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Sources and transport of nitrogen in arid urban watersheds

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Abstract

Urban watersheds are often sources of nitrogen (N) to downstream systems, contributing to poor water quality. However, it is unknown which components (e.g., land cover and stormwater infrastructure type) of urban watersheds contribute to N export and which may be sites of retention. In this study we investigated which watershed characteristics control N sourcing, biogeochemical processing of nitrate (NO_3^-) during storms, and the amount of rainfall N that is retained within urban watersheds. We used triple isotopes of NO_3^- ($\delta^{15}N$, $\delta^{18}O$, and $\Delta^{17}O$) to identify sources and transformations of NO_3^- during storms from 10 nested arid urban watersheds that varied in stormwater infrastructure type and drainage area. Stormwater infrastructure and land cover—retention basins, pipes, and grass cover—dictated the sourcing of NO_3^- in runoff. Urban watersheds were strong sinks or sources of N to stormwater depending on runoff, which in turn was inversely related to retention basin density and positively related to imperviousness and precipitation. Our results suggest that watershed characteristics control the sources and transport of inorganic N in urban stormwater but that retention of inorganic N at the timescale of individual runoff events is controlled by hydrologic, rather than biogeochemical, mechanisms.

Introduction

Urban watersheds are often sources of nitrogen (N) and other pollutants to downstream systems[1–4]. At the same time, numerous studies have documented high rates of N retention in urban watersheds[2,5–7], albeit usually not as high as those of non-urban systems. Retention (here defined as the difference between inputs and watershed export[2,7]) includes internal processes such as denitrification or volatilization that result in gaseous loss of N from the watershed and thereby reduce the N load in runoff. N may also be retained in watersheds via immobilization in soils and/or assimilation into plant or microbial biomass, or it may simply be stored due to lack of hydrologic transport. Whatever the mechanism, it is clear that urban watersheds have some capacity to modulate pollutant loads to downstream ecosystems. However, we do not know which watershed features (e.g., land-use or cover types, stormwater infrastructure features) contribute most to N export and which may be sites of retention, making it difficult to manage urban nonpoint source N pollution.

Observed high N retention rates in urban watersheds have led to an effort to identify specific locations within watersheds that support high rates of N retention, so-called "hotspots"(sensu McClain et al.[8]). Terrestrial ecologists have focused largely on the role of residential landscapes—yards—as potential hotspots [9–11], whereas aquatic ecologists have studied streams and stormwater infrastructure features as sites of N removal[12–19]. The potential rates of denitrification in urban yards [10,11] and retention basins [13,16] are very high, and a recent study in Tucson, AZ found large fluxes of nitrous oxide (N_2O) from urban ephemeral stream channels following wetting[19], suggesting that these systems may also be hotspots of N removal. However, it is not clear how the biogeochemical functioning of these systems affects N retention and transport at the watershed scale. Furthermore, the relative importance of yards compared

with streams and stormwater infrastructure features as hotspots of N removal has not been determined.

The sources of N in urban stormwater are also not always well understood. Sourcing studies in mesic cities[4,20,21] show that atmospheric NO_3^- and sewage or septic waste are the dominant sources of NO_3^- in urban surface waters[4,20], but these generalizations may not apply to newer cities in arid regions[22]. Deep groundwater tables in arid (relative to mesic cities) may reduce the importance of leaks from sanitary sewers as a source of N to streams, and hydrologic differences between cities, such as precipitation regimes and subsurface hydrology, may also alter opportunities for biogeochemical N transformations. Furthermore, urban landscaping in arid cities includes not only mesic lawns, but also "xeriscapes" that are planted with drought-tolerant plants. Differences in the management and ecological functioning of these systems[11] may lead to patterns of N sources and transformations that differ from those observed in mesic cities. In addition, recent conceptual advances have suggested that urban biogeochemistry varies across scales[23], yet it is unknown how N sources might vary with watershed size.

Previous findings in Arizona[24–26] demonstrated that stormwater N export is primarily a function of runoff, with biogeochemical processes playing a minor role. However, other research has found that increasing hydrologic residence time increases opportunities for biogeochemical transformations across a range of ecosystem scales from individual small streams to large watersheds [27–30]. Furthermore, Hale et al.[26] found that spatial and temporal patterns of event-specific N export can be variable. Wet N deposition is highly variable in both space and time[31]; yet how this variability in wet N deposition translates to spatial and temporal patterns of stormwater N export has not been evaluated. Thus, the overarching aim of this study was to

104 understand mechanisms and watershed structural controls regulating the source and retention of
105 N in urban stormwater systems.
106 Specifically, the first question we addressed was: (Q1) At the timescale of rainfall-runoff
107 events, how much dissolved inorganic N is exported from watersheds in runoff compared to N
108 inputs via rainfall? To determine the extent to which N exported in flow is derived directly from
109 precipitation, we then asked: (Q2) What are the sources and transformations of stormwater NO_3^-
110 in arid urban watersheds? To refine further our understanding of variability in sources of
111 stormwater NO_3^-, we asked: (Q3) Which watershed features (land cover and stormwater
112 infrastructure) are important in determining source characteristics?
113
114 **Methods**
115 *Study Site*
116 N sourcing and retention were evaluated in the Central Arizona–Phoenix Long-Term
117 Ecological Research (CAP LTER) study area, located in the Phoenix, AZ metropolitan region
118 (hereafter Phoenix). Phoenix is a rapidly growing urban area with a population of ~4.3 million
119 and an extensively modified hydrologic system[32–35]. It is located in the Sonoran Desert, where
120 the climate is hot and dry. Precipitation averages 180 mm annually, but ranges widely within and
121 between years. On average, about half of the annual rainfall falls during the summer monsoon
122 season, and half falls during the passages of winter frontal storm systems. Summer convective
123 storms have intense localized rainfall, whereas winter storms tend to feature longer duration,
124 low-intensity rains over broader areas.
125 Stormwater in Phoenix, as in other cities, is managed with a variety of stormwater
126 infrastructure designs, including storm sewers, engineered open channels, and retention basins.

