

## Combined effects of leaf litter inputs and a flood on nutrient retention in a Mediterranean mountain stream during fall

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### *Abstract*

This study examined the effect of increasing in-channel leaf standing stocks on hydrologic transient storage and nutrient retention in a Mediterranean mountain stream. A flood at the end of the leaf fall period provided the opportunity to examine the effect of abrupt removal of much of the leaf material. Twenty-one chloride additions were performed from October to December 2004. In 13 of these, we also added ammonium and phosphate to estimate nutrient uptake lengths and uptake velocities to assess nutrient retention. The one-dimensional transport with inflow and storage (OTIS) model was used to estimate transient water storage parameters. Although discharge remained constant during leaf fall, water residence time increased because of in-channel litter accumulation, as did nutrient uptake velocity. Flooding reduced leaf benthic standing stocks by 65% and dramatically altered hydraulic and nutrient retention properties of the channel. After recession, the stream rapidly recovered in terms of nutrient retention, especially for phosphate. Abrupt changes in discharge under flood conditions largely determined the variability in stream nutrient retention. However, leaf litter inputs played an important role in nutrient dynamics during constant flow. Because both the flood regime and the timing of leaf fall are being regionally altered by climate change, our results have implications for stream nutrient dynamics under climate change scenarios.

Intense leaf fall from deciduous riparian vegetation is of major importance for both the community structure (Wallace et al. 1997) and metabolism (Crenshaw et al. 2002) of streams. Leaf litter inputs provide large quantities of energy to headwater streams that typically exhibit low levels of primary productivity (Fisher and Likens 1973). The ecological relevance of these inputs is well recognized,

especially in temperate regions (Wallace et al. 1997). Streams in Mediterranean regions, in contrast to those from more humid climates, are characterized by high interannual variability in the intensity and frequency of floods as well as by periods of intermittent flow. In addition, in Northern Hemisphere Mediterranean regions higher leaf litter input coincides with periods of high flood frequency, low temperature, and low autotrophic activity (Gasith and Resh 1999). Therefore, the residence time of the allochthonous matter in Mediterranean streams may be much shorter than in temperate streams because it enters shortly before or in conjunction with flooding. In consequence, the ecological relevance of this allochthonous energy source may depend on the timing of flood events relative to leaf inputs.

Mediterranean regions are among the most vulnerable to climate change (Schröter et al. 2005). In these regions, both a change in the frequency and intensity of rains and an increase in temperatures are expected (Christensen and Christensen 2004). Under this scenario, it is likely that alterations in the regimes of autumnal leaf inputs and flooding will have implications for stream metabolism and

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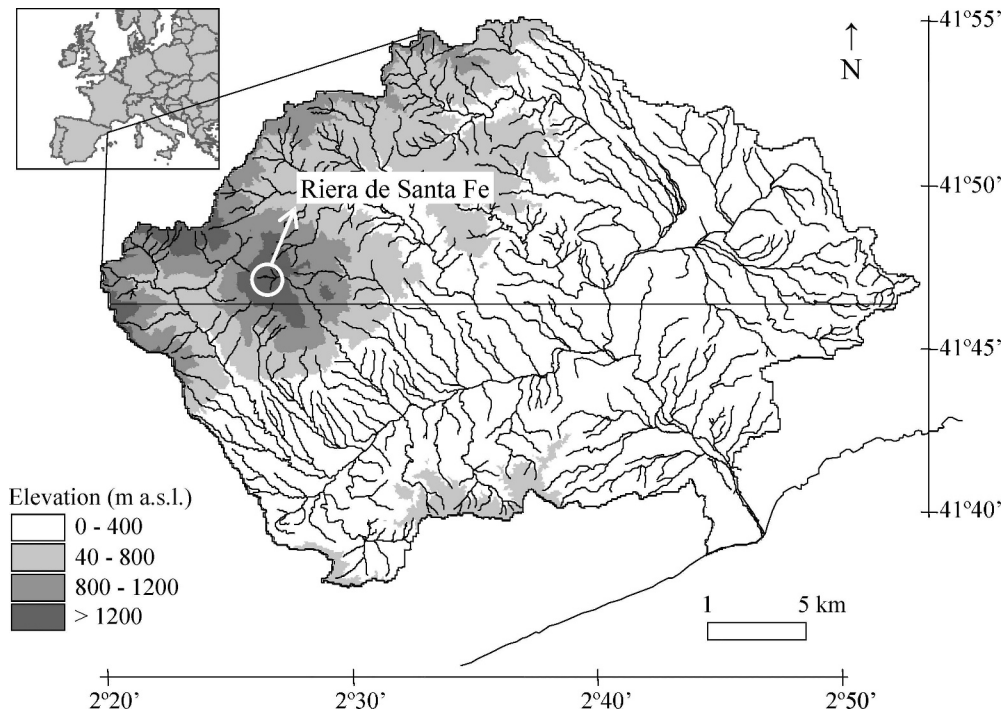


Fig. 1. Map showing general location of Riera de Santa Fe in Europe and in the La Tordera catchment.

biogeochemistry. The effects of autumnal leaf litter inputs on stream biota (Maamri et al. 1997) and metabolism (Acuña et al. 2004) have been studied previously in Mediterranean streams, but little is known about their effect on nutrient retention. In addition, methodological constraints on measuring nutrient retention under flood conditions, together with the unpredictability and high rate of change of these episodic events, have restricted the number of studies assessing flood effects on nutrient retention (but *see* Martí et al. 1997).

Nutrient retention in stream ecosystems is a combination of hydrologic, biologic, and chemical retention (Valett et al. 1996). Hydrologic retention is influenced by discharge and the hydraulic and morphologic properties of the stream channel, which determine the extent of the transient water storage (i.e., water moving at slower velocity than the average velocity in the channel, relative to the free flowing water). The magnitude of the transient water storage can be relevant for nutrient retention, because the interaction between stream biota and available nutrients is greater in transient storage zones than in the free flowing water (Triska et al. 1989). Therefore, it has been hypothesized that the influence of in-stream processes on stream nutrient concentrations increases with transient water storage. However, literature results conflict (Mulholland et al. 1997; Hall et al. 2002; Ensign and Doyle 2005), possibly because transient water storage can originate in a variety of channel structures that delay water transport (e.g., eddies, back waters, side channels, streambed irregularities, pools, mats of filamentous green algae, hyporheic zones, and organic debris dams), which may contribute differently to nutrient retention across streams or within streams over time.

