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Influence of shifting flow paths on nitrogen concentrations during monsoon floods, San Pedro River, Arizona

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[1] Hydrologic flow paths control transport, and therefore are a major constraint on the cycling and availability of nutrients within stream ecosystems. This control is particularly evident in semiarid streams, where hydrologic connectivity between stream, riparian, and upland systems increases greatly during storms in the rainy season. We measured chloride concentrations in base flow, precipitation, soil water, and stream water to quantify the hydrologic connectivity and solute flux between soil water, groundwater, and the stream channel during six summer floods in 2001 (a wet year; 25 cm winter rain) and 2002 (a dry year; 5 cm winter rain) in the San Pedro River, southeastern Arizona. This hydrologic information was used to evaluate observed patterns in nitrate, dissolved organic nitrogen (DON) and dissolved organic carbon (DOC) concentrations in floods. The first floods of each year showed increased stream nitrate concentration that was approximately two orders of magnitude higher than base flow concentration. DOC consistently doubled to tripled during storm events, while DON in 2001 showed no response and showed a marked increase in 2002. A chloride mixing model indicated that soil and groundwater contributions to storm water discharge were related to antecedent conditions and to flood magnitude. Soil and groundwater contributions were the highest early in the 2001 monsoon season following the wet winter, much lower early in 2002 following a dry winter, and lowest during the largest floods of the 2002 monsoon season when flows were derived primarily from precipitation and overland flow. Stream water nitrate-N concentrations during floods were consistently 0.2–0.5 mg/L higher in 2002 than during 2001, suggesting greater over-winter accumulation of soil nitrate during the drier year. This result is consistent with higher mean nitrate-N concentrations in soil water of the riparian zone in 2002 (3.1 mg/L) than in 2001 (0.56 mg/L). These data highlight the importance of seasonal and interannual variability of hydrology in semiarid regions, and the role of water availability in driving patterns of soil nutrient accumulation and their transport to the stream.

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1. Introduction

[2] Streams in semiarid regions are hydrologically disconnected from terrestrial uplands except during isolated runoff events. In contrast to most streams in mesic areas, hillslope-water contributions to streams like the San Pedro River are minimal during dry periods, with perennial flow primarily supplied by regional and riparian groundwater much of the year [*Grimm*, 1992; *Grimm and Fisher*, 1992; *Brooks and Lemon*, 2007; *Baillie et al.*, 2007]. Episodic floods during the summer monsoon, however, potentially create new and redirect existing hydrologic flow paths that carry associated nutrient, solute, and sediment loads to the active channel [*Salmon et al.*, 2001]. Although terrestrial-aquatic linkage is known to be restricted to these episodic events, the role of the riparian zone in mediating this linkage is not well understood.

[3] In the southwestern United States, particularly in the Sonoran and Chihuahua Deserts of Arizona and New Mexico, precipitation mainly occurs during two periods: widespread, long-duration, low-intensity rainfall in the winter months; and short-duration, high-intensity, generally localized rainfall during summer. Summer rainfall provides 60% of total annual rainfall [*Sheppard et al.*, 2002]. High flow, beginning as overland runoff and quickly coalescing into the ephemeral and intermittent stream network, connects otherwise hydrologically disconnected upland and

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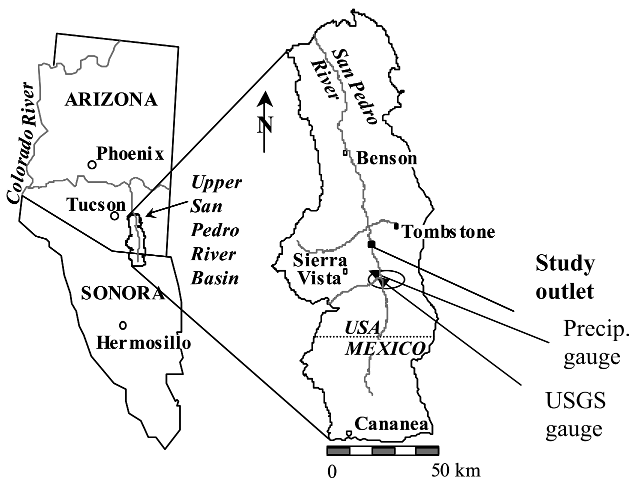

Figure 1. Study site location in the San Pedro River in southeastern Arizona. The sampling site is located at the outlet of the perennial reach of the river.

riparian ecosystems [*Belnap et al.*, 2005; *Welter et al.*, 2005]. These episodic events drive rapid material transfers between compartments in a catchment, flushing water and solutes from distant upland soils or from adjacent stream banks to surface waters. Conversely, the absence of a hydrologic transport vector during dry periods may cause otherwise mobile solutes to accumulate [*Michalski et al.*, 2004; *Meixner and Fenn*, 2004]. For example, *Grimm and Fisher* [1992] found that nitrate in floods in Sycamore Creek, Arizona was negatively correlated with the number of floods in the prior three years, and suggested that upland soil accumulation could explain this pattern. *Welter et al.* [2005] subsequently confirmed that ammonium accumulates in upland Sonoran Desert soils between floods, is transported to streams during floods but is nitrified during transport along these surface flow paths. Similarly, *Michalski et al.* [2004] showed that atmospherically derived nitrate accumulated during the summer dry season and was later flushed out during winter storm events in the chaparral of southern California. Solute accumulation likely occurs in lowland riparian soils as well, but this process has been investigated only by artificial rewetting experiments [*Heffernan and Sponseller*, 2004].

[4] Of solutes stored during dry periods and mobilized by floods, nitrogen (N) is of particular interest since it can limit primary production in both streams [e.g., *Grimm and Fisher*, 1986] and terrestrial ecosystems [e.g., *Hooper and Johnson*, 1999] of the desert Southwest. Nitrogen limitation implies that the biological demand for N exceeds inputs [*Redfield*, 1958; *Perakis*, 2002], and that significant N loss from an N-limited system should be minimized. Mobilization and redistribution of N during episodic events may, however, contribute to N limitation in semiarid riparian systems because rapid N losses from soil may be physically, rather than biologically, controlled [cf. *Vitousek et al.*, 1998]. Such nutrient movement, on the other hand, may represent a significant source of N to streams.

