

Subsystems, flowpaths, and the spatial variability of nitrogen in a fluvial ecosystem

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Abstract Nutrient dynamics in rivers affect biogeochemical fluxes from land to oceans and the atmosphere. Fluvial ecosystems are thus important environments for understanding spatial variability in nutrient concentrations. At the San Pedro River in semi-arid Arizona, USA, we investigated how variability in dissolved inorganic nitrogen (DIN) was regulated by subsystem type and hydrological flowpaths. The three subsystems we compared were the riparian zone, parafluvial (gravel bar) zone, and surface stream. DIN concentration was greater in the riparian zone than in the surface stream, suggesting that the riparian zone retains DIN and is a source of N for the surface stream. Parafluvial zones were too

variable to generalize how they regulate DIN. Our hypothesis that subsystem type regulates DIN oxidation was too simple. The riparian and parafluvial zones host a mosaic of oxidizing and reducing conditions, as they exhibited highly variable ammonium to nitrate ($\text{NH}_4^+:\text{NO}_3^-$) ratios. Surface stream DIN was dominated by NO_3^- . Along a subsurface flowpath in the riparian zone, we did not observe spatial covariation among the N forms and transformations involved in mineralization. We also compared spatial variability in solute concentrations between flowpaths and non-flowpath reference areas. Our mixed results suggest that spatial variability is regulated in part by flowpaths, but also by solute-specific processing length along a flowpath. To understand the distribution of N in fluvial ecosystems, subsystem type and flowpaths are readily discernable guides, but they should be coupled with other mechanistic factors such as biota and soil type.

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Introduction

Human activities have affected global biogeochemical cycles by modifying material flux among

the atmosphere, land, and water (Grimm et al. 2003). These changes have highlighted the importance of fluvial ecosystems (Peterson et al. 2001) because they encompass terrestrial–aquatic boundaries and are defined by flux. Fluvial ecosystems connect ground and surface water (Grimm and Fisher 1984; Grimm 1996; Schade et al. 2005). And, the direction and magnitude of fluxes within fluvial ecosystems regulate the fluxes of greenhouse gases and pollutants from them to the atmosphere, lakes, and estuaries (Fisher et al. 1998, 2004; Groffman et al. 2003; Sponseller and Fisher 2006). Fluvial ecosystems are thus critical forums for understanding spatial variability in nutrient concentrations.

Spatial variability in nutrient concentrations has gained increasing attention (Broadbent et al. 1980; Smith 1986; Pringle 1990; Evans and Ehleringer 1993; Gross et al. 1995; Burke et al. 1999; Dent and Grimm 1999; Jenerette et al. 2006; Lewis et al. 2006). This pervasive phenomenon derives from heterogeneity in the relative rates of biogeochemical functions performed by the components of an ecosystem. Because ecosystem components—biota, soils, landforms, and flowpaths—regulate one another through feedbacks (after Carpenter 2003), they are organized into a limited number of configurations, or subsystems.

Investigating whether subsystems have distinct biogeochemistries is particularly important since other conceptual frameworks assume it, such as the general hypothesis that the spatial arrangement of subsystems influences net ecosystem functions like nutrient retention (Fisher et al. 2004). In fluvial ecosystems, different subsystems host varied nitrogen (N) transformations (Jones et al. 1995; Grimm and Petrone 1997; Hedin et al. 1998; Schade et al. 2001; Pinay et al. 2003; Groffman et al. 2005). Their net effects impinge directly on water quality and the N balance of the whole catchment (Perakis and Hedin 2002; Bernhardt et al. 2003).

Fluvial ecosystems comprise many subsystems, including the surface stream, hyporheic zone, parafluvial zone, and riparian zone (Fisher et al. 1998). The surface stream is the visibly flowing water and the hyporheic zone is the underlying saturated sediment. The parafluvial zone is the unconsolidated sediment deposited as typically

unvegetated sand and gravel bars. These three subsystems lie within the annually flooded channel of a stream or river. The riparian zone lies between the channel and the terrestrial uplands. We thus define a fluvial ecosystem as the portion of a catchment that is not the terrestrial uplands. In the U.S. Southwest, this portion is easy to visually delimit, since the low gradient, forested floodplains of the riparian zone contrast sharply with the sloped, scrub and grass uplands.

Here, we investigate whether spatial variability in the concentration and form (oxidation state) of inorganic N in a fluvial ecosystem is regulated by subsystem type and by hydrologic flowpaths, which are particularly important components of fluvial ecosystems. We focus on inorganic N because it can limit surface stream and riparian zone productivity (Grimm and Fisher 1986; Adair and Binkley 2002), N release from riparian soils can impair air and surface water quality, and changes to hydrologic transport can alter how fluvial ecosystems process N (Pinay et al. 2002; Groffman et al. 2003).

We test two hypotheses. First, we hypothesize that the concentration and form of dissolved inorganic N (DIN) are regulated by subsystem. Subsystems differ in ecosystem components, and thus should differ in several N cycling processes. If this hypothesis is supported, data should match the prediction (P1-1) that DIN varies among subsystems. Data should also match the second prediction (P1-2) that the dominant form of N in the DIN pool will shift from ammonium (NH_4^+) in the riparian zone to nitrate (NO_3^-) in the surface stream. We expect dominance by either form in the parafluvial zone. Riparian zones are generally reducing environments (Hill 1996; Hedin et al. 1998; Gold et al. 2001), surface streams are generally oxidizing environments, and parafluvial zones express oxidizing (Holmes et al. 1994; Henry and Fisher 2003) and reducing (Schade et al. 2001) conditions. This prediction implies that dissolved oxygen (DO) concentration will be inversely correlated with $\text{NH}_4^+:\text{NO}_3^-$, and will differ among subsystems accordingly.