We sampled rain and runoff from10 nested urban watersheds that varied in stormwater infrastructure type and drainage area (see Hale et al.[26] and Supplemental Information for site information and descriptions of infrastructure designs). Due to the arid climate, these watersheds do not have baseflow and produce runoff only in response to rain. Land use in the seven smallest watersheds was characterized as predominately residential; these watersheds differed in area and stormwater infrastructure design. The two smallest watersheds (6-10 ha) were drained by surface drainage by pipes only. The other five small watersheds ranged from 18 ha to 141 ha in size and were drained primarily by pipes, engineered channels, or retention basins. The three largest watersheds (1,662-20,247 ha) had a mix of land uses (residential, commercial, industrial, and open desert) and stormwater infrastructure types, and are herein referred to as "integrator" watersheds.

Event N Retention

Stormwater and precipitation samples were collected for all storm events from August 2010 to August 2012. Detailed methods for estimating retention of dissolved inorganic N (DIN) for each event can be found in the Supplemental Information. Automated pump samplers [ISCO® (Lincoln, Nebraska, USA)] were used to collect discrete stormwater samples from the outlet of each watershed during storm events. Stage height was monitored using ISCO® 730 bubbler modules. Rainfall for discrete rainfall events was collected in acid-washed, 1-L bottles fitted with a funnel and stopper that were co-located with pump sampler locations and deployed immediately prior to storms. Rainfall samples were collected for 4 events for which there was the best coverage of sites: 5 Nov 2011, 7 Nov 2011, 13 Dec 2011, and 30 Jul 2012, enabling us to estimate event-scale DIN budgets across the watersheds. Rainfall and runoff samples were

centrifuged to remove particulate material and analyzed for NH_4^+ and NO_3^- using a Lachat Quick Chem 8000 Flow Injection Analyzer.

Event-scale DIN retention was then calculated as a proportion:

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

where the DIN load in rainfall was calculated by multiplying the rainfall DIN concentration by watershed area and rainfall depth, and the runoff, DIN was calculated by multiplying the DIN concentrations in runoff (extrapolated over the hydrograph from time-discrete measurements) by discharge (Hale et al.[26]; further detail on methods used in the Supplemental Information).

Isotopic Analysis

Analysis of N and O isotopes of NO_3^- was performed on water from three storms, 5 Oct 2010, 7 Nov 2011, and 13 Dec 2011, during which the majority of the watersheds flowed. These rainfall (N=21) and stormwater (N=180) samples were filtered through ashed Whatman GF/F filters and frozen immediately. We also collected soil and impervious-surface samples for NO_3^- isotopic analysis (see Supplemental Information for details). Briefly, 5-cm deep soil cores were sieved to 2 mm and extracted with nanopure water. To characterize N sources from impervious surfaces, a small-diameter (470 cm^2) PVC ring fitted with foam tape was used to create a temporary seal with concrete (i.e., sidewalks) and asphalt surfaces (i.e., roads). Then, 1 L of deionized water was added and agitated to ensure dissolution of any soluble material that had accumulated on the surface. The resulting solution was collected using a peristaltic pump. These water samples were transported on ice to the laboratory where they were processed using the same protocols as for stormwater runoff.

Frozen water samples were shipped on ice to the Purdue Stable Isotope Facility for isotopic analysis of NO_3^- ($\delta^{18}O$, $\delta^{17}O$, and $\delta^{15}N$) using the denitrifier gold-tube thermal-reduction method[36–38]. NO_3^- was denitrified to N_2O by a pure culture of denitrifying bacteria. The N_2O samples were then thermally decomposed into N_2 and O_2, which were subsequently analyzed for $\delta^{15}N$, $\delta^{17}O$, and $\delta^{18}O$ on a Delta V Plus Thermo-Finnegan isotope ratio mass spectrometer. We report $\delta^{15}N$ relative to air-N_2, and $\delta^{17}O$ and $\delta^{18}O$ relative to the Vienna Standard Mean Ocean Water (VSMOW), where:

$$\delta = (R_{sample}/R_{standard} - 1) \times 1000,$$

and R is the ratio of the heavy to light isotope of the sample and the known standard. Precision of the $\delta^{15}N$ values was ±0.4‰, for $\delta^{18}O$ ±1.0‰, and for $\delta^{17}O$ ±0.3‰, based on replicate analysis of the working standards and calibrations.

Isotope mixing analysis was used to determine the fraction (f) of stormwater NO_3^- from atmospheric, fertilizer, and nitrified soil sources: $f_{atm} + f_{fert} + f_{nit} = 1$. $\Delta^{17}O$ values were used to estimate the fractional contribution of atmospheric NO_3^- (f_{atm}) to stormwater. Atmospheric NO_3^- is anomalously enriched in ^{17}O as a result of ^{17}O-enriched ozone that is then transferred to NO_3^- during the oxidation of NO_x[39,40]. The difference between the $\delta^{17}O$ value predicted by mass-dependent biological fractionation (described by relationship: $\delta^{17}O = 0.52(\delta^{18}O)$) and the $\delta^{17}O$ value of atmospheric NO_3^- is positive and is denoted $\Delta^{17}O$ [39]. $\Delta^{17}O$ values are conserved during mass-dependent fractionation (e.g., during denitrification) and can be used as a tracer of atmospheric NO_3^- deposition. The f_{atm} was estimated using[39–41]:

$$f_{atm} = \frac{\Delta^{17}O_{sample}}{\Delta^{17}O_{atmosphere}}$$

The runoff NO_3^- isotopic values were transformed using f_{atm} to remove the atmospheric NO_3^- $\delta^{15}N$ and $\delta^{18}O$ contribution in the runoff NO_3^- following the methods of Dejwakh et al.[41]:

$$\delta^{18}O_{trans} = (\delta^{18}O_{runoff} - f_{atm}(\delta^{18}O_{atm}))/ (1-f_{atm})$$

$$\delta^{15}N_{trans} = (\delta^{15}N_{runoff} - f_{atm}(\delta^{15}N_{atm}))/ (1-f_{atm})$$

where $\delta^{18}O_{trans}$ and $\delta^{15}N_{trans}$ are the isotopic values with the atmospheric signal removed and $\delta^{15}N_{atm}$ and $\delta^{18}O_{atm}$ are the average isotopic values of rainfall NO_3^-.

