological outcomes. The ecological characteristics of residential landscapes and the human drivers of landscape management have been the focus of disciplinary studies, often at a single scale of analysis. However, an interdisciplinary examination of residential landscapes is needed to understand the feedbacks and tradeoffs of these complex adaptive social-ecological systems as a whole. Our aim is to synthesize the diversity of perspectives, scales of analysis, and findings from the literature in order to 1) contribute to a holistic, interdisciplinary understanding of residential landscapes and 2) identify research needs while providing a robust conceptual approach for future studies. We synthesize 256 studies from the literature and develop an interdisciplinary, multi-scalar framework on residential landscape dynamics.
From our synthesis, we find that complex human drivers, including attitudinal, structural, and institutional factors at multiple scales, influence management practices, which in turn determine biophysical characteristics of residential landscapes. However, gaps exist in our interdisciplinary understanding of residential landscapes within four key but understudied areas: 1) the link between social drivers and ecological outcomes of management decisions, 2) the ecosystem services provided by these landscapes to residents, 3) the interactions of social drivers and ecological characteristics across scales, and 4) generalizations of patterns and processes across cities. Our holistic perspective will help to guide future interdisciplinary collaborations to integrate theories and research methods across geographic locations and spatial scales.
INTRODUCTION

Residential landscapes are a primary setting of everyday interactions between humans and the environment (Bhatti and Church 2001). Approximately 75% of people in developed regions live in urbanized areas, and an estimated 41% of urban land area is used for homes and their surroundings (UN 2010; Nowak et al. 1996). Within the outdoor area surrounding homes (hereafter, “landscapes” or “yards”), turfgrass yards are highly managed ecosystems that rival corn as the most extensive irrigated crop in the US (Milesi et al. 2005). Along with gardens and more “natural” appearing lawn alternatives, these landscapes embody the idealized preferences and socially constrained practices of residents (Jenkins 1994; Robbins 2007). Similar to well studied agricultural systems (e.g., Matson et al. 1998; Tilman et al. 2002), residential landscapes provide important amenities while contributing to both intended and unintended environmental consequences (Martin 2008; Larson et al. 2009a). Residential landscapes are complex adaptive systems (sensu Holland 1995), in which multiple social and biophysical processes and feedbacks occur at a range of scales, from parcels and neighborhoods to watersheds and larger-scale regions. Thus, understanding the tradeoffs and feedbacks associated with these coupled human-natural systems necessitates interdisciplinary research that considers a variety of spatial scales.

Both social and natural science research have long explored human-environment interactions using disciplinary approaches. Previous residential landscape studies have been conducted primarily from social (e.g., Askew and McGuirk 2004) or ecological (e.g., Sperling and Lortie 2010) perspectives, typically focusing on a single scale of
analysis. At the household-scale, for instance, social scientists have studied residents’ preferences for certain yard features (e.g., Larson et al. 2009a), while ecologists have explored biodiversity (e.g., Smith et al. 2006c) often with social surveys and observational field studies, respectively. Broader-scale studies have examined residential land-use/land-cover patterns, commonly with remote sensing imagery and geospatial technology in single regions (e.g., Grove et al. 2006a). The nascent field of urban ecology has begun to examine coupled human-environment interactions using interdisciplinary approaches (Pickett et al. 1997; Collins et al. 2000; Grimm et al. 2000), with limited but increasing attention to residential landscapes (Byrne and Grewal 2008).

However, disparate disciplinary perspectives, analytical methods, and different scales of analysis render generalizations difficult and limit an integrated understanding of residential landscape dynamics.

Here, our aim is to synthesize disciplinary perspectives and scales of analysis from the literature in order to 1) contribute to a holistic, integrated understanding of the causes, consequences, and feedbacks related to residential landscapes as complex social-ecological systems, and 2) identify compelling research directions while providing a robust conceptual approach to guide future studies. We, thus, critically review the growing body of residential landscapes literature to synthesize the social-ecological interconnections across scales within this system. From our review, we examine temporal trends of research regarding residential landscapes. We also develop an interdisciplinary framework that encompasses multiple scales and disciplinary perspectives to guide future interdisciplinary research on the human drivers of landscaping practices and the ecological outcomes of those landscaping decisions. Our
interdisciplinary approach advances a holistic understanding of feedbacks and tradeoffs associated with residential landscapes as a model social-ecological system, and it provides a guide for future integrated research and theories. In the following sections, we synthesize findings from the literature across the system components at the household (parcel), neighborhood, and broader-scales, including: the ecological properties, function and ecosystem services of residential landscapes; the land management decisions that create and maintain these ecosystems; the social drivers—attitudinal, structural, and institutional—of those practices; and long-lasting legacies from past decisions that influence yard structure, management, and ecosystem services. Finally, we conclude by highlighting knowledge gaps and suggesting directions for future research on residential landscapes as complex human-environment systems.

METHODS

To review publications related to residential landscapes, we searched titles, abstracts and author keywords within Web of Science, EbscoHost, and other relevant journals not included in these databases (e.g., Urban Ecosystems) using the following a priori key terms (alone and in combination): resident*, hous*, yard, garden, landscap*, lawn, turf*. Asterisks indicate partial search words for which multiple word derivations may be relevant (e.g., resident and residential). Terms were searched in several combinations using “AND” and “OR” statements, primarily by combining terms to represent our interest in residential households and yards (e.g., resident* OR hous* AND yard OR garden OR landscap* OR lawn). Keyword searches were repeated in multiple
combinations until no new relevant publications were found. Along with exhaustive searches, we identified additional publications from references of articles obtained in the database searches. Articles that did not specifically address or examine data regarding privately managed residential properties and their residents were excluded, as they were beyond the scope of our research. This focus narrows our review to mostly outdoor spaces of developed urban and suburban regions where single-family residences dominate. It thus excludes some residential settings (e.g., apartment complexes) that do not have private outdoor landscapes. In total, 256 studies were critically reviewed.

For each article, we first identified the dominant research question(s), then grouped publications by related topics and reviewed them for themes, results, and methodological approaches. Because our intent is to advance an interdisciplinary understanding of residential landscapes, we focused on the commonalities, differences, strengths, and weaknesses from the literature collectively, while identifying areas for future research.

In this paper, we reviewed “multidisciplinary” studies through which several different fields explore questions or system dynamics from single disciplinary perspectives. We use the term “interdisciplinary” specifically to encompass research that integrates more than one disciplinary approach in addressing questions collectively from both social and ecological perspectives. In addition to examining the change in multidisciplinary and interdisciplinary research on residential landscapes over time, we classified articles into three overarching categories, natural science, social science, or both (interdisciplinary), based on the article’s research objective and methods. For example, research examining fertilizer use is classified as “social science” if residents were surveyed or interviewed about their landscaping practices or personal attributes (e.g. demographics); as “natural
“science” if ecological properties were examined as a result of fertilization; or “interdisciplinary” if a combination of methods or approaches was used.

In the preliminary stages of our research, we initially conceived of a framework encompassing relevant disciplinary and interdisciplinary perspectives. The initial conception drew on social and ecological approaches, ranging from human-ecological theories of behavior (e.g., the value-belief-norm model; Stern 2000) to broad interdisciplinary frameworks in urban ecology (e.g., highlighting key social and ecological patterns and processes, such as demographics and institutions, as well as ecosystem functions and services; Grimm et al. 2000; Pickett et al. 2001; Redman et al. 2004). We then further developed and refined the framework’s system components (boxes and arrows) based on our literature review specific to residential landscapes. The framework synthesizes the major relationships emerging from theoretical and empirical evidence in the published literature on the social-ecology of yard management. The framework focuses on the bi-directional interactions between the drivers of residents’ practices, the resulting ecological properties and processes, ecosystem services, legacy effects, and the feedbacks that reinforce or constrain land management. While such linkages could be addressed for other social-ecological systems or contexts, such as the management of public parks, we maintain a focus on privately owned residential landscapes as a prominent everyday setting for human-environment interactions in urban ecosystems.
FINDINGS

Ecology of residential landscapes

Cities are heterogeneous ecosystems with complex ecological properties and processes (Band et al. 2005). Humans directly and indirectly impact urban—and residential—ecological characteristics through management of built and biotic infrastructure as well as alteration of climate conditions and food webs, among other ecosystem elements. Most studies on residential landscapes have been conducted using methods from natural science disciplines (68% of all 256 studies; Fig. 1) with a focus on ecological properties of yards at the household-scale (56% of 174 ecology studies from natural science and interdisciplinary papers). Fewer studies explore ecological functioning and services (41% of 174 ecology studies), or ecological properties at larger scales (27% of 174 ecology studies).

Ecological properties of residential landscapes: The biotic and abiotic physical characteristics of yards include various groundcovers, species composition and abundance, soil properties and microclimates (Fig. 2a, Ecological Properties). Residential landscapes cover approximately a quarter of the land within cities, and nearly half of residential land is vegetated (Gaston et al. 2005; Mathieu et al. 2007). While biophysical properties are heterogeneous within and between individual residential properties, they follow predictable patterns based primarily on yard size, housing density and age, homeowner socioeconomic and lifestyle factors, management practices, vegetation composition, and legacies of former land use (Table 1). At broader scales
across cities, residential biophysical patterns are commonly examined in relation to regional climate and aggregated household and social data.

*Ecological properties at the household-scale:* Green lawns with shade trees are often perceived as a homogeneous manifestation of “the American Dream,” as they are ubiquitous across United States (US) cities in diverse biomes (Jenkins 1994; Bormann et al. 2001). Yet at the parcel-scale, residential landscape structure varies considerably within and between neighborhoods (Martin et al. 2003; Gaston et al. 2005; Crow et al. 2006; Kirkpatrick et al. 2007; Luck et al. 2009; yet see Loram et al. 2008b).

Groundcovers vary between grass, bare soil, rocks, and impervious surfaces (e.g. pools, patios, parking areas), with numerous grass, herb, shrub, and tree species (Henderson et al. 1998; Zmyslony and Gagnon 1998; Martin et al. 2003; Thompson et al. 2004; Daniels and Kirkpatrick 2006a; Smith et al. 2006c; Loram et al. 2008a; Luck et al. 2009). To understand this seemingly random suite of species and structures, investigators have classified yards into distinct morphologies. In an arid region, Martin and colleagues (2003) identified three yard types based on vegetation and water-use intensity: “mesic” yards with turfgrass and shade trees, “xeric” yards with gravel and drought-adapted plants, and “oasis” yards that contain both mesic and xeric features. In a temperate climate, Daniels & Kirkpatrick (2006a) identified distinct categories based on vegetation architecture, including height and percent cover. A number of studies show that parcel-scale landscape variability is less random than perceived. For example, the area of yard structures such as patios, cultivated borders, and vegetation canopy is positively correlated to yard size (Table 1; Richards et al. 1984; Smith et al. 2005; Daniels and Kirkpatrick 2006a; Smith et al. 2006c; Kirkpatrick et al. 2007; Loram et al. 2008b) and
socioeconomic characteristics of homeowners (Martin et al. 2004; Kirkpatrick et al. 2007; Luck et al. 2009), and it is negatively correlated with housing density (Smith et al. 2005; Marco et al. 2008).

Plant community composition also varies among households, but patterns emerge across studies. Non-native species that originate from many parts of the world dominate the flora of residential landscapes, making up 67-88% of all woody species (Livingston et al. 2003; Thompson et al. 2003; Smith et al. 2006c; Acar et al. 2007; Loram et al. 2008a; Marco et al. 2008). However, indigenous lawn species are far greater in European cities and tropical regions than elsewhere (Stewart et al. 2009; Akinnifesi et al. 2010). Most individual exotics are reported at very low frequencies, suggesting an overall high diversity and turnover of non-native species (Thompson et al. 2003; Acar et al. 2007; Loram et al. 2008a; Marco et al. 2008). Although species richness and diversity are often positively related to yard size (Thompson et al. 2004; Smith et al. 2006c), this relationship may vary by region, as it is not consistent across studies (Table 1; Albuquerque et al. 2005; Stewart et al. 2009). Finally, in some instances species composition in yards is related to housing age (Smith et al. 2005; Acar et al. 2007). For example, in Turkey, younger housing had a greater variety of ornamental species and older residential areas had traditional, functional gardens (e.g., fruiting trees; Acar et al. 2007).

Most residential vegetation studies focus on front yards because they are readily surveyed through field observations; however, a few highlight differences in front and backyard biotic structure (Dorney et al. 1984; Richards et al. 1984; Daniels and Kirkpatrick 2006a; Loram et al. 2007). Although the paucity of data prevents
generalization, front yards are often more highly manicured than backyards, likely due to their visibility to the public (Richards et al. 1984; Daniels and Kirkpatrick 2006a; Larsen and Harlan 2006; Larson et al. 2009a). In contrast, backyards are more likely to contain flower and vegetable gardens and a greater extent of grass than front yards (Richards et al. 1984; Daniels and Kirkpatrick 2006a). However, newer suburban developments tend to have larger houses and smaller backyards than in older communities, which may affect how the backyard is utilized and managed (Hall 2010).

Patterns in vegetation and management practices at the household-scale have diverse, often taxon-specific, consequences for the abundance and diversity of invertebrate species that utilize yards as habitat or resources (Livingston et al. 2003; Raupp et al. 2010). For instance, yard habitat structure influences the abundance of ground-dwelling organisms (e.g., Byrne 2007). Some ground arthropods, such as spiders and harvestmen, thrive in mesic (grass) yards compared to other yard types, likely due to the productivity and resource availability associated with irrigation (Shochat et al. 2004; Cook and Faeth 2006). However, lawns with varying management (e.g., chemical versus no chemical inputs) exhibit little difference in arthropod (e.g., Collembolas) and nematode abundance (Byrne and Bruns 2004; Cheng et al. 2008). Abundance of ground invertebrates, such as earthworms, is inversely related to soil bulk density (Smetak et al. 2007; Byrne et al. 2008) while some winged and non-winged invertebrate abundance is positively correlated with aboveground characteristics such as vegetation richness and plant structure (Table 1; Smith et al. 2006b; Sperling and Lortie 2010).

Similar to some natural ecosystems (Waide et al. 1999; Mittelbach et al. 2001), residential faunal diversity can be negatively related to plant productivity. Invertebrate
species richness is often lower in lawns than in less productive xeric yards (McIntyre and Hostetler 2001; Shochat et al. 2004; yet see Cook and Faeth 2006), although species richness increases near the lawn’s edge where species mix from adjacent habitats (e.g., shrub borders; Smith et al. 2006a). Additionally, plant species composition within yards, for example native versus non-native species, is especially important to butterfly, bee, and bird populations (Table 1; Germaine et al. 1998; Marzluff and Ewing 2001; Yahner 2001; Chace and Walsh 2006; Daniels and Kirkpatrick 2006b; French et al. 2005; Fetridge et al. 2008; Aurora et al. 2009; Burghardt et al. 2009).

Urban biotic and abiotic characteristics, as well as human actions, affect soil physical and chemical properties, leading to a divergence from native soils (e.g., Golubiewski 2006; Pouyat et al. 2007). Pickett and Cadenasso (2009) characterized urban soils based on the five factors of soil formation (Jenny 1941)—soil parent material, the effect of time, species composition, topography, and microclimate—in addition to human impacts. Parent material of urban and residential areas is generally distinguished from native soils by disturbances from urban development and construction, resulting in a mixed substrate and compaction (Effland and Pouyat 1997; Lehmann and Stahr 2007). Over time, older residential soils tend to have lower bulk density and contain larger total pools of organic carbon (C) and nitrogen (N) than newer residential properties, regardless of location across the US (Table 1; Law et al. 2004; Scharenbroch 2005; Golubiewski 2006; Smetak et al. 2007; Pouyat et al. 2009).

Species composition, current and past land uses, and human management also impact residential soil characteristics and related microclimates. Soil organic C storage is generally higher in residential yards compared to surrounding native forests (Pouyat et al. 2007). Urban biotic and abiotic characteristics, as well as human actions, affect soil physical and chemical properties, leading to a divergence from native soils (e.g., Golubiewski 2006; Pouyat et al. 2007). Pickett and Cadenasso (2009) characterized urban soils based on the five factors of soil formation (Jenny 1941)—soil parent material, the effect of time, species composition, topography, and microclimate—in addition to human impacts. Parent material of urban and residential areas is generally distinguished from native soils by disturbances from urban development and construction, resulting in a mixed substrate and compaction (Effland and Pouyat 1997; Lehmann and Stahr 2007). Over time, older residential soils tend to have lower bulk density and contain larger total pools of organic carbon (C) and nitrogen (N) than newer residential properties, regardless of location across the US (Table 1; Law et al. 2004; Scharenbroch 2005; Golubiewski 2006; Smetak et al. 2007; Pouyat et al. 2009).

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grasslands (Kaye et al. 2005; Golubiewski 2006), and deserts (Jenerette et al. 2006; Kaye et al. 2008), and it is positively correlated with fertilization, irrigation, and returning grass clippings (Pouyat et al. 2002; Qian et al. 2003; Pouyat et al. 2009). Plant available phosphorus (P) is greater in lawns than native prairies, but lower than in other cultivated lands such as farms (Bennett et al. 2005). In addition, residential soils are affected by legacies of former land cover or land use decisions. Due to antecedent soil fertility, soils from lawns on former agricultural fields contain larger pools of soil organic matter, C, N, and bioavailable P than soils from residential properties that were previously desert (Hope et al. 2005; Lewis et al. 2006; Davies and Hall 2010). Finally, plant communities, landscape characteristics, and management practices such as irrigation combine to create cooler microclimates through evapotranspiration (Bonan 2000; Coutts et al. 2007; Jenerette et al. 2007; Tratalos et al. 2007b; Baris et al. 2009; Shashua-Bar et al. 2009; Peters and McFadden 2010), which in turn regulates soil moisture (Trudgill et al. 2010).

Ecological properties at neighborhood and broader-scales: When aggregated, heterogeneous ecological properties within parcels lead to broad patterns at regional and larger scales. Houses clustered in close proximity within a neighborhood often share related yard characteristics (Zmyslony and Gagnon 1998, 2000; but see Kirkpatrick et al. 2009). Vegetation cover is inversely associated with housing and population density (Iverson and Cook 2000; Marco et al. 2008; Luck et al. 2009; Boone et al. 2010). Additionally, both floral diversity and cover are inversely related to neighborhood age (Martin et al. 2004; Hope et al. 2006; yet see Grove et al. 2006b who report a quadratic relationship). This finding is contrary to the fundamental ecological theory of island
biogeography, which predicts a positive relationship between age of site and diversity (MacArthur and Wilson 2001). Vegetation diversity and cover across neighborhoods is positively related to socioeconomic advantage, education, and lifestyle factors that reflect group identity and social status (Table 1; Iverson and Cook 2000; Hope et al. 2003; Martin et al. 2004; Grove et al. 2006b; Mennis 2006; Tratalos et al. 2007b; Luck et al. 2009; Boone et al. 2010). Similarly, invasive plant richness is positively related to income, low-density housing, and area of urban-wildland interface at the county scale (Gavier-Pizarro et al. 2010). Despite general patterns, the geographic context and historic processes of urban growth are important factors in predicting current vegetation trends (Luck et al. 2009; Boone et al. 2010). In Detroit, Michigan, for example, vegetation cover was positively associated with exurban growth and economic development, but also neighborhood abandonment in low-income, inner-city neighborhoods (Ryznar and Wagner 2001). At the city scale, US residential tree cover is dictated by climate as it varies predictably by biome, from 31% in forested cities, 19% in grassland cities to 17% in desert cities (Nowak et al. 1996).

The distribution and composition of fauna across residential neighborhoods, particularly species with large ranges, are negatively affected by landscape patchiness and fragmentation. As predicted by the theory of island biogeography, bird, butterfly, and small mammal abundance and diversity increase with habitat area (Chamberlain et al. 2004; Daniels and Kirkpatrick 2006b; Baker and Harris 2007; Evans et al. 2009), neighborhood age (Edgar and Kershaw 1994; Yahner 2001; yet see Loss et al. 2009), and proximity to natural habitats, source populations, and corridors (Germaine et al. 1998; Daniels and Kirkpatrick 2006b; Baker and Harris 2007; Loss et al. 2009). In addition,
residential landscapes in conjunction with local open, green spaces may form a large urban matrix of habitats, corridors and resources that can provide beneficial services to urban species (James et al. 2009; Goddard et al. 2010). At larger city-scales, faunal species abundance is often greater in urban areas, while diversity is lower or different in composition compared to surrounding native ecosystems (Marzluff and Ewing 2001; Shochat et al. 2004; Chace and Walsh 2006; Cook and Faeth 2006; McKinney 2006; Catterall et al. 2010). While some common trends exist, patterns often vary by species, region, or method and scale of analysis (Smith et al. 2006b; Smith et al. 2006d). For instance, bird, butterfly and small mammal abundance and richness vary between positive, negative and non-linear relationships with housing density (Germaine et al. 1998; Germaine et al. 2001; Yahner 2001; Baker and Harris 2007; Tratalos et al. 2007a; Evans et al. 2009; Hourigan et al. 2010).

**Ecological functioning and ecosystem services of residential landscapes:** Biophysical properties regulate material and energy flow between humans, non-human biota, soils, water, the atmosphere, and other ecosystems (Fig. 2b, *Ecological Function*). Ecological functions include cycling of water and elements, as well as trophic dynamics. Together, ecosystem properties and functions provide many services to people (MEA 2005; Fig. 2c, *Ecosystem Services*). Like their native counterparts, managed landscapes regulate ecological properties and processes such as microclimate and pollination (regulating services), provide support for other services through primary production and nutrient cycling (supporting services), and produce goods such as food resources (provisioning services; Beard and Green 1994). In addition, residential yards offer key, social amenities such as a sense of place for people and communities (cultural services).
Finally, human actions and natural causes (e.g., storms) are sometimes responsible for negative ecosystem services, or “disservices” such as air or water pollution, that result in social and ecological costs (Tratalos et al. 2007b; Grimm et al. 2008).

To date, most studies on ecological functioning in yards have been conducted at the parcel-scale (86% of 72 studies focused on ecological processes), with the exception of some research on surface temperatures (Jenerette et al. 2007) and watershed-scale nutrient budgets (Groffman et al. 2004). While residential outdoor spaces can provide numerous services to residents, few studies explicitly examine the ecosystem services and disservices of residential landscapes. Collectively, studies show that ecosystem processes in residential landscapes often differ in rate, magnitude or variability from those in surrounding native biomes due to human impacts on yard composition and water and nutrient availability through management practices (Table 2).

Irrigation, species composition, and plant physiological processes affect water fluxes among residential yards and other ecosystem components, such as the atmosphere. Similar to native ecosystems, the areal extent of residential vegetated ground and canopy cover is positively related to evapotranspiration—the loss of water from soil and vegetation to the surrounding atmosphere (Bonan 2000; Martin et al. 2007; Shashua-Bar et al. 2009). Evapotranspiration creates a positive service, cooling air around homes and potentially reducing energy use for air conditioning (Huang et al. 1987; Bonan 2000; Coutts et al. 2007; Georgi and Dimitriou 2010). One study estimated air conditioning costs can be reduced by approximately 2% per residential tree (Simpson and McPherson 1998), although tree species vary in their effects on human thermal comfort (Georgi and Dimitriou 2010). Likewise, irrigated mesic landscapes mitigate surface temperatures
better than impervious surfaces or less-irrigated yards (Bonan 2000; Martin et al. 2007). At the neighborhood scale, high pavement cover and housing density are positively related to warmer land surface temperatures, while increased vegetation cover cools temperatures and may reduce human heat stress and other urban heat island effects (Stabler et al. 2005; Harlan et al. 2006; Jenerette et al. 2007; Buyantuyev and Wu 2010; Su et al. 2010).

Potential tradeoffs between ecosystem services exist, for example, between water and energy use for varying types of residential landscapes. While highly productive yards might mitigate energy use and heat stress, they require more water and, in turn, intensive pruning that incurs the cost of labor and time (Martin 2008). Yards with drought-adapted vegetation require less water than lawns, but irrigation of xeric yards is often not adjusted for seasonal changes in evapotranspiration and results in over-watering (Martin 2001; Sovocool et al. 2006; St Hilaire et al. 2008). Moreover, high irrigation rates and pruning can cause vegetation to use water less efficiently, as well as decrease the potential to store carbon (Stabler 2008; Martin 2008). Recognizing the tradeoffs between lawns and xeric yards, some residents intentionally choose “oasis”-type yards to achieve “best of both worlds” benefits in desert cities, such as Phoenix, Arizona (Larson et al. 2009a).

Like all ecosystems, residential landscapes support trophic exchange between non-human organisms through predation and herbivory. Species’ mobility and resource demands, along with the variety of habitats and human management practices make it difficult to identify trends across yards and for specific species (Smith et al. 2006b; Smith et al. 2006d). However, managed landscapes generally contain more abundant and less seasonally variable resources than many native ecosystems (Shochat et al. 2006),
particularly with supplementary nest boxes and feeders (Gaston et al. 2005; Fuller et al. 2008; Davies et al. 2009). Thus, competitive interactions and top-down versus bottom-up trophic controls are altered, which in turn shifts faunal species composition and predation rates (Faeth et al. 2005; Cook and Faeth 2006; Shochat et al. 2006). For instance, synanthropic species (species associated with humans) may exploit urban resources, thereby out-competing non-synanthropic species and preventing them from adapting to the urban environment (Shochat et al. 2010). An increase in urban exploiter species, who likely thrive in highly managed residential yards, may shift community assemblages toward biotic homogenization in cities (McKinney 2006). Additionally, altered urban floral and faunal communities may impact ecosystem services, such as biodiversity, pollination, seed dispersal, and beneficial pest regulation (Andersson et al. 2007; Davies et al. 2009; Doody et al. 2010).

Yard properties and management practices also influence C cycling, a primary life-supporting service. Methane (CH$_4$) is a carbon-based greenhouse gas and is generally consumed by microbial processes in well-drained soils. Rates of CH$_4$ uptake—or consumption—decline with N enrichment associated with fertilization and atmospheric deposition (Groffman and Pouyat 2009). Fertilized lawn soils consume CH$_4$ at lower rates than native soils or can even become a CH$_4$ source—an ecosystem disamenity (Kaye et al. 2004; Groffman and Pouyat 2009). While lawn CH$_4$ consumption rates are similarly low across studies, they vary little among different irrigation and fertilization treatments in urban lawns (Livesley et al. 2010).

Carbon dioxide (CO$_2$), another greenhouse gas, is a product of metabolic respiration and a primary requirement for photosynthesis. Through microbial and root respiration,
soils within some residential groundcover types emit more CO$_2$ than others, likely due to optimal soil temperature, moisture, and organic C available for microbial activity in managed landscapes (Green and Oleksyszyn 2002; Koerner and Klopatek 2002; Byrne et al. 2008). Overall, lawn soil CO$_2$ emissions are high relative to eastern temperate forests, agricultural fields, and native grasslands (Kaye et al. 2005; Groffman et al. 2009).

Through photosynthesis, CO$_2$ is transformed into organic matter that supports plant growth and C storage, particularly in highly irrigated yards and older landscapes with low disturbance and high vegetation productivity (e.g., Golubiewski 2006; Stabler 2008; Townsend-Small and Czimczik 2010).

Like carbon, N is an essential element for life and is affected by ecological properties and management of yards. At the parcel-scale in arid regions, fertilized lawn soils emit more nitrous oxide (N$_2$O), another greenhouse gas, than soils of native grasslands, deserts, agricultural land, or xeric, rock-covered yards (Kaye et al. 2004; Hall et al. 2008; Hall et al. 2009). However in temperate climates, rates of denitrification, a microbial process that produces N$_2$O in soils, does not differ between lawn and other organic-rich native forest soils or unmanaged old fields, which may be a result of similar soil moisture (Byrne 2006; Groffman et al. 2009). N$_2$O emissions from lawn soils are explained by a direct relationship to soil moisture (Bijoor et al. 2008; Hall et al. 2008; Groffman et al. 2009; Livesley et al. 2010), fertilizer application (Bijoor et al. 2008; Livesley et al. 2010; Townsend-Small and Czimczik 2010), and soil temperature (Bijoor et al. 2008; Hall et al. 2008). Due to the areal extent of fertilized grass lawns within cities and the urban heat island, parcel-scale management practices may contribute substantially to regional biosphere-atmosphere gas dynamics (Bijoor et al. 2008). For example, regular
fertilization and irrigation reduces seasonal variation in soil gas fluxes, such as N$_2$O and nitric oxide, a reactive gas that contributes to regional smog (Hall et al. 2008).

Excess soil nitrate (NO$_3^-$) is a common concern near urban and agricultural areas where leaching and runoff from fertilizer can contaminate groundwater or downstream ecosystems, creating an ecosystem disservice (Petrovic 1990; Groffman et al. 2004). Lawn soils tend to leach more NO$_3^-$ than native forest soils, but less than agricultural soils (Groffman et al. 2009). Lawn NO$_3^-$ leaching is dependent on water and fertilizer applications, soil texture (Petrovic 1990), and turfgrass species (Liu et al. 1997; Erickson et al. 2001). Nitrate leaching rates are particularly high in new yards where management may be more intense (Law et al. 2004; Oki et al. 2007), whereas older lawns with lower runoff rates are better at retaining excess nutrients and mitigating water pollution (Groffman et al. 2004; Pickett et al. 2008; Raciti et al. 2008). Similarly, grass yards can be relatively efficient at retaining NO$_3^-$ when they have high soil organic matter and actively growing microbial communities characteristic of older, undisturbed soils (Qian et al. 2003; Groffman et al. 2004; Raciti et al. 2008; Groffman et al. 2009).

Arguably, the most important services provided by residential landscapes are cultural, as they promote human mental and physical well-being and are places for recreation and gathering with family and friends (Beard and Green 1994; Matsuoka and Kaplan 2008; Abraham et al. 2010). Indeed, residents report a sense of comfort in their yards (Crow et al. 2006), as well as greater neighborhood satisfaction and social interactions when surrounded by more open space and trees (Kweon et al. 2010; Uslu and Gokce 2010). Outdoor space is often considered a functional extension of the home, designed and managed to meet aesthetic and recreational preferences (Jenkins 1994; Bhatti and Church...
2001; Martin et al. 2003; Larsen and Harlan 2006; Larson et al. 2009a). In many areas of the world, yards provide subsistence “homegardens,” with not only ornamental species, but also supplementary food and medicinal flora (Albuquerque et al. 2005; Eichemberg et al. 2009; Huai and Hamilton 2009; Kabir and Webb 2009). Yards also benefit human health through connections to the outdoors (Bhatti and Church 2001; Fuller et al. 2007; Tzoulas et al. 2007), and offer a “sense of place,” reminding residents of native ecosystems, their geographic place of origin, or particular settings such as “home” or “nature” (Larson et al. 2009a). Finally, landscaping is frequently perceived as an indicator of property investment and value, which may lead to community cohesiveness (Grove et al. 2006b; Robbins 2007).

Management decisions

Residents alter ecological properties and functions of their landscapes by installing and removing vegetation and impervious cover, using various irrigation technologies, mowing, pruning, and determining the timing, amount, and frequency of water and chemical inputs (Fig. 2d, Management Decisions). Thus far, residential landscape management research has mostly been conducted at the household-scale (83% of 39 management studies) through social surveys on landscaping practices and related social drivers. Our literature synthesis shows that management practices vary by the primary caretaker (e.g., resident versus professional service), knowledge of different management strategies, yard cover, irrigation technology (Table 3), and residents’ personal ideals and attributes, such as aesthetic preferences and income (Table 4).
Yard management varies between do-it-yourself approaches and professional services with predictable differences in yard “quality.” In surveys from Ohio, North Carolina and Oregon, approximately 16–43% of households use professional landscaping services (Robbins et al. 2001; Osmond and Hardy 2004; Nielson and Smith 2005), while 70% of US households cared for at least one aspect of their own yard (NGA 2007). Professionally maintained yards often rank higher in aesthetic lawn quality, as measured through grass color (greenness) and a lack of weeds (monoculture), than do-it-yourself approaches (Cheng et al. 2008; Alumai et al. 2009). Lush, green monoculture lawns result from frequent irrigation, herbicide application, and the use of time-release fertilizers (Nielson and Smith 2005).

More than half of US households apply synthetic fertilizers to their yards, but the variability in application rate, timing and amount is high (Robbins et al. 2001; Law et al. 2004; Osmond and Hardy 2004). Do-it-yourself approaches result in a significant range of fertilizer application rates (e.g., 10-370 kg N ha\(^{-1}\) yr\(^{-1}\); Robbins et al. 2001; Law et al. 2004; Osmond and Hardy 2004). In contrast, professional management services have a smaller range of application rates (e.g. 100-161 kg N ha\(^{-1}\) yr\(^{-1}\)), but apply with greater frequency compared to residents (Osmond and Platt 2000; Law et al. 2004). Overall, fertilizer use can be predicted by yard greenness (Zhou et al. 2008). When asked, residents report adjusting fertilizer application rates based on soil tests, land-cover type, season, and product instructions (Osmond and Hardy 2004). However, interviews from Oregon reveal that only 20% read packaging labels, and the remainder “just know” the appropriate application rates or learn from their family and friends (Nielson and Smith 2005).
In national and local surveys of residents, nearly half returned grass clippings to the yard, which reduces the need for fertilizers (NGA 2004; Osmond and Hardy 2004).

Nearly 75% of US households use chemical yard pesticides, including herbicides, insecticides and fungicides (Kiely et al. 2004). Similarly, across four North Carolina cities, an average of 60% of households (range 35–91%) used pesticides (Osmond and Hardy 2004). Both residents and professional landscapers apply pesticides to control insects (i.e. insecticides) and weeds (i.e. herbicides) more than fungicides (Braman et al. 1997; Kiely et al. 2004; Osmond and Hardy 2004). Like fertilizer, pesticide use is related to groundcover, as a Phoenix study found that insecticides and herbicides were used less on grass yards than rock yards (Larson et al. 2010). Thus, xeric yards present potential tradeoffs between water use and environmental toxicity, which could negatively affect human health (e.g., Karr et al. 2007), beneficial urban organisms, or downstream water quality (e.g., Blanchoud et al. 2004; Struger and Fletcher 2007). Integrated pest management offers opportunities to reduce these tradeoffs and the environmental and economic consequences (Braman et al. 2000; Klingeman et al. 2009; Alumai et al. 2010).

Watering practices depend on yard cover, irrigation technology and decisions about how much and when to water. Physical yard features such as turfgrass, lot area, and house area are positive predictors of water use for pools and irrigation, which together constitute the majority of municipal and residential water consumption (Table 4; Mayer et al. 1999; Troy and Holloway 2004; Sovocool et al. 2006; Balling and Gober 2007; Guhathakurta and Gober 2007; Wentz and Gober 2007; Harlan et al. 2009). Highly manicured lawns use significantly more water than the average yard (Askew and McGuirk 2004), while xeric yards require less water, maintenance costs, and time
However, over-watering is endemic in many yards (Nielson and Smith 2005; Salvador et al. 2011). In somewhat counterintuitive findings, households with automated irrigation systems, including relatively efficient drip-irrigation, tend to use more water than households with hand-held or movable sprinklers (Mayer et al. 1999; Martin 2001; Syme et al. 2004; Endter-Wada et al. 2008). Automated systems are often programmed at high rates, regardless of season and the needs of plants (Martin 2001). A recent survey found that regional water shortages are more likely to drive homeowners to conserve outdoor water than price increases or environmental concerns (St Hilaire et al. 2010). Yard water conservation efforts should target changing groundcover, species composition, irrigation technology, and homeowner education (Kjelgren et al. 2000).

**Multi-scalar human drivers of residential landscape attributes and management**

Numerous social theories and studies inform our understanding of the driving forces affecting landscape management and, in turn, the ecological outcomes of human behavior. Within the residential landscape literature, drivers of human behavior have been studied primarily at the household-scale (74% of 84 studies on human drivers), despite myriad factors across multiple scales that influence management practices and preferences of homeowners. These factors include personal attributes, neighborhood institutions, government policies, and broad-scale political-economic forces (Fig. 2; Table 4). Across the studies reviewed here, attitudinal factors (e.g. environmental values) and household characteristics (e.g. demographics) have been most closely examined as the drivers of individual land management decisions. Overall, residents’ values and attitudes have limited influence on landscaping practices, in part because institutional and
structural forces facilitate and constrain people’s choices at household, neighborhoods and larger scales.

