The influence of riparian evapotranspiration on stream hydrology and nitrogen retention in a subhumid Mediterranean catchment

Anna Lupon[1], Susana Bernal[1,2], Sílvia Poblador[1], Eugènia Martí[2], Francesc Sabater[1,3]

[1] Department d'Ecologia, Universitat de Barcelona, Av. Diagonal 643, 08028, Barcelona, Spain.
5 [2] Integrative Freshwater Ecology Group, Center for Advanced Studies of Blanes (CEAB-CSIC), Accés a la Cala Sant Francesc 14, 17300, Blanes, Spain.
[3] CREAF, Campus de Bellaterra (UAB) Edifici C, 08193, Cerdanyola del Vallès, Spain.

Correspondance to: Anna Lupon (alupon@ub.edu)

Abstract. Riparian evapotranspiration (ET) can influence stream hydrology at catchment scale by
10 promoting the net loss of water from the stream towards the riparian zone (i.e., stream hydrological retention). However, the consequences of stream hydrological retention on nitrogen dynamics are not well understood. To fill this gap of knowledge, we investigated changes in riparian ET, stream discharge, and nutrient chemistry in two contiguous reaches (headwater and valley) with contrasted riparian forest size in a small forested Mediterranean catchment. Additionally, riparian groundwater
15 level (h_{gw}) was measured at the valley reach. The temporal pattern of riparian ET was similar between reaches, and was positively correlated with h_{gw} ($\rho = 0.60$) and negatively correlated with net riparian groundwater inputs ($\rho < -0.55$). During the vegetative period, stream hydrological retention occurred mostly at the valley reach (59% of the time), and was accompanied by in-stream nitrate release and ammonium uptake. During the dormant period, when the stream gained water from riparian
20 groundwater, results showed small influences of riparian ET on stream hydrology and nitrogen concentrations. Despite being a small component of annual water budgets (4.5%), our results highlight that riparian ET drives stream and groundwater hydrology in this Mediterranean catchment and, furthermore, question the potential of the riparian zone as a natural filter of nitrogen loads.

Keywords. Stream hydrological retention, riparian evapotranspiration, net groundwater inputs, in-
25 stream nitrification, Mediterranean headwater catchment.

1. Introduction

The study of riparian zones has been of growing interest during last decades because they can reduce the pervasive effects of excessive anthropogenic nitrogen (N) inputs in forested, agricultural, and urban ecosystems across the globe (Hill, 1996; Pert et al., 2010). Since they can affect both the timing and magnitude of N delivery to downstream ecosystems, riparian zones are currently considered hot spots of N removal within catchments (McClain et al., 2003; Vidon et al., 2010). The high capacity of riparian zones to reduce terrestrial N inputs stems from the biogeochemical conditions at their unique interface location between upland and streams, which favors ammonium (NH_4^+) and nitrate (NO_3^-) biological uptake from shallow groundwater via plant assimilation and microbial denitrification (Clément et al., 2003; Vidon et al., 2010).

The capacity of riparian zones to diminish inorganic N loads critically relies on the hydrological connectivity between upland, riparian, and stream ecosystems because it directly influences water flow paths, and thereby whether groundwater N interacts with organic-rich soils (Mayer et al., 2007; Pinay et al., 2000). During wet conditions, the N retention in riparian zones is high because continuous upland groundwater inputs and the rising water table in flat riparian areas can promote the contact of groundwater with shallow riparian soils (Ranalli and Macalady, 2010; Vidon and Hill, 2004). However, little is known about the efficiency of riparian zones to diminish N inputs during dry conditions, when the hydrological connectivity between uplands and riparian zones tends to decrease at the valley bottom of catchments (Covino and McGlynn, 2007; Detty and McGuire, 2010; Jencso et al., 2009; Ocampo et al., 2006). Low or zero water inputs from uplands can drop the riparian groundwater level far below the organic-rich and rhizosphere soil layers, and consequently, diminish the capacity of riparian zones for removing groundwater N (Burt et al., 2002; Hefting et al., 2004). Conversely, hydrological disconnection between uplands and riparian zones can favor the lateral movement of water from the stream toward the riparian aquifer (defined here as stream hydrological retention), which can enhance denitrification and biological uptake of stream nitrate at the stream-riparian edge (Duval and Hill, 2007; Martí et al., 1997; Rassam et al., 2006; Schade et al., 2005).

The riparian groundwater level and the hydrological exchange between the stream and riparian groundwater can be directly influenced by the activity of riparian trees, which can consume high amounts of water during the vegetative period. Riparian evapotranspiration (ET) can drive diel fluctuations of stream discharge and seasonal patterns of riparian groundwater table and soil moisture (Brooks et al., 2009; Burt et al., 2002; Gribovszki et al., 2010). Thus, riparian trees could affect the strength, location, and duration of the predominant flow path, and consequently, influence the capacity

of riparian zones to reduce N not only from upland groundwater inputs, but also from stream water. In
this line of thought, previous studies have reported decreases in stream N concentration along losing
stream reaches attributed to N uptake at the stream-riparian edge (Bernal and Sabater, 2012; Dent et
al., 2007; Rassam et al., 2006). Yet, there has been little research focused on the influence of riparian
ET on upland-riparian-stream hydrological exchange and its potential to promote variations in stream
N concentrations and fluxes.

This study aims to investigate the influence of riparian ET on stream hydrological retention, and its
consequences on stream N concentrations in a small forested Mediterranean catchment. To do so, we
compared riparian tree ET between a headwater reach with limited riparian forest and a contiguous
valley reach with well-developed riparian forest. First, we expected higher riparian ET, and thus,
higher stream hydrological retention at the valley reach, especially during the vegetative period.
Second, we expected that differences in stream N concentration between the headwater and valley
reach will reflect differences in riparian N cycling coupled to the dominant direction of water flow
between the riparian zone and the stream. Based on longitudinal changes observed in semiarid streams
(Bernal and Sabater, 2012; Dent et al., 2007), we expected decreases in N concentration along the two
reaches, but especially at the valley reach because of higher stream hydrological retention. The results
of this study contribute to our understanding of the interaction between riparian ET and fluxes of water
and nutrients at the stream-riparian edge. This knowledge could have implications for water resource
management, as well as for anticipating how riparian zones and stream water chemistry could respond
to decreases in water availability induced by climate change.

2. Study site

The Font del Regàs catchment is located in the Montseny Natural Park, NE Spain (41º50'N, 2º30'E).
The climate is subhumid Mediterranean, with mild winters, wet springs, and dry summers. Annual
precipitation is 925 ± 151 mm, with < 1% of annual precipitation falling as snow. Mean annual
temperature averages 12.1 ± 2.5 ºC (mean ± SD, period 1940-2000, Catalan Metereologic Service).
Atmospheric inorganic N deposition ranges from 15 to 30 kg ha^{-1} yr^{-1} and does not show any temporal
trend (period 1983-2007; Àvila and Rodà, 2012).

The catchment area is 14.2 km^2 and its altitude ranges from 500 to 1500 m above the sea level (a.s.l.)
(Figure 1). The catchment is dominated by biotitic granite and it has steep slopes (28%) (Institut
Cartogràfic de Catalunya, 2010). Evergreen oak (*Quercus ilex*) and European beech (*Fagus sylvatica*)
forests cover 54% and 38% of the catchment, respectively (Figure 1). Upland soils (pH ~ 6) are sandy,
with a 3 cm deep O horizon followed by a 5 to 15 cm deep A horizon. There is no snowpack in hillslope

areas and upland soils are generally > 0 ºC. The riparian forest covers the 6% of the catchment area and it is almost flat (slope perpendicular to stream < 10%). Riparian width increases from 6 to 28 m along the catchment and the total basal area of riparian trees increases by 12-fold. Note that by total basal area we are referring to the sum of individual tree basal area as defined later in the text. Black

95   alder (*Alnus glutinosa*), black locust (*Robinea pseudoacacia*), sycamore (*Platanus x hispanica*), European ash (*Fraxinus excelsior*), and black poplar (*Populus nigra)* are the most abundant tree species in the riparian forest. Riparian soils (pH ~ 7) are sandy-loam, with a 5 cm deep organic layer followed by a 30 cm deep A horizon.