A second mixing model was used to separate the fractions of fertilizer NO_3^- (hereafter $NO_3^-_{fert}$) and microbially nitrified NO_3^- (hereafter $NO_3^-_{nit}$):

$$f_{fert} = (1 - f_{atm}) \times \frac{(\delta^{18}O_{trans} - \delta^{18}O_{soil})}{(\delta^{18}O_{fert} - \delta^{18}O_{soil})}$$

where f_{fert} is the fractional contribution of fertilizer to runoff NO_3^- as a fraction. The fractional contribution of $NO_3^-_{nit}$ (f_{nit}) was calculated by difference (1-(f_{atm}+f_{fert})). An average $\delta^{18}O$ value of 21‰ for $NO_3^-_{fert}$[42] and the average measured $\delta^{18}O$ of soil NO_3^- were used as isotope end-members in the mixing model. We assessed the sensitivity of our results to the $\delta^{18}O$ value of fertilizer by also assessing the model for the minimum (17‰) and maximum (25‰) reported $\delta^{18}O$ values for NO_3^- fertilizer.

Statistical Analysis

All data were transformed as needed to meet assumptions of normality and homogeneity of variance. One-way analysis of variance (ANOVA) was used to test for differences in isotopic composition of NO_3^- across different source types (rain, mesic, xeric, concrete, asphalt). To understand watershed controls on NO_3^- sources, we used multiple linear regression to characterize relationships between land cover (% impervious, grass, and soil cover), stormwater infrastructure (density of retention basins, pipes, and channels), storm variables (runoff coefficient, storm duration, rain-free and flow-free days preceding the event, and rain depth) and the proportion of NO_3^- sources (f_{atm}, f_{fert}, f_{nit}) in stormwater runoff. Pearson correlation was used

to determine the relationship between $\delta^{18}O$ values and $\delta^{15}N$ values of NO_3^- within events. All statistical analyses were conducted in R version 2.15.1 (www.r-project.org).

Results and Discussion

Urban watersheds can be strong sinks or sources of N to stormwater

Inputs of DIN in rainfall varied considerably across sites and events, ranging from 0.02 kg/ha to 0.32 kg/ha, and total event DIN export also ranged widely, from < 0.001 to 0.78 kg DIN/ha (Fig. 1). Most of the study watersheds were sinks for N at the timescale of discrete rainfall-runoff events, although the pipe- and surface-drained watersheds were sometimes sources of N downstream (Q1). Study watersheds were sinks rather than sources of DIN in 25 out of 29 events. DIN retention ranged from -314% to nearly 100% of rainfall inputs.

To our knowledge, these retention rates are the first reported at rainfall-runoff event timescales in urban watersheds, and some of the highest reported in the literature for urban watersheds across all timescales. Event N balances in the study watersheds reported here were also more variable than previous measures of urban watershed-scale N retention, varying in both the order of magnitude of retention as well as the sign (e.g., source vs. sink). By comparison, annual N retention in suburban watersheds of the Northeast ranged from 35 to 85% of annual inputs [2,4,6,7].

Much of the variation in DIN retention was due to variation in runoff, as has been observed at annual scales[4,7]. The proportion of DIN retained by each watershed was significantly related to the event runoff coefficient (runoff/precipitation; ANCOVA, $F_{(1, 25)}=28.72$, $p<0.0001$), and there was a significant interaction with the number of no-flow days preceding the storm (ANCOVA: $F_{(1,25)}=5.231$, p=0.03, Fig. 2), although no-flow days alone was not a significant

predictor (ANCOVA: $F_{(1,25)}$=2.199, p=0.15). The interaction with antecedent conditions, the number of days with no flow preceding the event, was such that retention was decreased by increasing no flow days. This suggests that drier antecedent conditions allow accumulation of N within the watershed, providing more sources of N to stormwater and reducing overall retention.

Watersheds with runoff coefficients greater than ~0.45 tended to be weak sinks or even sources depending on the site and the event. Runoff coefficients in these study watersheds, in turn, were strongly and negatively related to retention basin density and watershed area and positively related to impervious cover and precipitation (Hale et al.[26]). In these watersheds, therefore, retention basin density was associated with increased DIN retention at the watershed scale, whereas the imperviousness and precipitation was associated with decreased DIN retention at the watershed scale. Larger watersheds also had lower runoff coefficients and therefore retained more DIN, as noted by Lewis and Grimm[43].

Sources of NO_3^- in urban stormwater

The isotopic composition of NO_3^- varied significantly across rainfall, soil, and impervious surfaces (Fig. 3). Values of $\delta^{15}N\text{-}NO_3^-$ varied among source types, with higher $\delta^{15}N$ values in soil and impervious surfaces (potential watershed sources) than in rain (Fig. 3, Supplemental Information). Values of $\delta^{18}O$ and $\Delta^{17}O$ of NO_3^- in rainfall were significantly higher than both impervious surface and soil sources (Fig. 3). Within watersheds, NO_3^- collected from impervious surfaces had the highest $\delta^{18}O$ and $\Delta^{17}O$ values. The isotopic composition of NO_3^- from xeric and mesic yards did not differ (Fig. 3).