*Household-scale human drivers:* Residents are the fundamental local actors making landscaping decisions in front and backyards, where residents’ individual attitudes and social characteristics influence yard preferences and management practices. Following Stern (2000), we distinguish between the cognitive realm of residents’ values and attitudinal judgments versus other factors (i.e., context, habits and personal attributes) that facilitate or constrain decisions (Fig. 2e, *Household Scale Human Drivers*). In our framework, cognitive factors encompass attitudes and related judgments, such as values, beliefs, and norms, while household and urban structure involves personal and property attributes such as wealth and housing age. Overall, attitudinal factors influence landscaping preferences and behaviors in complex but limited ways, with specific beliefs and attitudes (e.g., about one’s own conservation practices relative to others) affecting landscaping practices more so than general judgments (e.g., broad-based environmental worldviews; Larson et al. 2010). As further detailed below, we also find from our review that household and property attributes, such as income or property size, appear to impose stronger constraints on landscaping decisions and ecological characteristics than attitudinal or cognitive factors at the household-scale (Table 4).

Residents’ landscape preferences, or intentional desires, are not always in agreement with realized yard choices, particularly in public front yards (Hurd 2006; Larsen and Harlan 2006). This disconnect, attributed to broader institutional and structural constraints that inhibit preferences from being realized, is less significant in private backyards where preferences are more closely aligned with actual landscapes (Larsen and
Harlan 2006). Front and backyard preferences differed in a Phoenix survey, along with
the rationales for residents’ choices across these public and private spheres (Larson et al.
2009a; see also Goffman 1959 and Stern 2000 for a discussion of public versus private-
shere actions). Thus, front yards may reflect a display of social status or adherence to
neighborhood norms or rules, whereas backyards reflect residents’ ideals or
“dreamscapes” based on personal values and lifestyles (Larsen and Harlan 2006).

In qualitative studies, residents’ stated reasons for their landscaping preferences
reflect value-based priorities. For example, aesthetic preferences are often a top priority
in explaining groundcover and management choices (Martin et al. 2003; Spinti et al.
2004; Nielson and Smith 2005; Hirsch and Baxter 2009), in addition to the familiarity of
landscapes, microclimate effects, and health factors (Larson et al. 2009a). Resident
preferences for well-manicured versus natural or “messy” looking alternative landscapes
vary based on aesthetic, safety, and environmental concerns (Jorgensen et al. 2007;
Mustafa et al. 2010; Zheng et al. 2011). Residents invoke environmental concerns as a
landscaping priority, yet their perceptions of the ecological outcomes of various
landscapes are mixed. Many people choose xeric landscaping for water conservation,
while environmental benefits such as air quality are linked to grass and other yard types
(Larson et al. 2009a). Additionally, grassy yards are chosen as safe, comfortable, and
“homey” places for leisure activities, especially in backyards. Landscaping choices often
reflect their utilitarian value for leisure, especially to provide recreational opportunities,
minimize maintenance requirements, and address safety concerns (Harlan et al. 2006;
Larson et al. 2009a). Yard choices also reflect non-utilitarian values concerning family
and social priorities such as feeling proud about one’s yard (Feagan and Ripmeester 1999; Endter-Wada et al. 2008; Hirsch and Baxter 2009). As such, landscapes represent symbolic expressions of residents’ identity (Larsen and Harlan 2006; Mustafa et al. 2010), while reflecting personal and social ideals based on what people think is important and how they subjectively view the world around them (Larson et al. 2009a). Thus, existing landscaping may influence people’s decisions to purchase a particular home or manage their yard in a certain way.

As broad-based notions of what is important in life (Schwartz 1994), values influence specific beliefs and attitudes about how the world works and what goals and actions are most desirable (Whittaker et al. 2006). Attitudinal constructs, which encompass a range of concerns, worldviews, and other types of evaluative (positive or negative) judgments, have been conceptualized and measured in myriad and often ambiguous ways, complicating comparisons across studies (Kaiser et al. 1999; Dunlap and Jones 2002; Dietz et al. 2005). However, past research that quantitatively examines attitudinal factors and landscaping choices indicates complex relationships between environmental values and ecologically friendly landscaping practices (Larson et al. 2010). For example, pro-environmental values—measured by Dunlap’s New Ecological Paradigm scale and “concern” about water scarcity—do not always translate into preferences for water-conserving xeric landscapes (Yabiku et al. 2008). Similarly, environmentally oriented people and those with heightened environmental “concern” tend to manage their yards more intensively than others, specifically with conventional chemical inputs (Templeton et al. 1999; Robbins et al. 2001; Robbins and Birkenholtz 2003). These counterintuitive
findings are consistent with the social construction of nature, wherein residents view green lawns as “nature,” even in a desert environment (Larson et al. 2009a).

Other landscape management practices, such as water use, are also influenced by personal beliefs, attitudes, and overriding social pressures in complex ways. Outdoor water use is often attributed to the belief that yards contribute to a property’s economic value (Nielson and Smith 2005; Endter-Wada et al. 2008). However, the link between water use and other attitudinal judgments is mixed. For example, preferences for a lush, green landscape explained outdoor water use in Australia (Askew and McGuirk 2004), but not in arid regions of the US like Utah and Arizona (Endter-Wada et al. 2008; Harlan et al. 2009). Positive attitudes toward water conservation practices explained reduced water use in Australia (Syme et al. 2004), while in a Mexican study, the belief that neighbors use water wastefully diminished conservation in outdoor irrigation practices (Corral-Verdugo et al. 2002; Corral-Verdugo et al. 2003). Differences across studies may be attributed to the geographic context of the research or the particular types of value-based judgments examined, with specific beliefs and attitudes about behaviors being more influential than broad-based values or concerns.

As a specific type of belief, normative views about how people should maintain their yard to meet others’ expectations also influence environmental behaviors (Ajzen 1985; Stern 2000). Few studies of residential landscaping practices empirically examine norms. In the few studies available, residents often explain their management practices by citing neighborly expectations and pressures (Nielson and Smith 2005) or referencing their neighbors’ preferences more so than broad social norms (e.g., maintaining a monocultural lawn; Nassauer et al. 2009). Similarly, the desire for social acceptance was positively
related to the desire to conserve water, but did not translate to reduced water use (Syme et al. 2004). This finding highlights the tenuous relationship between what people say and what they do.

In addition to attitudinal drivers, personal attributes, interests and abilities of human actors drive landscape characteristics and management practices at the household-scale. Income, for instance, is positively associated with vegetation cover (e.g., Mennis 2006; Boone et al. 2010). This positive relationship is described by ecologists as a “luxury effect” resulting from the financial ability to create ecologically-rich landscapes, and by social scientists as a “prestige effect” involving symbolic displays of identity and social status beyond economic wherewithal (Martin et al. 2004; Kinzig et al. 2005; Grove et al. 2006; Hope et al. 2006; Troy et al. 2007). Yet, financial resources, as well as time constraints, influence management choices by restricting the capacity to modify landscapes (Templeton et al. 1999; Hurd et al. 2006; Boone et al. 2010). Specifically, income predicts landscape preferences (Larsen and Harlan 2006), irrigation time, and outdoor water consumption (Osmond and Hardy 2004; Sovocool et al. 2006; Harlan et al. 2009; Polebitski and Palmer 2010). Middle-income residents, however, tend to prefer grass (Larsen and Harlan 2006) and apply the most fertilizers (Osmond and Platt 2000; Law et al. 2004). On the other hand, wealthy residents and homeowners more often use pesticides than others (Steer et al. 2006; Templeton et al. 2008) and are willing to pay more for locally grown native plants (Curtis and Cowee 2010).

Finally, other personal and property attributes further shape management decisions. In Baltimore, lawn care expenditures are positively related to income, but also predicted by education, median house value, and home ownership (Zhou et al. 2009). In the
Southwestern US, long-term residents, those with young children, and women prefer lawns more than xeric landscapes (Martin et al. 2003; Spinti et al. 2004; Larsen and Harlan 2006; Yabiku et al. 2008; Larson et al. 2009a). Gender differences are attributed to the socialized duties of women as primary housekeepers and caregivers of children, while men commonly manage the yard and thus prefer more maintenance-free landscape types (Yabiku et al. 2008; Larson et al. 2009a). Property values, another indicator of affluence and social status, are also a good predictor of water consumption (Sovocool et al. 2006) and chemical use (Templeton et al. 1999; Robbins et al. 2001; Robbins and Sharp 2003a). Finally, housing age is commonly related to particular front yard landscape types (Larsen and Harlan 2006) and is positively associated to vegetation cover (Grove et al. 2006a; Grove et al. 2006b).

*Neighborhood scale human drivers:* Neighborhoods are fundamental units that shape landscape patterns within cities, due in part to developments with similar characteristics and in part to social institutions that foster or inhibit landscaping decisions both formally or informally (Feagan and Ripmeester 1999; Fig. 2f, *Neighborhood Scale Human Drivers*). As organizing mechanisms for human actions, institutions are the rules, norms, and shared strategies that endure through social organization and interaction (Crawford and Ostrom 1995). Formal institutions include rules and restrictions codified in legal policies, while informal institutions encompass shared norms and non-codified codes of conduct. These factors partially explain the divergence between front and backyard choices, with social institutions operating to maintain the collective interests of residents in visible outdoor areas while constraining individuals’ choices (Table 4).
Formal institutions at the neighborhood scale drive resident landscaping practices through direct governance mechanisms. For example, homeowner association covenants, codes and restrictions (HOA CCRs), which are more prevalent in the US than other parts of the world, stipulate what residents can and cannot do to their homes and yards (McKenzie 1994). As private governing bodies, HOAs and similar organizations enforce pre-existing land-use regulations, approve (or deny) landscape changes, collect dues, maintain common areas, and aim to uphold property values and “community standards” (McKenzie 1994; Robbins 2007; Cheshire et al. 2009). While HOAs have the potential to regulate ecosystem services and water conservation, CCRs rarely govern outdoor water use explicitly but do regulate irrigation technology and restrict plant composition and height (Dyckman 2008). Yet the particular stipulations vary across neighborhoods; for example, some CCRs prohibit grass lawns while others require them in addition regulating pest and weed management. In Phoenix, HOA neighborhoods had fewer trees, more shrubs, and less turfgrass than non-HOA neighborhoods (Martin et al. 2003). These patterns are also likely linked to housing age, as developments with HOAs tend to be younger subdivisions (Larsen and Harlan 2006).

Although informal institutions, such as norms and customs, are not legally enforceable, the threat of social exclusion (or other informal penalties) shapes individual decisions to behave within widely accepted or perceived expectations. For example, the traditional lawn is ubiquitous in urban yards, partly as a result of neighborhood peer pressure and social conformity (Jenkins 1994; Askew and McGuirk 2004; Steinberg 2006; Robbins 2007). Well-kept lawns are commonly thought to reflect positively on the character, standards and value of the neighborhood (Feagan and Ripmeester 1999;
Most residential landscape studies offer only theoretical explanations for these social pressures, with anecdotal or minimal evidence. Few empirical studies have focused on understanding landscaping norms and how they operate across individuals, neighborhoods, or distinct regions. Together, formal and informal institutions can inhibit individuals from realizing their personal preferences and ideals, but they also explain why actual landscaping choices or yard structure deviate from residents’ values or attitudes.

**Municipal and broader-scale drivers:** At broader-scales, institutional and political-economic factors regulate landscaping decisions, enabling or constraining individuals’ choices (Fig. 2g, Municipal-Regional Scale Human Drivers). Despite their importance, limited research has focused on the broad-scale drivers of yard management, such as formal government ordinances and key political-economic players like the yard-care industry or large-scale housing developers (43% of 84 human driver studies). Additionally, less is known about the relationship between residents’ decisions and broad-scale informal institutions, such as shared customs and notions about a region’s identity (Table 4).

Similar to HOAs, local government ordinances and restrictions formally control lawn maintenance or front yard structure. For example, some planning and development codes restrict the hard surfacing (paving) of yards or new driveways to reduce local flooding (Stone 2004; Perry and Nawaz 2008; Shaffer et al. 2009). Municipal regulations often also dictate landscape structure or appearance through legal limits on grass height to avoid “nuisance” yards (Feagan and Ripmeester 1999; Robbins et al. 2001; Robbins 2007). Recent regulations in Canada banned cosmetic use of pesticides (Sandberg and
Foster 2005) in an attempt to address environmental concerns related to lawn care. For similar reasons, water-use restrictions in the Boston area now limit irrigation of lawns and gardens (Hill and Polsky 2007). Curiously, while relatively humid regions such as Boston, Massachusetts and Miami, Florida have implemented outdoor irrigation restrictions, arid cities such as Phoenix lack regulations on residential water use even in a ten-year drought (Larson et al. 2009b). As Hill and Polsky (2007) explain, municipal decisions to regulate water are a function of political will and tolerance for water supply versus demand, rather than simple responses to hydroclimatic conditions.

Marketing and other political-economic factors reinforce the notion of a “perfect” lawn to promote happy homes and idyllic communities (Robbins et al. 2001). The commercial production of yard chemicals during post-war mid-1900s codified the ability to maintain the ideal American landscape and, thus, promoted the commodification of yards (Jackson 1985; Jenkins 1994; Bormann et al. 2001; Robbins and Sharp 2003a). Adhering to industry standards, residents are entrenched in the marketing of chemical and yard-care corporations that perpetuate the consumption of lawns (Jenkins 1994; Bormann et al. 2001; Robbins and Sharp 2003a; Robbins 2007) and alternative landscapes, despite their perceived lower inputs (Mustafa et al. 2010). To alter this cycle, neighborhood institutions and municipal controls may be necessary to break residents from social pressures and economic forces (Robbins 2007; Nassauer et al. 2009).

Developers’ decisions also structure landscaping patterns and regulations that maintain neighborhood and regional characteristics (Coiacetto 2007; Cheshire et al. 2009). The development industry has powerful influence over broad-scale social-ecological outcomes, with similar building and greening strategies for master planned...
communities and the ability to enact CCRs in new subdivisions (McGuirk and Dowling 2007; Dyckman 2008; Song et al. 2009). Many residents in fact prefer the master planned communities for their aesthetic uniformity and well-manicured landscapes, as well as a sense of social distinction (Dowling et al. 2010). Although driven mostly by profits, developers are influenced and constrained by consumer preferences, as well as municipal ordinances, past land uses and infrastructure, water and material costs, and the potential ecosystem services provided by yards (Coiacetto 2007; He and Jia 2007; Dyckman 2008; Bowman and Thompson 2009; Mohamed 2009).

Finally, shared regional identities influence residents’ landscaping ideals and preferences. Place-based identity and the “sense of place” may vary over time, leading to “cultural landscapes” reflecting shared customs, developers’ original decisions, and residents’ ideals (Gobster et al. 2007; Romig 2010). For example, preferences for lush yards by long-time Phoenix residents are influenced by the promotion of Phoenix as an “oasis”—where “the desert is a myth” (Larson et al. 2009b). In contrast, residents of Tucson, Arizona embrace tourism campaigns that promote the desert setting (Prytherch 2002), where xeric yards are more prevalent and rates of water use are lower than Phoenix. Thus, the sense of place promoted in particular areas may have lasting effects by socializing residents to cultural landscaping practices and ideals (Larson et al. 2009a).

Legacy effects

Landscape legacies manifest at multiple scales through historic land-use decisions, preexisting land-cover, and urban development patterns. Legacies result from numerous social and ecological forces, ultimately affecting ecological structure, function and
services for centuries to millennia (Redman 1999; Foster et al. 2003; Lewis et al. 2006; Fig. 2h, Legacy Effects). Few studies, however, highlight the strong influence of historic trajectories on residential land management (4% of all 256 studies). The landscaping choices and consumption patterns of previous residents, which may have been driven by local climate, culture or available supplies, often create long-lasting legacies (Dow 2000; Alp et al. 2010; Boone et al. 2010). Recent studies suggest neighborhood land cover is better predicted by previous, rather than current, socio-economic and lifestyle characteristics in neighborhoods (Luck et al. 2009; Boone et al. 2010). Further, previous land-cover decisions continue to shape cultural expectations, for example, to maintain traditional lawn yards in historic neighborhoods of Phoenix (Larson et al. 2009a).

At larger scales, ecological legacies are a feature of the prevailing decisions of developers and previously established infrastructure or land uses. Developers’ original landscaping and infrastructure choices (e.g., irrigation technology) and the use of conventional versus alternative design principles may have long-lasting effects on regional characteristics that go unchanged due to cost constraints or CCR regulations (Larsen and Harlan 2006; Dyckman 2008; Conway 2009). Historic and present-day access to infrastructure also impacts landscape structure and management practices. As is the case of many Phoenix neighborhoods, water rights and canals used for early crop irrigation were easily transitioned into flood irrigation systems that now maintain lush lawns in the desert (Gober and Trapido-Lurie 2006). Similarly, yards built on previously farmed land in Phoenix have fewer woody species (Hope et al. 2003) and greater soil nutrients than those built on non-agrarian, desert lands (Lewis et al. 2006).
DISCUSSION AND FUTURE RESEARCH DIRECTIONS

Residential landscapes are an ideal setting to examine human (resident)-environment (yard) interactions. Residential landscapes research can integrate disciplinary perspectives across a common system, while serving as a model for studying social-ecological complexity in other systems (Baker et al. 2007). From over 250 papers published on residential landscapes (Fig. 1), most early studies focused on identifying the components of the residential landscape system (Fig. 2) from theory-driven strengths within social and natural science disciplines, often at single scales of analysis. As the field has matured, interdisciplinary studies have become more common, addressing the interactions between people and their surrounding home environment using mixed methodologies (Fig. 1). Still, further research is needed to understand interactions between the drivers of land management decisions and social or ecological outcomes across multiple scales. Interdisciplinary research can especially elucidate the tradeoffs and multi-scalar dynamics associated with human-environment systems.

Conceptual frameworks are useful tools for illustrating the links between disparate disciplinary perspectives or research in a common, interconnected system. Our approach builds upon existing urban ecosystem frameworks (e.g., Grimm et al. 2000; Pickett et al. 2001; Redman et al. 2004) by applying the causes, consequences, and feedbacks specific to residential land management to the broad components of previous social-ecological frameworks. While recent interdisciplinary frameworks have explored specific components of urban systems, such as public green spaces (James et al. 2009) and residential yard management at the parcel scale (Byrne and Grewal 2009), our framework
distinctively adds an essential cross-scalar perspective that considers the parcel scale as well as neighborhood and broader, regional dynamics of landscaping decisions. In particular, the framework uniquely highlights the multiple scales of social drivers that influence household decisions regarding their outdoor space. The framework herein is useful in pinpointing areas for future disciplinary and integrated research for social-ecological systems broadly and residential landscapes specifically, as further described below and in Table 5. Although specific to residents’ land management decisions, our framework could be adapted and refined for other social-ecological systems or contexts, such as public outdoor spaces managed by government officials.

Future research on residential landscapes will benefit from forging interdisciplinary theories with a common vocabulary and integrative approaches (Table 5). Disciplinary framing of research questions with varying theories and epistemologies is a commonly encountered barrier to effective collaboration on complex systems such as residential landscapes (Eigenbrode et al. 2007; Miller et al. 2008). For example, while social scientists recognize that residents create their own version of “nature”—both mentally and materially—in their well-manicured yards (i.e., following theories about the social construction of nature), ecologists traditionally consider a “natural landscape” to more closely represent the properties and functioning of the undisturbed, surrounding native ecosystem (Feagan and Ripmeester 1999). Nevertheless, this barrier can be overcome if scientists work collaboratively outside of their disciplinary training. Integrative approaches with strong conceptual foundations, including concepts like ecosystem services that bridge ecological functions with the values people ascribe to them and conceptual frameworks such as the one presented here, will facilitate this work.
In addition to developing integrated theoretical foundations, research is also needed on understudied system components (boxes Fig. 2) and interactions (arrows Fig. 2) of the residential landscape system. Ecologically, most studies are limited by their focus on ecosystem properties in front yards, but would benefit from examining how ecological properties and processes vary across public (front) and private (backyard) spaces within residential parcels (Table 5). For example, few ecological studies have examined backyards, or distinguish between front and backyards. This is in part due to available methods that rely on from-the-street observations or remote sensing, which coarsely classifies land use and land cover. Social science research, however, has identified variation in the drivers of landscaping practices of the public and private spheres of typical single-family residences. Thus, front and backyards are likely to have distinct landscapes and management practices, and in turn, ecological patterns and processes.

Beyond parcels, the neighborhood to regional ecology of residential landscapes largely remains unknown, particularly in terms of broad-scale ecosystem functioning and services (Table 5). The heterogeneous urban matrix and diversity of management choices at the household-scale make regional generalizations difficult. Further exploration is needed to identify the potential tradeoffs between the ecological outcomes of management practices at all scales, particularly those that lead to ecosystem services and disservices (Table 5). Future research should also link multi-scalar remote sensing technology with ground-level investigations of ecological functioning and social drivers to broaden understanding of cross-scalar feedbacks between the drivers of management practices and their ecological outcomes.
Many household-scale ecological studies note the importance of landscape management practices, yet few quantitatively account for variability in water and chemical inputs. The logistical constraints associated with replication and managing individual resident’s behaviors across multiple study plots make quantifying specific practices difficult. However, empirical research (e.g., Law et al. 2004) suggests chemical inputs vary not only among neighbors, but also between do-it-yourself and professional yard care managers. By generalizing yard care based on professional standards and not accounting for residents’ actual management practices, ecologists cannot accurately calculate variation in ecological properties and functions at the parcel-scale. Inaccurate generalizations about yard management also hinder realistic predictions of ecological processes at broader-scales. Controlled experiments can test the relationship between management practices and plot-scale variables or variables that are easily assessed at larger scales like lawn greenness or microclimate. Integrating social science methods, such as resident surveys about management practices, with ecological field studies will be essential to quantitatively capture the impacts of disparate landscaping practices and understand the heterogeneity of ecological characteristics among parcels (Table 5). Similarly, modeling tools such as the Household Flux Calculator (Baker et al. 2007) will help to identify the distribution and outcomes of various management strategies across households and cities.

In the social sciences, the human drivers of management decisions are relatively well studied, particularly at the household-scale. However, the variety of social constructs, research methods, and cross-scalar feedbacks result in mixed findings and are difficult to generalize (Table 4). For example, due to the disparate ways in which cognitive
judgments are conceived, the magnitude of and interaction between attitudinal factors and landscape management remains unclear. Future research can begin to clarify conflicting findings through consistent conceptualizations of human drivers, particularly cognitive factors, and the use of common methods and definitions (Table 5). Additionally, the relationship between individual agent-based drivers and broad-scale structural drivers of landscaping decisions is unclear. While the field of ecology routinely examines biophysical processes at multiple scales (Wu et al. 2006), many social scientists tend to favor a particular scale or unit of analysis (e.g., households in Larsen and Harlan 2005 versus the broader political economy in Robbins and Sharp 2003b). Social theories about the multi-scalar drivers of human decision-making are therefore underdeveloped, especially in relation to land management and resulting ecological patterns and processes. This is mainly due to the lack of studies examining drivers across scales and different socio-political contexts or locations. Multi-scalar and cross-site research that takes advantage of mixed methodologies, both qualitative and quantitative, will assist in clarifying the multiple influences on human decisions and in explaining disconnects between attitudes, preferences, and behaviors across varying contexts.

Legacy effects from previous land-use/land-cover and management decisions have not been studied extensively in residential landscapes, but they influence social-ecological outcomes and current or future landscaping decisions. A historical perspective provides important context for feedbacks that operate not only across temporal and spatial scales, but also between humans and the environment. Future research will benefit from documenting former land cover, land use, and social context as well as understanding the temporal or spatial patterns that emerge from these (Table 5; Dow
2000). For example, if individuals’ preferences for water-conserving landscapes grow, developers and large-scale market economies may begin to accommodate these new preferences. While shifts in broader institutions are often slow, changes in these institutions may ultimately feedback to affect resident’s management decisions and choice of home based on the existing landscape. In the future, these choices will be a legacy of past decisions, playing a role in how landscapes are managed over time.

Finally, systematic comparisons of social and ecological patterns and interactions are needed across diverse cities and scales using comparable methods (Table 5). Most previous studies have taken a case-specific approach focused on parcel- or household-scale research questions in a single region. Narrow focus on a single geographic context may conceal patterns that diverge in different biophysical (e.g., climatic or physiographic) and social (e.g., political or demographic) contexts. Cross-site research will reveal how and what human-environment patterns and processes emerge in distinct geographies or across diverse settings. Future cross-site research will thereby contribute to generalizable knowledge as well as nuanced, contextual understanding of complex social-ecological interactions that are place-specific.

CONCLUSIONS

Our synthesis of the growing body of literature on residential landscape social- ecology reveals a number of interesting trends and future research opportunities. While a great deal of research has focused on the parcel-household-scale in a single city, the social drivers and ecological characteristics of residential landscapes in fact vary across
scales, from distinct landscape patches within parcels (e.g. front versus backyards), to households, neighborhoods and regions. Additionally, research efforts to date have focused primarily on the individual components of the system, such as the ecological structure of yards or social factors that affect human choices (i.e. the boxes in Fig. 2), and far less is known about the interactions and tradeoffs that occur among these components (i.e. the arrows in Fig. 2). The social and ecological components of the residential landscape system intersect most clearly within two key but understudied areas, the link between drivers and outcomes of management decisions made by people, and the ecosystem services provided by these landscapes to residents (Table 5). In addition, patterns and feedbacks that emerge across scales, as well as across multiple sites and regions, have not been extensively studied and are not well understood.

The synthesis and framework we present draws on insights that emerged from the cumulative social, ecological and interdisciplinary literature on residential landscapes. The suggested integrated conceptual approach brings together disparate, disciplinary research to clarify patterns and dynamics between system components. In addition, this framework advances integrative urban social-ecological theory and research. Residential landscapes are a dominant land use within urban systems, and their management at parcel and broader-scales will have important implications for human well-being, urban ecological functioning, and the continued provision of ecosystem services. Thus, understanding the feedbacks and tradeoffs between human drivers, ecological outcomes and ecosystem services must also coincide with planning and management strategies at multiple scales that maximize benefits to both people and the environment.
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<th>Ecological property</th>
<th>Related explanatory factors</th>
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|                      | Regional climate & urbanization patterns & distance to native ecosystem & Former land use & Habitat fragmentation & Former farmland & Total forest area & Forest age & Woody vegetation & Woody vegetation & Management practices & Socioeconomic & lifestyle factors & Neighborhood age & Housing & density & Yard size & 
|                      | 73 |

The relationships shown here are dominant trends from the residential landscapes literature; however, faunal composition trends may vary by species and region. The relationships indicate the following: (+) indicates a positive relationship; (-) indicates an inverse relationship; (+/-) indicates a mixed relationship; (+) symbols indicate a positive relationship; and blank cells indicate no findings have been reported in the residential landscapes literature. However, faunal composition trends may vary by species and region.
**TABLE 2**: Variables most related to ecological functioning and ecosystem services of residential landscapes across the literature. Symbols as in Table 1

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<th>Ecological function and ecosystem services</th>
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<td>Ecological Structure</td>
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<td>Ground &amp; canopy cover</td>
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<td>Water fluxes (Regulating service)</td>
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<td>Faunal interactions (Regulating service)</td>
<td>Trophic dynamics</td>
</tr>
<tr>
<td>Soil-plant-atmosphere exchange and nutrient cycling (Regulating &amp; supporting services)</td>
<td>Methane (CH$_4$) consumption</td>
</tr>
<tr>
<td></td>
<td>Carbon dioxide (CO$_2$) emissions</td>
</tr>
<tr>
<td></td>
<td>Carbon sequestration</td>
</tr>
<tr>
<td></td>
<td>Nitrous oxide (N$_2$O) emissions</td>
</tr>
<tr>
<td></td>
<td>Nitrate (NO$_3^-$) leaching</td>
</tr>
<tr>
<td>Plant and faunal functions (Regulating, supporting &amp; provisioning services)</td>
<td>Primary production</td>
</tr>
<tr>
<td></td>
<td>Plant gas exchange</td>
</tr>
<tr>
<td></td>
<td>Pollination</td>
</tr>
<tr>
<td></td>
<td>Beneficial predation</td>
</tr>
<tr>
<td></td>
<td>Habitat provisions</td>
</tr>
<tr>
<td></td>
<td>Subsistence provisions</td>
</tr>
<tr>
<td>Landscape functions (Cultural services)</td>
<td>Cooling</td>
</tr>
<tr>
<td></td>
<td>Sense of place</td>
</tr>
<tr>
<td></td>
<td>Social cohesion</td>
</tr>
<tr>
<td></td>
<td>Leisure and recreation</td>
</tr>
<tr>
<td></td>
<td>Property values</td>
</tr>
</tbody>
</table>
TABLE 3: Variables most related to residential landscape management decisions across the literature. Filled symbols (●) indicate variables are strongly related; open symbols (○) indicate mixed or an indirect relationship; plus (+) symbols indicate a positive relationship; blank cells indicate no findings have been reported.

<table>
<thead>
<tr>
<th>Landscape management decisions</th>
<th>Related explanatory factors</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Knowledge of appropriate application rate, amount, etc.</td>
</tr>
<tr>
<td>Fertilization rate &amp; frequency</td>
<td>○</td>
</tr>
<tr>
<td>Pesticide use (herbicides, insecticides, etc.)</td>
<td>●</td>
</tr>
<tr>
<td>Water use</td>
<td>○</td>
</tr>
</tbody>
</table>
TABLE 4: Variables most related to multi-scalar human drivers of residents' preferences and management practices across the literature. Symbols as in Table 3.

<table>
<thead>
<tr>
<th>Related explanatory factors</th>
<th>Preferences</th>
<th>Yards</th>
<th>Irrigation</th>
<th>Fertilizer use</th>
<th>Pesticide use</th>
<th>Lawn care expenditure</th>
<th>Landscape management decisions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Development &amp; policy</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Urbanism &amp; city structure</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
</tr>
<tr>
<td>Social &amp; cultural factors</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
<td>Political economy</td>
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<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
<td>Homeownership</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
<td>Income</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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<tr>
<td>Gender</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
<td>●</td>
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</tbody>
</table>

Homeowner associations often do not directly regulate irrigation, pesticide, or fertilizer use; however, they do require certain yard appearances, which often necessitate the use of these management practices.
TABLE 5: Future research opportunities within and across scales, geographic contexts, and disciplines to advance the study of human-environment interactions within residential landscape settings

<table>
<thead>
<tr>
<th>Ecological properties &amp; processes</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Patterns across front/backyards, neighborhood, regional &amp; larger scales</td>
<td></td>
</tr>
<tr>
<td>• Comparable methods across studies</td>
<td></td>
</tr>
<tr>
<td>• Ecological patterns across geographic contexts</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Ecosystem services</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Ecosystem services as an interdisciplinary concept &amp; tool</td>
<td></td>
</tr>
<tr>
<td>• Tradeoffs between ecosystem services &amp; management practices</td>
<td></td>
</tr>
<tr>
<td>• Dynamics of ecosystem services across scales</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Management decisions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Explicit link between human drivers, management decisions, and ecological &amp; social outcomes</td>
<td></td>
</tr>
<tr>
<td>• Variability in landscaping decisions across contexts &amp; scales</td>
<td></td>
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</tbody>
</table>

<table>
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<tr>
<th>Multi-scalar human drivers</th>
<th></th>
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</thead>
<tbody>
<tr>
<td>• Clear, comparable attitudinal constructs &amp; measurements</td>
<td></td>
</tr>
<tr>
<td>• Social drivers linked to ecological outcomes across private &amp; public spaces</td>
<td></td>
</tr>
<tr>
<td>• Interactions between human drivers across scales</td>
<td></td>
</tr>
<tr>
<td>• Role of institutions (formal &amp; informal) &amp; political-economic forces</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Legacy effects</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Link between social &amp; ecological legacies &amp; current or future decisions</td>
<td></td>
</tr>
<tr>
<td>• Influence of historic land-use/land-cover &amp; geographic context on present-day decisions</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Integrated social-ecological research</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>• Interdisciplinary social-ecological theory, concepts &amp; methods applied across geographic contexts &amp; scales</td>
<td></td>
</tr>
</tbody>
</table>
**FIGURE 1:** Number of publications (1980 – 2010, total N = 256) on social and ecological aspects of residential landscapes, categorized by natural science topics (n = 135), social science topics (n = 64), and those that are interdisciplinary (n = 57) in focus and methodology. Years 1980 - 1992 are grouped together because of the small number (8) of relevant literature published over the 12 year time period.
FIGURE 2: Conceptual framework of multi-scalar social-ecological interactions of residential landscapes. Arrows represent interactions between framework components.
CHAPTER 3

ATMOSPHERIC NITROGEN DEPOSITION IN A LARGE SEMI-ARID CITY IS LOWER THAN EXPECTED: FINDINGS FROM A METHODS COMPARISON

ABSTRACT

Cities occupy a small land area globally, yet atmospheric compounds generated from human-dominated ecosystems have significant impacts on protected lands. Atmospheric nitrogen (N) deposition alters ecosystems, including biogeochemical cycling, primary production, and community composition. In arid ecosystems, considerable uncertainty surrounds estimates of atmospheric N inputs due to heterogeneous precipitation patterns and difficulties in quantifying dry deposition. I employed multiple approaches to quantify spatial and temporal patterns of N deposition at locations within Phoenix, Arizona and the surrounding native desert. I compared N deposition measured by ion-exchange resin (IER) collectors (bulk and throughfall, 2006–2013), and N deposition estimated by the inferential method using passive samplers (atmospheric N concentrations x deposition velocity; 2010-2012). Over two summer and winter seasons, I co-located samplers to directly compare methods for quantifying total and dry N deposition. Rates of total (wet and dry) N deposition estimated with throughfall collectors (3.3 kg N ha\(^{-1}\) yr\(^{-1}\)) had minimal spatial variation and were significantly lower than expected based on model and other aridland estimates. Despite minimal spatial variation, N deposition varied temporally. For example, total N throughfall deposition was greatest in the summer monsoon season and best predicted by the frequency of
precipitation events. Contrary to throughfall estimates, inferential methods indicated elevated N deposition—in the form of ammonia, nitrogen oxides, and nitric acid deposition—was restricted to the urban core (6.4 kg N ha\(^{-1}\) yr\(^{-1}\)). Overall, throughfall methods significantly underestimated total and dry deposition particularly in the urban region and in the winter season. By accounting for the potential underestimation by throughfall, I predicted average long-term N deposition in the region was 7.3 kg N ha\(^{-1}\) yr\(^{-1}\), which more closely approximated the modeled regional deposition but was still relatively low compared to other arid regions. Inconsistencies between approaches reveal how uncertainties related to quantifying dry deposition, as well as site characteristics and deposition velocities easily confound N deposition estimates. These findings highlight the need for and benefit of mixed methods to quantify wet and dry N deposition in arid systems. Overall, despite the size and population of arid Phoenix, N deposition was lower than expected compared to other cities, but was greatest in the urban core compared to the outlying desert.
INTRODUCTION

Increased human activities have led to elevated concentrations of atmospheric reactive nitrogen (N) worldwide (Vitousek et al. 1997; Galloway et al. 2004; Dentener et al. 2006). Emissions of oxidized and reduced N gases are transported downwind of urban and agricultural sources until they form secondary products or are removed from the atmosphere to surfaces through rainfall (wet deposition), cloud vapor, or adsorption of gases and particles (dry deposition). Rates of N deposition and the ecological effects have been well characterized in many ecosystems with high rainfall, including temperate and boreal forests, mesic grasslands, and heathlands (Lovett 1994; Aber et al. 1998; Galloway et al. 2004; Holland et al. 2005; Weathers et al. 2006; Bobbink et al. 2010; Pardo et al. 2011). In these regions, N deposition has increased during decades of urban and industrial growth and is projected to continue rising, with significant consequences for biogeochemical cycling and biotic composition (Phoenix et al. 2006; Dentener et al. 2006; Bobbink et al. 2010). Arid and semi-arid ecosystems cover over a third of the globe’s land area and future urban growth is expected to disproportionately occur in developing arid and semi-arid grassland and shrublands worldwide (UN 2009). Nitrogen deposition is thus expected to increase in dryland ecosystems, which likely respond differently than N-limited ecosystems where water does not constrain plant production. Yet, the quantification of N deposition in dryland regions has received far less attention than in more temperate ecosystems. And, where aridland N deposition has been quantified, there are many uncertainties and challenges in quantifying dry deposition and inputs from spatially and temporally patchy precipitation events (Fenn et al. 2009).
Arid and semi-arid ecosystems are especially sensitive to small anthropogenic changes, such as elevated N (Fenn, Baron, et al. 2003; Pardo et al. 2011). Significant portions of aridland ecosystems are predicted to receive atmospheric N inputs at or above the desert critical load—the level of deposition between 3-8 kg N ha\(^{-1}\) yr\(^{-1}\) at which ecological changes occur (Fenn et al. 2010; Pardo et al. 2011). For example, in the semi-arid southwestern and western United States (US), dry deposition alone is estimated within the range of the critical load and as high as 14 - 35 kg N ha\(^{-1}\) yr\(^{-1}\) (Alonso, Bytnerowicz, and Boarman 2005; L. E. Rao et al. 2009; Cisneros et al. 2010). Nitrogen inputs above the critical load in aridlands result in increased annual herbaceous plant growth, a loss of native desert vegetation, increased fire frequency, and lake eutrophication (Brooks 2003; Fenn, Baron, et al. 2003; Baron 2006; Báez et al. 2007; L. E. Rao, Allen, and Meixner 2010). The low N critical load in drylands highlights the importance of accurately assessing total atmospheric inputs to arid systems and capturing the pulsed wet deposition and dry deposition over long time periods. In order to better predict when and where deposition will occur for more effective management and protection of native ecosystems, a better understanding of the patterns and drivers of N deposition is needed.

