



## Abstract

Headwater streams have a strong capacity to transform and retain nutrients, and thus, a longitudinal decrease in stream nutrient concentrations would be expected from in-stream nutrient removal alone. Yet, a number of other factors within the catchment, including biogeochemical processing within the riparian zone and export to streams, can contribute to stream nutrient concentration, which may overcome the effect of in-stream biogeochemical processing. To explore this idea, we analyzed the longitudinal patterns of stream and riparian groundwater concentrations for chloride ( $\text{Cl}^-$ ), nitrate ( $\text{NO}_3^-$ ), ammonium ( $\text{NH}_4^+$ ), and phosphate ( $\text{PO}_4^{3-}$ ) along a 3.7 km reach at an annual scale. The reach showed a gradual increase in stream and riparian width, riparian tree basal area, and abundance of riparian  $\text{N}_2$ -fixing tree species. Concentrations of  $\text{Cl}^-$  indicated a strong hydrological connection at the riparian-stream edge. However, stream and riparian groundwater nutrient concentrations showed a moderate to null correlation, suggesting high biogeochemical processing at the riparian-stream edge and within the stream. A mass balance approach along the reach indicated that, on average, in-stream net nutrient uptake prevailed over release for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , but not for  $\text{NO}_3^-$ . On an annual basis, in-stream processes contributed to change stream input fluxes by 11 %, 26 %, and 29 % for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ , respectively. Yet, longitudinal trends in concentration were not consistent with the prevailing in-stream biogeochemical processes. During the riparian dormant period, stream concentration decreased along the reach for  $\text{NO}_3^-$ , but increased for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ . During the riparian vegetative period,  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  increased along the reach while  $\text{NH}_4^+$  showed no clear pattern. These longitudinal trends were partially related to riparian forest features and groundwater inputs, especially for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ . Our study suggests that even though in-stream biogeochemical processing was substantial, the riparian zone can modulate the longitudinal variation in stream nutrient chemistry in this headwater stream.

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## 1 Introduction

Stream water chemistry integrates hydrological and biogeochemical processes occurring within its drainage area, and thus, the temporal variation of stream solute concentrations at the catchment outlet is considered a good indicator of the response of terrestrial and aquatic ecosystems to environmental drivers (Bormann and Likens, 1967; Bernhardt et al., 2003; Houlton et al., 2003). Less attention has been paid to the spatial variation of water chemistry along the stream, though it can be considerable important because stream nutrient concentrations are influenced by changes in hydrological flow paths, vegetation cover, and soil characteristics as catchment size increases (Dent and Grimm, 1999; Likens and Buso, 2006). For instance, spatial variation in nutrient concentration along the stream has been attributed to changes in soil nitrification rates (Bohlen et al., 2001), soil organic carbon availability (Johnson et al., 2000), and organic soil depth across altitudinal gradients (Lawrence et al., 2000). Moreover, nutrient cycling within the riparian zone can strongly influence stream nutrient concentrations along the stream not only because these ecosystems are hot spots of biogeochemical processing (McClain et al., 2003; Vidon et al., 2010), but also because processes occurring in near stream areas have a major influence on stream water chemistry than those occurring in faraway locations (Ross et al., 2012). Finally, biogeochemical processes within the stream and at the riparian-stream edge can also influence stream nutrient chemistry along the stream (Peterson et al., 2001; Dent et al., 2007).

Our understanding of nutrient biogeochemistry within riparian zones and streams is mainly based on field studies performed at the plot scale and at small stream reaches of few hundreds meters. These empirical studies have widely demonstrated the potential of riparian and stream ecosystems as sinks or sources of nutrients (Peterson et al., 2001; Sabater et al., 2003; Mayer et al., 2007). Riparian and stream biota are capable to decrease the concentration of essential nutrients, such as dissolved inorganic nitrogen and phosphate, either in groundwater or in the stream water column, especially with increasing water storage and residence time (Valett et al., 1996; Hedin

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et al., 1998; Peterson et al., 2001; Vidon and Hill, 2004). Conversely, some riparian forests can become sources rather than sinks of nutrients when  $N_2$ -fixing species predominate (Helfield and Naiman, 2002; Compton et al., 2003). Moreover, there is an intimate hydrological link between riparian and stream ecosystems that can result in strong biogeochemical feedbacks between these two compartments as frequently described in the scientific literature (e.g., Morrice et al., 1997; Martí et al., 2000; Bernal and Sabater, 2012). However, studies integrating biogeochemical processes at these two nearby ecosystems are rare (but see Dent et al., 2007).