For this study, we selected two contiguous stream reaches with contrasting riparian forest (i.e., the

100   headwater and valley reach) (Figure 1). The headwater reach (750-550 m a.s.l.) is 1760 m long and drains 6.74 km^2 (Table 1). The reach is flanked by a 5-15 m wide riparian forest that covers ~5% of the drainage area. *A. glutinosa*, *F. excelsior*, and *P. nigra* represent 51%, 26%, and 23% of the total basal area, respectively. The valley reach (550-500 m a.s.l.) is 1160 m long and drains an additional area of 4.42 km^2 (i.e., total catchment area at this reach is 11.16 km^2). The reach is flanked by a 10-25

105   m wide riparian forest that covers ~10% of the drainage area. *A. glutinosa*, *F. excelsior*, *P. nigra*, and *R. pseudoacacia* represents 53%, 27%, 11%, and 9% of the total basal area, respectively. The two stream reaches show well-preserved channel morphology, with a riffle-run structure and low slopes (< 5%) along the reaches. The streambed is mainly composed by rock (~30%), cobbles (~25%), and gravel (~15%) at the headwater reach, whereas rock (~25%), cobbles (~30%), and sand (~30%) are

110   the dominant substrates at the valley reach. The stream channel is, on average, 2 and 3 m wide for the headwater and the valley reach, respectively. During the study period, riparian groundwater (< 1.5 m from the stream channel) flowed well below the soil surface in the two reaches (0.5 ± 0.1 m; averaged from 14 wells, 7 by reach, n = 82) (Bernal et al. 2015).

3. Materials and methods

115   **3.1. Field sampling and chemical water analysis**

To characterize the riparian forest, we inventoried 14 riparian forest plots of 30 m long × riparian width (5-20 m) (7 plots by reach, ca. 5% of the riparian area). In each plot, we identified each tree individual at species level and measured its diameter breast height (*DBH*, in cm) and its basal area (*BA* = π * (*DBH* / 2)^2, in cm^2). For each tree species i, we calculated the area-specific *BA* (*BA$_{sp,i}$*, in m^2 of *BA* per

120   km^2 of riparian area) by dividing the total *BA* for a given species by the total area of the inventoried riparian plots, either for the headwater (0.23 km^2) or valley (0.21 km^2) reach.

During two consecutive water years (from September 2010 to August 2012), we monitored three stream sampling sites (up-, mid-, and down-stream sites), which constituted the top and the bottom of the headwater and valley reaches. Stream water level was recorded at 15 min intervals at each sampling site with a water pressure transducer (HOBO U20-001-04). Fortnightly, stream discharge (Q, in L s^{-1}) was measured using the "slug" chloride addition technique (Gordon et al., 1992). We used the regression between discharge and stream water level measurements to infer Q values at 15 min intervals during the study period (n = 57, 60, and 61 for up-, mid- and down-stream sites, respectively; in all cases: $R^2 > 0.97$; Figure S1). In order to compare stream discharge among the three sites, we calculated area-specific stream discharge (Q', in mm d^{-1}) by dividing Q by drainage area. Riparian groundwater level (h_{gw}, in cm below soil surface (b.s.s.)) was recorded at 15 min intervals with a water pressure transducer (HOBO U20-001-04) in a 1.8 m long PVC well (3 cm Ø) placed ~3 m from the stream channel edge at the down-stream site (Figure 1).

Stream water samples were collected daily (at noon) from each sampling site with an auto-sampler (Teledyne Isco Model 1612) and taken to the laboratory every 10 days. Auto-samplers were installed about 1 m below ground to keep water samples fresh and prevent biogeochemical transformations (Figure S2). From August 2010 to December 2011, discharge and water chemistry was measured every 2 months at the three permanent tributaries discharging to Font del Regàs stream (Figure 1). We used pre-acid-washed polyethylene bottles to collect water samples after triple rinsing them with stream water. All water samples were filtered (Whatman GF/F, 0.7 μm pore Ø) and kept cold (< 4ºC) until laboratory analysis (< 24 h after collection). Water samples were analyzed for dissolved inorganic N (DIN; NO_3^- and NH_4^+) and chloride (Cl^-), which was used as hydrological tracer (Kirchner et al., 2001). Cl^- was analyzed by ionic chromatography (Compact IC-761, Methrom). NO_3^- was analyzed by the cadmium reduction method (Keeney and Nelson, 1982) using a Technicon Autoanalyzer (Technicon, 1976). NH_4^+ was manually analyzed by the salicilate-nitropruside method (Baethgen and Alley, 1989) using a spectrophotometer (PharmaSpec UV-1700 SHIMADZU).

3.2. Riparian evapotranspiration

From September 2010 to August 2012, we calculated diel variations in stream discharge at the up-, mid-, and down-stream sites (Q_{lost}, in m^3 d^{-1}) by subtracting daily Q to the stream discharge obtained by linearly interpolating maxima Q (measured between 0:00-3:00h) between two consecutive days. We used only stream discharge during base flow conditions (i.e., changes in $Q < 10\%$ in 24 h) to avoid any confounding effect associated with storm events. During the vegetative period, we attributed Q_{lost} to water withdrawal by riparian tree roots from either the riparian aquifer or directly from the stream

channel (Cadol et al., 2012). Given that there was no snowpack in the study catchment, Q_{lost} during the dormant period was attributed to water withdrawal by riparian understory vegetation (Roberts, 1983) and/or by upland evergreen trees (Savé et al., 1999). Furthermore, we estimated riparian ET along each reach as the difference in Q_{lost} measured at the bottom and at the top of the reach and by assuming that Q_{lost} measured at each particular site integrated the riparian ET upstream from that point. Riparian ET (ΔQ_{lost}, in m^3 m^{-1} d^{-1}) was weighted by stream length for comparison purposes. For the valley reach, we compared ΔQ_{lost} values with diel variations in h_{gw} to explore the influence of riparian ET on the riparian groundwater level.

To explore the relation between diel cycles in stream discharge and the activity of riparian trees, we compared ΔQ_{lost} with an independent estimate of riparian transpiration based on mean monthly sap flow measurements of the dominant riparian trees (8 individuals of *A. glutinosa,* 5 individuals of *F. excelsior*, 5 individuals of *P. nigra*, and 12 individuals of *R. pseudoacacia*). Sap flow was measured using constant thermal dissipation sensors (Granier, 1985). Each sensor consisted of two probes (10-20 mm long) inserted in the north-side of the trunk at breast height 10 cm apart. The upper probe was heated at constant temperature. The thermal difference between probes was scanned at 10 s intervals and recorded as 15 min average with a data-logger (CR1000, Campbell Inc.). Then, thermal differences were related to sap flux density (in dm^3 of water per m^2 of *BA* and minute) following the original calibration of Granier (1985). More details can be found in Nadal-Sala et al. (2013).

For each reach, we calculated the transpiration of the riparian tree community (T_{rip}, in m^3 m^{-1} d^{-1}) with:

$$T_{rip} = (\Sigma_{i=1}^{n} T_i \times BA_{sp,i}) \times A \ / \ x \qquad (1)$$

where T_i is monthly mean daily transpiration (in dm^3 of water per m^2 of *BA* and day) and $BA_{sp,i}$ is the area-specific basal area (in m^2 BA km^{-2}) of each tree species *i*, A is the riparian area (in km^2), and x is the reach length (in m). Values of mean monthly *T* were recorded at the valley of the catchment from January to August 2012 (Nadal-Sala et al., 2013).