Atmospheric N inputs are expected to be particularly high in arid regions influenced by urbanization compared to more remote arid lands. For example, empirical estimates of N deposition range between 30 - 60 kg N ha\(^{-1}\) yr\(^{-1}\) in the metropolitan regions of Los Angeles, California and the large Chinese cities of Urumqi and Beijing (Bytnerowitz and Fenn 1996; Fenn et al. 2003; Pan et al. 2012; Li et al. 2013). Yet, in the sixth largest city in the US, estimates of N deposition in Phoenix, Arizona and the surrounding Sonoran
Desert are an order of magnitude lower (3-6 kg N ha\(^{-1}\) yr\(^{-1}\)) than other arid urban regions and than regional models predict (Baker et al. 2001; Fenn, Haeuber, et al. 2003; Lohse et al. 2008). It is uncertain if the modeled or empirical estimates in Phoenix are more accurate. In particular, dry deposition, which can contribute significantly to N inputs in arid systems, can be difficult to quantify empirically (Lohse et al. 2008). On the other hand, modeled estimates of wet and dry N deposition are often generated from regional-scale models, such as the Community Multi-scale Air Quality (CMAQ) model, or national monitoring networks for wet and dry deposition. Both the CMAQ model and monitoring networks are limited in their spatial resolution or ability to capture spatial heterogeneity, particularly near urban systems and in patchy arid systems, and have been found to over- or underestimate local-scale deposition (Holland et al. 2005; Fenn, Haeuber, et al. 2003; Fenn et al. 2013; Bettez and Groffman 2013). Overall, the large discrepancy between modeled and empirical rates of N deposition highlights the difficulty in estimating deposition in urban aridland systems (Lohse et al. 2008).

While wet deposition during rainy seasons is expected to be an important seasonal input to arid systems (Báez et al. 2007; Li et al. 2013), dry deposition is thought to contribute up to 80% of atmospheric inputs to arid landscapes where limited precipitation is spatially and temporally heterogeneous (Hanson and Lindberg 1991; Lohse et al. 2008; Fenn et al. 2010; Li et al. 2013). Dry N deposition, however, is challenging to quantify because of short gaseous atmospheric life spans, volatilization, saturated leaf surfaces, or biological uptake (Hanson and Lindberg 1991; Lovett 1994; Asman, Sutton, and Schjørring 1998; Golden et al. 2008; Fenn et al. 2013). For example, throughfall monitoring—a method used in many ecosystems to measure wet and dry ammonium
(NH₄) and nitrate (NO₃)—may underestimate N deposition in arid systems when leaf surfaces become saturated with dry deposition during long periods without rain (Fenn et al. 2000; Fenn et al. 2009). Dry deposition can be estimated from the inferential method based on atmospheric concentrations of ammonia (NH₃), nitrogen oxides (NOₓ), and nitric acid (HNO₃) and the deposition velocity (Vₜ) of each N compound. Deposition velocities—requiring site-specific meteorological, vegetation, and landscape characteristics—can also be difficult to quantify and compound the uncertainty of dry deposition estimates for a region (Wesely and Hicks 2000; Krupa and Legge 2000).

More accurate N deposition estimates may be obtained by employing multiple empirical monitoring techniques that can be extrapolated locally and regionally with modeled N deposition estimates (Holland et al. 2005; Fenn et al. 2013). Quantifying both wet and dry N fluxes and capturing their seasonal variability is important for accurately estimating total ecosystem inputs and effectively mitigating and managing the resulting ecological consequences.

Given the largely unknown rates of total N deposition—and dry deposition in particular—in arid systems and the uncertainty in drivers and individual sampling methods, I asked, what are spatial and temporal patterns and dominant drivers of total (wet and dry) N deposition in arid regions? Using the Phoenix metropolitan region where N deposition estimates are uncertain and the surrounding Sonoran Desert as a case study, I employed multiple sampling approaches to quantify N deposition. I used throughfall (wet and dry) and bulk (wet) collectors to examine long-term seasonal dynamics of N deposition in urban and outlying desert locations. I also employed the inferential method to compare dry deposition across seasons and urban and outlying
desert locations. Inferential estimates of dry deposition can provide an indication of the upper bounds of potential dry deposition in the system, which can then be used in combination with other methods to approximate total deposition.

Overall, I expected total N deposition to differ spatially and seasonally, largely dependent upon precipitation patterns and proximity to urban areas. Similar to other arid urban regions, I expected N deposition to exceed the desert critical load. In particular, I expected the highest deposition rates to occur in the urban region near emissions sources. Following modeled estimates, I also expected deposition to be high in outlying desert locations to the east where downwind deposition was predicted to be higher than in other remote areas. Due to seasonal differences in wet inputs, I expected higher total deposition during the rainy seasons. Yet due to the patchy precipitation, I hypothesized dry deposition would account for a majority of total annual deposition.

To test the drivers of N deposition, I hypothesized that not only the amount of precipitation but also the timing of rain events and location relative to urban areas would be an important predictor of N deposition patterns. For example, I expected metrics of extended dry periods, such as the number of antecedent dry days and the number of consecutive rain-free days, would improve the estimates of total wet and dry (throughfall) deposition, whereas wet (bulk) deposition would be better predicted by total precipitation and the number of rainy days. In addition to rainfall, I expected site-specific meteorological variables (temperature and relative humidity) and urban characteristics (e.g. traffic density) to be strong drivers of total N deposition patterns.
METHODS

Site Characteristics

The Phoenix metropolitan area situated in the northern Sonoran Desert is an ideal case study to examine N deposition in drylands as a result of urbanization. Phoenix has been characterized as one of the fastest growing urban areas in the US (Gober 2006). With rapid urban sprawl housing a population of over 4 million, the Phoenix metropolitan region and the surrounding Sonoran Desert experience the effects of land use conversion, the urban heat island, and elevated reactive N gas emissions (Brazel et al. 2000; Baker et al. 2001; Grimm and Redman 2004). The ecological effects of N deposition are expected to lead to changes in primary production and community composition with cascading effects on ecosystem services such as ecosystem N retention (Hall et al 2011). Yet, rates of atmospheric N inputs from urban and agricultural emissions to the ecosystem are largely unknown, and accurate estimates are further compounded by the difficulty in quantifying dry deposition. Accurate N flux estimates are important for predicting the ecological consequences of N inputs to ecosystems and evaluating the effectiveness of conservation and N emission control policies (Holland et al. 2005; Lovett 2013).

The Phoenix metropolitan region provides a unique study system for examining the effects of urbanization on arid ecosystems. Municipal ordinances have preserved large remnant patches of native Sonoran Desert within the metropolitan area, making an urban-rural comparison possible between urban remnant desert and outlying desert locations. The Sonoran Desert is characterized by unique vegetation, precipitation and wind patterns. Drought tolerant cacti (e.g. Saguaro, *Carnegiea gigantea*), shrubs (e.g. creosote
bush, *Larrea tridentata*), and winter herbaceous vegetation dominate the landscape. Average annual precipitation is 208 mm with bimodal winter (October – March) and monsoon summer (June – September) seasonal rains (NOAA 2010), and there is a precipitation gradient across the valley with highest rainfall at slightly higher elevations to the east (Table 1). In addition, the average minimum and maximum daily temperatures in the region are 17 and 31°C, respectively (NOAA 2010).

Finally, the Phoenix valley has complex topography resulting in atmospheric mixing patterns that shift daily and seasonally affecting spatial and temporal distribution of atmospheric compounds (Nunnermacker et al. 2004; Wang and Ostoja-Starzewski 2004; Lee, Fernando, and Grossman-Clarke 2007). The unstable summer atmosphere leads to significant atmospheric mixing throughout the valley, while the more stable winter atmosphere and winter inversion create less vertical mixing. For example, the winter atmosphere tends to settle in the urban core in the early morning until mid-day warming of the eastern mountains and winds from the west causes the atmosphere near the mountains to rise and mix, at which time it is replaced by atmospheric wind from the city center. In the evening, cooling temperatures cause the air to settle back into the valley.

*Long-term N deposition monitoring*

*Monitoring site characteristics:* In order to examine my questions regarding long-term N deposition across seasons and urban and remote locations, I continuously monitored N deposition at 15 sites within the 6400 km² Central Arizona-Phoenix Long-term Ecological Research (CAP LTER) area from March 2006 – December 2013. Five monitoring sites were located within urban desert remnant patches (urban locations, n =
5) and 5 sites each were located to the west and east of Phoenix in protected desert preserves (outlying locations, n = 10; Figure 1; Table 1). One urban site (Mountain View Park, MVP) had limited sampling after 2007 because of frequent human disturbance of field equipment. All sites have similar sandy loam soils, vegetation dominated by drought tolerant creosote bush, and are part of an extensive manipulative N and phosphorus addition experiment measuring ecosystem variables across the landscape (Hall et al. 2011; Sponseller et al. 2012).

**Measuring bulk and throughfall NO$_3$ and NH$_4$ deposition:** With ion exchange resin (IER) collectors, I measured bulk (wet) deposition in interplant open spaces and throughfall (wet and dry) deposition under the dominant shrub. Both bulk and throughfall collectors were deployed with 2 replicates at each site. Collectors were deployed continuously over four 3-month sampling intervals per year (n = 31 sampling intervals from 2006 - 2013) – approximately January to March, March to June, June to September, and September to December. Collectors were in the field for an average deployment of 89 days (range: 35 – 121 days in the field across all sites and periods). Replicate bulk and throughfall subsamples were averaged for each site and period (15 sites x 31 periods, n = 465). Dry deposition was estimated by taking the difference of throughfall and bulk deposition (after averaging the subsamples) for each site and period. Similarly, the ratio of NH$_4$:NO$_3$ in throughfall and bulk deposition was calculated for each site and period after averaging subsamples. The actual number of samples varies for throughfall (n = 419), bulk (n = 410) and dry deposition (n = 395) due to some missing, broken or contaminated field samples, as well as the minimal sampling at MVP.
Bulk and throughfall IER collectors were built with a modified design following Fenn and Poth (2004) and Simkin and colleagues (2004). For each sampling period, IER collectors were made with hydrochloric acid-washed supplies. Each IER collector consisted of a 12” PVC pipe filled with 60 mL Monosphere Dowex Resin (Dow Chemical Company). The resin-filled pipe was closed on one end with a PVC cap with 5 – 7 holes drilled for drainage and filled with glass wool to prevent resin loss. On the other end of the resin-filled PVC pipe, nitex screening was used to prevent debris in the resin and a plastic funnel was placed onto the top. The funnel was covered with mesh and a bird spikes to prevent debris contamination of the resin.

In the field, bulk collectors were installed 1.5 meters above the ground on rebar in open space areas without canopy cover. Throughfall collectors were placed under *L. tridentata*, where 2-ft holes were dug and filled partly with aquarium rocks to allow for drainage during rain events. All IER collectors (including the funnels and the *L. tridentata* branches for throughfall collectors) were rinsed with 500 mL di-ionized water before being collected at the end of the sampling period. In addition, field blanks were prepared without a funnel and instead capped on both ends. Field blanks were deployed at one urban (DBG) and two outlying sites (WTM and LDP) with three replicates at each site for both bulk and throughfall field blanks.

After exposed samplers were collected in the field, NH\textsubscript{4} and NO\textsubscript{3} ions were extracted from each resin sample with 200 mL 2M potassium chloride (KCl) solution. KCl-resin slurries were shaken for one hour and then filtered through Whatman 42 filters pre-leached with KCl. In addition, three KCl extract blanks were prepared. All KCl extracts were analyzed on the continuous flow injection Lachat QuikChem 8000 (Lachat
Instruments) for NH₄ and NO₃. Data were corrected for extract blanks and field blanks from the from their corresponding landscape location. There were no field blanks deployed between March 2006 – December 2007, thus samples from these periods were corrected with an average of field blanks from the following four sampling periods.

With N concentrations (mg N-NO₃ L⁻¹ and mg N-NH₄ L⁻¹) from the KCl extract solutions, I calculated N deposition (kg N ha⁻¹ yr⁻¹) for each site and period. N deposition was estimated based on the volume of extract solution (0.2 L), open area of the funnel (314 cm²) on each collector, and the number of days each sampler was deployed in the field.

_Estimating dry deposition with multiple sampling approaches_

_Monitoring site characteristics: Using passive filter samplers and the inferential method, I estimated gaseous N concentrations and dry N deposition, respectively, at two locations (open symbols Figure 1). This two-site design was chosen to compare N concentrations and dry deposition at an urban location with expected high atmospheric N concentrations and an outlying desert location with expected low N concentrations. The anticipated difference in N deposition makes an ideal set-up for comparing the dry deposition estimated by IER collectors (described above) and the inferential method. In addition, the outlying location at Lost Dutchman State Park (LDP) is approximately 65 km east of Phoenix and is co-located with one of the long-term monitoring sites described above. The urban site is located in a dense residential neighborhood near central Phoenix. The urban site is also a monitoring location for the Arizona Air Quality_
department. Both sites have a meteorological tower operated by the CAP LTER that provided site-specific data for calculating deposition velocities of each N species.

Measuring gaseous NH$_3$, NO$_x$, and HNO$_3$ concentrations and estimating dry deposition: At both locations, I measured concentrations of NO$_x$, NH$_3$, and HNO$_3$ using co-located passive samplers. NO$_x$, NH$_3$, and HNO$_3$ are expected to make up the predominant reduced and oxidized N gases that deposit to surfaces and have ecological consequences (Holland et al. 2005). Passive samplers were deployed for consecutive 2-3 week intervals over two summer seasons (3 and 4 summer sampling intervals in 2010 and 2011, respectively) and two winter seasons (4 and 3 sampling intervals in 2010-2011 winter and 2011-2012 winter, respectively). NH$_3$ and NO$_x$ samplers were deployed with 2 replicate samplers per site per sampling interval (NH$_3$: 4 replicates/site, NO$_x$ and NO$_2$: 2 replicates each/site). Similar to NO$_x$ and NH$_3$, four replicate HNO$_3$ samplers were deployed during each sampling interval at a site. Replicates were averaged by site and sampling interval.

Ammonia and NO$_x$ (NO$_x$ and NO$_2$) concentrations were measured using Ogawa Teflon passive samplers and Ogawa impregnated filter pads (Koutrakis et al. 1993; Roadman et al. 2003). Ambient NH$_3$ concentrations were collected on filter pads coated with citric acid, which forms ammonium citrate in the presence of NH$_3$. Ambient NO$_x$ concentrations were collected by simultaneously exposing NO$_2$ and NO$_x$ filter pads that together were used to calculate total NO$_x$ (details of the calculations below). Ambient NO$_2$ filters were coated with triethanolamine (TEA) and NO$_x$ filter pads with TEA and PTIO (2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl). TEA reacts to form nitrite (NO$_2^-$) and PTIO is a free radical reagent to scavenge NO and NO$_2$ simultaneously.
Nitric acid samplers were designed following methods developed by Bytnerowicz and colleagues (2005) set-up using nylon membrane filters (Pall brand Nylasorb nylon membrane filters, 1.0μm, 47mm) to collect ambient air absorbed as NO₃. For each site and sampling period, one additional sampler was set-up as a field blank for each filter type.

Passive samplers were all transported to and from the field in a sealed bag within a sealed plastic container. In the field, passive samplers were installed under a protective cover to block direct sun and rain at approximately 2 meters above ground and away from tall vegetation and structures. Field blanks were prepared and transported to the field sites the same as samplers that were deployed. However, field blanks were returned to the lab immediately after the field samples were deployed and remained sealed on a lab bench at room temperature during the sampling period.

At the end of each sampling period, exposed filters were transported to the lab, where they were transferred to a sealed 20-ml acid-washed glass vial. Dry filters were stored in the freezer until analysis. Each filter was extracted separately with double de-ionized water (DI) directly before analysis and shaken on a shaker table at 165 rpm for 15 minutes. NH₃, NO and NO₂ filters were extracted with 8 mL DI water and HNO₃ filters with 20 mL DI water. NH₃ and HNO₃ samples were filtered through a 0.02 μm syringe filter (Acrodisc 13mm, 0.2 μm nylon syringe filters to prevent clogging in the analytical instrument) and analyzed in duplicates on a Dionex ion chromatograph (Dionex Corporation): NH₃ samples for ammonium and HNO₃ samples for nitrate. NO and NO₂ filters were analyzed for nitrite on the continuous flow injection Lachat Quikchem (Lachat Instruments). The field blanks were extracted and analyzed the same as the
exposed filters. I also analyzed extraction blanks (unexposed “blank” filters that were extracted and analyzed with each set of samples). I averaged duplicate samples from the same sampling period and corrected each with the corresponding blank.

Calculating N concentrations and dry deposition: Gaseous N concentrations and dry deposition rates were calculated using a variety of methods. Ammonia concentrations were calculated following Ogawa protocol (equation 1) based on exposure time, extract concentration and volume and the site-specific diffusion coefficient based on meteorological variables. In equation 1, \( \text{NH}_4 (\mu g \text{ mL}^{-1}) \) is the concentration of the sample extract, 17.04 (\( \mu g \mu mol^{-1} \)) is the molecular weight of \( \text{NH}_3 \), 14.01 (\( \mu g \mu mol^{-1} \)) is molecular weight of N, and 24.45 is the constant conversion factor for volume to mass of an ideal gas at standard temperature and pressure. The alpha conversion factor converts \( \text{NH}_4 \) to \( \text{NH}_3 \) concentration by molecular weight and includes the mass transfer diffusion coefficient – or sampling rate – that was calculated based on the geometry of the sampler and the molecular diffusivity of the gas using site-specific meteorological variables during each sampling period (Roadman et al. 2003). I calculated the \( \alpha \) conversion factor for \( \text{NH}_3 \) following Roadman and colleagues (2003) based on average temperature during the sampling interval.

\[
\text{NH}_3 \left( \frac{\mu g N}{m^3} \right) = \frac{\text{NH}_4 \left( \frac{\mu g}{mL} \right) \times \text{Extract volume (mL)} \times a \left( \frac{\text{mg min}}{\mu g} \right) \times 17.04 \left( \frac{\mu g}{\mu mol} \right) \times 14.01 \left( \frac{\mu g}{\mu mol} \right) \times 24.45 \left( \frac{m^3}{\mu mol} \right)}{\text{Exposure time (min)}} \quad (1)
\]

Nitrogen dioxide gaseous concentrations were calculated similarly to \( \text{NH}_3 \) following Ogawa protocol (Equation 2). \( \text{NO}_2 (\mu g \text{ mL}^{-1}) \) is the concentration of the sample extract from the \( \text{NO}_2 \) filter pad, 46.01 (\( \mu g \mu mol^{-1} \)) is the molecular weight of \( \text{NO}_2 \), and the \( \alpha \)
conversion factor was calculated specifically for each site and sampling period based on temperature, relative humidity and vapor pressure of water.

\[
NO_2 \left( \frac{\mu g N}{m^3} \right) = \frac{NO_2 \left( \frac{\mu g}{mL} \right) \times Extract \ volume \ (mL) \times a \left( \frac{ppb \cdot min}{\mu g} \right)}{Exposure \ time \ (min) \times 46.01 \left( \frac{\mu g}{pmol} \right) \times 14.01 \left( \frac{\mu g}{pmol} \right)}
\]

Total NO\textsubscript{x} gaseous concentrations were determined by summing NO and NO\textsubscript{2} concentrations. Since there is no \( \alpha \) conversion factor for NO\textsubscript{x} (the combination of NO and NO\textsubscript{2}), the concentration of NO and NO\textsubscript{2} was determined separately and then summed. NO was calculated by subtracting the extract concentrations of NO\textsubscript{2} from the corresponding NO\textsubscript{x} sample from the same site and interval. Then, following Equation 2, NO concentration (\( \mu g N \text{ m}^{-3} \)) was calculated using an NO specific \( \alpha \) conversion factor and the molecular weight of NO.

HNO\textsubscript{3} concentrations were calculated using the Bytnerowitz et al (2005) calibration curve of absorbed NO\textsubscript{3} on each filter when exposed to particular HNO\textsubscript{3} dose in controlled conditions (slope = 69.498 (hour m\textsuperscript{-3}); equation 3).

\[
HNO_3 \left( \frac{\mu g N}{m^3} \right) = \frac{NO_3 \left( \frac{\mu g}{mL} \right) \times Extract \ volume \ (mL) \times 69.498 \left( \frac{hour}{m^3} \right)}{Exposure \ time \ (hour) \times 63.02 \left( \frac{\mu g}{pmol} \right)}
\]

Using the inferential method, I estimated dry N deposition based on the concentrations from the passive samplers (equations 1 – 3) and estimated deposition velocities (\( V_d \text{ cm sec}^{-1} \)) for each gaseous N species (equation 4). I used deposition velocities previously estimated by the scholars in the CAP LTER network for the outlying desert site (Gonzalez, unpublished data; Table 2). While deposition velocities vary between sites due to different vegetation structure and meteorological conditions, the deposition velocities I used for each N species were comparable to those used in other
arid and urban-arid ecosystem studies (Wesely and Hicks 2000; Zhang, Brook, and Vet 2003; Pan et al. 2012; Delon et al. 2012; Li et al. 2013).

$$Deposition \ (kg \ N \ ha^{-1} \ yr^{-1}) = N \ Concentration \ * \ V_d$$ (4)

To examine the accuracy of long-term N deposition estimates from IER collectors within my study site, I compared total deposition estimated from multiple sampling approaches. At the urban and outlying location, I co-located bulk and throughfall IER collectors with the passive filter samples described above. I planted a *L. tridentata* shrub at the urban comparison site (an empty dirt lot with meteorological monitoring equipment) in order to collect throughfall using the same method as in the outlying location. The IER collectors were deployed continuously over the same sampling intervals each season (installed at the beginning of the first sampling period with passive filter samplers and collected at the end of the last sampling interval per season). The IER collectors were analyzed for NH$_4$ and NO$_3$ with the same methods described above.

In order to compare total (wet and dry) N deposition estimates, I compared total N deposition estimated from throughfall (wet and dry) to total N deposition estimated by adding wet bulk deposition with dry deposition calculated from the inferential method.

**Meteorological and urban site characteristics**

**Meteorological variables**: I gathered several site characteristics, including meteorological variables that were averaged (or summed for precipitation) over each sampling interval. Precipitation, relative humidity, temperature and wind speed and direction were downloaded from the nearest meteorological monitoring stations (Table 1; FCDMC 2013; see Appendix 1 for meteorological stations). In order to address the
temporal variability in precipitation during sampling intervals, I calculated 5 precipitation metrics, in addition to total precipitation, for each sampling interval. Metrics included 1) the number of rainy days per interval, 2) a ratio of the number of rainy days to rain-free days in each sampling interval, 3) the longest number of consecutive rain-free days per interval, 4) the antecedent dry days, which was calculated as the number of consecutive dry days before the first rain event for each sampling interval (including rain-free days from the previous period), and 5) the antecedent dry days specific to the period. The distinction between the last two metrics is expected to be important for explaining variability in throughfall versus bulk deposition, respectively, where bulk deposition is expected to be dependent only upon precipitation while throughfall may capture accumulated dry deposition from the previous sampling interval.

*Urbanization variables:* I also calculated several anthropogenic related site characteristics. These include housing density, traffic density, and percentage of urban land use within a 10 km buffer area around each site (Table 1). The number of households in each buffer area was calculated with 2010 Census block data including all census blocks that overlapped the perimeter of the 10 km buffer (using the spatial join tool in ArcGIS 10.0). I calculated housing density by summing the total number of households and dividing by the land area (households km$^{-2}$). Similarly, I calculated traffic density using 2008 average weekday traffic counts, including heavy and light duty traffic on freeways and arterial roads, modeled from the TransCAD travel demand model (Maricopa Association of Government’s Transportation Division; modeled data shared by Ron Pope, Maricopa Air Quality Department). Using ArcGIS, the traffic density was calculated by summing the traffic count or all the roads within the 10 km buffer around
each site (including road segments overlapping the perimeter of the buffer based on Spatial Join tool) and dividing by the total length of roadways within the buffer.

**Data analyses**

Statistical analyses were conducted using R (R Core Team, 2014). Dependent variables were transformed to meet basic parametric assumptions to compare N deposition between locations, seasons, and years using analysis of variance. Aggregating temporal data to examine spatial patterns, I used a two-way ANOVA to compare N deposition among sites and regions (outlying west, urban and outlying east). I then aggregated across sites to compare inter and intra annual temporal variability of N deposition.

I used multiple linear regression analyses to determine the main predictors of N deposition (throughfall, bulk, and estimated dry) across the Phoenix metropolitan region. To test the importance of the timing of precipitation, I first ran multiple linear regression analyses with only the precipitation metrics. Next, I included all site characteristics into the initial model. I used a backward stepwise approach, such that predictor variables were removed from the full model stepwise to determine the most predictive power and parsimonious model based on AIC scores, adjusted $R^2$ and reduced multi-collinearity among independent variables.

For N concentrations and dry N deposition measured between 2010 – 2012, I compared HNO$_3$, NH$_3$, NO$_x$ individually and total N (HNO$_3$ + NH$_3$ + NO$_x$) as concentrations and deposition by site location and season using a two-way ANOVA.
Throughfall measurements were expected to capture both wet and dry deposition in an ecosystem. Yet, throughfall has the potential to underestimate dry deposition in arid systems where dry deposition can saturate leaf surfaces during extended periods without rain (Fenn et al 2009). In order to examine this potential underestimation in throughfall deposition, I compared two estimates of total (wet and dry) N deposition measured with co-located samplers. Specifically, I compared total throughfall N deposition with total deposition estimated by adding wet deposition collected in bulk IER samplers and dry deposition estimated from the co-located passive gas collectors. Based on these alternative methods of calculating total N deposition, I calculated the percent of total N deposition underestimated by throughfall following equation 5.

\[
\text{% underestimate by throughfall} = 100 - \left(\frac{\text{throughfall}}{\text{bulk + dry inferential}}\right)
\]  

(5)

RESULTS

Long-term N deposition

From 2006 – 2013, mean total inorganic N (NH$_4$ + NO$_3$) throughfall deposition in the region was 3.3 (+/- 0.1) kg N ha$^{-1}$ yr$^{-1}$ and ranged from 0.2 – 18.0 kg N ha$^{-1}$ yr$^{-1}$ (Table 3). Throughfall deposition, measuring both wet and dry deposited N, was significantly greater than wet bulk deposition (2.0 +/- 0.1 kg N ha$^{-1}$ yr$^{-1}$, ranging between 0.07 – 11.8 kg N ha$^{-1}$ yr$^{-1}$). Estimated using the difference between throughfall and bulk collectors, dry deposition was 42% of total deposition (0-97%; Table 3) and the median dry:wet deposition across all sites of was 0.83 (0 - 29.5).
Across the region, NH$_4$ fluxes were greater than NO$_3$. The average NH$_4$:NO$_3$ ratio was 2.8 (+/-0.2) and 1.5 (+/-0.1) in throughfall and bulk deposition, respectively, across all sites (Table 3). On average, NH$_4$ was 68% (36-97%) of total throughfall deposition and 53% (0-86%) of wet bulk deposition. Additionally, variability of NO$_3$ fluxes (65% CV) was lower than NH$_4$ fluxes (93% CV) in throughfall across sites and years, and was similarly true for wet bulk and dry deposition (Table 3, Appendix 2).

**Spatial variability of N deposition:** Averaged across seasons and years, total (NH$_4$ + NO$_3$) throughfall deposition was significantly different among sites (two-way ANOVA, p = 0.006) and minimally different among regions (p = 0.06). Total urban N throughfall was minimally greater than both outlying west (p = 0.1) and east (p = 0.09). Across sites, total throughfall deposition was significantly greater at MVP than two outlying sites (outlying west EMW and outlying east SRR, Table 3). However, N deposition collection at MVP ended in 2007 due to human destruction of field samples in the urban park. When MVP is removed from the analysis, the differences between region are no longer significant (p = 0.15) and throughfall deposition at the DBG was minimally significantly greater than at SRR (p = 0.1).

On the other hand, the patterns of NH$_4$:NO$_3$ and NH$_4$ and NO$_3$ individually in throughfall differed from total (NH$_4$ + NO$_3$) throughfall deposition. The ratio of NH$_4$:NO$_3$ in total throughfall did not differ significantly among sites (two way ANOVA, p = 0.2). Yet, the outlying west desert region had significantly higher NH$_4$:NO$_3$ than both the urban and outlying east desert regions (p <0.001, Table 3). Examining NH$_4$ and NO$_3$ deposition individually, average NO$_3$ in throughfall was significantly greater in the city than in outlying sites to east or west of Phoenix (p < 0.001), while NH$_4$ in throughfall
did not differ between regions (p = 0.14; data not shown). Across sites, urban DBG and PWP and one outlying east site (MCN) had greater NO$_3$ throughfall deposition than outlying west EME and EMW (p = 0.004). NH$_4$ was significantly greater at MVP than outlying site EME and SRR (p = 0.02).

Total N (NH$_4$ + NO$_3$) in wet bulk deposition was not significantly different among sites (two-way ANOVA, p = 0.9), but was significantly lower in the outlying west region than urban or outlying east region (p = 0.02, Table 3). NH$_4$:NO$_3$ ratio in wet deposition followed a similar pattern; it did not differ among sites (two-way ANOVA, p = 0.12), but was significantly lower in the outlying west location than outlying east (p = 0.009).

Dry deposition was more variable than throughfall or bulk deposition. Total (NH$_4$ + NO$_3$) dry N deposition was significantly lower in the outlying east desert than urban or outlying west desert regions (two-way ANOVA, p < 0.001, Table 3). Total dry deposition also varied by site (p < 0.005, Table 3). DBG (urban), SNW and SNE (west sites) were significantly greater than outlying east: LDP, SRR and outlying west: EME.

Temporal variation of N deposition: N deposition varied both intra-annually and inter-annually. Seasonally across all sites, NO$_3$, NH$_4$ and total N (NH$_4$ + NO$_3$) throughfall was greatest between June to September (p<0.001; Figure 2). NH$_4$ and total N deposition in all other times of the year (January-March, March-June, and September-December) did not significantly differ. In contrast, NO$_3$ in throughfall was significantly lower between March and June than other periods. Similarly, wet bulk total (NH$_4$ + NO$_3$) deposition was the greatest during the summer monsoon season of June – September, while the relatively dry season between March and June had significantly lower deposition than January – March and June – September (p < 0001). Dry total (NH$_4$
+ NO₃) deposition was significantly greater in summer monsoon season between June – September than all other seasons (p = 0.01)

Significant inter-annual variation was predominately a result of deposition rates measured in 2006, which had an anomalously high period of N deposition between June – September 2006 (June-September 2006 average throughfall across all sites was 12.7 +/- 0.8 kg N ha⁻¹ yr⁻¹ compared to the same period during other years that ranged between 2.2 - 7.1 kg N ha⁻¹ yr⁻¹; Figure 2). Averaged across sites, total N throughfall was significantly greater in 2006 than all other years (p<0.001). When this period was removed as an outlier, N deposition in 2006 was still significantly greater than in 2009 (p = 0.04) a year of below-average precipitation (Figure 2). The differences in total N throughfall deposition across all other years were minimal and not significant. There were minimal significant differences in wet bulk deposition across years (p = 0.06), but there were no significant differences among years in post-hoc pairwise tests. However, dry deposition was significantly lower in 2009 than in 2008 (p = 0.04).

Drivers of long-term N deposition: I expected the variability in the timing of the precipitation to be an important driver of N deposition in arid systems; thus, I analyzed throughfall, bulk, and dry N deposition based on precipitation metrics alone (i.e., excluding other site-specific variables). To compare the relative importance of timing in rain events, I compared standardized beta coefficients (st β) from a best fit multiple regression model. The initial full model started with all 6 precipitation metrics (Throughfall ~ Precipitation + Rainy days:Dry days + # Rainy Days + Longest consecutive dry days + Antecedent Dry Days + Antecedent dry days by period), and I removed non-significant independent variables stepwise based on AIC scores. For
throughfall, the best fit model (Table 4, $F(5,412) = 60.6$, $p < 0.001$, adj $R^2 = 0.42$) included all the precipitation metrics, except antecedent dry days by period. Based on the standardized beta coefficients of each variable, the ratio of rainy days to dry days ($st \beta = 0.82$) and number of rainy days per period ($st \beta = -0.49$) had the greatest relative importance and all other variables were less important (total precipitation ($st \beta = 0.19$), # consecutive dry days ($st \beta = -0.20$), and antecedent dry days ($st \beta = 0.15$)). The most parsimonious model predicting bulk deposition was a better fit (i.e. higher adjusted $R^2$) than throughfall and included all precipitation metrics (Table 4, $F(6,402) = 89.1$, $p<0.001$, adj $R^2 = 0.56$). Similar to throughfall, the ratio of rainy days to dry days ($st \beta = 1.1$) and number of rainy days per period ($st \beta = -0.85$) were the most important predictors of wet deposition, followed by total precipitation ($st \beta = 0.31$), the antecedent dry days ($st \beta = 0.21$), the longest consecutive number of dry days ($st \beta = -0.20$), and antecedent dry days within the period ($st \beta = -0.13$). Unsurprisingly, the final model predicting dry deposition from precipitation metrics explained little variation and only included two predictors: the number of rainy days per period ($st \beta = 0.30$) and the number of antecedent dry days ($st \beta = 0.10$; Table 4, $F(2,392) = 17.8$, $p < 0.001$, adj $R^2 = 0.08$)).

In addition to the timing of precipitation, I also expected site-specific factors related to meteorological variables and urbanization to be important predictors of N deposition. To test this, I used a more extensive multiple regression model following the same backward stepwise procedure as above. The full initial models included the precipitation metrics (as described above), meteorological variables (average temperature, relative humidity, wind speed and wind direction), as well as site characteristics such as elevation, housing density, traffic density, and percent urban land cover within a 10 km
buffer area around each site (Table 5). Throughfall was best predicted by a model including independent predictors of temperature (st ß = 0.50), relative humidity (st ß = 0.36), ratio of rain days to dry days (st ß = 0.32), the number of rainy days (st ß = -0.31), total precipitation (st ß = 0.27), as well as the longest consecutive number of dry days, percent urban land cover, average wind speed, and elevation (Table 5; F(9,369) = 52.9, p <0.001, adj R² = 0.55).

A mixture of precipitation metrics, meteorological and urbanization factors explained more variability in wet deposition than throughfall or dry deposition models. The most parsimonious model describing wet deposition (Table 5; F(8, 370) = 114, p < 0.001, adj R² = 0.71) including the number of rainy days (st ß = -0.69), the ratio of wet days to dry days (st ß = 0.68), temperature (st ß = 0.55), percent urban land cover (st ß = 0.39), relative humidity (st ß = 0.37), housing density (st ß = -0.34), precipitation (st ß = 0.33), and longest number of consecutive dry days (-0.19). The variability in dry deposition, on the other hand, was not well predicted by the final model (Table 5; F(6, 357) = 12.2, p < 0.001, adj R² = 0.16). The predictors in the dry deposition model included housing density (st ß = 0.60), traffic density (st ß = -0.33), number of rainy days (st ß = 0.30), average wind speed (st ß = 0.17), temperature (st ß = 0.14), and elevation (st ß = -0.11).

