Author responses to reviewer comments on the manuscript entitled

"The influence of riparian evapotranspiration on stream hydrology and nitrogen retention

in a subhumid Mediterranean catchment"

By Anna Lupon, Susana Bernal, Sílvia Poblador, Eugènia Martí and Francesc Sabater

Dear reviewers and Prof. Cristian Stamm (Editor of HESS),

Many thanks for you thoughtful review comments on the paper "The influence of riparian evapotranspiration on stream hydrology and nitrogen retention in a subhumid Mediterranean catchment". We feel thankful for your positive and constructive comments such as that "*this paper is straightforward and convincing*" or that "*the authors did a commendable job*". Moreover, we think that your comments and edits on the paper have been of great help to improve its quality and clarity.

We have taken into consideration all the comments highlighted by you and we have worked thoroughly to tackle most of them. According to your comments, we now explain in more detail sap-flux measurements, chemical data analysis, and both riparian and stream characteristics. Moreover, we have clarified the interpretation of diurnal signals of stream discharge during the dormant period. Following your advice, we do now provide some explanation for the low evapotranspiration rates; and temperature has been included as a potential driver of in-stream nitrification. We have also toned down our conclusions regarding the effect of riparian evapotranspiration on stream nitrogen loads at annual scale. Finally, we have added the graphs requested by you as supplementary materials.

Below we provide the answer to each of your comments. In case of not following completely your suggestions, we have stated why. Please, do not hesitate to contact us if you considered that further clarifications are needed.

Looking forward hearing from you soon,

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cc: Susana Bernal, Sílvia Poblador, Eugènia Martí, Francesc Sabater

Editor comments

Detailed comments:

L.20: What is about the nitrogen budget? **Answer:** Unfortunately, we could not directly calculate the influence of riparian trees on catchment N budgets because tree N uptake was not measured.

L.35: What do you mean here (and elsewhere) with "reduce": changing the oxidative status of N compounds? **Answer:** We mean "diminish" or "lowered". Changes in the text according to this have been done (lines 38, 45).

L.39: Why is the residence time large during wet conditions? **Answer:** We have clarified that high water residence time can occur when the water table rises up during wet conditions in flat riparian areas (Ranalli and Macalady, 2010) (lines 41-43).

L.57: Why should a losing streams show decreasing N concentrations in the stream? If you only have a losing stream you diminish the load but do not change the concentration in the stream unless other fate processes are affected (e.g., fraction of water exchanging between the hyporheic zone and the stream). Please explain. This is essential also for understanding your hypothesis (L. 70). Answer: In previous studies, decreases in stream N concentration along losing stream reaches have been attributed to high N uptake rates at the stream-riparian edge. We have added this statement in the manuscript (lines 62-64).

L.67: "direction of water flow. . . " Answer: OK (line 73).

L.72: "paramount" seems slightly overstated to me. **Answer:** OK, now this sentence reads as follow: "this knowledge <u>could</u> <u>have implications</u> for water resource management" (lines 78-80).

L.79-80: Is there any temporal trend in N deposition over the years or are these interannual variations? **Answer:** According to Àvila and Rodà (2012), bulk nitrogen deposition did not significantly vary from 1983 to 2007. Therefore, there has not been any substantial temporal trend in N deposition over the past decades (lines 86-87).

L.85: How do you define the riparian zone? Is it based on vegetation (species composition), pedology or terrain? Please explain. This seems also essential for the subsequent discussion (e.g., Fig. 6). Answer: Riparian zone is defined based on vegetation. We do now refer to "riparian forest" in order to clarify such definition through the manuscript.

L.86: In which direction do you measure the slope here? The steepest descent or perpendicular to the river? Slopes < 10% are not necessarily almost flat. **Answer:** Slopes were measured perpendicular to the river by using a theodolite. This procedure has been included in the manuscript (line 94).

L.87: The increase of the basal area is not clear to me, sorry. **Answer:** We have clarify the sentence indicating that the total basal area of riparian trees (based on tree diameter at breast height) <u>increases by 12-fold</u> along the study stream reach (lines 94-97).

L.117-118: Please show the scatter plots for this regression in the Supplementary Material. Answer: OK, now this information is provided in Figure S1 (Supplementary materials, pp. 31).

L.123: How frequently were samples taken to the lab and processed? Where there any measures taken to prevent nitrification or any other changes of N forms? **Answer:** Samples collected with auto-samplers were carried to the lab every 10 days (lines 136-137). Auto-samplers were installed about 1 m below ground for keeping water samples in a fresh environment with small changes in temperature, which prevents biogeochemical transformations within auto-samplers (lines 137-138). We have followed the same procedure in previous studies, and despite not taken any especial measure to prevent nitrification, we have never found substantial differences between grab samples and samples kept in the auto-samplers for this period of time. To illustrate that, below we show the graphs that compare chloride (conservative tracer), ammonium, and nitrate concentrations between samples collected by the two methods (grab vs auto-samplers) (Figure R1). 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. The

good match between the two types of samples as well as the small relative root-mean-square error (< 3%) suggest that biogeochemical transformation was minimal within the auto-sampler bottles (Figure R1).