Despite the impressive body of knowledge showing the potential of riparian zones and stream ecosystems to modify either groundwater or stream nutrient concentrations, our ability to upscale those reach- and plot-scale measurements is limited because hydrological and biogeochemical processes can vary substantially along the stream (Covino and McGlynn, 2007; Jencso et al., 2010). The assessment of the spatial variation in nutrient concentration along the stream can be useful to overcome this limitation and contribute to our understanding of controls on stream nutrient chemistry and ecosystem-level processes (Dent and Grimm, 1999; Lawrence et al., 2000). We propose that the influence of riparian and in-stream biogeochemical processes on stream nutrient chemistry could be inferred from the longitudinal variation of stream nutrient concentrations and fluxes along natural gradients with an increasing presence of these ecosystems (for instance, from headwaters to the valley bottom). Physiographic features such as riparian and stream size can change markedly across relatively short distances in headwater streams compared to lowland streams (Uehlinger, 2000), which makes headwater catchments good model systems for investigating drivers of longitudinal patterns in stream nutrient concentration and their temporal variation.

The goal of this study was to gain a more comprehensive view of the influence of biogeochemical processes at the riparian–stream interface (including the riparian zone, the riparian-stream edge, and the stream channel) on stream nutrient chemistry and fluxes in a headwater forested catchment. To this end, we explored the longitudinal variation of riparian groundwater nutrient inputs (nitrate, ammonium, and phosphate)

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to the stream as well as in-stream net nutrient uptake along a 3.7 km reach. The upper most site of the reach drained hillslope forests and it had almost no riparian trees while the stream was wider and sandier, and it was flanked by a well-developed riparian forest at the downier most site. We sampled during both, the dormant and vegetative period to investigate if the longitudinal pattern of stream water chemistry was influenced by the seasonality of biological processes. We expected a decrease in nutrient concentrations along the stream reach, and a subsequent decrease in area-specific nutrient fluxes, if nutrient retention at the riparian-stream interface increases from headwaters to the valley bottom. Alternatively, an increasing trend in stream nutrient concentrations and fluxes would indicate a limited ability of this riparian-stream interface to reduce nutrient inputs from adjacent terrestrial ecosystems.

## 2 Study site

The research was conducted in the Font del Regàs catchment (14.2 km<sup>2</sup>), located in the Montseny Natural Park, NE Spain (41°50' N, 2°30' E, 300–1200 m a.s.l.) during the period 2010–2011 (Fig. 1). Total inorganic N deposition in this area oscillates between 15–30 kg N ha<sup>-1</sup> year<sup>-1</sup> (Àvila and Rodà 2012). The climate at the Montseny Mountains is subhumid Mediterranean. The long-term mean annual precipitation is 925 ± 151 mm and the long-term mean annual air temperature is 12.1 ± 2.5 °C (mean ± SD, period: 1940–2000, Catalan Metereologic Service: <http://www.meteo.cat/servmet/index.html>). During the study period, mean annual precipitation (975 mm) and temperature (12.9 °C) fall well within the long-term average (data from a meteorological station within the study catchment).

The catchment is dominated by biotitic granite (ICC, 2010) and it has steep slopes (28 %). Evergreen oak (*Quercus ilex*) and beech (*Fagus sylvatica*) forests cover 54 % and 38 % of the catchment area, respectively (Fig. 1). The upper part of the catchment (2 %) is covered by heathlands and grasslands (ICC, 2010). Hillslope soils (pH ~ 6) are

sandy, with high content of rocks (33–36%). Soils at the hillslopes have a 3 cm depth O-horizon and a 5 to 15 cm depth A-horizon (averaged from 10 soil profiles).