**Gaseous N concentrations and dry deposition**

*Nitric acid concentrations:* Gaseous HNO₃ concentrations ranged between 0.1 – 0.7 µg N m⁻³ in the urban location and 0.1 – 0.5 µg N m⁻³ in the outlying location. While concentrations were low, in a two-way comparison between location and season, HNO₃ was significantly greater in the urban (0.4 +/- 0.1 µg N m⁻³) than outlying location (0.3
Ammonia concentrations: Average gaseous NH$_3$ concentrations ranged between 4.3 – 11.1 µg N m$^{-3}$ in urban location and 0.3 – 2.0 µg N m$^{-3}$ in outlying location. Urban gaseous NH$_3$ concentration (6.6 µg N m$^{-3}$ +/- 0.6) was significantly greater than outlying concentrations (1.0 µg N m$^{-3}$ +/- 0.2, p < 0.001, Figure 3). In two-way ANOVA, gaseous NH$_3$ did not significantly differ between seasons and there were no interactions between season and location (p > 0.1).

Nitrogen oxide concentrations: Urban gaseous NO$_x$ concentrations ranged from 2.0 – 16.5 µg N m$^{-3}$ and were significantly greater (9.1 µg N m$^{-3}$ +/- 1.4) than outlying east concentrations (0.6 µg N m$^{-3}$ +/- 0.2, range 0.3 – 1.0 µg N m$^{-3}$, p < 0.001, Figure 3). As a main effect, season was only minimally significant, with NO$_x$ concentration greater in the winter (6.1 µg N m$^{-3}$ +/- 1.7) than in the summer (3.0 µg N m$^{-3}$ +/- 1.3, p = 0.07) due to variability between sites and seasons. However, in the urban location NO$_x$ concentration in winter was significantly greater than in summer, whereas in the outlying location the opposite trend was significant (p = 0.03).

Dry deposition of gaseous nitrogen species: Dry deposition fluxes were calculated with the inferential method using the empirical concentrations measured at the urban and outlying site described above. I estimated deposition fluxes using the average deposition velocity from a local Sonoran Desert study as the most probable, site-specific deposition velocity for this study (Table 2). Across both sites and years, total dry N deposition was comprised of 41% (+/- 3%) NH$_3$, 36% (+/- 5%) HNO$_3$, and 22% (+/- 2%) NO$_x$. The
percent of NH₃ deposition was significantly greater in the winter than summer season (p = 0.003), and in the urban location compared to outlying desert (p < 0.001, Figure 4). HNO₃ followed the opposite pattern: significantly greater in the summer than winter (p < 0.001) and in the outlying compared to the urban location (p < 0.001; Figure 4). NOₓ, however, was significantly greater in the urban than the outlying desert location (p < 0.001; Figure 4), but did not differ by season. Total urban dry N deposition (HNO₃ + NH₃ + NOₓ, 6.4 +/- 0.4 kg N ha⁻¹ yr⁻¹) was significantly greater than total outlying dry N deposition (1.8 +/- 0.2, p < 0.001; Figure 5, Table 6). When averaged across locations, differences by season were minimal, but winter tended to have lower rates of deposition than summer, particularly at the outlying site (Figure 5).

**Total N deposition comparison**

*N deposition estimates from co-located throughfall and bulk collectors:* During the corresponding sampling periods in the summer and winter of 2010 - 2012, I measured NH₄-NO₃ fluxes with ion exchange resin samplers. Similar to long-term N deposition estimates with IER samplers in urban and outlying locations, average throughfall deposition was 3.1 +/- 0.6 kg N ha⁻¹ yr⁻¹. Deposition rates were not significantly different between the urban and outlying sites (p = 0.5), but summer deposition at both sites (urban = 4.1 +/- 0.6, outlying 4.3 +/- 0.4 kg N ha⁻¹ yr⁻¹) was significantly greater than winter deposition (urban = 2.1 +/- 0.6, outlying 1.2 kg N ha⁻¹ yr⁻¹, p = 0.007, data summarized in Table 6). Like the long-term bulk N deposition estimates, bulk wet deposition was lower than total throughfall (wet and dry), bulk wet deposition was similar between locations (p = 0.7), and bulk deposition was significantly greater in the summer than winter season (p
The throughfall and bulk N deposition estimates described here were also comparable to the throughfall and bulk N deposition estimates from the same periods from the long-term N deposition sampling.

Total N deposition correction: Across sites and years (summer 2010 - winter 2012), total throughfall deposition was significantly less than total deposition estimated by bulk and dry deposition methods (paired t-test, t = 4.4, df = 7, p = 0.003). Overall, throughfall underestimated total deposition by an average of 54%. In other words, N deposition measured in throughfall was 46% of total deposition estimated by adding wet bulk deposition and dry deposition estimated by the inferential method. Throughfall was a better measure of total deposition in the outlying location, where the underestimation of total deposition in the outlying location (41 +/- 21%) was lower than in the urban location (67 +/- 14%, t = -2.0, p = 0.1). Compared by season, throughfall was a better predictor of total wet and dry deposition in the summer (average 40 +/- 20% underestimation by throughfall) than in the winter (average 67 +/- 14% underestimate by throughfall, t = -2.2, p = 0.07, Table 6). The discrepancy between seasonal estimates may be due, in part, to the high gaseous NOx and NH3 concentrations in the winter (Figures 3 & 5). In addition, the stable atmospheric conditions in the Phoenix region during the winter months suggests the urban atmospheric N is more likely to be deposited locally near the source and lead to greater dry deposition in the city during the winter season.

To better estimate total long-term N deposition patterns, I modeled total N deposition in the region accounting for the underestimation in throughfall. While there were seasonal and regional trends in the underestimation of total deposition from throughfall (Table 6), the differences between locations or season were not overwhelmingly
significant and variances are high. Thus, I used a simple model and predicted new estimates of total N deposition based on the average 54% underestimation across both locations and seasons (predicted N deposition = long-term throughfall / 0.46).

Based on this “correction,” the mean predicted total N deposition in the region increases from 3.3 kg N ha$^{-1}$ yr$^{-1}$ (in throughfall) to 7.3 (+/- 0.3) kg N ha$^{-1}$ yr$^{-1}$ (range 0.4 – 39.2 kg N ha$^{-1}$ yr$^{-1}$). The overall patterns followed those of throughfall. For example, the predicted total N deposition did not significantly differ among regions (urban: 8.2 +/- 0.6, outlying east: 6.7 +/- 0.4, and outlying west: 7.0 +/- 0.5 kg N ha$^{-1}$ yr$^{-1}$), but was significantly greater in the summer monsoon season (June – September, 12.7 +/- 0.3 kg N ha$^{-1}$ yr$^{-1}$, p< 0.001) than in the other seasons (January – March: 5.7 +/- 0.3 kg N ha$^{-1}$ yr$^{-1}$, March – June: 5.1 +/- 0.3 kg N ha$^{-1}$ yr$^{-1}$, September – December: 5.5 +/- 0.3 kg N ha$^{-1}$ yr$^{-1}$).

DISCUSSION

Patterns of N deposition in a large semi-arid city and surrounding native ecosystem

In the Phoenix metropolitan region and surrounding Sonoran Desert, N deposition rates across the region were surprisingly low. From 2006 - 2013, total wet and dry (throughfall) N deposition was on average 3.3 kg N ha$^{-1}$ yr$^{-1}$ (Table 3). Urban throughfall deposition (3.8 kg kg N ha$^{-1}$ yr$^{-1}$) tended to be higher than in the outlying desert (Figure 2, Table 3). Yet, contrary to expectations, the average rates were only minimally different. Similarly, neither total (throughfall) nor wet deposition varied among the 15 sites throughout the metropolitan and surrounding Sonoran Desert (Table 3). While total deposition was comparable between the urban and outlying desert regions, wet deposition
was greater in the native desert to the east of Phoenix than the native desert west of Phoenix (Table 3). Compared to the other sites, the eastern region has a slight elevation gain that creates a precipitation gradient east of the urban region with more frequent rainfall events (Table 1 and 5). In contrast, dry deposition was greater in the outlying region to the west of Phoenix where agriculture is predominant (Table 3).

Observed N deposition rates were consistent with those previously reported in this region using wet-dry buckets from 2000 – 2005. Lohse and colleagues (2008) found mean wet and dry NH₄-NO₃ deposition across the region was approximately 4 kg N ha⁻¹ yr⁻¹ with few differences among sites, though dry deposition tended to be highest to the west of the urban center. However, the authors noted N deposition was lower than expected and highlighted the potential underestimation of dry fine particulate and gaseous forms of N deposition by wet-dry buckets in arid systems (Lohse et al. 2008).

Based on deposition in other cities as well as Phoenix specific modeled estimates, I expected significantly higher N inputs than observed, particularly to the east where downwind deposition was expected to be higher. For example, the 2006 CMAQ model estimated average urban deposition in Phoenix to be 18-20 kg N ha⁻¹ yr⁻¹ and previous models estimated similar rates with N deposition in the downwind region as high as 25 kg N ha⁻¹ yr⁻¹ (Baker et al. 2001; Fenn, Haeuber, et al. 2003). The empirical estimates in this study may be lower than modeled deposition because these models incorporate all forms of deposition, including particulate, aerosol and gas phase N that are difficult to quantify in field measurements. Deposition in the Phoenix region was also surprisingly low given the deposition rates reported in other large metropolitan systems, such as Los Angeles, Baltimore, Boston, and several cities in China. The average deposition rate
across these cities was 15 kg N ha\(^{-1}\) yr\(^{-1}\) and often exceeded 30-60 kg N ha\(^{-1}\) yr\(^{-1}\) (Alonso, Bytnerowicz, and Boarman 2005; L. E. Rao and Allen 2010; Cisneros et al. 2010; Pan et al. 2012; P. Rao et al. 2013; Bettez and Groffman 2013; Li et al. 2013). Higher rates of N deposition in some cities may be explained, in part, by significantly more precipitation, less seasonal variability, a higher proportion of wet deposition, and characteristics related to traffic and housing density. Lower rates of dry deposition in more temperate regions may lead to more accurate total N deposition estimates.

Dry deposition is difficult to estimate in arid and semi-arid ecosystems due to prolonged dry periods, and sporadic and spatially heterogeneous rain during the wetter seasons. I estimated dry deposition with multiple approaches in order to better account for the dry component of deposition. First, I estimated dry deposition from the IER collectors by calculating the difference between throughfall and bulk (wet) measurements, where throughfall is expected to capture wet and dry deposition that accumulates on leaf surfaces above the throughfall collector. Bulk deposition is expected to primarily collect wet deposition. Though some dry deposition may enter the bulk collectors, little dry deposition is expected to collect on the surface of the plastic funnels of bulk deposition collectors. The average rate of dry deposition across the region by the IER collectors was 1.4 (+/- 0.1) kg N ha\(^{-1}\) yr\(^{-1}\) (Table 3; range 0 – 7.9 N ha\(^{-1}\) yr\(^{-1}\)). Mean dry deposition from IER collectors across sites only accounted for 29 – 55% (average 42 +/- 1%) of total deposition (Table 3). While dry deposition estimates from IER collectors were comparable to those reported previously in the Phoenix region (Lohse et al. 2008), they are lower than expected based on estimates up to 80% from other urban arid studies (Li et al. 2013).
Second, I estimated dry deposition based on the inferential method using empirical measurements of gaseous N concentrations in an urban and outlying location. Average dry N deposition estimated by the inferential method (4.4 +/- 0.5 kg N ha\(^{-1}\) yr\(^{-1}\), range 0.8 – 9.3 kg N ha yr) was higher than dry deposition estimated by IER collectors. Dry deposition estimates in the outlying desert were comparable between methods (1.1 and 1.8 kg N ha\(^{-1}\) yr\(^{-1}\) from dry throughfall vs inferential estimates, respectively). Yet, urban dry deposition estimates differed more substantially. Urban dry deposition estimated by IER collectors was 31% (1.6 kg N ha\(^{-1}\) yr\(^{-1}\)) greater than the outlying dry deposition. In contrast, urban dry deposition estimated by inferential method was 72% (6.4 +/- 0.4 kg N ha\(^{-1}\) yr\(^{-1}\)) higher than outlying dry deposition estimates from the same method. Overall, with the inferential method, dry deposition was approximately 74% of total deposition in the urban region and 40% of total deposition in the outlying Sonoran Desert.

Patterns of high dry deposition in the city resulted directly from higher gaseous N concentrations in the urban region than the outlying Sonoran Desert (Figure 3). N concentrations in HNO\(_3\), NH\(_3\), and NO\(_x\) were all greater in the city than in the outlying Sonoran Desert (Figure 3). These patterns are similar to those reported in other urban regions, though only two other studies measure all three compounds concurrently (Li et al. 2013; Zbieranowski and Aherne 2012). In particular, NH\(_3\) gaseous concentrations were comparable to those previously measured in Phoenix and other arid urban regions (Watson et al. 1994; Bytnerowicz, Omasa, and Paoletti 2007; Sather et al. 2008; Salem, Soliman, and El-Haty 2009; Li et al. 2013). Gaseous NO\(_x\) concentrations were also an important component of the urban atmosphere, particularly during the winter months, and were similar to those collected by the same method in other cites (Sather et al. 2007;
Moodley, Singh, and Govender 2011; Li et al. 2013). Higher winter NO\textsubscript{x} concentrations can be attributed to reduced photo-oxidation of this common pollutant from vehicle exhaust as a result of lower temperatures and fewer daylight hours (Sather et al. 2007; Afif et al. 2009; Li et al. 2013). While NO\textsubscript{x} gas concentrations were greater than both gaseous NH\textsubscript{3} and HNO\textsubscript{3}, NO\textsubscript{x} deposition velocities are low (Table 2) and thus NO\textsubscript{x} contributes a relatively smaller amount to deposition than gaseous NH\textsubscript{3} or HNO\textsubscript{3}. HNO\textsubscript{3} and NH\textsubscript{3}, on the other hand, are highly soluble, reactive gases that deposit closer to their sources. With high deposition velocities, even relatively small concentrations can significantly affect the total deposition fluxes (Hanson and Lindberg 1991; Zhang, Brook, and Vet 2003; Schwede et al. 2011). Comparable to throughfall NH\textsubscript{4}\textsubscript{4}:NO\textsubscript{3} (Table 3) and as in other studies (Cisneros et al. 2010; Pan et al. 2012), NH\textsubscript{3} was the most significant component of dry N deposition in the city, while outlying deposition was primarily made up of HNO\textsubscript{3} (Figure 5). In California’s San Joaquin Valley near Fresno, estimates of summer dry N deposition ranged from 0.4 – 15 kg N ha\textsuperscript{-1} yr\textsuperscript{-1}, where NH\textsubscript{3} made up between 62-88% of N (Cisneros et al. 2010). In Phoenix, NH\textsubscript{3} dry deposition only made up 41% of total dry deposition across seasons (Figure 4). NH\textsubscript{3} concentrations and deposition are expected to increase, however, as the projected N emissions in the US are likely to shift from predominantly oxidized N to predominantly reduced N emissions by 2050 (Ellis et al. 2013).

**Drivers and sources of N deposition in an arid metropolitan region**

Though spatial variation in N deposition was minimal in the Phoenix metropolitan region, N deposition varied seasonally, and seasonal precipitation was an important
predictor of deposition. The Sonoran Desert is characterized by bimodal precipitation in the winter and summer. Following rainfall patterns, I expected similar deposition rates in the summer and winter rainy seasons. Yet, the summer monsoon season (June – September) had higher rates of total (wet and dry) deposition (5.8 kg N ha\(^{-1}\) yr\(^{-1}\)) than other times throughout the year, including during the winter rainy season (Figure 2; average range 2.3-2.7 kg N ha\(^{-1}\) yr\(^{-1}\)). Like other arid systems, Sonoran Desert summer monsoon precipitation was a strong predictor of summer N deposition (Báez et al. 2007; Lohse et al. 2008; Li et al. 2013). Unlike other studies that measured wet deposition in rainfall collectors, I examined both wet and total throughfall deposition and found summer precipitation was strongly correlated to both (correlation coefficient 0.68 and 0.63 for summer total (throughfall) and wet (bulk) deposition, respectively, based on Spearman’s rho rank correlation; Appendix 3). Similar to summer patterns, winter precipitation was also correlated (0.56 correlation coefficient) with winter total (throughfall) deposition, though winter precipitation was more strongly related (0.83 correlation coefficient) to winter wet (bulk) deposition (Appendix 3). The strength of the winter relationships suggests wet deposition was more dependent on the amount of rainfall during the winter season than total throughfall deposition.

To further investigate the relationship between precipitation and N deposition, I calculated several metrics to capture the timing of rainfall over the integrated 3-month N deposition sampling intervals. In addition to total precipitation, these metrics included the number of rainy days per interval, a proportion of rainy days to dry days in each interval, and the longest consecutive span of dry days per period (Appendix 3). I expected N deposition, and throughfall in particular, to be related to the timing and
frequency of precipitation rather than just total precipitation. From best fit multiple regression models, both throughfall and wet bulk deposition were most strongly related to precipitation metrics describing the number of rain events (Table 4; e.g. the proportion of rainy days relative to the dry days and the absolute number of days in which it rained during each sampling interval). Though total precipitation was an important positive predictor of deposition, the number of consecutive dry days was negatively related to deposition indicating less deposition during longer spans without rain. Together, these relationships highlight that aridland total N deposition rates are higher when there are more frequent rainfall events. These trends lend support to the hypothesis that total deposition, in particular the dry component, may be underestimated during long dry periods when leaf surfaces become saturated (prohibiting further collection of N deposition on the surface of leaves during dry periods) or when particulate N volatilizes from leaf surfaces during hot periods.

In addition to precipitation as a primary driver of N deposition, I also examined the influence of other site-specific characteristics, including other meteorological variables, elevation, and factors related to urbanization that were expected to influence N deposition and increase model predictability. Temperature and relative humidity were primary factors explaining throughfall deposition (Table 5). Temperature and relative humidity are seasonally dependent, and along with the precipitation metrics described above, explain the patterns of higher summer N deposition. Total throughfall deposition was also related to the percentage of urban land cover surrounding each monitoring site, wind speed and elevation (Table 5). The same overall set of factors described wet deposition, though the timing of precipitation was relatively more important than temperature and
relative humidity in explaining the variability of wet N inputs. On the other hand, long-
term dry deposition (calculated as difference in throughfall and bulk deposition) was best
predicted by housing and traffic density relative to other site characteristics such as
number of rainy days, wind speed, temperature and elevation. The predictors of dry
deposition match well with high urban dry deposition estimates based on inferential
calculations, where highly reactive NH$_3$ and HNO$_3$ are deposited closer to their sources.

The spatial distribution of NH$_4$ and NO$_3$ and their various gaseous components can be
an important indicator of the source of deposition in the region (Holland et al. 2005; P.
Rao et al. 2013; Li et al. 2013). For example, high NH$_4$:NO$_3$ suggests atmospheric NH$_3$
inputs to ecosystems from agricultural sources (N fertilizer applications and animal
husbandry), although NH$_3$ can also be a secondary pollutant of motor vehicles. On the
other hand, lower NH$_4$:NO$_3$ ratios indicate sources of NO$_x$ from industrial combustion
that are deposited as NO$_3$ in precipitation. Average NH$_4$:NO$_3$ in long-term throughfall
deposition was approximately 2.8 across the Phoenix and outlying desert region, and NH$_4$
was 67% (36-97%) of total throughfall across sites and seasons. While NH$_4$ in thoughfall
deposition did not vary among regions, the NO$_3$ deposition was significantly greater in
the city than in the outlying desert to the west, indicating fewer sources of combustion in
the outlying desert. Similar to the other urban studies, NH$_4$:NO$_3$ in throughfall was
lower (2.3) in Phoenix urban sites where housing and traffic density are highest (Table 3,
(Holland et al. 2005; P. Rao et al. 2013; Li et al. 2013; Pan et al. 2012; Bettez and
Groffman 2013; Lovett et al. 2000)). In contrast, the high NH$_4$:NO$_3$ (3.7) west of
Phoenix indicated a likely contribution of NH$_3$ from agriculture in the outlying region
more than NO$_3$ from industrial and fossil fuel combustion (Table 3).
Underestimation of N deposition in arid systems

The underestimation of N deposition – particularly dry deposition in arid regions – is a common concern (Lohse et al. 2008). To address these uncertainties, I integrated multiple methods to more accurately estimate total and dry deposition. In comparing total deposition estimated by throughfall with total deposition estimated by wet deposition (from bulk measurement) and dry deposition (from inferential estimates), I found that throughfall underestimated total deposition by an average of 54%. Throughfall was better at estimating total deposition in the outlying desert regions and during the summer months where dry deposition is expected to be lower and more frequent rain events are important for accurately capturing total deposition (e.g. Figure 5). Throughfall has also been reported by other studies to underestimate deposition when compared with alternative wet and dry deposition estimates (Weathers et al. 2000; Fenn et al. 2013). For example, Fenn and colleagues (2013) noted throughfall in western forests may underestimate total wet and dry N deposition by 20-40%, and up to 80% during winter months as a result of N uptake through plant leaves. Throughfall underestimation may result from potential leaf uptake or retention of N by *L. tridentata* or possible difficulty in rinsing N from sticky *L. tridentata* leaves. Though *L. tridentata* leaf uptake and retention were not specifically tested here (see Padgett et al. 1999), leaf uptake was expected to be relatively minor, because throughfall estimates were significantly higher than wet bulk deposition for both NH₄ and NO₃. Rather, leaf saturation and volatilization from leaf surfaces are likely to be the primary reason for the underestimation of total deposition, especially during long dry periods.
To account for the underestimation of long-term N deposition in this arid region, I predicted N deposition estimates based on long-term throughfall measurements and the average percent by which throughfall underestimates total deposition (54%) based on the inferential method. Accounting for the underestimation, average total deposition across the region and study period is predicted to be 7.3 (+/- 0.3) kg N ha\(^{-1}\) yr\(^{-1}\) (range between 0.4 – 39.2 kg N ha\(^{-1}\) yr\(^{-1}\)) and average summer deposition is 12.7 (+/- 0.8) kg N ha\(^{-1}\) yr\(^{-1}\) (Figure 6). The corrected deposition estimates more closely approximate those of the CMAQ model and other arid urban regions, but are still lower than expected for a large metropolitan region. In addition, the predicted long-term N deposition rates across the region are at the upper limit of the expected range (3 – 8 kg N ha\(^{-1}\) yr\(^{-1}\)) for aridland N critical loads (Fenn et al. 2010; Pardo et al. 2011). Long-term deposition above the critical load has potentially significant ecological effects on ecosystem processes and primary producer community composition (Brooks 2003; Báez et al. 2007; L. E. Rao, Allen, and Meixner 2010).

_Uncertainties in urban arid N deposition estimates_

Despite using multiple methods to estimate N deposition in the region, many uncertainties remain and total N deposition estimates in this study may be conservative for several reasons. First, dissolved organic nitrogen (DON), which in some systems is a significant component of atmospheric N deposition though may be relatively minor in arid regions, was not accounted for in empirical monitoring (e.g. see Jiang et al. 2013; Cornell 2011; Neff et al. 2002). Second, the variability in atmospheric compounds is also driven by the complex topography and seasonal and diurnal atmospheric mixing.
patterns in the Phoenix valley (Wang and Ostoja-Starzewski 2004; Nunnermacker et al. 2004; Lee, Fernando, and Grossman-Clarke 2007; Lohse et al. 2008). In the summer, the atmosphere tends to be more unstable causing significant mixing and increased movement and deposition of gaseous particles. On the other hand, vertical flux of gaseous particles is more limited when the atmosphere is more stable during winter months, though the stable atmosphere and winter inversion also allows gaseous concentrations to build up in the city atmosphere. I aimed to account for these factors by including elevation and meteorological variables such as wind speed and direction in analyses. However, the urban topography (i.e. building height) was not accounted for and the average meteorological variables integrated over a 3-month sampling interval likely did not have enough temporal resolution to capture their importance in driving patterns of atmospheric N in the region.

Finally, as noted, dry deposition is difficult to accurately estimate from all methods. Passive samplers, including throughfall and passive gaseous samplers, have a low temporal resolution such that it is only possible to estimate integrated time-averaged fluxes (Golden et al. 2008). For similar reasons, it is difficult to connect atmospheric concentrations and deposition to vegetation and ecosystem responses (Golden et al. 2008). Overall, this contributes to the uncertainty and underestimation of throughfall rates because of leaf saturation, biological uptake, or volatilization during hot periods. With the inferential method, there are additional uncertainties associated with deposition velocity estimates, which are highly dependent on the meteorological variables, surface characteristics, and the height and heterogeneity of the surrounding landscape (Wesely and Hicks 2000). Deposition velocities tend to be lower in semi-arid and sparse
vegetation areas than in denser canopy forests (Hanson and Lindberg 1991). In contrast, deposition velocities in urban regions tend to be higher (Zhang, Brook, and Vet 2003; Zhang et al. 2009). Yet, few studies have empirically modeled or tested deposition velocities in arid urban cities, and thus there are potential uncertainties in arid dry deposition estimates.

To calculate dry deposition from the inferential method in this study, I applied an average deposition velocity for each N species estimated for the Sonoran Desert (Table 2). However, even when concentrations are similar, the application of slightly different deposition velocities across locations or seasons can change the deposition estimate by a factor of 2-3 (Schwede et al. 2011). For example, applying the deposition velocities used for estimating deposition in several Chinese cities located in semi-arid regions (HNO$_3$: 1.7, NH$_3$: 0.28, NO$_2$: 0.2 cm sec$^{-1}$; Table 2; Pan et al. 2012; Li et al. 2013), the dry deposition estimates calculated by the inferential method in the Phoenix region would increase by an average of 61% (64% in the city and 58% in desert regions). Based on the higher deposition velocities, the average urban and outlying desert dry deposition could be as high as 10.6 and 2.8 kg N ha$^{-1}$ yr$^{-1}$, respectively (compared to 6.4 and 1.8 kg N ha$^{-1}$ yr$^{-1}$ estimated with the Sonoran Desert deposition velocities). This further increases the likelihood of significant underestimation of total deposition in throughfall measurements. For example, underestimation by throughfall is expected to increase to 65% when dry deposition is calculated with the higher deposition velocities compared to 54% underestimation when calculated with Sonoran Desert specific deposition velocities. Overall, the Sonoran Desert deposition velocities are comparable to those used in the other arid and urban-arid studies and are expected to be the best estimate for this system.
(Table 2, e.g. Zhang et al 2003, Pan et al 2013, Adon et al 2013, Li et al 2013).

However, estimates with higher dryland deposition velocities highlight the potential upper range of deposition in this large semi-arid metropolitan region.

CONCLUSION

Overall, despite the size and population of Phoenix, N deposition was lower than expected compared to other large arid cities. Lower than expected deposition was likely due, in part, to the difficulty in quantifying dry deposition in arid ecosystems where precipitation patterns are spatially and temporally patchy. Inconsistencies between N deposition sampling approaches reveal the difficulties in accurately estimating dry deposition, as well as how uncertainties related to quantifying site characteristics and deposition velocities can easily confound N deposition estimates.

By accounting for dry deposition with multiple methods, predicted total wet and dry deposition in the region was expected to be in the upper range of the aridland N critical load. Both inferential and throughfall methods indicate the highest deposition rates were restricted to the urban core, though deposition to ecosystems in the outlying region also exceeded predicted critical loads. Despite relatively low levels compared to other arid and urban regions, changes in ecosystem structure and function are likely to occur at the current rates of deposition, particularly in rainy years where microbial communities are expected to be more active (Collins et al. 2008; Hall et al. 2011) and where chronic low levels of N inputs can have significant impacts on community structure (Clark and
Tilman 2008). My findings highlight the need for and benefit of mixed methods to more accurately quantify wet and dry N deposition in arid systems.
ACKNOWLEDGEMENTS

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REFERENCES


Compounds: A Review of Leaf, Canopy and Non-Foliar Measurements.”


TABLE 1: Site characteristics of N deposition monitoring sites. Site characteristics of remnant desert preserves in metropolitan region of Phoenix, AZ (urban) and in outlying native desert to the east and west of the city.

<table>
<thead>
<tr>
<th>Location</th>
<th>Elevation (m)</th>
<th>Traffic density</th>
<th>Housing density</th>
<th>Mean (annual) temperature (°C)</th>
<th>Mean (annual) relative humidity (%)</th>
<th>Mean (annual) precipitation (mm)</th>
<th>Mean (annual) wind speed (mph)</th>
<th>Mean (annual) wind direction (degrees)</th>
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</table>

*Distance to city was calculated in ArcGIS 9.3 based on Euclidean distance from the location to urban center of Phoenix, AZ.

^Traffic (average weekday traffic/mile of road) and housing density (average households/km²) are based on 10km buffer surrounding each site location.

#Temperature, relative humidity, precipitation, wind speed and direction, annual average for 2006-2013; all meteorological data from nearest FCDMC met station (see Appendix 1).
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<td>Pan et al, 2013</td>
<td>Semi-arid, urban</td>
<td>3.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Zhang et al, 2003</td>
<td>Semi-arid, urban</td>
<td>0.6 - 0.9</td>
<td>0.2 - 0.3</td>
</tr>
<tr>
<td>Zbieranowski &amp; Aherne, 2012</td>
<td>Urban</td>
<td>1.9</td>
<td>0.4</td>
</tr>
<tr>
<td>Redling et al, 2013</td>
<td>Urban</td>
<td>0.18</td>
<td>0.3</td>
</tr>
<tr>
<td>Zhang et al, 2003</td>
<td>Urban</td>
<td>4.7</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Table 2: Average (and/or range when available) deposition velocities (cm/sec) for arid, semi-arid, and urban ecosystems.
### TABLE 3: Throughfall, bulk, and dry N deposition across sites. Average (+/− 1SE) throughfall (wet and dry), bulk (wet), and dry (throughfall – bulk) total N deposition (NH₄⁺ + NO₃⁻, kg N ha⁻¹ yr⁻¹) at each site averaged across all seasons and years. Mean (+/− SE) percent dry deposition at each site. Different letters within a column indicate significantly different means among sites.

<table>
<thead>
<tr>
<th>Site</th>
<th>(NH₄⁺ + NO₃⁻) Throughfall (wet and dry)</th>
<th>(NH₄⁺ + NO₃⁻) Bulk (wet)</th>
<th>(NH₄⁺ + NO₃⁻) Dry (throughfall – bulk)</th>
<th>Total N deposition (NH₄⁺ + NO₃⁻) (wet and dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EME</td>
<td>2.7 (0.4)ab</td>
<td>4.0 (1.2)a</td>
<td>1.2 (0.4)ab</td>
<td>31.7 (4.7)a</td>
</tr>
<tr>
<td>EMW</td>
<td>2.6 (0.5)a</td>
<td>2.7 (0.3)a</td>
<td>1.7 (0.2)a</td>
<td>38.6 (4.2)ac</td>
</tr>
<tr>
<td>SNE</td>
<td>3.7 (0.6)ab</td>
<td>5.1 (1.5)a</td>
<td>1.5 (0.3)a</td>
<td>55.7 (4.7)bc</td>
</tr>
<tr>
<td>SNW</td>
<td>3.9 (0.5)ab</td>
<td>4.1 (0.7)a</td>
<td>1.6 (0.3)a</td>
<td>59.4 (4.5)c</td>
</tr>
<tr>
<td>WTM</td>
<td>3.3 (0.6)ab</td>
<td>2.7 (0.4)a</td>
<td>1.7 (0.3)a</td>
<td>46.6 (4.5)c</td>
</tr>
<tr>
<td>DBG</td>
<td>4.3 (0.6)c</td>
<td>3.7 (0.2)c</td>
<td>1.2 (0.1)c</td>
<td>45.9 (2.2)</td>
</tr>
<tr>
<td>MVP</td>
<td>8.4 (3.1)c</td>
<td>5.1 (2.5)a</td>
<td>2.9 (NA)a</td>
<td>55.3 (2.5)bc</td>
</tr>
<tr>
<td>PWP</td>
<td>3.8 (0.5)ab</td>
<td>1.9 (0.2)a</td>
<td>2.2 (0.4)ab</td>
<td>44.5 (4.1)c</td>
</tr>
<tr>
<td>SME</td>
<td>3.2 (0.4)ab</td>
<td>2.3 (0.2)a</td>
<td>2.1 (0.4)ab</td>
<td>34.3 (4.1)c</td>
</tr>
<tr>
<td>SMW</td>
<td>3.1 (0.4)ab</td>
<td>2.2 (0.2)a</td>
<td>2.0 (0.4)ab</td>
<td>39.7 (4.3)c</td>
</tr>
<tr>
<td>LDP</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
<td>ND</td>
</tr>
<tr>
<td>Urban</td>
<td>3.8 (0.3)</td>
<td>2.3 (0.1)</td>
<td>2.1 (0.2)</td>
<td>43.4 (2.0)</td>
</tr>
<tr>
<td>Outlying East</td>
<td>3.1 (0.2)</td>
<td>2.3 (0.1)</td>
<td>2.1 (0.2)</td>
<td>37.0 (2.0)</td>
</tr>
<tr>
<td>Outlying West</td>
<td>3.2 (0.2)</td>
<td>2.3 (0.1)</td>
<td>2.1 (0.2)</td>
<td>32.0 (2.0)</td>
</tr>
<tr>
<td>Overall Mean (SE)</td>
<td>3.3# (0.1)</td>
<td>2.0 (0.1)</td>
<td>1.5 (0.1)</td>
<td>41.9 (1.2)</td>
</tr>
</tbody>
</table>

% dry = % dry deposition of total deposition (throughfall)

Dry NH₄⁺:NO₃ is not reported; many dry NH₄ and NO₃ estimates are zero. % dry = % dry deposition of total deposition (throughfall)
TABLE 4: Predicting N deposition from precipitation variables. Multiple regression parameters and significant predictors of N throughfall, bulk and dry deposition from the best-fit model for each. All predictors listed are significant (p < 0.05).

<table>
<thead>
<tr>
<th>Predictor</th>
<th>Bulk deposition</th>
<th>Thoroughfall deposition</th>
<th>Dry deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td># Rainy days : # Dry days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Longest # consecutive dry days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antecedent dry days by period</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Antecedent dry days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total precipitation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of rain days</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Model statistics</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\[ F(5, 412) = 60.6, p < 0.001, \text{adj R}^2 = 0.42 \]
\[ F(6, 402) = 89.1, p < 0.001, \text{adj R}^2 = 0.56 \]
\[ F(2, 392) = 17.9, p < 0.001, \text{adj R}^2 = 0.08 \]
### TABLE 5: Predicting N deposition from precipitation and site characteristics variables

Multiple regression parameters and significant predictors of N throughfall, bulk and dry deposition from the best fit model for each. All predictors listed are significant ($p < 0.05$).

<table>
<thead>
<tr>
<th>Variable</th>
<th>Throughfall dep.</th>
<th>Bulk dep.</th>
<th>Dry dep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total precipitation (mm)</td>
<td>$1.5 \times 10^{-3}$</td>
<td>$0.14 \times 10^{-3}$</td>
<td>$0.27 \times 10^{-3}$</td>
</tr>
<tr>
<td>Number of rain days</td>
<td>$0.96 \times 10^{-3}$</td>
<td>$0.32 \times 10^{-3}$</td>
<td>$0.05 \times 10^{-3}$</td>
</tr>
<tr>
<td># Rainy days : # Dry days</td>
<td>$1.2 \times 10^{-2}$</td>
<td>$0.0 \times 10^{-2}$</td>
<td>$10.0 \times 10^{-2}$</td>
</tr>
<tr>
<td>Longest # consecutive dry days</td>
<td>$-2.7 \times 10^{-4}$</td>
<td>$-0.18 \times 10^{-4}$</td>
<td>$-0.10 \times 10^{-4}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$4.1 \times 10^{-3}$</td>
<td>$0.02 \times 10^{-3}$</td>
<td>$0.01 \times 10^{-3}$</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>$-3.1 \times 10^{-4}$</td>
<td>$-0.34 \times 10^{-4}$</td>
<td>$-0.07 \times 10^{-4}$</td>
</tr>
<tr>
<td>Housing density</td>
<td>$-2.7 \times 10^{-6}$</td>
<td>$-0.33 \times 10^{-6}$</td>
<td>$-0.03 \times 10^{-6}$</td>
</tr>
<tr>
<td>Percent urban land cover</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$0.16 \times 10^{-3}$</td>
<td>$0.08 \times 10^{-3}$</td>
</tr>
<tr>
<td>Wind speed</td>
<td>$4.0 \times 10^{-3}$</td>
<td>$0.21 \times 10^{-3}$</td>
<td>$0.04 \times 10^{-3}$</td>
</tr>
<tr>
<td>Elevation</td>
<td>$-2.7 \times 10^{-4}$</td>
<td>$-0.10 \times 10^{-4}$</td>
<td>$-0.02 \times 10^{-4}$</td>
</tr>
<tr>
<td>Relative humidity</td>
<td>$4.0 \times 10^{-3}$</td>
<td>$0.21 \times 10^{-3}$</td>
<td>$0.04 \times 10^{-3}$</td>
</tr>
<tr>
<td>Percent urban land cover</td>
<td>$1.0 \times 10^{-3}$</td>
<td>$0.16 \times 10^{-3}$</td>
<td>$0.08 \times 10^{-3}$</td>
</tr>
<tr>
<td>Wind speed</td>
<td>$4.0 \times 10^{-3}$</td>
<td>$0.21 \times 10^{-3}$</td>
<td>$0.04 \times 10^{-3}$</td>
</tr>
<tr>
<td>Elevation</td>
<td>$-2.7 \times 10^{-4}$</td>
<td>$-0.10 \times 10^{-4}$</td>
<td>$-0.02 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Model statistics**

- $F(9, 369) = 52.9, p < 0.001$, adj $R^2 = 0.55$
- $F(8, 370) = 114, p < 0.001$, adj $R^2 = 0.71$
- $F(6, 357) = 12.2, p < 0.001$, adj $R^2 = 0.16$
### TABLE 6: Total N deposition estimates from multiple methods, and percent difference in N deposition estimates.

