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N retention and transformation in urban streams

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Abstract. Nutrient spiraling in theory and application provides a framework for comparing nutrient retention efficiency of urban streams to relatively unaltered streams. Previous research indicated that streams of the southwestern USA deserts are highly retentive of N because of N limitation, high productivity, and high channel complexity (in particular, extensive transient storage associated with the hyporheic zone). Most southwestern urban streams have extensively modified channels and experience N loading from urban runoff and inputs of NO_3^--contaminated groundwater. Therefore, we predicted southwestern urban streams are neither N-limited nor retentive. For some urban streams, however, restoration efforts reestablish flow in long-dry channels, create nonstructural flood-management solutions, and design riparian areas as a public recreation amenity. These human modifications may, in part, restore N retention functions if channel complexity and heterogeneity are as important to N retention efficiency as believed. We conducted experimental tracer studies using ^{15}N-NO_3^-, as part of the Lotic Intersite Nitrogen eXperiment (LINX) project, and several separate nutrient-addition experiments (using slight increases in NO_3^- concentration), to evaluate N retention in southwestern urban streams. We present preliminary results of those experiments, comparing results to similar experiments in unaltered streams to test our predictions. Our results allow an evaluation of the use of nutrient spiraling metrics as a tool for assessing the status of stream ecosystem services in urban restoration projects.

Key words: nitrogen, nutrient spiraling, uptake velocity, uptake length, channel modification, nitrogen limitation, ecosystem services, designer ecosystems.

Urbanization directly alters the land cover of a small proportion of the Earth's terrestrial area, yet it has profound and far-reaching indirect effects on biogeochemical cycles, the hydrological cycle, biodiversity, climatic change, and land transformation well beyond cities. Cities are now home to >½ of the world's population; these burgeoning urban populations have high resource needs but no longer rely on their immediate hinterlands to support their demands for food or fuel (e.g., Folke et al. 1997). Moreover, rising atmospheric CO_2 concentration is ample evidence that assimilation of a city's waste products is no longer restricted just to nearby ecosystems (Luck et al. 2001). For an urban area such as metropolitan Phoenix, Arizona, N inputs are very high and overwhelmingly human-mediated, and annual N retention (excess of input over output) exceeds total annual N inputs (from N_2 fixation and atmospheric deposition) to surrounding desert ecosystems (Baker et al. 2001). Thus, an important corollary to the generalization that humans have doubled

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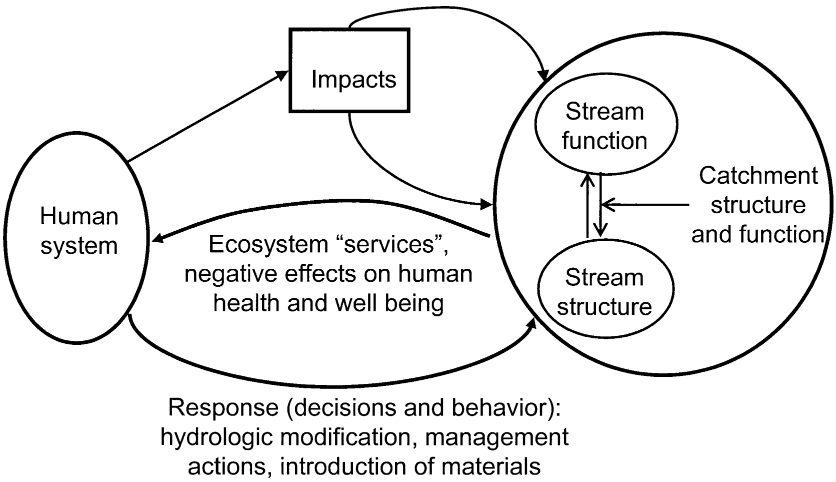

FIG. 1. Since Hynes's (1975) seminal paper, stream ecologists often have sought explanation for patterns in stream structure and function by invoking influences from the surrounding catchment. Urbanization is conceived as a human impact on streams, although we stress a more complete conceptual model that recognizes the bidirectional interaction between humans and streams and their catchments. Provision of ecosystem services or risks (e.g., flooding or impaired water quality) is met with responses at individual and collective levels, some of which may have negative effects on streams while others may improve stream ecosystems that would otherwise be severely impaired. Recognition that urban streams are highly modified landscapes may allow humans to design or restore these ecosystems to maximize ecosystem services and minimize risk.

N input to terrestrial ecosystems is that the N is unevenly distributed, and is especially abundant within urban ecosystems.

Direct landcover changes associated with urbanization are particularly destructive to stream ecosystems. The literature shows many examples of paving over, dewatering, channelizing, canalizing, and otherwise altering streams themselves (reviewed by Paul and Meyer 2001). Changes in upland areas also affect streams because both infiltration and peak flows are altered by increased impervious surface constructed during urbanization (Leopold 1968, Corbett et al. 1997, Walsh et al. 2005). In turn, high imperviousness (i.e., proportion of a catchment covered by impervious surfaces) has been linked to stream impairment (Arnold and Gibbons 1996), most often to losses of biodiversity or of sensitive species of benthic organisms. However, little research has addressed how changes associated with urbanization affect a basic ecosystem service like nutrient retention (but see Meyer 1997, Paul and Meyer 2001, Groffman et al. 2005, Meyer et al. 2005). Moreover, rather than simply cataloguing human impacts, ecologists must begin to examine the feedbacks to and from the social system to better understand the coupled human–natural ecosystem (Pickett et al. 1997, 2001, Collins et al. 2000, Grimm et al. 2000; Fig. 1).

Stream ecosystems are heterogeneous landscapes of interacting subsystems strongly connected to surrounding terrestrial and downstream recipient ecosystems, including groundwater, lakes, large rivers, and coastal ecosystems (Dahm et al. 1998, Fisher et al. 1998). Because of this multidirectional connectivity, streams integrate processes of their uplands and contribute to the character of recipient ecosystems. Streams are like arteries because they shunt materials through a larger system although, unlike arteries, they have significant capacity to transform and retain materials. Retention and transformation processes are important ecosystem services that are, as yet, not fully understood for most stream ecosystems. In particular, the consequences for recipient ecosystems of nutrient retention in streams modified by urbanization and other landuse changes are largely unexplored.

N retention is defined in our paper (and elsewhere; Peterson et al. 2001) as the difference between input to and output from an ecosystem. In practice, outputs via hydrologic vectors usually are measured and other outputs, like gas fluxes, which are more difficult to measure, are included in retention because the N is not lost to downstream recipient ecosystems. In other words, the fate of the N retained is storage and recycling within the ecosystem or gaseous output. Streams and riparian zones may be ''hot spots'' of N retention (Groffman et al. 1993, 1996, Alexander et al. 2000, Gold et al. 2001, Peterson et al. 2001), where a hot spot is a region of relatively high reaction rates (uptake, or denitrification in this case) relative to the surrounding matrix (McClain et al. 2003; see also Groffman et al. 2005).