Second, we hypothesize that the concentration of DIN is regulated by hydrologic flowpaths. Flowpaths transport reactants and products to and from sites of N processing (McClain

et al. 2003). Thus, one prediction (P2-1) is that along a flowpath, we will observe spatial covariation between concentrations of various N forms and rates of the processes that produce and consume them. Here, we specifically investigate pools and processes related to N mineralization. Additionally, a flowpath enhances linkages among some points by flowing between them, and constrains or prevents linkages among others by not flowing between them. Thus, a second prediction (P2-2) is that solute concentrations are less heterogeneous among points in proportion to the degree that those points communicate by a flowpath. For instance, nutrient concentrations may be less spatially variable along fast flowpaths through media affording little opportunity for uptake than along slow flowpaths through media affording ample opportunity for uptake (Lewis et al. 2006).

Methods

Setting

Predictions were compared against data from three sampling programs conducted along two reaches of the San Pedro River fluvial ecosystem, in semi-arid southeastern Arizona, USA (Fig. 1). Gray Hawk Ranch (GHR) and Boquillas (BOQ) are 400–500 m long, separated by 16 km, and have a similar channel slope of 0.3%. The more upstream reach, GHR, is 30 km north of the México–U.S. border. Samples were collected in various years (2001–2004) during May and June when temperatures are high and discharge is low and has been low for several months (Fig. 2). This stability in discharge preceding and during our sampling campaigns is important to the context of our study. It ensures that the three sampling programs were conducted under similar hydrologic conditions, and can thus be related to one another. Had this research been conducted at other times of the year, results might have been different and, importantly, other conceptual frameworks may have been needed to interpret the data. For instance, discharge that had been high and variable could have produced flowpaths that (i) were faster, (ii) switched directions

owing to changes in hydraulic head (e.g., riparian-to-channel flow could switch to channel-to-riparian flow), and (iii) ran closer to the soil surface. All of these flowpath characteristics would have consequences for N biogeochemistry.

At GHR, the former channel runs along the base of a mesquite (*Prosopis velutina*) bosque terrace at the distal edge of the riparian zone (Fig. 1). Like the active channel, this relict channel is bounded by a cottonwood (*Populus fremontii*)-willow (*Salix goodingii*) forest. Below the surface soil of the relict channel is a region of seasonal saturation (RoSS), which is intermittently saturated owing to water table fluctuations (Baker et al. 2000; Harms 2004).

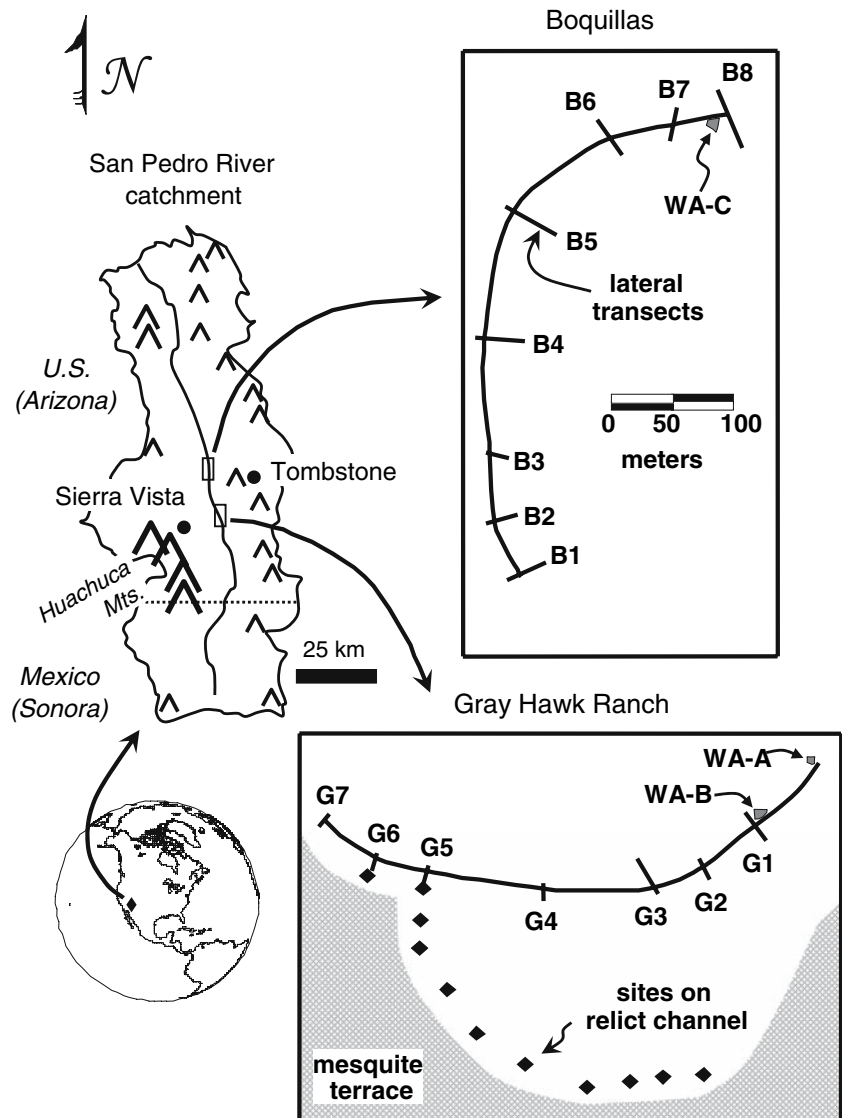
We presume that the relict channel is a preferential route for groundwater flow. Thus, points on the relict channel are probably interlinked by a single flowpath (with additional in- and out-flows possible), whereas other points in the riparian zone are not. Even points located on the banks of the active channel will not communicate by a single flowpath moving longitudinally (parallel to the active channel). These bank-side points will be intersected by numerous flowpaths, many with a lateral orientation (perpendicular to the channel) flowing to or from the channel (e.g., Schade et al. 2005).