<table>
<thead>
<tr>
<th>Location</th>
<th>Season</th>
<th>Year</th>
<th>Total (throughfall wet and dry)</th>
<th>Total (bulk wet + inferential dry)</th>
<th>Throughfall underestimate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mean (SD)</td>
<td>Mean (SD)</td>
<td></td>
</tr>
<tr>
<td>Outlying</td>
<td>Summer</td>
<td>2010</td>
<td>4.7 (1.1 + 6.2)</td>
<td>5.9 (2.6 + 6.9)</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>2010</td>
<td>1.4 (2.9 + 1.1)</td>
<td>4.0 (2.9 + 1.1)</td>
<td>64</td>
</tr>
<tr>
<td>Urban</td>
<td>Summer</td>
<td>2010</td>
<td>5.1 (4.0 + 7.8)</td>
<td>11.8 (4.0 + 7.8)</td>
<td>57</td>
</tr>
<tr>
<td></td>
<td>Winter</td>
<td>2010</td>
<td>3.1 (2.6 + 6.5)</td>
<td>9.0 (2.6 + 6.5)</td>
<td>65</td>
</tr>
</tbody>
</table>

Deposition Estimates % difference in methods

The percentage that throughfall (wet and dry) deposition underestimate local (wet bulk + dry) deposition by sampling period and location. Urban location between 2010 - 2012. Percent difference in local N deposition estimates (throughfall versus bulk + dry) is calculated with co-located throughfall and bulk ER collectors and passive gas exchange samplers (inferential method) an N deposition (kg).
FIGURE 1: Long-term N deposition monitoring sites. Long-term N deposition monitoring sites within protected native desert in outlying west, urban, and outlying east locations in the CAP LTER study site. Open symbols indicate the sites used for monitoring N concentrations and estimating dry N deposition in 2010 – 2012.
**FIGURE 2**: Long term seasonal average of N throughfall deposition and precipitation. Mean (+/- 1SE) N throughfall (wet and dry) deposition (\(\text{NH}_4\)-\(\text{NO}_3\), kg N ha\(^{-1}\) yr\(^{-1}\), bottom) and precipitation (mm, top) during each season in outlying native desert east and west of Phoenix metropolitan region, and within the urban region. Sampling intervals approximately January – March, March – June, June – September, September – December.
FIGURE 3: Mean ambient HNO$_3$, NH$_3$, and NO$_x$ concentrations at urban and outlying location between 2010 – 2012. Mean (+/- SE) HNO$_3$, NH$_3$, and NO$_x$ ambient concentrations (µg N m$^{-3}$) at outlying and urban locations between 2010 – 2012. Significance values from 2-way ANOVA comparing location (urban, outlying) and season (summer, winter).
**FIGURE 4:** Percent HNO$_3$, NH$_3$, and NO$_x$ of total dry N deposition. Mean (+/- SE) percent HNO$_3$, NH$_3$, and NO$_x$ of total dry N deposition in outlying native desert and an urban location between 2010 – 2012. Dry deposition was estimated by the inferential method.
FIGURE 5: Urban and outlying dry N deposition estimated by the inferential method. Dry N deposition (kg N ha$^{-1}$ yr$^{-1}$) calculated by the inferential method from measured N concentrations and average deposition velocities estimated for the Sonoran Desert.
FIGURE 6: Predicted total N deposition across multiple seasons. Predicted seasonal deposition (NH₄-NO₃ wet and dry, kg N ha⁻¹ yr⁻¹, between January – March, March – June, June – September, and September to December) estimated for each region by accounting for the underestimation of measured throughfall. Solid line indicates mean across all sites and seasons (7.3 kg N ha⁻¹ yr⁻¹) and dashed lines indicate lower (3 kg N ha⁻¹ yr⁻¹) and upper (8 kg N ha⁻¹ yr⁻¹) estimates for the critical load in arid ecosystems.
Table 1: Flood Control District of Maricopa County (FCDMC) station IDs for the nearest meteorological station to the corresponding N deposition monitoring site.

<table>
<thead>
<tr>
<th>Location</th>
<th>FCDMC station name(s)</th>
<th>Precipitation station ID</th>
<th>Wind speed station ID</th>
<th>Wind direction station ID</th>
<th>Relative humidity station ID</th>
<th>Temperature station ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlying West</td>
<td>Outlying West</td>
<td>6845, 6860</td>
<td>6897</td>
<td>6897</td>
<td>6891</td>
<td>6892</td>
</tr>
<tr>
<td>Estrella Mountain East</td>
<td>Estrella Mountain East (EME)</td>
<td>6891</td>
<td>6892</td>
<td>6891</td>
<td>6892</td>
<td></td>
</tr>
<tr>
<td>Outlying East</td>
<td>Lost Dutchman Park</td>
<td>6675, CAP LTER</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>McDowell Mountain North</td>
<td>McDowell Mountain North (MCN)</td>
<td>5975</td>
<td>5907</td>
<td>5917</td>
<td>5951</td>
<td></td>
</tr>
<tr>
<td>McDowell Mountain South</td>
<td>McDowell Mountain South (MCS)</td>
<td>4660</td>
<td>5975</td>
<td>5907</td>
<td>5917</td>
<td></td>
</tr>
<tr>
<td>Sonoran National Monument East</td>
<td>Mobile (Upper Waterman)</td>
<td>6965</td>
<td>6900</td>
<td>6967</td>
<td>6971</td>
<td></td>
</tr>
<tr>
<td>Sonoran National Monument West</td>
<td>Gila Bend (Landfill) (Maricopa Mountains) (Upper Waterman)</td>
<td>6955</td>
<td>6900</td>
<td>6907</td>
<td>6917</td>
<td></td>
</tr>
<tr>
<td>Salt River Recreation Area</td>
<td>Saguaro Lake (Granite Reef)</td>
<td>4565</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Usery Mountain Park</td>
<td>Usery Mountain Park</td>
<td>6650</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Phoenix Dam</td>
<td>Phoenix Dam</td>
<td>4635</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mountain View Park</td>
<td>Mountain View Park</td>
<td>6510</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South Mountain East</td>
<td>South Mountain East</td>
<td>6510</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>South Mountain West</td>
<td>South Mountain West</td>
<td>6525</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban West</td>
<td>Desert Botanical Garden (DBG)</td>
<td>4520</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Desert Botanical Garden (DBG)</td>
<td>Apache Trail (CAP LTER)</td>
<td>6675</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CITATION FOR DATA: Flood Control District of Maricopa County (FCDMC) meteorological data were downloaded for 2006–2013. If more than one site is listed in a column, data were averaged.
### APPENDIX 2

**Table 1:** Descriptive statistics for throughfall (wet and dry), bulk (wet), and dry (throughfall – bulk) deposition (kg N ha\(^{-1}\) yr\(^{-1}\)) across all years and locations.

<table>
<thead>
<tr>
<th>Throughfall (wet + dry), n = 419</th>
<th>Total</th>
<th>NH4</th>
<th>NO3</th>
<th>NH4:NO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>3.3</td>
<td>2.4</td>
<td>1.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Median</td>
<td>2.6</td>
<td>1.8</td>
<td>0.8</td>
<td>2.1</td>
</tr>
<tr>
<td>SD</td>
<td>2.7</td>
<td>2.2</td>
<td>0.6</td>
<td>3.2</td>
</tr>
<tr>
<td>SE</td>
<td>0.1</td>
<td>0.1</td>
<td>0.03</td>
<td>0.2</td>
</tr>
<tr>
<td>%CV</td>
<td>80%</td>
<td>93%</td>
<td>65%</td>
<td>114%</td>
</tr>
<tr>
<td>Range</td>
<td>0.2 - 18.0</td>
<td>0.09 - 15.2</td>
<td>0.07 - 3.1</td>
<td>0.6 - 36.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bulk (wet), n = 410</th>
<th>Total</th>
<th>NH4</th>
<th>NO3</th>
<th>NH4:NO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>2.0</td>
<td>1.2</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Median</td>
<td>1.3</td>
<td>0.8</td>
<td>0.6</td>
<td>1.2</td>
</tr>
<tr>
<td>SD</td>
<td>2.0</td>
<td>1.6</td>
<td>0.5</td>
<td>1.2</td>
</tr>
<tr>
<td>SE</td>
<td>0.1</td>
<td>0.08</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td>%CV</td>
<td>102%</td>
<td>133%</td>
<td>65%</td>
<td>79%</td>
</tr>
<tr>
<td>Range</td>
<td>0.07 - 11.8</td>
<td>0 - 10.0</td>
<td>0.05 - 2.9</td>
<td>0.6 - 6.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Dry (Throughfall - Bulk), n = 395</th>
<th>Total</th>
<th>NH4</th>
<th>NO3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>1.4</td>
<td>1.1</td>
<td>0.3</td>
</tr>
<tr>
<td>Median</td>
<td>1.0</td>
<td>0.8</td>
<td>0.2</td>
</tr>
<tr>
<td>SD</td>
<td>1.4</td>
<td>1.1</td>
<td>0.4</td>
</tr>
<tr>
<td>SE</td>
<td>0.07</td>
<td>0.06</td>
<td>0.02</td>
</tr>
<tr>
<td>%CV</td>
<td>96%</td>
<td>102%</td>
<td>129%</td>
</tr>
<tr>
<td>Range</td>
<td>0 - 7.9</td>
<td>0 - 7.5</td>
<td>0 - 2.0</td>
</tr>
</tbody>
</table>
### Table 1: Non-parametric spearman rho correlation R coefficients between precipitation metrics and total N throughfall (wet and dry) and bulk (wet) deposition. Correlations include annual means (2006 – 2013), and winter (January – March) and summer monsoon (June – September) seasons. All correlations were significant (p < 0.05).

<table>
<thead>
<tr>
<th>Metric</th>
<th>Annual</th>
<th>Winter</th>
<th>Summer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Throughfall (wet and dry)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precipitation (mm)</td>
<td>0.52</td>
<td>0.56</td>
<td>0.68</td>
</tr>
<tr>
<td>Rainy days:dry days</td>
<td>0.58</td>
<td>0.53</td>
<td>0.66</td>
</tr>
<tr>
<td>Number of rainy days</td>
<td>0.55</td>
<td>0.55</td>
<td>0.69</td>
</tr>
<tr>
<td>Antecedent dry days</td>
<td>-0.19</td>
<td>-0.55</td>
<td>-0.40</td>
</tr>
<tr>
<td>Longest # consecutive dry days</td>
<td>-0.53</td>
<td>-0.31</td>
<td>-0.48</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bulk (wet)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Annual</td>
<td>0.56</td>
<td>0.55</td>
<td>0.68</td>
</tr>
<tr>
<td>Winter</td>
<td>0.72</td>
<td>0.68</td>
<td>0.83</td>
</tr>
<tr>
<td>Summer</td>
<td>0.83</td>
<td>0.63</td>
<td>0.63</td>
</tr>
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</table>

See methods for a description of each precipitation metric.
CHAPTER 4
CHARACTERIZATION OF THE ‘ECOLOGICAL AIRSHED’ OF NEAR-URBAN PROTECTED ECOSYSTEMS

ABSTRACT

Atmospheric compounds generated by cities are expected to have significant impacts on protected lands in urban and surrounding native ecosystems. Gaseous reactive nitrogen (N), ozone (O$_3$) and carbon dioxide (CO$_2$) are generated by human activities and individually act as a resource or stressor to ecosystems, but their co-occurring distribution is unknown. Air quality monitoring programs routinely measure O$_3$ and nitrogen oxides (NO$_x$) in residential areas to meet human health regulations, while other ecologically important compounds such as ground-level CO$_2$ and reactive N are not monitored in either cities or remote protected lands. Using a spatially extensive design, I characterized the “ecological airshed” of native protected ecosystems within and surrounding Phoenix, Arizona by quantifying the spatial and temporal distribution of biologically relevant atmospheric compounds, including nitric acid (HNO$_3$), ammonia (NH$_3$), NO$_x$, O$_3$, and CO$_2$. Additionally, I measured N and O$_3$ concentrations along a 1500 meter transect representing a distance-from-city gradient from the exterior edge to the interior of a large open space native preserve. I found that CO$_2$, reactive N and O$_3$ co-occur in both urban and outlying protected areas at elevated levels likely to affect the ecological structure and functioning of ecosystems. Carbon dioxide and N concentrations, as well as N deposition, consistently co-occur at higher levels within urban open space areas...
compared to the outlying native ecosystem. For example, summer N deposition to urban ecosystems was up to 42% greater than native ecosystems outside of the city. In the outlying locations, N deposition rates were within or above the estimated critical load (3 – 8 kg N ha\(^{-1}\) yr\(^{-1}\) for deserts) at which ecological impacts from elevated N inputs are expected to occur. Mean daily CO\(_2\) concentrations were highest within the city (396 ppm), yet urban CO\(_2\) patterns were primarily characterized by high diurnal fluctuations (average 373 – 443 ppm) that reflect anthropogenic activities, such as rush hour traffic. Though summer average O\(_3\) concentrations were 11% lower within the city, urban-based real-time monitors show that ecosystems within and outside of the city experience periods of high acute O\(_3\) exposure. In native desert locations to the west of the city, all three pollutants occur at elevated levels where CO\(_2\) concentrations mimic those in the urban area as a result of extensive agricultural fields. This study is the first to identify the distinct spatial pattern of co-occurring, ecologically important urban pollutants within protected lands. The affects of the urban atmosphere on ecosystems, in combination with other factors related to urbanization such as elevated temperatures, may lead to longer-term consequences for ecosystem structure, functioning and services. My findings highlight the need for air quality monitoring with an expanded repertoire of compounds known to affect ecosystem services and biological processes in both urban and remote native ecosystems.
INTRODUCTION

Cities occupy only a small percentage of Earth’s land surface, but urban-generated compounds affect air quality and ecosystems at local, regional and global-scales (Dentener et al. 2006; George et al. 2007; Gurney et al. 2009). Atmospheric compounds are frequently transported far beyond the urban or political boundaries in which they are produced and regulated (Akimoto 2003; Monks et al. 2009). Despite the distance from human activities, native ecosystems can be exposed to elevated levels of ecologically important urban air pollutants, such as reactive nitrogen (N), ozone (O₃), and carbon dioxide (CO₂). Decades of research has found these pollutants act individually as a resource or stressor to ecosystems, and more recent research highlights the potential non-additive effects of the pollutants in combination (Long et al. 2004; Karnosky et al. 2007; Bobbink et al. 2010). Yet, to date, no studies have estimated the co-occurrence of CO₂, N, and O₃ within or near urban areas, and thus the distribution and extent to which these common pollutants co-occur is unknown. In this study, I examined the spatial and temporal distribution of CO₂, O₃, and gaseous reactive N concentrations and deposition in native desert ecosystems within and surrounding the major metropolitan area of Phoenix, Arizona. Identifying the land area affected by the co-distribution of these atmospheric compounds within and beyond the urban boundary—the “ecological airshed”—is an important step for setting effective management and conservation strategies to protect native ecosystems and the ecosystem services they provide.

Pollutant standards and regulatory monitoring are increasingly common in both developed and developing cities (Molina and Molina 2004; Parrish et al. 2011), yet the
spatial distribution of the urban “ecological airshed” is unknown. Air quality has improved in the last several decades in some large cities, such as Los Angeles and New York City in the United States (Parrish et al. 2011). However, as cities in developing nations become more industrialized and expand in population and land cover worldwide, air pollutants continue to exceed regulatory standards and are of growing public concern (Molina and Molina 2004; Parrish et al. 2011; Seto, Güneralp, and Hutyra 2012). Yet, air quality regulations primarily focus on human health and do not account for potential ecosystem impacts (Paoletti and Manning 2007; Lovett et al. 2009; Hidy and Pennell 2010). Further, the spatial resolution of air quality monitoring is often restricted to residential or industrial areas to meet human health regulations with a focus on O$_3$, carbon monoxide (CO), particulate matter, and oxidized sulfur and N compounds (USEPA Clear Air Act). Other compounds, such as surface level CO$_2$, may be monitored in remote regions for background levels, but are less frequently monitored near cities despite their expected elevated concentrations near human activities and ecological significance. Air quality models exist to address these gaps, but their spatial and temporal resolution is often inadequate to examine the variability and magnitude of ecosystem exposure at local scales. Overall, additional monitoring is needed with an expanded repertoire of compounds to monitor the distribution of the “ecological airshed” in order to identify the affected ecosystems and develop air quality regulations that protect both humans and the environment.

Despite general improvements in air quality, elevated CO$_2$, O$_3$, and N generated from human activities are expected to influence native ecosystems worldwide (IPCC 2013). For example, human-mediated agricultural and combustion activities have significantly
increased concentrations of reactive N gas emissions (Galloway et al. 2008). Atmospheric N deposits to ecosystem surfaces as reduced (ammonium (NH$_4^+$), ammonia (NH$_3$)) and oxidized forms of N (Lovett 1994). Nitrogen deposition has important consequences on ecosystems and plant community composition by alleviating nutrient limitation and stimulating primary production (Aber et al. 1998; Clark and Tilman 2008; Payne et al. 2013). Similarly, CO$_2$ is a natural product of ecosystem processes (e.g. respiration), but CO$_2$ emissions are greatest in and near cities—creating an expected “urban CO$_2$ dome”—as a result of energy combustion (Idso, Idso, and Balling Jr. 2001; Pataki et al. 2006; George et al. 2007; Gurney et al. 2009; Duren and Miller 2012). CO$_2$ is a greenhouse gas affecting climate change, but also a key resource for photosynthesis (IPCC 2013). Ozone, on the other hand, is a product resulting from photodegradation (e.g., oxidation) of CO and volatile organic carbon compounds (VOCs) in the presence of NO$_x$ (Finlayson-Pitts and Pitts 2000). Tropospheric O$_3$ has negative health implications for humans, as well as toxic effects on plant physiology leading to reduced growth or early senescence (Karnosky et al. 2007; Ainsworth et al. 2012). In addition to the individual effects of each pollutant, the pollutants in combination can have synergistic or antagonistic affects on ecosystems and primary producers (Payne et al. 2011; Templer 2013; Smith et al. 2014). Yet, no studies have estimated the co-occurrence of CO$_2$, N, and O$_3$ within or near urban areas in order to determine the land area affected or to estimate ecosystem responses to the co-occurring pollutants on a larger scale.

In order to address this gap, I asked, what is the spatial and temporal co-distribution of CO$_2$, N, and O$_3$ concentrations (the “ecological airshed”) in protected desert areas in and surrounding the major metropolitan region of Phoenix, AZ? Arid and semi-arid
ecosystems cover over a third of the globe’s land area on which much of the world’s new urban growth is expected to occur (UN 2009, 2011). Further, dryland ecosystems are predicted to be especially sensitive to regional and global anthropogenic changes, such as elevated CO$_2$ and other urban generated pollutants (Melillo et al. 1993; Pardo et al. 2011). Phoenix, Arizona is situated in the northern Sonoran Desert, where over 4 million people reside with significant impacts on air quality. For example, Phoenix experienced 40 O$_3$ non-attainment days in 2012 and 2013 in which 8-hour average concentrations exceeded the US EPA standard (75 ppb). Predicted mean annual N deposition in the metro Phoenix area is expected to be approximately 7 kg N ha$^{-1}$ yr$^{-1}$ with seasonal averages ranging between 5 – 13 kg N ha$^{-1}$ yr$^{-1}$ (Cook et al. In prep). Finally, intense anthropogenic activities create a “CO$_2$ dome” along roads that also varies with distance from the city and land cover (Idso, Idso, and Balling Jr. 1998; Idso, Idso, and Balling Jr. 2001; Day et al. 2002; Wentz et al. 2002; Koerner and Klopatek 2002). The spatial and temporal co-distribution of these compounds has not been widely investigated within or beyond the urban boundary.

To examine the spatial and temporal distribution of urban air quality, I monitored local and regional patterns of CO$_2$, O$_3$, and reactive gaseous N concentrations in native protected desert ecosystems in the urban and outlying regions of the Phoenix metropolitan area. Based on ambient gaseous N concentrations, I also estimated N deposition to ecosystems in order to better account for the N fluxes to the landscape relative to the critical load. The N critical load is the rate of deposition at which ecological changes occur in ecosystems and is estimated for desert ecosystems between 3-8 kg N ha$^{-1}$ yr$^{-1}$ (Fenn et al. 2010; Pardo et al. 2011). In addition, I examined the
small-scale variability of N and O₃ concentrations along a transect from the exterior to interior of a large protected desert area within the city. I expected the distribution of each compound to vary as a result of a suite of biophysical and anthropogenic variables (Wentz et al. 2002; Nunnermacker et al. 2004; Wang and Ostoja-Starzewski 2004; Lee, Fernando, and Grossman-Clarke 2007). For example, I expected CO₂ and N to be highest within urban areas closer to human generated sources of emissions. O₃ concentrations, in contrast, were expected to be highest outside of the city due to urban O₃ titration in the presence of higher urban NOₓ. Despite differences in peak concentrations, I expected native ecosystems within and surrounding the city to be exposed to co-occurring CO₂, O₃, and N at levels that impact ecosystems.

METHODS

Experimental design and site characteristics

I monitored CO₂, O₃ and N with co-located passive and active atmospheric samplers in sites with varying proximity to the urban center of Phoenix, Arizona. Phoenix is an ideal location to explore the “ecological airshed” of cities. Several large remnant native desert areas have been preserved within the Phoenix municipal area and at the outlying edge of current urban development, and these preserves make a useful urban-rural gradient for examining the effects of urbanization and proximity to the city on the native ecosystem. Following other ecological studies in the Phoenix region (Hall et al. 2011; Sponseller et al. 2012), I used a gradient of monitoring sites in the preserves within the city (“urban”) and in protected native desert areas at the edge and outside of the urban boundary (“outlying”).
Specifically, I measured $O_3$ and gaseous N concentrations with passive samplers at 10 sites: two outlying west of Phoenix (n = 2), four urban (n = 4), and four outlying east of Phoenix (n = 4, Table 1, Figure 1). At three of these locations (one outlying west, urban and outlying east site), I continuously monitored CO$_2$ concentration with non-dispersive infrared gas analyzers. All sites except one (the calibration site) are located in protected open space desert preserves that range in size and distance from the urban center (Table 1). In addition, the sites fall along a natural elevation and precipitation gradient that increases to the east of Phoenix (Table 1). All sites have a similar vegetation structure, dominated by drought tolerant shrubs, *Larrea tridentata* and *Ambrosia deltoidea*, and diverse annual grasses and forbs in the spring. The calibration site (39$^{th}$ Ave and Earll Drive) is located in a dense residential neighborhood in west-central Phoenix and was chosen to calibrate samplers with continuous air quality monitors operated by the Maricopa Air Quality Department (AQD) and temperature and relative humidity monitors located on a meteorological tower operated by the Central Arizona–Phoenix Long-term Ecological Research (CAP LTER) program. Finally, to examine small-scale spatial variability of pollutants, I examined reactive N and $O_3$ concentrations at five equally spaced points along a 1500 meter transect extending from the edge to the interior of the largest protected open space area within the city (South Mountain, Figure 1).

At all locations, I measured concentrations of NO$_x$, NH$_3$, HNO$_3$, and O$_3$ using co-located passive samplers for five consecutive 2 - 3 week intervals over a summer season (May 17 – August 14, 2013; see Appendix 1 for specific dates). Due to limited supplies NH$_3$ was only sampled during the first, third and fourth sampling intervals, while NO and NO$_2$ were sampled during the second and fifth sampling intervals (Appendix 1). HNO$_3$
and O₃ were both measured continuously throughout the summer. NH₃ samples were deployed with 2 duplicate filters per sampler. NOₓ, NO₂, HNO₃ and O₃ samples only included 1 filter (or one set of two O₃ filters that were analyzed together) per site per sampling interval (NH₃: 2 duplicate samples/site, NOₓ, NO₂, HNO₃, and O₃: 1 sample each/site). CO₂ was monitored with infrared gas analyzers nearly continuously from June 2013 to March 2014 (See Appendix 1 for specific dates).

**O₃ and N field collection and analyses**

Ammonia, NOₓ (NO and NO₂), and O₃ gaseous concentrations were measured using Ogawa Teflon passive samplers and Ogawa impregnated fiber filter pads (Koutrakis et al. 1993; Roadman et al. 2003). Ambient NH₃ concentrations were collected on filter pads coated with citric acid, which forms ammonium citrate in the presence of NH₃. NOₓ concentrations were captured by simultaneously exposing NO₂ and NOₓ filter pads that together were used to calculate total NOₓ based on site-specific meteorological variables (details of the calculations described below). Ambient NO₂ filters were coated with triethanolamine (TEA) and NOₓ filter pads with TEA and PTIO (2-phenyl-4,4,5,5-tetramethylimidazoline-3-oxide-1-oxyl). TEA reacts to form nitrite (NO₂⁻) and PTIO is a free radical reagent to scavenge NO and NO₂ simultaneously. Finally, O₃ concentrations were collected on filters coated with NO₂⁻ that is oxidized to nitrate (NO₃⁻) when exposed to O₃. Nitric acid (HNO₃) samplers were designed and deployed following methods developed by Bytnerowitz and colleagues (2005) using nylon membrane filters (Pall brand Nylasorb nylon membrane filters, 1.0µm, 47mm) to collect ambient air absorbed as NO₃⁻.
Passive samplers were all transported to and from the field in a sealed bag within a sealed plastic container. All passive samplers were installed in the field with a protective cover to block direct sun and rain at 2 meters above ground and in open areas away from shrubs, trees, taller vegetation and built structures (Figure 2). For each compound and sampling period, one additional sampler was set-up as a field blank for each filter type. Field blanks were transported to the field sites in a sealed bag with the samples being deployed, but were returned to the lab immediately after the field samples were installed and remained sealed on a lab bench at room temperature during the sampling interval.

Filters were extracted for chemical products according to methods described in the Ogawa protocols (ogawausa.com) and by Bytnerowicz and colleagues (2005). At the end of each sampling period, exposed filters were transferred to and sealed in a 20 ml acid-washed glass vial. Dry filters were stored in the freezer until analysis. Each filter was extracted separately with double de-ionized water (DI) immediately before analysis and shaken on a shaker table at 165 rpm for 15 minutes. NH$_3$, NO and NO$_2$ filters were extracted with 8 mL DI water, and O$_3$ and HNO$_3$ filters were extracted together with 5 and 20 mL DI water, respectively. O$_3$ extracts were diluted in 1:5 dilution in DI water by adding 1mL of extract to 4 mL DI water. NH$_3$, O$_3$, and HNO$_3$ extracts were filtered through a 0.2 μm syringe filter (Acrodisc 13mm, 0.2 μm nylon syringe filters to prevent clogging in the analytical instrument) and analyzed in duplicates on a Dionex ion chromatograph (Dionex Corporation): NH$_3$ samples for ammonium (NH$_4$); O$_3$ and HNO$_3$ samples for NO$_3^-$. NO$_x$ and NO$_2$ filters were analyzed colorimetrically for nitrite with Lachat Quikchem continuous flow injection instrument (Lachat Instruments). The field blanks were extracted and analyzed at the same time as exposed filters, as were extract
blanks (additional unexposed “blank” filters) with each set of samples. I averaged duplicate samples from the same sampling period and corrected each with the corresponding field blank.

**Calculating \(O_2\) and \(N\) concentrations and dry \(N\) deposition**

Gaseous \(N\) concentrations and dry deposition rates were calculated using a variety of methods. Ammonia concentrations were calculated following Ogawa protocol (equation 1) based on exposure time, extract concentration and volume and the site-specific diffusion coefficient based on meteorological variables. In equation 1, \(NH_4\) (\(\mu g\ mL^{-1}\)) is the concentration of the sample extract, 17.04 (\(\mu g\ \mu mol^{-1}\)) is the molecular weight of \(NH_3\), 14.01 (\(\mu g\ \mu mol^{-1}\)) is molecular weight of \(N\), and 24.45 is the constant conversion factor for volume to mass of an ideal gas at standard temperature and pressure. The alpha conversion factor converts \(NH_4\) to \(NH_3\) concentration by molecular weight and includes the mass transfer diffusion coefficient – or sampling rate – that is calculated based on the geometry of the sampler and the molecular diffusivity of the gas using site-specific meteorological variables during each sampling period (Roadman et al. 2003). I calculated \(\alpha\) conversion factor for \(NH_3\) based on Roadman and colleagues (2003) which is based on average temperature during the sampling period.

\[
NH_3\left(\frac{\mu g\ N}{m^3}\right) = \frac{NH_4\left(\frac{\mu g}{mL}\right) \times \text{Extract volume (mL)} \times a\left(\frac{pg}{mL}\right) \times 17.04\left(\frac{\mu g}{\mu mol}\right) \times 14.01\left(\frac{\mu g}{\mu mol}\right)}{\text{Exposure time (min)}} \times 24.45\left(\frac{m^3}{\mu mol}\right) \times 17.04\left(\frac{\mu g}{\mu mol}\right) \tag{1}
\]

Nitrogen dioxide gaseous concentrations were calculated similarly to \(NH_3\) following Ogawa protocol (Equation 2). \(NO_2\) (\(\mu g\ mL^{-1}\)) is the concentration of the sample extract...
from the NO₂ filter pad, 46.01(μg μmol⁻¹) is the molecular weight of NO₂, and the α conversion factor is calculated specifically for each site and sampling period based on temperature, relative humidity and vapor pressure of water.

\[
NO₂ \left( \frac{μgN}{m^3} \right) = \frac{NO₂ \left( \frac{μg}{m^3} \right) \times Extract \; volume \; (mL) \times α \left( \frac{ppb \cdot min}{μg} \right)}{Exposure \; time \; (min)} \times \frac{46.01 \left( \frac{μg}{μmol} \right)}{24.45 \left( \frac{m^3}{μmol} \right)} \times 14.01 \left( \frac{μg}{μmol} \right)
\]

Total NOₓ gaseous concentrations were determined by summing NO and NO₂ concentrations. Since there is no α conversion factor for NOₓ (the combination of NO and NO₂), the concentration of NO and NO₂ was determined separately and then summed. NO was calculated by subtracting the extract concentrations of NO₂ from the corresponding NOₓ sample from the same site and period. Then, following Equation 2, NO concentration (μgN m⁻³) was calculated using an NO specific α conversion factor and the molecular weight of NO.

HNO₃ concentrations were calculated using the Bytnerowicz and colleagues (2005) calibration curve of absorbed NO₃ on each filter when exposed to particular HNO₃ dose in controlled conditions (slope = 69.498 (hour m⁻³); equation 3).

\[
HNO₃ \left( \frac{μgN}{m^3} \right) = \frac{NO₃ \left( \frac{μg}{m^3} \right) \times Extract \; volume \; (mL) \times 69.498 \left( \frac{hour}{m^3} \right)}{Exposure \; time \; (hour)} \times 14.01 \left( \frac{μg}{μmol} \right) \times 63.02 \left( \frac{μg}{μmol} \right)
\]

Ozone concentrations were calculated using Equation 4 from the Ogawa O₃ protocol. In equation 4, NO₃ is the sample extract concentration from the O₃ filter pads and 18.09 is the constant conversion factor that incorporates the sampling rate (21.8 mL min⁻¹) and molecular weight conversion from NO₃ to O₃.

\[
O₃ (ppb) = \frac{NO₃ \left( \frac{μg}{m^3} \right) \times Extract \; volume \; (mL) \times 18.09 \left( \frac{mL}{μg \; NO₃} \right) \times 1000}{Exposure \; time \; (min)}
\]
As this study is focused on estimating the ecological airshed to determine the extent and impact of urban pollutants on ecosystems, I estimated N deposition rates from N concentrations to use as an indicator of the amount of N reaching the ecosystem. Nitrogen deposition rates, rather than concentration values, are also useful for determining where N inputs to the ecosystem exceed the critical load data. Using the inferential method, I estimated dry N deposition fluxes (Equation 5) based on the concentrations from the passive samplers (equations 1 - 3) and estimated deposition velocities ($V_d$, cm sec$^{-1}$) for each gaseous N species.

$$Deposition \ (kg \ N \ ha^{-1} \ yr^{-1}) = N \ Concentration * V_d$$  (5)

Across all sites and periods, I uniformly applied an average deposition velocity (NO: 0.01 cm sec$^{-1}$, NO$_2$: 0.14 cm sec$^{-1}$, HNO$_3$: 1.2 cm sec$^{-1}$, and NH$_3$: 0.15 cm sec$^{-1}$) previously estimated for each compound at an outlying Sonoran Desert site in the CAP LTER region (Gonzalez, unpublished data). While deposition velocities likely vary between sites due to differences in vegetation structure and meteorological conditions, the deposition velocities I used for each N species were comparable to those used in other arid and urban-arid ecosystem studies (Wesely and Hicks 2000; Zhang, Brook, and Vet 2003; Pan et al. 2012; Delon et al. 2012; Li et al. 2013).

**Monitoring CO$_2$ concentrations**

Real-time CO$_2$ concentrations were monitored with 6 non-dispersive infrared gas analyzers (IRGA, CM-0018, CO$_2$meter, Ormand Beach, Fl). These particular CO$_2$ sensors were chosen because they are inexpensive and portable with built-in data loggers for CO$_2$ concentrations, temperature and relative humidity. Recording data every 10
minutes, the IRGAs can log for about six-week intervals. Finally, the IRGAs were battery operated for easy deployment in remote desert sites without electricity.

CO₂ monitoring occurred at 3 sites in the Phoenix region: one outlying west (EME), one urban (DBG), and one outlying east (MCS; Table 1, Figure 2). At each site, 2 CO₂ IRGAs were installed on rebar: one each at 2 and 0.5 meters above the ground in open areas away from shrub and tree vegetation. I monitored CO₂ at 2 meters in order to capture ambient concentrations at a similar height to those monitored in other studies (Idso, Idso, and Balling Jr. 2001) and at 0.5 meters to test if near surface ambient CO₂ concentrations —closer to the height of desert herbaceous vegetation—differ from 2-meter concentrations. Sensors were placed under a hard plastic protective shield (approximately 100 cm diameter and 10 cm side height) to protect it from direct sunlight and rain. CO₂ monitoring began on 11 June 2013, and concentrations (ppm) were recorded every 10 minutes continuously until 14 March 2014. Data were downloaded and batteries replaced in each sensor every 2–5 weeks throughout the sampling period. At each site, there were some sensor or data logging errors, creating some gaps in the continuous long-term data (see Appendix 1 for specific dates).