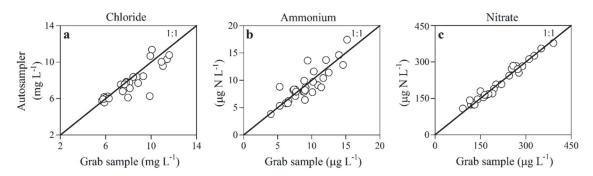


Figure R1. Comparison of stream water chemistry measured by grab samples vs auto-samplers (Figure R1). The samples collected with auto-samplers were taken in the same day than the manual ones, but the formers were then kept in the auto-sampler between 1-10 days. Data is shown for (a) chloride, (b) ammonium 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.

L.126: Please indicate these four locations on the map. Answer: OK, locations are now included on the map (see new Figure 1).

L.147: How was sap flow measured? **Answer:** 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 dm³ H₂O m⁻² *BA* min⁻¹) following the original calibration of Granier (1985). Following your suggestion, we have included this brief description of sap flow measurements in the methods section (lines 167-173).

L.154: What does n stand for? **Answer:** "n" stand for the number of months. We have removed it from the manuscript to avoid confusions with the number of species in equation 3.

L.167: Please show actual data as scatter plots in the Supplementary Material. **Answer:** OK. Please see new Figure S2 (panel a) (Supplementary materials, pp. 32).

L.177: I suppose the last term of the right hand side is added not subtracted. **Answer:** That's right. Thank you for noticing. We changed Equation 3 accordingly (line 205).

L.182: Again, please show the actual data in the Supplementary Material. **Answer:** OK. These data are now provided in Figure S2 (panels b-d) (Supplementary materials, pp. 32).

L.188-190: Again, please show the actual data in the Supplementary Material. **Answer:** OK. These data are now provided in Table S1 (Supplementary materials, pp. 33).

L.252: A higher values implies lower water table levels, correct? **Answer:** Yes, we have now clarified it in the manuscript (lines 284-285).

L. 292: What are possible reasons for such low values? **Answer:** The truth is that we are not sure about it. One explanation could be because of low solar radiation (Aguilar et al. 2010). The study catchment is quite V-shaped and the riparian forest is in a topographically-shaded area. On average, solar radiation arriving to the riparian canopy is 36 ± 18 W m⁻² d⁻¹; that is 80% less than in the open areas of the catchment (Poblador, unpublished data). This potential explanation has been included in the discussion (lines 328-331).

L.301: What are there references used for Fig. 6? How large (percentage of catchment) are the riparian areas in the respective studies? **Answer:** References are now included as Supplementary material. Moreover, Table S2 now shows the percentage of the catchment covered by riparian areas, which ranges from 2% to 15% (pp. 34).

L.352 - 361: I have problems to follow your argument: On L. 354 you state that the fluxes into and out of the valley reach during the vegetative period were similar and that nitrate export would have been about 15% higher without water lost to the riparian area (L. 357). During the dormant period, the nitrate fluxes are larger (about 18 mg N s⁻¹) without a change along the reach. Under the assumption that the dormant and vegetative period each last 6 months, this indicates that the effect size is in the order of 5% of the annual nitrate export. Is this substantial? **Answer**: That's right; on annual terms, the riparian zone does not have a remarkable influence on nitrate exports from the catchment. Accordingly, we now argue that "these back-ofthe-envelope calculations highlight that riparian ET and stream-riparian hydrological exchange can substantially influence stream N fluxes during some time-windows of the year, despite it may have small implications for N fluxes at annual scale" (lines 407-409).

L.371: What about temperature and pH? Both are known to have an important influence on nitrification rates in streams and temperature will exhibit a pronounced seasonal pattern, I assume (e.g., Laursen & Seitzinger, 2004; Warwick, 1986). **Answer:** Following your advice, we have included in the manuscript that warm temperatures in summer could also stimulate in-stream mineralization and nitrification at the valley reach (Laursen and Seitzinger, 2004) (lines 378-379; 418-421). However, we do not have evidences that stream pH changed over the year at the down-stream site (pH = 7.6 ± 0.3 , n = 58; unpublished data). Therefore, we have decided not to include this explanation, unless you consider it would add value to the discussion.

L. 373: See comment above: strong regulation seems to strong an expression here. **Answer:** Thanks, we have toned down our conclusions in this regard. We now state "ET can regulate the spatio-temporal pattern of stream water fluxes in Mediterranean regions" (lines 422-424).

Reviewer #1

Major concern:

The only major point is that there is no differentiation between winter and summer type diurnal signal therefore false calculation/interpretation of Q_{lost} in the dormant season. Q_{lost} estimation (used in paper) is good only for summer type signal. But in dormant season there is another so called winter type signal, which has a different shape and phase than summer type. The inducing effect of winter type signal is freezing and thawing not ET (see e.g. Lundquist and Cayan 2002, Gribovszki et al. 2010).