[5] The few studies that have addressed N movement during floods in arid and semiarid regions [*Fisher and Minckley*, 1978; *Grimm and Fisher*, 1992; *Marti et al.*, 2000] focused on Sycamore Creek, a small stream in central Arizona. Although these studies showed interannual variability in N transport during floods, they did not include hydrograph analyses to distinguish the effects of upland and riparian areas as sources or sinks of N in the stream. Knowledge of the mechanisms driving groundwater and soil-water contributions to flood discharge is key to understanding nutrient input to the channel, because a large nutrient pool typically accumulates in catchment soils over the dry season [*Michalski et al.*, 2004; *Meixner and Fenn*, 2004]. Furthermore, riparian soils may act as either a source or sink of N to the stream depending on hydrologic flow paths and hydrologic and solute residence time.

[6] We investigate the timing and magnitude of nutrient inputs to a semiarid stream during summer floods in two contrasting years: 2001 (a wet year) and 2002 (a dry year). Specific research questions were: (1) How do antecedent conditions influence water sources for event flow? and (2) How do nutrient concentrations and fluxes vary according to changes in stream-source waters due to high-flow monsoon events and soil conditions prior to the monsoon season?

2. Site Description

[7] The San Pedro River is located in southeastern Arizona and flows northward approximately 225 km from its headwaters in Sonora, Mexico, to the Gila River in central Arizona (Figure 1). The upper San Pedro basin is bounded by the Huachuca Mountains to the west, the Mule Mountains and Tombstone Hills to the east, and extends several km across the U.S.-Mexico border [*Pool and Coes*, 1999]. Limited agricultural activity on either side of the border consists of open-range grazing with a few areas of irrigated alfalfa. This crop is typically irrigated overhead, is fertilized infrequently only with phosphorus, and has little to no return flow to the river. Land use in the remainder of the basin is rangeland, with limited forest areas (%?) and small urbanizing centers in Sierra Vista, Tombstone and Cananea (%?).The study outlet (drainage area of 3196 km^2) is located in a section of the corridor characterized by a meandering stream within a wider, shallow channel containing numerous gravel bars and point bars.

[8] We selected a sampling site at the downstream end of the perennial section of the San Pedro River, within the San Pedro River National Conservation Area in the upper basin (Figure 1). The study reach is a section of the river-riparian corridor characterized by a meandering stream within a wider, shallow channel containing numerous gravel bars and point bars. Regional phreatophytes that populate the riparian zone include Fremont cottonwoods (*Populus fremontii*) and Goodding willows (*Salix gooddingii*) [*Snyder and Williams*, 2000]; mesquite trees (*Prosopis velutina*) populate the higher terraces on both sides of the river, and seepwillow shrubs (*Baccharis salicifolia* and *B. emoryi*) have colonized active-channel gravel bars. Several wider floodplain forests alternate along the length of the river where meanders once occurred, including one within our study site. See *Snyder and Williams* [2000] and *Stromberg* [1993] for a more detailed description of the study area.

[9] The two years of our study contrasted sharply and provided a good comparison, falling near two ends of a

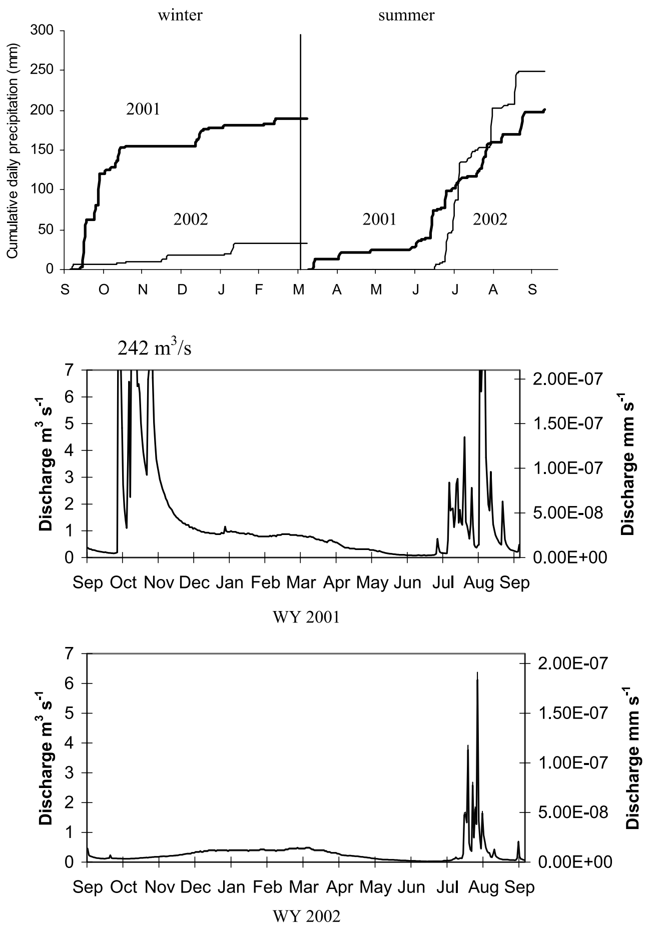

Figure 2. Rainfall measured approximately 4 km upstream from the study site during winter and summer 2000–2001 and 2001–2002 (top). Average daily discharge from a USGS stream gauge approximately 7.4 km upstream from the study site in WY 2001 (middle) and WY 2002 (bottom).

hydrologic continuum. Rainfall measured nearby (~4 km upstream) indicated wetter conditions in the 2001 water year (2001 water year was from 1 October 2000–30 September 2001) than in the 2002 water year (Figure 2) [*Scott et al.*, 2004] (see also http://www.wrh.noaa.gov/tucson/climate/reports.html). Daily discharge measured at a nearby United States Geological Survey (USGS) stream gauge (station #09471000, San Pedro River at Charleston, ~7.4 km upstream of the study site) showed higher stream flow in the 2001 water year compared to the 2002 water year (Figure 2). Summer flood events in this system are generally highly localized intense summer convective storms that create localized runoff events that propagate through stream networks depending on antecedent conditions, wetter prior conditions lead to larger travel distances and total flood flow volumes [*Goodrich et al.*, 1997].