The riparian zone covers 6% of the catchment area and on average the slope is < 10%. Riparian soils (pH ~ 7) are sandy-loam with low rock content (13%) and a 5 cm depth organic layer followed by a 30 cm depth A-horizon (averaged from 5 soil profiles). Along the 3.7 km stream reach, the width of the riparian zone increases from 6 to 32 m, and the total basal area of riparian trees increases by 12-folds (based on forest inventories of 30 m plots every ca. 150 m) (Fig. 2a). *Alnus glutinosa*, *Robinia pseudoacacia*, *Platanus hybrida*, and *Fraxinus excelsior* are the most abundant riparian tree species followed by *Corylus avellana*, *Populus tremula*, *P. nigra*, and *Sambucus nigra*. The abundance of N<sub>2</sub>-fixing species (*A. glutinosa* and *R. pseudoacacia*) increases along the longitudinal profile, representing 0% and > 60% of the total basal area of riparian trees at the top and at the bottom of the longitudinal profile, respectively (Fig. 2a). During base flow conditions, riparian groundwater (< 1.5 m from the stream channel) flows well below the soil surface (0.5 ± 0.1 m) and thus, the interaction with the riparian organic soil is minimal (averaged from 15 piezometers, *n* = 165) (Fig. 2b). During the period of study, riparian groundwater temperature ranged from 5.3 °C to 19.5 °C.

The geomorphology of the stream bed changes along the 3.7 km stream reach. Along the first km of the longitudinal profile, the stream bed is mainly composed by rocks and cobbles (70%) with a small contribution of sand (~ 10%), whereas at the valley bottom sands and gravels represent 44% of the stream substrate and the presence of rocks is minor (14%). Moreover, the wet width of the stream channel increases from 1.5 to 3 m along the reach (Fig. 2c). During the study period, stream water temperature ranged from 5 to 17.7 °C.

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### 3 Materials and methods

#### 3.1 Field sampling and laboratory analysis

We selected 15 sampling sites along the 3.7 km study reach. The distance between consecutive sampling sites ranged from 110 to 600 m (Fig. 1). At each sampling site, we installed a 1 m long PVC piezometer (3 cm Ø) in the riparian zone at ~ 1.5 m from the stream channel.

We sampled stream water and riparian groundwater from each sampling site every 2 months from August 2010 to December 2011. We used pre-acid washed polyethylene bottles to collect water samples after triple-rinsing them with either stream or groundwater. On each sampling date, we also measured dissolved O<sub>2</sub> concentration (DO, in mg L<sup>-1</sup>) and water temperature (*T*, in °C) with an YSI ProODO device in both, stream water and in riparian groundwater. We avoid sampling soon after storms to ensure that our measurements were representative of base flow conditions, when the influence of biogeochemical processes at the riparian-stream interface on stream nutrient concentrations and fluxes is expected to be the highest. On each sampling date and at each sampling site, we measured groundwater table elevation (in m below soil surface) with a water level sensor (Eijkelkamp 11.03.30) as well as wet width (in m), stream discharge (*Q*, in L s<sup>-1</sup>), and water velocity (m s<sup>-1</sup>). *Q* and water velocity were estimated with the slug-addition technique by adding 1 L of NaCl-enriched solution to the stream (electrical conductivity = 75–90 mS cm<sup>-1</sup>, *n* = 11) (Gordon et al., 2004).

On each sampling date, we also collect stream water and measured *Q* at the four main tributaries discharging to the Font del Regàs stream (Fig. 1). These data was used for mass balance calculations (see below).

Water samples were filtered through pre-ashed GF/F filters (Whatman®), and kept cold (< 4 °C) until laboratory analysis (< 24 h after collection). Chloride (Cl<sup>-</sup>) was used as a conservative hydrological tracer and analyzed by ionic chromatography (Compact IC-761, Methrom). Nitrate (NO<sub>3</sub><sup>-</sup>) was analyzed by the cadmium reduction method

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(Keeney and Nelson, 1982) using a Technicon Autoanalyzer (Technicon, 1976). Ammonium ( $\text{NH}_4^+$ ) was manually analyzed by the salicylate-nitroprusside method (Baethgen and Alley, 1989) using a spectrophotometer (PharmaSpec UV-1700 SHIMADZU). Phosphate ( $\text{PO}_4^{3-}$ ) was manually analyzed by the acidic molybdate method (Murphy and Riley, 1962) using a spectrophotometer (PharmaSpec UV-1700 SHIMADZU).