Sample collection and processing

Survey of two reaches

Our first sampling program was in 2001. Samples were collected from riparian, parafluvial, and surface stream sites, which were located on 15 lateral transects (eight at BOQ and seven at GHR; Fig. 1). At each reach, lateral transects were separated by 50–100 m of channel length. At each riparian and parafluvial site, subsurface water was sampled with a peristaltic pump (GeoPump, Inc., Medina, NY, USA) from a polyvinylchloride well, screened over the bottom 0.5–1.0 m and installed to about 1 m below the water table, as recorded in February 2001. Surface stream samples were collected by dipping bottles into the thalweg to half the water depth. Each polyethylene bottle was pre-washed in

Fig. 1 Location and spatial extent of our study sites. In the inset of the whole catchment, flow is from south to north. Lateral transects, on which sites were located for the 2001 survey of the two reaches, are individually labeled for each reach. At each reach, flow starts at transect number 1. Polygons denote well arrays (WA) A, B, and C, sampled in the 2002 survey. Relict channel sites at GHR are marked with diamonds. Aerial views of sites are marked on Google Earth. The link to the placemark can be found by visiting bbs.keyhole.com, and searching the Nature and Geography forum for either “Lewis San Pedro fluvial ecosystem sites” in the keyword field or “dblewis” in the username field

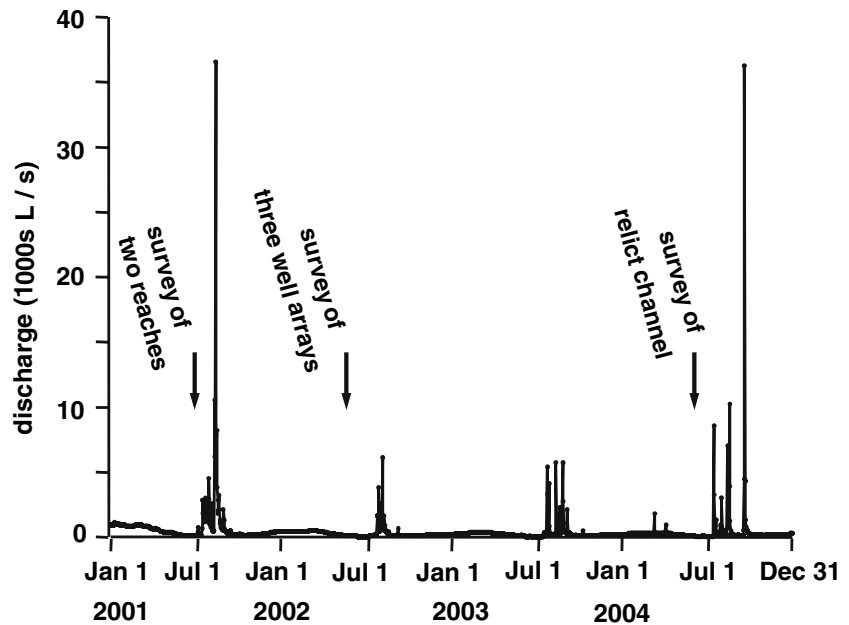


1.2 M HCl in the laboratory, and was rinsed in situ, immediately prior to sample collection, with water from its assigned site. Sampling proceeded in an upstream direction.

Water samples were collected in triplicate from each site. Separate nutrient concentration values for each of the three samples were averaged to yield one datum per solute per site. Samples were maintained on ice until analyses within 72 h at the Goldwater Environmental Laboratory of Arizona State University, in Tempe, Arizona. Prior to analyses, water was centrifuged (Beckman J2-HS Centrifuge, Beckman Coulter, Inc., Fullerton, CA, USA) at 10^4

RPM for 10 min. We analyzed supernatant colorimetrically (Lachat QC8000, Lachat Instruments, Milwaukee, WI, USA). We used the cadmium–copper reduction method for nitrite (NO_2)–N + NO_3 –N (hereafter NO_3 –N) and the phenol–hypochlorite method for NH_4 –N. DIN equals the total mass of N atoms in NO_3^- and NH_4^+ . We measured DO from all sites using a handheld probe (YSI 85, YSI, Inc., Yellow Springs, OH, USA). We measured surface stream DO by directly inserting the probe into the stream, and well water DO by inserting the probe into a 15-cm deep cup into which we continuously pumped bubble-free water.

Fig. 2 Discharge during study period. Line is fit through daily mean values. Data are from USGS station 09471000, San Pedro River at Charleston, AZ. Arrows point to dates on which the various surveys were conducted



Survey of three well arrays

In our second sampling program, we examined the parafluvial–riparian boundary. In 2002, we installed an array of 34–38 wells on each of three gravel bars (Fig. 1). Wells were separated by 2–3 m. Each array was rectangular or trapezoidal with 45–111 m² area. We laid each array across the gravel bar (parafluvial zone), and included one row of wells on the parafluvial–riparian boundary and one in the adjacent riparian zone. We pumped water from wells for analyses of NH₄⁺, NO₃⁻, and DO, as above. Next, we injected bromide (Br⁻), a conservative tracer, into an upstream parafluvial well in each array. Injections persisted until breakthrough curves for downstream wells exhibited plateaus. To monitor tracers, we analyzed well water in situ for Br⁻ concentration with an ion selective electrode (Orion Model 290A, Boston, MA, USA). From wells where tracers were found early on, we continued sampling for 28 h, at 0.5–1.0 h intervals, until breakthrough curves returned to near pre-injection levels. We monitored other wells less frequently.

Relict channel

In our third sampling program, we examined N in soil and groundwater along the relict channel at GHR (Fig. 1). We sampled groundwater via wells from six sites in 2001 and eight sites in 2004. We determined concentrations of NH₄⁺, NO₃⁻, and dissolved organic N (DON). DON equals total N minus DIN. Total N was determined via oxidation of N-containing compounds with alkaline persulfate/UV digestion at 90°C, and then colorimetric analysis for NO₃⁻. In 2004, we cored and sieved (2 mm) soil for net ammonification and nitrification potentials from 11 sites. Ammonification and nitrification were measured from surface soils (0–15 cm depth) and soils within the RoSS. Ammonification and nitrification are the changes in soil NH₄⁺ and NO₃⁻, respectively, extractable with 2 M potassium chloride (KCl), when soil is incubated aerobically for 28 days in the laboratory at field capacity moisture.