Nutrient retention results in reduction of nutrient delivery to recipient systems, and thus can be seen as an essential ecosystem service (Postel and Carpenter 1997). At larger scales than the stream reach typically studied, other features of landscapes also may be important sites of nutrient retention. Thus, we posed a key question in our quest to learn how N retention capacity is altered by urbanization: what are the important sites of N retention in urban landscapes? The answer to this question not only requires incorporation of the heterogeneity of multiple landuse types, hydrologic infrastructure, and stream modification, but also an understanding of how decisions and behavior of the human ecosystem affect and are affected by the stream and its catchment (Fig. 1).

Background and theory of nutrient spiraling

The characteristic unidirectional flow of stream ecosystems has dictated modification of nutrient cycling theory developed for terrestrial or lentic ecosystems. In particular, scientists studying nutrient spiraling in streams have developed 3 main metrics that together yield much information about nutrient retention: uptake length (S_w), uptake rate (U), and uptake velocity (v_f). S_w is the mean stream distance traveled by a nutrient atom or ion between its release from the benthic zone and subsequent removal from the water column, U is the mass of nutrient removed from the water column per unit area of stream bottom per unit time, and v_f is the vertical velocity at which nutrients move from the water column to the site of uptake in the benthic zone. The above 3 metrics are related to one another by the following equations:

$$S_w = \frac{QC}{Uw} \quad [1]$$

$$U = v_f C \quad [2]$$

$$v_f = \frac{Q}{S_w w} \quad [3]$$

where C = nutrient concentration, w = stream width, and Q = discharge ($Q = v_{water}$ wz; v_{water} = water velocity, z = water depth). Although there has been some disagreement in the literature over which is the most useful of these metrics, we agree with the Stream Solute Workshop (1990) and Doyle et al. (2003) that each metric contains useful information and all 3 should be reported. Short S_w, high U, and high v_f, in general, indicate a high nutrient retention capacity. S_w is highly dependent on physical channel features, such as Q (Newbold et al. 1981). From equation 1, S_w is directly proportional to the nutrient flux (QC); therefore, for a given C and U, S_w will increase linearly with Q. Similarly, if Q and U remain constant, S_w will increase with increasing concentration. This behavior makes sense because, as Q increases, v_{water} usually also increases, resulting in a decreased travel time in the reach. A decrease in travel time will likely lessen the contact time between nutrients and assimilation sites, resulting in a longer S_w.

Biological uptake in streams is often assumed to follow saturation kinetics, such as the Michealis–Menten kinetics of enzymatic reactions (Dodds et al. 2002). As a result, the shape of the U vs substrate concentration ($[NO_3^-]$) curve follows this general form. At low $[NO_3^-]$, U follows a linear, 1st-order kinetic model, with U increasing in proportion to $[NO_3^-]$. At some value of $[NO_3^-]$, U reaches saturation because sites of nutrient assimilation are overwhelmed at higher nutrient levels. Thereafter, as $[NO_3^-]$ in streamwater increases, U remains constant (i.e., assumes zero-order kinetic behavior). v_f is directly related to U (equation 2) by C, so the shape of the v_f vs $[NO_3^-]$ curve will be the same as the U vs $[NO_3^-]$ curve. Therefore, as C increases, the rate at which nutrients move towards sites of assimilation (v_f) decreases. Overall, nutrient uptake behavior in unaltered streams conforms reasonably well to these theoretical expectations (Newbold et al. 1981, Peterson et al. 2001, Valett et al. 2002). For urban streams, we asked whether relationships between the 3 nutrient spiraling metrics and Q or C conformed to those established for unaltered streams.

N spiraling theory holds that high N retention, whatever the metric or mechanism, is associated with high primary productivity, N limitation, and/or complex channel form (Peterson et al. 2001, Valett et al. 2002, Hall and Tank 2003, Webster et al. 2003). U is likely to be high because of high algal demand for N in productive streams; indeed, Hall and Tank (2003) showed that gross primary productivity explained 75% of variation in v_f for NO_3^- in high-light streams in Wyoming, USA. Based strictly on the stoichiometry of primary production, greater retention when the ratio of primary production to ecosystem respiration (P:R) >1 would be expected; however, decomposer heterotrophs also may account for N uptake, especially under N-poor conditions. Indeed, all biota capable of taking up inorganic N should do so more efficiently under N limitation, leading to shorter S_w. Valett et al. (2002) showed that North Carolina streams in old-growth systems were more retentive than streams in recently logged areas: S_w was shorter, and U and v_f were significantly higher in the old-growth than the logged ecosystems. In forested ecosystems, metabolism is dominated by heterotrophic respiration and P:R can be low (Minshall et al. 1983), in contrast to the urban streams discussed in our paper. Last, hydrologic retention is higher in heterogeneous channels than in simple ones, so higher channel complexity leads to greater contact time of water and nutrients with sites of assimilation or denitrification, and thus higher retention. Channel complexity includes such features as backwaters, hyporheic zones, lateral bars associated with meanders, and even biotic patches such as beds of aquatic vascular plants or macroalgal mats. Valett et al. (2002) attributed much of the difference between streams in old-growth and logged areas to differences in channel complexity.

We explored how urban streams differed from their nonurban counterparts in capacity for N retention. We tested predictions based on N spiraling theory using data from the southwest region of the Lotic Intersite Nitrogen eXperiment, phase 2 (LINX2) project. This preliminary data set did not yet include the full complement of urban, agricultural, and desert streams under investigation, so our experimental design was not sufficiently robust to draw rigorous conclusions; however, the data set was supplemented with information from several other sources to address this question. We asked how urbanization altered the position of streams along the 3 axes (productivity, N limitation, and complexity), and hence, whether urban streams exhibited a higher or a reduced capacity for nutrient retention relative to their unaltered counterparts. Modifications to urban streams are well known, and include indirect changes in catchment land cover (especially imperviousness), increased N loading (through enhanced atmospheric N deposition and fertilizer use) within the catchment, direct alteration of channel morphometry (straightening, deepening, lining, or even paving over streams), and changes in hydrologic flowpaths and amount of water supplied to streams.

Methods

Our assessment of differences between urban and unaltered streams of the American Southwest is based on a compilation of data from several sources. We conducted NO_3^--addition and $^{15}NO_3^-$-injection experiments in 5 urban streams in metropolitan Phoenix and Albuquerque, and in 2 unaltered desert streams in central Arizona. We also measured longitudinal water chemistry in 7 additional urban streams, and used nutrient-diffusing substrata to determine seasonal changes in nutrient limitation in one urban stream in New Mexico. Detailed description of study sites, and of the native, agrarian, or urbanized landscapes (below), illustrates the range of modifications and alterations characteristic of urban streams in this arid/semi-arid region.