3.3. Mass balance calculations

Net riparian groundwater inputs to stream. To examine the temporal and spatial pattern of stream hydrological retention, we measured the hydrological exchange between riparian groundwater and stream water bodies at reach scale. The contribution of mean daily net riparian groundwater inputs to stream discharge (Q_{gw}) was estimated with:

$$Q_{gw} = Q_{bot} - Q_{top} - Q_{trib} \qquad (2)$$

where Q_{top} and Q_{bot} are mean daily discharge measured at the top and at the bottom of the reach, respectively; and Q_{trib} is mean daily discharge at the permanent tributaries (all in L s^{-1}). For the headwater reach, Q_{top} and Q_{bot} were the discharge at the up- and mid-stream sites, respectively; while we used the discharge at the mid- and down-stream sites for the valley reach. For each stream site, mean daily discharge was the average of Q for each day. To estimate mean daily discharge at each tributary, we used the best fit model (logarithmic model) between Q measured at each tributary and at the up-stream site within the same day (for each of the three tributaries: $R^2 > 0.97$, n = 11, p < 0.001; Figure S3). Values of $Q_{gw} > 0$ indicate the movement of water from the riparian zone to the stream (i.e. net gaining stream), while values of $Q_{gw} < 0$ indicate a net loss of water from the stream towards the riparian zone. Therefore, $Q_{gw} < 0$ was used as an indicator of stream hydrological retention (Covino et al., 2010).

Chemical signature of riparian groundwater and stream water. We used a mass balance approach to investigate whether changes in stream water Cl$^-$, NO$_3^-$, and NH$_4^+$ concentrations along the valley reach could be explained by hydrological mixing between riparian groundwater and stream water. The mass balance was focused at the valley reach, where water and N retention were expected to be the highest. Only discharge and solute concentrations during base flow conditions were used for the mass balance approach. For each day, we calculated a predicted concentration for the down-stream site with the following mass balance:

$$Q_{bot} \times C_{bot} = Q_{top} \times C_{top} + Q_{gw} \times C_{gw} + Q_{trib} \times C_{trib} \qquad (3)$$

where Q_{top}, Q_{bot}, Q_{trib}, and Q_{gw} are as in Eq. 2 (all in L s^{-1}). C_{top} and C_{bot} are daily solute concentrations measured at the top and at the bottom of the reach, respectively (in mg L^{-1}). C_{trib} is daily solute concentration at the tributaries (in mg L^{-1}), which was estimated by fitting the best fit model (logarithmic model) between solute concentration measured at each tributary and at the up-stream site within the same day (for each of the three tributaries and for the three solute: $R^2 > 0.78$; in all cases: n = 11, p < 0.001; Figure S3). Although this may be a rough estimation of solute concentrations at the tributaries, it was a useful procedure for inferring riparian groundwater chemistry at daily time steps. Finally, C_{gw} is daily solute concentration in riparian groundwater (in mg L^{-1}). For periods of $Q_{gw} < 0$, we considered that C_{gw} equaled C_{top}. For periods of $Q_{gw} > 0$, we assumed similar riparian groundwater chemistry between the headwater and valley reaches. In this case, C_{gw} at the headwater reach was inferred from eq. 3 by assuming that there was no biological reactivity within the stream channel. The predicted C_{gw} showed a good match with the concentrations measured at 7 wells installed along the

headwater reach (< 2 m from the stream), with median C_{gw} differing < 5%, 7%, and 10% for Cl⁻, NO₃⁻
, and NH₄⁺, respectively (Bernal et al., 2015) (Table S1).

For each day, we calculated the ratio between observed and predicted solute concentrations (Obs:Pred ratio). For Cl⁻ (hydrological tracer), we expected Obs:Pred ratios close to 1 if there are no additional water sources contributing to stream discharge at the valley reach. For NO₃⁻ and NH₄⁺, Obs:Pred < 1 and Q_{gw} < 0 was interpreted as in-stream biological N retention via assimilatory uptake (for NO₃⁻ and NH₄⁺), nitrification (for NH₄⁺) and/or denitrification (for NO₃⁻). We interpreted Obs:Pred > 1 and Q_{gw} < 0 as either in-stream mineralization (for NH₄⁺) or nitrification (for NO₃⁻). For Q_{gw} > 0 (net gaining stream), Obs:Pred ≠ 1 was interpreted as differences in riparian groundwater nutrient concentration between the headwater and the valley reaches. We used the relative difference between measured and predicted C_{gw} at the headwater reach as a threshold to determine when observed and predicted concentrations differed significantly from each other (±1.05, ±1.07, and ±1.1 for Cl⁻, NO₃⁻, and NH₄⁺ concentrations, respectively).

3.4. Statistical analysis

To investigate the influence of riparian ET on stream discharge and stream water chemistry, we split the data set into vegetative and dormant periods. We considered that the vegetative period was compressed between the onset (April) and offset (October) of riparian tree evapotranspiration (Nadal-Sala et al., 2013).

For each reach, we investigated differences in Q', Q_{gw}, mean daily h_{gw} and stream solute concentrations between the two periods with a Wilcoxon rank sum test (Zar, 2010). For each period, the occurrence of stream hydrological retention was calculated by counting the number of days with Q_{gw} < 0. For each reach, we further explored the relationship between T_{rip}, ΔQ_{lost} and Q_{gw} with a Spearman correlation. Spearman correlation was also used to analyze the relationship between ΔQ_{lost} and mean daily h_{gw} at the valley reach.

To explore whether stream hydrological retention influenced stream NO₃⁻ and NH₄⁺ concentrations at the valley reach, we examined the relationship between Q_{gw} and Obs:Pred ratios measured at the down-stream site with Spearman correlations. For each solute, we further compared the Obs:Pred ratio between days with Q_{gw} > 0 and Q_{gw} < 0 with a Wilcoxon rank sum test (Zar, 2010).

All the statistical analyses were carried out with the R 2.15.1 statistical software (R-project 2012). We chose non-parametric statistical tests because the residuals of both stream discharge and solute

245   concentrations were not normally distributed (Shapiro test, p < 0.05). In all cases, differences were considered statistically significant when p < 0.01.

4. Results

4.1. Seasonal and diel patterns of stream discharge and whole-reach riparian ET

During the study period, median annual Q was 15.9, 53.9, and 62.4 L s^{-1} at the up-, mid-, and down-
250   stream sites, respectively. The three sites showed the same seasonal pattern, characterized by a strong decline in Q during the vegetative period (Figure 2a). As expressed by catchment area, median annual Q' was 0.65, 0.53, and 0.41 mm d^{-1} at the up-, mid-, and down-stream sites, respectively. In all sites, Q' was significantly higher during the dormant than during the vegetative period (Wilcoxon test, p < 0.01).

255   Diel variations in stream discharge occurred during the whole year, with maxima in early morning (3-6 am) and minima in early afternoon (2-5 pm). During the dormant period, diel discharge variations were relatively small at the three sites (Q_{lost} < 2% of mean daily Q). Values of Q_{lost} increased during the vegetative period and showed a marked longitudinal pattern, median values being 36, 219, and 340 m^3 d^{-1} at the up-, mid-, and down-stream sites, respectively. At the three sites, Q_{lost} increased from
260   April to June, peaked in summer (July-August), and then decreased until November. In the summer peak, Q_{lost} accounted for the 7%, 15%, and 19% of mean daily Q at the up-, mid-, and down-stream sites, respectively. This seasonal pattern of Q_{lost} was consistent for the two studied water years.

During the vegetative period, riparian ET was lower at the headwater than at the valley reach as indicated by ΔQ_{lost} (0.12 vs. 0.17 m^3 m^{-1} d^{-1}) and T_{rip} (0.31 vs. 0.49 m^3 m^{-1} d^{-1}). There was a strong and
265   positive relationship between T_{rip} and ΔQ_{lost} for both the headwater and valley reach (Figure 3a). Both T_{rip} and ΔQ_{lost} peaked in summer (July-August) and showed minima in winter (January-March). At the valley reach, there was a positive relationship between ΔQ_{lost} and diel variations in h_{gw} (Spearman coefficient [ρ] = 0.58, p < 0.001, n = 277).