## 3.2 Data analysis

The seasonality of biological activity at the riparian-stream interface can strongly affect both, groundwater nutrient concentrations and in-stream biogeochemical processes (Groffman et al., 1992; Hill et al., 2001). Therefore, the data set was separated in two groups based on sampling dates during the vegetative and dormant season (7 and 4 sampling dates, respectively). We considered the vegetative period of the riparian forest starting at the beginning of leave out (April) and ending at the peak of leave-litter fall (October), coinciding with the onset and offset of riparian tree evapotranspiration respectively (Nadal-Sala et al., 2013).

### 3.2.1 Longitudinal patterns in stream discharge, groundwater inputs, and solute concentrations and fluxes

We examined the longitudinal pattern of stream discharge, groundwater inputs, and stream solute concentrations and fluxes along the reach for each season. On each sampling date, the contribution of groundwater inputs to surface water along the reach ( $Q_{\text{gw}}$ ) was estimated as the difference in  $Q$  between 2 consecutive sampling sites (Covino et al., 2010). We calculated the instantaneous area-specific stream discharge ( $Q_{\text{spf}}$ , in  $\text{L km}^{-2} \text{s}^{-1}$ ) at each sampling site. We used  $Q_{\text{spf}}$  rather than  $Q$  in order to compare water and solute fluxes from the 15 nested catchments considered along the 3.7 km stream reach. The instantaneous area-specific solute fluxes ( $F_{\text{spf}}$ , in  $\text{mg km}^{-2} \text{s}^{-1}$ ) were calculated by multiplying  $Q_{\text{spf}}$  by stream solute concentration ( $C_{\text{sw}}$ ) at each sampling site.

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We examined the longitudinal pattern of  $Q_{\text{gw}}$ ,  $Q_{\text{spf}}$ ,  $F_{\text{spf}}$ , and  $C_{\text{sw}}$  by applying simple linear regression models. Moreover, we evaluated the degree of variability of stream water chemistry along the reach by calculating the coefficient of variation (CV) of stream solute concentrations for both, sampling sites on the same sampling date and sampling dates for each sampling site. Furthermore, we applied generalized linear models (glm) to investigate whether the longitudinal pattern of  $C_{\text{sw}}$  for each nutrient was associated to changes in stream geomorphology, riparian groundwater, and riparian forest features. For each nutrient and period, the dependent variable was the mean value obtained from all sampling dates for each sampling site along the reach. The predictor variables were distance to the upper most site ( $D$ ), riparian groundwater concentration for the same nutrient (RC), as well as a suite of variables related to riparian forest features and stream geomorphology. Total basal area of riparian trees (BA) and riparian width (RW) were included as proxies of the riparian forest size. The relative contribution of the basal area of  $\text{N}_2$ -fixing species to BA (NBA) was included as a proxy of species composition. Stream wet width (SW), water velocity ( $V$ ), and the percentage of sands in stream bed ( $S$ ) were included as a proxy of stream geomorphology and the size of the hyporheic zone (a major pool of heterotrophic activity) (Jones and Holmes, 1996).

For a given nutrient, we expected  $D$  to be the only significant predictor variable if the longitudinal pattern of  $C_{\text{sw}}$  is not related to any of the riparian and stream predictors included in the model. We first performed a stepwise model selection based on Akaike's Information Criteria (AIC) to select the simplest model minimizing the loss of information (min AIC) (Burnham and Anderson, 2001). For each dependent variable, we retained all models that were close to the best available model, that is those models with an  $\Delta_i < 4$ , being  $\Delta_i = \text{AIC}_i - \text{minAIC}$  (Burnham and Anderson, 2002). For each nutrient and period, we calculated the relative likelihood ( $L_i$ ) for each retained model to assess which of them was the most likely (i.e., the one that maximizes the likelihood) (Burnham and Anderson, 2002). Moreover,  $L_i$  values were normalized to obtain

the Akaike weights ( $w_i = L_i / \sum_{r=1}^r L_r$ ), which can be interpreted as the probability that a model is the best model given the available data and the set of candidate models (Burnham and Anderson, 2001). Finally, we used analysis of variance tests (ANOVA) to calculate the goodness of fit of each retained model and to compare it against the best available model (Zar, 2010).