Study sites

The arid and semiarid southwestern USA has seen rapid urbanization since the end of World War II. The largest city of Arizona, Phoenix, and that of New Mexico, Albuquerque, support >3.5 and ~1 million current inhabitants, respectively, and have grown from small agricultural communities at the beginning of the 1900s. Agriculture has lost ground in the past 1 to 2 decades; the Phoenix urban area expanded nearly 3-fold from 1975 to 1995, whereas agricultural lands during this period were reduced by 30%. Similarly, in Albuquerque, 56.7 km^2 of agricultural lands were irrigated in 1975 vs only 38.8 km^2 in 1992, a 32% reduction (McAda 1996). Historically, these cities developed in the midst of the desert because of the rivers that supply them: the Salt and Gila rivers in Phoenix, and the Rio Grande in Albuquerque (Fig. 2A, B). Arizonans built 5 upstream dams on the Salt River to ensure water supply; the lowermost dam diverts all of the remaining flow of the Salt River into canals, which diverge and spread onto the landscape of the Phoenix basin, once mostly agriculture but now largely urban and suburban lands (Fig. 2A). The Agua Fria River (AFR) and Sycamore Creek (SYC) are 2 unimpounded desert streams within the larger region of central Arizona. Neither stream flows in its lowermost reaches except during large floods. Other streams are either impounded above the city or are ephemeral; thus, there are no naturally perennial, larger streams in metropolitan Phoenix. By contrast, the Rio Grande still flows through Albuquerque, but has a reticulate network of >500 km of diversion and conveyance channels along its length (Fig. 2B).

SYC is a much-studied stream at ~700 m elevation located northeast of Phoenix (Fig. 2A). We include spiraling data from the LINX1 experiment done in 1997 in this stream (E. Martí, Centre d'Estudis Avançats de Blanes, and NBG, unpublished data), and from data in Martí et al. (1997), to compare with our urban stream data. SYC has been extensively described elsewhere (Fisher et al. 1982, Grimm 1987, Martí et al. 1997), and is a shallow, clear stream containing coarse sand and fine cobble substrata covered by epilithic diatoms, filamentous green algae (especially *Cladophora glomerata*), and cyanobacteria. The latter was not abundant during late-spring experiments. SYC is N-limited (Grimm 1992) and has an extensive hyporheic zone (Valett et al. 1994). AFR is a desert stream ~110 km north of Phoenix (elevation ~1100 m; Fig. 2A). The study reach had a mean width of 3 m, a mean depth of 10 to 15 cm, and Q ranging from 15 to 20 L/s. The reach is in a small canyon, although the channel receives full sunlight, with surrounding native vegetation consisting of mesquite and cottonwood (as in SYC). Substrata in the channel during the study were 40% coarse sand with epilithic diatoms, 15% *Cladophora glomerata*, 35% *Nasturtium* sp., and 10% *Cynodon dactylon*.

Urban streams in Phoenix and Albuquerque differed visually from the above unaltered desert streams. Channels of some of the urban streams were sediment-lined whereas others were cement-lined. Indian Bend Wash (IBW) runs through an urban park in Scottsdale, Arizona, and consists of a series of lakes connected by several small stream segments (Fig. 2A). The park was constructed as a nonstructural flood-management system and to provide recreation for surrounding neighborhoods. The study reach was a deeply incised earthen channel, with ~40% shade from surrounding park trees; the channel was ~4 m wide and 25 cm deep, and Q was ~30 L/s. NO_3^- concentration during the experiment was 100 μg N/L, which was atypically low for this site (WJR, unpublished data). Gila Drain (GRD) is an earthen ditch in the southern Phoenix metropolitan area that delivers irrigation water to surrounding neighborhoods from one of the main water-supply canals (Fig. 2A). The drain was ~3 m wide and 50 cm deep, and Q ranged from ~50 to 150 L/s. Based on several survey trips to the site, $[NO_3^-]$ ranged from 0.7 to 3 mg N/L. The channel bottom was ~45% sand and organic material, 45% epilithon on sand and cobble, and 10% grasses scattered along banks. The drain had full sunlight with steep banks consisting of unconsolidated soil and gravel. Highline Canal (HLC) is a 4- to 5-km-long concrete canal in southern Phoenix (Fig. 2A). The canal was in full sun-

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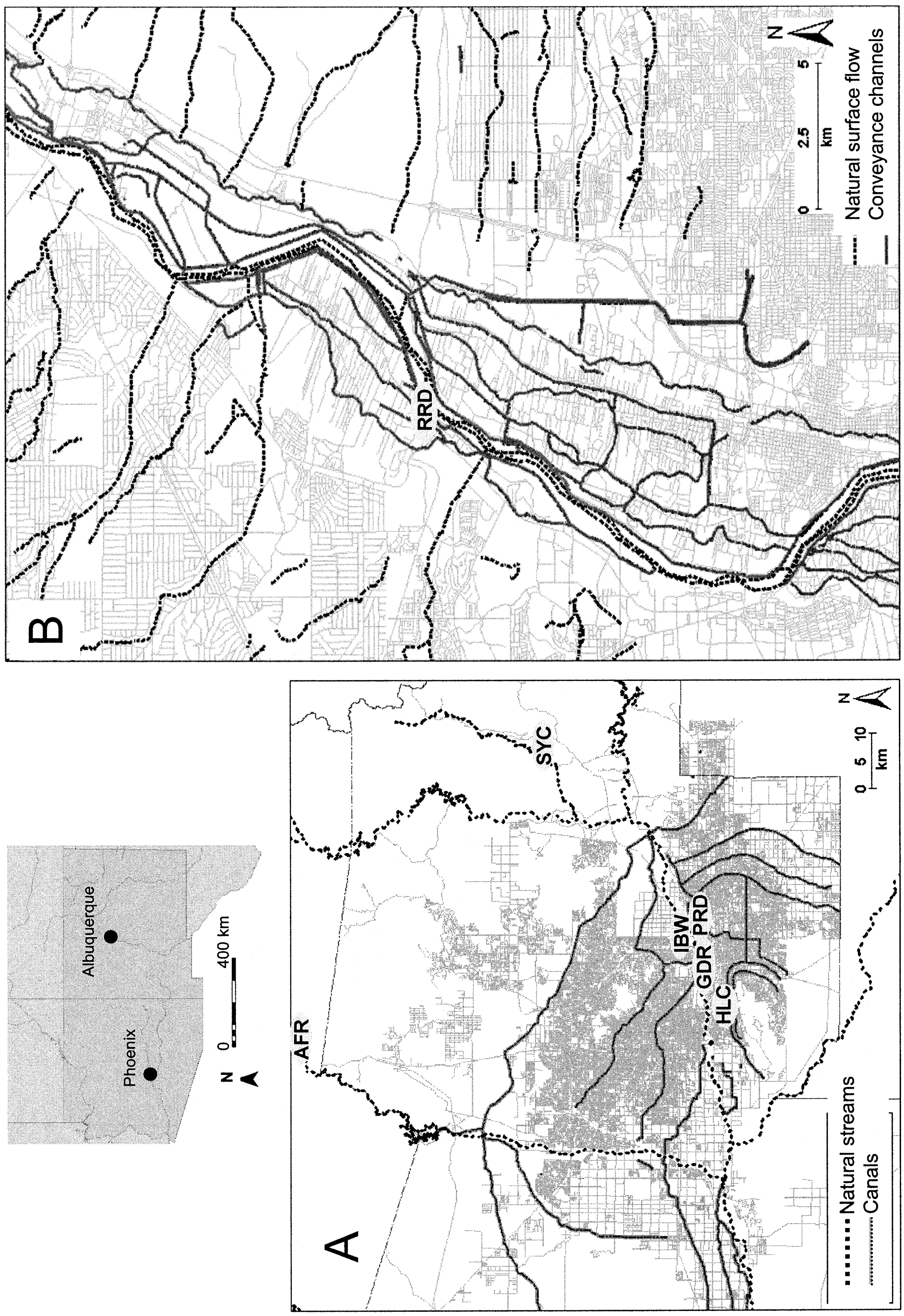
FIG. 2. Natural and constructed waterways in Phoenix (A) and Albuquerque (B) metropolitan areas, located in Arizona and New Mexico, southwestern USA (location map, upper left). Study sites are: Sycamore Creek (SYC); Agua Fria River (AFR); Indian Bend Wash (IBW); Highline Canal (HLC); Gila Drain (GDR); Price Road Drain (PRD); and Rio Rancho Drain (RRD). Street grids for both cities give an approximation of the degree of urbanization. Note the irrigation pattern differs between the two cities, with a canal distributary system spreading out over the broad Phoenix basin from a single point on the Salt River (Granite Reef Dam), and a network of conveyance channels running to and from the Rio Grande in Albuquerque, where irrigation is more closely associated with the river.