Data analyses

Data were log₁₀ transformed where necessary to normalize variance and prevent heteroskedastic

residuals. All analyses were evaluated at $\alpha = 0.05$, adjusted as needed for two-tailed tests and multiple comparisons.

P1-1: DIN varies among subsystems

With data from the survey of the two reaches, we tested the interactive effects of subsystem and reach on DIN concentration. We used a two-way analysis of variance (ANOVA). Where only the subsystem term was significant, we pooled data from both reaches and used a one-way ANOVA with a Bonferroni post-hoc test (adjusted for three comparisons) to investigate pairwise comparisons between subsystems. We used the same approach with data from the well arrays to test the interactive effects of subsystem and array on DIN concentrations. For the arrays, subsystems were the parafluvial zone, the parafluvial–riparian interface, and the riparian zone. Since an array included only one row of wells in each of the riparian zone and interface, we represented the parafluvial zone with only the row through its mid-section.

We compared DIN among subsystems at eight cross-sections of the river. Five were a lateral transect with at least one site per subsystem. To obtain three more cross-sections with at least one site per subsystem, we combined data from two lateral transects separated by 50 m (e.g., G1 and

G2, Fig. 1). On each cross-section, we ranked subsystems by DIN, and compiled a subsystem \times rank frequency table. We used a log-linear model to compare this table with a table of expected frequencies (value in every cell = number of cross-sections/3 ranks).

P1-2: Dominant form of N differs among subsystems

To examine sources of variation in DO and in the relative concentrations of NO_3^- and NH_4^+ , we used similar analyses as for P1-1, but with DO concentration and the molar ratio $\text{NH}_4^+:\text{NO}_3^-$ as dependent variables. We used regression to also examine whether $\text{NH}_4^+:\text{NO}_3^-$ was inversely correlated with DO.

P2-1: Covariation along flowpaths

With data from the relict channel, we conducted three types of analysis to investigate correlations among N forms and transformations involved in mineralization (Table 1). First, we regressed Y against X , with n = number of sites at which both were measured. This direct analysis ignores spatial relationships between the two variables. Second, we regressed Y against X spatially lagged by one site (Y versus X from one site upstream). Third, we used regression to determine whether

Table 1 Three types of relationships examined for the N forms and transformations in N mineralization

Y	X	Type of analysis and hypothesized sign		
		Direct	Lagged	Delta
Comparisons within a soil stratum				
Soil NH_4^+	Ammonification	+	n.s.	+
Nitrification	Soil NH_4^+	+	n.s.	+
Soil NO_3^-	Nitrification	+	n.s.	+
Comparisons across strata				
RoSS ammonif.	GW DON	+		+
GW NH_4^+	RoSS ammonif.	+		+
RoSS nitrif.	GW NH_4^+	+		+
GW NO_3^-	RoSS nitrif.	+		+
Comparisons in the groundwater				
NH_4^+	DON	n.s.	n.s.	n.s.
NO_3^-	NH_4^+	n.s.	n.s.	n.s.

Data are from the relict channel at GHR. Comparisons within a soil stratum were conducted for both surface and RoSS soil layers. Lagged analyses were not conducted for comparisons across strata. Nitrification and ammonification are potential net rates determined under laboratory conditions. ‘GW’ denotes groundwater. *A priori*, relationships are predicted to be either positive (+) or not specified (n.s.)

the magnitude and direction of change, per meter, in Y (ΔY) was correlated with ΔX . In direct and delta-type analyses, we predicted positive relations between N pools and potential rates of the processes that produce or consume them. For pairs of solutes, and for lagged analyses, expectations for both positive and negative relationships seem reasonable, so we did not predict sign and evaluated significance with a two-tailed test. Significance tests were further adjusted for the number of comparisons made for a type of analysis within or across strata (soil layer or groundwater). Regardless of P -value, relationships were deemed insignificant if they relied on points with leverage >0.6 , or if they exhibited the wrong sign.

P2-2: Flowpaths reduce heterogeneity

We conducted two analyses with data from the reach surveys to test whether spatial heterogeneity in DO and DIN concentrations was least among surface stream sites, intermediate among parafluvial zone sites, and greatest among riparian zone sites. This expectation recognizes that surface streams sites are interlinked by a single, rapid flowpath (the surface stream) while riparian zone sites are probably not (see *Setting*, above). First, we calculated Δ DIN and Δ DO (as for ΔY , above) between points on the longitudinal axis for each subsystem, with n = number of intervals between points. We used a one-way ANOVA to test whether $|\Delta$ solute| exhibited the pattern of riparian zone $>$ parafluvial zone $>$ surface stream, with a Bonferroni correction for three comparisons. To limit the number of analyses, we do not analyze NH_4^+ and NO_3^- , as P2-2 is not about N oxidation.

Second, we tested the expectation that the coefficient of variation (CV) among sites in DO and DIN concentrations would decrease from riparian zone to parafluvial zone to surface stream. We determined whether the difference in CV (δ CV) between subsystems deviated from δ CV expected at random. We used a null model to re-assign the data of each site to any site in the survey. From the random distribution, we calculated δ CV for each pair of subsystems. This

procedure was conducted 10^4 times. For each pair of subsystems, we then determined whether the real δ CV was greater than 98.3% of the 10^4 randomly generated δ CVs ($\alpha = 0.05$ adjusted for three pairwise comparisons between subsystems per solute).