The CO₂ IRGAs have a repeatability of +/- 20 ppm and an accuracy of +/- 30ppm (CO₂ meter.com). In order to account for variability among sensors and ensure consistency in readings across sites, I calculated a sensor specific correction (i.e. an offset factor) to apply to the data for each sampling period. Correction factors were determined by simultaneously logging ambient CO₂ concentrations with the field CO₂ IRGAs and a calibrated LiCOR IRGA (Li-8100 calibrated at LiCOR, Lincoln Nebraska). The Li-8100 is an automated CO₂ soil flux system, but for this purpose was set up to draw ambient air
and simultaneously record CO$_2$ concentrations with the field sensors every 15 seconds. A correction factor was calculated based on the average difference in CO$_2$ readings between the Li-8100 and each sampler and applied to the corresponding sampling periods. Correction factors tended to increase over time, but were relatively consistent within a sampler. Correction values ranged among samplers from minimal offset value of -0.8 ppm (average +/- 5.5 SD across sampling periods at EME) to the maximum offset of -33.0 ppm (average +/- 11.9 SD across sampling periods at MCS). A negative offset indicates the field sensors were consistently higher than actual concentrations. The data reported here are corrected CO$_2$ values.

**Data analyses**

Each pollutant (HNO$_3$, NH$_3$, NO$_x$, total reactive N, O$_3$, CO$_2$) was transformed when needed to meet basic assumptions of normality and homogeneity of variances. When data could not meet these assumptions, I used non-parametric Kruskal Wallis test to compare ranked means. For O$_3$ and N, I first examined differences in mean concentration (O$_3$, HNO$_3$, NH$_3$, NO$_x$, and total N) among sampling locations with one-way ANOVA (O$_3$) and Kruskal Wallis (all N concentrations). Next, I compared summer O$_3$ concentrations and N deposition among location (outlying west, urban and outlying east) and the sampling period (see Appendix 1) with a two-way ANOVA. I used bonferroni adjustment in the post-hoc comparisons in order to account for multiple pairwise comparisons. Statistical analyses were conducted using R (R Core Team, 2014).

Ambient CO$_2$ concentrations, monitored over a longer continuous time frame, were analyzed by sampling height (0.5 and 2 meter), site location (EME, DBG, MCS), season
(summer: June – August, winter: December – March), diurnal patterns, and monthly concentration. At each site and sampling height, raw 10 minute data were summarized as hourly means to examine the diurnal fluxes (n = 24). I also compared daily means over the entire study period (at 2 meter and 0.5 meter height respectively, n = 263 and 221 at MCS, n = 195 and 80 at DBG, and n = 247 and 248 at EME, see Appendix 1 for specific dates), and over the summer (June – August 2013) and winter (December 2013- March 2014) seasons, separately. Differences in mean site and monthly concentrations were compared within each season with a two-way ANOVA. I used bonferroni adjustment in the pairwise post-hoc comparisons to account for inflated error due to multiple comparisons among means.

RESULTS

Ozone

During summer (mid-May to mid-August), average two-week summer O₃ concentrations ranged from a low of 31.9 ppb at the urban Desert Botanical Garden (DBG) site to 65.4 ppb at McDowell Mountain South (MCS) to the east of Phoenix (Table 2). Mean O₃ concentrations were significantly higher at MCS than the urban 39th Ave site, but did not significantly differ among other locations (one-way ANOVA, F(9,38) = 2.2, p = 0.04, Table 2). Averaged across sites, summer O₃ concentrations were higher in the middle of summer (Period 3, F(4,45) = 23.4, p < 0.001; Figure 3) and 11% higher on average to the east of the city (48.1 ± 1.4 ppb) than in urban (42.8 ± 1.3 ppb) locations (two-way ANOVA, F(2,45) = 9.1, p < 0.001, Figure 4).
Nitric Acid

Summer HNO₃ concentrations ranged from 0.3 – 1.5 µg N m⁻³ across sites, but were not significantly different among sites (Kruskal-Wallis, χ² = 10.1, df = 9, p = 0.3, Table 2). Summer HNO₃ two-week average deposition followed the same pattern. Summer HNO₃ deposition ranged from 1.1 kg N ha⁻¹ yr⁻¹ at White Tank Mountains (WTM) to 5.5 kg N ha⁻¹ yr⁻¹ at DBG (Table 3). Averaged across sites, summer HNO₃ deposition differed significantly by location relative to the city (two way ANOVA, F(2, 33) = 16.5, p<0.001; Figure 4) and period of summer sampling (two way ANOVA, F(4, 33), = 22.0, p < 0.001). Summer season HNO₃ deposition was significantly greater in the city (3.2 ± 0.3 kg N ha⁻¹ yr⁻¹) than in sites outlying to the east (2.3 ± 0.2 kg N ha⁻¹ yr⁻¹) or west (2.1 ± 0.3 kg N ha⁻¹ yr⁻¹) and was higher in the middle of the summer (periods 2 – 4) than the final period during early August (not shown).

Ammonia

Summer NH₃ concentrations ranged from 2.4 – 14.1 µg N m⁻³ (Table 2). While there was a large range in NH₃ concentrations, mean NH₃ did not significantly differ among sites (Kruskal-Wallis, χ² = 16.5, df = 9, p = 0.06, Table 2). Summer NH₃ deposition rates were lowest in the outlying sites to the east and west of the city with deposition as low as 1.2 kg N ha⁻¹ yr⁻¹ (Table 3). The highest ammonia fluxes were 6.7 kg N ha⁻¹ yr⁻¹ at urban 39th Ave site (Table 3). Averaged across sites, NH₃ fluxes were significantly higher during the third and fourth periods than the first period in early summer (two-way
ANOVA, \(F_{(2, 20)} = 26.2, p <0.001, \) data not shown). In addition, mean fluxes were significantly higher in the urban \((4.2 \pm 0.4 \text{ kg N ha}^{-1} \text{ yr}^{-1})\) than outlying desert to the east \((2.1 \pm 0.2 \text{ kg N ha}^{-1} \text{ yr}^{-1}; \) two-way ANOVA, \(F_{(2,20)} = 26.8, p < 0.001, \) Figure 4). In contrast, urban \(\text{NH}_3\) deposition did not differ from the outlying west sites \((3.0 \pm 0.5 \text{ kg N ha}^{-1} \text{ yr}^{-1})\).

**Nitrogen oxide**

Summer \(\text{NO}_x\) concentrations ranged between \(0.1 – 1.2 \mu \text{g N m}^{-3}\) with the highest concentrations within the urban region (Table 2). \(\text{NO}_x\) concentrations at urban 39th Ave \((1.7 \pm 0.2 \mu \text{g N m}^{-3})\) and DBG \((1.1 \pm 0.1 \mu \text{g N m}^{-3})\) were significantly higher than \(\text{NO}_x\) concentrations to the east or west of Phoenix \((0.2 – 0.3 \mu \text{g N m}^{-3}; \text{Kruskal-Wallis, } \chi^2 = 16.9, \text{df} = 9, p = 0.04, \) Table 2). When calculated as deposition, summer \(\text{NO}_x\) fluxes were low compared to deposition of other N compounds in this study, ranging from 0.04 in the outlying regions to 0.7 kg N ha\(^{-1}\) yr\(^{-1}\) in an urban site (Table 3). Despite overall low values, when averaged across sites, \(\text{NO}_x\) deposition was greatest in urban compared to outlying locations (two way ANOVA, \(F_{(2, 13)} = 11.2, p < 0.001, \) Figure 4). Nitrogen oxide fluxes did not differ by summer period (two-way ANOVA, \(F_{(3, 13)} = 1.5, p = 0.3\)).

**Total dry N deposition**

Total dry N concentration was determined by summing the concentrations of HNO\(_3\), \(\text{NH}_3\), and \(\text{NO}_x\) for each site and sampling period. Because \(\text{NH}_3\) and \(\text{NO}_x\) were only sampled during a subset of the season’s sampling periods, the seasonal average of each
compound at the corresponding site was substituted for missing sampling periods in order to estimate the total concentration for all sites and periods. Total summer N concentrations ranged between 3.1 – 16.6 µg N m\(^{-3}\) and differed significantly by site (Kruskal-Wallis, \(\chi^2 = 34.3, \text{df} = 9, p < 0.001\), Table 2). Nitrogen concentrations at 39\(^{th}\) Ave (13.2 +/- 2.8 µg N m\(^{-3}\)) were significantly higher than all other sites except urban DBG (10.8 +/- 1.9 µg N m\(^{-3}\)) and SMW (10.3 +/- 3.2 µg N m\(^{-3}\), Table 2). In addition, DBG and SMW were also significantly higher than three outlying east sites (Table 2).

Total dry N fluxes varied from 2.4 – 11.1 kg N ha\(^{-1}\) yr\(^{-1}\) and differed significantly by location relative to the city (Figures 3 and 4). Averaged across sites during the summer, urban total dry N deposition (7.8 ± 0.4 kg N ha\(^{-1}\) yr\(^{-1}\)) was significantly greater than to the east (4.5 ± 0.2 kg N ha\(^{-1}\) yr\(^{-1}\)) or west (5.1 ± 0.5 kg N ha\(^{-1}\) yr\(^{-1}\), two-way ANOVA, \(F_{(2, 45)} = 72, p< 0.001\), Figure 4). Note, these values only account for dry deposition.

At the urban locations, NH\(_3\) constitutes an average 53 +/- 6% of total dry N deposition in the region, with the remainder from HNO\(_3\) (42 +/- 8%) and NO\(_x\) (5 +/- 3%). In the outlying west sites, NH\(_3\) also makes up the highest proportion of fluxes (58 +/- 5% of total) compared to 40% (+/- 5) from HNO\(_3\). On the other hand, the outlying east sites had more even distribution than the west sites of NH\(_3\) and HNO\(_3\), 50% (+/- 7) and 48% (+/- 7) of the total dry deposition, respectively. Among all locations, the proportion of NO\(_x\) fluxes were variable but tended to be higher in the city, composing 5% (+/- 3%) of total urban N deposition, compared to 1% (+/- 0.2) and 2% (+/- 0.5) in the locations west and east of the city, respectively.
**Carbon dioxide concentrations**

The urban and outlying locations had distinct CO$_2$ patterns that were most pronounced at the 2 meter compared to 0.5 meter sampling height (Figures 5 - 8). At 2 meters above ground, annual mean CO$_2$ concentrations were greater in the urban (396 ppm +/- 29 ppm) and outlying west sites (392 +/- 26 ppm) than CO$_2$ at the outlying east site 382 ppm (+/- 10 ppm). Urban CO$_2$ patterns had greater diurnal variation than concentrations in the outlying locations. In the urban locations, the difference between mean daily minimum (374 ppm) and maximum (443 ppm) values was 69 ppm. In outlying desert to the west (EME), the mean daily minimum and maximum was 377 and 426 ppm, respectively, with a range of 49 ppm. In contrast, the mean diurnal variation in the outlying location to the east (MCS) was only 19 ppm with daily average minimum and maximum ranging between 373 - 393 ppm.

At 0.5 m sampling height, CO$_2$ patterns were more similar among sites (Figures 6 and 8). Averaged across the year, the average concentration was 386 ppm at all sites. Mean daily minimum and maximum values were also similar among sites. The mean daily low concentrations were 372, 373, and 374 ppm at urban, west, and east sites respectively. The mean daily maximum CO$_2$ concentration was 410 ppm at both urban and west sites and 399 ppm at the east site.

At all sites, CO$_2$ concentrations varied seasonally and tended to be higher in the winter than summer. Average daily winter concentrations were significantly greater at west (404 +/- 34 ppm) and urban (416 +/- 32 ppm) locations than east site (386 +/- 8 ppm; p < 0.001, Figure 4). Winter monthly patterns were not consistent among sites. Similar patterns among the sites were observed in the summer, yet the daily mean
concentration at each site was lower in the summer than winter season (west 385 +/- 11 ppm, urban 387 +/- 15 ppm, and east 381 +/- 11 ppm, p < 0.001, Figure 6).

During the summer dates corresponding to N and O\textsubscript{3} sampling, mean 2 meter CO\textsubscript{2} concentrations were significantly greater in the city (392 +/- 12 ppm) and to the west of the city (387 +/- 11 ppm) than to the east of the city (382 +/- 12 ppm, Figure 4). In addition, diurnal variation in median daily min and max CO\textsubscript{2} concentrations was greater at the urban site (71 ppm, range 374 - 445 ppm) compared to the west site (50 ppm, range 371-421 ppm) and east site (45 ppm, range 365 – 410 ppm).

\textit{Edge-interior open space transect}

Ozone concentrations and N deposition along the edge-interior open space transect were comparable to those in other urban locations in this study. Contrary to expectations, there were few differences among sampling locations on the transect. Ozone concentrations ranged between 40 – 54 ppb during summer 2013, but were not significantly different among sites on the 1500m transect (Table 4, Kruskal-Wallis, $\chi^2 = 1.2$, df = 4, p = 0.9). However, similar to O\textsubscript{3} trends at the regional-scale, O\textsubscript{3} concentrations were highest during mid summer sampling interval (3: 11 June – 12 July) and significantly decreased in the following two sampling intervals (Table 4; Kruskal-Wallis, $\chi^2 = 12.5$, df = 2, p = 0.002).

Total (HNO\textsubscript{3} + NO\textsubscript{x} + NH\textsubscript{3}) N deposition along the transect ranged between 6.0 – 10.3 kg N ha\textsuperscript{-1} yr\textsuperscript{-1}, but did not differ significantly among locations (Table 4; Kruskal-Wallis, $\chi^2 = 1.9$, df = 2, p = 0.8). The same pattern held true for each individual species
(HNO₃, NH₃, NOₓ) of total N deposition. Finally, averaged across all transect sites, there were no significant differences (p > 0.05) in N deposition between summer sampling intervals (Table 4).

DISCUSSION

*Spatial and temporal co-occurrence of CO₂, O₃ and N in an urban “ecological airshed”*

I examined the extent and spatial-temporal variability of human-generated pollutants in native ecosystems within and beyond the urban boundaries of the major metropolitan region of Phoenix, Arizona. No previous studies have examined CO₂, O₃, and reactive N in combination to determine the extent to which they form an “ecological airshed” of biologically important pollutants near and far from their sources.

I found that O₃, reactive N, and CO₂ co-occur in both urban and outlying protected areas at elevated levels likely to affect the ecological structure and functioning of ecosystems. Carbon dioxide and N concentrations, as well as N deposition, consistently co-occur at higher levels within urban open space areas compared to the outlying native ecosystem. For example, N deposition rates across all locations were within or above the estimated critical load range, but summer N deposition to urban ecosystems was up to 42% greater than native ecosystems outside of the city. Similarly, mean daily CO₂ concentrations were highest within the city (396 ppm mean annual CO₂). The main difference between urban and outlying CO₂ concentrations, however, is reflected in the diurnal patterns influenced by anthropogenic activities. Urban CO₂ fluctuates following anthropogenic pulses, such as vehicular emissions from morning and evening rush hour
traffic. Despite the distance from major roadways, urban open space preserves experience average daily maximum concentrations of 443 ppm compared to maximum 393 ppm daily maximum values in an outlying native ecosystem. The average daily CO₂ fluctuation in cities is 69 ppm, which is 72% greater diurnal variability than in the outlying native ecosystem to the east of the city. Though summer average O₃ concentrations were 11% lower within the city, urban-based real-time monitors show that ecosystems within and outside of the city experience periods of high acute O₃ exposure. In addition, long-term O₃ exposure at concentrations comparable to the urban region can have significant impacts on ecosystems (Paoletti and Manning 2007).

Despite the distance from the city and human activities, outlying native ecosystems are also within the urban ecological airshed and experience elevated combinations of all three pollutants. Though lower than in the city, N inputs into the outlying native ecosystem occur at rates that have predicted consequences for primary producers resulting in increased annual herbaceous plant growth, a loss of native desert vegetation, and increased fire frequency (Brooks 2003; Báez et al. 2007; Rao, Allen, and Meixner 2010; Vourlitis 2012). Nitrogen deposition in outlying areas co-occurs with elevated summer O₃ concentrations to the east of Phoenix, following the dominant meteorological patterns in the valley (Ellis et al. 2000; Lee et al. 2008). In native ecosystems to the west of the city, CO₂ concentrations mimic those in the urban area and thus all three pollutants occur at elevated levels. While cities only cover a small percentage of the Earth’s land surface, these results highlight the impact of concentrated urban human activity on ecosystems beyond the urban boundaries.
Summer regional $O_3$ patterns

Summer ozone concentrations varied spatially across the urban and outlying native ecosystem. Similar to patterns previously reported in this region, the highest mean $O_3$ concentrations were primarily found beyond the urban borders (Atkinson-Palombo, Miller, and Balling Jr. 2006; Blanchard, Tanenbaum, and Lawson 2008). In particular, mean $O_3$ concentrations in the native desert to the east of the city were 11% greater than within the city (Figure 4). While vehicle emissions are the main source of anthropogenically produced precursors to $O_3$, the high $O_3$ concentrations outside of the city are likely due to transport of urban $O_3$ plumes to downwind locations and the titration of $O_3$ in the city center. $O_3$ titration leads to a diurnal fluctuation in which urban $O_3$ concentration dips significantly at night in the presence of high concentrations of NOx ($NO + O_3 \rightarrow NO_2 + O_2$; Finlayson-Pitts and Pitts 2000). With lower traffic density and vehicle emissions in the outlying locations (Table 1), $O_3$ titration is also expected to be lower in the outlying regions.

The passive sampling methods employed in this study have many benefits (e.g. inexpensive, low maintenance) and can be used to estimate ecosystem exposure to pollutants over longer, integrated periods. However, the passive samplers do not capture the diurnal variability, peak concentrations, or acute short-term $O_3$ exposure that can be important for ecosystem consequences. For example, on shorter temporal scales (1 and 8 hour averages), Phoenix urban $O_3$ concentrations were frequently higher than in outlying locations, despite higher long-term averages in the outlying desert regions (Pope and Wu 2014). Similarly, I compared hourly $O_3$ concentrations collected by the Maricopa County Air Quality Department (AQD) at the calibration site during summer 2013.
Hourly O₃ concentrations ranged between 67 – 94 ppb and the daily maximum 8-hour O₃ concentrations exceeded the 75 ppb EPA standard on 3 days during the study period. In comparison, the mean concentrations across the five summer sampling intervals measured by the Maricopa County AQD (31.2 – 40.1 ppb) were similar to the co-located passive samplers at the same site in this study (32.4 – 41.4 ppb).

Overall, both long-term and short-term O₃ concentrations and exposure estimates are important for estimating ecological impacts of O₃ (Paoletti and Manning 2007). For example, plants exhibit sensitivity to long-term O₃ exposure near 40 ppb, as well as to short-term acute exposure at peak concentrations (Paoletti and Manning 2007; Ainsworth et al. 2012). Further, this highlights that while ecosystem exposure to O₃ may be lower in the urban regions compared to outlying regions, the ecological consequences within the city may still be significant. In addition to phytotoxic effects on vegetation, short-term acute exposure that occurs throughout the urban and outlying regions can have negative human health implications.

**Regional N concentration and deposition**

Summer total N concentrations and deposition rates were higher within the urban open space preserves compared to the outlying native ecosystem. Urban open space areas, which are characterized by higher surrounding traffic and housing density than the outlying locations, had 49% and 33% higher total N (HNO₃ + NH₃ + NOₓ) concentrations than the outlying east and west native ecosystems respectively (up to 16.6 µg N m⁻³; Table 3). Across all location, NH₃ concentrations (ranging between 2.6 – 14.1 µg N m⁻³) were comparable to other urban arid systems and NH₃ was the predominant N species.
contributing over 80% to total N concentrations in the region (Watson et al. 1994; Alonso, Bytnerowicz, and Boarman 2005; Cisneros et al. 2010; Li et al. 2013). While NH₃ emissions typically result from agricultural sources, NH₃ is also a secondary pollutant of motor vehicles (Holland et al. 2005). In contrast, HNO₃ and NOₓ made up a proportionally smaller amount, typically less than 10%, of the total atmospheric N concentrations (Table 3). Though NOₓ acts as a precursor to O₃ formation during warm summer months, summer NOₓ concentrations were highest in the city near emission sources (Table 3).

Using the inferential method to estimate N inputs to the ecosystem, summer mean dry deposition in the city (7.8 kg N ha⁻¹ yr⁻¹) was greater than in the outlying protected native ecosystem (4.5 – 5.1 kg N ha⁻¹ yr⁻¹). Urban deposition was comparable to dry N deposition estimated using the same methods for previous summers in the region (2010 – 2011 summers 6.4 +/- 0.4 kgN ha⁻¹ yr⁻¹; Cook et al, In prep). However, dry deposition in the outlying region was substantially higher than reported for previous summers (1.8 +/- 0.2 kg N ha⁻¹ yr⁻¹), which is attributed to the increased sampling and spatial coverage in this study.

Despite the variability in N deposition among locations, the total N deposition in both urban and outlying native ecosystems in the Phoenix region was within or exceeded the critical loads. Recent estimates of N critical loads for desert ecosystems range from 2–20 kg N ha⁻¹ yr⁻¹, depending on species composition and water availability (Allen et al. 2006; Fenn et al. 2010; Rao et al. 2010; Pardo et al. 2011). Some models predict a smaller range between 3–8 kg N ha⁻¹ yr⁻¹, though the critical loads in deserts have only been estimated by a few studies and uncertainties in the best estimate are high (Fenn et al. 2010).
2010; Rao et al. 2010). Nevertheless, dry deposition alone in the Phoenix region was estimated to be within this critical load range with potential ecological consequences for the native ecosystem. In addition, wet N deposition can also be an important input, particularly during the monsoon summer season (Báez et al. 2007; Lohse et al. 2008; Li et al. 2013). Previous estimates of summer wet:dry N deposition using co-located passive and bulk ion exchange samplers found dry deposition in the summer months was about 69% of the total deposition in the urban region and 44% in the outlying regions (Cook et al, In Prep). Based on these ratios and dry deposition measurements from this study, I predicted total wet and dry deposition for the region to be 11.2 (+/- 2.9) kg N ha\(^{-1}\) y\(^{-1}\) in the urban open preserves, with the highest deposition occurring at the most urbanized locations (39\(^{th}\) Ave and DBG at 15.1 and 16.1 kg N ha\(^{-1}\) y\(^{-1}\), respectively). In the outlying Sonoran Desert east and west of the city, the average total wet and dry deposition was predicted to be 10.4 (+/- 2.4) and 11.9 (+/- 3.7) kg N ha\(^{-1}\) y\(^{-1}\), respectively. Thus, accounting for both wet and dry N inputs, the current rates of deposition within the urban region and in outlying protected native ecosystems are likely to affect primary production, species composition, and belowground processes, particularly in years of above average precipitation.

**Regional and temporal CO\(_2\) concentrations**

I examined patterns of ambient CO\(_2\) concentrations at 2 and 0.5 meters above ground in remote desert sites and in a desert preserves within the urban ecosystem. With consecutive measurements that capture diurnal, seasonal, and annual variability between native ecosystems in urban and outlying locations, I found the urban CO\(_2\) dome varies by
season, sampling height, and extent into the native desert. These findings expand our understanding about urban CO₂ characteristics beyond those along the major roadways on which it has previously been examined in the Phoenix region.

Urban CO₂ concentrations measured at 2 meters above ground were characterized by high diurnal variability (Figure 5, 6). Mean annual urban CO₂ concentrations in the city were 396 ppm (+/- 29). Urban CO₂ concentrations had 30 and 73% larger daily fluctuations (69 ppm) than the outlying native ecosystem to the west and east of the city, respectively (49 ppm at outlying west site and 19 ppm at outlying east site). While this pattern is true for other urban-rural comparisons (Idso, Idso, and Balling Jr. 2001; Day et al. 2002; Grimmond et al. 2002; Nasrallah et al. 2003; Coutts, Beringer, and Tapper 2007; Helfter et al. 2011; García, Sánchez, and Pérez 2012; Song and Wang 2012), the amplitude of the urban diurnal CO₂ flux was greater than reported elsewhere and likely due in part to the complex topography in the Phoenix region (Wang and Ostoja-Starzewski 2004). Like more remote locations, ambient urban CO₂ concentrations follow biological processes of respiration (high pre-dawn concentrations), photosynthesis (low mid-day CO₂ concentrations), and the meteorological effects of convective mixing. However, urban CO₂ variability is also influenced by anthropogenic activities, such that urbanized areas with high population, traffic and employment density are important sources of CO₂ (Koerner and Klopatek 2002; Wentz et al. 2002; Pataki et al. 2006; Pataki et al. 2007). In particular, vehicular emissions are expected to contribute up to 80% of CO₂ emissions in the Phoenix region (Koerner and Klopatek 2002). Even away from major roadways within the open space preserve, the urban diurnal CO₂ fluctuations
appear to be augmented by anthropogenic pulses such as morning and evening rush hour traffic (Koerner and Klopatek 2002; Pataki et al. 2007).

Contrary to expectations, ambient CO\textsubscript{2} patterns in remote outlying native ecosystems were not always lower than in the city. Characterized by relatively low surrounding housing and traffic density in comparison to the urban location (Table 1), I expected both outlying sites to be on the outskirts of the urban CO\textsubscript{2} dome and have overall lower CO\textsubscript{2} concentrations and diurnal variability. While mean annual CO\textsubscript{2} was lowest in the outlying site to the east of the city (382 +/- 10 ppm, 2 meters), CO\textsubscript{2} concentrations in the outlying west site (392 +/- 26 ppm) were more similar to urban patterns (Figure 5, 6). Despite the remote western location, agriculture is a predominant land use in the region west of Phoenix, and agricultural soils can be a significant contributor to CO\textsubscript{2} emissions (Koerner and Klopatek 2002). For example, compared to desert soil CO\textsubscript{2} efflux (< 2 g CO\textsubscript{2} m\textsuperscript{-2} day\textsuperscript{-1}), agricultural soils have high CO\textsubscript{2} emissions similar to mesic landscapes (20 - 30 g CO\textsubscript{2} m\textsuperscript{-2} day\textsuperscript{-1}, Koerner and Klopatek 2002). The agricultural emissions likely contribute to the higher than expected CO\textsubscript{2} concentrations at the outlying western location. In addition, the timing of seasonal agricultural activities (e.g. tilling, planting, and irrigation) may affect the diurnal fluctuations of CO\textsubscript{2} monitored in the outlying desert. The variation among sites may also be attributed, in part, to the local vegetation structure within each site. For example, while all sites are characterized by a mix of \textit{A. deltoidea} and \textit{L tridentata}, the urban site is also situated near a large mesic park, which can be a significant source of CO\textsubscript{2} from mesic soils (Koerner and Klopatek 2002). While site differences in vegetation may affect the local scale strength of CO\textsubscript{2} sources and sinks,
these differences are expected to be minimal in comparison to the human dominated CO$_2$ sources of vehicle and agricultural soil emissions.

Seasonally, winter CO$_2$ concentrations and diurnal variability at all locations were greater than in the summer, which can be explained by a combination of biological and human dominated factors. For example, reduced water stress and mild temperatures during the winter season make biological activity from microbial communities and primary producers an important contributor of ecosystem CO$_2$ fluxes (Noy-Meir 1973). For example, Pataki and colleagues (2007) estimated up to 60% of CO$_2$ fluxes in Salt Lake City, UT originated from biological respiration during the growing season in the region. In other large cities, such as London, the elevated winter CO$_2$ concentrations are attributed to increased human consumption of fossil fuels for heating (Helfter et al. 2011). Though less likely in this system, elevated winter CO$_2$ concentrations may result from the winter inversion layer that reduces the atmospheric mixing in the region (Pataki et al. 2007). The stable atmosphere with low wind speeds leads to less vertical mixing and less dispersion of the CO$_2$. Thus, winter CO$_2$ emissions that are generated from human or biological activity “build up,” particularly during evening and early morning hours, such as at the urban and outlying west site (Day et al. 2002). The outlying east location did not follow the same seasonal patterns. This may be a result of the distance from anthropogenic CO$_2$ sources or the higher elevation where the site is less affected by the winter inversion and experiences higher wind turbulence (Table 1).

At 0.5 meters above ground, CO$_2$ concentrations were more consistent; mean annual CO$_2$ was 386 (+/- 14ppm) at all three locations. The consistent and lower concentrations at 0.5 meter compared to 2 meter concentrations reflect the similarity in local ecosystem
characteristics of native desert soils and their low CO₂ efflux (Koerner and Klopatek 2002). In addition, these results suggest relatively little atmospheric mixing between the ground level and above shrub canopy (~2 meters), particularly in comparison to the regional atmospheric mixing patterns. The 0.5 meter monitoring better represents the exposure of herbaceous plants and soil microbial communities in native ecosystems. Thus, despite close proximity to anthropogenic CO₂ sources, low lying herbaceous vegetation and the soil microbial communities in urban open spaces may be “shielded” from the elevated CO₂ concentrations typically reported in urban regions. While CO₂ concentrations are continuing to rise globally (IPCC 2014), these findings have important implications for considering ecosystem responses to future predicted elevated CO₂.

*Urban “ecological airshed” extends to interior of urban open space preserve*

While regional urban and outlying locations differed in atmospheric O₃ and reactive N, variability was minimal on a smaller-scale from the exterior to interior of an open space preserved native ecosystem within the city. I expected the more remote interior of the park to be less influenced by the ecological airshed than the exterior areas. For example, I expected N deposition to decline toward the interior of the open space and away from major anthropogenic sources as a result of high deposition velocities. However, while total N and O₃ concentrations were comparable to those in other urban open space areas, they did not differ along the edge to interior transect. Overall, these findings suggest a well-mixed atmosphere widely distributes urban pollutants. Thus, the urban ecological airshed extends into the interior of even the largest municipal open space preserves of the native ecosystems.
CONCLUSION

Global urban land area is expected to triple by 2030 and more than 65% of the world’s population is predicted to live in cities by 2050 (United Nations 2012; Seto, Güneralp, and Hutyra 2012). Human activities concentrated in growing urban centers are significant sources of atmospheric pollutants, including CO$_2$, reactive N, and O$_3$, that affect air quality, human health, ecosystem services, and ecological functioning (IPCC 2013). My findings highlight that the urban “ecological airshed” extends well beyond the urban boundary where biologically relevant pollutants co-occur in remote areas at levels that affect ecosystem structure and function. It is particularly important to identify the extent of land area exposed to human-generated pollutants in an urban “ecological airshed” as existing urban air quality conditions have been found to affect growth and physiological functioning of primary producers with likely long-term feedbacks on native ecosystem structure, function, and the provision of ecosystem services (Gregg, Jones, and Dawson 2003; Gregg, Jones, and Dawson 2006). These findings highlight the need and urgency to adopt air quality monitoring and regulations that include a full suite of ecologically relevant compounds to protect the surrounding natural environments and ecosystem services.
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REFERENCES


TABLE 1: Site characteristics within open space preserves in Phoenix, Arizona. Site characteristics within open space preserves in the metropolitan region of Phoenix, AZ (urban) and in outlying native ecosystems to the east and west of the city.

<table>
<thead>
<tr>
<th>Location</th>
<th>Elevation (m)</th>
<th>Distance to City (km)</th>
<th>Traffic Density</th>
<th>Housing Density</th>
<th>Mean Temperature (°C)</th>
<th>Mean Relative Humidity (%)</th>
<th>Total Precipitation (mm)</th>
<th>Mean Annual Precipitation (mm)</th>
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<tr>
<td>Outlying East</td>
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<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>Lost Dutchman Park (LDP)</td>
<td>214.4</td>
<td>996</td>
<td>21.2</td>
<td>24.9</td>
<td>3.3</td>
<td>32.8</td>
<td>10.2</td>
<td>168.3</td>
</tr>
<tr>
<td>Outlying East</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lost Dutchman Park (LDP)</td>
<td>214.4</td>
<td>996</td>
<td>21.2</td>
<td>24.9</td>
<td>3.3</td>
<td>32.8</td>
<td>10.2</td>
<td>168.3</td>
</tr>
<tr>
<td>West Salt River Recreation Area (SRRA)</td>
<td>161.7</td>
<td>376</td>
<td>24.9</td>
<td>32.8</td>
<td>7</td>
<td>6.4</td>
<td>23.2</td>
<td>142.9</td>
</tr>
<tr>
<td>Piestawa Peak (PWP)</td>
<td>189.3</td>
<td>412</td>
<td>32.8</td>
<td>6.4</td>
<td>12</td>
<td>31.2</td>
<td>24.0</td>
<td>164.0</td>
</tr>
<tr>
<td>McDowell Mountain South (MCS)</td>
<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.2</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>McDowell Sonoran Preserve (MSP)</td>
<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>Salt River (SR)</td>
<td>189.3</td>
<td>412</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>South Mountain Vertex (SMV)</td>
<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>Desert Botanical Garden (DBG)</td>
<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>Outlying West</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>White Tank Mountain (WTM)</td>
<td>145.3</td>
<td>396</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
<tr>
<td>McDowell Sonoran Preserve (MSP)</td>
<td>192.0</td>
<td>429</td>
<td>32.8</td>
<td>31.1</td>
<td>15</td>
<td>31.1</td>
<td>10.2</td>
<td>154.0</td>
</tr>
</tbody>
</table>

Ozone and nitrogen concentrations were monitored at all locations. Carbon dioxide was monitored at a subset of sites (EME, DBG, and MCS).
TABLE 2: Range and two-three week mean (SD) O$_3$, HNO$_3$, NH$_3$, NO$_x$, and total N concentrations (µg m$^{-3}$) during summer 2013. Different letters represent significantly different means among sites (pairwise comparison post-hoc test).

<table>
<thead>
<tr>
<th>Location</th>
<th>Site Name</th>
<th>O$_3$(ppb)</th>
<th>HNO$_3$(µg N/m$^3$)</th>
<th>NH$_3$(µg N/m$^3$)</th>
<th>NO$_x$(µg N/m$^3$)</th>
<th>Total N (µg N/m$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlying West</td>
<td>WTM</td>
<td>42.3 - 56.0</td>
<td>0.7 (5.5)</td>
<td>0.1 (0.3)</td>
<td>0.0 (0.1)</td>
<td>2.6 (0.1)</td>
</tr>
<tr>
<td>Outlying East</td>
<td>SR</td>
<td>42.2 - 55.8</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td>Urban</td>
<td>DBG</td>
<td>43.0 - 55.4</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>PWP</td>
<td>43.0 - 55.4</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>SMW</td>
<td>43.0 - 55.4</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>39th Ave</td>
<td>39.2 - 48.6</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>SRR</td>
<td>39.2 - 48.6</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>MCS</td>
<td>42.2 - 55.8</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>MSP</td>
<td>42.2 - 55.8</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>LDP</td>
<td>42.2 - 55.8</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>LDP</td>
<td>42.2 - 55.8</td>
<td>0.4 (0.6)</td>
<td>0.0 (0.1)</td>
<td>0.0 (0.1)</td>
<td>2.5 (0.1)</td>
</tr>
</tbody>
</table>

Different means among sites (pairwise comparison post-hoc test).
<table>
<thead>
<tr>
<th>Location</th>
<th>Name</th>
<th>Range (kg N ha⁻¹ yr⁻¹)</th>
<th>Mean (kg N ha⁻¹ yr⁻¹)</th>
<th>SD (kg N ha⁻¹ yr⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>East Outlying</td>
<td>WTM</td>
<td>1.1 (0.3)</td>
<td>2.2 (1.0)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td></td>
<td>EMW</td>
<td>1.2 (0.3)</td>
<td>2.8 (1.6)</td>
<td>0.7 (0.2)</td>
</tr>
<tr>
<td></td>
<td>DBG</td>
<td>1.4 (0.2)</td>
<td>3.9 (1.5)</td>
<td>1.5 (0.6)</td>
</tr>
<tr>
<td></td>
<td>PWP</td>
<td>1.8 (0.2)</td>
<td>4.8 (2.0)</td>
<td>0.9 (0.3)</td>
</tr>
<tr>
<td></td>
<td>SMW</td>
<td>1.6 (0.1)</td>
<td>3.1 (1.6)</td>
<td>1.1 (0.1)</td>
</tr>
<tr>
<td></td>
<td>39th Ave</td>
<td>1.4 (0.1)</td>
<td>4.4 (2.0)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td></td>
<td>SRR</td>
<td>1.3 (0.1)</td>
<td>4.1 (1.8)</td>
<td>0.5 (0.1)</td>
</tr>
<tr>
<td></td>
<td>MCS</td>
<td>1.4 (0.1)</td>
<td>4.3 (1.8)</td>
<td>0.4 (0.1)</td>
</tr>
<tr>
<td></td>
<td>MSP</td>
<td>1.6 (0.1)</td>
<td>4.8 (2.0)</td>
<td>0.3 (0.1)</td>
</tr>
<tr>
<td></td>
<td>LDP</td>
<td>1.5 (0.1)</td>
<td>3.8 (1.6)</td>
<td>0.8 (0.2)</td>
</tr>
</tbody>
</table>

Deposition was estimated by the inferential method using measured N concentrations and average Sonoran Desert deposition velocities.
Ozone and N sampling only occurred along the transect during the final three sampling periods of Summer 2013.