Isotopic evidence suggests that fertilizer, atmospheric, and microbial sources all contribute to NO_3^- in stormwater (Fig. 4). Overall, fertilizer was the largest source of NO_3^- in

stormwater, contributing from 6 to 65% of stormwater runoff NO_3^- loads (44% on average; Fig. 5). These values are very high compared to other urban studies that have found fertilizer to be only a minor component of stormwater NO_3^- [4,20,44]. The contribution of fertilizer NO_3^- was not strongly sensitive to the $\delta^{18}O$ value of fertilizer chosen. The mean fertilizer contribution ranged from 38% to 50% depending on the $\delta^{18}O$. We attribute the high $NO_3^-_{fert}$ contribution to very high amounts of fertilizer used in Phoenix: annual fertilizer N inputs, estimated at 223 kg N ha lawn^{-1} y^{-1} by Baker et al.[5], are likely one to two orders of magnitude higher than those from atmospheric deposition. Assuming that 50% of all pervious areas are fertilized[5], this would be the equivalent of 69 to 130 kg N ha^{-1} y^{-1} input via fertilization, an order of magnitude larger than estimates of total annual N deposition of <6 to 18 kg/ha [45,46].

As in previous studies[4,20,47,48], we found that f_{atm} in urban stormwater was high, averaging 34%. The contribution of $NO_3^-_{atm}$ to total NO_3^- export from watersheds ranged from 4 to 53% across all observed events (Fig. 5), and observations of f_{atm} for individual samples within events ranged much more widely (0 to 80% over all samples). Previous work has found that while wastewater is a major source of N to urban baseflow, atmospheric sources tend to dominate during storms[4,20,44,47], which, due to the absence of baseflow, was the only component of flow measured in this study. This pattern of increased f_{atm} under high flows is common across climates and land-use types[44,48–51]. A review by Curtis et al.[51] found that $NO_3^-_{atm}$ could comprise up to 100% of stream NO_3^- in forested watersheds during high-flow and snowmelt events. In other urban watersheds, f_{atm} ranges widely, but has been observed to contribute up to 94% of NO_3^- in streamflow during storms[4].

Microbially nitrified NO_3^- contributed an average of 24% of NO_3^- in stormwater runoff, though this source varied across events and sites as well (range = 0 to 75%; Fig. 5). The largest

284 microbial contribution to stormwater NO_3^- (75%) was observed at the largest watershed scale
285 (20,247 ha), in the Indian Bend Wash watershed. All other watersheds had f_{nit} between 0 and
286 38%. Although the f_{nit} was small relative to fertilizer and atmospheric sources for most
287 watersheds, the presence of microbially nitrified NO_3^- suggests active biogeochemical
288 processing in these urban watersheds. Evidence discussed below suggests these microbially
289 mediated biogeochemical transformations occur between, rather than during events.
290
291 *NO_3^- sources are related to land cover and infrastructure, not hydrologic factors*
292 The contribution of NO_3^- from atmospheric and microbial sources was significantly
293 related to land cover and stormwater infrastructure characteristics, but not to storm
294 characteristics. The contribution of $NO_3^-{}_{fert}$ was not significantly related to any watershed or
295 storm characteristics. Although fertilizer use is likely related to pervious cover, the timing of
296 fertilizer applications may vary within a watershed, obscuring any relationship between land
297 cover and f_{fert}. Unlike previous studies[20,44,47,52], we did not find a significant relationship between
298 f_{atm} and total or connected impervious surface cover. We did find, however, that % grass and the
299 density of retention basins were inversely correlated with f_{atm}. The maximum observed f_{atm} within
300 an event was significantly and negatively related to the amount of grass cover within a watershed
301 ($R^2 = 0.44$, $p = 0.002$), but was not significantly related to any other watershed or storm
302 characteristics. The f_{atm} of total event NO_3^- loads, however, was significantly and negatively
303 related to the density of retention basins and significantly and positively related to the density of
304 pipes within a watershed (multiple regression: total $R^2 = 0.49$, $p = 0.004$). This result suggests
305 that grass cover and retention basins either remove $NO_3^-{}_{atm}$, or that NO_3^- from other sources
306 (fertilizer or microbial nitrification) mask the atmospheric fraction. The positive relationship

between f_{atm} and pipe density suggests that pipes act as inactive conduits between impervious surfaces and watershed outlets and reduce opportunities for both NO_3^- transformations and the introduction of additional NO_3^- sources.

Previous work has suggested that impervious areas act as collectors of atmospheric deposition and should therefore be good predictors of atmospheric NO_3^- contribution[20,44,47,52]. In contrast, our results suggest that grass cover and stormwater infrastructure together influence f_{atm} in stormwater. Atmospheric NO_3^- deposition to yards is dwarfed by inputs of fertilizer N, which dilutes the atmospheric signal. However, despite much greater inputs to yards, the amount of NO_3^- stored in topsoil was less than amount stored on impervious surfaces (Supplemental Information, Fig. S2). Our results suggest that the high rates of denitrification documented in yards [9–11,15] and stormwater retention basins[13,17,35] rapidly consume the anthropogenic inputs of NO_3^-, thus altering its isotopic composition.

Whereas f_{atm} was lower in watersheds with high retention basin density, the contribution of $NO_3^-{}_{nit}$ to stormwater NO_3^- loads was positively correlated with the density of retention basins within watersheds ($R^2 = 0.37$, $p = 0.006$). This result provides further evidence that these stormwater features are important sites of biogeochemical activity. Although recent work in Tucson, AZ has demonstrated that ephemeral urban channels are biogeochemical hotspots[18,19,24], we did not find a relationship between channel density and f_{nit}.

No evidence of denitrification occurring during runoff events

We found no isotopic evidence of denitrification during rainfall-runoff events, suggesting that NO_3^- retention at the event scale is via hydrologic mechanisms. A significant positive relationship between $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values would indicate denitrification[42];

no such relationship was found. At the two surface-drained watersheds there were significant negative correlations between $\delta^{15}N$ and $\delta^{18}O$ ($\rho = -0.87$, $p < 0.05$ and $\rho = -0.63$, $p < 0.05$) during the 13 December 2011 event. These results support findings from other studies suggesting that variation in NO_3^- isotopes in urban[4,20,47,48,50,53] and non-urban[48,49] waters is primarily a result of the mixing of sources rather than biogeochemical processing along flowpaths during runoff events. Across a range of land uses, isotopic evidence of denitrification at the watershed scale has only been documented during baseflow conditions and is largely limited to agricultural watersheds [4,21,54]. It is important to note that a lack of isotopic evidence of denitrification does not preclude its occurrence. Several previous studies have noted that heterogeneous sources of NO_3^- can obscure signals of denitrification[21,52], and the wide variety of landscape management practices within our study watersheds would likely mask any isotopic signals of denitrification during events. That said, isotopic evidence of denitrification was documented in a suburban watershed[4] with similar land cover to our study watersheds (though in a different climate).