In two more analyses for P2-2, we tested the expectation that heterogeneity would be less among sites that communicate by the same flowpath than among sites that do not. First, at GHR, we used ANOVA to compare $|\Delta$ DIN| and $|\Delta$ DO| among sites on the relict channel versus among riparian sites along the active channel (thought to not occupy a single flowpath; see *Setting*). For each group, n = the number of intervals between points. Second, we used the tracer injections to identify flowpaths through well arrays. We compared CV in DO and DIN among the k points on each tracer-identified flowpath versus 3000 other CV values, where each was calculated among an equal number (k) of randomly selected wells in the same array but not on the flowpath. We determined whether the flowpath CV was less than 97.5% of the non-flowpath CVs ($\alpha = 0.05$ adjusted for comparisons on two arrays per solute). In each array, the number of combinations of k wells from the set of non-flowpath, parafluvial wells is >3000 .

Results

P1-1: DIN varies among subsystems

The survey of the two reaches revealed that DIN concentration was greater in the riparian zone than in the surface stream (Fig. 3). The concentration in the parafluvial zone was intermediate, and not significantly different from that of the other subsystems. The reach and reach \times subsystem terms were not significant (Table 2A). In the survey of the well arrays, the array \times subsystem term was significant ($P < 0.001$), indicating that the among-subsystems contrasts in DIN were different among arrays. We thus conducted a separate one-way ANOVA for each array (Table 3A), with a Bonferroni post-hoc pairwise

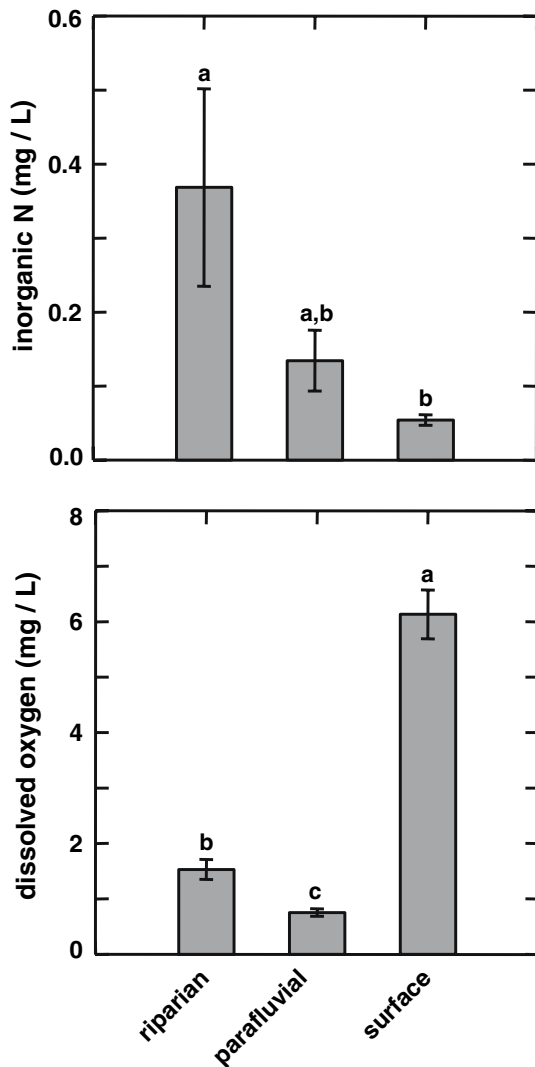


Fig. 3 Comparisons of DIN and DO among subsystems. Data are from the survey of the BOQ and GHR reaches, and are pooled between reaches. Analyses were performed using log₁₀-transformed data. Untransformed means \pm one standard error are displayed. Subsystems with significantly different solute concentrations are indicated by different letters

comparison of subsystems. DIN did not differ among subsystems in array A, was greatest in the parafluvial zone in array B, and was greatest in the riparian zone in array C (Fig. 4). In the cross-sections, the greatest DIN concentration was most often observed in the riparian zone (7 of 8 cross-sections), the intermediate concentration was most often observed in the parafluvial zone (5 of 8), and the lowest concentration was most

often observed in the surface stream (6 of 8). These frequencies deviate from the expected even distribution of ranks among subsystems (likelihood ratio Chi-square = 23.3, $df = 4$, $P < 0.001$).

P1-2: Dominant form of N differs among subsystems

In the survey of the reaches, there were no differences in $\text{NH}_4^+:\text{NO}_3^-$ among subsystems or between reaches (Table 2B). The riparian zone exhibited both the highest and lowest values for this ratio, and the surface stream DIN pool was always dominated by NO_3^- (Fig. 5). In the survey of the well arrays, the interaction term was significant ($P < 0.001$), so we tested the effect of subsystem in each array, separately (Table 3B). The ratio did not differ among subsystems in array A, was least in the parafluvial zone in array B, and exhibited the rank riparian zone > interface > parafluvial zone in array C (Fig. 4). Among our eight cross-sections, the ranking of subsystems by $\text{NH}_4^+:\text{NO}_3^-$ was variable and thus rank frequencies were evenly distributed (likelihood ratio Chi-square = 7.3, $df = 4$, $P = 0.121$).

In both the two-reach and the well-array surveys, $\text{NH}_4^+:\text{NO}_3^-$ was negatively correlated with DO ($P = 0.007$ for reaches, and $P = 0.021$ for arrays). However, DO explained relatively little variability in this ratio (Fig. 6).