### 3.2.2 Sources of variation of stream nutrient concentration along the reach

We investigated whether the observed longitudinal patterns were driven either by riparian groundwater inputs, in-stream biogeochemical processing, or a combination of both. First, we explored the possibility that changes in stream nutrient concentration along the reach were related to the longitudinal variation of nutrient concentration in riparian groundwater. For each period, we analyzed whether nutrient concentrations differed between stream water and riparian groundwater by using a Wilcoxon paired sum rank test (Zar, 2010). Because redox conditions can strongly control biogeochemical processes, we calculated an empirical chemical index (CI) as a proxy of redox conditions and we compared CI values between stream water and riparian groundwater. The CI is the logarithm of the ratio between DO and  $\text{N-NH}_4^+$  concentration and thus, it shows lower values under low DO concentration than under fully aerobic conditions (Vázquez et al., 2011).

Moreover, we examined the degree of hydrological interaction at the riparian-stream edge by exploring the relationship between  $\text{Cl}^-$  concentrations measured at riparian groundwater and stream water with a Spearman correlation. For each period, we quantified the difference between  $\text{Cl}^-$  concentrations in the two water bodies by calculating

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divergences from the 1 : 1 line with the relative root mean square error (RRMSE, in %):

$$\text{RRMSE} = \frac{\sqrt{\sum_{i=1}^n (C_{\text{sw}} - C_{\text{gw}})^2}}{n \cdot \overline{C_{\text{gw}}}} \cdot 100 \quad (1)$$

where  $C_{\text{sw}}$  and  $C_{\text{gw}}$  are stream and riparian groundwater solute concentrations, respectively,  $n$  is the total number of observations, and  $\overline{C_{\text{gw}}}$  is the average of  $C_{\text{gw}}$ . A strong correlation and a low RRMSE between stream and riparian groundwater  $\text{Cl}^-$  concentrations indicate a strong hydrological connection between the two water bodies. Similarly, we examined the correlation between riparian groundwater and stream nutrient concentrations during the study period. We expected weak correlations and high RRMSE values between nutrient concentrations measured at the two compartments if groundwater nutrients are cycled at the riparian-stream edge.

Second, we investigated the influence of in-stream biogeochemical processes on the longitudinal pattern of stream nutrient concentrations by applying a mass balance approach (Roberts and Mulholland, 2007). For each nutrient, we calculated changes in stream flux between consecutive sampling sites ( $F_{\text{sw}}$ , in  $\mu\text{g m}^{-1} \text{s}^{-1}$ ), being  $F_{\text{sw}}$  the net flux resulting from in-stream uptake and release processes along a particular stream segment (von Schiller et al., 2011). We referred  $F_{\text{sw}}$  by unit of stream length in order to compare net changes in stream flux between consecutive segments differing in length. For each sampling date and for each nutrient,  $F_{\text{sw}}$  was approximated with:

$$F_{\text{sw}} = (F_{\text{top}} + F_{\text{ef}} + F_{\text{gw}} - F_{\text{bot}}) / X, \quad (2)$$

where  $F_{\text{top}}$  and  $F_{\text{bot}}$ , are the nutrient flux at the top and at the bottom of each stream segment,  $F_{\text{gw}}$  is the nutrient flux from groundwater inputs, and  $F_{\text{ef}}$  is the nutrient flux from effluent inputs for those reaches including a tributary (all in  $\mu\text{g s}^{-1}$ ).  $F_{\text{top}}$  and  $F_{\text{bot}}$  were calculated by multiplying  $Q$  by  $C_{\text{sw}}$  at the top and at the bottom of the segment,