4.2. Net riparian groundwater inputs and groundwater table elevation

270   Median annual Q_{gw} was positive at the headwater reach (11.2 L s^{-1}), but negative at the valley reach (-0.5 L s^{-1}). The two reaches showed lower Q_{gw} values during the vegetative period compared to the dormant period, though differences were larger at the valley reach (Table 2, Figure 2c). The two reaches showed a negative correlation between Q_{gw} and ΔQ_{lost} (headwater: ρ = -0.57, p < 0.001, n = 273; valley: ρ = -0.79, p < 0.001, n = 286) (Figure 3b).

275   Stream hydrological retention ($Q_{gw} < 0$) was more frequent at the valley reach compared to the headwater reach (27% vs 4% of the time on an annual basis). During the vegetative period, $Q_{gw} < 0$ occurred from May to September (59% of the time) at the valley reach, while it occurred only in July and August at the headwater reach (15% of the time). During the dormant period, days with $Q_{gw} < 0$ were infrequent (< 3% of the time) for the valley reach and nil for the headwater reach.

280   At the down-stream site, median annual h_{gw} was 70 cm b.s.s. and showed higher values (i.e. lower water table levels) during the vegetative period compared to the dormant period (Figure 2d, Table 2). There was a moderate positive correlation between mean daily h_{gw} and ΔQ_{lost} ($\rho = 0.60$, $p < 0.001$, n = 277).

4.3. Stream solute concentrations

285   Stream Cl^- concentration was lower at the up- than at the mid- and down-stream sites for both the vegetative and dormant periods (Table 3). The up-stream site showed no differences in stream Cl^- concentration between the two periods, while the mid- and down-stream sites showed lower Cl^- concentration during the dormant than during the vegetative period (Table 3). The highest stream NO_3^- concentration was observed at the up-steam site and the lowest at the mid-stream site (Table 3). Stream
290   NO_3^- concentration was higher during the dormant than during the vegetative period at the up- and mid-stream sites, while no seasonal pattern was observed at the down-stream site (Table 3). Stream NH_4^+ concentration was higher at the up- than at the down-stream site. The three sites showed higher stream NH_4^+ concentration during the vegetative than during the dormant period (Table 3).

4.4. Comparison between observed and predicted stream solute concentrations at the down-
295   **stream site**

During the study period, there was a good match between observed stream Cl^- concentrations at the down-stream site and those predicted by hydrological mixing as indicated by Obs:Pred ratios ~ 1 (Figure 4a). For NO_3^-, Obs:Pred ratios were close to 1 during the dormant period, while increased up to 1.95 during the vegetative period (Figure 4b). For NH_4^+, Obs:Pred ratios were higher during the
300   dormant period (~1.15) than during the vegetative period (from 0.29 to 0.87) (Figure 4c).

The relationship between Obs:Pred ratios and Q_{gw} was null for Cl^- ($\rho = 0.2$, $p > 0.05$), negative for NO_3^-, and positive for NH_4^+ (Figure 5). For NO_3^-, Obs:Pred ratios were significantly higher for $Q_{gw} < 0$ than for $Q_{gw} > 0$, while the opposite pattern was observed for NH_4^+ (for the two solutes: Wilcoxon test, $Z > Z_{0.05}$, $p < 0.01$).

5. Discussion

5.1. Influence of riparian ET on stream and riparian groundwater hydrology

Our results revealed that riparian ET can influence stream and riparian groundwater hydrology, though its relevance varies depending on the time scale considered. On a sub-daily basis, the strong relationship between T_{rip}, diel variation in h_{gw}, and ΔQ_{lost} suggests that riparian vegetation drives diel fluctuations in stream discharge likely by taking up water from the riparian aquifer (Cadol et al., 2012; Gribovszki et al., 2010; Lundquist and Cayan, 2002). However, the fact that ΔQ_{lost} values were lower than those of T_{rip} suggest that riparian trees fed also on soil water. This result concurs with previous studies showing that riparian tree species can obtain between 30-90% of their water requirements from the surface soil (0-50 cm depth) (Brooks et al., 2009; Sánchez-Pérez et al., 2008; Snyder and Williams, 2000). On a seasonal basis, riparian ET influenced the temporal pattern of both stream and groundwater hydrology because ΔQ_{lost} was negatively related to $Q_{gw,}$ and positively related to mean daily h_{gw}. In agreement, previous studies have reported that riparian water demand (0.5-5 mm d^{-1}) can severely drop the groundwater table (Sabater and Bernal, 2011; Schilling, 2007) and decrease the amount of groundwater entering to streams by 30-100% (Dahm et al., 2002; Folch and Ferrer, 2015; Kellogg et al., 2008). On an annual basis, riparian transpiration at the study site (350-450 mm yr^{-1}) was small compared to published values of ET for other riparian forest worldwide (400-1300 mm yr^{-1}) (Scott et al., 2008) as well as compared to oak and beech upland forests (600-900 mm yr^{-1}) (Àvila et al., 1996; Llorens and Domingo, 2007). These low ET values could partially be explained by the low radiation reaching the riparian canopy (36 ± 18 W m^{-2} d^{-1}) compared to the radiation reaching non-shaded areas of the catchment (270 ± 70 W m^{-2} d^{-1}; unpublished data), a phenomenon already described in the literature (Aguilar et al. 2010). The relatively low ET values, together with the fact that the riparian forest occupied a small area of the catchment (6%), resulted in a minimal contribution (4.5%) of riparian transpiration to the annual water budget for this catchment. This estimate is similar to values reported for tropical (Cadol et al., 2012), temperate (e.g. Petrone et al., 2007; Salemi et al., 2012), and Mediterranean (e.g. Bernal and Sabater, 2012; Folch and Ferrer, 2015; Wine and Zou, 2012) systems, while being several folds lower than values reported for semiarid and dry lands regions (Contreras et al., 2011; Dahm et al., 2002; Doble et al., 2006) (Figure 6). Together, these results suggest that the relative contribution of riparian ET to catchment water depletion across biomes could be explained by differences in water availability (Figure 6 and Table S2). Therefore, the potential of riparian forests to control catchment and stream hydrology at both large and fine time scales could dramatically increase in regions experiencing some degree of water limitation (P/PET <1).

In concordance to our expectations, the influence of riparian ET on stream hydrology varied along the stream continuum, likely due to changes in the balance between water availability and water demand. At the up-stream site, maxima Q_{lost} values (7% of mean daily Q) were similar to values reported for systems with no water limitation (Bond et al., 2002; Cadol et al., 2012), while maxima Q_{lost} values for the down-stream site (19% of mean daily Q) were close to those reported for water-limited systems (Lundquist and Cayan, 2002). Stream hydrological retention occurred mostly at the valley reach, where riparian forest was well developed, thus suggesting higher riparian water requirements at the valley bottom (Bernal and Sabater, 2012; Covino and McGlynn, 2007; Montreuil et al., 2011). Yet, the increase in stream hydrological retention along the stream could be favored by additional factors such as longitudinal changes in channel geomorphology, riparian topography, upland-riparian hydrological connectivity, or the hydraulic gradient between the riparian aquifer and the stream (Covino et al., 2010; Detty and McGuire, 2010; Duval and Hill, 2006; Jencso et al., 2009; Vidon and Hill, 2004). Overall, our results suggest that, despite being insignificant for catchment water budgets, riparian ET exerted a strong influence on diel and seasonal patterns of riparian groundwater table and stream discharge likely due to the proximity and strong hydrological connectivity between these two water bodies.

5.2. Influence of stream hydrological retention on stream N concentrations

In contrast to our expectation, the prevalence of stream hydrological retention during the vegetative period at the valley reach was accompanied by an increase of stream NO_3^- concentrations (Obs:Pred > 1). This result suggests NO_3^- release within the stream channel, which conflicts with previous studies reporting NO_3^- uptake at the stream-riparian edge in net losing reaches (Bernal and Sabater, 2012; Duval and Hill, 2007; Rassam et al., 2006). Biological NO_3^- uptake at the stream-riparian edge typically occurs when a large volume of water flows directly or remains long time in anoxic zones within the rhizosphere and/or the organic-rich soils flanking the stream channel (Duval and Hill, 2007; Schade et al., 2005). At Font del Regàs, however, there was a permanent disconnection between riparian groundwater and surface soil layers, which may have limited the occurrence of microbial denitrification and plant NO_3^- uptake during periods of stream hydrological retention (Burt et al., 2002; Hefting et al., 2004).