B
RRD
0 2.5 5
km
N
Natural surface flow
Conveyance channels
Albuquerque
Phoenix
0 400 km
N
A
AFR
SYC
IBW
PRD
GDR
HLC
0 5 10
km
N
Natural streams
Canals

light, had a mean channel width of 2 m, a mean depth of 40 to 60 cm, and consisted of exposed concrete along 90 to 95% of the wetted perimeter. Q ranged between 300 and 500 L/s. Source waters for this canal were a mixture of agricultural runoff, urban runoff, and groundwater pumping. As a result, background Q and [NO_3^-] were highly variable; daily Q could vary by 20% and [NO_3^-] could change by almost 1 mg N L^{-1} d^{-1} (RWS, unpublished data). Mean [NO_3^-] ranged from 2 to 6 mg N/L depending on sampling time. Approximately 5% of the concrete channel was covered by *Nostoc* colonies and small filamentous algal mats growing on cobble that fell into the canal. Price Road Drain (PRD) is a steep-walled, concrete-lined channel near the intersection of 2 major highways transporting urban runoff from a 260-km^2 area of eastern Phoenix (Fig. 2A). Mean width was 4 m, depth was ~20 to 25 cm, and Q was ~180 L/s. Background [NO_3^-] was always high, ranging from 2.5 to 6 mg N/L during most sample dates. The channel was 95% exposed concrete and ~5% weeds and grasses growing in cracks of the channel. Water from this site flows into the Salt River channel, which has been highly modified to reduce flooding in the Phoenix metropolitan area.

The Rio Rancho Drain (RRD) runs parallel to the middle Rio Grande in Albuquerque (Fig. 2B). The drain is used for irrigation and transportation of runoff from the surrounding neighborhood, a suburban landscape consisting of 25 to 40% imperviousness and 60 to 75% lawns. Mean channel width and depth were 4.4 m and 20 cm, respectively, and Q was ~30 L/s, with a [NO_3^-] of ~15 μg N/L. The site was in full sunlight during the study with bankside vegetation (herbaceous weeds and grasses) shading parts of the channel. Biota and predominant substrata in the channel were 10% green algae (Zynematales spp. and *C. glomerata*), 53% aquatic plants (48% *Myriophyllum* sp., 5% *Potamogeton* sp.), and 37% fine silt.

Nutrient surveys and seasonal nutrient limitation

Water samples were collected at each site and analyzed for nutrients and Cl^-, the latter used as a conservative tracer, at intervals along reaches of 10 to 100 m. Pre-acid-washed polyethylene bottles were used to collect samples, which were immediately stored on ice and analyzed within 24 h after centrifugation to remove large particles. Concentrations of NH_4^+, NO_3^-, soluble reactive P (SRP), and Cl^- were determined using a continuous-flow-injection analyzer (Lachat QC8000), and were expressed as mass of nutrient element. Spiraling metrics (equations 1–3) were calculated from background changes in concentration after correction for dilution using [Cl^-] data (after Martí et al. 1997).

Seasonal nutrient-enrichment bioassays were used in RRD to assess its nutrient limitation status. Q varied seasonally from 0.74 to 39.9 L/s, with the lowest flows occurring in winter and spring. Bioassays using clay-pot substrata enriched with PO_4^{-3}-P (as K_3PO_4), NO_3^--N (as $NaNO_3$), both PO_4^{-3}-P and NO_3^--N, or controls with neither nutrient (Grimm and Fisher 1986, Pringle and Triska 1996) were conducted seasonally (July 2002, November 2002, January 2003, April 2003). The amount of accumulated biomass on each stream substratum was measured as ash-free dry mass (AFDM, mg/cm^2) and chlorophyll *a* (chl-*a*, μg/cm^2) after 3-wk incubations (5 replicates per treatment). A significant difference in biomass between enriched and control substrata was assumed to indicate limitation of biomass production by the enriched nutrient.