These results are in contrast to previous studies that have identified yards[11], retention basins[13,35], and channels[18,19] as hotspots of biogeochemical activity. It may be that these biogeochemical retention mechanisms are small relative to hydrologic retention mechanisms during runoff events due to retention of most rainfall in some watersheds (Fig. 2). Alternatively, retention mechanisms, such as denitrification, may be balanced by processes that increase the availability of N, or biogeochemical transformations may not be spatially or temporally consistent enough to observe at the watershed scale. For example, Gallo et al.[18] found that grass-lined channels had highly variable source-sink dynamics during runoff events and were a source of solutes in nearly half of observations. In another Tucson study, pervious channel density was associated with decreases in NO_2^- and NH_4^+ concentrations but had no relationship with NO_3^- or

dissolved organic N concentrations[24]. However, biogeochemical processes that are triggered by rainfall events may be sustained for extended periods of time after events[19], suggesting that gaseous N losses may be significant between events even if they do not affect concentrations of N in stormwater.

Sources and transport of stormwater NO_3^- across scales

The largest study watershed, Indian Bend Wash (IBW), differed substantially from the others in its isotopic composition of NO_3^-. Nitrate in IBW was dominated by $NO_3^-{}_{nit}$ (75%), with some contribution from fertilizer and very little $NO_3^-{}_{atm}$ (Fig. 5). The sampling location for IBW is located below a large flood-management system that includes a lake and stream system and a large grassy floodplain[34]. Between storms, the lakes are kept filled by pumping groundwater[34]. It is likely that this groundwater contributes to stormwater, an interpretation that is consistent with the very high concentrations of NO_3^- observed at IBW during the 13 December 2011 event compared to rainwater and runoff from all other watersheds (data not shown). The isotopic signature of NO_3^- at IBW was not only distinct, but was also much less variable than the signature of NO_3^- at the other sites, suggesting that most of the NO_3^- was coming from a different, more homogeneous source—probably groundwater.

The dramatic difference in NO_3^- sources between IBW and the other watersheds highlights the difficulty of scaling biogeochemical results in urban watersheds. The classic River Continuum Concept (RCC)[55] was developed to explain gradual and continuous longitudinal changes in stream and river geomorphology and ecology. An implicit assumption of this model was that small-scale observations can be scaled up to predict patterns in larger rivers. Thorp[56] recently argued that concepts such as the RCC fall short because spatial heterogeneity and cross-

scale interactions in watersheds create nonlinearities and thresholds that make it impossible to predict large scale patterns simply by scaling up small scale observations. Despite these failings of the RCC, the concept has been recently adapted in urban watershed systems as the Urban Watershed Continuum[23]. We suggest that the issues discussed by Thorp[56] are especially important in urban watersheds, where nonlinearities and thresholds are generated not only by ecological processes, but by social processes as well. As watershed scale increases in urban watersheds, the complexity and heterogeneity of human behaviors and engineered structures increases. New human behaviors emerge at larger scales that complicate our efforts to scale up small-scale observations.

In this study, NO_3^- sourcing changed nonlinearly across scales (Fig. 6). NO_3^- sources were similar across all watersheds, regardless of watershed size, but it was the introduction of a new human behavior (groundwater inputs), rather than a specific scale, that caused change in N biogeochemistry. If we were to move to even larger scales, we would likely find that wastewater effluent and agricultural irrigation return flow introduce new sources of NO_3^- to flow (Fig. 6). Heterogeneity in NO_3^- sources across and within urban watersheds makes it is extremely difficult to accurately scale up from small to large watershed scales.

Implications for arid urban stormwater management

The results of this study have significant implications for stormwater management in arid cities. Larson and Grimm[35] reported high rates of potential denitrification in stormwater retention basins in the Phoenix area, and Hale et al.[26] reported that N delivery was negatively related to the density of retention basins in a watershed. However, our isotopic results suggest that, even though retention basins change the isotopic composition of NO_3^- in stormwater, the mechanisms

399 driving N retention at the scale of rainfall-runoff events are primarily hydrologic, not
400 biogeochemical. This finding is particularly important because Larson and Grimm[35] found
401 differences in the potential rates of denitrification between xeric and grassy retention basins and
402 suggested that grassy retention basins may be more effective at removing N from stormwater
403 than xeric basins. Retention basin landscaping may be important for understanding the fate of N
404 once it has been retained in a basin. It is unclear whether N retained during storm events leaches
405 into the soil (possibly creating a groundwater pollution problem), remains stored in the retention
406 basins (to possibly be transported in subsequent storm events), is assimilated into vegetation, or
407 is converted to N gases (which may or may not be greenhouse gases)[18,19]. That retention basins
408 change the sources of NO_3^- but not the amount in stormwater suggests that these features are
409 biogeochemically active between events, but not necessarily in ways that are relevant for
410 stormwater quality protection at rainfall-runoff event timescales. Our results, in demonstrating
411 the importance of hydrology as a control on stormwater N delivery, suggest that these
412 differences in retention basin landscaping and biogeochemistry may not matter at the watershed
413 scale, as long as the basins retain water.
414

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421 ecosystems (SNAZ). Land cover classifications, based on National Agricultural Imagery

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Supporting Information

Detailed descriptions of study site and methods; Table S1. Characteristics of study watersheds; Table S2. Mean (standard deviation) of rainfall characteristics across the reported events, and rainfall depth across all storm events measured from August 2010 to August 2012; Figure S1. Location of study watersheds; Figure S2. Amount of NO_3^- stored on watershed surfaces.