Answer: We completely agree. In temperate catchments there is usually a freezing and thawing diel signal characterized by a dawn minima and early afternoon maxima (Lunquist and Cayan, 2002). However, this type of signal does not usually occur in Mediterranean catchments, such as Font del Regàs, because there is no snow pack and soils are always > 0 °C (except some few days during particularly cold winters, which was not the case during the study period). Instead, we observed a tinny diel variation in stream discharge during winter, with maxima in early morning (3-6 am) and minima in early afternoon (2-5 pm). Similarly to the vegetative period, this type of signal is typically induced by tree evapotranspiration (Lunquist and Cayan, 2002). We agree with the reviewer that this signal cannot come from riparian evapotranspiration because riparian trees do not have leaves during winter time. Most likely, diel variations in winter result from the evapotranspiration of riparian understory vegetation (Roberts, 1983) and upland evergreen oaks (Savé et al., 1999). We have rewritten the methods and results sections to clearly explain (i) that there is no snow pack in our catchment (Section 2, lines 83-84; 92-93) and (ii) that winter diel signals probably result from riparian understory vegetation and hillslope evergreen oak forests (Section 3.2, lines 156-158; Section 4.1, lines 258-259).

Detailed comments:

Ln.15: subscript (lowercase). Answer: OK (lines 15; 16).

Ln.87: You have to define basal area here because this is the first mention in text. How can be basal area 22776 m²/ha? *Is this basal area the same as BA later defined in line 108?* **Answer:** Yes, it was the same basal area. However, there was a mistake in the numbers, we apologize. We have changed the sentence in order to define basal area and to clarify its meaning (lines 94-97) (please, see our answer to Editor's comment, who also highlighted this issue).

Ln.95. Longitudinal slope of reaches would be also informative. **Answer:** OK, we have added this information in the study site section (line 109-110).

Ln.100: It would be better to characterize h_{gw} not only for the valley reach, because as you mentioned in line 189 you have piezometers also along the headwater reach. Are there any differences between the water table levels or dynamic? Hydraulic conductivity values for streambed and riparian aquifer (if you have information about it) would also be informative. Answer: The two reaches show similar riparian groundwater level. To illustrate that, below we show the comparison of the temporal pattern of near stream riparian groundwater (< 1.5 m from the stream channel) measured in 7 wells along each stream reach. Groundwater level was measured every 2 months from August 2010 to December 2011 as a part of a parallel study (Bernal et al., 2015). On average, groundwater level was 0.5 ± 0.1 m below the soil surface in both reaches (Figure R2). Following your advice, we have included this information in the study site section (lines 113-115). Unfortunately, we did not measure hydraulic conductivity.

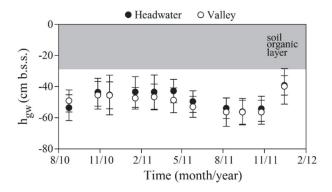


Figure R2. Temporal pattern of near stream groundwater level (h_{gw}) measured at the headwater and valley reaches during the period August 2010-December 2011. Circles are mean values for 7 wells located along each selected study reach, and whiskers denote the standard deviation. Both reaches showed similar temporal pattern (Wilcoxon paired rank sum test, p > 0.1, n = 82), being mean groundwater level 0.5 ± 1 cm below the soil surface.

Ln.107: BA needs to be defined where it is used first. See earlier comment. Answer: OK. Please, see our answer to your earlier comment to see how the definition of BA has been introduced in the text.

Ln.115: Pressure transducer (instead of water sensor). Answer: OK (line 127; 134).

Ln.122: Why had not you also installed another piezometer with a pressure transducer at the headwater reach (it is only a question of interest)? **Answer:** We agree that it would have been of a great help to install an additional piezometer at the headwater reach. We realized about that when the study was already ongoing. The study was initially designed to understand the influence of riparian zones on stream discharge, and in particular of stream hydrological retention. To this end, we decided to use the diel variation in stream discharge at the two reaches to estimate riparian ET. As the study evolved, we realized that it would be a great piece of information to show the close hydrological link between riparian groundwater and stream discharge by comparing the diel variation of discharge with the variation in riparian groundwater table. In this sense, we considered high temporal resolution data on riparian groundwater table at the valley bottom collected by Silvia Poblador (as

part of her PhD) to complement the current study. Despite we could only made these measurements for the valley reach, we still think that it is an added value for the paper.

Ln.135: This Q_lost estimation is good only for summer type signal. But in dormant season there is another so called winter type signal, which has a different shape and phase than summer type. The inducing effect of winter type signal is freezing and thawing not ET (see e.g. Lundquist and Cayan 2002, Gribovszki et al. 2010). Answer: That's right, as we mentioned earlier in our response, these winter signal is not observed at Font del Regàs, probably because the winter signal with maxima in early morning and minima in early afternoon, which may correspond to evapotranspiration by understory and hillslope evergreen oak forests. We have clarified this issue in the methods and results sections (lines 156-158; 258-259).

Ln.144: Why had not you calculated ripartian ET from diurnal signal of h_gw . There are a lot of methods available for calculation (see comparison of methods e.g. in Fahle and Dietrich 2014). Answer: As we mention in our earlier responses, the goal of our study was to evaluate the effect of riparian ET on stream discharge, in particular on stream hydrological retention. Variability in riparian groundwater level was not our central target. This is why we used the Cadol et al. (2012) method to calculate riparian ET from stream discharge rather than from groundwater level variations (e.g. White, 1932). Furthermore, we only had groundwater data for the valley reach, which would not allow us making direct comparison of riparian ET (measured from groundwater) between the two reaches.