The presence of in-channel vegetation (Harvey et al. 2003), debris dams (Lautz et al. 2006), flow obstacles (Ensign and Doyle 2005), and complex stream morphology (Gücker and Boëchat 2004) enlarges transient storage zones relative to main channel cross-sectional area. In temperate streams with well developed riparian forests, autumnal litter inputs may naturally modify channel hydraulic properties, increasing transient water storage (Haggard and Storm 2003). Ecologically, leaf litter constitutes an external input of energy and resources to stream communities and provides new colonization substrata for microbial communities. Therefore, an increase in transient water storage coupled to enhanced microbial colonization during leaf fall can result in a hot nutrient retention moment (*sensu* McClain et al. 2003). Mulholland et al. (1985) attributed temporal variation in phosphate retention efficiency to the availability of benthic organic matter in streams, showing that it was greatest during leaf fall. Nevertheless, several studies have also shown that discharge is a key factor in controlling stream nutrient retention efficiency. In general, rising discharge lowers nutrient retention, which may override or counterbalance other effects such as the accumulation of benthic organic matter. This pattern is consistent both for variation across streams (Peterson et al. 2001; Hall et al. 2002; Martí et al. 2004) and for temporal variation within a stream (Butturini and Sabater 1998). Floods not only suddenly increase discharge, but also dramatically affect stream biota and decrease stream nutrient retention (Martí et al. 1997). Little is currently known about the subsequent recovery of streams from high discharge events.

In this study we present insights into the combined effects of leaf litter inputs and flooding on in-stream

nutrient retention. The aims of this study were (1) to examine how autumnal accumulation of leaf litter modifies the hydraulic properties of the channel, including transient water storage, (2) to evaluate nutrient retention response during this period, and (3) to examine its relationship with leaf accumulation and hydraulic properties. The occurrence of a flood just after all trees had completely lost their leaves enabled us to examine flood effects and subsequent responses of both hydraulic properties and in-stream nutrient retention to the abrupt removal of much of the accumulated leaf litter.

## Methods

**Study site**—The study was conducted in Riera de Santa Fe, a second-order tributary of La Tordera stream in the natural protected area of Parc Natural del Montseny in the northeastern Iberian Peninsula (50 km north of Barcelona, Spain; Fig. 1). At the study site (1,180 m a.s.l.) the stream drains a 2.15 km<sup>2</sup> catchment dominated by siliceous geology and forested primarily with *Fagus sylvatica* at lower elevations and *Abies alba* at higher elevations. Mean annual precipitation is 1,200 mm and occurs mostly during autumn and spring. Precipitation occasionally falls as snow during the coldest months (December and January). Stream flow is permanent, with a mean discharge of 16.2 L s<sup>-1</sup> (biweekly 2004–2005). During floods, which occur mostly during spring and autumn, stream discharge can increase by more than two orders of magnitude.

We selected a morphologically homogeneous 140-m reach, dominated by pools and riffles and with a slope of 0.094 m m<sup>-1</sup>. The streambed was composed of cobbles (47%), boulders (25%), and pebbles (21%) with patches of gravel (5%) and sand (1%). The riparian vegetation was well developed and dominated by trees (*Fagus sylvatica*) with some shrubs (*Sambucus nigra*).

**Sampling strategy**—Between October and December 2004 we assessed the temporal variation in hydraulic and nutrient retention parameters relative to variation in leaf benthic standing stocks and stream discharge. The leaf fall period began in the first week of October and lasted through November. We sampled benthic litter weekly in October, then at least twice weekly through November until all the trees had lost their leaves. In the first week of December, a major flood washed out 65% of the leaf biomass. To assess the temporal variation in hydraulic and nutrient retention parameters as the flood receded, we then sampled three times a week through December. In total, 21 samplings were completed during the study period (Oct–Dec 2004).

On each sampling date, we conducted a short-term conservative tracer (Cl<sup>-</sup> as NaCl) addition at constant rate to estimate transient water storage parameters. In 13 additions we also added ammonium (NH<sub>4</sub>-N) (as NH<sub>4</sub>Cl) and PO<sub>4</sub>-P (as Na(H<sub>2</sub>PO<sub>4</sub>)·2H<sub>2</sub>O) to estimate nutrient retention metrics. Additions began at approximately 11:00 h and lasted until conductivity reached a plateau indicating complete mixing at the bottom of the reach (i.e., 2–3 h). Conductivity was automatically recorded every

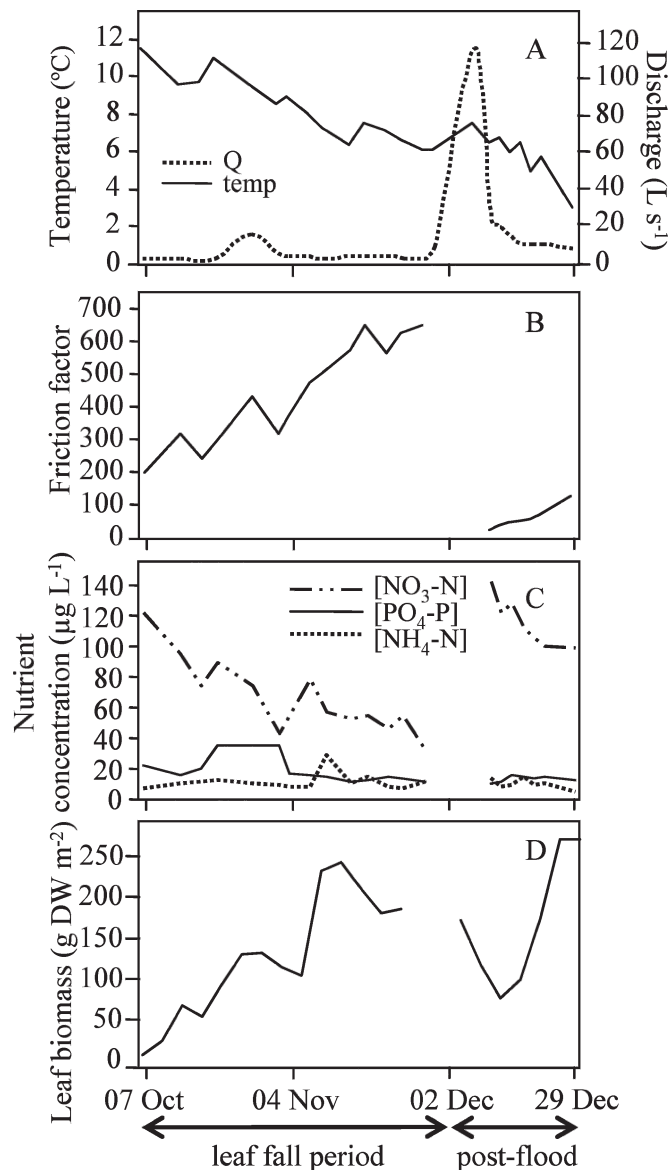


Fig. 2. Temporal variation of (A) stream discharge and water temperature, (B) Darcy–Weisbach friction factor, (C) ambient nutrient concentrations, and (D) leaf standing stocks in the stream channel during the study period. The break in the lines corresponds to the onset of flooding.