3. Methods

3.1. Sample Collection and Analysis

[10] Water samples were collected during 6 large floods in the 2001 and 2002 summer seasons: including the second large flood of the 2001 season and 5 floods over a three-week period in 2002, including the first flood of the season. Stage height was measured on our site using a pressure transducer in a stilling well and data logger, a MiniTroll® unit manufactured by InSitu, Inc. Discharge was calculated using a stage-discharge relationship and rating curve. The rating curve for discharge values below 6 $m^3\ s^{-1}$ was developed onsite. For discharge values above 6 $m^3\ s^{-1}$, a non-linear Muskingum-routing algorithm [*Birkhead and James*, 1998] was used to extend the rating curve based on observations at the USGS Charleston gauge.

[11] Flood samples were collected using ISCO stream autosamplers programmed to collect 1-L samples every 0.5–2 hours. Samples were transferred from the ISCO autosamplers to HDPE plastic bottles for inorganic chemical analysis. Collection and autosampler bottles were soaked in Milli-Q distilled, deionized water for at least 24 hours and rinsed 2–3 additional times with deionized water. Additionally grab sample bottles were rinsed with sample water 2–3 times before filling. Samples were immediately transferred to a cooler with ice and returned to the lab for analyses most samples were collected within 24 hours of when sample was pulled from river. The anions chloride and nitrate were measured on a Dionex DX-600 ion chromatograph (IC) within 48 hours of collection of samples from the field. Before analysis, samples were filtered into IC vials using 0.45-μm acetate filters. Precipitation samples were collected using plastic funnels connected to bottles, rinsed with Milli-Q water, mounted approximately 0.5 m above ground on rebar or fence posts.

[12] Upon return of samples from the field, sample aliquots were transferred to amber glass bottles for total organic carbon and total nitrogen analyses. Samples were filtered immediately using precombusted (5 hours, 450°C) Whatman GF/F glass-fiber filters, and then stored in amber bottles in the dark at 4°C until analysis. Water samples were analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a high-temperature combustion oxidation (HTCO) method [*Cauwet*, 1999] on a Shimadzu TOC-5050(A) Total Organic Carbon Analyzer and an Antek 9000 Total Nitrogen Analyzer, respectively. Total organic nitrogen was calculated by difference (Total dissolved nitrogen concentration – measured nitrate concentration = dissolved organic nitrogen). Based on past studies conducted in regional desert streams including the San Pedro River, we did not measure for ammonium for all samples [*Fisher et al.*, 1982; *Holmes et al.*, 1998; *Brooks and Lemon*, 2007]. In 2001 a few samples (32) were analyzed for ammonium and concentrations averaged less than 0.03 mg-N L^{-1} verifying previous results that NH_4^+-N concentrations are typically 0 to 5% of DIN and often below detection limits and thus ammonium analysis was suspended. For all analyses, United States National Institute of Standards and Technology standards and blind spikes were used to ensure the accuracy of the analysis. Duplicates were analyzed to ensure analytical precision. For TDN, nitrate-N and chloride detection limit was 0.05 mg/L, for TOC detection limit was 0.10 mg/L.

[13] Soil-water samples were collected periodically through Teflon tubing attached to suction lysimeters made of stainless steel with a pore size < 0.1 μm. Three nests of lysimeters were installed along the left bank, immediately

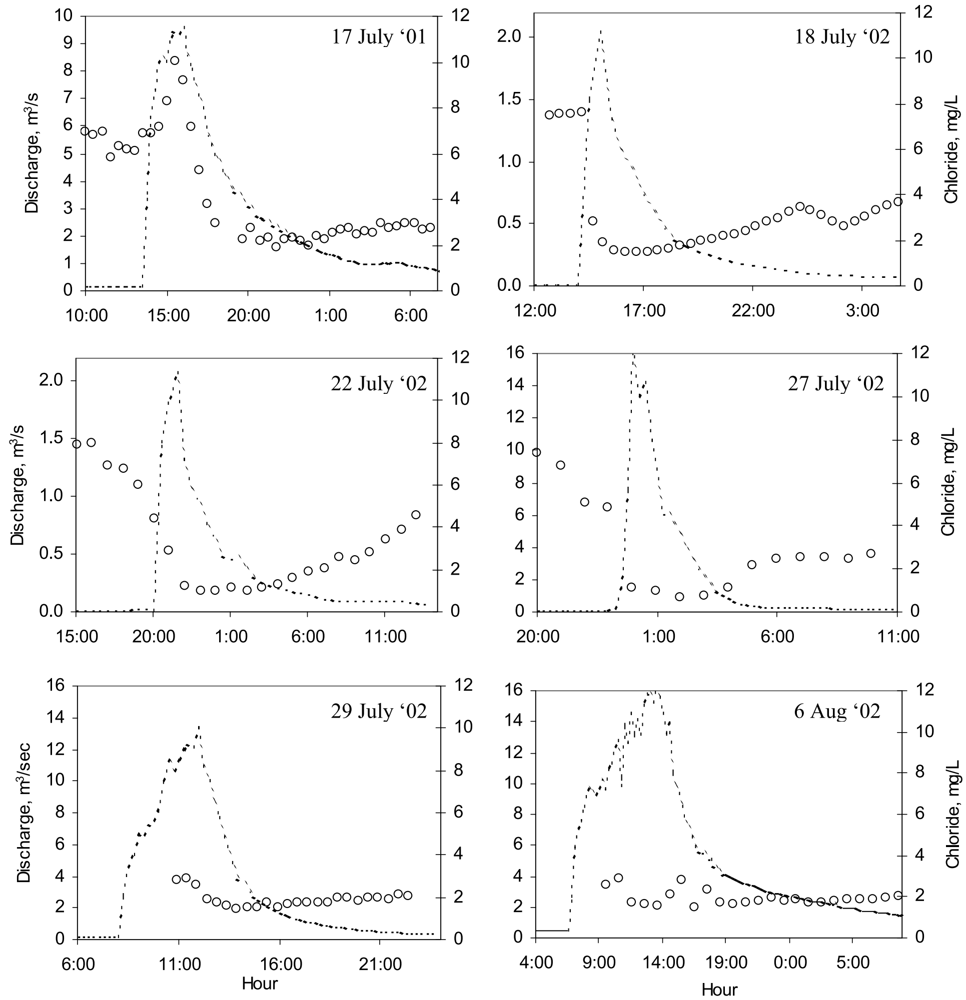

Figure 3. Stream chloride concentrations during 6 floods in 2001 and 2002 (circles). Dotted line is flood discharge.

adjacent to the stream channel at locations (separated by 100–250 m) where soils permitted installation. Lysimeters sampled water at depths between 0.5 and 1.4 m. Soil-water samples were preserved, stored and analyzed in the same manner as stream samples. Shallow groundwater samples were collected from 45 PVC wells with 1.5-m screens installed in spring 2001 in channel gravel bars, near-stream banks, and the floodplain. Groundwater samples were collected monthly to bimonthly from February through December 2001 in triplicate, clean HDPE plastic bottles, and were returned to the lab on ice for analysis within 48 hours. Analyses on filtered samples were by ion chromatography or on a Lachat Quickchem® automated analysis system for major anions.