Ln.197-199: I do not understand this sentence. Please clarify it. **Answer:** OK, the sentence now reads as follow: "For $Q_{gw} > 0$ (net gaining stream), Obs:Pred $\neq 1$ was interpreted as differences in riparian groundwater nutrient concentration between the headwater and the valley reaches" (lines 226-227).

Ln.228: Please take care of. It is probably a winter type signal. **Answer:** Many thanks for the advice. We have checked diel variations in discharge and, although being small, they show the shape and phase of ET induced signals. Please, see our earlier comments on this regard.

Ln.238: In dormant season (Jan-March) a winter type signal is typical, and it is not caused by T_{rip} (*or* ET_{rip}). **Answer:** That is true; evapotranspiration by riparian trees could not induce diel cycles of in-stream discharge in winter. Most likely, either riparian understory or evergreen oak forest is inducing such diel cycles in Font del Regàs catchment. Please, see our earlier comments on this regard.

Ln.343-351: Please, take into account that under 10°C the nitrification is very slow. **Answer:** This is a good point. However, empirical results from a parallel study in Font del Regàs indicated relatively high net nitrification rates ($0.84 \pm 0.23 \text{ mg N kg}^{-1}$ day⁻¹, n = 36) in riparian soils during winter, when soil temperature ranged between 5-10°C (Lupon et al., 2016). These results suggest that soil nitrification was likely not limited by temperature in the study area, while supporting the idea that high rates of nitrification can promote N export from the riparian zone to the stream during the dormant season (lines 395-397).

Reviewer #2

Major concern:

This paper seeks to determine the role of riparian vegetation on controlling duration and extent of stream recharge to nearstream aquifers, termed stream hydrological retention by the authors, and concomitant changes to forms of inorganic nitrogen. This is no easy task, as the processes involved are hard to link as they operate at different spatial and temporal scales. None the less, the authors have done a commendable job, providing enough correlative data to strongly suggest water table drawdowns are indeed induced by ET, which leads to increased stream hydrologic retention. That this would also be associated with increased rates of nitrification is novel. I recommend publication with hopefully minor revisions. My most important concerns with the manuscript involve separation of the chemistry data to look at time periods that strictly align with periods of net discharge losses (unless I've misread how the data were grouped), and the presentation of the methods with respect to the ET determinations.

Answer: Many thanks for your positive and constructive comments of the paper. Regarding how data was analyzed, only discharge and solute concentrations during base flow conditions (i.e., when changes in discharge were < 10% in 24 h) were included in the analysis. The same data set was used to investigate differences between the vegetative and dormant periods (i.e. Wilcoxon rank sum test) as well as for the mass balance approach. We have clarified this issue in the methods section (lines 202-203).

Furthermore, and following both the reviewer and editor suggestions, we have included more information regarding how sapflux measurements were carried out in the field (lines 167-173). Please, see our responses to the editor, who has also highlighted this issue.

Detailed comments:

Study Area: I'm confused as to how the valley reach drained less of the catchment area than the headwater reach. Figure 1 indicates the sites are both located on the main stem of the river, which should mean the total catchment area being drained at any point along the stream increases as you move downstream. Answer: That is right; what we wanted to say is that the valley reach drains an additional area of 4.42 km² on top of the drainage area of the headwater reach (i.e. 11.16 km² in total). We have clarified this in the study site section (lines 105-106).

Results Section 4.3: I'm not sure the approach presented here is the most fruitful. Lumping the whole dataset together for each sampling point to compare means in phases of the year probably confounds the interpretation. The authors have already removed storm flow data from their Q analysis, would it not make sense to also do that for the solute analysis? Surely the few rain events during the vegetative periods will lead to unique N & Cl responses than what the authors are striving towards; that is, N flushing as Qgw becomes more positive. Why not try to look only at solute differences during base flow? Answer: That is right, we completely agree. Indeed, to avoid any interference from stormflow data, we only used solute concentrations measured during base flow conditions when exploring differences between the two periods as well as when calculating mass balance approaches. We have clarified this procedure in the methods section (lines 202-203).

Discussion Section 5.2: The authors point out the previous literature on losing reaches has found net nitrate removal from the stream water. It might be worth mentioning here that net nitrification leading to ammonium losses and nitrate increases in other stream type are not uncommon (Triska et al., 1990, 1993 for early data). This highlights the importance of in-stream (in-hyporheic zone) N transformations that would be (mostly) disconnected from whether the stream is gaining or losing water to the riparian zone. Answer: This is an interesting point; thanks for highlighting this issue. For instance, both Triska et al. (1993) and Dent et al. (2007) reported an increase in nitrate concentration along the stream despite measuring high denitrification rates at the stream-riparian interface. In both cases, such increase in nitrate concentration was attributed to instream (or hyporheic) nitrification. Ultimately, these results suggest that processes occurring within the stream surface channel or in the hyporheic zone can overwhelm those occurring within the stream-riparian edge, especially during periods of high hydrological retention. We have included this idea in the discussion section (lines 386-388).

L35: change "relays" to "relies" Answer: OK (line 38).

L58-60: The tone set here is too negative to their purposes. "There is little empirical evidence" sounds like people have studied riparian ET – nitrogen cycling before and not found any linkage. I think the authors are trying to say that there has been very little investigation into this linkage. **Answer:** Thanks. The sentence now reads as follows: "there has been <u>little</u> research focused on the influence of riparian ET on upland-riparian-stream hydrological exchange" (lines 64-66).