Solute injection and ^{15}N-injection experiments

Nutrient additions with NO_3^- were conducted to determine uptake parameters at each of the sites. Solutions of $NaNO_3$ and NaBr were pumped into each stream for 4 h at a known rate (20–88 mL/min, depending on Q and background [NO_3^-]) using a fluid-metering pump (FMI, Inc., Syosset, New York), to raise streamwater [NO_3^-] by ~0.25 mg N/L. Five to 8 samples were taken along a 200- to 250-m reach at each site for background [NO_3^-] and [Br^-] and at the end of the 4-h injection period (plateau samples). Plateau samples for [NO_3^-] were background-corrected and Br^- in the injection solution was used as a conservative tracer to account for dilution along the reach. Each 60-mL sample was filtered in the field using Whatman GF/F filters and kept at 4°C until analysis (usually within 6 h of collection). NO_3^- and Br^- were analyzed using a continuous-flow-injection analyzer (Lachat QC8000). S_w for NO_3^- was determined from the slope of the regression of ln-corrected [NO_3^-] plotted against downstream

TABLE 1. Comparison of nutrient concentrations (means, with limits in parentheses) in an urban stream survey and in Indian Bend Wash over a 2-y period (WJR, unpublished data) with those from long-term data (Grimm 1992, Marti et al. 1997, and NBG, unpublished data) and a one-time extensive spatial survey (Dent and Grimm 1999) of Sycamore Creek, Arizona. Urban streams surveyed include the Salt River, Indian Bend Wash, and urban canals and drains (Fig. 2A). ND = no data, SRP = soluble reactive P.

Parameter	Urban stream survey	Indian Bend Wash (time)	Sycamore Creek (time)	Sycamore Creek (space)
NH_4^+-N (μg/L)	39 (4–96)	40 (5–161)	16 (0–~100)	ND
NO_3^--N (μgL)	1392 (5–4024)	1629 (18–6645)	95 (0–450)	35 (0–279)
SRP (μg/L)	67 (23–128)	31 (6–132)	48 (20–80)	28 (2–59)
N:P	51 (0.3–99)	84 (0.3–572)	~6 (0–60)	4 (0–29)
Number of cases	7	44	211	260

distance (Stream Solute Workshop 1990). Once S_w was determined, U and v_f for NO_3^- were calculated using equations 2 and 3.

Channel complexity was evaluated by qualitative examination of Br^- curves. A stream with a small transient-storage zone should exhibit a "square" curve of Br^- concentration over time, whereas the rise and tail of the Br^- curve should be spread out in more complex channels.

At a subset of sites (AFR, RRD, IBW, HLC), a similar experiment was done between April and November 2003, but with $K^{15}NO_3^-$ as the NO_3^- source. Injections of ^{15}N maintain ambient concentration (<10% increase), so S_w reflects actual gross uptake rates. Injection experiments lasted 24 h with the final (plateau) samples collected at noon. At HLC, a 4-h injection was done because of the rapid time to reach plateau and the excessive cost of using isotopes, although plateau samples were collected at noon, as at the other sites. Similar to the NO_3^--addition experiments, injection rate was dependent upon background [NO_3^-] and Q, ranging from 20 to 55 mL/min. S_w was determined from $\ln^{15}N$ flux plotted against distance (Mulholland et al. 2004):

$$^{15}N_{flux} = AR_{bc}\,[NO_3^-\text{-}N]Q \qquad [4]$$

where AR_{bc} is the background-corrected atomic ratio (Mulholland et al. 2004). Samples were processed for $^{15}NO_3^-$ using a modified version of the alkaline-headspace-diffusion method of Sigman et al. (1997) as described by Mulholland et al. (2004).

Results

Urban streams in Phoenix and Albuquerque contrasted with nearby unaltered desert streams in having higher amounts of fine sediment, less-complex channels, and generally higher nutrient concentrations. NO_3^- concentration in AFR was temporally variable, ranging from >1000 to <10 μg N/L, but showing consistent longitudinal decline during all sample dates—patterns consistent with long-term observations within SYC (Grimm 1992, Dent and Grimm 1999; Table 1). NO_3^- concentrations in urban streams often were high, although there were some cases of low [NO_3^-] and correspondingly low N:P (ratio of inorganic N to SRP; Table 1). In contrast, [NH_4^+] in the urban streams surveyed were not substantially different than SYC (range 4–96 μg/L for the urban streams cf. 0–100 μg/L for SYC over time; Table 1). Earthen channels in the urban settings had higher silt and other fine sediment (e.g., 37 and 45% in RRD and GDR, respectively) than unaltered streams (0–10% in SYC and AFR). Concrete-lined canals (PRD, HLC) had low channel complexity, lacking fine sediment, sinuosity, backwaters, or variations in width or depth.

No nutrient limitation was observed in RRD during summer and autumn (Fig. 3A, B). N possibly limited AFDM (winter; Fig. 3B) and chl-*a* (spring; Fig. 3A) accumulation; data were most persuasive for spring, as chl-a responded to both N and N+P enrichments (Fig. 3A).

As part of the NO_3^--addition and ^{15}N-injection experiments, Br^- was added to streams to determine hydrologic parameters. The temporal pattern of Br^- tracer concentration in SYC contrasted sharply with the urban streams HLC and RRD (Fig. 4). The Br^- curve for the desert stream AFR, however, resembled those of the urban streams more than SYC.

Background declines in nutrients with down-

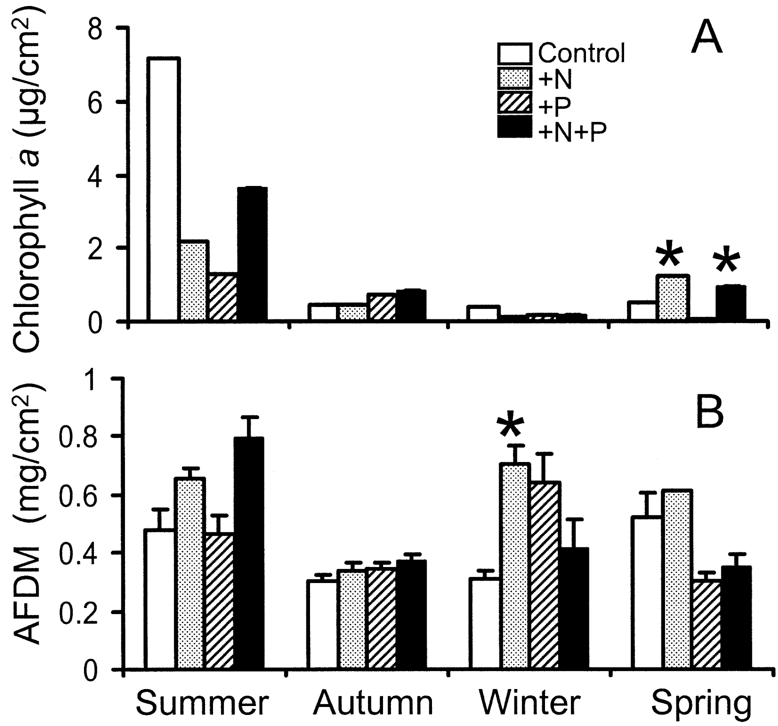


FIG. 3. Responses of chlorophyll *a* (A) and ash-free dry mass (AFDM, B) to nutrient enrichment in the Rio Rancho Drain, Albuquerque, over 4 seasons in 2002–2003. Asterisks denote responses that were significantly greater than controls.