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588 FIGURE CAPTIONS

589 Figure 1. Inputs of DIN in rainfall (positive values) and outputs in runoff (negative values) for
590 each site during 4 storms. Only data on NO_3^- and NH_4^+ are shown. Note that fluxes for each
591 event are not plotted on the same scale. Events for which there was no runoff, and therefore
592 nodata, are indicated by "nd." Note that for events with no runoff data, rainfall data are not
593 shown. Sites are arranged by drainage area.

594 Figure 2. Proportion of DIN retained by each watershed was significantly related to runoff
595 coefficient (ANCOVA, $F_{(1, 25)}$=28.72, p<0.0001), and there was a significant interaction with the
596 number of no flow days preceding the storm (ANCOVA: $F_{(1,25)}$=5.231, p=0.03).

597 Figure 3. Isotopic characteristics of NO_3^- in rainfall and sources within watersheds. Statistics are
598 results from one-way ANOVA. Boxes with different letters are significantly different at $p < 0.05$
599 using Tukey's HSD.

600 Figure 4. Dual isotope plot of means and standard deviations across all soil, rainfall, and runoff
601 samples across all events. a) untransformed means and standard deviations. In plot b, runoff data
602 has been transformed to remove atmospheric signal. Ranges of $\delta^{15}N$ and $\delta^{18}O$ values are shown
603 (from Kendall 2007).

604 Figure 5. Mean contribution of different NO_3^- sources to stormwater NO_3^- across all watersheds.

605 Figure 6. Illustration of observed and hypothesized changes in NO_3^- sources across scales in
606 Phoenix watersheds.

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610 FIGURES

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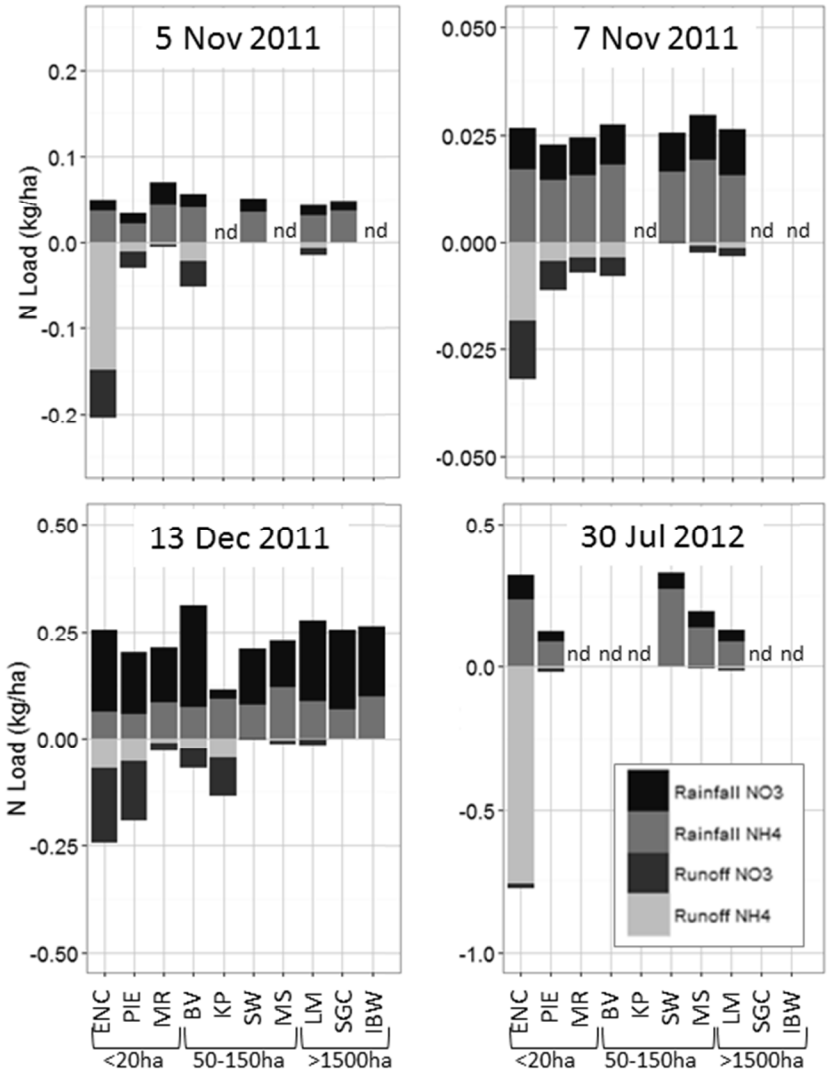

612

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616 events with no runoff data, rainfall data are not shown. Sites are arranged by drainage area.

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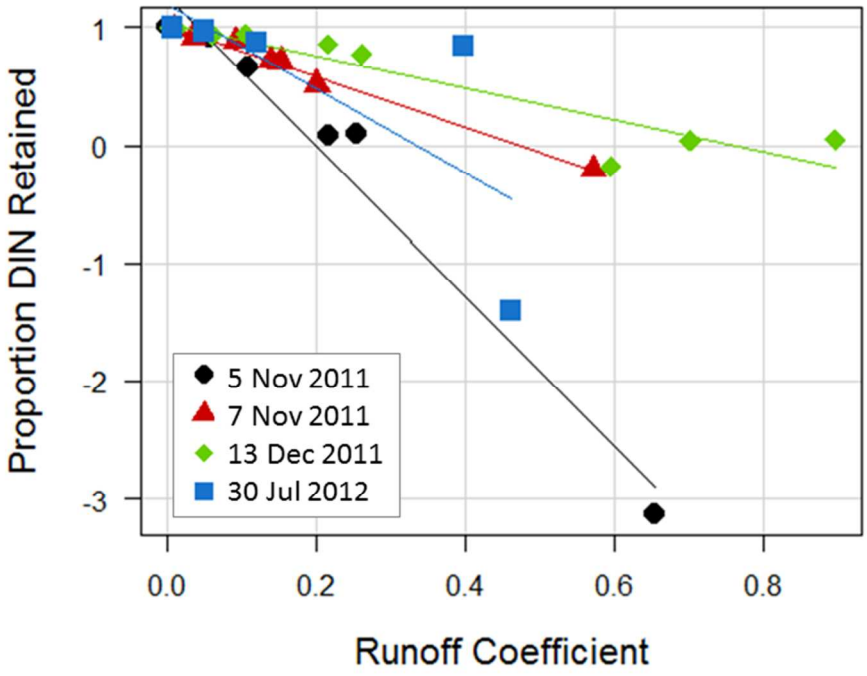