L106: were the forest inventories done as straight-line transects of 30-m length, or were they plots 30-m long, perhaps also by 30-m wide? **Answer:** Plots were 30 m long and their width varied from 5-20 m depending on the width of the riparian forest. We have clarified this in the manuscript (lines 118-119).

L108: the upper case version of pi is used in the basal area calculation, rather than the lower case. **Answer:** OK, thanks. We have changed it accordingly (line 95).

L115: insert "transducer" or "sensor" after "water pressure." Answer: OK (lines 127; 134).

L121: more information is necessary on the piezometer. Was it a piezometer or a well? Wells are slotted throughout their length and measure groundwater level. Piezometers are only perforated for some specific interval (less than its entire length) and measure hydraulic head at that specific depth (which may differ quite a bit from the water table). Answer: Yes thanks for noticing it. We have indicated throughout the manuscript as well as in Figure 1 that we installed wells.

L152-153: I feel more information on the tree transpiration / sap flow measurements is needed. I realize they were taken from the Nadal-Sala et al. (2013) study; however, it seems pretty central to the present paper and the reader should not have to go to another source for so crucial a measurement technique. Answer: Following the reviewer suggestion, we do now provide more information regarding sap flow measurements (lines 167-173). Please, see our responses to the editor, who also highlighted this issue.

L250-251: Figure 2c refutes this statement. There appear to be at least a few days around January / February, 2012 with Qgw < 0 *in the valley reach.* **Answer:** The reviewer is totally right; thanks for noticing. During the dormant period, days with Qgw < 0 occurred during 6 days (< 3% of the time) at the valley reach. We have changed results and Table 2 accordingly (lines 282-283).

L334: Change "suite" to "suit." Answer: OK (line 375).

L366: Change "stronly" to "strongly." Answer: OK (line 415).

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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 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

- 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} (ρ = 0.60) and negatively correlated with net riparian groundwater inputs (ρ < -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 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
- 25 **Keywords.** Stream hydrological retention, riparian evapotranspiration, net groundwater inputs, instream nitrification, Mediterranean headwater catchment.

1. Introduction

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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 35 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 <u>diminish</u> inorganic N critically relyrelies on the hydrological connectivity between upland, riparian, and stream ecosystems because it directly 40 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 large residence times and the contact of groundwater with shallow riparian soils (Ranalli and Macalady, 2010; Vidon and Hill, 2004). However, little is known about the efficiency 45 of riparian zones to reduce 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 50 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).

55 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 <u>attributed to N uptake at the stream-riparian edge</u> (Bernal and Sabater, 2012; Dent et al., 2007; Rassam et al., 2006). Yet, there has been little <u>evidence of research focused on</u> 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 forest and a 70 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 75 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 be of paramount importance have implications for water resource management, as well as for anticipating 80 how riparian zones and stream water chemistry¹ 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 (41°50'N, 2°30'E). The climate is subhumid Mediterranean, with mild winters, wet springs, and dry summers. Annual precipitation is 925 ± 151 mm,-<u>with < 1% of annual precipitation falling as snow</u>. Mean annual temperature averages 12.1 ± 2.5 °C (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 km² and its altitude ranges from 500 to 1500 m above the sea level (a.s.l.) 90 (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 °C. 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 –($BA = \pi$ * (DBH / 2)², with DBH being the tree diameter at breast height) increases from 118 to 22776 m² ha⁻¹ by 12-fold along the catchment. 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 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 headwater and valley reach) (Figure 1). The headwater reach (750-550 m a.s.l.) was 1760 m long and drained 6.74 km² (Table 1). The reach was flanked by a 5-15 m wide riparian forest that covered ~5% of the drainage area. A. glutinosa, F. excelsior, and P. nigra represented 51%, 26%, and 23% of 105 the total basal area, respectively. The valley reach (550-500 m a.s.l.) was 1160 m long and drained an additional area of 4.42 km² (i.e., total catchment area at this reach was 11.16 km²). The reach was flanked by a 10-25 m wide riparian forest that covered $\sim 10\%$ of the drainage area. A. glutinosa, F. excelsior, P. nigra, and R. pseudoacacia represented 53%, 27%, 11%, and 9% of the total basal area, 110 respectively. The two stream reaches showed well-preserved channel morphology, with a riffle-run structure and $\frac{1}{1}$ struc (~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. In the two reaches, 115 riparian groundwater (< 1.5 m from the stream channel) flowed well below the soil surface (0.5 ± 0.1 m; averaged from 14 wells, 7 by reach, n = 82) (Bernal et al. 2015).