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respectively.  $F_{\text{gw}}$  was estimated by multiplying groundwater inputs ( $Q_{\text{gw}}$ ) by nutrient concentration in riparian groundwater ( $C_{\text{gw}}$ ). For gaining segments ( $Q_{\text{gw}} > 0$ ),  $C_{\text{gw}}$  was the average between groundwater nutrient concentration at the top and bottom of the reach. For losing segments ( $Q_{\text{gw}} < 0$ ), we assumed that  $C_{\text{gw}}$  averaged  $C_{\text{top}}$  and  $C_{\text{bot}}$  of each segment. For those cases in which stream segments received water from a tributary,  $F_{\text{ef}}$  was calculated by multiplying  $Q$  and  $C$  at the outlet of the tributary. Finally,  $x$  (in m) is the length of the segment between two consecutive sampling sites. The same approach was applied for  $\text{Cl}^-$ , which we used as a hydrological reference because it is a conservative solute little affected by biogeochemical processes. For  $\text{Cl}^-$ , we expected  $F_{\text{sw}} \sim 0$  if upstream water and riparian groundwater inputs account for most of the stream  $\text{Cl}^-$  flux. For nutrients,  $F_{\text{sw}}$  can be positive (uptake > release), negative (uptake < release) or nil (uptake  $\sim$  release). Therefore, we expected  $F_{\text{sw}} \neq 0$  if in-stream uptake and release processes do not fully counterbalance each other (von Schiller et al., 2011).

To investigate whether stream segments were consistently acting as net sinks or net sources of nutrients, we calculated the frequency of  $F_{\text{sw}} > 0$  and  $F_{\text{sw}} < 0$  for each nutrient and for each segment during the period of study. For each nutrient, we considered  $F_{\text{sw}} \neq 0$  when the absolute value of  $F_{\text{sw}}$  was larger than its standard error (SE). Moreover, we evaluated the relevance of  $F_{\text{sw}}$  compared to input solute fluxes by calculating the ratio between  $F_{\text{sw}}$  (in absolute values) and the total input flux ( $F_{\text{in}}$ ) for each segment, solute, and sampling date.  $F_{\text{in}}$  was the sum of  $F_{\text{top}}$ ,  $F_{\text{ef}}$ , and  $F_{\text{gw}}$  (the latter was included only for gaining segments). We interpreted a high  $|F_{\text{sw}}/F_{\text{in}}|$  ratio as a strong potential of in-stream processes to modify groundwater and upstream inputs.

All statistical analyses were carried out with R packages (stats, MASS). We chose non-parametric tests for our statistical analysis because not all data sets had a normal distribution. In all cases, differences were considered significant if  $p < 0.01$ , unless stated differently.

## 4 Results

### 4.1 Hydrological characterization of the stream reach

During the study period, mean  $Q_{\text{spf}}$  decreased from  $9.8 \pm 1.6$  [mean  $\pm$  SE] to  $6.2 \pm 1.3 \text{ L km}^{-2} \text{ s}^{-1}$  from the top to the bottom of the reach (linear regression [ln.reg],  $r^2 = 0.79$ , degrees of freedom [df] = 14,  $F = 51.4$ ,  $p < 0.0001$ ) (Fig. 3a). There were no statistical differences in  $Q_{\text{spf}}$  between the dormant and vegetative period (Wilcoxon rank sum test,  $p > 0.05$ ), and both seasons showed a similar longitudinal pattern. In contrast to  $Q_{\text{spf}}$ , stream  $\text{Cl}^-$  concentrations showed a 40 % increase along the reach (ln.reg,  $r^2 = 0.88$ , df = 14,  $F = 44.6$ ,  $p < 0.0001$ ) (Fig. 3b). The two seasons showed a similar longitudinal pattern, though stream  $\text{Cl}^-$  concentrations were lower during the dormant than during the vegetative period (Wilcoxon rank sum test,  $Z = -6.4$ ,  $p < 0.0001$ ) (Table 1). During the period of study, the CV of  $\text{Cl}^-$  concentrations for a given sampling site ranged from 22.5 % to 39.6 %, though this variability did not follow a longitudinal pattern (ln.reg,  $p > 0.05$ ).