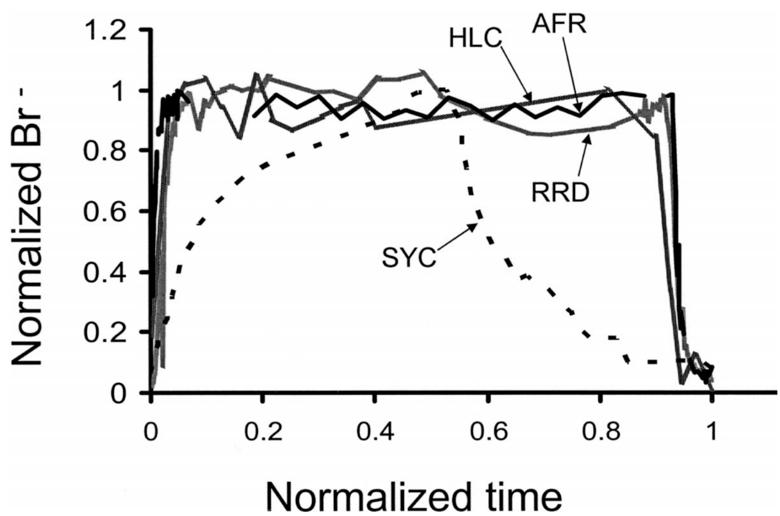


FIG. 4. Normalized time-course of Br^- concentration during addition experiments in 2 urban streams (HLC, RRD) and 2 desert streams (AFR, SYC), showing the contrast of streams with very little transient storage (HLC, RRD, and AFR) with a stream with a large transient storage zone (SYC). Stream abbreviations as in Fig. 2.

TABLE 2. Comparison of uptake lengths (S_w) of NO_3^--N and NH_4^+-N for urban streams and Sycamore Creek (SYC), Arizona. S_w values were calculated from background (bkgd) longitudinal change in nutrient concentration (used only if regression of corrected nutrient concentration [C] vs longitudinal distance was significant at $\alpha = 0.1$) for the urban streams survey, and reported in Marti et al. (1997) for SYC.

	Urban stream survey	SYC
S_w-NO_3^-–bkgd (m)	400–5000 ($n = 2$)	10–200
S_w-NH_4^+–bkgd (m)	−200–700 ($n = 4$)	2–80

stream flow indicated net retention of ions. In the urban streams, only 2 and 4 of the 7 streams showed significant longitudinal patterns in [NO_3^-] and [NH_4^+], respectively, each yielding longer S_w than SYC (Table 2). N retention as indicated by the 3 spiraling metrics was lower in urban streams than in unaltered desert streams. In fact, when streams were ranked by [NO_3^-], channel type was arrayed from unaltered streams with the shortest S_w to concrete-lined streams with the longest S_w (Table 3). The four ^{15}N-injection experiments reported also showed higher N retention capacity in unaltered than in urban streams (Table 3).

S_w of urban streams was significantly correlated with both Q ($r = 0.92$; Fig. 5A) and [NO_3^-] ($r = 0.97$; Fig. 5B), but the 2 desert streams had lower S_w at comparable Q and [NO_3^-] (Fig 5A, B). U and v_f also were positively correlated with [NO_3^-] ($r = 0.88$ [Fig. 5C] and 0.67 [Fig. 5D], respectively) for the urban streams; U of SYC and AFR conformed to the urban stream data (Fig. 5C), whereas v_f for SYC and AFR was higher than the urban streams at comparable [NO_3^-] (Fig. 5D).

Discussion

Our analysis of the data presented here centers on the 3 axes hypothesized to influence N retention capacity: productivity, N limitation, and channel complexity. How does urbanization alter the position of aridland streams along these axes? Given knowledge of changes in these 3 variables, are predictions about retention supported by our preliminary N spiraling data? Urban streams in the US Southwest have a potential for high primary productivity, both from macroalgae and vascular plants, although primary productivity data are not yet available. Most of the study streams had abundant primary producers, except HLC, which was so channelized that high flows probably prevented much algal establishment on substrata. These streams are unshaded and often experience high nutrient concentrations, so primary productivity could be as high as, or higher than, in nearby desert streams. However, one factor that might alter this expectation is human response to high algal or macrophyte biomass. In fact, al-

TABLE 3. N spiraling metrics for urban and unaltered streams in the US Southwest, based upon experimental NO_3^- additions and $^{15}NO_3^-$ injections. Q = discharge, S_w = uptake length, U = uptake rate, v_f = uptake velocity. Stream abbreviations as in Fig. 2.

Site	Channel type	NO_3^- (μg/L)	Q (L/s)	S_w (m)	U (μg N m^{-2} s^{-1})	v_f (mm/s)
NO_3^- additions						
AFR	Unaltered	5	15.4	67	0.38	0.077
SYC	Unaltered	21	55	90	4.3	0.200
RRD	Earthen	18	27.4	294	0.38	0.021
IBW	Earthen	100	49	555	2.2	0.022
GDR	Earthen	1220	113	526	87	0.072
PRD	Concrete	5241	187	833	294	0.056
HLC	Concrete	6111	306	1245	734	0.120
^{15}N injections						
AFR	Unaltered	0.4	10	36	0.040	0.094
RRD	Earthen	7	14	84	0.433	0.038
IBW	Earthen	202	69	609	2.962	0.026
HLC	Concrete	4747	502	1245	1231	0.269

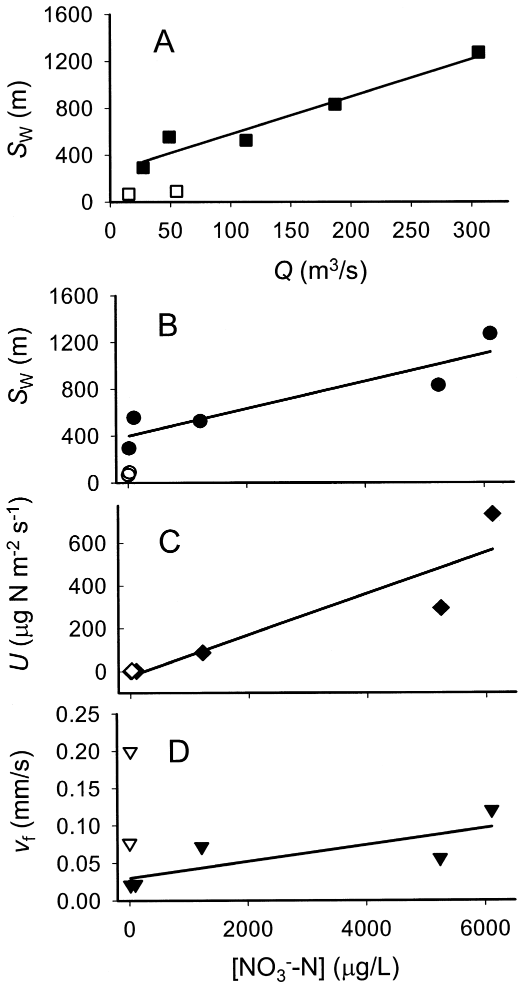


FIG. 5. Comparison of uptake length (S_w), uptake rate (U), and uptake velocity (v_f) between urban (filled symbols) and desert (open symbols) streams, expressed as a function of discharge (Q) (S_w only, A) and NO_3-N concentration (B–D). Regression lines included for urban streams only.

gicides and herbicides are regularly added to IBW, HLC, and GDR to prevent plant growth (WJR, personal observations). Application of herbicides is a clear example of how human interactions and feedbacks can confound simple expectations of stream ecosystem responses (Fig. 1).

