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

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Abstract. Riparian evapotranspiration (ET) can influence stream hydrology at catchment scale by 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 level (hgw) was measured at the valley reach. The temporal pattern of riparian ET was similar between reaches, was positively correlated with hgw ($\rho = 0.60$), and negatively correlated with net riparian groundwater inputs ($\rho < -0.55$). During the vegetative period, stream hydrological retention occurred only 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 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-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 derives 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 reduce inorganic N critically relays 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 large residence times favor 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 reduce 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 of stream nitrate at the stream-riparian interface (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 for upland groundwater inputs, but also for stream water. In this line of thought, previous studies have reported decreases in stream N concentration along losing stream reaches (Bernal and Sabater, 2012; Dent et al., 2007; Rassam et al., 2006). Yet, there is little empirical evidence of 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 zone 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 between the riparian zone and the stream. Based on longitudinal changes in systems with some water scarcity (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 interface. This knowledge could be of paramount importance 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, and mean annual temperature averages 12.1 ± 2.5 ℃ (mean ± SD, period 1940-2000, Catalan Metereologic Service). Atmospheric inorganic N deposition ranges from 15 to 30 kg

80   ha^{-1} yr^{-1} (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 Cartografic 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,

85   with a 3 cm deep O horizon followed by a 5 to 15 cm deep A horizon. The riparian zone covers the 6% of the catchment area and it is almost flat (slope < 10%), and its width increases from 6 to 28 m along the catchment. The total basal area of riparian trees increases from 118 to 22776 m^2 ha^{-1} along the stream. Black 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.

90   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 zone (the headwater and valley reach) (Figure 1). The headwater reach (750-550 m a.s.l.) was 1760 m long and drained 6.74 km^2 (Table 1). The reach was flanked by a 5-15 m wide riparian forest that covered ~5% of the drainage

95   area. *A. glutinosa*, *F. excelsior*, and *P. nigra* represented 51%, 26%, and 23% of the total basal area, respectively. The valley reach (550-500 m a.s.l.) was 1160 m long and drained 4.42 km^2. The reach was flanked by a 10-25 m wide riparian forest that covered ~10% of the drainage area. *A. glutinosa*, *F. excelsior*, *P. nigra*, and *R. pseudoacacia* represented 53%, 27%, 11%, and 9% of the total basal area, respectively. The two stream reaches showed a well-preserved channel morphology with a riffle-run

100   structure. The streambed was mainly composed by rock (~30%), cobbles (~25%), and gravel (~15%) at the headwater reach, whereas rock (~25%), cobbles (~30%), and sand (~30%) were the dominant substrates at the valley reach. The stream channel was, on average, 2 and 3 m wide for the headwater and the valley reach, respectively.

3. Materials and methods

3.1. Field sampling and chemical water analysis

To characterize the riparian zone, we inventoried 14 riparian forest plots of 30 m long each (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 at breast height (DBH, in cm) and its basal area (BA, in cm^2) with $BA = \Pi * (DBH / 2)^2$. For each tree species i, we calculated the area-specific BA (BA_i, in m^2 of BA per ha 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 (2.3 ha) or valley (2.1 ha) 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 (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 (n = 57, 60, and 61 for up-, mid- and down-stream sites, respectively; in all cases: R^2 > 0.97). 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 sensor (HOBO U20-001-04) in a 1.8 m long PVC piezometer (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). From August 2010 to December 2011, stream discharge and stream chemistry was measured every 2 months at the four 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

130 (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

135 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. We attributed Q_{lost} to water withdrawal by riparian tree roots from

140 either the riparian aquifer or directly from the stream channel (Cadol et al., 2012). 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

145 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 tree (*A. glutinosa, F. excelsior*, *P. nigra*, and *R. pseudoacacia*). For each reach, we calculated the transpiration of the riparian tree community (T_{rip}, in $m^3 m^{-1} d^{-1}$) with:

150 $$T_{rip} = (\Sigma_{i=1}^{n} T_i \times BA_i) / x \tag{1}$$

where T_i is monthly mean daily transpiration (in dm^3 of water per m^2 of BA and day) and BA_i is the area-specific basal area (in m^2 BA ha^{-1}) of each tree species i, 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) (n = 8).

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 (log-log) between Q measured at each tributary and at the up-stream site within the same day (for each of the four tributaries: $R^2 > 0.92$, $n = 18$, $p < 0.001$). 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. 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

180   concentration at the tributaries (in mg L^{-1}), which was estimated by fitting the best fit model (log-log) between solute concentration measured at each tributary and at the up-stream site within the same day (for each of the four tributaries and for the three solute: R^2 > 0.70; in all cases: n = 18, p < 0.001). 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

185   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 piezometers installed along the headwater reach (< 2 m from the stream), with median C_{gw}

190   differing < 5%, 7%, and 10% for Cl$^-$, NO$_3^-$, and NH$_4^+$, respectively (Bernal et al., 2015).