5 seconds using a conductivity meter (WTW, model LF 340) connected to a data logger (Campbell Scientific) placed at the bottom of the reach. On the dates of nutrient addition, we measured conductivity and collected water samples at eight locations along the reach before the addition and once conductivity reached a plateau. Water samples for chemical analyses were collected using 50-mL syringes. At each location, two replicates were collected for ambient concentrations and five for plateau concentrations. Water samples were filtered in the field using Whatman GF/F fiberglass filters (0.7 µm pore diameter) and refrigerated until analysis. NH<sub>4</sub>-N, nitrate (NO<sub>3</sub>-N), nitrite (NO<sub>2</sub>-N), and soluble reactive phosphorus (SRP) concentrations were analyzed following standard colori-

Table 1. Temporal variation in nutrient uptake length ( $S_w$ ), uptake length ratio ( $S_w \text{ NH}_4\text{-N} : S_w \text{ PO}_4\text{-P}$ ), nutrient uptake velocity ( $V_f$ ), uptake velocity ratio ( $V_f \text{ NH}_4\text{-N} : V_f \text{ PO}_4\text{-P}$ ), and DIN : P molar ratio during the study period.

Date	$S_w$ (m)			$V_f$ (mm min <sup>-1</sup> )		$V_f$ ratio	DIN : P molar ratio
	PO <sub>4</sub> -P	NH <sub>4</sub> -N	$S_w$ ratio	PO <sub>4</sub> -P	NH <sub>4</sub> -N		
Leaf fall period							
07 Oct 04	287.3	60.5	0.21	0.40	1.89	4.75	14.8
21 Oct 04	135.8	51.3	0.38	0.71	1.87	2.65	6.6
04 Nov 04	223.1	44.4	0.20	0.71	3.56	5.03	9.3
11 Nov 04	251.0	55.7	0.22	0.49	2.22	4.51	14.9
26 Nov 04	196.6	51.9	0.26	0.66	2.49	3.79	11.5
30 Nov 04	—	30.0	—	—	5.70	—	10.3
Post-flood period							
13 Dec 04	1312.2	416.4	0.32	0.55	1.73	3.15	45.4
15 Dec 04	825.2	551.5	0.67	0.68	1.01	1.50	32.9
17 Dec 04	665.6	299.9	0.45	0.68	1.50	2.22	24.0
19 Dec 04	585.2	240.8	0.41	0.55	1.34	2.43	24.0
21 Dec 04	429.3	227.6	0.53	0.61	1.15	1.89	22.8
23 Dec 04	287.2	148.6	0.52	0.88	1.70	1.93	21.0
29 Dec 04	202.5	92.5	0.46	1.16	2.54	2.19	22.9

metric methods (APHA 1998) using Bran+Luebbe auto-analyzers (TRAACS for NO<sub>3</sub>-N, NO<sub>2</sub>-N, and SRP, and Technicon for NH<sub>4</sub>-N). On average, the nutrient additions increased NH<sub>4</sub>-N and SRP concentrations by  $14.4 \pm 7.6$  and  $6.8 \pm 2.7$  fold above ambient concentrations, respectively. Despite this variability in enrichment levels, we did not find a significant relationship between the degree of enrichment and uptake lengths or uptake velocities.

Water temperature at each sampling station was determined several times over the course of each addition, and values were averaged. Discharge ( $Q$ , L s<sup>-1</sup>) and average water velocity ( $u$ , m s<sup>-1</sup>) were measured using the time–curve conductivity data recorded at the bottom of the reach. Calculation of  $u$  was done by dividing the reach length by the time needed to increase the conductivity to one half of the plateau (i.e., nominal travel time).  $Q$  calculation was based on a tracer mass balance approach.

Along the reach, we defined 29 channel transects at 5-m intervals. On each sampling date at each transect we measured the channel wetted width ( $w$ , m) and a cross-sectional profile (every 20 cm) of water depth ( $h$ , m) and estimated the percentage coverage by different kinds of substrata. A measure of channel roughness was calculated by solving the Darcy–Weisbach equation

$$f = (8ghs)/u^2 \quad (1)$$

where  $f$  is the friction factor coefficient,  $g$  is the gravitational acceleration (9.8 m s<sup>-2</sup>), and  $s$  (m m<sup>-1</sup>) is the streambed slope. This coefficient was used as an integrative measure of the temporal changes in both discharge and leaf standing stocks.

Finally, on each sampling date we visually estimated the percentage of stream surface that was covered by leaves and the percentage occupied by pools and riffles. These estimates were made for each stream segment between every consecutive transect. Pools and riffles were categorized according to flow types following River Habitat Survey guidelines (EA 2003). Estimated percentages for

each stream segment were then used to calculate the surface area for each habitat type (i.e., pools or riffles). Leaf standing stock was determined by sampling twenty-four 20 cm × 20 cm quadrats on each sampling date. Half of the samples were collected in pools and half in riffles to account for differences in leaf accumulation patterns associated with each habitat type. Leaf samples were dried and weighed to determine dry weight (g DW m<sup>-2</sup>).

*Estimation of transient water storage parameters*—The magnitude of transient water storage zones was quantified using the one-dimensional transport model with inflow and storage (OTIS, Runkel 1998) to obtain two parameters: (2) the transient water storage zone ( $A_s$ , m<sup>2</sup>) and (2) the water exchange coefficient ( $k_1$ , s<sup>-1</sup>) between the free flowing water and the transient storage zone.

The cross-sectional area of the stream channel ( $A$ ) was calculated by dividing  $Q$  by  $u$  and was used to obtain the ratio between the cross section of the transient water storage zone and that of the surface stream channel ( $A_s : A$ ). This was used to estimate  $k_2$  (the water exchange coefficient between the transient storage zone and the free flowing water) as

$$\frac{A_s}{A} = \frac{k_1}{k_2} \quad (2)$$

Before applying the OTIS model to the conductivity time-series data, we calculated the Damkohler number (DaI) to evaluate whether the selected reach length ( $L$ ) was appropriate (Wagner and Harvey 1997). DaI was estimated as

$$\text{DaI} = ((k_1 + k_2)L)/u \quad (3)$$

Although estimated hydraulic uncertainties are lowest at DaI values ~1.0, values of 0.5 to 5 have been considered acceptable (Hall et al. 2002; Ensign and Doyle 2005). If the reach length is too short (DaI < 0.5), not enough water enters the transient storage zone to estimate transient water

storage parameters properly. Conversely, DaI values  $>5$  indicate that dispersion dominates the shape of the solute concentration curve.

Relationships between hydraulic parameters (i.e.,  $w$ ,  $h$ ,  $u$ ,  $A_s$ ,  $A_s:A$ ,  $k_1$ , and  $k_2$ ) and discharge or leaf benthic standing stocks were examined using univariate regression analyses. The level of significance considered was  $p < 0.05$ .

*Calculation of nutrient retention metrics*—Two nutrient retention metrics were estimated from the short-term nutrient additions at constant rate: nutrient uptake length ( $S_w$ , m) and nutrient uptake velocity ( $V_f$ ,  $m\ s^{-1}$ ), also referred to as mass-transfer coefficient (Stream Solute Workshop 1990).  $S_w$ , the average distance traveled by a nutrient molecule before being removed from the water column, was calculated based on the variation in tracer nutrient concentrations along the reach at plateau conditions (corrected for ambient levels) and by the variation in conductivity using the following equation:

$$N_x = N_0 e^{-bx} \quad (4)$$

where  $N$  is the nutrient concentration at the first sampling station ( $N_0$ ) and at the sampling station located  $x$  m downstream ( $N_x$ ), and  $b$  is the nutrient retention coefficient ( $m^{-1}$ ).  $S_w$  is the inverse of this coefficient (i.e.,  $S_w = -b^{-1}$ ) and is inversely proportional to stream nutrient retention efficiency. Simple linear regression analysis was used to determine the degree of significance of the  $S_w$  values (accepted significance level was  $p < 0.05$ ). The ratio between  $S_w$  for ammonium and phosphate (i.e.,  $S_w-NH_4:S_w-PO_4$ , Martí and Sabater 1996) was calculated to compare the relative retention efficiency of the two nutrients among sampling dates.