TABLE 4: Range and mean (SD) of ozone concentrations, and nitric and total N deposition (HNO$_3$+NH$_3$+NO$_x$) along edge-to-interior transect of protected urban open space. Sampled dates: 11/June, 12/July, 30/July, 14/August

<table>
<thead>
<tr>
<th>Transect locations</th>
<th>O$_3$ (ppb)</th>
<th>NO (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>NO$_2$ (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>NH$_3$ (kg N ha$^{-1}$ yr$^{-1}$)</th>
<th>Total N (kg N ha$^{-1}$ yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exterior, Site 1</td>
<td>40.0 - 42.6</td>
<td>0.2 (0.3)</td>
<td>1.5 (2.1)</td>
<td>0.1 (0.2)</td>
<td>1.8 (2.6)</td>
</tr>
<tr>
<td>Interior, Site 2</td>
<td>41.2 - 43.5</td>
<td>0.2 (0.3)</td>
<td>1.5 (2.1)</td>
<td>0.1 (0.2)</td>
<td>1.8 (2.6)</td>
</tr>
<tr>
<td>Site 3</td>
<td>41.4 - 43.7</td>
<td>0.2 (0.3)</td>
<td>1.5 (2.1)</td>
<td>0.1 (0.2)</td>
<td>1.8 (2.6)</td>
</tr>
<tr>
<td>Site 4</td>
<td>41.6 - 43.9</td>
<td>0.2 (0.3)</td>
<td>1.5 (2.1)</td>
<td>0.1 (0.2)</td>
<td>1.8 (2.6)</td>
</tr>
<tr>
<td>Interior, Site 5</td>
<td>40.9 - 42.5</td>
<td>0.2 (0.3)</td>
<td>1.5 (2.1)</td>
<td>0.1 (0.2)</td>
<td>1.8 (2.6)</td>
</tr>
</tbody>
</table>

Data are reported by location along the transect (n = 3 sampling intervals) and by sampling interval (n = 5 locations).
**FIGURE 1:** Nitrogen, O$_3$, and CO$_2$ monitoring sites in metropolitan region of Phoenix, Arizona. Nitrogen (NH$_3$, NO$_x$, and HNO$_3$), O$_3$, and CO$_2$ monitoring sites in the metropolitan region of Phoenix, Arizona. O$_3$ and N were measured at all sites. Open symbols indicate CO$_2$ monitoring locations. Starred diamond indicates location of the edge-to-interior urban open space transect. All monitoring sites are located within protected Sonoran Desert areas, except the urban calibration site (hatched diamond) which is located in a dense residential neighborhood.
FIGURE 2: Field set-up for measuring ambient atmospheric gaseous concentrations. Field set-up for measuring ambient NH$_3$, NO$_x$, HNO$_3$, O$_3$, and CO$_2$ concentrations. (A) NH$_3$, NO$_x$, HNO$_3$, and O$_3$ passive samplers were installed 2 meters above ground under protective covers to block direct sun and rain during 2 week sampling intervals. (B) Infrared gas analyzers (IRGAs) were installed at 2 and 0.5 meters above ground to continuously monitor ambient CO$_2$ concentrations. (C) View of CO$_2$ and N passive samplers installed at 2 meters above ground in a native desert location.
FIGURE 3: N deposition, O₃, and CO₂ in outlying and urban locations over 5 summer sampling intervals. Summer 2013 mean (+/− SE) dry N deposition (HNO₃ + NH₃ + NOₓ, kg N ha⁻¹ yr⁻¹), O₃ (triangles, ppb), and CO₂ (circles, ppm at 2 meters) in outlying west (W), urban (U), and outlying east (E) native open space preserves. Dates indicate the collection date for each 2-3 week sampling period. There were no CO₂ data from the first period. Solid horizontal lines are reference for 20 and 60 ppb O₃.
FIGURE 4: Mean summer N deposition, O$_3$, and CO$_2$ in outlying and urban locations. Summer 2013 mean (+/- SE) dry N deposition (HNO$_3$ + NH$_3$ + NO$_x$, kg N ha$^{-1}$ yr$^{-1}$), O$_3$ (triangles, ppb), and CO$_2$ (circles, ppm at 2 meters) in outlying west, urban, and outlying east native open space preserves. Different letters within a pollutant indicate significantly different means. Horizontal lines are reference to O$_3$ scale.
FIGURE 5: Summer hourly urban and outlying CO₂ concentrations at 2 meters above ground. Summer 2013 hourly CO₂ concentrations (ppm) at 2 meters averaged (+/- 1SE) by month (June (circle), July (square), and August (diamond)) at outlying west, urban and outlying east sites. Dashed lines are summer averages per site; black line indicates 400 ppm for reference. Insets show monthly median, 1st and 3rd quartile (box), minimum and maximum (whiskers) CO₂ by month at each site. Different letters indicate significantly different CO₂ concentrations within a site.
FIGURE 6: Winter hourly urban and outlying CO\textsubscript{2} concentrations at 2 meters above ground. Winter 2013-2014 hourly CO\textsubscript{2} concentrations (ppm) at 2 meters averaged (+/-1SE) by month (December (circle), January (square), February (diamond), and March (triangle)) at outlying west, urban and outlying east sites. Dashed lines are winter season site average; black line indicates 400 ppm for reference. Insets show monthly median, 1\textsuperscript{st} and 3\textsuperscript{rd} quartile (box), minimum and maximum (whiskers) CO\textsubscript{2} by month at each site. Different letters indicate significantly different CO\textsubscript{2} concentrations within a site.
FIGURE 7: Summer hourly urban and outlying CO$_2$ concentrations at 0.5 meters above ground. Summer 2013 hourly CO$_2$ concentrations (ppm) at 0.52 meters averaged (+/- 1SE) by month (June (circle), July (square), and August (diamond)) at outlying west, urban and outlying east sites. Dashed lines are summer averages per site; black line indicates 400 ppm for reference. Insets show monthly median, 1$^{st}$ and 3$^{rd}$ quartile (box), minimum and maximum (whiskers) CO$_2$ by month at each site. Different letters indicate significantly different CO$_2$ concentrations within a site.
FIGURE 8: Winter hourly urban and outlying CO$_2$ concentrations at 0.5 meters above ground. Winter 2013-2014 hourly CO$_2$ concentrations (ppm) at 0.5 meters averaged (+/-1SE) by month (December (circle), January (square), February (diamond), and March (triangle)) at outlying west, urban and outlying east sites. Dashed lines are winter averages per site; black line indicates 400 ppm for reference. Insets show monthly median, 1$^{st}$ and 3$^{rd}$ quartile (box), minimum and maximum (whiskers) CO$_2$ by month at each site. Different letters indicate significantly different CO$_2$ concentrations within a site. There were no data recorded at 0.5 meters at the urban site due to sensor error.
APPENDIX 1

**TABLE 1**: Dates of sample deployment and number (n) of sites within each region (outlying west, urban and outlying east) at which each atmospheric compound was monitored during summer 2013.

<table>
<thead>
<tr>
<th>Location</th>
<th>Deployment date</th>
<th>Collection date</th>
<th>Carbon dioxide</th>
<th>Ozone</th>
<th>Nitric acid</th>
<th>Ammonia</th>
<th>Nitrogen oxides</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outlying West</td>
<td>May 17</td>
<td>June 11</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>June 11</td>
<td>June 26</td>
<td>1</td>
<td>2</td>
<td>ND</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>June 26</td>
<td>July 12</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>ND</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>July 12</td>
<td>July 30</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>ND</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>July 30</td>
<td>August 14</td>
<td>1</td>
<td>2</td>
<td>ND</td>
<td>2</td>
<td>ND</td>
</tr>
<tr>
<td>Urban</td>
<td>May 17</td>
<td>June 11</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>4</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>June 11</td>
<td>June 26</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>ND</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>June 26</td>
<td>July 12</td>
<td>1</td>
<td>8</td>
<td>8</td>
<td>ND</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>July 12</td>
<td>July 30</td>
<td>1</td>
<td>8</td>
<td>8</td>
<td>ND</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>July 30</td>
<td>August 14</td>
<td>1</td>
<td>8</td>
<td>ND</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Outlying East</td>
<td>May 17</td>
<td>June 11</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>ND</td>
</tr>
<tr>
<td></td>
<td>June 11</td>
<td>June 26</td>
<td>1</td>
<td>3</td>
<td>ND</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>June 26</td>
<td>July 12</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>ND</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>July 12</td>
<td>July 30</td>
<td>1</td>
<td>4</td>
<td>4</td>
<td>ND</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>July 30</td>
<td>August 14</td>
<td>1</td>
<td>4</td>
<td>ND</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

ND = No data. Sampling at MSP (outlying east) and along the SMW transect (urban) did not occur during first two summer periods. Due to limited sampling equipment, ammonia and nitrogen oxides were sampled during opposite periods, except in the urban location where sampling occurred.
**TABLE 2:** Mean (SD) daily CO$_2$ concentrations (ppm) during each collection period in 2013 and 2014. CO$_2$ concentrations were recorded every 10 minutes at 2 and 0.5 meters above ground at each location (raw data were first averaged by day before calculating daily mean concentration).

<table>
<thead>
<tr>
<th>Collection Dates</th>
<th>Outlying West (EME)</th>
<th>Urban (DBG)</th>
<th>Outlying East (MCS)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 m</td>
<td>0.5 m</td>
<td>2 m</td>
</tr>
<tr>
<td>June 11 - June 26 2013</td>
<td>391 (7)</td>
<td>ND</td>
<td>393 (7)</td>
</tr>
<tr>
<td>June 26 - Jul 12 2013</td>
<td>390 (2)</td>
<td>377 (7)</td>
<td>390 (4)</td>
</tr>
<tr>
<td>July 12 - July 30 2013</td>
<td>388 (9)</td>
<td>386 (6)</td>
<td>ND</td>
</tr>
<tr>
<td>July 30 - August 14 2013</td>
<td>379 (7)</td>
<td>ND</td>
<td>391 (6)</td>
</tr>
<tr>
<td>August 14 - September 10 2013</td>
<td>381 (8)</td>
<td>383 (7)</td>
<td>378 (9)</td>
</tr>
<tr>
<td>September 10 - October 3 2013</td>
<td>374 (7)</td>
<td>378 (5)</td>
<td>377 (9)</td>
</tr>
<tr>
<td>October 3 - November 6 2013</td>
<td>383 (3)</td>
<td>385 (3)</td>
<td>393 (9)</td>
</tr>
<tr>
<td>November 6 - December 9 2013</td>
<td>410 (24)</td>
<td>393 (11)</td>
<td>411 (23)</td>
</tr>
<tr>
<td>December 9 - January 7 2014</td>
<td>408 (15)</td>
<td>389 (9)</td>
<td>ND</td>
</tr>
<tr>
<td>January 7 - February 7 2014</td>
<td>ND</td>
<td>383 (5)</td>
<td>ND</td>
</tr>
<tr>
<td>February 7 - March 14 2014</td>
<td>398 (18)</td>
<td>391 (9)</td>
<td>415 (14)</td>
</tr>
</tbody>
</table>

ND = No data recorded during the collection period due to sensor error.
APPENDIX 2

TABLE 1: Flood Control District of Maricopa County (FCDMC) station IDs for the
nearest meteorological station to the corresponding N, CO2, or O3 monitoring site.
FCDMC meteorological data were downloaded for the study period (summer 2013). If
more than one site is listed in a column, data were averaged.

Table,1:,Flood(Control(District(of(Maricopa(County((FCDMC)(station(IDs(for(the(nearest(meteorological(station(to(the(corresponding(nitrogen,(
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CHAPTER 5
SYNERGISTIC NET EFFECTS OF URBAN AIR POLLUTION ON ECOSYSTEMS

ABSTRACT

Plants and ecosystems are rarely exposed to a single pollutant, yet research on the effects of co-occurring atmospheric compounds is limited. Carbon dioxide (CO$_2$), ozone (O$_3$), and nitrogen (N) deposition are elevated in and around cities, affecting air quality at local to global scales. Despite the ecological relevance of CO$_2$, O$_3$, and N as both stressors and resources for primary producers, their combined impacts at current and future concentrations are unknown. To address this gap, I ask, what is the sensitivity of primary producers to co-occurring CO$_2$, O$_3$, and N? Using the Central Arizona Phoenix Long Term Ecological Research (CAP LTER) site as a model system, I examined the net effect of elevated concentrations of CO$_2$, O$_3$, and N on growth and physiological responses of dominant native (*Pectocarya recurvata*) and non-native (*Schismus arabicus*) Sonoran Desert winter herbaceous vegetation. Growth of both species was additive (sum of individual responses) when exposed to two factor combinations (O$_3$ x N, CO$_2$ x N, and CO$_2$ x O$_3$) but synergistic (amplifying, i.e. greater than the sum of individual effects) in response to CO$_2$, O$_3$ and N combined. Elevated CO$_2$ mitigated the negative effects of O$_3$ exposure for the non-native grass but had minimal protective effect against high O$_3$ concentrations for the native forb. Contrary to expectations, elevated N did not have a significant individual influence on the responses of either species. Differences in species’ responses to current and future urban air pollution may lead to long-term
changes in plant community composition of protected ecosystems. Overall, these findings highlight the vulnerability of native ecosystems to current and future air pollution over the long term and provide empirical evidence for future policies addressing ecosystem sensitivity to multiple stressors in current and predicted future environmental conditions.
INTRODUCTION

Atmospheric pollutants generated from human activities can affect air quality and ecosystems at local, regional, and global-scales (Dentener et al. 2006; Grimm et al. 2008; Monks et al. 2009). Though cities are point sources of greenhouse gases and other pollutants, urban-generated atmospheric compounds are not restricted to the political boundaries in which they are regulated or monitored (Akimoto 2003; Monks et al. 2009). Thus, despite their distance from cities, protected native lands are exposed to elevated concentrations of atmospheric carbon dioxide (CO₂), reactive nitrogen (N), and ozone (O₃) from cities (Cook et al. In prep). Individually, these compounds act as either resources or stressors to primary producers, with potentially cascading effects across trophic levels. Yet little is known about the net impacts of these co-occurring ecologically important compounds on ecosystem structure or function. Unaccounted for synergistic or antagonistic effects of multiple pollutants may explain recent regional and global changes in primary production, carbon and N storage, and community structure (Sala et al. 2000; S. D. Smith et al. 2000; Ollinger et al. 2002; Shaw et al. 2002).

With over 65% of the world’s population expected to live in cities by 2050 and urban land cover expected to triple by 2030, ecosystems will increasingly be exposed to elevated CO₂, O₃, and N deposition with cascading impacts on ecosystem processes (IPCC 2014; Seto, Güneralp, and Hutyra 2012; United Nations 2012). For example, by 2030 reactive N deposition above 10 kg N ha⁻¹ yr⁻¹ is expected to affect up to 35% of Earth’s terrestrial land (Dentener et al. 2006). Elevated reactive N gas emissions and deposition from agriculture and combustion activities alleviate nutrient limitation in
terrestrial and aquatic ecosystems, stimulating primary production and altering biogeochemical cycling (Aber et al. 1998; Brooks 2003; Báez et al. 2007; Elser et al. 2007; LeBauer and Treseder 2008). Similarly, CO$_2$—a greenhouse gas and key reactant in photosynthesis—is elevated in and near cities as a result of combustion processes (Idso, Idso, and Balling Jr. 2001; George et al. 2007; Bergeron and Strachan 2011). In some species, elevated CO$_2$ can increase the efficiency of plant N-use and water-use, thus alleviating water stress and increasing production (Long et al. 2004; Housman et al. 2006); though in other species, elevated CO$_2$ has minimal effect on primary producers (Morgan et al. 2004; Dukes et al. 2005). On the other hand, tropospheric O$_3$—a secondary, widely dispersed pollutant—has negative effects on plant physiology, leading to leaf and cellular damage, reduced growth, and early senescence with consequences for community composition (Bytnerowicz et al. 1988; Karnosky et al. 2007; Ainsworth et al. 2012; Lombardozzi, Sparks, and Bonan 2013). Atmospheric concentrations of CO$_2$ and tropospheric O$_3$ are both expected to increase 40% globally by 2100 (Horowitz 2006; IPCC 2014).

Plants and ecosystems are rarely exposed to a single pollutant (Fangmeier et al. 2002; Lovett et al. 2009) and the combined effects of pollutants can have cascading affects on plant growth, physiological functioning, community composition, and competition. Current global change research has focused on quantifying interactions between land-cover changes (e.g. biological invasion, grazing, and fire), climate-related variables (e.g., precipitation and temperature), and select atmospheric variables (e.g., CO$_2$ and N deposition; Sala et al. 2000; Zavaleta et al. 2003; Henry et al. 2006). These pioneering studies have shown that ecological responses are likely to be synergistic (amplifying or
greater than the sum of individual effects) or antagonistic (canceling or less than sum of individual effects) rather than simply additive (Sala et al. 2000; Shaw et al. 2002; Rustad 2008; but see Zavaleta et al. 2003). However, in order to ensure quantifiable effect sizes in complex systems, experimental treatments are often larger than near-future, or even long-term expected conditions (e.g., additions of 7 g N m\(^{-2}\) yr\(^{-1}\) when atmospheric N deposition is \(\sim\)0.5 g m\(^{-2}\) yr\(^{-1}\); e.g., Zavaleta et al. 2003; Weiss 1999; or +300 ppm CO\(_2\) when expected increases are +150 ppm CO\(_2\); e.g., Shaw et al. 2002). In fact, most ecosystems experience small, incremental changes in atmospheric composition over the long-term (M. D. Smith, Knapp, and Collins 2009), and large pulses do not represent current—or often predicted future—concentrations or gradual rates of change that are occurring worldwide (Luo and Reynolds 1999; Shen et al. 2008). Additionally, large experimental changes in ambient conditions make it difficult to test mechanisms, sensitivity, and feedbacks (e.g., down-regulation, Ashmore 2002).

Understanding the plant or ecosystem responses at expected levels is essential to examining threshold responses and informing regional critical loads. Critical loads are the level of pollution at which significant ecological effects are expected to occur from elevated N inputs (Fenn et al. 2010; Pardo et al. 2011). To date, critical loads have been determined only for single pollutants, such as N, and thus do not account for more realistic scenarios of exposure to co-occurring compounds. Examining the sensitivity and critical levels relevant to interacting pollutants in native ecosystems will provide empirical evidence to establish frameworks for protection of ecosystem services in addition to human health (Groffman et al. 2006).
Airsheds exposed to elevated CO\textsubscript{2} and N deposition are often simultaneously exposed to elevated O\textsubscript{3} concentrations. Elevated CO\textsubscript{2} can reduce the negative physiological impacts of O\textsubscript{3} by minimizing stomatal conductance and intercellular O\textsubscript{3} exposure (Cardoso-Vilhena and Barnes 2001; Reid and Fiscus 2008; Ainsworth et al. 2012). The interactive effects of CO\textsubscript{2} and O\textsubscript{3} are dependent on plant physiological traits, leading to synergistic or antagonistic eco-physiological responses in different ecosystems (Long et al. 2004; Lindroth 2010). Similarly, the net effects of elevated CO\textsubscript{2} and N vary across ecosystems based on plant N uptake, soil moisture, temperature, additional nutrient limitations, and species composition (Shaw et al. 2002; Dukes et al. 2005; Reich et al. 2006; Dijkstra et al. 2010; Langley and Megonigal 2010; Reich and Hobbie 2013).

Only a few studies have empirically quantified the ecosystem consequences of elevated CO\textsubscript{2}, N and O\textsubscript{3} together. In well-watered agricultural crops, CO\textsubscript{2} mitigates O\textsubscript{3} damage, and elevated N has little additional influence (Heagle et al. 1999; Cardoso-Vilhena and Barnes 2001). However, agricultural plants have different physiological responses to environmental stressors than wild plants, because they are bred for net production under high water and nutrient conditions (sensu Chapin 1980; Chapin 1991). Modeled ecosystem responses to elevated CO\textsubscript{2}, N and O\textsubscript{3} predict potential future feedbacks in temperate forested ecosystems with increased evapotranspiration and reduced N-induced carbon sinks (Ollinger et al. 2002; Felzer et al. 2009). Yet in a field study across an urban-rural gradient, Gregg and colleagues (2003) found high rural O\textsubscript{3} concentrations most strongly influenced plant growth compared to other atmospheric components. Overall, however, net physiological, ecosystem, or community responses to realistic combinations of CO\textsubscript{2}, N, and O\textsubscript{3} are difficult to predict from the currently limited
research (Sala et al. 2000; Aber et al. 2002; Krupa 2003; Bassin et al. 2009; Lindroth 2010) and there have been several recent calls for research investigating more realistic scenarios in which ecosystems are exposed to elevated CO₂, N, and O₃ together (Karnosky et al. 2007; Rustad 2008; Templer 2013).

Given the unknown ecological impacts of air pollution in urban and surrounding ecosystems around the world, I asked, what is the sensitivity of primary producers to co-occurring CO₂, O₃, and N at realistic and expected future concentrations? I modeled the experimental designed based on current and predicted near-future air quality conditions in the metropolitan region of Phoenix, Arizona and the surrounding native desert ecosystem. Dryland ecosystems are predicted to be especially sensitive to regional and global anthropogenic changes (Melillo et al. 1993). For example, elevated CO₂ is expected to alleviate water limitation by increasing plant water-use efficiency (Smith et al 1997), which would in turn increase primary production and rates of nutrient cycling. Further, in lower productivity systems where primary producers are often co-limited by more than one resource, the effects of multiple changes may be interactive. Within this context, I examined the net effect of elevated levels of CO₂, O₃, and N on growth and physiological responses of two dominant herbaceous plant species, a native forb (*Pectocarya recurvata*) and a non-native graminoid (*Schismus arabicus*). Ephemeral desert plants are ideal candidates to examine mechanistic dose responses and interacting feedbacks related to multiple pollutants. Winter herbaceous plants respond quickly to small changes in the environment and have a relatively short growing season (Sala and Lauenroth 1982). In addition, winter ephemeral plant production provides multiple ecosystem services, such as attractive wildflowers, food for herbivores, and a ‘vernal
dam’ preventing inorganic N losses (Venable and Pake 1999; Hall et al. 2011). Thus, I expected the co-occurring pollutants would have synergistic or antagonistic effects, rather than simply additive responses, on plant growth and physiological parameters.

METHODS

*Experimental design*

In a six-week, multi-factorial dose-response experiment, I examined the dominant native and non-native Sonoran Desert winter herbaceous plant growth and physiological responses to varying combinations of CO$_2$, O$_3$ and N. Between January and March 2013, I conducted a fumigation experiment at the University of California, Riverside and USFS Fire Lab greenhouse facilities in Riverside, California. Using continuously stirred tank reactor (CSTR) fumigation chambers, I grew plants in full factorial treatment combinations of CO$_2$ (ambient (400 ppm), 550, and 700 ppm gaseous fumigation), O$_3$ (ambient (15 ppb), 60, and 100 ppb gaseous fumigation), and N (ambient, +4, +8 kgN ha$^{-1}$ yr$^{-1}$ applied as ammonium nitrate, n = 27 treatments for each species). Individual plants (n = 15-17 individuals per species) were grown without competition as subsamples within each treatment. Two to three individuals of each species were successively harvested every 7-10 days throughout the experiment, and the subsamples were then averaged for each harvest.
**Study species**

Winter desert herbaceous plants respond quickly, have a short growing season and are well suited to test short-term feedbacks and sensitivities. *Pectocarya recurvata* (Boraginaceae), a forb, and *Schismus arabicus* (Poaceae), a graminoid, are two dominant native and non-native species, respectively, within the Sonoran Desert and Central Arizona-Phoenix Long-term Ecological Research (CAP LTER) site encompassing the Phoenix metropolitan region (CAP LTER species composition database). *P. recurvata* and *S. arabicus* differ in key functional traits, such as relative growth rate (RGR) and water use efficiency (WUE) related to stomatal conductance and stress tolerance. For example, *P. recurvata* is characterized by low RGR and high WUE, whereas *S. arabicus* tends to have high RGR and low WUE (Huxman et al. 2008; Angert et al. 2009). In addition, these species have been examined previously in studies of their eco-physiological responses and thus methods to account for their small leaf area have been previously established (Huxman et al. 2008; Angert et al. 2009; Gremer et al. 2012).

Seeds for each species were collected in Spring 2012 in native Sonoran Desert locations east of Phoenix, Arizona (Salt River Recreation Area or Lost Dutchman Park) and stored in a cool, dark, dry place until the experiment. In December 2012, all seeds were soaked in 200 ppm Gibbarellic Acid (GA$_3$) for 24 hours to stimulate germination. At the end of 24-hour soak, seeds were transferred to small germinating trays and grown in a mix of vermiculite and arid zone potting soil (Sunshine Mix #4, SunGro Horticulture, Agawam, MA). Germination occurred in a greenhouse with natural diurnal light and trays were watered every 2-3 days. Approximately 4 weeks after germination, individual seedlings were transplanted into separate “cone-tainers” (individual plastic cells, Stuewe
& Sons, Inc Tangent, OR) to exclude competition from the experiment. An arid zone potting soil (Sunshine Mix #4) was used in all cone-tainers to minimize additional variation. Plants were established in the individual cone-tainers for 5-7 days before beginning experimental treatments. Throughout the six-week fumigation experiment, plants were watered with de-ionized water every 5-7 days.

**Experimental treatment set-up**

I used 9 CSTR chambers, each 1.35 m diameter x 1.35 m height (Figure 1) located within one greenhouse for simultaneous exposure of plants under similar temperature, humidity, and air-flow conditions (Padgett et al. 2004). With a continuously moving impeller and exchange of air, the CSTR chambers ensure even mixing of gases throughout the chamber. I used a gas delivery and monitoring system to regulate diurnal fluctuations of O₃ and maintain a consistent daily CO₂ concentration in each chamber.

**Carbon dioxide and ozone fumigation:** Carbon dioxide was distributed directly to each chamber from a 50 lb pressurized CO₂ gas canister regulated by a flow meter and manifold system. Chambers receiving elevated CO₂ concentrations each contained an infrared gas analyzer (IRGA) with an integrated relay system (iSense CM-0043, CO₂ meter, Ormand Beach, Fl) and solenoid valve to regulate CO₂ gas flow into the chamber. Each chamber’s IRGA was programmed to maintain the specified CO₂ concentration by measuring CO₂ within the chamber every 10 seconds and opening or closing the flow valve as needed to meet the specified range of CO₂. Three chambers were fumigated with approximately 700 ppm CO₂ (daily average for high CO₂ treatments), three chambers with 550 ppm CO₂ (daily average for mid-level CO₂
treatments), and three chambers received no CO₂ inputs for ambient concentrations approximately 400 ppm CO₂ (low-level ambient CO₂ treatments, Table 1).

Ozone was generated from charcoal filtered air by electrical discharge (Griffin O₃ synthesizer, Griffin Technics Corp Lodi, NJ). Oxygen was released between 9:00 and 18:00 daily into electrostatic ozone generator and then distributed through a manifold system to each chamber at a specified O₃ concentration. Each chamber concentration was adjusted via flow meters such that desired peak O₃ concentration remained stable throughout the day. Three chambers were set up to be fumigated with approximately 100 ppb O₃ (daytime average for high O₃ treatment), three chambers with 60 ppb O₃ (daytime average for mid level O₃ treatment), and three chambers were not fumigated with O₃ and had an ambient concentration of approximately 15 ppb O₃ (low-level ambient treatment, Table 1). The chambers for each treatment were chosen randomly (Appendix 1). Carbon dioxide and O₃ concentrations simulated in this experiment represent current and predicted near-term future levels in the Phoenix metropolitan region (Idso, Idso, and Balling Jr. 2001; Wentz et al. 2002).

Ozone and Carbon Dioxide monitoring: Ozone and CO₂ concentrations were recorded in each chamber once every hour (taken as an average over 5 minute intervals) throughout the day. Air was pumped from an individual chamber through a scani-valve for six-minute intervals into a Dasibi O₃ analyzer (Dasibi Environmental Corp, CA) and a CO₂ IRGA (PP System EMG-4, MA) set-up independently of IRGAs inside each chamber. Both monitoring instruments were integrated with a chart recorder (Cole Palmer, Vernon Hills, IL) and PC data logger (Dataram 4, Thermo Instruments) for continuous data recording throughout the experiment.
**N additions:** Individual plants from each species were randomly divided into 3 groups (n = 15-17) to receive N treatments. N fertilizer was applied as ammonium nitrate (NH$_4$-NO$_3$) in de-ionized water solution made at concentrations equivalent to 0 (deionized water only), +4, and +8 kg N ha$^{-1}$ yr$^{-1}$. NH$_4$-NO$_3$ solution was applied in four applications approximately every 10 – 12 days starting on day 1 of the experiment. Water trays were placed under the plants to capture any dripping; water trays were specific only to plants in the same N treatment. N treatments represented the range of ambient N deposition across the Phoenix urban-rural gradient (Lohse et al. 2008).

**Response variables**

I sampled plants from each treatment approximately every 7-10 days for a total of 5 sampling periods. However, the majority of remaining *P. recurvata* individuals in all treatments had senesced around the 4$^{th}$ sampling, and thus only *S. arabicus* was sampled five times in each treatment. At each “harvest,” I sampled 2-3 individual plants per species from each treatment (e.g., 2 species x 2 individuals x 27 treatments = 108 plants sampled per harvest). At each sampling, it took approximately 3-4 days to process and analyze all individuals; plants remained in the treatment chambers until the day they were to be sampled. Individuals were analyzed as pseudo-replicates and then averaged by treatment and sampling date to test the effects of CO$_2$, O$_3$, and N individually and in combination on each species’ dry mass, growth rate, and physiological characteristics.

**Physiological Fluorescence measurements:** Chlorophyll fluorescence measurements were taken to quantify physiological stress on the Photosystem II (PS II) apparatus.
Each individual with minimal disturbance (plant intact in cone-tainer) was moved from the treatment chamber and placed in a dark box for at least 30 minutes to dark-adapt the plants for chlorophyll fluorescence measurements.

Fluorescence was measured using a portable modulated chlorophyll fluorometer (PAM-2000, Heinz Walz, Germany) following procedures described by Gremer and colleagues (2012) for small desert annual herbaceous species. Specifically, following the dark adaptation period, I used a non-saturating light pulse to measure initial fluorescence (Fo) and then a saturating light to estimate maximum fluorescence (Fm). Next, I applied an actinic light for 120 seconds before a second saturating pulse. Fluorescence level was measured before and after this second pulse to yield F's and F'm, respectively. The response to far-red light was then measured (F'o). Based on each response, I calculated the variable fluorescence (Fv = Fm – Fo), the maximum quantum yield of PSII (Fv/Fm) and the effective quantum yield of PS II (hereafter “yield”; yield = F'm-F's/F'm; Maxwell and Johnson 2000). Photosynthetic yield is a measure broadly describing photosynthetic stress by measuring light driven electron transport and CO₂ assimilation, where lower yield values indicate a more stressed PS II (Henriques 2009).

Leaf Area and Dry Mass: After fluorometric measurements were complete, plants were cut at the soil surface to separate below and aboveground biomass. Aboveground parts were then separated using forceps into leaf, stem, and reproductive parts, and belowground root mass was cleaned from potting soil. Reproductive biomass included any visible flower, bud or nutlet. Leaf area was measured using a portable leaf area meter (LI-COR 3000C, LI-COR Environmental, Nebraska). Leaves were placed flat without overlap between two clear plastic sheathes that passed through the LI-3000C.
sensor head. Leaf area was measured three times for each sample and averaged for final area. For samples in which the leaves were too big to measure without overlap, the sample was divided into sub-samples, each measured as stated above, and the final averages were added together for the total leaf area for that individual. Finally, biomass was dried at 60°C for 48 hours and then weighed.

Data analyses

I analyzed treatment effects using linear mixed models in order to determine which factors (CO₂, O₃, and N) best predicted response variables for each species (lme4 package in R, R Core Team, 2014). The fixed effects included CO₂, O₃ and N treatments as single, additive (e.g., CO₂ + O₃) and interactive factors (e.g., CO₂ * O₃). Chamber was included in each model as a random effect in order to account for potential unmeasured differences among chambers. In order to test my hypotheses regarding the sensitivity of plants to single and co-occurring pollutants, I separately tested models with elevated CO₂, O₃, and N treatments as single fixed factors, combined additive terms or interactions terms (Table 2). I ran separate models for each species and dependent variable, including growth rate (aboveground biomass day⁻¹) and physiological effective quantum yield of PS II (yield is unitless).

Growth rate data were log transformed to meet basic assumptions of the linear mixed models. The growth rate did not differ between the final sampling periods (sampling period 4 and 5 for S. arabicus (F(1,167) = 1.5, p = 0.2) and sampling period 3 and 4 for P. recurvata (F(1,134) = 0.2, p = 0.7)), and so data were combined within each species for the final sampling periods in order to increase sample size for peak growth rate models. The
yield data were not aggregated. *S. arabicus* yield was analyzed from the fifth sampling, and *P. recurvata* yield was analyzed for the third sampling as this is before *P. recurvata* individuals began to senesce so the effects across all treatment combinations could be analyzed.

To examine the importance of individual and co-occurring factors, I compared the goodness of fit of candidate mixed model results using Akaike’s information criterion adjusted for finite samples (AICc, Table 2). The AICc accounts for small sample sizes and lower AICc indicate a better goodness of fit (Burnham and Anderson 2002). The difference between AICc scores (Δ AICc = Model AICc – Best fit (lowest AICc) model AICc) was calculated to assist in choosing the best model. Models with Δ AICc less than 3 are more likely to be an alternative choice for best model compared to models with Δ AICc greater than 3 (Burnham and Anderson 2002). Candidate best models were nested and compared via likelihood ratio comparison tests in order to determine which individual, or set of additive or interaction factors are most important for predicting the response variable. After the best fit model was chosen, I compared each treatment to the control in each model with Dunnett’s (Dunnett 1955) many-to-one comparison test with a Bonferroni correction to account for potential inflated error from multiple comparisons.

Finally, I tested if the global change factors have an overall additive, synergistic, or antagonistic effect. I calculated the predicted net effect (relative percent difference from the control) as the sum of individual treatments of elevated CO₂, O₃, or N. I compared the predicted net effect to the corresponding observed effects from empirical treatment combinations. For example, the predicted net growth rate of *S. arabicus* grown in combined elevated CO₂ and O₃ is 33.5% (33.5% is the sum of +44.3% net increased
growth when grown in 700 ppm CO$_2$ and -10.9% change when grown in 100 ppb O$_3$). The observed net growth in the combined treatment of CO$_2$ and O$_3$ is 25.5% (difference between predicted and observed = 8%). When the predicted change is equal (or comparable (<10% difference) to the observed change, this is an overall additive effect of the treatments. If the predicted change is more than 10% lower than observed change, the net response is synergistic (greater than the sum of individual effects), and if the predicted change is more than 10% greater than the observed response, the net response is antagonistic (less than the sum of individual effects).

RESULTS

At peak growth, the best fit models to explain growth rate of the non-native graminoid (S. arabicus) and native forb (P. recurvata) differed. S. arabicus’ growth rate and yield were best predicted by models including the interaction between CO$_2$ and O$_3$ (Table 2). P. recurvata’s growth rate was best predicted by O$_3$ alone while a model including both CO$_2$ and O$_3$ was the best fit to describe physiological yield. Overall, elevated N or the interaction of N with CO$_2$ or O$_3$ was a minimally important predictor for the growth rate or yield of either species in this experiment (Table 2).