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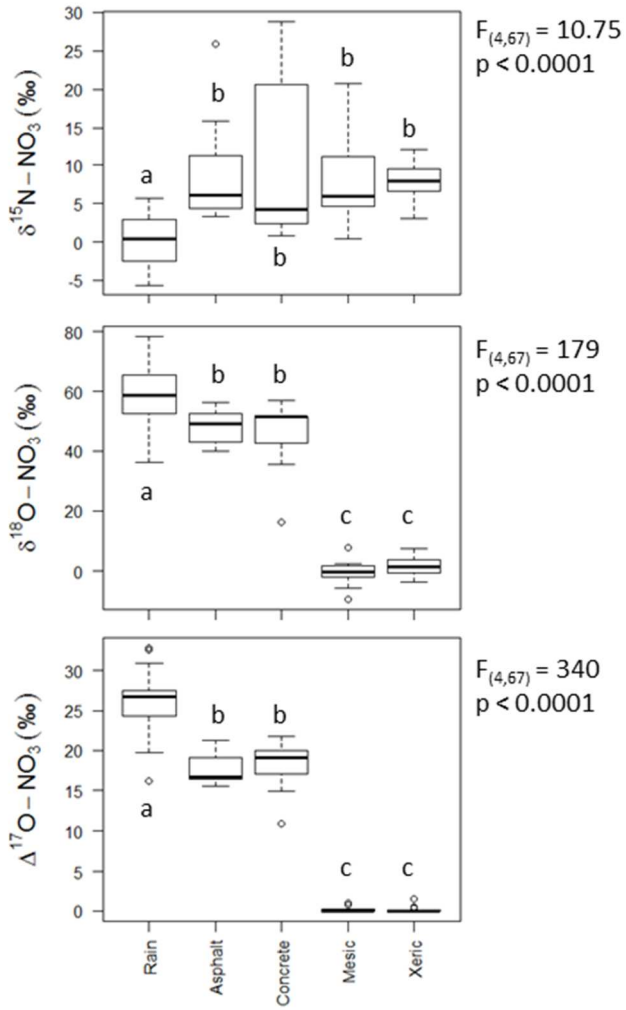

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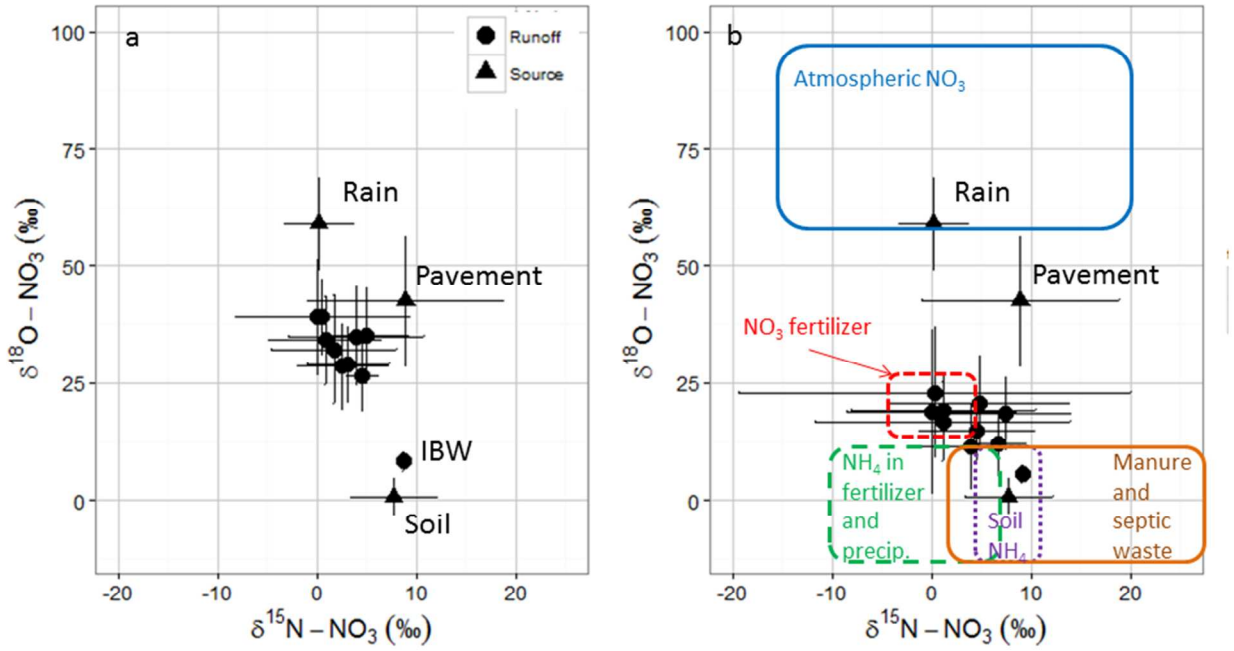
624 Figure 3. Isotopic characteristics of NO_3^- in rainfall and other potential sources within

625 watersheds. Statistics are results from one-way ANOVA. Boxes with different letters are

626 significantly different at $p < 0.05$ using Tukey's HSD. Mesic indicates yards with turf grass,

627 while Xeric indicates xeriscaped yards (i.e., low water use plants).