Furthermore, in-stream NO_3^- release was accompanied by NH_4^+ uptake (Obs:Pred < 1), suggesting that in-stream nitrification prevailed at the valley reach. Previous studies have reported sustained in-stream nitrification in well-oxygenated, slow water flowing, hyporheic zones (Dent et al., 2007; Jones et al., 1995; Triska et al., 1990), and also when stored leaf packs are rich in organic N and labile carbon (Mineau et al., 2011; Starry et al., 2005). The two aforementioned explanations suit at Font del Regàs

because the valley reach had inputs of N-rich leaf litter (Bernal et al., 2015) and a well-oxygenated

370 hyporheic zone (~7 mg O_2 L^{-1}, unpublished data) during periods of stream hydrological retention. Moreover, in-stream nitrification in summer could be stimulated by warm water temperatures (Laursen and Seitzinger, 2004) and both low discharge (< 30 L s^{-1}) and stream depth (< 15 cm), which ultimately could favor the contact between nutrients and the microbial communities. Alternatively, differences in NO_3^- and NH_4^+ concentrations between the headwater and the valley reach could be explained by

375 hydrological mixing with unaccounted water sources, such as deep groundwater (Clément et al., 2003) or riparian N-rich soils (Hill, 2011). However, these two explanations were discarded because small mismatches between observed and predicted Cl^- concentrations indicate that the mixing model included the main water sources contributing to stream discharge. Together, these results suggest that processes occurring within the stream surface channel or in the hyporheic zone can overwhelm those

380 occurring at the stream-riparian edge, especially during periods of high hydrological retention.

During the dormant period, when the two reaches gained water from the riparian groundwater, Obs:Pred ratios at the down-stream site were ≥ 1 for both NO_3^- and NH_4^+. This finding does not support previous studies showing that riparian zones increase their N buffer capacity from headwaters to valley bottom (Montreuil et al., 2011; Rassam et al., 2006). For NO_3^-, this pattern could be explained by

385 limited riparian denitrification, given that (i) NO_3^- availability was low in groundwater arriving from uplands (< 1 mg L^{-1}; unpublished data), and (ii) groundwater and organic-rich soils were hydrologically disconnected even during the dormant period. Additionally, high rates of N mineralization and nitrification in the riparian soil during winter (0.84 ± 0.23 mg N kg^{-1} day^{-1}) could promote N export from the riparian zone to the stream at the valley reach (Lupon et al., 2016).

390 The influence of in-stream N cycling on N export ultimately depends on water fluxes and the hydrological exchange between riparian and stream ecosystems, which vary over the year. During the vegetative period, NO_3^- fluxes entering and exiting the valley reach were similar (median = 8.8 and 8.9 mg N s^{-1}, respectively) mostly because the increase in stream NO_3^- concentration at the valley reach was counterbalanced by the loss of water from the stream towards the riparian zone induced by riparian

395 ET. Otherwise, NO_3^- export to downstream ecosystems would have been 15% higher. Similarly, during the dormant period, there were no differences between input and output NO_3^- fluxes at the valley reach, but in this case discharge and NO_3^- concentrations were similar between the top and the bottom of the reach (Q = 110 vs. 113 L s^{-1} and NO_3^- = 0.166 vs. 0.168 mg N L^{-1}). These back-of-the-envelope calculations highlight that riparian ET and stream-riparian hydrological exchange can substantially

400 influence stream N fluxes during some time-windows of the year, despite it may have small implications for N fluxes at annual scale.

6. Conclusions

Our study adds to the growing evidence demonstrating that riparian ET is a key process for understanding temporal patterns of stream discharge and hydrological processes at the stream-riparian edge in small forested catchments, despite its modest contribution to annual water budgets (Folch and Ferrer, 2015; Medici et al., 2008). Riparian ET strongly controlled the temporal pattern of net groundwater inputs and stream discharge across daily and seasonal scales. From a network perspective, the influence of riparian ET on stream hydrology increased along the stream continuum and promoted stream hydrological retention at the valley reach. In contrast to previous studies, high stream hydrological retention was accompanied by increases in nitrate concentrations, likely due to in-stream nitrification enhanced by low stream flows, large stocks of N rich leaf litter, warm conditions and well oxygenated hyporheic zones. In addition, we found no clear evidence of riparian effects on stream N dynamics during the dormant period. Our findings highlight that riparian ET can regulate the spatio-temporal pattern of stream water fluxes in Mediterranean regions and question the N buffering capacity of Mediterranean riparian zones at catchment scale.

Author contribution

AL, SB, and FS designed the experiment. AL, SB, and SP carried them out. AL performed all laboratory analysis. AL analyzed the data set and prepared the manuscript with contributions from SB, SP, EM, and FS.

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Tables

Table 1. Reach length, catchment drainage area, percentage of riparian area, width of the riparian zone, and total basal area of riparian trees for the headwater and valley reaches.

	Reach characteristics			Riparian zone characteristics	
	Length (m)	Drainage Area (km^2)	Area (%)	Mean Width (m)	Total Basal Area (m^2 BA)
Headwater	1760	6.74	4.9	12	822
Valley	1161	4.42	9.9	19	1354

600   **Table 2.** Net groundwater inputs to stream discharge (Q_{gw}), number of days with stream hydrological retention ($Q_{gw} < 0$) and groundwater depth (h_{gw}) for the vegetative and dormant period, respectively. The number of cases is shown in parentheses for each group. For Q_{gw} and h_{gw}, data is shown as median ± interquartile range [25th, 75th], and asterisk indicate statistically significant differences between the two periods (Wilcoxon rank sum test, * $p < 0.01$).

605

		Vegetative	**Dormant**
Q_{gw} **(L s^{-1})**	Headwater	10.4 [6.9, 13.2] (373)	11.8 [10.4, 15.7] (237)*
	Valley	-5.3 [-10.1, 2.1] (373)	6.0 [3.6, 9.0] (237)*
$Q_{gw} < 0$ **(days)**	Headwater	57 (373)	0 (237)
	Valley	219 (373)	6 (237)
h_{gw} **(cm b.s.s.)**	Headwater	—	—
	Valley	72.3 [68.7, 76.2] (256)	69.6 [65.3, 70.7] (189)*

Table 3. Median and interquartile range [25th, 75th] of stream solute concentrations at each sampling site for the vegetative and dormant periods. The number of cases is shown in parentheses for each group. The asterisks indicate statistically significant differences between the two periods (Wilcoxon rank sum test, * p < 0.01).

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		Vegetative	Dormant
Cl^- (mg L^{-1})	Up-stream site	6.1 [5.7, 6.5] (281)	6.0 [5.8, 6.2] (176)
	Mid-stream site	8.0 [7.7, 8.4] (333)	7.4 [7.2, 8.6] (220)*
	Down-stream site	8.3 [7.9, 8.8] (302)	7.7 [7.5, 7.8] (184)*
NO_3^- (µg N L^{-1})	Up-stream site	238 [216, 247] (284)	238 [212, 298] (202)*
	Mid-stream site	149 [141, 164] (324)	166[152, 190] (234)*
	Down-stream site	166 [156, 180] (300)	168 [150, 186] (184)
NH_4^+ (µg N L^{-1})	Up-stream site	10.8 [8.2, 14.4] (281)	9.2 [6.8, 10.8] (170)*
	Mid-stream site	10.0 [7.2, 13.7] (344)	8.7 [6.6, 10.8] (229)*
	Down-stream site	9.2 [6.8, 12.7] (310)	8.0 [6.3, 10.4] (147)*