The degree of N limitation changes with urbanization, although we were surprised that streams were not consistently N loaded (Table 1). In comparing urban systems to SYC, where extensive time-series and spatial surface-water nutrient data exist, we found urban streams had higher inorganic N concentration and N:P, although there were incidents where N:P<16, which is presumed to be a point of transition from P to N limitation (i.e., Redfield Ratio; Redfield 1958). Of the 2 major inorganic N species, NO_3^- concentration was more elevated than NH_4^+ concentration in urban streams compared with unaltered streams.

Although N limitation was observed in RRD only during spring (Fig. 3A), nutrient-addition experiments also showed that NO_3^- U was highest, S_w was lowest, and background NO_3^- levels were highest in the spring (LHZ, unpublished data); thus, if N limitation occurs, it appears to be transient. Similar nutrient-enrichment bioassays in IBW showed no evidence of N limitation, and seasonal assays showed P limitation in summer only (A. M. Goettl, Arizona State University, and NBG, unpublished data), although the possibility exists that N limitation or co-limitation may occur following storms (i.e., during high P loads and relatively low N concentrations; WJR, unpublished data). Interestingly, stormwater chemistry data for many urban storm drains and ephemeral streams in the Phoenix metropolitan area suggest that loading from storms tends to promote N limitation as often as P limitation. N to P ratios center on the Redfield Ratio, with ~53% of data points suggesting potential N limitation (Grimm et al. 2004). This result is surprising, given that transportable N accumulates on asphalt surfaces well in excess of P (Hope et al. 2004); however, clearly either P is enriched during transport or there are localized sites of N retention between such surfaces and stormwater drains (Hope et al. 2004), i.e., possible hot spots of N retention within this desert city.

Last, along the channel-complexity axis, urban streams in the US Southwest exhibit a range of characteristics because of differences in their substrata (earthen vs concrete) and degree of channelization, incision, and straightening. Stream ecologists often use additions of conservative tracers to determine transient storage zone size, an indicator of channel complexity (Webster and Erman 1996). The shape of the temporal patterns of tracer concentration permits qualitative assessment of transient storage zone size and hence complexity. The highly lagged increase and decrease in Br^- concentration in SYC, compared with the square pattern for HLC, RRD, and AFR (Fig. 4) likely reflects the well-known extensive hyporheic zone of SYC and its rapid exchange between surface and subsurface water (Grimm and Fisher 1984, Valett et al. 1990, 1994). The urban streams all had much lower complexity as judged by transient-storage calculations (RWS, unpublished data) than did SYC.

Are predictions about N retention capacity of urban streams supported?

We hypothesized that N retention would be lower in urban than in unaltered desert streams: S_w would be longer, U lower, and v_f smaller than in SYC or AFR. Our preliminary results, from background nutrient surveys and nutrient-addition and stable-isotope-injection experiments, allowed testing of these predictions.

Background [NO_3^-] declines characterize many desert streams in succession following flood disturbance (Fisher et al. 1982, Grimm 1987), allowing calculation of spiraling metrics that approximate net, rather than gross, uptake (Martí et al. 1997). Declines of both [NO_3^-] and [NH_4^+] were rare in urban streams and, when measurable, they yielded much longer S_w than observed for SYC (Table 2).

NO_3^--addition experiments provided the largest data set using comparable methods, so we used these data to evaluate whether spiraling metrics conformed to our expectations that S_w would increase linearly with Q and [NO_3^-], and that U would exhibit a saturating function and v_f a negative exponential function with [NO_3^-]. Our data for the urban streams conformed to predictions for S_w, but not U and v_f. Interestingly, regardless of how well urban streams fit predictions, they behaved differently than AFR and SYC. In particular, for both S_w and v_f, we observed a similar offset of the desert streams from the pattern exhibited by the urban streams (Fig. 5A, B, and D), especially for v_f of SYC (Fig. 5D), the stream with the greater channel complexity (cf. Fig. 4). These patterns are intriguing but preliminary, and indicate the possibility of distinct behavior of urban streams.

NO_3^--injection experiments also showed urban streams to be less retentive than their unaltered counterparts (Table 3). For the 4 streams with both ^{15}N-injection and NO_3^--addition data (AFR, RRD, IBW, HLC; Table 3), estimates of S_w were usually lower and v_f higher using injections than for additions, a result that has been reported by LINX1 researchers and others (Mulholland et al. 1990, 2002, Martí et al. 1997). Whatever the experimental method used, clearly the large suite of changes associated with urbanization—possibly, changes along axes of primary productivity, N limitation, and channel complexity—are associated with loss of N retention capacity. Our data were insufficient to assign relative roles to the 3 axes, but a comparison between IBW and RRD, urban streams with similar substrata but different [NO_3^-], implicated N loading as a primary factor. The concrete-lined streams had the highest [NO_3^-] and the longest S_w; their high N loads were perhaps not surprising given that there was little instream biotic structure to reduce loads (see also Groffman et al. 2005). Further, the short S_w of unaltered AFR, despite its square [Br^-] response curve (Fig. 4), implicated either N loading or productivity over complexity as important factors controlling retention capacity. However, the [Br^-] curve is possibly an inadequate characterization of complexity, particularly if slower transient storage pools are not captured by this method (Harvey et al. 1996).