We calculated  $V_f$  by dividing  $u$  times  $h$  by  $S_w$ .  $V_f$  indicates the rate at which a molecule of a nutrient is removed from the water column and is a good indicator of the stream nutrient demand across variable flows (Hall et al. 2002).

Relationships between nutrient retention metrics (i.e.,  $S_w$  and  $V_f$ ) and hydrologic and hydraulic parameters or leaf benthic standing stocks were examined using univariate regression analyses. The level of significance considered was  $p < 0.05$ . All statistical analyses were done using SPSS for Windows (version 12.0, SPSS, Chicago).

## Results

*Environmental characterization during the study period*—During the leaf fall period (07 October to 02 December),  $Q$  remained almost constant at around  $8\ L\ s^{-1}$ . However, just after defoliation was complete on 10 December, a large storm increased  $Q$  from  $7\ L\ s^{-1}$  to  $124\ L\ s^{-1}$  (Fig. 2A). After the flood,  $Q$  receded rapidly, but at the end of the study the stream was still twice its pre-storm discharge. During the study, water temperature steadily declined from  $12^\circ C$  to  $3^\circ C$  (Fig. 2A) and was unaffected by changes in discharge. The values of the friction factor  $f$  increased three-fold during the leaf fall period from 205 to 657 (Fig. 2B), dramatically decreased just after the flood, and

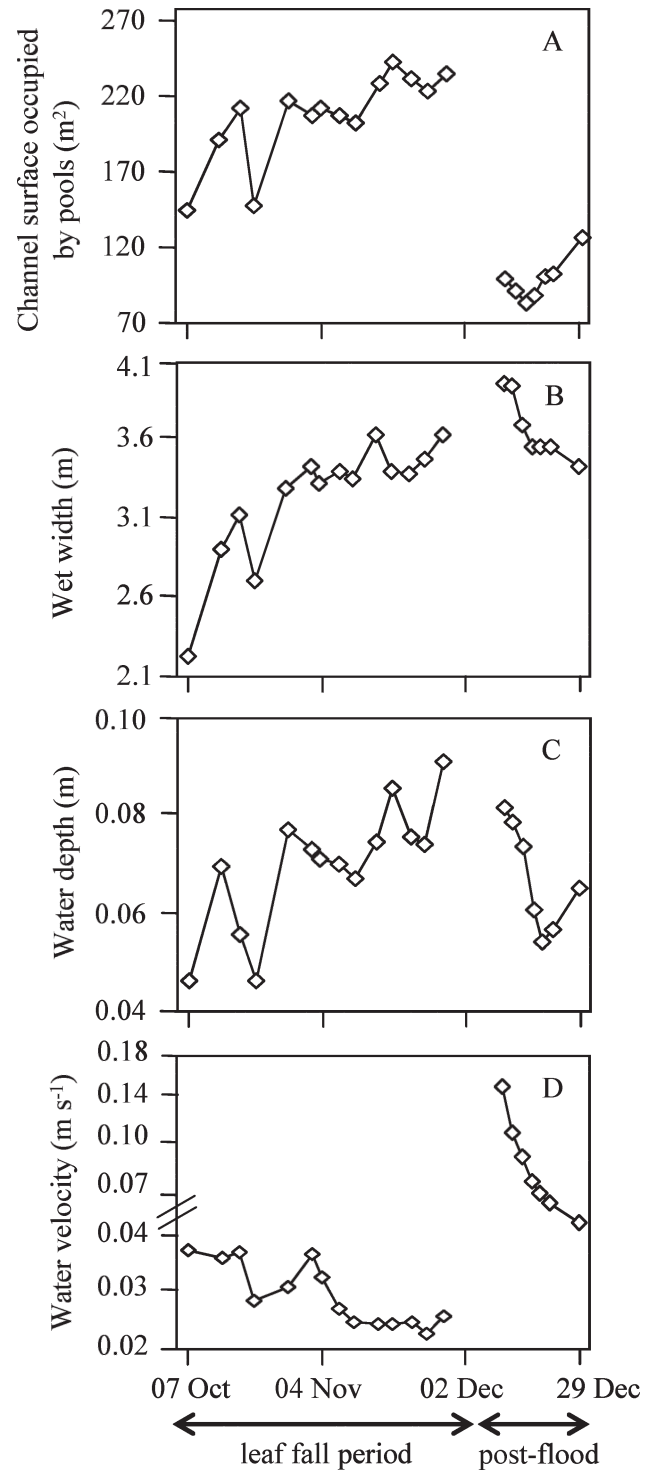


Fig. 3. (A) Surface area of the stream channel dominated by pools, (B) average channel wetted width, (C) average water depth, and (D) average water velocity during the study period. The break in the lines corresponds to the onset of flooding.

gradually increased afterward. By the end of the study,  $f$  was still five-fold less than the pre-flood values. Concentrations of SRP and  $NH_4-N$  remained low throughout the study (mean  $\pm 1$  SE were  $14.4 \pm 8.2\ \mu g\ P\ L^{-1}$  and  $8.3 \pm$

Table 2. Temporal variation of hydraulic parameters during the study period. Discharge (Q), dispersion (D), cross-sectional area of the transient storage ( $A_s$ ), transient storage exchange rates ( $k_1$ , from channel to transient storage, and  $k_2$ , from transient storage to main channel), ratio of the cross-sectional area of the transient storage zone to the cross-sectional area of the stream ( $A_s:A$ ), and Damkohler number (DaI).

Date	Q (L s <sup>-1</sup> )	D (m <sup>2</sup> s <sup>-1</sup> )	$A_s$ (m <sup>2</sup> )	$k_1 \times 10^{-3}$ (s <sup>-1</sup> )	$k_2 \times 10^{-3}$ (s <sup>-1</sup> )	$A_s:A$	DaI
Leaf fall period							
14 Oct 04	6.53	0.07	0.036	0.25	0.88	0.29	3.96
18 Oct 04	8.90	0.08	0.045	0.14	0.61	0.23	2.58
21 Oct 04	6.19	0.09	0.039	0.14	0.54	0.26	2.79
28 Oct 04	20.76	0.14	0.042	0.08	0.54	0.07	2.28
02 Nov 04	9.70	0.08	0.036	0.14	0.82	0.17	3.33
04 Nov 04	8.18	0.10	0.041	0.12	0.56	0.22	2.55
16 Nov 04	8.34	0.08	0.050	0.10	0.43	0.23	2.44
19 Nov 04	8.55	0.07	0.063	0.12	0.42	0.29	2.44
23 Nov 04	7.76	0.08	0.054	0.10	0.39	0.26	2.20
30 Nov 04	6.69	0.07	0.053	0.12	0.40	0.30	2.31
Post-flood period							
13 Dec 04	28.72	0.22	0.022	0.50	4.05	0.12	4.27
15 Dec 04	23.65	0.23	0.029	0.22	1.48	0.15	2.00
17 Dec 04	18.94	0.20	0.032	0.20	1.08	0.18	1.74
19 Dec 04	15.34	0.18	0.033	0.21	1.02	0.21	1.95
21 Dec 04	14.25	0.17	0.030	0.21	1.11	0.19	2.30
23 Dec 04	15.47	0.17	0.041	0.20	0.93	0.22	2.13
29 Dec 04	11.61	0.15	0.043	0.19	0.75	0.25	2.18