Non-native species responses under single and combined factors

The model including the interaction between elevated CO$_2$ and O$_3$ was the best predictive model of S. arabicus growth rate (Table 2). The best-fit model CO$_2$ * O$_3$ was determined by AICc value and likelihood ratio comparison between CO$_2$ + O$_3$ and CO$_2$ *
O3 ($\chi^2 = 9.1$, p = 0.06). Nitrogen was not a significant factor in the growth rate model for *S. arabicus* (Table 2). As single factors, elevated CO2 increased growth rate and O3 exposure decreased the growth rate of *S. arabicus* (Figure 2, top panel). In combination, elevated CO2 mitigated the negative effects from exposure to elevated O3 (Figure 2, top panel). *S. arabicus* growth rate increased 34 and 44% in the elevated 550 ppm and 700 ppm CO2 treatments, respectively, compared to growth rate in ambient 400 ppm CO2 (averaged across all levels of O3 exposure, main effect of CO2 not shown). In contrast, growth rate decreased 5 and 11% in 60 ppb and 100 ppb O3 treatments compared to ambient 15 ppb O3 exposure (averaged across all levels of CO2 exposure, main effect of O3 not shown). At ambient O3, CO2 increased *S. arabicus* growth rate by an average 18% (9.7 +/- 0.6 mg day$^{-1}$) and 36% (11.1 +/- 0.5 mg day$^{-1}$) in 550 ppm and 700 ppm CO2 treatments, respectively, compared to the control (8.2 +/- 0.3 mg day$^{-1}$; Figure 2 top panel). At ambient CO2, O3 as a single factor decreased growth rate by 9% (7.5 +/- 0.3 mg day$^{-1}$) and 23% (6.3 +/- 0.2 mg day$^{-1}$; Figure 2 top panel) under in 60 ppb and 100 ppb O3 exposure. However, at elevated CO2 concentrations, O3 damage was mitigated and there was a net positive increase in *S. arabicus*’ growth rate compared to the control (Dunnett’s test, p < 0.05 all high CO2 treatments, Figure 2 top panel).

Similar to growth rate, the model accounting for the interaction between CO2 and O3 was the best predictive model of *S. arabicus* photosynthetic yield (i.e. model with lowest AICc score and no additional models with $\Delta$ AICc < 3; Table 2). Nitrogen was not significantly related to photosynthetic yield in *S. arabicus* (Table 2). In ambient CO2, photosynthetic yield was 54% (0.17 +/- 0.05) and 57% (0.16 +/- 0.04) lower than the control in the 60 ppb and 100 ppb O3 treatments, respectively (Dunnett’s test, p < 0.05, 217
A similar pattern followed for O₃ exposure at 550 ppm CO₂. In contrast, in high CO₂ (700 ppm) exposure, photosynthetic yield did not differ from the control at any level of O₃ exposure (Dunnett’s test, p > 0.1 all high CO₂ treatments, Figure 2 bottom panel). The non-significant result, in comparison to the significant negative effects of O₃ alone, indicates the negative impacts of O₃ observed at lower CO₂ concentrations were mitigated under elevated CO₂.

*Native species affected most by O₃*

Contrary to *S. arabicus*, *P. recurvata’s* growth rate was best fit by a single factor model (Table 2, best fit model O₃), and growth rate was not dependent on the interaction between CO₂ and O₃. Nitrogen was not significantly related to *P. recurvata* growth (Table 2). While the CO₂ + O₃ additive model and O₃ single factor growth rate models had similar low AICc scores (Table 2), adding CO₂ to the model did not significantly increase the model’s predictive power of *P. recurvata’s* growth rate (likelihood ratio comparison, $\chi^2 = 2.5$, p = 0.3). The growth rate of *P. recurvata* was negatively affected by exposure to elevated O₃ concentrations. At ambient CO₂, *P. recurvata’s* growth rate decreased only 3% (4.7 +/- 0.6 mg day⁻¹) in the 60 ppb O₃ treatment compared to the control (4.7 +/- 0.7 mg day⁻¹), but decreased 57% (2.0 +/- 0.5 mg day⁻¹) under high O₃ (100 ppb) compared to the control (4.8 +/- 0.7 mg day⁻¹, Figure 3, top panel). While exposure to elevated CO₂ increased growth rate by 10% and 30% in 550 and 700 ppm CO₂, respectively, the increased growth rate was not significantly different from the control due to variability among O₃ treatments, variability of individual responses within treatments, and low sample size (Figure 3, top panel).
For the photosynthetic yield of *P. recurvata*, multiple mixed models were equally plausible best-fit candidates based on low AICc scores (Table 2, Δ AICc < 3). The model including CO₂ and O₃ without the interaction term (CO₂ + O₃) provided significantly better fit and lower residual error than the model with interaction term or O₃ alone (CO₂ + O₃, likelihood ratio comparison test $\chi^2 = 15.1, p < 0.001$). Elevated CO₂ increased photosynthetic yield 34% at ambient O₃ and 30% at mid-levels of O₃, both of which are significantly greater than the control treatment (Dunnett’s test, p < 0.005, Figure 3, bottom panel). At ambient CO₂, yield was reduced under the high O₃ by 25% compared to the control, but was not significantly different than the control (Dunnett’s test, p = 0.2). Like *S. arabicus*, N was not significantly related to *P. recurvata* photosynthetic yield (Table 2).

### Additive and non-additive effects of combined factors

I compared the percent change in growth rate (relative to the control) between species in the single factor high treatments (700 ppm CO₂, 100 ppb O₃, and 8 kg N ha⁻¹ yr⁻¹) and the combinations of these high treatments (Figure 4). Overall, non-native *S. arabicus* had net positive change in most treatments with only slight declines (-11%) in growth rate in high O₃ treatments (100 ppb; Figure 4). In contrast, native *P. recurvata* was more sensitive to elevated O₃. For example, the growth rate of *P. recurvata* declined 49% in high O₃ exposure compared to the control (Figure 4). N only had a slight positive effect on *S. arabicus* (+5%) and no effect (-0.2%) on the growth rate of *P. recurvata* (Figure 4).

Combined elevated CO₂ and N (CO₂ * N, Figure 4) increased growth rate 57 and 49% compared to the control for *S. arabicus* and *P. recurvata*, respectively. In contrast,
combined elevated O$_3$ and N decreased growth rate 6% and 58% for *S. arabicus* and *P. recurvata*, respectively. N appeared to have a slight positive impact on the growth of *S. arabicus* where percent change in the combined O$_3$ and N was lower (less negative) compared to that when exposed to O$_3$ alone. On the other hand, the response of *P. recurvata* was a greater decline (more negative) in growth rate in the combined treatment compared to O$_3$ alone. The greatest difference between species was in their response to combined CO$_2$ and O$_3$. The growth rate of *P. recurvata* decreased 30% from the control in combined CO$_2$ and O$_3$, while the growth rate of *S. arabicus* increased 25% despite co-occurring exposure to 100 ppb O$_3$ (Figure 4). Finally, when exposed to all three pollutants in combination (CO$_2$ x O$_3$ x N), there was a net positive increase in growth rate by 49 and 11% for *S. arabicus* and *P. recurvata*, respectively.

In order to further investigate if the combined factors had an overall additive, synergistic or antagonistic effect, I compared the predicted responses (summed effects from individual treatments in combined high [700ppm CO$_2$, 100ppb O$_3$, and 8 kgN ha$^{-1}$ yr$^{-1}$] and middle [550ppm CO$_2$, 60ppb O$_3$, and 4 kgN ha$^{-1}$ yr$^{-1}$] treatments) to the observed responses in corresponding experimental treatment combinations. Overall, there was net positive growth in treatment combinations of CO$_2$ x N (Figure 4; triangles Figure 5) and CO$_2$ x O$_3$ x N for both species (Figure 4; diamonds, Figure 5), and net negative (less than the control) growth in combined O$_3$ and N for both species (Figure 4; circles, Figure 5). Contrary to my expectations, the majority of *S. arabicus’* growth rate responses to co-occurring pollutants were additive (i.e. predicted response approximately equals observed along the 1:1 line, Figure 5), while *P. recurvata* responses were more mixed.
For *S. arabicus* (dark grey and black symbols Figure 5), the observed growth effects were additive for all the two-way treatment combinations (CO\(_2\) x O\(_3\), CO\(_2\) x N, and O\(_3\) x N). However, there was a synergistic effect from all three pollutants combined (CO\(_2\) x O\(_3\) x N, diamonds Figure 5). The predicted net increase in *S. arabicus*’ growth rate in high treatments (700 ppm CO\(_2\) x 100 ppb O\(_3\) x 8 kg N ha\(^{-1}\) yr\(^{-1}\) N) was 38% compared to the observed 49% actual net increase in growth compared to the control (11% difference indicating a net synergistic effect, black diamond Figure 5). In the middle level treatments, predicted net increase in growth rate was 28% compared to 40% actual observed net increase (12% difference). The net effect of all three pollutants combined was greater than in two-way combinations of CO\(_2\) and O\(_3\) (-9% difference, square Figure 5). Thus, removing the effect of N appears to change the net response, though N was not a significant factor in the linear mixed models (Figure 5).

Similar to *S. arabicus*, *P. recurvata*’s growth rate responses (open and light grey symbols, Figure 5) were additive in two-way combinations of CO\(_2\) and O\(_3\) (squares, Figure 5) and synergistic in response to all three pollutants combined (CO\(_2\) x O\(_3\) x N, diamonds, Figure 5). *P. recurvata*’s growth rate was predicted to decrease 23% when exposed concurrently to all three pollutants, however the observed response was a net increase of 11% compared to the control (34% difference indicating synergistic response, grey diamond Figure 5). There was also a synergistic response in the middle level treatments where the growth rate was predicted to increase 7%, but actually increased 30% (23% difference indicating synergistic response). I also observed net synergistic responses of *P. recurvata* grown in two-way combinations of elevated CO\(_2\) and N (triangles, Figure 5). In contrast, the net effect of O\(_3\) and N tended to be antagonistic 221.
where there was a predicted decrease of 49% in the high treatments and 9% in the middle level treatments, but observed growth rate decreased 58% and 19%, respectively, a greater decrease than expected (circles, Figure 5). *P. recurvata*’s net negative growth as a result of O₃ exposure (Figure 5 circles and squares) highlights the significance of O₃ as a main influence on the native species’ growth (Figures 3 and 4).

DISCUSSION

I investigated the ecological impact of multiple ecologically relevant atmospheric compounds (CO₂, N, and O₃) on the growth and physiological yield of the dominant native and non-native Sonoran Desert herbaceous species. Overall, I found the two most frequently encountered species in this system, which differ in functional type and physiological tradeoffs, also differed in net responses and sensitivities to co-occurring pollutants. The non-native graminoid *S. arabicus*, characterized by high relative growth rate (RGR) and low water use efficiency (WUE), was most strongly influenced by elevated CO₂. Elevated CO₂ led to net positive growth of *S. arabicus*, despite the physiological stress of O₃ on growth and photochemistry (Figure 2). In contrast, the native forb *P. recurvata*, characterized by high WUE and low RGR, showed positive physiological response to elevated CO₂, but no accelerated growth (Figure 3). *P. recurvata* grew more slowly than controls under elevated O₃ (Figure 3). Contrary to my expectations, elevated N had a minimal and non-significant impact on growth or physiological functioning for *S. arabicus* or *P. recurvata* (Table 2, Figure 4). Finally, I found that growth rate responses to combinations of two factors (O₃ x N, CO₂ x N, and
CO₂ x O₃) were largely additive (sum of individual responses) for the non-native species, while the native species responses were more frequently synergistic (amplifying or greater than the sum of individual effects, Figure 5). Overall, net responses to three-way combinations of co-occurring CO₂, O₃ and N were synergistic for both species, though the synergistic effect was more strongly apparent for the native forb (P. recurvata) than the non-native graminoid (S. arabicus, Figure 5).

**Responses to co-occurring pollutants**

The growth rate and physiological yield of both native and non-native species were affected differently by CO₂ and O₃ individually and in combination. At current global CO₂ concentrations (i.e. concentrations comparable to ambient CO₂ levels in this experiment), exposure to high O₃ concentrations (100 ppb) reduced growth rate by 23% and 57% for the non-native and native species, respectively (Figure 2 & 3). The species differed, however, in their response to elevated CO₂. Elevated CO₂ mitigated the negative impacts of O₃ exposure for the non-native. S. arabicus had net positive growth (greater than the control) when grown in 700 ppm CO₂, regardless of co-occurring exposure to 60 or 100 ppb O₃ concentrations (Figure 2, Figure 5). In contrast, elevated CO₂ concentrations neither increased the growth rate in the native forb nor as strongly mitigated the negative effects of elevated O₃ as seen in S. arabicus (Figure 3).

Desert annual species differ in functional traits along a gradient of physiological tradeoffs between WUE and RGR and these differences can affect growth and physiological responses to elevated pollutants. For example, P. recurvata is characterized by relatively low stomatal conductance, high WUE and low RGR, whereas
S. arabicus tends to have higher stomatal conductance, RGR and lower WUE (Huxman et al. 2008; Angert et al. 2007; Angert et al. 2009). As expected, the peak growth rate of S. arabicus (8.2 +/- 0.3 mg day^{-1}) was higher than P. recurvata in ambient conditions (4.8 +/- 0.7 mg day^{-1}, Figure 2 & 3). I also expected S. arabicus to be more sensitive to exposure to elevated atmospheric pollutants, and O_3 in particular, as a result of higher relative stomatal conductance. The oxidative stress of O_3 damage is strongly correlated with stomatal conductance and directly impacts the photosynthetic mechanisms, Rubisco, and chlorophyll content (Reich and Amundson 1985). I measured photosynthetic quantum yield with chlorophyll fluorescence as an indicator of photosynthetic stress from exposure to pollutants. As expected, S. arabicus had significant physiological stress in response to elevated O_3, whereas P. recurvata did not exhibit lower yields or physiological stress from O_3 exposure. S. arabicus’ yield was reduced up to 57% when exposed to elevated O_3 at ambient (400 ppm) and enriched (550 ppm) CO_2 (Figure 2). Yet, as with growth rate, photosynthetic stress of S. arabicus at high O_3 was reduced when concurrently exposed to elevated CO_2 (Figure 2). The net positive physiological response of S. arabicus in part explains the mechanism for net positive growth in elevated O_3 and CO_2. As CO_2 concentrations rise and the photosynthetic need for CO_2 uptake is reduced, stomatal conductance is also reduced, which in turn minimizes the flux of O_3 into the leaf and mitigates O_3 stress and damage (Cardoso-Vilhena and Barnes 2001; Cardoso-Vilhena et al. 2004). Despite the physiological stress from O_3 exposure, the net positive growth rate highlights the plasticity of S. arabicus to respond and adapt to increasing environmental conditions and concentrations of co-occurring pollutants.
The physiological response of native *P. recurvata* was more variable. Elevated CO$_2$ increased photosynthetic yield up to 34% in some treatments, yet elevated O$_3$ did not significantly reduce yield of the native species (Figure 3). Characterized by relatively low stomatal conductance, physiological damage from O$_3$ is minimal in *P. recurvata* indicating the *P. recurvata* may be more physiologically stress tolerant. However, despite the minimal physiological response to elevated O$_3$, the growth rate of *P. recurvata* was significantly reduced when exposed to high (100 ppb) O$_3$ concentrations as a result of observed physical damage and necrosis of leaf biomass. Overall, the physical damage and lack of interaction between CO$_2$ and O$_3$ suggests the non-native species has less plasticity to respond to changing environmental conditions.

Contrary to my expectations, elevated N had minimal predictive power in explaining growth or physiological responses of either species (Table 2, Figure 4). I expected elevated N in combination with elevated CO$_2$ would reduce co-limitations on growth and lead to synergistic effects on growth rate (Shen et al. 2008). For example, I saw additive growth rate responses when plants were exposed to co-occurring CO$_2$ and O$_3$, but in combinations including elevated N, the responses were synergistic (diamonds above the 1:1 line, Figure 5). The lack of power in the models including N (Table 2) to predict these synergistic relationships may be due, in part, to low sample size in the combined CO$_2$, O$_3$, N treatments. However, the limited N impact in this experiment was also consistent with a multi-year field study from the Sonoran Desert, in which desert herbaceous biomass did not differ between urban and outlying locations despite larger soil inorganic N pools and higher N deposition in the urban locations (Hall et al. 2011). In wet years, N was limiting to desert herbaceous plants, and plants responded under high
rates of N additions (60 kg N ha\(^{-1}\) yr\(^{-1}\)) in a field manipulation experiment. Similarly, the desert herbaceous species in my study may not be responsive to relatively low N inputs (8 kg N ha\(^{-1}\) yr\(^{-1}\) applied in this study compared to 60 kg N ha\(^{-1}\) yr\(^{-1}\) in field manipulation) that are characteristic of the N deposited in the Phoenix region, even under well-watered conditions. Overall, however, background inorganic N in the homogenized soil mixture used as a growing medium likely explains the minimal effects of my experimental N treatments. High background levels in the soil (~45 ppm) most likely overshadowed the N I applied as ammonium nitrate in solution to simulate 4 and 8 kg N ha\(^{-1}\) yr\(^{-1}\) deposition (6 and 12 ppm respectively). Thus, I expect N may not have been limiting for the plants in any of the treatments.

**Predicted impacts of water co-limitation**

In arid ecosystems where water is the main limiting factor, aridland plants are expected to respond differently to environmental factors, such as elevated CO\(_2\), depending on water availability. I maintained well-watered plants and elevated soil moisture to reduce variability in the high number of treatment. Similar to findings in other arid studies, I found elevated CO\(_2\) in high water conditions increased non-native grass biomass more than the native species (S. D. Smith et al. 2000). However, I expect my data may best describe the “potential” growth rate when WUE is less essential to the survival in well-watered conditions, and the results may vary under more water-limited conditions. For example, in a long-term manipulative experiment in the Mojave Desert, herbaceous plants have increased production and reproductive allocation in response to elevated CO\(_2\) in wet years but not drought years, which can significantly influence the
long-term dominance of native and non-native species (S. D. Smith et al. 2000; Housman et al. 2006; S. D. Smith et al. 2014). In contrast, other studies report mixed effects of elevated CO\textsubscript{2} on biomass during wet and dry years, where in drier years elevated CO\textsubscript{2} in arid ecosystems results in greater water use efficiency, in turn leading to increased soil moisture and the potential for increased N mineralization and uptake (Morgan et al. 2004; Dijkstra et al. 2010). Thus, aridland C\textsubscript{3} herbaceous production is expected to increase non-linearly in response to elevated CO\textsubscript{2} and N (i.e., a synergistic effect) in wet years, while in dry years the effects would be antagonistic (Shen et al 2008). In addition to the effects of elevated CO\textsubscript{2} concentrations, this study is novel in also testing the co-occurring impacts of other pollutants. I found the non-native species was particularly sensitive to elevated O\textsubscript{3} exposure at 60 and 100 ppb O\textsubscript{3} (Figure 2). Under more water-limited conditions, I would expect \textit{S. arabicus} to be less sensitive to O\textsubscript{3} with perhaps greater interactive effects in combinations of elevated CO\textsubscript{2} and O\textsubscript{3}.

Finally, herbaceous annual plants’ functional traits of WUE and RGR, which are consistent across years and experimental conditions (e.g. greenhouse vs field experiment), can be translated to a tradeoff in fitness under different environmental conditions, such as water availability (Kimball et al. 2012). For example, in wet years, high RGR species (e.g. \textit{S. arabicus}) are expected to outperform species with lower RGR and higher WUE (e.g. \textit{P. recurvata}) as a result of greater plasticity and an ability to exploit resources (Kimball et al. 2012). The findings in this study support this, as elevated CO\textsubscript{2} concentrations led to an overall increased growth rate of \textit{S. arabicus} despite damage from elevated O\textsubscript{3}. As in other studies, I expect that in drier conditions, the native forb may be favored due to its relatively high WUE and ability to tolerate physiological
stress (S. D. Smith et al. 2014). Yet, our findings highlight the native forb’s susceptibility to O₃ damage to leaves, despite low physiological stress. These results also highlight the important role of water as a driving factor in arid ecosystem responses to multiple pollutants and the need to test co-occurring factors with water as an additional constraint.

*Synergistic responses to realistic co-occurring pollutants*

I expected co-occurring elevated pollutants to have interactive effects leading to overall net synergistic or antagonistic growth responses in each species. With the full factorial dose response design, I was able to ask if net growth rates were simply additive and could have been predicted by studying each factor individually, or if responses were synergistic or antagonistic requiring a more complex model to predict the results. Overall, I found co-occurring elevated CO₂ and O₃ had an interactive effect on the photosynthetic yield and growth rate of non-native *S. arabicus*, such that CO₂ largely mitigated the negative effects of elevated O₃ (Table 2, Figure 3). On the other hand, net negative growth of *P. recurvata* was observed in the same treatment (Figures 2 and 3). These results suggest that CO₂ was a stronger driver of *S. arabicus* growth, while O₃ was the stronger control on *P. recurvata* growth. Nevertheless, despite the significant interaction between CO₂ and O₃ for *S. arabicus*, the net growth rate of both species was additive in combinations of CO₂ and O₃ (i.e., predicted and observed effects were equal; squares, Figure 5). On the other hand, both species had net synergistic growth rate responses to combined CO₂, O₃, and N (Figure 5). *P. recurvata* also had a synergistic growth response to elevated CO₂ and N (Figure 5). Though N was not a significant
factor in the models, likely due to the background soil N used in this experiment, the non-additive results suggest possible synergistic responses of both species grown in the ecological airshed of cities, in which elevated CO₂, O₃, and N deposition co-occur. It is essential to identify when ecosystem response may be synergistic or antagonistic, as possible non-additive responses increase the complexity of systems models needed to accurately predict future ecological outcomes. Additional multi-factor experiments and models are needed to assess the potential synergistic responses to realistic combinations of elevated CO₂, O₃, and N in combination with species interactions and other co-occurring global changes such as altered temperature and precipitation patterns (Bytnerowicz et al 2013, Templer 2013).

**Implications of urban air quality for primary producers and ecosystems**

Current and future levels of multiple pollutants may lead to long-term changes in plant community composition, yet species and community responses to co-occurring future levels of CO₂, O₃, and N are unknown. For example, elevated N deposition is expected to reduce species diversity even at chronic, low levels of N inputs to an ecosystem (Clark and Tilman 2008; Payne et al. 2013). On the other hand, elevated CO₂ has mixed effects on changing community composition (Potvin and Vasseur 1997; Zavaleta et al. 2003). Yet, in combination, elevated CO₂ has been found to mitigate the negative effects of N deposition on species loss (Reich 2009). These studies, however, do not account for the co-occurring exposure to elevated CO₂, N, and O₃ in the “ecological airshed” in native ecosystems surrounding cities (Cook et al in prep).
Though I did not test community-level responses to co-occurring CO2, N, and O3, the net responses of the dominant species of the Sonoran Desert differed, such that the non-native species will be favored in predicted future environmental conditions. In combinations of predicted current and future CO2 and O3 concentrations, the non-native species had overall net positive growth despite co-occurring O3 and negative physiological responses to O3. This suggests elevated CO2 had a protective effect for the non-native species under high stress. While the native species responded similarly with reduced growth in elevated O3, native *P. recurvata* was less physiologically sensitive to O3. Overall, elevated CO2 did not have the same mitigating effects on O3 responses for the native species. The different net responses could lead to the non-native species exploitation of resources and outcompeting the native species within the urban “ecological airshed.” The eco-physiological tradeoffs between WUE and RGR in part explain the current co-existence of Sonoran Desert species, as well as the variability in how species respond to current and predicted future urban pollutants (Angert et al. 2009; Kimball et al. 2012). However, additional changing environmental patterns, such as longer periods of drought and increased temperature, will interact with eco-physiological traits and elevated pollutant levels with potential cascading impacts on the co-existence, competition, and dominance of herbaceous species (Kimball et al 2012). More research is needed to specifically link the eco-physiological responses of species to community level changes in order to better predict changing ecosystem structure (Suding et al. 2008; Crous et al. 2010). Changes to the community structure can have important ecosystem consequences: for example, altered community composition of arid grasslands may lead
to increased fire frequency and altered ecosystem services, such as the ability to store carbon and N (S. D. Smith et al. 2000; Hall et al. 2011).

CONCLUSION

Decades of research have shown that plant processes are sensitive to altered climate and elevated concentrations of CO$_2$, N, or O$_3$ alone, as they function as both resources and stressors for primary producers (Long et al. 2004; Karnosky et al. 2007; Bobbink et al. 2010). While CO$_2$, O$_3$ and N are expected to be elevated concurrently as a result of human activities, particularly in and around cities, no research to date has examined their co-occurring impacts at concentrations that reflect current and predicted future levels along urban-rural gradients. These results show that native ecosystems are vulnerable to current and future air pollution over the long-term. The findings in this study highlight that current and predicted future air quality conditions in and around urban regions can have important impacts, including interactive and synergistic effects, on individual species growth and physiological functioning with potential cascading impacts on the community composition of protected ecosystems.
ACKNOWLEDGEMENTS

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**TABLE 1:** CO$_2$ and O$_3$ concentrations in treatment chambers. Mean (SD) CO$_2$ (ppm, 24 hour average) and O$_3$ (ppb (0900 – 1800 daytime average) concentrations in treatment chambers (averaged within a chamber for 24 hour period) and within treatments (n = 3 chambers averaged per treatment) during the study period. Plus signs indicate ambient (+), mid (++), and high (+++) fumigation treatments.

<table>
<thead>
<tr>
<th>Carbon dioxide (ppm)</th>
<th>Ozone (ppb)</th>
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<tbody>
<tr>
<td><strong>Individual chamber</strong></td>
<td></td>
</tr>
<tr>
<td>+ 419.5 (26.3)</td>
<td>+ 15.2 (7.4)</td>
</tr>
<tr>
<td>+ 409.7 (18.9)</td>
<td>++ 60.1 (22.0)</td>
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<td>+ 410.4 (18.9)</td>
<td>+++ 93.4 (21.2)</td>
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<td>++ 539.4 (45.4)</td>
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<td>+++ 659.1 (73.2)</td>
<td>+++ 95.3 (26.3)</td>
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TABLE 2: Linear mixed model results showing individual, additive or interactive effects on growth rate and photosynthetic yield. Linear mixed model results showing elevated CO$_2$, O$_3$, and N as individual, additive or interactive effects on growth rate (mg day$^{-1}$) and photosynthetic yield for non-native *S. arabicus* and native *P. recurvata* species. Akaike’s information criterion value for finite samples (AICc) and delta (ΔAICc) are reported as goodness of fit for each model. Lowest AICc and delta AICc (< 3) are italicized to indicate the best explanatory models, and the selected best fit model (chosen based on likelihood ratio comparison test) is bolded.

<table>
<thead>
<tr>
<th></th>
<th>Non-native <em>S. arabicus</em></th>
<th>Native <em>P. recurvata</em></th>
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CO$_2$, O$_3$ and N (and their interactions) are included as fixed effects and growth chamber is included as a random effect in all models.
FIGURE 1: CSTR chambers in UC Riverside greenhouse. Nine Continuously Stirred Tank Reactor (CSTR) chambers at UC Riverside used for the multi-factor dose response fumigation experiment to test the co-occurring effects of CO$_2$, O$_3$ and N.
FIGURE 2: Growth (mg day\(^{-1}\)) and photosynthetic yield of *S. arabicus* grown in ambient and elevated CO\(_2\) and O\(_3\). Average (+/- 1SE growth rate (mg day\(^{-1}\), top) and photosynthetic yield (unitless, bottom) for *S. arabicus* in single and combined CO\(_2\) and O\(_3\) treatments. Dashed horizontal line represents control average (ambient CO\(_2\) and ambient O\(_3\)). Asterisks indicate significantly different means from control based on Dunnett’s comparison with Bonferroni adjustment.
FIGURE 3: Growth (mg day$^{-1}$) and photosynthetic yield of *P. recurvata* grown in ambient and elevated CO$_2$ and O$_3$. Average (+/- 1SE growth rate (mg day$^{-1}$, top) and photosynthetic yield (unitless, bottom) for *P. recurvata* in single and combined CO$_2$ and O$_3$ treatments. Dashed horizontal line represents control average (ambient CO$_2$ and ambient O$_3$). Asterisks indicate significantly different means from control based on Dunnett’s comparison with Bonferroni adjustment.
**FIGURE 4:** Observed percent relative change in growth rate. Observed percent relative change in growth rate (compared to the control defined as ambient CO$_2$, O$_3$, and/or N for each treatment combination) for non-native graminoid (*S. arabicus*, dark grey) and native forb (*P. recurvata*, light grey) in single and combined high CO$_2$ (700 ppm), O$_3$ (100 ppb), and N (8 kg N ha$^{-1}$ yr$^{-1}$) treatments.
FIGURE 5: Additive and non-additive effects based on predicted and observed percent relative change in growth rate of *S. arabicus* and *P. recurvata*. Predicted and observed percent change in growth rate (from the control defined as ambient CO$_2$, O$_3$, and/or N for each treatment combination). Predicted responses are the sum of percent change from individual treatments (CO$_2$ + O$_3$, CO$_2$ + N, etc) and observed responses are from empirically combined treatments. Combinations shown for high (black) and middle (dark grey) treatments for *S. arabicus* and high (light grey) and middle (open) treatments for *P. recurvata*. Points along the dashed 1:1 line indicate additive responses, below the line are antagonistic effects and above the line are synergistic effects. Ellipses highlight the different species responses.
TABLE 1: Multi-factor dose response treatment combinations within each chamber: O$_3$ and CO$_2$ were delivered by gas fumigation for desired concentrations within each chamber and N was applied as three levels of NH$_4$-NO$_3$ within each chamber.

<table>
<thead>
<tr>
<th>Chamber</th>
<th>O$_3$ (ppb)</th>
<th>N (kg/ha/yr)</th>
<th>CO$_2$ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1: (Control)</td>
<td>Ambient (~15)</td>
<td>0, 4, 8</td>
<td>Ambient (~400)</td>
</tr>
<tr>
<td>2:</td>
<td>15</td>
<td>0, 4, 8</td>
<td>550</td>
</tr>
<tr>
<td>3:</td>
<td>15</td>
<td>0, 4, 8</td>
<td>700</td>
</tr>
<tr>
<td>4:</td>
<td>60</td>
<td>0, 4, 8</td>
<td>400</td>
</tr>
<tr>
<td>5:</td>
<td>60</td>
<td>0, 4, 8</td>
<td>550</td>
</tr>
<tr>
<td>6:</td>
<td>60</td>
<td>0, 4, 8</td>
<td>700</td>
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<tr>
<td>7:</td>
<td>100</td>
<td>0, 4, 8</td>
<td>400</td>
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<tr>
<td>8:</td>
<td>100</td>
<td>0, 4, 8</td>
<td>550</td>
</tr>
<tr>
<td>9:</td>
<td>100</td>
<td>0, 4, 8</td>
<td>700</td>
</tr>
</tbody>
</table>
CHAPTER 6

CONCLUDING REMARKS

In this conclusion, I synthesize the main research findings from each chapter and highlight the major contributions of this research, and then point to next steps and management implications.

SYNTHESIS OF MAJOR RESEARCH FINDINGS

Chapter 2: Examining the drivers of people’s actions and in turn the ecological outcome of those actions in highly managed systems, I found that a complex set of individual and institutional social characteristics drives people’s choices, which in turn affect ecological structure and functioning across scales from yards to cities (Larson et al. 2010; Cook, Hall, and Larson 2012). This work demonstrates the link between individuals’ decision-making and ecosystem service provisioning in highly managed urban ecosystems. In addition, this research highlights the importance of an interdisciplinary and multi-scalar approach to understanding complex human-ecological systems.

Chapter 3: Overall, total nitrogen (N) deposition in the Phoenix metropolitan region and surrounding Sonoran Desert was lower (7.3 kg N ha\(^{-1}\) yr\(^{-1}\)) than expected compared to similar ecosystems, but within the range of the dryland N critical load. The dryland critical load, estimated between 3 – 8 kg N ha\(^{-1}\) yr\(^{-1}\), is the level at which ecological changes are expected to occur as a result of elevated N inputs (Fenn et al. 2010; Pardo et al. 2012).
al. 2011). Despite low regional estimated deposition rates, N inputs from arid cities into the surrounding native ecosystem are likely to have significant ecological consequences, particularly with long-term accumulation and in years of above average precipitation. Using multiple sampling approaches to address the uncertainties related to quantifying N deposition in dryland systems, I found that dry N deposition was highest within the urban region, and primarily predicted by proximity to sources of N emissions. In contrast, patterns of total and wet deposition were mainly driven by meteorological variables and the timing and frequency of rainfall events. My results highlight the importance of employing multiple measurement techniques to accurately assess seasonal trends of wet and dry N deposition and their distribution across the landscape.

Chapter 4: This study is the first to identify the distinct spatial pattern of co-occurring, ecologically important pollutants within protected lands. The urban “ecological airshed,” is created by elevated concentrations and deposition of biologically important urban-generated compounds. I found that the “ecological airshed” extends far into the outlying native ecosystem at levels that are likely to affect ecosystem structure and function. The impacts of the urban atmosphere on ecosystems, in combination with other factors related to urbanization such as elevated temperatures, may lead to longer-term consequences for ecosystem structure, functioning, and services. My findings show the need for air quality monitoring with an expanded repertoire of compounds known to affect ecosystem services and biological processes in both urban and remote native ecosystems.
Chapter 5: Under current and predicted future air quality conditions, herbaceous desert species responded differently suggesting potential cascading long-term consequences for community composition in native ecosystems. The non-native species (*Schismus arabicus*) grew rapidly in all treatments despite physiological stress under high O$_3$ concentrations. In contrast, the native species (*Pectocarya recurvata*) was more sensitive to O$_3$ and, unlike the non-native species, did not experience the protective cover of elevated CO$_2$. Elevated CO$_2$ mitigated negative effects of O$_3$ for the non-native species and suggests that *S. arabicus* may be favored over *P. recurvata* when exposed to future air quality conditions. In addition, species responses were synergistic in combinations of CO$_2$, O$_3$, and N. Overall, these results provide empirical evidence for future nuanced policies addressing ecosystem sensitivity to multiple pollutants in native landscapes.

NEXT STEPS AND IMPLICATIONS FOR FUTURE MANAGEMENT

Global urban land area is expected to triple by 2030 and more than 65% of the world’s population is predicted to live in cities by 2050 (United Nations 2012; Seto, Güneralp, and Hutyra 2012). Human activities concentrated in growing urban centers are significant sources of atmospheric pollutants – including CO$_2$, reactive N, and O$_3$ – that affect air quality, human health, ecosystem services, and ecological functioning (IPCC 2014). My findings highlight that the urban “ecological airshed” extends well beyond the urban boundary where ecologically relevant pollutants co-occur in remote areas at levels that likely affect ecosystem structure and function. I also found that existing urban air quality conditions can affect growth and physiological functioning of primary producers.
with potential long-term feedbacks on native ecosystem structure, function, and the provision of ecosystem services (Gregg, Jones, and Dawson 2003; Gregg, Jones, and Dawson 2006). Identifying the extent of land area exposed to human-generated pollutants in an urban “ecological airshed” highlights the need and urgency to adopt air quality monitoring and regulations that include a full suite of ecologically relevant compounds to protect the surrounding natural environments and ecosystem services.

Neither current air quality nor conservation policies typically account for the realistic scenarios in which multiple urban pollutants co-occur with potential synergistic or antagonistic impacts on outlying ecosystems and human health (Clair et al. 2011). Air-quality regulations with a primary focus on human health and secondarily on visibility and ecosystem impacts. Thus, air quality regulations mainly focus on multiple pollutants only with regard to atmospheric chemical reactions between precursors and pollutants of interest for human health (e.g. VOC, NO\(_x\), and O\(_3\); Finlayson-Pitts & Pitts 2000). While conservation plans seek to preserve native ecosystems, they frequently do not account for the influence of air pollutants that cross political and municipal boundaries (Lovett et al. 2009). In order to more effectively manage and address air quality concerns for humans and ecosystems, there are many changes to current regulations that are needed. For example, new regulatory policies should 1) consider a more inclusive suite of pollutants that affect humans and ecosystems, 2) monitor ambient concentrations in areas of human and ecosystem exposure, 3) model projected changes in air quality under different scenarios, 4) regulate emissions, and 5) test and account for ecological and human exposure, risks, and responses to multiple pollutants (Hidy and Pennell 2010).
Critical loads are an example framework developed in the European Union and United States that account for ecosystem exposure and risk. To date, critical loads have been determined only for single pollutants, such as N deposition, rather than accounting for multiple, often more realistic exposure of ecosystems to co-occurring compounds. Similarly, air quality regulations focused on human health address individual pollutants, such as O₃ or particulate matter. I propose that a multi-pollutant critical load framework would be an effective tool to regulate and examine both ecosystem and human exposure to multiple relevant stressors. This would be an important step in addressing the resulting environmental and human health impacts from air quality conditions. My research highlights the extent of the “ecological airshed” and that existing urban air quality conditions can alter ecosystem structure and functioning in nearby native ecosystems. These findings on multiple interacting pollutants provide initial empirical evidence and first steps for establishing nuanced regulations to protect ecosystems and human health through a multi-pollutant critical load.
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