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 NO$_3^-$ and NH$_4^+$, Obs:Pred < 1 and $Q_{gw} <$ 0 was interpreted as in-stream biological N retention via assimilatory uptake (for NO$_3^-$ and NH$_4^+$),

195   nitrification (for NH$_4^+$) and/or denitrification (for NO$_3^-$). We interpreted Obs:Pred > 1 and $Q_{gw} < 0$ as either in-stream mineralization (for NH$_4^+$) or nitrification (for NO$_3^-$). When the stream was gaining water in net terms ($Q_{gw} > 0$), values of Obs:Pred ≠ 1 were interpreted as an indication of differences in riparian groundwater chemistry between the headwater and valley reach. We used the relative difference between measured and predicted C_{gw} at the headwater reach as a threshold to determine when observed and

200   predicted concentrations differed significantly from each other (±1.05, ±1.07, and ±1.1 for Cl$^-$, NO$_3^-$, and NH$_4^+$ 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

205 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

210 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 NO_3^- and NH_4^+ concentrations at the valley reach, we examined the relationship between Q_{gw} and Obs:Pred ratios measured at the down-stream

215 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 concentrations were not normally distributed (Shapiro test, $p < 0.05$). In all cases, differences were

220 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-stream sites, respectively. The three sites showed the same seasonal pattern, characterized by a strong

225 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, $p < 0.01$).

During the dormant period, diel variations in stream discharge were relatively small at the three sites, Q_{lost} accounting for $< 2\%$ of mean daily Q. Values of Q_{lost} increased during the vegetative period and showed

230   a marked longitudinal pattern being median values 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 April to June, peaked in summer (July-August), and then decreased until November. During 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.

235   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 positive relationship between T_{rip} and ΔQ_{lost} for both the headwater and valley reach (Figure3a). 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

240   $[\rho] = 0.58$, $p < 0.001$, $n = 277$).

4.2. Net riparian groundwater inputs and groundwater table elevation

During the study period, 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).

245   The two reaches showed a negative correlation between Q_{gw} and ΔQ_{lost} (headwater: $\rho = -0.57$, $p < 0.001$, $n = 273$; valley: $\rho = -0.79$, $p < 0.001$, $n = 286$) (Figure 3b).

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

250   headwater reach (15% of the time). There were no days with $Q_{gw} < 0$ during the dormant period at any of the two reaches.

At the down-stream site, median annual h_{gw} was 70 cm b.s.s. and showed higher values 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

During the study period, stream Cl^- concentration was lower at the up- than at the mid- and down-stream sites during 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 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-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 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

280 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

285 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 diminish the groundwater table (Sabater and Bernal, 2011; Schilling, 2007) and decrease the amount of groundwater entering to

290 streams by 30-100% (Dahm et al., 2002; Folch and Ferrer, 2015; Kellogg et al., 2008). On an annual basis, riparian transpiration (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 relatively low values, together with the fact that riparian forests occupied a small area of the catchment (6%), resulted

295 in a minimal contribution (4.5%) of riparian transpiration to the annual catchment water budget. Our estimates are 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). Together, these results

300 suggest that the relative contribution of riparian ET to catchment water depletion across biomes could be explained by differences in water availability (Figure 6). 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 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 interface in net losing reaches (Bernal and Sabater, 2012; Duval and Hill, 2007; Rassam et al., 2006). Biological NO_3^- uptake at the stream-riparian interface 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).

330   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), 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 suite at Font del Regàs because the valley reach had

335   extra inputs of N-rich leaf litter (Bernal et al., 2015) and a well-oxygenated hyporheic zone (~7 mg O_2 L^{-1}, unpublished data) during periods of stream hydrological retention. Moreover, both low discharge (< 30 L s^{-1}) and stream depth (< 15 cm) during summer could favor the contact between nutrients and microbial community. Alternatively, differences in NO_3^- and NH_4^+ concentrations between the headwater and the valley reach could be explained by hydrological mixing with unaccounted water sources, such as deep

340   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.

During the dormant season, 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

345   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 limited riparian denitrification, given that both NO_3^- availability was low in groundwater arriving from uplands (< 1 mg L^{-1}; unpublished data) and that groundwater and organic-rich soils were hydrologically disconnected even during the dormant period. Additionally, high rates of N mineralization and nitrification in the riparian

350   soil could promote N export from the riparian zone to the stream at the valley reach (Lupon et al., in review).