5.0  $\mu\text{g N L}^{-1}$ , respectively; Fig. 2C). In contrast,  $\text{NO}_3\text{-N}$  concentration decreased from 122  $\mu\text{g N L}^{-1}$  to 30  $\mu\text{g N L}^{-1}$  during leaf fall, increased sharply after the flood (to 252  $\mu\text{g N L}^{-1}$ ), and then decreased again. Due to the variation in  $\text{NO}_3\text{-N}$  concentration, the dissolved inorganic nitrogen to phosphorus concentration molar ratio (DIN:P) varied from a mean of  $11.3 \pm 4.0$  before the flood to 45.4 just after the flood, after which it decreased gradually to 22.9 by the end of the study (Table 1). Leaves accumulated in the stream channel during the leaf fall period from 9.3 g DW  $\text{m}^{-2}$  to 217.5 g DW  $\text{m}^{-2}$  (Fig. 2D). After the flood, 65% of leaf benthic standing stocks were washed from the reach, decreasing stocks to 77.1 g DW  $\text{m}^{-2}$ . Two weeks after the disturbance, in-channel leaf standing stocks had recovered to pre-flood levels (Fig. 2D).

*Temporal variation of hydraulic parameters*—During leaf fall, the percentage of reach surface area dominated by pools increased from 51% to 67% (141  $\text{m}^2$  to 339  $\text{m}^2$ ; Fig. 3A). The decrease of leaf standing stocks after the flood coincided with a sharp decrease in the proportion of reach surface area dominated by pools. Once the flood receded, pool area increased again, but by the end of the study was still less than before (Fig. 3A).

Because Q was relatively constant during the leaf fall period, the observed changes in the relative proportion of habitat types resulted in a gradual increase of the average channel  $w$  and  $h$  (Fig. 3B,C) and a concomitant decrease in average  $u$  (Fig. 3D). During this period, the variation in these parameters was significantly related to the total biomass (g DW  $\text{m}^{-2}$ ) of leaves accumulated in the stream channel ( $w = 1.7\text{biomass}^{0.14}$ ,  $R^2 = 0.87$ ,  $p < 0.001$ ,  $\text{df} = 12$ ;  $h = 0.03\text{biomass}^{0.17}$ ,  $R^2 = 0.58$ ,  $p < 0.005$ ,  $\text{df} = 12$ ;  $u = 0.04e^{-0.0013\text{biomass}}$ ,  $R^2 = 0.53$ ,  $p < 0.005$ ,  $\text{df} = 12$ ). During

the flood, mean  $w$  increased from 3.6 m to 3.9 m, mean  $h$  decreased from 9 cm to 8 cm, and  $u$  increased five-fold. Once the flood receded, all of these parameters returned nearly to pre-flood values.

The Damkohler number ranged between 1.7 and 4.3 (Table 2), and therefore hydraulic parameters estimated with the OTIS model were considered reliable.  $A_s$  gradually increased over the leaf fall period (Table 2) and positively correlated with leaf benthic standing stocks ( $A_s = 0.4e^{0.002\text{biomass}}$ ,  $R^2 = 0.46$ ,  $p < 0.050$ ,  $\text{df} = 8$ ). In contrast,  $k_1$  and  $k_2$  slightly decreased during this period and were negatively correlated with leaf benthic standing stocks ( $k_1 = 0.0004-0.0001\ln(\text{biomass})$ ,  $R^2 = 0.59$ ,  $p = 0.010$ ,  $\text{df} = 8$  and  $k_2 = 0.0008e^{-0.003\text{biomass}}$ ,  $R^2 = 0.58$ ,  $p < 0.010$ ,  $\text{df} = 8$ ). The flood had opposite effects on the hydraulic parameters (Table 2). After the flood,  $A_s$  decreased 2.4-fold and  $k_1$  and  $k_2$  increased 4.2-fold and 10-fold, respectively. During discharge recession,  $A_s$  tended to increase and  $k_1$  and  $k_2$  tended to decrease, but at the end of the sampling period  $A_s$  had not fully recovered to pre-flood values and  $k_1$  and  $k_2$  were still two times greater than pre-flood values.

Combining all dates,  $A_s:A$  and  $A_s$  were negatively correlated with Q ( $A_s:A = 0.27e^{-0.03Q}$ ,  $R^2 = 0.63$ ,  $p < 0.001$ ,  $\text{df} = 15$ ;  $A_s = 0.05e^{-0.02Q}$ ,  $R^2 = 0.36$ ,  $p < 0.050$ ,  $\text{df} = 15$ ), whereas  $k_1$  and  $k_2$  were positively correlated to Q ( $k_1 = 6.4 \times 10^{-5} + 9.1 \times 10^{-6}Q$ ,  $R^2 = 0.42$ ,  $p = 0.005$ ,  $\text{df} = 15$ ; and  $k_2 = 0.0003e^{0.07Q}$ ,  $R^2 = 0.69$ ,  $p < 0.001$ ,  $\text{df} = 15$ ). No transient water storage parameter was significantly related to litter accumulation when all the sampling dates were combined. Much of the variability in  $A_s$ ,  $k_1$ , and  $k_2$  was explained by the friction factor coefficient,  $f$  ( $A_s = 0.013f^{0.219}$ ,  $R^2 = 0.74$ ,  $p < 0.001$ ,  $\text{df} = 15$ ;  $k_1 = 0.001f^{-0.33}$ ,  $R^2 = 0.69$ ,  $p < 0.001$ ,  $\text{df} = 15$ ;  $k_2 = 0.009f^{-0.48}$ ,  $R^2 = 0.77$ ,  $p < 0.001$ ,  $\text{df} = 15$ ).