DO concentration did not differ between reaches, but did among subsystems (Table 2C). DO was greatest in the surface stream, intermediate in the riparian zone, and lowest in the parafluvial zone (Fig. 3). In the survey of the well arrays, the interaction term was significant ($P < 0.001$), so we again tested the effect of subsystem in each array, separately (Table 3C). In array B, DO concentration was greater in the parafluvial zone than in either the interface or riparian zone (Fig. 4). In arrays A and C, DO did not differ among subsystems. In our analysis of cross-sections, the greatest DO concentration was always observed in the surface stream (6 of 6 cross-sections), the intermediate concentration was most often observed in the riparian zone (5 of 6), and the lowest concentration was most often observed in the parafluvial zone (5 of 6; two

Table 2 Two-way ANOVA of log₁₀-transformed data from the survey of the two reaches for (A) DIN, (B) NH₄⁺:NO₃⁻, and (C) DO

Source	<i>F</i> -ratio	<i>P</i> -value	Pairwise comparison of subsystems (Bonferroni <i>P</i> -value)		
(A) DIN	(<i>n</i> = 71 sites)			Riparian	Parafluvial
Reach	0.02	0.897	Parafluvial	0.448	
Subsystem	3.45	0.037	Surface	0.042	0.805
Interaction	1.78	0.177			
(B) NH ₄ ⁺ :NO ₃ ⁻	(<i>n</i> = 71 sites)				
Reach	0.39	0.534	Parafluvial	n.a.	
Subsystem	1.37	0.262	Surface	n.a.	n.a.
Interaction	0.25	0.778			
(C) DO	(<i>n</i> = 69 sites)				
Reach	0.91	0.344	Parafluvial	0.019	
Subsystem	39.36	<0.001	Surface	< 0.001	<0.001
Interaction	0.63	0.537			

Statistics for the reach and subsystem terms are from models without the interaction term, which was dropped (and the model refit) upon determining its insignificance. No post-hoc test was conducted for NH₄⁺:NO₃⁻ owing to the insignificance of the subsystem term

cross-sections with incomplete DO data were excluded from this analysis). These frequencies deviate from expected (likelihood ratio Chi-square = 28.7, *df* = 4, *P* < 0.001).

P2-1: Covariation along flowpaths

Along the relict channel at GHR, pairs of variables in the N mineralization process (Table 1) did not exhibit correlation in direct, spatially lagged, or delta-type relationships.

Table 3 One-way ANOVA for the effect of subsystem on (A) DIN, (B) NH₄⁺:NO₃⁻, and (C) DO

Array	<i>N</i>	<i>F</i> -ratio	<i>P</i> -value
(A) DIN			
A	18	0.84	0.451
B	24	7.32	0.004
C	18	13.60	<0.001
(B) NH ₄ ⁺ :NO ₃ ⁻			
A	18	0.00	0.996
B	24	48.10	<0.001
C	18	14.91	<0.001
(C) DO			
A	18	0.65	0.537
B	16	8.92	0.002
C	18	4.19	0.048

Analyses are of log₁₀-transformed data from the well arrays. Tests were done separately for each array owing to a significant subsystem x array term in a two-way ANOVA (see Results). The “*N*” column lists sample size (number of wells)

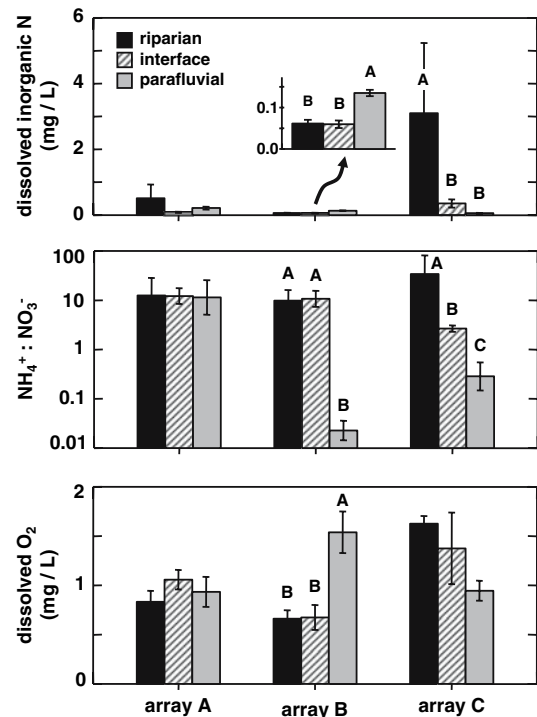


Fig. 4 Comparisons of DIN, NH₄⁺:NO₃⁻, and DO among subsystems for each well array. Analyses were performed using log₁₀-transformed data. Untransformed means ± one standard error are displayed. For an array and solute, subsystems with significantly different solute concentrations are indicated by different letters. Where bars are not marked with letters, no significant differences among subsystems were detected for that array and solute

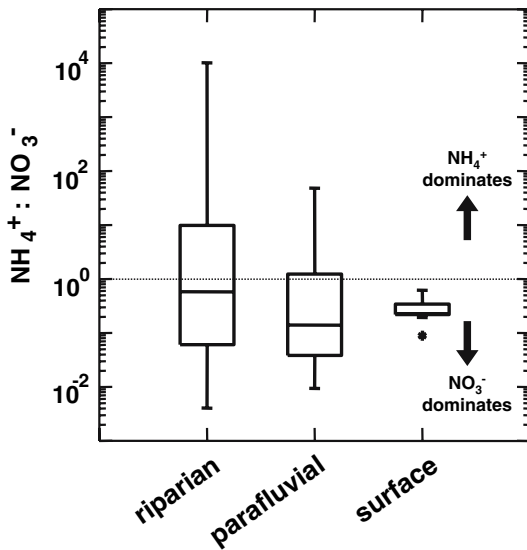


Fig. 5 Box and whisker plots displaying variability in $\text{NH}_4^+:\text{NO}_3^-$ for each subsystem. Data are from the survey of the BOQ and GHR reaches, and are pooled between reaches. Mean values do not differ among subsystems. A box encompasses an interquartile range (magnitude = H), with the median denoted by a horizontal line. Whiskers span data within a range of $1.5 \times H$ above and below the interquartile range. Individual points denote data beyond this range