There was a strong correlation between stream and riparian groundwater  $\text{Cl}^-$  concentrations, and the relationship between them resulted in low RRMSE values for both, the dormant and vegetative periods (Fig. 4a and Table 2). On average, stream segments along the reach gained water from groundwater at a rate of  $0.34 \pm 0.2 \text{ L km}^{-2} \text{ s}^{-1}$ , which represented ca. 5 % of mean  $Q_{\text{spf}}$  (Fig. 3c). No stream segment was either consistently gaining or losing water over time. All the segments lost water towards the riparian zone at least on one occasion, and 3 of them lost water in  $> 60$  % of the sampling dates. Stream water loses towards the riparian zone ( $Q_{\text{gw}} < 0 \text{ L km}^{-2} \text{ s}^{-1}$ ) were detected during 39 % and 43 % of the cases during the dormant and vegetative period, respectively.

The mean net change in  $\text{Cl}^-$  flux within stream segments was  $0.1 \pm 0.04 \text{ mg m}^{-1} \text{ s}^{-1}$ , which was a small fraction of the total  $\text{Cl}^-$  input flux ( $|F_{\text{sw}}/F_{\text{in}}| < 10$  %). Thus, the mass

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balance approach indicated that the stream  $\text{Cl}^-$  flux was mainly explained by upstream water and riparian groundwater inputs, and that additional water sources were unlikely.

## 4.2 Variability of stream nutrient concentrations and fluxes along the reach

Stream nutrient concentrations varied over space (along the stream for the same sampling date) and over time (among sampling dates for a single sampling site). On a single date, the CV of stream nutrient concentrations along the reach averaged 27 %, 36 % and 51 % for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$  respectively, being this CV similar between the dormant and vegetative period (Wilcoxon rank sum test, for the three nutrients  $p > 0.05$ ). The CV of stream  $\text{NO}_3^-$  and  $\text{NH}_4^+$  concentrations did not show a longitudinal pattern (in the two cases,  $\ln.\text{reg}$ ,  $p > 0.05$ ), while it decreased along the reach for  $\text{PO}_4^{3-}$  ( $r^2 = 0.56$ ,  $df = 14$ ,  $F = 16.9$ ,  $p < 0.005$ ). For a given sampling site, the CV of stream nutrient concentration during the study period averaged 47 %, 41 %, and 53 % for  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{PO}_4^{3-}$ , respectively. Thus, the variability of stream  $\text{NO}_3^-$  concentrations was higher over time than over space, though differences in concentration between the dormant and vegetative period were not statistically significant (Wilcoxon rank sum test,  $p > 0.05$ ) (Table 1). In contrast, stream  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  concentrations were higher during the vegetative than during the dormant period (Wilcoxon rank sum test,  $Z_{\text{NH}_4} = -3.5$  and  $Z_{\text{PO}_4} = -6.6$ , for both nutrients  $p < 0.001$ ) (Table 1).

The longitudinal pattern of stream nutrient concentrations differed between seasons. During the dormant period, mean stream  $\text{NO}_3^-$  concentration decreased along the reach from  $285 \pm 30$  to  $222 \pm 33 \mu\text{g N-NO}_3^- \text{L}^{-1}$ , especially along the first km ( $\ln.\text{reg}$ ,  $r^2 = 0.47$ ,  $df = 15$ ,  $F = 11.4$ ,  $p < 0.005$ ) (Fig. 5a). According to the glm results, this decrease was positively related to the basal area of riparian trees (BA), and negatively related to both, water velocity ( $V$ ) and abundance of  $\text{N}_2$ -fixing species (NBA) (Table 3). During the vegetative period, mean stream  $\text{NO}_3^-$  concentrations increased by 60 % along the last km of the reach (from  $218 \pm 39$  to  $342 \pm 44 \mu\text{g N-NO}_3^- \text{L}^{-1}$ ) and thus, there was not a consistent linear longitudinal pattern (Fig. 5a). The best models explaining

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the variability of stream  $\text{NO}_3^-$  concentrations during the vegetative period included variables related to both, stream geomorphology ( $Q$  and  $WW$ ) and riparian features (NBA and BA) (Table 3).