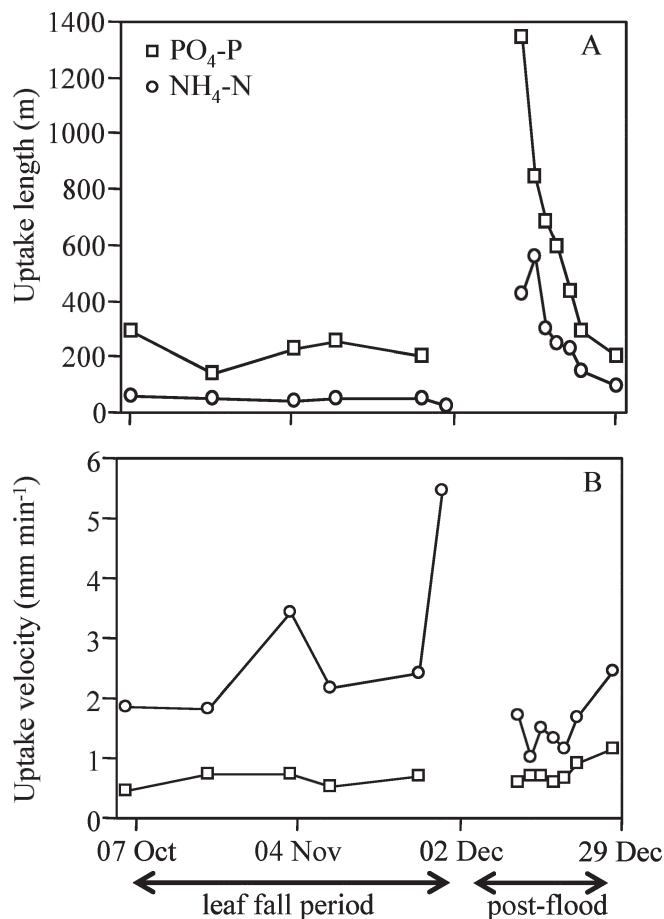


Fig. 4. (A) Temporal variation of uptake length ( $S_w$ ) and (B) uptake velocity ( $V_f$ ) during the study period for  $\text{PO}_4\text{-P}$  (squares) and  $\text{NH}_4\text{-N}$  (circles). The abrupt increases in nutrient uptake lengths coincided with the onset of flooding.

**Temporal variation of nutrient retention metrics**—During the leaf fall period,  $S_w$  did not show a clear temporal trend for either nutrient. On average,  $S_w\text{-PO}_4$  and  $S_w\text{-NH}_4$  were relatively short (i.e., mean  $\pm$  1 SE were  $219 \pm 57$  m and  $49 \pm 11$  m, respectively).  $S_w\text{-NH}_4$  was on average four times shorter than  $S_w\text{-PO}_4$ ; thus, the  $S_w\text{-NH}_4:S_w\text{-PO}_4$  ratio was consistently  $<1$  (Table 1). The flood caused a dramatic increase in  $S_w$  for both nutrients (Fig. 4A). This effect was greater for  $S_w\text{-NH}_4$  (eight times longer than pre-flood values) than for  $S_w\text{-PO}_4$  (6.7 times longer than pre-flood values). After the flood,  $S_w$  of the two nutrients gradually shortened with stream discharge, almost returning to average pre-flood values by the end of the study. The recovery rate, estimated from a post-flood decrease in  $S_w$  with time, for  $S_w\text{-PO}_4$  ( $-1.01 \text{ d}^{-1}$ ) was significantly greater than that for  $S_w\text{-NH}_4$  ( $-0.89 \text{ d}^{-1}$ ;  $p < 0.05$ , Wilcoxon test for two related variables).

Values of  $V_f\text{-NH}_4$  were on average  $3.0 \pm 1.2$  times greater than those of  $V_f\text{-PO}_4$  (Table 1).  $V_f$  tended to gradually increase as leaves accumulated in the channel (Fig. 4B). The flood decreased both  $V_f\text{-PO}_4$  and  $V_f\text{-NH}_4$  (1.2 times and 1.4 times, respectively).  $V_f\text{-PO}_4$  increased gradually post-flood, reaching slightly greater values than pre-flood.  $V_f\text{-NH}_4$  remained low after the flood, gradually

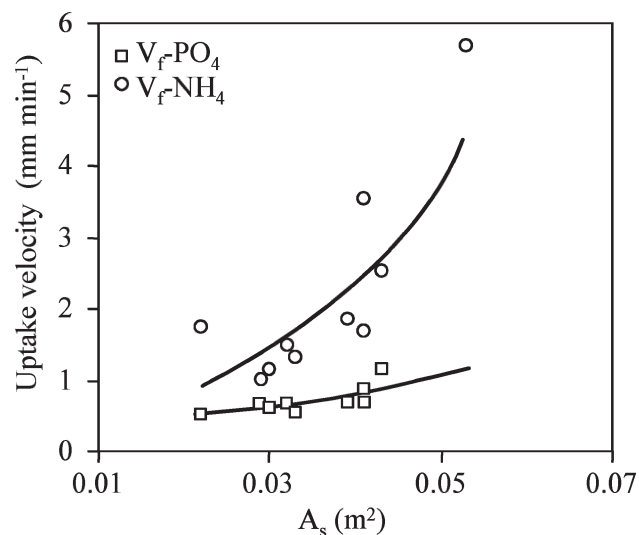


Fig. 5. Relationships between transient storage and nutrient uptake velocities ( $V_f\text{-PO}_4 = 0.29e^{25.93A_s}$ ,  $R^2 = 0.59$ ,  $p < 0.050$ ,  $df = 7$ ;  $V_f\text{-NH}_4 = 0.33e^{48.37A_s}$ ,  $R^2 = 0.65$ ,  $p = 0.005$ ,  $df = 8$ ) for  $\text{PO}_4\text{-P}$  (squares) and  $\text{NH}_4\text{-N}$  (circles).

increasing as discharge receded (Fig. 4B). Regression analyses showed that  $V_f\text{-PO}_4$  was related to leaf benthic standing stocks and temperature (Table 3).  $V_f\text{-NH}_4$  was negatively correlated to DIN concentration and the DIN:P molar ratio (Table 3). No significant relationship was found between  $V_f$  and SRP concentration. Both  $V_f\text{-PO}_4$  and  $V_f\text{-NH}_4$  were positively related to  $A_s$  (Fig. 5).

## Discussion

**Influence of leaf litter inputs and the flood on hydraulic parameters**—The large quantity of accumulated leaves during the leaf fall period, coinciding with low and stable discharge, affected the relative dominance of habitat type and hydraulic characteristics of the reach. Leaf inputs tended to accumulate at the head of the riffles favoring the formation of small leaf-debris dams, which increased the upstream pool surface area. Shifting proportions of habitat types presumably induced the observed change in hydraulic properties. As leaves accumulated on the stream channel, it became wider and deeper, water velocity decreased, and channel roughness increased. These changes caused a gradual change in transient water storage parameters. The increase in  $A_s$  indicates an increased volume of water in transient storage zones, consistent with previous findings on the physical effect of leaf litter accumulation (Hart et al. 1999; Haggard and Storm 2003; Jin and Ward 2005). In addition, the gradual decrease in  $k_1$  and  $k_2$  during the leaf fall period indicates weakened connectivity between the slow and fast flowing hydrologic compartments. Together, these changes in the hydraulic template, mostly driven by litter inputs, increased the water residence time and enhanced the opportunity for nutrient uptake by microbial communities.