Implications of reduced N retention in urban streams

N retention is a basic ecosystem service that summarizes N cycle processes and their impact on adjacent, connecting ecosystems. If urban streams have a reduced capacity to retain N, as judged by their longer S_w, then recipient systems downstream of urban areas will receive higher N loads. In the southwestern US deserts, recipient systems are the highly endangered riparian ecosystems of large rivers such as the Gila River and the Rio Grande, the Gulf of California (Mexico), which receives low quantities of poor-quality water from the Colorado River, and regional aquifers. Groundwater is an important source of irrigation and domestic water in both Arizona and New Mexico, but threats to both supply and quality exist. In the Phoenix metropolitan area, for example, groundwater NO_3^- concentrations exceed federal drinking water standards. The US Geological Survey's National Water-Quality Assessment Program has shown higher N loads downstream from urban areas (Nolan and Stoner 2000), but we do not know the extent to which such higher loads

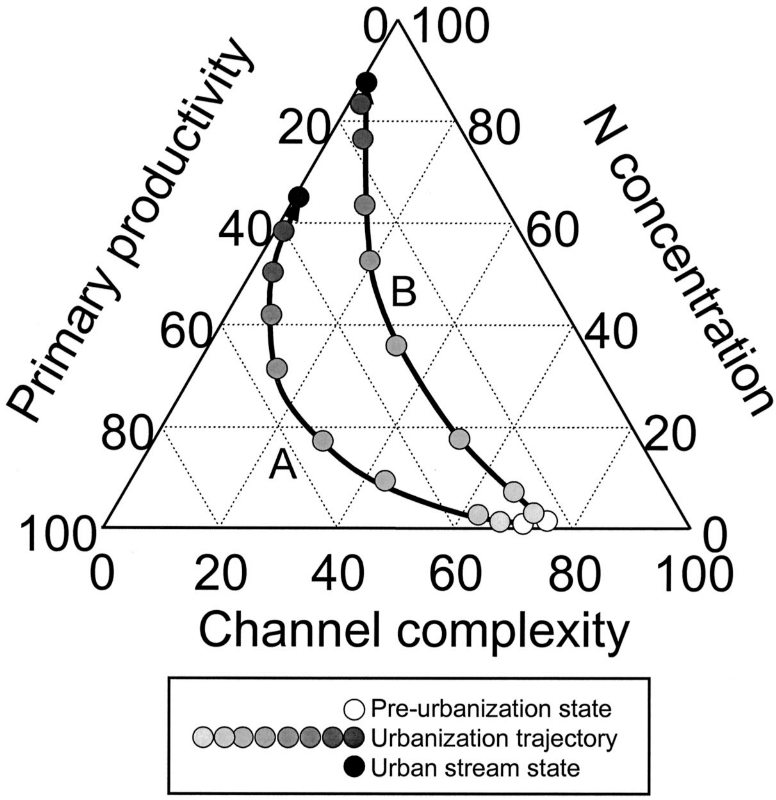


FIG. 6. Ternary diagrams may be used to plot points (streams here), according to the relative contribution (0–100%) of 3 distinct variables. Diagrams were constrained because the combined load on the 3 axes sums to 1. Assuming appropriate metrics for each variable could be developed, streams could be plotted according to their relative channel complexity, primary productivity, and N concentration (the inverse of N limitation). In this hypothetical example, 2 possible cases are shown as an unaltered stream is converted to an urban stream with increased N availability and with decreased channel complexity. In the 1st case (trajectory A), primary productivity is hypothesized to increase because of increased light availability, whereas in the 2nd case (trajectory B), management efforts result in a reduction of primary productivity. We hypothesize that, when plotted in such a fashion, urban and unaltered streams will cluster within distinct groups, reflecting important differences along these axes. Depiction of a given stream's position on the 3 axes that control N spiraling may be a useful means for managers and planners to visualize and design for maximizing N retention capacity.

are attributable to higher inputs, reduced retention, or both. If reduced retention is the primary cause, then at least 2 questions need to be asked: 1) How can urban streams be managed, changed, or even designed to maximize their capacity for N retention? and 2) If streams are not the hot spots of N retention in urban landscapes, then can other features of these landscapes provide this important ecosystem service?

Research in the Central Arizona–Phoenix Long-Term Ecological Research project provides some insight into the 2nd question. We have learned that aquatic ecosystems are largely disconnected from the terrestrial uplands except during storms. This disconnection is no different than desert streams such as SYC (Grimm and Fisher 1992); however, the hydrologic flowpaths taken by storm runoff are manipulated and, in many cases, purposefully designed in the urban ecosystem. Stormwater chemistry is unique for any given combination of storm characteristics (e.g., rainfall intensity, amount, or timing) and catchment features (e.g., imperviousness, arrangement of different types of land cover, structure of water-conveyance networks, or catchment size; Lewis 2002); thus, nutrient loads delivered to large rivers and streams during events connecting uplands and streams may be a function of distribution and number of retention features in the landscape. Evidence for this contention includes lower than expected N loads in actual runoff compared to that predicted by the amount of N stored on asphalt surfaces (Hope et al. 2004), and results from studies of urban retention basins and artificial lakes. Retention basins are grassy, common areas that receive street runoff from the surrounding neighborhood during storms, and are required features of all new developments. These retention basins quickly route water to the subsurface by dry wells, but during standing-water periods they may be important hot spots for N retention because they exhibit high denitrification potentials (Zhu et al. 2004). Artificial lakes also receive runoff from surrounding urbanized uplands. Preliminary evidence from IBW suggests that denitrification is higher in lakes than in either the connecting stream segments or bordering grassy floodplains (WJR, unpublished data). A definitive understanding of distribution of N retention hot spots across the urban landscape will require synthesis of these disparate studies, but we suggest that hot spots are likely to have shifted from stream riparian zones to artificially created aquatic and terrestrial landscape features such as lakes and retention basins.

Serious consideration should be given to the question of how engineers, planners, and managers can design and maintain urban streams to maximize the benefit received from any capacity to retain N. Most urban design or stream management focuses on flood control, minimizing unsightly primary producers, or reducing water-quality hazards (real or perceived), whereas the ecosystem service of N retention is scarcely known among decision makers. We contend that urban streams, particularly when they are as drastically altered as has occurred in desert cities of the US Southwest, are not good candidates for restoration; however, they provide excellent opportunities for creation of ''designer ecosystems'' that maintain some of the features and services that streams can provide (Palmer et al. 2004). We need a better understanding of N retention along the axes of primary productivity, N limitation, and complexity to best determine how to design retentive urban streams, and we need to know how urban streams change along these axes (Fig. 6). Which of these factors plays the greatest role in conveying high retention capacity? Which is most easily controlled or manipulated? Last, assuming humans are able to control or manipulate one of these axes, which factor produces the greatest response? These questions are difficult to answer because, in many cases, the respective roles of the 3 axes are not fully understood, even for unaltered streams. Moreover, the possibility that urbanization has resulted in a fundamental change in stream ecosystem structure and function, i.e., a ''regime shift'' (sensu Carpenter 2003) that has placed urban streams in a different stability region altogether, makes it difficult to simply transfer our understanding from unaltered streams to urban streams. Nevertheless, as the world becomes increasingly urbanized, and because these issues center on the places we live, we believe it is imperative that stream ecologists give these ideas full attention.

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