3. Materials and methods

3.1. Field sampling and chemical water analysis

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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 at breast height (DBH, in cm) and its basal area (BA, in ^{cm2}) with BA = $\Pi * (DBH / 2)^2 DBH$ (in cm) and its *BA* (in cm²). For each tree species *i*, we calculated the area-specific *BA* (*BA*_{*i*}, in m² 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 (0.23 km²) or valley (0.21 km²) 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: R² > 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 \emptyset) 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. 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 (< 4°C) until laboratory analysis (< 24 h after collection). Water samples were analyzed for dissolved inorganic N (DIN; NO₃⁻ and NH₄⁺) and chloride (Cl⁻), which was used as hydrological tracer (Kirchner et al., 2001). Cl⁻ was analyzed by ionic chromatography (Compact IC-761, Methrom). NO₃⁻ was analyzed by the cadmium reduction method (Keeney and Nelson, 1982) using a Technicon Autoanalyzer (Technicon, 1976). NH₄⁺ was manually analyzed by the salicilate-nitropruside method (Baethgen and Alley, 1989) using a spectrophotometer (PharmaSpec UV-1700 SHIMADZU).

3.2. Riparian evapotranspiration

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From September 2010 to August 2012, we calculated diel variations in stream discharge at the up-, mid-, and down-stream sites (Q_{lost} , in m³ 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 m³ 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.

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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 dm³ of water per m² 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 $(T_{rip}, \text{ in } \text{m}^3 \text{ m}^{-1} \text{ d}^{-1})$ with:

$$T_{rip} = \left(\sum_{i=1}^{n} T_i \times BA_i\right) / \mathbf{x} \tag{1}$$

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where T_i is monthly mean daily transpiration (in dm³ of water per m² of *BA* and day) and *BA_i* is the area-specific basal area (in m² 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:

$$Q_{gw} = Q_{bot} - Q_{top} - Q_{trib}$$
⁽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 190 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 < 100195 0.001; Figure S2). 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).

200 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 205 site with the following mass balance:

$$Q_{bot} \times C_{bot} = Q_{top} \times C_{top} + Q_{gw} \times C_{gw} + Q_{trib} \times C_{trib}$$
(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 210 model (logarithmic model) between solute concentration measured at each tributary and at the upstream 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 S2). 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 215 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 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).

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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⁻). When the stream was gaining water in net terms (Qgw > 0), values of Obs:Pred \neq 1 were interpreted 230 as an indication of differences in riparian groundwater chemistry between the headwater and valley reach. For $Q_{gw} > 0$ (net gaining stream), Obs:Pred $\neq 1$ was interpreted as differences in riparian groundwater nutrient concentration 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 predicted concentrations differed significantly from each other (±1.05, ±1.07, and ± 1.1 for Cl⁻, NO₃⁻, and NH₄⁺ concentrations, respectively).

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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



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

255 **4. Results**

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

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During the study period, median annual Q was 15.9, 53.9, and 62.4 L s⁻¹ at the up-, mid-, and downstream 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).

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 m³ 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. 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 m³ m⁻¹ d⁻¹) and T_{rip} (0.31 vs. 0.49 m³ m⁻¹ d⁻¹). There was a strong and positive relationship between T_{rip} and ΔQ_{lost} for both the headwater and valley reach (Figure 3a).

275 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

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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: $\rho = -0.57$, 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 headwater reach (15% of the time). There were no days with $Q_{gw} < 0$ during the dormant period at any of the two reaches. – 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.

290 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

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 NO₃⁻ concentration was observed at the up-steam site and the lowest at the mid-stream site (Table 3).
Stream NO₃⁻ 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. The three sites showed higher stream NH₄⁺ concentration during the vegetative than during the dormant period (Table 3).

305 4.4. Comparison between observed and predicted stream solute concentrations at the downstream 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 NO₃, Obs:Pred ratios were close to 1 during the dormant period, while increased up

to 1.95 during the vegetative period (Figure 4b). For NH₄⁺, Obs:Pred ratios were higher during the 310 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 NO₃, and positive for NH₄⁺ (Figure 5). For NO₃, Obs:Pred ratios were significantly higher for $Q_{gw} <$ 0 than for $Q_{gw} > 0$, while the opposite pattern was observed for NH₄⁺ (for the two solutes: Wilcoxon test, $Z > Z_{0.05}$, p < 0.01).

5. Discussion

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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 320 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 325 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) 330 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).

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In concordance to our expectations, the influence of riparian ET on stream hydrology varied along 350 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 waterlimited systems (Lundquist and Cayan, 2002). Stream hydrological retention occurred mostly at the 355 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 360 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.

365 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

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> 1). This result suggests NO₃⁻ release within the stream channel, which conflicts with previous studies reporting NO₃⁻ uptake at the stream-riparian edge in net losing reaches (Bernal and Sabater, 2012; Duval and Hill, 2007; Rassam et al., 2006). Biological NO₃⁻ 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 NO₃⁻ uptake during periods of stream hydrological retention (Burt et al., 2002; Hefting et al., 2004).

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Furthermore, in-stream NO₃⁻ release was accompanied by NH₄⁺ uptake (Obs:Pred < 1), suggesting that in-stream nitrification prevailed at the valley reach. Previous studies have reported sustained instream nitrification in well-oxygenated, slow water flowing, hyporheic zones (Dent et al., 2007; 380 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 suite at Font del Regàs because the valley reach had inputs of N-rich leaf litter (Bernal et al., 2015) and a well-oxygenated hyporheic zone (~7 mg O₂ 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 385 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 hydrological mixing with unaccounted water sources, such as deep groundwater (Clément et al., 2003) or riparian N-rich soils (Hill, 2011). However, these two 390 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 occurring at the stream-riparian edge, especially during periods of high hydrological retention.