Flooding greatly reduced the influence of litter accumulation on channel hydraulics. Whereas changes driven by leaf litter inputs were gradual (weeks), changes due to the

Table 3. Regressions of uptake velocities on environmental variables (leaf biomass as dry weight, water temperature, dissolved inorganic nitrogen concentration [DIN] and DIN:P molar ratio) during the study period.

	$V_f\text{-PO}_4$ (mm min <sup>-1</sup> )	$V_f\text{-NH}_4$ (mm min <sup>-1</sup> )
Biomass (g DW m <sup>-2</sup> )	$V_f\text{-PO}_4=0.42\text{biomass}-0.002$ $R^2=0.55, p<0.010, \text{df}=10$	no sign.
Temperature (°C)	$V_f\text{-PO}_4=1.40-0.38\ln(\text{temp})$ $R^2=0.47, p<0.050, \text{df}=10$	no sign.
[DIN] (ppb)	no sign	$V_f\text{-NH}_4=14.75-2.73\ln[\text{DIN}]$ $R^2=0.75, p<0.001, \text{df}=11$
DIN:P	no sign.	$V_f\text{-NH}_4=8.82[\text{DIN:P}]^{-0.52}$ $R^2=0.37, p<0.050, \text{df}=11$

No sign. no significant relationship.

flood were abrupt (days). The abrupt increase in discharge significantly increased water velocity, decreased relative transient water storage (i.e., reduced  $A_s$  and  $A_s:A$ ) and increased connectivity between low and high flow hydrologic compartments (i.e., greater  $k_1$  and  $k_2$ ). These findings are similar to those of Martí et al. (1997) for a Sonoran Desert stream (Arizona). The changes observed in the study stream just after the flood could be the result of both the washout of a high proportion of leaves from the channel, which reduced surface obstructions, and an increase in the cross-sectional area ( $A$ ) of the channel. These changes likely reduced the influence of streambed topography on surface-water flow, decreasing the relative importance of  $A_s$ . Conversely, after recession, transient water storage parameters returned to pre-flood values faster than discharge. This was probably because of lateral leaf litter inputs from adjacent riparian soil, which created zones of slow moving water in the stream channel. These results suggest that most variation in transient water storage was associated with surface-water compartments rather than modification of subchannel flow paths in the hyporheic zone.

Considering all sampling dates, stream discharge accounted for the largest proportion of the variability in the hydraulic parameters. However, when we focus on low flow conditions, our results indicate that leaf standing stocks primarily influenced stream hydraulics. Variation in transient water storage parameters was related to leaf benthic standing stocks only during leaf fall, when discharge was low; however, this relationship was not significant for the entire study period. In contrast, we found a negative relationship between  $A_s:A$  and discharge using the complete data set. In a study with similar results, D'Angelo et al. (1993) argued that at high discharge transiently stored water is more quickly incorporated into the main flow, but at low discharge is stored more independently of the main flow. Results from previous studies relating  $A_s$  and  $Q$  are inconsistent. Whereas no relationship has been found for some streams (e.g., Hart et al. 1999), others agree with the present study (Valett et al. 1996; Martí et al. 1997; Butturini and Sabater 1999). Similarly, the positive relationship between  $k_1$  and  $k_2$  and discharge found in this study agrees with some previous studies (Hart et al. 1999), but contrasts with others who either found no relationship between exchange coefficient

and discharge (Butturini and Sabater 1999; Hall et al. 2002; Jin and Ward 2005) or found an inverse relationship (D'Angelo et al. 1993; Martí et al. 1997).

In order to test if our results obey a general pattern, we compiled data from 17 studies done across several streams worldwide ( $n = 187$ ) to see if a significant relation between transient water storage parameters and discharge emerged. Results from this analysis revealed significant relationships between these parameters and streamflow across all the streams considered (Fig. 6), supporting results from our study. Nevertheless, the percentage of variation of transient water storage parameters explained by discharge considering the compiled data was less than that obtained considering only data from the present study, probably reflecting the variable location and nature of the transient water storage zones in each particular stream.

*Combined effects of leaf litter inputs and the flood on nutrient retention*—The two nutrient retention metrics ( $S_w$  and  $V_f$ ) helped to determine the relative influence of both leaf inputs and flooding on stream nutrient retention. Leaf litter inputs played an important role in  $\text{PO}_4$  and  $\text{NH}_4$  retention during stable  $Q$  although abrupt flooding and subsequent flood recession largely controlled the overall variability in nutrient retention. To our knowledge, this study is the first of its kind with sufficiently intensive sampling to evaluate stream nutrient retention to gradual and abrupt changes over a short time scale.

The observed nutrient retention responses (both  $S_w$  and  $V_f$ ) for  $\text{PO}_4$  and  $\text{NH}_4$  were in line with headwater streams elsewhere (e.g., see Peterson et al. 2001; Hall et al. 2002; Webster et al. 2003). Retention of both nutrients was relatively high during leaf fall. In addition, the  $S_w\text{-NH}_4:S_w\text{-PO}_4$  ratios, which were consistently  $<1$ , indicate greater efficiency in retaining  $\text{NH}_4$  than  $\text{PO}_4$  regardless of leaf benthic standing stocks or stream discharge. A similar pattern was previously reported from another stream in the same region (Martí and Sabater 1996).

In contrast to our expectations,  $\text{PO}_4$  and  $\text{NH}_4$  retention efficiencies (i.e.,  $S_w$ ) remained relatively constant during the leaf fall period, when discharge was relatively constant and low, despite the clear increase in the additional energy resource from the leaf inputs and in transient water storage size. The lack of relationship between  $S_w\text{-PO}_4$  and leaf litter accumulation agrees with D'Angelo et al. (1991), but