3.2. Mixing Model Equation

[14] We used chloride in a mixing model to estimate groundwater and soil-water input to summer floods in 2001 and 2002. Groundwater-chloride concentration was used to separate water that has interacted extensively with porous media, or reactive water (groundwater and soil water), and water that has had brief or no contact with porous media, or unreactive water (precipitation and overland flow). The flow of reactive water is:

$$Q_r = \left[Q_s \times \frac{(C_s - C_{unr})}{(C_r - C_{unr})}\right] \tag{1}$$

where Q is discharge, C is tracer concentration, and subscripts *r, s, and unr* represent reactive water (groundwater and soil water), stream, and unreactive water (precipitation and overland flow), respectively. Flow attributed to unreactive water was estimated by subtracting the flow of reactive water from total discharge:

$$Q_{unr} = Q_s - Q_r \tag{2}$$

4. Results and Modeling

4.1. Hydrologic Conditions

[15] Peak discharge during the 2001 flood was approximately 10 m^3/s and its duration was approximately 16 hours (from time of flood front to approximate return to base flow

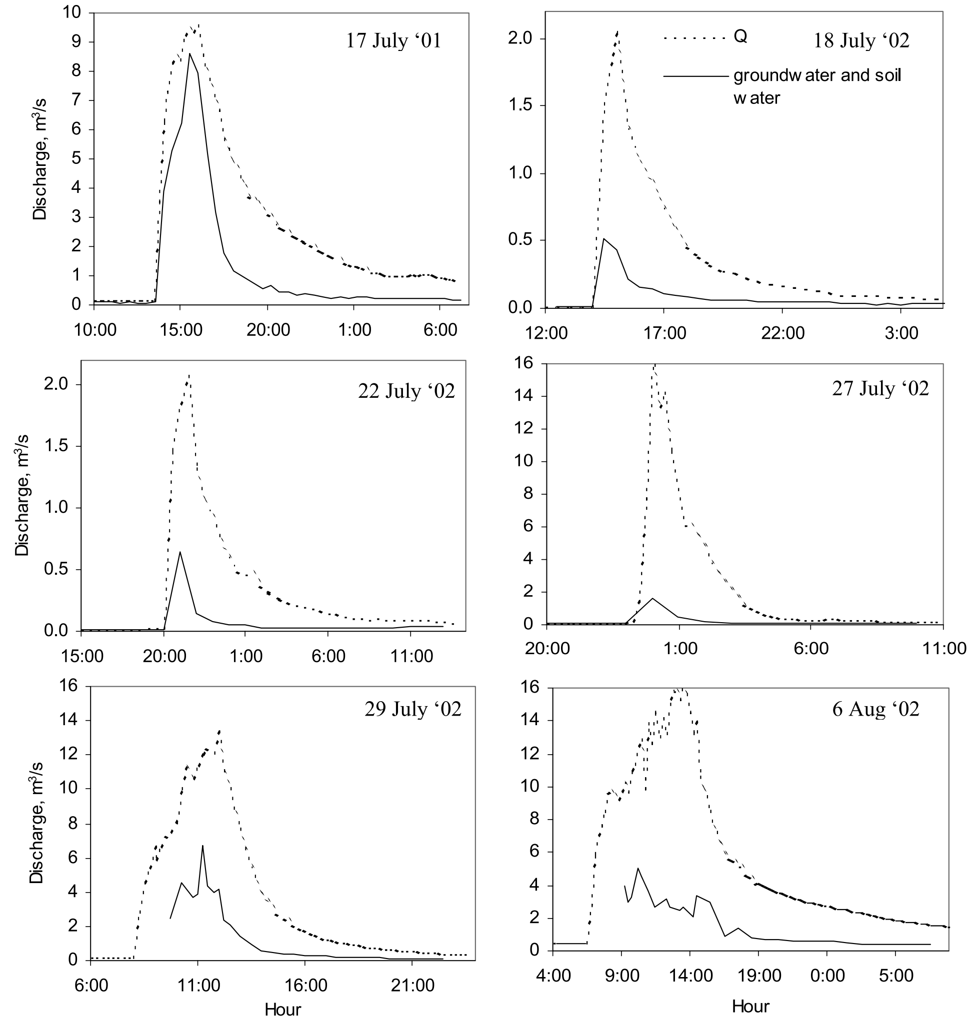

Figure 4. Chloride mixing model results for 2001 and 2002 floods.

conditions), and peak discharges during the 2002 floods ranged from 2–17 m^3/s. The duration of early and mid-season 2002 floods ranged from 7 to 10 hours, whereas late-season floods (July 29 and August 6) were 12 and 27 hours in duration, respectively. Early-season flood hydrographs were characterized by a more rapid increase in discharge with the flood front, whereas later-season floods showed a slower rise in the hydrograph (29 July and 6 August 2002) (Figure 3).

4.2. Chloride Chemistry and Mixing Model Results

[16] Chloride end members used in mixing-model analyses were determined from base flow in June of each year (immediately before the onset of the monsoon). These samples provided average chloride end-member concentrations for reactive water of 11 mg/L (CV 5%) in 2001 and 7.5 mg/L (CV of 4%) in 2002. These values compare to regional groundwater-chloride concentrations of 6.4 mg/L [*Wahi*, 2005; *Baillie et al.*, 2007]. Chloride concentration for the precipitation plus overland-flow end-member of 0.4 mg/L was based on several chloride-concentration measurements in ephemeral flows at gauged locations within Walnut Gulch, an experimental watershed that drains into the San Pedro River immediately downstream of our site (D. Goodrich, Agricultural Research Service, personal communication, 2003). This value compares to average measured concentrations of 0.2 mg/L in precipitation. Because relatively little precipitation falls directly on the channel, we chose to use the higher value from Walnut Gulch to ensure that overland flow was included in the unreactive water estimates.

