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Mixed method approach to assess atmospheric nitrogen deposition in arid and semi-arid ecosystems☆

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ABSTRACT

Arid and semi-arid ecosystems (aridlands) cover a third of Earth's terrestrial surface and contain organisms that are sensitive to low level atmospheric pollutants. Atmospheric nitrogen (N) inputs to aridlands are likely to cause changes in plant community composition, fire frequency, and carbon cycling and storage. However, few studies have documented long-term rates of atmospheric N inputs in aridlands because dry deposition is technically difficult to quantify, and extensive sampling is needed to capture fluxes with spatially and temporally heterogeneous rainfall patterns. Here, we quantified long-term spatial and temporal patterns of inorganic N deposition in protected aridland ecosystems across an extensive urban-rural gradient using multiple sampling methods. We compared long-term rates of N deposition from ion-exchange resin (IER) collectors (bulk and throughfall, 2006–2015), wet-dry bucket collectors (2006–2015), and dry deposition from the inferential method using passive samplers (2010–2012). From mixed approaches with IER collectors and inferential methods, we determined that 7.2 ± 0.4 kgNha^{-1}y^{-1} is deposited to protected Sonoran Desert within metropolitan Phoenix, Arizona and 6.1 ± 0.3 kgNha^{-1}y^{-1} in nearby desert ecosystems. Regional scale models overestimated deposition rates for our sampling period by 60% and misidentified hot spots of deposition across the airshed. By contrast, the easy-deployment IER throughfall collectors showed minimal spatial variation across the urban-rural gradient and underestimated deposition fluxes by 54%, largely because of underestimated dry deposition in throughfall. However, seasonal sampling of the IER collectors over 10 years allowed us to capture significant seasonal variation in N deposition and the importance of precipitation timing. These results, derived from the longest, spatially and temporally explicit dataset in drylands, highlight the need for long-term, mixed methods to estimate atmospheric nutrient enrichment to aridlands in a rapidly changing world.

1. 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). N gas emissions from urban and agricultural sources are transported downwind and deposited upon surfaces through rainfall (wet deposition), cloud vapor, and adsorption of gases and particles (dry deposition). Increasing rates of N deposition during decades of agricultural and industrial growth, and the significant ecological consequences of increased rates, have been well characterized in ecosystems with high rainfall (Lovett, 1994; Aber et al., 1998; Galloway et al., 2004; Holland et al., 2005; Dentener et al., 2006; Phoenix et al., 2006; Weathers et al., 2006; Pardo et al., 2011). However, N deposition is also expected to increase in dryland ecosystems where a disproportionate amount of future urban growth is anticipated (United Nations, 2014). While arid and semi-arid ecosystems cover over a third of the globe's land area, far more effort has been put into quantifying patterns of N deposition to mesic compared to aridland ecosystems.

Although water constrains primary production in aridlands, N availability significantly affects ecosystem functioning during wet

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periods and within landscape patches with prolonged access to soil water (Hall et al., 2011; Ladwig et al., 2012; Collins et al., 2014). However, precipitation variability in drylands decouples plant and soil processes, making it unlikely that arid ecosystem functioning will respond to N deposition according to the forest N saturation model in temperate ecosystems (*sensu* Aber et al., 2002; Hall et al., 2011). The few studies examining the effects of elevated N inputs to arid ecosystems have reported increases in annual herbaceous (but not perennial) plant growth, losses of native vegetation, and greater fire frequency (Brooks, 2003; Fenn et al., 2003a; Báez et al., 2007; Rao et al., 2010; Hall et al., 2011). Such responses, particularly during wet periods, may have cascading effects on ecosystem services, including carbon storage (Ochoa-Hueso et al., 2013; Poulter et al., 2014). Many aridland ecosystems are predicted to receive atmospheric N inputs at or above the desert critical load, the threshold at which many ecological changes occur (Fenn et al., 2010; Pardo et al., 2011). Deposition rates as low as 3–9 $kgNha^{-1}y^{-1}$ can alter the seasonal growth and composition of herbaceous plant communities (Fenn et al., 2003a, 2010; Pardo et al., 2011; Simkin et al., 2016). By comparison, in central and southern California, United States (US)—one of the few places where aridland N deposition has been well studied—dry deposition alone is estimated to be as high as 14–35 $kgNha^{-1}y^{-1}$ (Alonso et al., 2005; Rao et al., 2009; Cisneros et al., 2010).

Long-term atmospheric deposition in aridlands is challenging to estimate in part due to the pulsed nature of precipitation, where episodic and often intense, rainfall events punctuate long dry periods (Noy-Meir, 1973; Collins et al., 2014). Despite this, long-term monitoring is important for evaluating ecosystem changes, conservation strategies, and policies controlling N emissions (Holland et al., 2005; Lovett, 2013). For example, since the 1990 US Clean Air Act amendments, the composition of N deposition in the US has changed from primarily oxidized N (e.g., nitrogen oxides (NO_x)) to reduced N forms (e.g., ammonia (NH_3); Du et al., 2014; Li et al., 2016; Lloret and Valiela, 2016), reflecting a broad shift from industrial to agriculture sources. While changing patterns of N deposition have been examined at the national scale, much less is known about regional long-term deposition in aridlands. This study addresses the challenges of estimating aridland inorganic N deposition using multiple methods across an urban-rural and precipitation gradient to capture long-term and seasonal patterns of wet and dry N deposition.