The influence of in-stream N cycling on N export ultimately depends on water fluxes and the hydrological exchange between riparian and stream ecosystems. 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

355 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 ET. Otherwise, NO_3^- export to downstream ecosystems would have been 15% higher. Similarly, there were no differences between input and output NO_3^- fluxes at the valley reach during the dormant period, 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^-

360 $= 0.166$ vs. 0.168 mg N L^{-1}). These back-of-the-envelope calculations highlight that riparian ET and stream-riparian hydrological exchange can substantially influence stream N fluxes.

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 interface in small

365 forested catchments, despite its modest contribution to annual water budgets (Folch and Ferrer, 2015; Medici et al., 2008). Riparian ET stronly 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

370 accompanied by increases in nitrate concentrations, likely due to in-stream nitrification fueled by low stream flows, large stocks of N rich leaf litter, 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 strongly regulate the spatio-temporal pattern of stream water fluxes in Mediterranean regions and questions the N buffering capacity of Mediterranean riparian zones at

375 catchment scale.

Author contribution

A.L., S.B., and F.S. designed the experiment. A.L., S. B., and S.P. carried them out. A.L. performed all laboratory analysis. A.L. analyzed the data set and prepared the manuscript with contributions from S.B, S.P, E.M., and F.S.

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380

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535 **Tables**

Table 1. Reach length, catchment drainage area, percentage of riparian area, width of the riparian zone, and 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)	Tree Basal Area (m^2 BA m^{-1} stream)
Headwater	1760	6.74	4.9	12	0.28
Valley	1161	4.42	9.9	19	0.58

Table 2. Net groundwater inputs to stream discharge (Q_{gw}), number of days with stream hydrological
540   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 each variable, the asterisk indicates
statistically significant differences between the two periods (Wilcoxon rank sum test, * $p < 0.01$). For Q_{gw}
and h_{gw}, data is shown as median ± interquartile range [25th, 75th].

		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)	0 (237)
h_{gw} **(cm b.s.s.)**	Headwater	—	—
	Valley	72.3 [68.7, 76.2] (256)	69.6 [65.3, 70.7] (189)*

545   **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).

		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)*

550

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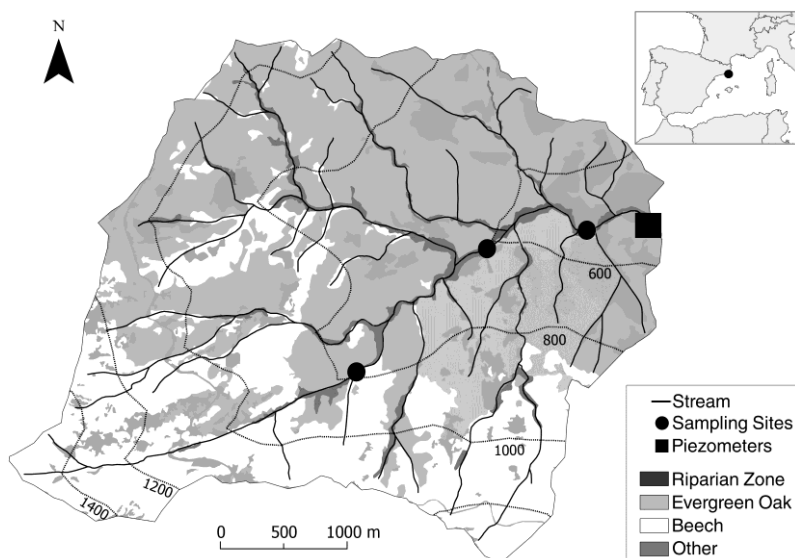
Figure 1. Map of the Font del Regàs catchment (Montseny Natural Park, NE Spain). The location of the three sampling sites (black circles) and the riparian plot where tree transpiration and groundwater level were measured (black square) are shown. The headwater reach is comprised between the up- and mid-stream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