[17] In the 17 July 2001 flood, stream chloride increased from approximately 7 mg/L to 10.6 mg/L at the flood peak and subsequently dropped to between 2 and 3 mg/L on the falling limb (Figure 3). In contrast, chloride concentration during early floods in 2002 decreased from base flow values of 7–9 mg/L to < 2 mg/L during the hydrograph peak, and then increased on the falling limb toward base flow concentrations. During the later-season floods that occurred on 29 July and 6 August, chloride concentration did not change considerably (between 2 and 4 mg/L) during peak or recession of the hydrograph (Figure 3).

[18] Results of the chloride mixing model showed that the amount of reactive-water contribution to each flood was greatest during peak flow. This pattern was most pronounced in early and midseason floods (17 July 2001, and 18 July, 22 July, and 27 July 2002) (Figure 4). The 17 July (2001) flood also had the greatest fraction of reactive water

Table 1. Discharge, Volume, and Percentage of Water Sources to Flood Flow During 2001 and 2002 Based on Cl^- Mixing Model Results[a]

				Percent	
Flood Date	Sequence	Maximum Discharge, m^3/s	Total Volume, m^3	Precipitation and Overland Flow	Reactive Water
2001					
17 July	2	9.6	2.10×10^5	54	46
2002					
18 July	1	2.0[b]	2.34×10^4	74	26
22 July	3	2.1[b]	2.74×10^4	81	19
27 July	6	16.4	1.10×10^5	89	11
29 July	9	13.4	2.22×10^5	76	24
6 August	15	16.3	5.72×10^5	81	19

[a]"Sequence" number represents what order the floods occurred in the entire sequence of flood events during the monsoon.
[b]Indicates an estimated maximum discharge based on stage height.

entering the stream over the entire period of the storm (46%; Table 1). In 2002, the first flood of the season had the greatest reactive input for that year (26%), while the 27 July flood had the lowest reactive water input (11%); this was also the first large flood (>3 m^3/s) of the season. The 22 July and 6 August floods resulted in similar estimates for reactive water input (19% each), while reactive water contributed 24% to the 29 July flood.

[19] Soil lysimeter measurements from the 2001 and 2002 summer season identified wide inter-annual and intra-seasonal variation in chloride concentration at the same location. Soil chloride concentration at the 1.2 m depth ranged from 5 to 50 mg/L (Table 2). The highest concentration was measured during the middle to late-monsoon season in 2002. Chloride concentrations measured in other soil lysimeters in 2001 also was high but did not reach the very high level measured in 2002.

4.3. Nitrate-N, DOC, and DON Chemistry

[20] Nitrate-N concentration during base flow was 0.02 mg/L in 2001. Nitrate-N concentration reached 0.4–0.6 mg/L during the 17 July 2001 flood (Figure 5). This event was the second large flood of the 2001 season, with a relatively high (0.22 mg N/L) preflood nitrate-N concentration that was the result of a flood of similar magnitude that occurred a few days before. The maximum nitrate-N concentration occurred shortly after peak discharge, followed by a decrease to 0.33 mg/L over the next several hours.

[21] Base flow nitrate-N concentration in 2002 was 0.04 mg/L. Nitrate increased rapidly during the flood front to a peak concentration of almost 0.9 mg/L during the 18 July flood and just above 0.6 mg/L on the 22 July flood. These first two floods of the 2002 season had higher nitrate concentrations compared to the July 2001 flood (Figure 5). In all cases, nitrate slowly returned to preflood concentration within several hours following peak discharge. During the 22 July flood, a rapid increase in stream nitrate concentration began at the onset of peak flow, though the nitrate peak lagged the discharge peak by about three and a half hours. Nitrate concentration showed a slow recovery to base flow concentration during the receding limb; however, an on-site rain event occurred during the night, probably resulting in the dilution in nitrate at approximately 0300 hrs (Figure 5).

[22] Discharge-nitrate patterns in the final three floods sampled during 2002 were notably delayed and differed from floods sampled earlier in season (Figure 5). Stream nitrate reached its highest concentration in 2002 during a two-day period in July, several hours after a small flood peak and three to four hours before the first of these later three large floods (27 July; Figure 5). The 27 July flood was the first large flood of the season (~16.4 m^3/s). Nitrate concentration decreased with peak flow from approximately 1 mg/L (the highest stream nitrate concentration in 2002) to just over 0.45 mg/L. The next two large floods (29 July and 6 August), were of similar magnitude as the 27 July flood (~13.4 and 16.3 m^3/s, respectively), but elevated flows lasted longer. Nitrate concentration was relatively unresponsive to peak flow, ranging between 0.5 to 0.75 mg/L during peak and the receding limb of both floods.

[23] Soil-water nitrate concentration was higher in 2002 (up to 41 mg L^{-1}) than in 2001 at the same location and a depth of approximately 1.2 m (Table 2). Middle and late season soil-water nitrate-N concentrations in 2001 were 1.2 mg/L (25 July; measured after at least two large floods) and 1.5 mg/L (21 August), respectively. Nitrate-N concentration measured at other lysimeter depths (0.5 to 1.4 m) and locations (250 m upstream and 100 m downstream of outlet) in 2001 varied between 0.02 mg/L and 0.33 mg/L. Nitrate-N concentration at these same locations in 2002 decreased from approximately 41 mg/L (25 July; measured after several early season small floods) to 5.8 mg/L (29 July) and 0.66 mg/L (13 August).

[24] Nitrate-N concentration measured in open precipitation (i.e., away from vegetation) in 2001 was 0.29 mg/L; in 2002, open-precipitation nitrate was 0.31 mg/L. Concentrations of 0.44 mg/L and 1.0 mg/L were measured in two throughfall samples collected under mesquite vegetation in 2002. Nitrate-N concentration in overland flow and runoff in nearby Walnut Gulch was 0.75 mg/L, and in groundwater, nitrate-N concentration was 0.33 mg/L.