Figures

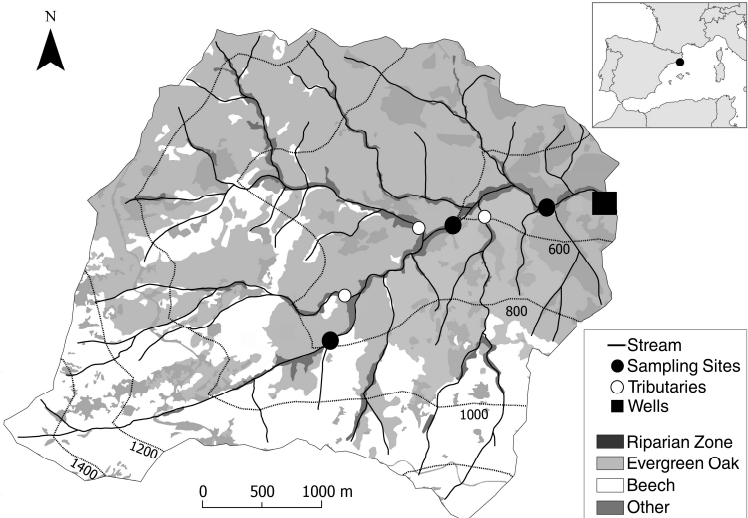



Figure 1. Map of the Font del Regàs catchment (Montseny Natural Park, NE Spain). The
615   location of the three sampling sites (black circles), tributaries (white circles) and the riparian plot
where tree transpiration and groundwater level were measured (black square) are shown. The
headwater reach is comprised between the up- and mid-stream sampling sites, while the valley
reach is comprised between the mid- and down-stream sampling sites.

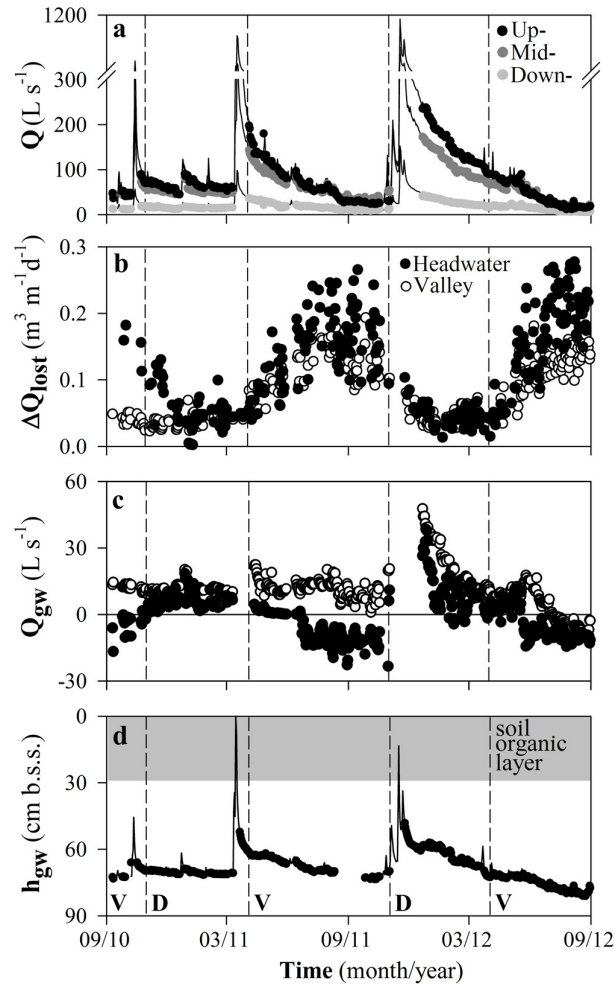



Figure 2. Temporal pattern for the period 2010-2012 of (a) stream discharge (Q) at the up- (light gray), mid- (dark gray) and down-stream (black) sites, (b) riparian evapotranspiration (ΔQ_{lost}) estimated as the difference in the diel variation in discharge between the top and the bottom of the headwater (white) and valley (black) reaches, (c) daily net riparian groundwater inputs (Q_{gw}) for the headwater (white) and valley (black) reaches, and (d) groundwater table fluctuation (h_{gw}) at the valley bottom. In panel (c), the $Q_{gw} = 0$ line is shown as a reference of nil net riparian to stream water inputs; $Q_{gw} > 0$ and < 0 indicates when the stream reach was net gaining and net losing water, respectively. In panel (d), the mean soil depth of the A horizon is indicated. V: vegetative period, D: dormant period.

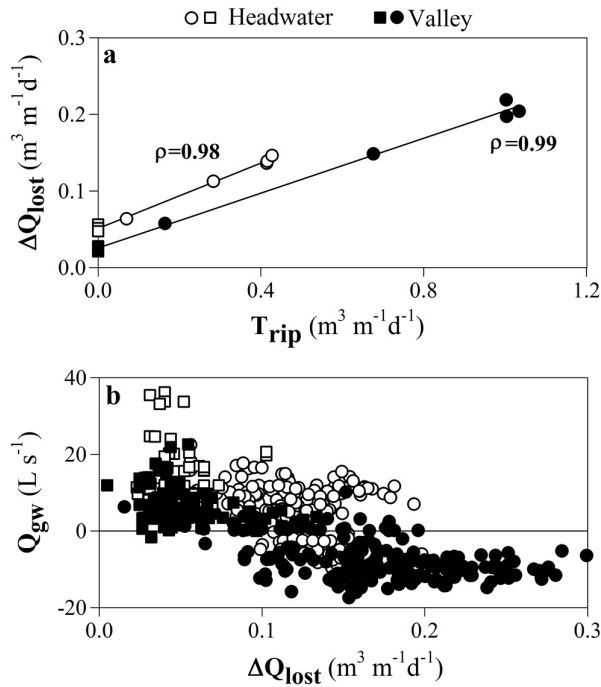



Figure 3. Relationship between (a) the monthly mean of daily riparian transpiration estimated from
sap-flow data (T_{rip}) and riparian evapotranspiration estimated as the difference in diel discharge
variation between the top and the bottom of each stream reach (ΔQ_{lost}), and (b) ΔQ_{lost} and daily net
riparian groundwater inputs (Q_{gw}) for the headwater (white) and valley (black) reaches. Data is shown
separately for the vegetative (circles) and dormant (squares) period. The Spearman coefficients are
indicated in (a) (in both cases: $p < 0.01$, n = 8). In (b), the Q_{gw} = 0 line is shown as a reference of nil
net riparian to stream water inputs; $Q_{gw} > 0$ and < 0 indicates when the stream reach was net gaining
and net losing water, respectively.

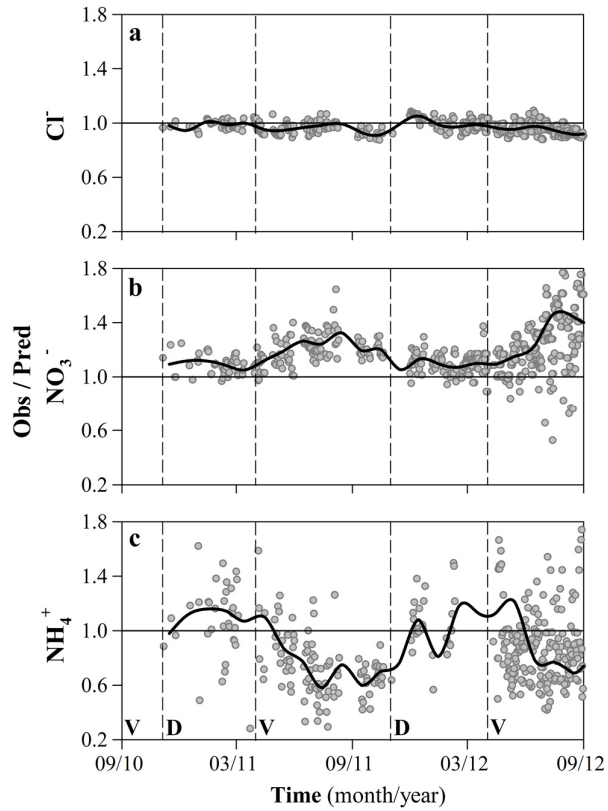
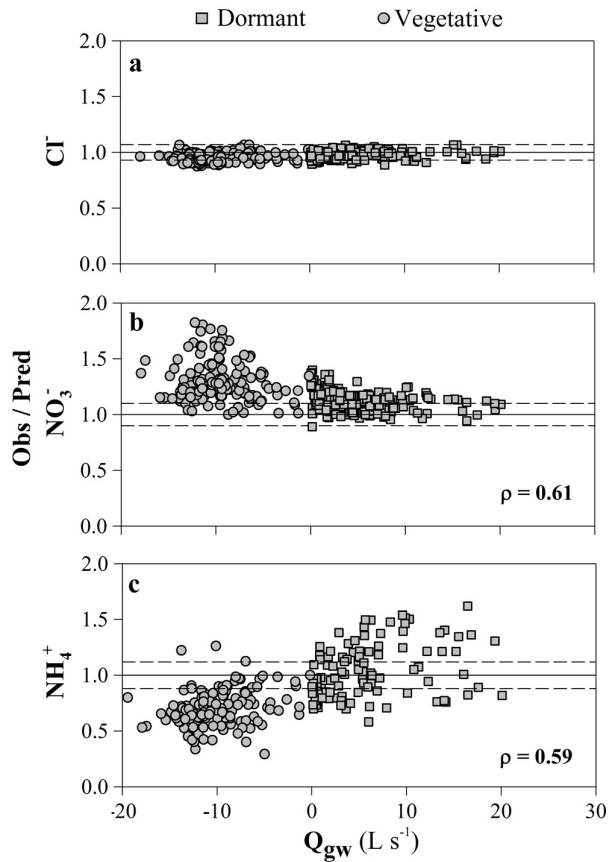