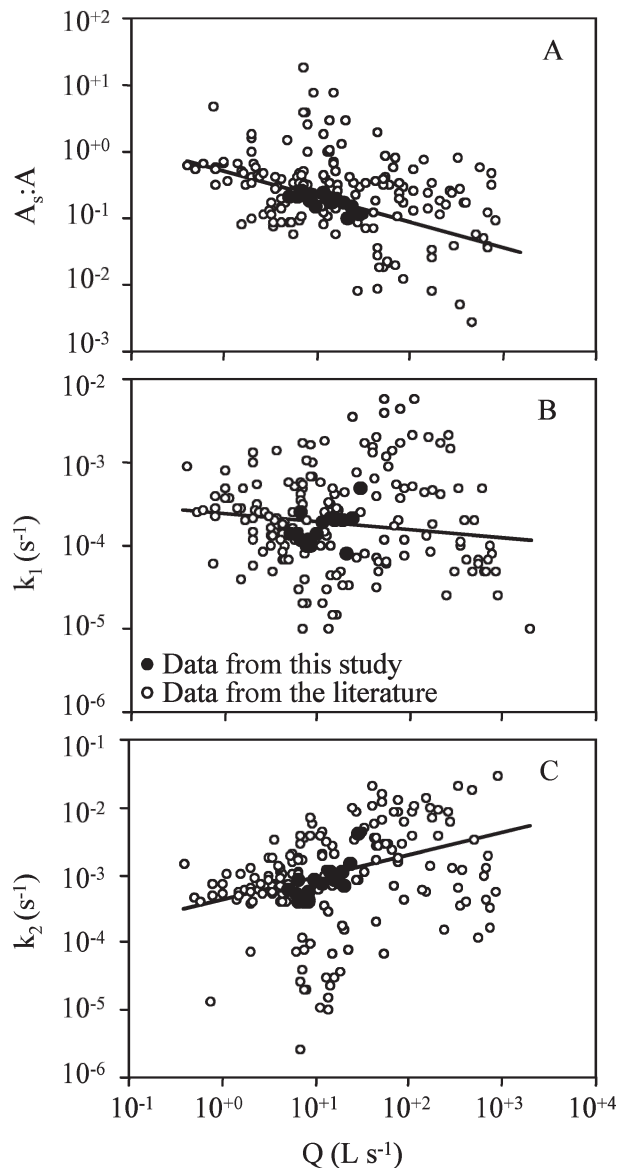


Fig. 6. Relationships between stream discharge and transient storage parameters: (A) transient storage ratio,  $A_s:A = 0.51Q - 0.28$ ,  $R^2 = 0.14$ ,  $p < 0.001$ ,  $df = 185$ , (B) exchange ratio from transient storage to main channel,  $k_1 = 0.0002e^{-0.0013Q}$ ,  $R^2 = 0.05$ ,  $p = 0.002$ ,  $df = 175$ , and (C) exchange ratio from main channel to transient storage,  $k_2 = -0.0003 + 0.001\ln Q$ ,  $R^2 = 0.17$ ,  $p < 0.001$ ,  $df = 170$ . Closed circles are data from the present study and open circles are data from Bencala and Walters (1983), Bencala et al. (1984), Bencala et al. (1990), Broshears et al. (1993), D'Angelo et al. (1993), Martí et al. (1997), Morrice et al. (1997), Mulholland et al. (1997), Butturini and Sabater (1999), Hart et al. (1999), Hall et al. (2002), Haggard and Storm (2003), Harvey et al. (2003), Webster et al. (2003), Ensign and Doyle (2005), Jin and Ward (2005), and Lautz et al. (2006).

contrasts with other studies, showing greater P retention efficiency during periods of benthic organic matter accumulation (Mulholland et al. 1985; Haggard and Storm 2003). Differences could be explained in part by the temporal scale of each study. Whereas previous studies were temporally extensive (annual), the present study was

temporally intensive (seasonal). Moreover, the relationship between  $\text{NH}_4$  retention efficiency and temporal shifts in benthic organic matter has seldom been addressed.

Nutrient retention efficiency is affected by both hydro-morphologic factors and biogeochemical processes.  $V_f$  corrects  $S_w$  for depth and velocity (Stream Solute Workshop 1990), and was more sensitive to benthic leaf accumulation and its influence on transient water storage parameters than  $S_w$ . The variation in  $V_f$  for both nutrients followed the increase in transient water storage ( $A_s$ ) both before and after the flood. At these two moments, transient water storage increased and there was a greater decoupling between fast and slow hydrologic compartments (i.e., reduced  $k_1$  and  $k_2$ ). These conditions may have favored the interaction between stream communities and available nutrients and thus increased stream nutrient demand. In addition, because leaf inputs increased the availability of energy-rich substrata, increased nutrient demand could also be directly associated with the development of microbial communities. Ensign and Doyle (2005) similarly observed a greater nutrient demand as superficial transient storage increased after baffles were installed in a channel. Other studies have found no significant relationships between transient storage parameters and  $V_f$  (e.g., Hall et al. 2002; Webster et al. 2003). In those studies, however, relationships were compared between different streams; therefore, the lack of relationships could be attributed to differences in the nature of the transient water storage and the associated biogeochemical processes.

The same arguments presented above could also explain the subtle differences in temporal patterns observed between  $\text{PO}_4$  and  $\text{NH}_4$  uptake velocities. For instance, temporal variation in  $V_f\text{-NH}_4$  was influenced by the increase in transient storage volume just like  $V_f\text{-PO}_4$ , but it was also negatively influenced by the availability of dissolved inorganic nitrogen (mostly in the form of  $\text{NO}_3$ ). Hall et al. (2002) found similar results and suggested that high  $\text{NO}_3$  concentration may alleviate microbial demand for  $\text{NH}_4$ , lowering  $V_f\text{-NH}_4$ .

The greatest temporal variability in nutrient retention metrics was related to the flood and its subsequent recession. Nutrient retention efficiency of  $\text{PO}_4$  and  $\text{NH}_4$  was significantly reduced after the flood. The increased discharge would be partly responsible (Martí et al. 1997). The flood also flushed out a high percentage of leaves, removing channel obstructions and exporting part of the microbial community. These effects likely contributed to the decreased post-flood nutrient demand. Therefore, the combination of physical factors (i.e., increase in water depth and velocity and reduction in transient water storage) and biological consequences (i.e., decrease in nutrient demand) resulted in reduced post-flood retention efficiency. The stream recovered relatively fast from disturbance. Based on the estimated recovery rates, average pre-flood  $S_w$  values for  $\text{PO}_4$  and  $\text{NH}_4$  were reached 22 days and 47 days after the flood, respectively. These values are within the range of those reported for  $S_w\text{-NO}_3$  in Sycamore Creek (Martí et al. 1997). In that study, the recovery in nutrient retention was attributed to a fast post-flood growth of algal communities. In the present study,  $S_w$  recovery could be

associated with a significant increase in  $\text{NH}_4$  and  $\text{PO}_4$  demand as discharge declined and leaves reaccumulated. Return to base flow stream discharge took 64 days, much longer than for  $S_w$ . This indicates that biogeochemical processes significantly contributed to the high resiliency (i.e., fast recovery capacity) in nutrient retention, presumably enhanced by the lateral leaf input.

In summary, the seasonal litter input not only modified the physical template of the stream reach, but also increased  $\text{PO}_4$  and  $\text{NH}_4$  demand, either directly through microbial demand or through increasing transient storage. The flood altered channel hydraulic properties and nutrient retention in the stream. However, once the flood receded, the stream exhibited fast recovery in nutrient retention, especially for  $\text{PO}_4$ , probably enhanced by the lateral input of riparian leaf litter. Therefore, the net contribution of leaf inputs to headwater stream metabolism over the leaf fall period appears to depend on the timing of floods relative to leaf fall. This has implications in the context of climate change because both the timing of leaf fall and flood regimes are expected to be influenced by climate change (Christensen and Christensen 2004). For example, Peñuelas et al. (2002) have reported that leaf fall has been delayed an average of 13 days relative to 1952 in the study area. Stream hydrologic regimes are also expected to change (McCarthy et al. 2001), with projections for the study region indicating an increase in extreme episodic storms and droughts. These changes may alter the timing of leaf fall and floods, with varying impacts on nutrient retention. Less flooding during the season of leaf fall would increase the residence time of leaves in the stream channel, enhancing nutrient retention. Conversely, an increase in flood frequency during leaf fall would result in leaf litter being periodically flushed from the headwaters and exported downstream to zones of higher flow and lower nutrient retention capacity.

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