[25] DON concentration during base flow was 0.12 mg/L in 2001 (not shown in figure as sample was taken in June), and changed very little during the 17 July 2001 flood (Figure 5). In 2002, base flow DON concentration was 0.1 mg/L, but it displayed a noticeable increase to 0.8 mg/L during the 18 July flood and to just above 0.4 mg/L during the 22 July flood. These first two floods of the 2002 season had higher DON concentrations compared to the July 2001

Table 2. Nitrate and Chloride Concentrations in Bank Soil Water[a]

Measurement date	Cl^-, mg/L	NO_3^-–N, mg/L
2001		
25 July	22	1.22
21 August	5	1.47
2002		
25 July	12	41
29 July	50	5.7
13 August	33	0.58

[a]Data are shown from a lysimeter at the outlet, at a depth of approximately 1.2 m.

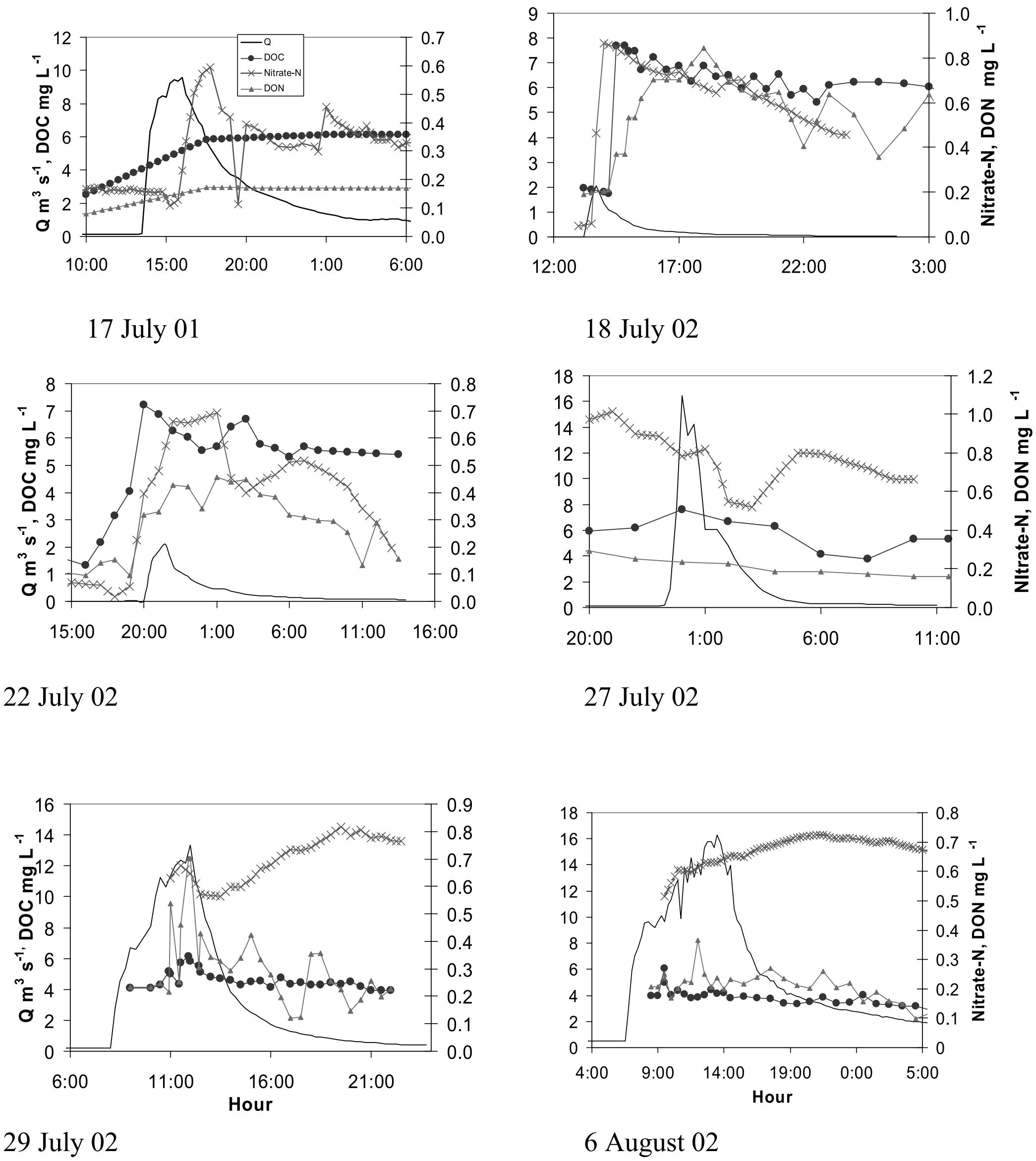

Figure 5. Stream water nitrate-N, DON and DOC concentrations during the floods in 2001 (top) and 2002 (middle and bottom). Q is solid line, DON is line with triangles, DOC is line with squares and Nitrate-N is line with crosses. Symbols indicate actual samples collected and analyzed. Note different axes.

flood (Figure 5). In all cases, DON remained elevated following the flood.

[26] Responses of DON differed between the last three 2002 sampled floods compared to the early-season floods (Figure 5). In the 27 July flood there was almost no change in DON, DON was highly variable during the 29 July flood, and little change in DON occurred during the 6 August event.

[27] DOC concentrations exhibited even less poststorm variability than DON concentrations. The 2001 storm as well as the first two 2002 storms show a generally large initial increase in DOC and then a plateau in concentrations during recession. The latter storms in 2002 show only a subtle increase in DOC during the storm event and a very gradual decline after peak flow.

[28] Notably the storm response of DOC is larger in 2002 than in 2001. When this information is combined with the DON data it is evident that the source of carbon is shifting during some storms. Notably in 2001 from a lower C:N carbon source to a higher C:N carbon source. In 2002 this trend is shifted with the during storm variability in DON and DOC indicating a relatively constant C:N ratio during storms [see also *Brooks and Lemon*, 2007].

5. Discussion

5.1. Water Sources

[29] The amount of reactive water (water in recent, extensive contact with porous media, i.e., soil or groundwater) contributing to flood flow in the San Pedro varied

depending upon antecedent conditions with wetter antecedent conditions leading to larger reactive water contributions. The highest percentage of reactive water in flood flow (46%) was calculated in the 2001 flood. We attribute this to the earlier occurrence of high-discharge storms in 2001 compared with the 2002 summer season (Figure 2). The highest reactive-water input to floods in 2002 (26%) occurred during the first flood of the season that was observed in this study. *Soulsby et al.* [2003] used an end-member mixing analysis to show that the mean subsurface-flow (soil-water) contribution to range from 10 to 52% during several storms in an agricultural watershed, similar to the results here. We expect that groundwater had a lesser contribution than soil water in most floods due to high stream flow, which may have induced a hydraulic gradient from stream to riparian groundwater [e.g., *Marti et al.*, 2000; *Malcolm et al.*, 2003].