Figure 4. Temporal pattern of the ratio between observed stream solute concentrations at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (c) ammonium during the period 2010-2012. Bold lines indicate the running median (the half-window is 7 days). The Obs:Pred =1 line is indicated as a reference. V: vegetative period, D: dormant period.

645   **Figure 5.** Relationship between mean daily net groundwater inputs (Q_{gw}) and the ratio between stream concentrations observed at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (b) ammonium. Data is shown separately for the vegetative (circles) and dormant (squares) period. The Spearman coefficient is shown in each case. The solid line indicates no differences between observed and predicted concentrations, and the dashed
650   lines indicate the uncertainty associated to the zero line as explained in the material and methods section.

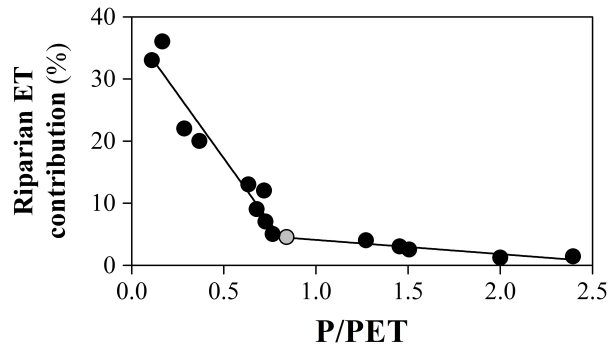



Figure 6. Relationship between the relative contribution of riparian evapotranspiration (ET) to annual catchment water depletion and the ratio between annual precipitation and potential evapotranspiration (P/PET) for a set of catchments worldwide (n = 15). Total water output fluxes from the catchment are stream discharge, catchment evapotranspiration, riparian evapotranspiration, and anthropogenic extraction (if applies). The Font del Regàs catchment (present study) is indicated with a gray circle. More information and references of the study sites are in Supplements (Table S2).

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Supplements of "The influence of riparian evapotranspiration on stream hydrology and nitrogen retention in a subhumid Mediterranean catchment"

Anna Lupon[1], Susana Bernal[1,2], Sílvia Poblador[1], Eugènia Martí[2], Francesc Sabater[1,3]

[1] Department d'Ecologia, Universitat de Barcelona, Av. Diagonal 643, 08028, Barcelona, Spain.
665   [2] Integrative Freshwater Ecology Group, Center for Advanced Studies of Blanes (CEAB-CSIC), Accés a la Cala Sant Francesc 14, 17300, Blanes, Spain.
[3] CREAF, Campus de Bellaterra (UAB) Edifici C, 08193, Cerdanyola del Vallès, Spain.

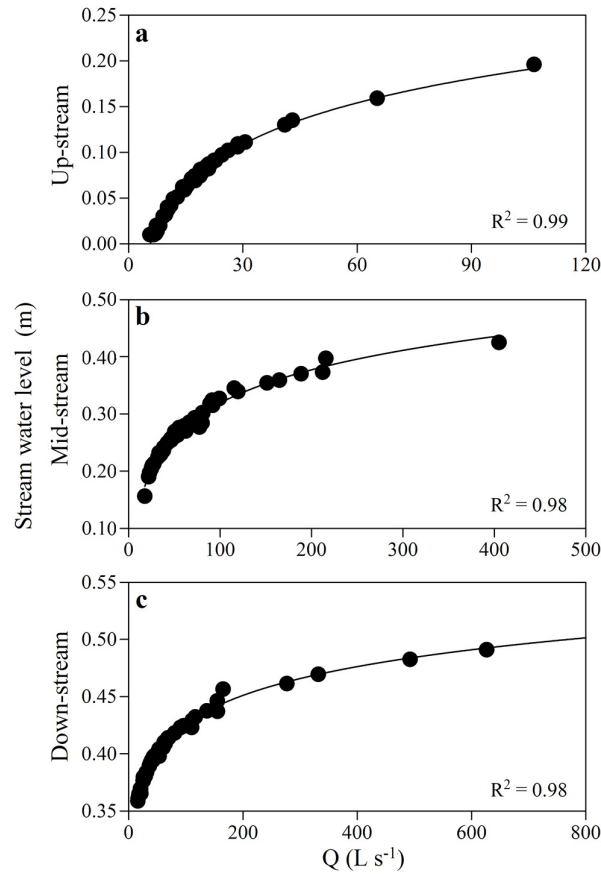
Correspondance to: Anna Lupon (alupon@ub.edu)