Most N deposition studies employ a single empirical or modeling approach to estimate wet and dry deposition over relatively short time periods. However, single approaches can lead to uncertainty under temporally and spatially heterogeneous environmental conditions common to aridlands. For example, throughfall measurements likely misrepresent deposition because leaf surfaces can become saturated with dry deposition during periods without rain and N may volatilize off surfaces before being washed into throughfall collectors (Fenn et al., 2000, 2009; Padgett et al., 2008). While wet deposition is an important seasonal input to arid systems (Báez et al., 2007; Li et al., 2013), dry deposition—much of which is expected to be dry NH_3—can contribute up to 80% of atmospheric inputs to arid landscapes between patchy storm events (Lohse et al., 2008; Fenn et al., 2010; Li et al., 2013, 2016). Dry deposition itself is challenging and costly to quantify because of the short life span of many atmospheric gases, volatilization, saturated leaf surfaces, and the bidirectional fluxes of NH_3 (Hanson and Lindberg, 1991; Lovett, 1994; Asman et al., 1998; Wesely and Hicks, 2000; Golden et al., 2008; Lohse et al., 2008; Fenn et al., 2013; Bytnerowicz et al., 2015).

Various N deposition modeling approaches also have limitations that introduce considerable uncertainty. For example, the inferential method estimates dry deposition based on deposition velocities and atmospheric concentrations of NH_3, NO_x, and nitric acid (HNO_3)—composing most of the deposited N gases (Holland et al., 2005). Deposition velocities are dependent on heterogeneous landscape characteristics, and the error in deposition velocity estimates propagate uncertainty of dry deposition (Schwede et al., 2011). Additional uncertainty arises from the bidirectional flux of NH_3, which is the difficult to quantify ecosystem-atmosphere exchange of N regulated by variable compensation points, atmospheric concentrations, canopy structure, and meteorological conditions (Asman et al., 1998; Zhang et al., 2010; Zhu et al., 2015b). Finally, N deposition estimates from regional-scale models (e.g., Community Multi-scale Air Quality (CMAQ) model) and national monitoring networks are limited in spatial resolution (e.g., 12 × 12-km; Fenn et al., 2003b; Holland et al., 2005; Bettez and Groffman, 2013; Fenn et al., 2013). In spatially heterogeneous aridland ecosystems, low-resolution models constrain the ability to examine habitat-scale deposition patterns that vary with topography and intermittent shrub cover.

In this paper, we use a unique long-term study that integrates multiple methods to address the question: what are the patterns and drivers of wet and dry inorganic N deposition in a dryland region? We assessed inorganic N deposition across a precipitation and urban-rural gradient encompassing several thousand km^2 in central Arizona in the northern Sonoran Desert. With rapid urban sprawl and over 4 million residents, the Phoenix metropolitan region and Sonoran Desert are affected by land use change, the urban heat island, and elevated reactive N gas emissions (Brazel et al., 2000; Baker et al., 2001; Grimm and Redman, 2004). Municipal ordinances have preserved large remnant patches of native Sonoran Desert arrayed along a precipitation gradient (ranging from 131 to 282 $mm\text{-}y^{-1}$; mean annual precipitation of 208-mm). This feature makes the region not only a unique study system for examining N deposition and its drivers in aridlands, but also a potentially critical carbon sink during a period of increasing anthropogenic carbon dioxide emissions (Poulter et al., 2014).

We quantified wet and/or dry inorganic N deposition continuously over 10 years (2006–2015) in the Central Arizona–Phoenix Long-Term Ecological Research (CAP LTER) study area using four different methods: co-located throughfall collectors (wet and dry deposition), bulk collectors (wet deposition), wet-dry buckets (wet and dry deposition), and passive atmospheric concentration samplers (dry deposition via inferential method). In this rapidly urbanizing area, we expected N deposition to vary spatially and seasonally, dependent on precipitation and proximity to urban activities. In particular, we predicted that the rate of inorganic N deposition would exceed the estimated desert critical load (3–9 $kgNha^{-1}y^{-1}$) with deposition primarily dominated by reduced forms of N. We also expected wet deposition patterns to follow a precipitation gradient from west to east (Table 1). Because storms are seasonal and spatially patchy, we expected the timing of rain and extended dry periods to affect the rate and form of N deposition. Thus, we predicted higher rates of wet N deposition during the semi-annual rainy seasons (i.e. associated with low-intensity winter storms and high-intensity summer monsoons) than dry seasons. However, overall, we expected dry deposition would compose the largest fraction of total annual inorganic N deposition due to long dry periods between rains.

2. Materials and methods

2.1. Wet and dry inorganic N (NH_4^++NO_3^-) deposition estimated from throughfall and bulk collectors

We measured bulk and throughfall ammonium (NH_4^+) and nitrate (NO_3^-) deposition continuously from March 2006 to June