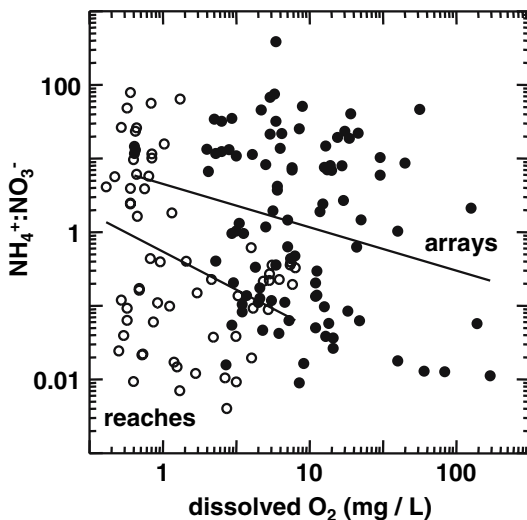


Fig. 6 Plot of $\text{NH}_4^+:\text{NO}_3^-$ versus DO. The relationship for reaches (open symbols) has $R^2 = 0.11$, and for arrays (filled symbols) has $R^2 = 0.06$. One reach point at (0.890, 10143) is not shown for graphical convenience, but was included in the statistical analysis

P2-2: Flowpaths reduce heterogeneity

In the survey of the reaches, longitudinal change in DIN was less in the surface stream than in the riparian and parafluvial zones (Bonferroni $P < 0.001$ for both comparisons, from ANOVA of $\log_{10}(|\Delta\text{DIN}|) = f(\text{subsystem})$; $n = 30$ longitudinal intervals and $F > 24.5$). Change in concentration ($\mu\text{g/l}$) per 100 m of channel length was 9.8 (1 standard error = 2.6) for the surface stream, 215 (92.5) for the parafluvial zone, and 605.4 (302.6) for the riparian zone. Longitudinal change in DO did not differ among subsystems.

Also in the survey of the two reaches, the CV in DIN concentration did not significantly differ among subsystems ($P > 0.017$). The CVs in DO for the surface stream (0.23) and parafluvial zone (0.34) were less ($P \leq 0.008$) than for the riparian zone (0.79).

At the GHR reach, $|\Delta\text{DIN}|$ and $|\Delta\text{DO}|$ did not differ between the riparian wells along the active channel and riparian wells on the relict channel.

From the injections into well arrays, we identified a flowpath in array B and another in array C. Neither flowpath crossed the parafluvial–riparian boundary. We found no flowpath in array A. In well array C, CV in DIN was lower among points on the flowpath than among points not on the flowpath ($P = 0.016$, i.e., flowpath $\text{CV} < \text{CV}$ from 98.4% of 3000 randomly chosen sets of non-flowpath wells). The same was not true in array B ($P > 0.025$). In both arrays B and C, the CV in DO was not different among points on versus off the flowpath.

Discussion

Anthropogenic changes of nutrient cycles have focused attention on fluxes among the atmosphere, land, and water. Because fluvial ecosystems can govern these fluxes (Peterson et al. 2001, Grimm et al. 2003), they are interesting and important environments for understanding spatial variability in nutrient concentrations. We evaluated support for two hypotheses, that (1) fluvial subsystem type and (2) flowpaths regulate the spatial distribution of DIN and its forms. We derived several expectations from these hypotheses. Only

Table 4 Evaluation of support for hypotheses. Table indicates whether data are consistent with the predictions from each hypothesis

Hypothesis 1: The concentration and form of DIN are regulated by subsystem type	Prediction consistent with data?
<i>Predictions 1.1 & 1.2: DIN concentration and form vary among subsystems</i>	
▶ ANOVA of reaches	DIN Yes NH ₄ ⁺ : NO ₃ ⁻ No DO Yes
▶ ANOVA of well arrays	DIN 2 of 3 arrays NH ₄ ⁺ : NO ₃ ⁻ 2 of 3 arrays DO 1 of 3 arrays
▶ Frequency table analysis of cross-sections	DIN Yes NH ₄ ⁺ : NO ₃ ⁻ No DO Yes
<hr/>	
Hypothesis 2: Spatial variability is regulated by hydrologic flowpaths	Prediction consistent with data?
<i>Predictions 2.1: N pools and process rates spatially covary along a flowpath</i>	
▶ Relict channel	all comparisons No
<hr/>	
<i>Predictions 2.2: Flowpaths reduce spatial variability</i>	
▶ Longitudinal change in reaches	DIN Yes DO No
▶ Analysis of CV in reaches	DIN No DO Yes
▶ Relict channel versus riparian bank wells	DIN No DO No
▶ CV in well arrays—on versus off flowpath	DIN 1 of 2 flowpaths DO No

a portion of them were consistent with data (Table 4). Here, we propose mechanisms for the expectations that were met, and discuss how generally they allow us to accept our hypotheses. We also offer possible explanations for expectations that were not met, and consider whether these failures are sufficient grounds for rejecting our hypotheses.

Hypothesis 1: the role of subsystems

Our first hypothesis was that subsystem type influences the concentration and oxidation state of DIN. The concentration part of this hypothesis appears true. DIN was greater in the riparian zone than in the surface stream, both on average (Fig. 3) and at every cross-section. From the strength of this pattern, we conclude that our hypothesis is supported.

Several mechanisms may explain this pattern of DIN distribution. Rates of N mineralization may be high in the riparian zone. Schade et al. (2002) found N mineralization (rather than hydrologic imports of DIN) great enough to

support the bulk of riparian primary productivity. Further, low DIN in the surface stream may derive from uptake by plants and microbes at the point of sub-surface water discharge into the surface stream (Henry and Fisher 2003), and immobilization of DIN as DON on recalcitrant molecules prior to N release into the surface water (Hedin et al. 1995).

High DIN in the riparian zone has implications for surface water quality and N transport within the fluvial ecosystem. This pattern suggests that riparian zones retain large pools of DIN and slow their transfer to surface waters. This retention is a particularly important function. The productivity of many streams is limited by the availability of N (Grimm and Fisher 1986). The large, riparian DIN pool is thus a subsidy for surface waters. Disturbances that rapidly mobilize this pool could enhance surface water productivity and algae growth.