395 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 NO₃⁻ and NH₄⁺. 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 NO₃, this pattern could be explained by 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-400

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 \pm 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).

The influence of in-stream N cycling on N export ultimately depends on water fluxes and the 405 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 NO₃⁻ concentration at the valley reach was counterbalanced by the loss of water from the stream towards the riparian zone induced by riparian ET. Otherwise, NO₃⁻ export to downstream ecosystems would have been 15% 410 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 NO₃⁻ = 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 -during some time-windows of the year, despite it may have small implications for N fluxes at annual scale. 415

6. Conclusions

- Our study adds to the growing evidence demonstrating that riparian ET is a key process for 420 understanding temporal patterns of stream discharge and hydrological processes at the streamriparian 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 425 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 strongly regulate the spatio-temporal pattern of stream water fluxes in Mediterranean regions and 430
 - 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.

Acknowledgments

We are thankful to Ada Pastor and Lídia Cañas for their invaluable assistance in the field, and to Dani Nadal for providing data on riparian tree evapotranspiration. Financial supported was provided by the Spanish Government through the projects MONTES-Consolider (CSD2008-00040MONTES), MEDFORESTREAM (CGL2011-30590), and MEDSOUL (CGL2014-59977-C3-2). AL was supported by a FPU PhD fellowship from the Spanish Ministry of Education and Science (AP-2009-3711) and the MEDSOUL project. SB work was funded by the Spanish Research Council (JAE-DOC027), the Spanish CICT (Juan de la Cierva contract JCI-2008-177), European Social Funds (FSE), and the NICUS (CGL-2014-55234-JIN) project. SP was supported by a FPI PhD fellowship from the Spanish Ministry of Education by a FPI PhD fellowship form the Spanish Ministry of Science (AP-2009-3711) and the NICUS (CGL-2014-55234-JIN) project. SP was supported by a FPI PhD fellowship from the Spanish Ministry of Economy and Competitiveness (BES-2012-054572). We also thank site cooperators, including Vichy Catalan and the Catalan Water Agency (ACA) for permission to sample at the Font del Regàs catchment.

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Tables

Table 1. Reach length, catchment drainage area, percentage of riparian area, width of the615riparian 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	

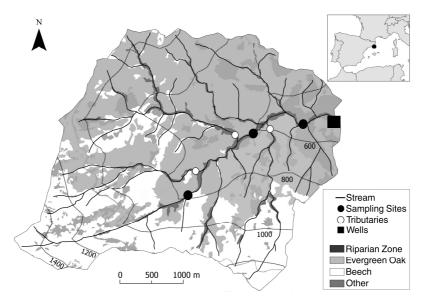
Table 2. Net groundwater inputs to stream discharge (Q_{gw}), number of days with stream hydrological retention ($Q_{gw} < 0$) and groundwater depth (h_{gw}) for the vegetative and dormant period, respectively. The number of cases is shown in parentheses for each group. For each variable, the asterisk 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 \pm 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)	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).

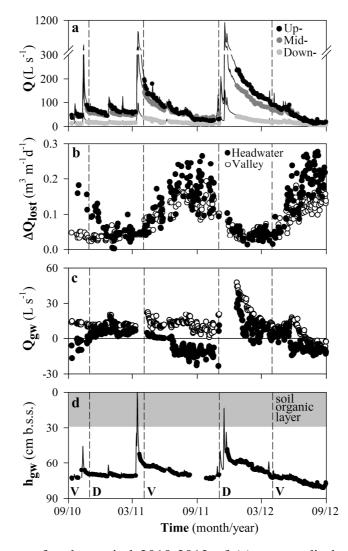
		Vegetative	Dormant
Cl ⁻ (mg L ⁻¹)	Up-stream site	6.1 [5.7, 6.5] (281)	6.0 [5.8, 6.2] (176)
	Mid-stream site	8.0 [7.7, 8.4] (333)	7.4 [7.2, 8.6] (220)*
	Down-stream site	8.3 [7.9, 8.8] (302)	7.7 [7.5, 7.8] (184)*
NO ₃ ⁻ (µg N L ⁻¹)	Up-stream site	238 [216, 247] (284)	238 [212, 298] (202)*
	Mid-stream site	149 [141, 164] (324)	166[152, 190] (234)*
	Down-stream site	166 [156, 180] (300)	168 [150, 186] (184)
NH4 ⁺ (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



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Figure 1. Map of the Font del Regàs catchment (Montseny Natural Park, NE Spain). The 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.



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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: 645 dormant period.

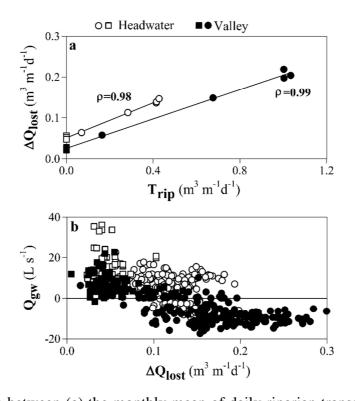


Figure 3. Relationship between (a) the monthly mean of daily riparian transpiration estimated from sap-flow data (T_{rip}) and riparian evapotranspiration estimated as the difference in diel discharge variation between the top and the bottom of each stream reach (ΔQ_{lost}), and (b) ΔQ_{lost} and daily 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.