555
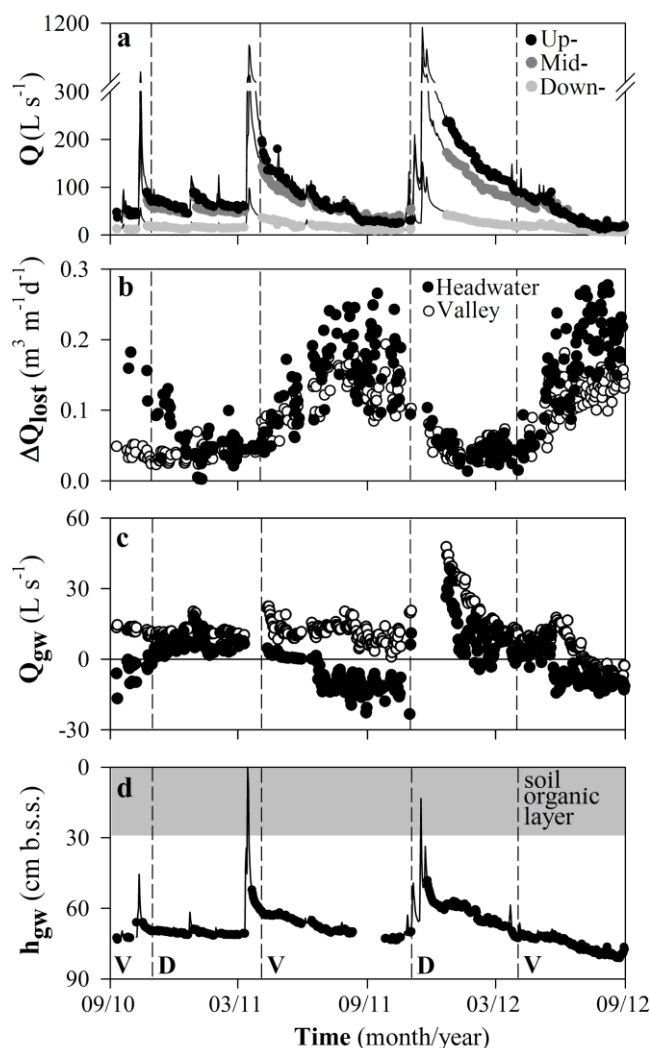
Figure 2. Temporal pattern for the period 2010-2012 of (a) stream discharge (Q) at the up- (light gray),
mid- (dark gray) and down-stream (black) sites, (b) riparian evapotranspiration (ΔQ_{lost}) estimated as the
difference in the diel variation in discharge between the top and the bottom of the headwater (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.
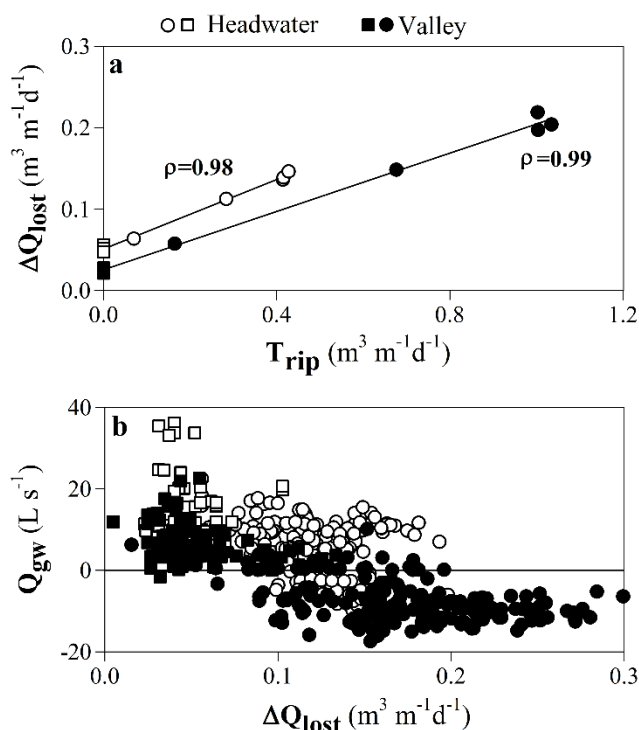
Figure 3. Relationship between (a) the monthly mean of daily riparian transpiration estimated from sap-flow data (T_{rip}) and riparian evapotranspiration estimated as the difference in diel discharge variation between the top and the bottom of each stream reach (ΔQ_{lost}), and (b) ΔQ_{lost} and daily 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.
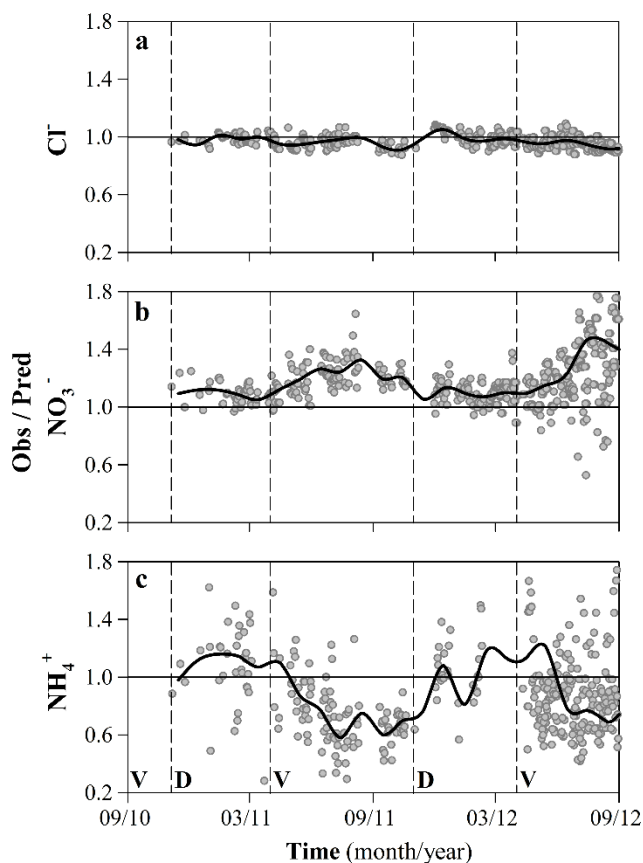
Figure 4. Temporal pattern of the ratio between observed stream solute concentrations at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (c) ammonium during