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Figure S1. Regressions between discharge (Q) and stream water level for the (a) up-stream, (b) mid-stream and (c) down-stream sites during the period 2010-2012. Circles are data from slug additions and lines are the regression models. The R^2 values are also shown for each case. n = 57, 60 and 61 for the up-, mid- and down-stream sites, respectively. These regressions were used to infer stream
675   discharge at 15 min intervals.
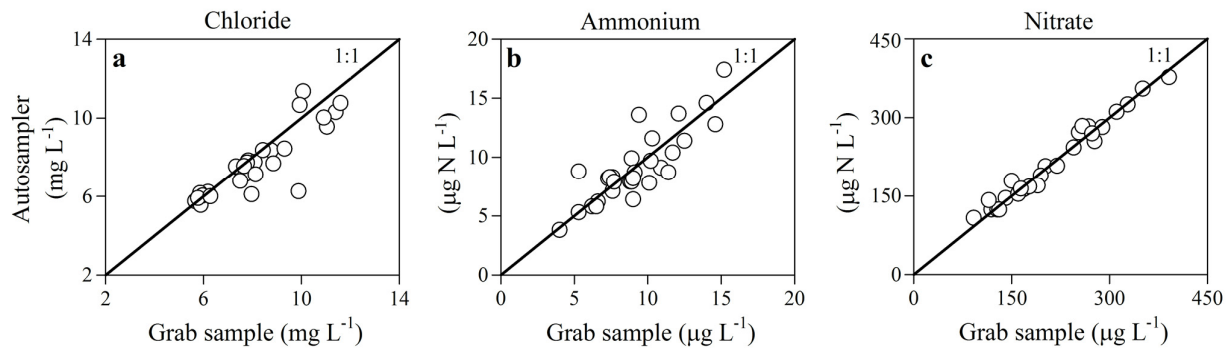
Figure S2. Comparison of stream water chemistry measured by grab samples vs auto-samplers. The samples collected with auto-samplers were taken in the same day than the manual ones, but the formers were then kept in the auto-sampler between 1-10 days. Data is shown for (a) chloride, (b) ammonium and (c) nitrate. The line 1:1 is also shown. The relative root-mean-square error was 3.1, 2.7 and 1.1% for chloride, ammonium and nitrate concentrations, respectively. The good match between the two types of samples suggest that biogeochemical transformation was minimal within the auto-sampler bottles.
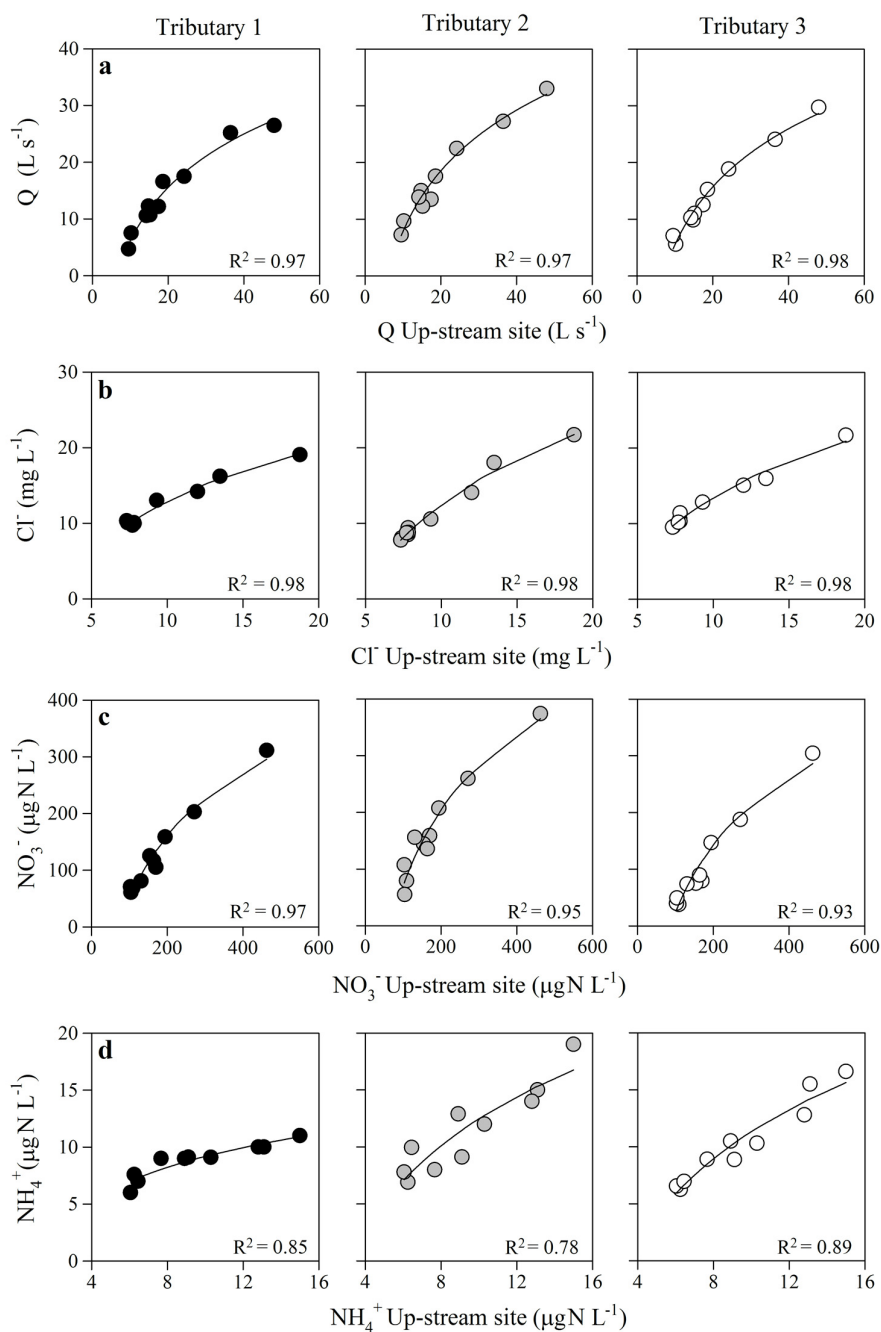
Figure S3. Relationship between values measured at the three main tributaries of the main steam and those measured at the up-stream site for (a) discharge and concentrations of (b) chloride, (c) nitrate, and (d) ammonium. Data was collected on the same day for a set of 11 synoptic field campaigns during the period 2010-2012 (Bernal et al., 2015). The line indicates the best fit (logarithmic model) and R^2 values are shown for each case. The regressions models were used to infer mean daily discharge and daily solute concentrations at each tributary from values measured at the upstream site, which were then used for mass balance calculations.

695 **Table S1.** Measured and predicted concentrations of riparian groundwater concentrations for chloride
(Cl⁻), nitrate (NO$_3^-$) and ammonium (NH$_4^+$) at the headwater reach during the study period. The relative
difference between measured and concentrations predicted from mass balance are also shown.
Groundwater concentrations were measured during a parallel study conducted in the catchment, and
are shown as the median value for the 7 wells installed along the headwater reach (< 2 m from the
700 stream) (Bernal et al., 2015). The concentrations predicted from the mass balance approach showed a
good match with measured concentrations, differing < 5%, 7%, and 10% for Cl⁻, NO$_3^-$, and NH$_4^+$,
respectively. This relative difference between measured and predicted groundwater concentrations at
the headwater reach was used as a threshold to determine when observed and predicted concentrations
at the down-stream site differed significantly from each other.

Day	Cl⁻ (mg L⁻¹)			NO$_3^-$ (µg N L⁻¹)			NH$_4^+$ (µg N L⁻¹)		
	Measured	Predicted	Diff (%)	Measured	Predicted	Diff (%)	Measured	Predicted	Diff (%)
24/08/2010	6.8	6.5	4	246	230	7	21	20	5
27/10/2010	6.3	5.7	5	428	404	6	43	39	9
22/11/2010	7.3	7	4	99	92	7	27	28	-4
19/01/2011	6.9	6.9	0	229	218	5	13	11	10
1/3/2011	6.9	6.6	4	360	351	3	28	27	4
12/4/2011	7	6.8	3	129	131	-2	31	30	3
26/05/2011	6.2	6.1	2	80	78	3	16	17	-6
9/8/2011	9.1	8.6	5	97	102	-5	26	25	4
13/09/2011	8.7	8.5	2	111	110	1	20	20	0
26/10/2011	6.2	5.9	5	223	212	5	24	25	-4
14/12/2011	7.2	7.4	-3	166	175	-5	18	16	10

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Table S2. Annual precipitation (P), annual potential evapotranspiration (PET), P/PET ratio, percentage of riparian area within the catchment (Rip Area) and riparian water depletion (RWD) for different catchments across climatic regions. This data set was used to build Figure 6 of the main manuscript.

Climate	P (mm yr^{-1})	PET (mm yr^{-1})	P/PET	Rip Area (%)	RWD (%)	Source
Arid	250	2280	0.11	8.4	33	Dahm et al., 2002
Arid	300	1800	0.17	11.7	36	Doble et al., 2006
Arid	400	1400	0.29	3-11	22	Contreras et al., 2011
Arid	255	693	0.37	---	20	Goodrich et al., 2000
Arid	570	900	0.63	---	13	Springer et al., 2006
Mediterranean	1296	1911	0.68	8.2	9	Scott, 1999
Mediterranean	780	1055	0.72	3.0	12	Folch and Ferrer, 2015
Mediterranean	850	1170	0.73	15.0	7	Wine and Zou, 2012
Mediterranean	750	990	0.77	2.1	5	Sabater and Bernal, 2011
Mediterranean	925	1100	0.84	6.0	3.6	Present Study
Temperate	1780	1400	1.27	8.4	4	Dunford and Fletcher, 1947
Temperate	858	590	1.45	8.0	3	Petrone et al., 2007
Temperate	1523	1011	1.51	---	2.5	Salemi et al., 2012
Temperate	1800	900	2.00	11.0	1.2	Dunford and Fletcher, 1947
Tropical	4370	1825	2.39	2.5-6.6	1.4	Cadol et al., 2012

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