[30] At the beginning of the 2002 season, most floods were small (<3 m^3 s^{-1}) and therefore were in contact with a smaller volume of riparian soil. As the season progressed, floods became larger and therefore were capable of flushing a larger volume of soil. The first large flood of the 2002 season (27 July, 16.4 m^3 s^{-1}) resulted in the smallest percentage of reactive-water input of all the 2002 floods measured (Table 1). Middle- and late-season floods (29 July and 6 August 2002) originated from storms that were further upstream than early-season floods (personal observation), and therefore had longer travel times. Additionally the broad hydrograph is indicative of a flood with longer travel time. Much of that soil volume, however, had likely been flushed by previous floods, and the volume of unflushed soil available in a given flood decreased with time and with the number of previous floods that occurred in and above our study area. These middle- and late-season floods had a lesser impact on solute concentrations exported to the stream because the stream and soil compartments were already well-mixed from previous floods, as was evident in the flood chemistry. The majority of soil water entered the stream during peak flow via the displacement of "old" soil water with new water infiltrating the soil. The receding limb and postflood base flow, however, may have been sustained by drainage from bank soils, especially later in the season after the soils had been thoroughly wetted [e.g., *Nyholm et al.*, 2003].

[31] The timing and magnitude of prior events, a flood's residence time in the channel, flood discharge, and antecedent soil-moisture conditions are all variables that affect reactive-water input to floods in semiarid catchments such as the San Pedro River. We were able to qualitatively differentiate between wet- and dry-soil conditions based on year-to-year climate variability in 2001 and 2002. Later-season floods were larger in both peak discharge and runoff volume, probably due to less bank infiltration in saturated conditions. Toward the end of the season, bank soils were no longer presenting material that could be flushed with flood water for the first time, thus any soil-water input to smaller floods that occurred after larger ones was essentially a mixture of stream and soil water from prior floods that moved through or was stored in the adjacent bank until the next event (e.g., 29 July and 6 August 2002; Figures 3 and 4). Soil flushing, rather than bank drainage, was the dominant process driving reactive-water input to flood flow, because reactive-water inputs to the stream peaked coincident with peak flow, indicating a flushing as opposed to a drainage mechanism [*Creed et al.*, 1996; *Chanat et al.*, 2002].

5.2. Solute Variability in Soils

[32] Temporal and spatial variations in flood end-member chemical composition should be addressed when determining the extent of mixing between both water and solute sources to floods [*Soulsby et al.*, 2003], since it has been shown that end-member compositions need not be stable over time [*Anderson et al.*, 1997]. Lysimeter data indicated high variability in chloride end-member composition (Table 2). Soil-water chloride concentrations are elevated at the beginning of the flood season due to evaporative concentration of solutes during the premonsoon dry season. The high variability is likely due to differences in time since the last soil-flushing event and the effectiveness of that flushing by percolating water, soil characteristics and differential rates of evapoconcentration at each sampling location. Soil-water chloride concentration at isolated locations probably decreases during a flood for two reasons: (1) Initial soil water that is high in chloride will be flushed from the bank and replaced by more dilute flood water; and (2) hydrologic gradients change as floods pass through the system, first flood waters force high-chloride waters out of the bank and then later, as the floodwaters drain from the bank, their lower chloride concentration becomes evident in streamflow. High soil-water chloride concentration in the riparian zone is expected because salts are left behind during evapotranspiration [*Duffy and Cusumano*, 1998; R. Scott, Agricultural Research Service, personal communication, 2003]. Particularly during dry periods infiltration is reduced and evapoconcentration causes enrichment of soil solutes in the unsaturated area below the root zone [*Hartsough et al.*, 2001; *Heffernan and Sponseller*, 2004]. *Hartsough et al.* [2001] found that soil-solute concentrations in the vadose zone were highest 2–3 m below the surface, due to flushing by precipitation and uptake by plants, keeping concentrations low nearer to the land surface. This process may be occurring in riparian-zone soils at our study site. The observed variability in soil-water chemistry complicates the calculation of reactive-water input to later-season floods.

[33] As a result we have used two constant end members depending on Cl^- composition one for unreactive water (overland flow and precipitation) of 0.4 mg L^{-1} and one for reactive water (soil and groundwaters) (11 mg L^{-1} in 2001 and 7.5 mg L^{-1} in 2002). Selecting higher Cl^- concentrations for reactive water would decrease the fraction of the reactive-water end member but leave in place the temporal pattern of its contribution to streamflow. However even doubling the Cl^- concentration in reactive water would not dramatically alter the conclusions we draw that wetter antecedent conditions increase the reactive water and inorganic nutrient contribution to the stream. Lower Cl^- concentrations do not make physical sense as they would lead to greater than 100% contributions of reactive water and negative contributions of unreactive water.

[34] Seasonal variability in soil-water nitrate that is available for flushing to the stream results from a combination of physical, chemical, and biological controls, including trans-

port, redox reactions, nitrification, denitrification, and uptake by plants and microorganisms. The most important physical control on soil-water nitrate is displacement by infiltrating flood water during high flow, primarily through translatory [*Chorley*, 1978] and macropore flow [*Buttle*, 1998]. Our data suggest that transport accounts for most of the loss of nitrate, given the large contribution of soil water to flood discharge, which carries with it accumulated solutes like nitrate. However, we cannot discount rapid denitrification as a factor in an event-based decrease in soil-water nitrate. Indeed, *Harms* [2004] showed rapid increases in denitrification enzyme activity following summer storms. It is likely that plant and microbial uptake caused a more gradual, seasonal decrease in soil-water nitrate (note lower values in Table 2 late in 2002 as well as lower stream nitrate values).