Results from the parafluvial zone do not clearly support the hypothesis that subsystems regulate DIN concentrations. Our several analyses were variable in whether, and how, parafluvial DIN

differed from DIN of other subsystems. Parafluvial zones host a variety of N transformations, including ammonification, nitrification, denitrification, and immobilization. The functioning of various patches of parafluvial zone (discrete gravel bars) may depend on their edaphic and hydrologic attributes. It remains in doubt whether we can generalize about the influence of parafluvial zones on DIN.

Our first hypothesis also held that subsystems regulated DIN form. This hypothesis appears too simplistic. Rather, multiple factors interact to control oxidation potential. The weak correlation between $\text{NH}_4^+:\text{NO}_3^-$ and DO suggests that DO alone is insufficient information for making expectations about DIN oxidation state. Though our data did not fully match our expectations, they did reveal interesting patterns. From the survey of the two reaches, data at every site matched our expectation that NO_3^- would dominate the DIN pool, and that DO would be high, in the surface stream. In the parafluvial and riparian zones, however, we did not observe increasing dominance by NH_4^+ . Rather, we observed increasing variability in $\text{NH}_4^+:\text{NO}_3^-$, suggesting that parafluvial and riparian zones host a mosaic of oxidizing and reducing conditions. Data from the well arrays complements this suggestion, as the three arrays presented different patterns of $\text{NH}_4^+:\text{NO}_3^-$ and DO across the riparian–parafluvial boundary. The many observations of high NO_3^- and DO in the riparian zone (Figs. 3, 5) precludes stereotyping riparian zones as reducing, denitrifying environments.

Hypothesis 2: the role of flowpaths

Our second hypothesis was that hydrologic flowpaths regulate the distribution of DIN by transporting reactants and products to and from sites of N processing (McClain et al. 2003). For instance, reactants (NO_3^-) fuelling processes (N immobilization) at the downstream end of a gravel bar are only available because they were delivered by flowpaths from their nearly exclusive point of production (via nitrification) at the upstream end (Henry and Fisher 2003). Likewise, this nitrification at the head of a gravel bar derives from short (<cm long) flowpaths sweeping

N and organic matter through a sequence of tightly coupled N-fixation, ammonification, and nitrification reactions (Holmes et al. 1994; Valett et al. 1994).

In a similar vein, we expected that N pools would be correlated with rates of N transformation along a flowpath in a relict channel. This expectation was not met, but we do not believe that this fact warrants discarding this hypothesis. No pair of variables in the N mineralization process (Table 1) exhibited a direct correlation, a spatially lagged correlation (lag \approx 30 m), or a correlation in their degree of change between two locations (delta-type). Despite these results, flowpaths may indeed generate spatial covariation between nutrient pools and process rates. However, detecting this covariation along a flowpath through a complex medium like a riparian zone may require sampling at a finer grain than 30 m.

Our second hypothesis also posits that flowpaths regulate the distribution of DIN by decreasing variability among the points it connects. The mixed support we found for this hypothesis suggests that our hypothesis should be modified. A better hypothesis would be that flowpaths and processing lengths, together, regulate spatial variability. As our original hypothesis posits, it still seems reasonable that two points will more likely exhibit similar solute concentrations if they are connected by a flowpath than if they are not. The degree of similarity, however, will likely be mediated by the rate of uptake per unit advective displacement of a molecule, i.e., by processing length (Fisher et al. 1998, Lewis et al. 2006). Processing length will differ among solutes and flowpath types. For instance, we found the most (albeit incomplete) support for this hypothesis in the analysis that contrasted the riparian zone with the surface stream. This analysis presented the greatest possible contrast in uptake rate per distance advective displacement (riparian zone \gg surface stream).

Generality

Conservative inductive reasoning suggests that any support we found for hypotheses applies only at this study area. We feel safe, however, inferring that our results are general over a broader area.

This is particularly true of DIN differences between the riparian zone and surface stream, as it was observed at multiple cross-sections on each of two different reaches. The geomorphology and flora of our study reaches are characteristic of Southwestern arid and semi-arid fluvial ecosystems (Stromberg 1993). Namely, the reaches have low gradients and wide floodplains forested with a cottonwood-willow association. Given that our reaches bear a representative physiognomy, similar results might be found over the middle San Pedro River and perhaps in other low gradient rivers with intact riparian zones throughout the Southwest.

While our results are general over a broader area, they might not be general over a broader portion of the year. That is, they may be general among years, but only during the May–June period of high temperature, no recent rainfall, and protracted periods of low discharge (Fig. 2). Flowpaths at other times of year might be faster, variable in direction, and shallower (i.e., closer to the ground surface), all with biogeochemical consequences. Faster flowpaths would cause more advective displacement of an N atom per cycle through the mineralization-immobilization sequence, i.e., a more open ecosystem. Switches in flowpath direction could result in the situation wherein a flowpath that once went from a reducing zone to an oxidizing zone now goes the other way. This switch would have important implications for N, as a reduction zone-to-oxidation zone flowpath would favor N mineralization (and thus N retention within the fluvial ecosystem), whereas an oxidation zone-to-reduction zone flowpath would favor denitrification (and thus a loss of N as a gas to the atmosphere). Flow closer to the ground surface would bring water in contact with solutes stored in the overlying soil (after Baker et al. 2000, Harms 2004), thus increasing nutrient concentrations in the flowpath, and contributing to heterogeneity among points along the flowpath.

Fluvial ecosystems link land to lakes, estuaries, and oceans. The functions they perform, such as nutrient retention, are thus important in a broader spatial context (Peterson et al. 2001). It is hypothesized that the capacity for fluvial ecosystems to perform these important functions

depends on the interweaving of diverse subsystems by a network of flowpaths (Fisher et al. 1998, 2004). Our results, albeit limited to one place in time, suggest that subsystem type and flowpaths, by being readily discernable, are useful for understanding the distribution of N. Because they explain only a limited amount of variability in N, however, they should be coupled with biota, soil type, and other mechanistic factors.

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