628

629 Figure 4. Dual isotope plot of means and standard deviations across all soil, rainfall, and runoff

630 samples across all events. (a) untransformed means and standard deviations. In plot b, runoff

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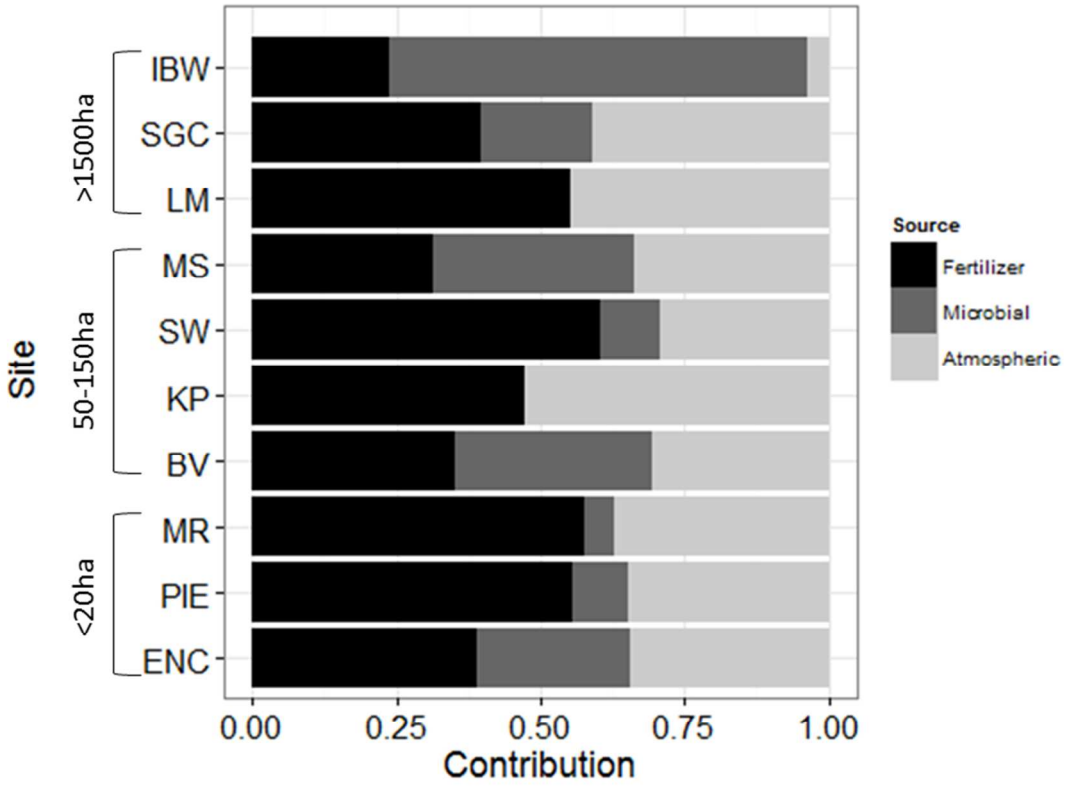

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635 Figure 5. Mean fractional contribution of different NO_3^- sources to stormwater NO_3^- for each

636 watershed. Sites (y-axis) are arranged by drainage area. See Supplemental Information for site

637 abbreviations and descriptions.

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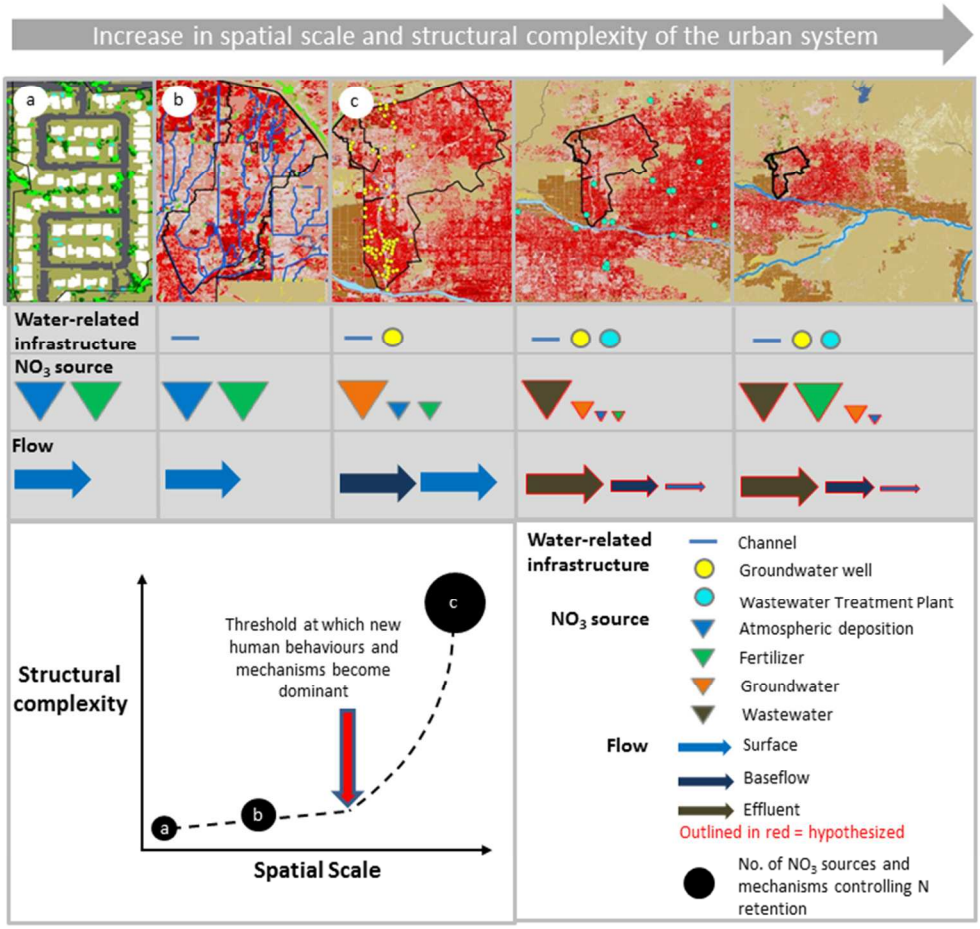

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644 Figure 6. Illustration of observed and hypothesized changes in NO_3^- sources across scales in

645 Phoenix watersheds.

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