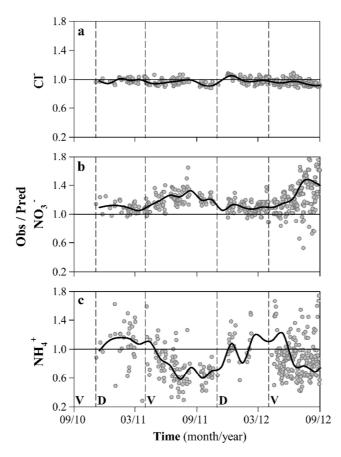


Figure 4. Temporal pattern of the ratio between observed stream solute concentrations at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (c) ammonium during the period 2010-2012. Bold lines indicate the running median (the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

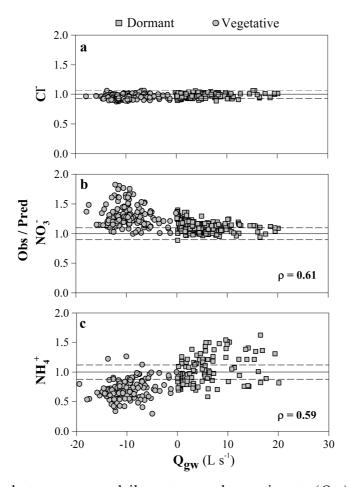


Figure 5. Relationship between mean daily net groundwater inputs (Q_{gw}) and the ratio between stream concentrations observed at the bottom of the valley reach (down-stream site) and those predicted from hydrological mixing for (a) chloride, (b) nitrate and (b) ammonium. Data is shown separately for 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.

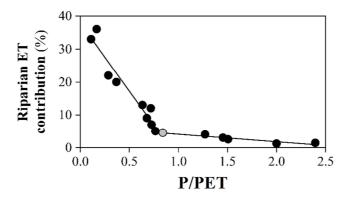


Figure 6. Relationship between the relative contribution of riparian evapotranspiration (ET) to annual catchment water depletion and the ratio between annual precipitation and potential evapotranspiration (P/PET) for a set of catchments worldwide (n = 15). Total water output fluxes
from the catchment 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 (Table S2).

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

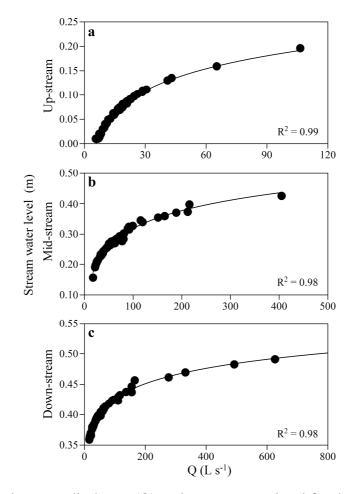
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Figure S1. Regressions between discharge (Q) and stream water level for the (a) up-stream, (b) midstream and (c) down-stream sites during the period 2010-2012. Circles are data from slug additions and lines are the regression models. The R^2 values 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 discharge at 15 min intervals.

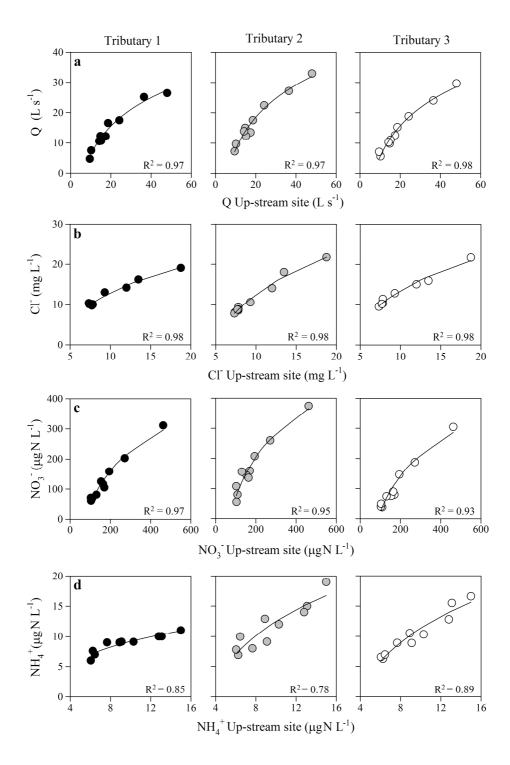


Figure S2. Relationship between values measured at the three main tributaries of the main steam and those measured at the up-stream site for (a) discharge and concentrations of (b) chloride, (c) nitrate, and (d) ammonium. Data was collected on the same day for a set of 11 synoptic field campaigns during 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.

Table S1. Measured and predicted concentrations of riparian groundwater concentrations for chloride (Cl⁻), nitrate (NO₃⁻) and ammonium (NH₄⁺) 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 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⁻, NO₃⁻, and NH₄⁺, 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 difference significantly from each other.

	$\operatorname{Cl}^{-}(\operatorname{mg} \operatorname{L}^{-1})$			$NO_{3}^{-}(\mu g N L^{-1})$			$NH_4^+ (\mu g N L^{-1})$		
Day	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

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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