5.3. Nutrient Variability as Influenced by Hydrology

[35] Solute concentrations in both soil water and in the stream during the monsoon season were lower in a year with wet antecedent soil-moisture conditions (2001) than during a year with ~80% lower antecedent precipitation (2002). During the dry season, hillslopes, the riparian zone, and the stream are disconnected and isolated, allowing potentially large, mobile nutrient pools to accumulate in riparian-zone soils. These solutes are mobilized during monsoon floods, when dry soils are flushed for the first time in several months. Our findings indicate that hydrologic connectivity is lower, and mobile-solute accumulation greater, during drier years. These findings are consistent with those of *Biron et al.* [1999], who showed that dry antecedent conditions in a small, forested catchment led to high stream and soil-water concentrations during flushing events, as well as *Brooks et al.* [1999], who showed that retention of N deposition was lower during dry years in headwater catchments in the Rocky Mountains. Similarly, *Burns et al.* [1998] demonstrated that soil nutrients were flushed from the soil early in storm flow in a humid, subtropical, forested catchment.

[36] In contrast with the general pattern of soil flushing early in floods observed both here and in other studies, the high stream water nitrate concentrations that occurred several hours after the 27 July 2002 flood did not coincide with peak flow. This later flush suggests an additional mechanism, beyond soil accumulation and flushing, that provides N to the stream (Figure 5). Possible sources of nitrate include bank drainage of previously mineralized and nitrified nitrogen that occurred during hydrograph recession, upwelling of nutrient-rich hyporheic water, parafluvial inputs (located lateral to the stream), or transport from an upstream event. The large increase in concentration after peak flow and during elevated stream discharge indicates that the most likely cause is large-scale bank drainage.

[37] Hyporheic and parafluvial zones of semiarid streams may be a significant source of nitrate to the surface stream [*Dent and Grimm*, 1999; *Holmes et al.*, 1998; *Valett et al.*, 1994]. It is unlikely, however, that hyporheic inputs were responsible for the high nitrate concentration we observed during floods, due to the minimal volume of water that the hyporheic zone is capable of contributing compared with total flood-water volume.

[38] Recent studies suggest that agricultural land upstream from our study site may be an N source to the river [*Brooks and Lemon*, 2007], resulting in highly variable N loading to the stream during the monsoon season. *Malcolm et al.* [2003] found that dissolved oxygen (DO) and nitrate-N concentrations in the hyporheic zone of a small agricultural stream were extremely variable with depth before a series of autumn storms; however, both DON and nitrate-N concentrations decreased during the events and became similar with depth among several sample sites in the stream, indicating a well-mixed system. The progression from higher and more variable stream-nitrate concentrations in early 2002 floods, to lower concentrations and muted variability in later-season floods, is likely is due to a slow transition from a system that is hydrologically disconnected and composed of small, heterogeneous pockets of nitrate-rich soil and sediment, to one that was both well mixed and had increased nutrient reaction rates.

[39] Of particular interest in the results for nutrient concentrations during storm events (Figure 5) is the fact that under wetter antecedent conditions nitrate is a more important contributor to total nitrogen than DON. This result can be seen in both 2001 (with the wetter preceding winter) and in 2002, with the earlier storms having relatively more DON than the later storms (Figures 5d–5f). This result is not terribly surprising as the availability of water with wetter antecedent conditions should increase microbial respiration and nitrogen mineralization and nitrification. Wetter conditions would also, as noted below, increase the volume of water available from the soil zone and thus the relative importance of nitrate in the stream. Some might consider the result counter-intuitive as since wetter conditions might be expected to lead to more denitrification but this situation is unlikely in the case of the San Pedro as wetter conditions are not likely to be enough to overcome the generally oxic conditions in groundwater.

5.4. Antecedent Conditions and Implications

[40] Wetter antecedent conditions limit accumulation of soil solutes and promote high soil-water input to floods compared with dry conditions. Thus, loading of solutes is reduced under wetter conditions. In our study, wetter winter conditions were responsible for a higher fraction of soil-water input to the 17 July 2001 flood, and consequently the lowest stream and soil-water nitrate concentrations seen in both years. Our results are the first data to show a clear connection between interannual climate variability and nutrient input to semiarid rivers, a connection hypothesized for a central Arizona catchment by *Grimm and Fisher* [1992] based on correlations between flood frequency and floodwater nitrate concentration.

[41] *Webb and Betancourt* [1992] suggested that seasonality of annual flooding in southwestern U.S. rivers may be changing due to directional climate change. Southern Arizona rivers such as the San Pedro, Gila, Santa Cruz, and San Francisco experience their largest floods during the winter months, due to the more widespread, frontal systems typical of this period. A change in these types of storms can cause a change in flood seasonality induced by climate variability, as seen on the Santa Cruz River, Arizona [*Webb and Betancourt*, 1992. Increasingly larger-magnitude floods could cause more rapid and elevated solute and nutrient

stream water concentrations during rainy seasons in southern Arizona rivers. In the presumed N-limited San Pedro River, rapid additions of nitrate during floods should have dramatic effects on aquatic primary production, which would be exacerbated by any anthropogenic sources of nitrate. This process may be especially important for land management practices and the coincidence of agricultural runoff with already elevated floodwater solute and nutrient concentrations.

6. Conclusions

[42] Our study has shown that during flood flows the greatest fraction of groundwater and soil water occurs during the flood peaks, and that this mechanism is the most likely avenue for solute loading to the stream. This is especially the case for wetter years, such as 2001, when there was a greater soil-water displacement into the stream due to moister preflood soil conditions. Nitrate accumulation in soil water during the relatively dry winter of 2002 resulted in floodwater and soil-water nitrate concentrations in summer 2002 that were higher than those measured during summer 2001 floods, which followed a wetter winter. Dry conditions in 2002 inhibited the movement and/or biogeochemical cycling of this highly concentrated and potentially mobile pool of soil solutes from the soil to the stream until the onset of the summer monsoon.

[43] We suggest that the wetter year resulted in high intersystem connectivity and in reduced availability of transportable nutrients due to the following: (1) five-fold higher precipitation in the winter of 2001 compared with winter 2002; (2) a larger first flood of the season, which occurred a few days before the 17 July 2001 flood and flushed some solutes from the soil; and (3) less-concentrated nutrient pools due to a smaller aerobic soil volume and more uptake by vegetation in the wetter year. Nitrate concentrations in late season 2002 floods were relatively unchanged during the peak and falling limb of the hydrograph, suggesting that (1) previous floods had exhausted the soil compartment of nitrate that accumulated over winter, and (2) increased water availability in soils promoted biological uptake or denitrification of N between storm events. The elevated flood-nitrate concentration later in the monsoon could be attributed to a longer residence time of flood water in the alluvial aquifer/channel and transport of flood water from upstream areas of the catchment.

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