the period 2010-2012. Bold lines indicate the running median (the half-window is 7 days). The Obs:Pred =1 line is indicated as a reference. V: vegetative period, D: dormant period.
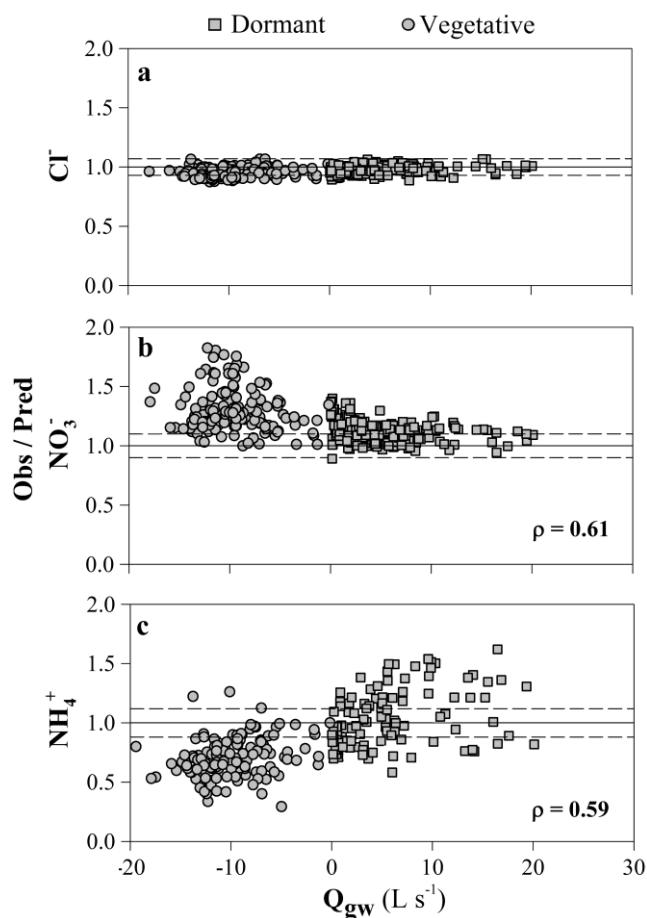
Figure 5. Relationship between mean daily net groundwater inputs (Q_{gw}) and the ratio between stream concentrations observed at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (b) ammonium. Data is shown separately for 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 lines indicate the uncertainty associated to the zero line as explained in the material and methods section.
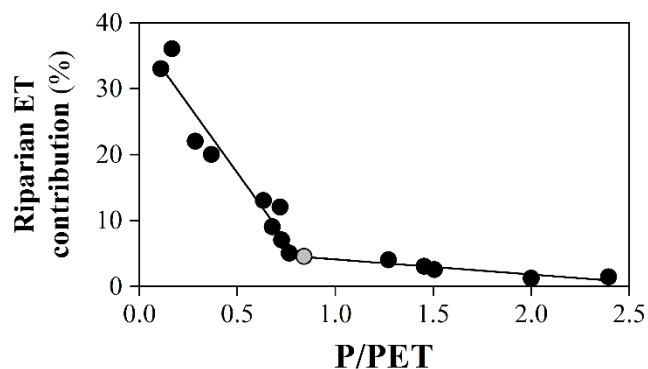
Figure 6. Relationship between the relative contribution of riparian evapotranspiration (ET) to annual catchment water depletion and the ratio between annual precipitation and potential evapotranspiration (P/PET) for a set of catchments worldwide (n = 15). Total water output fluxes from the catchment 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 1.