During the dormant period, stream  $\text{NH}_4^+$  concentration increased from  $9 \pm 1$  to  $10 \pm 2 \mu\text{g N-NH}_4^+ \text{L}^{-1}$  along the reach (ln.reg,  $r^2 = 0.42$ ,  $df = 15$ ,  $F = 9.6$ ,  $p < 0.01$ ) (Fig. 5b). In contrast, no clear longitudinal pattern was observed for stream  $\text{NH}_4^+$  concentrations during the vegetative period (Fig. 5b). None of the predictors included in the glm accounted for the longitudinal variability of stream  $\text{NH}_4^+$  concentrations during either, the dormant or vegetative period (Table 3).

Stream  $\text{PO}_4^{3-}$  concentrations showed an increasing longitudinal trend during the two seasons (dormant: ln.reg,  $r^2 = 0.53$ ,  $F = 14.6$ ,  $df = 14$ ,  $p < 0.01$ ; vegetative: ln.reg,  $r^2 = 0.46$ ,  $F = 11.21$ ,  $df = 14$ ,  $p < 0.01$ ) (Fig. 5c). For the two seasons, this longitudinal pattern was partially explained by the concentration of  $\text{PO}_4^{3-}$  in riparian groundwater (RC) among other variables related to both, stream geomorphology and riparian features (Table 3).

Stream nutrient fluxes along the reach were strongly influenced by the longitudinal pattern of stream discharge, especially for  $\text{NO}_3^-$  and  $\text{NH}_4^+$  for which the area-specific flux ( $F_{\text{spf}}$ ) decreased along the reach during the two seasons (Fig. 5a and b). In contrast, the  $F_{\text{spf}}$  for  $\text{PO}_4^{3-}$  did not follow any clear longitudinal pattern during either, the dormant or vegetative period (Fig. 5c).

### 4.3 Sources of longitudinal variation in stream nutrient concentration: riparian groundwater inputs and in-stream nutrient processing

The relationship between stream and riparian groundwater concentrations differed between nutrients and seasons. During the dormant period, stream and riparian groundwater  $\text{NO}_3^-$  concentrations were similar, while mean stream  $\text{NO}_3^-$  was 30 % higher than in riparian groundwater during the vegetative period (Table 1). During the two seasons, stream and riparian groundwater  $\text{NO}_3^-$  concentrations were positively correlated and

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showed relatively small RRMSE (Fig. 4b and Table 2). On average, stream  $\text{NH}_4^+$  concentrations were 2.5 fold lower than in riparian groundwater (Table 1), and there was no correlation between them during either the dormant or vegetative period (Fig. 4c and Table 2). During the dormant period, stream and riparian groundwater  $\text{PO}_4^{3-}$  concentrations were similar and showed a significant correlation between them (Tables 1 and 2). During the vegetative period,  $\text{PO}_4^{3-}$  concentrations were 2-fold lower in the stream than in riparian groundwater (Table 1), they showed no correlation, and relatively high RRMSE (Fig. 4d and Table 2). These differences in nutrient concentrations between the two water bodies were accompanied by lower chemical index values in riparian groundwater than in stream water (Table 1).

The influence of in-stream biogeochemical processing on stream fluxes differed among nutrients. During the study period, mean  $F_{\text{sw}}$  was positive for  $\text{NH}_4^+$  ( $0.6 \pm 0.2 \mu\text{g N m}^{-1} \text{s}^{-1}$ ) and  $\text{PO}_4^{3-}$  ( $0.2 \pm 0.4 \mu\text{g P m}^{-1} \text{s}^{-1}$ ), indicating that on average the stream was acting as a net sink for these nutrients. In contrast, mean  $F_{\text{sw}}$  was negative for  $\text{NO}_3^-$  ( $-0.5 \pm 1 \mu\text{g N m}^{-1} \text{s}^{-1}$ ), indicating that in-stream  $\text{NO}_3^-$  release prevailed over uptake. The magnitude of  $F_{\text{sw}}$  showed no consistent longitudinal pattern for any nutrient for either the vegetative or dormant period (for the three nutrients,  $\ln.\text{reg}$ ,  $p > 0.05$ ).

The capacity of in-stream processes to change stream input fluxes was smaller for  $\text{NO}_3^-$  ( $|F_{\text{sw}}/F_{\text{in}}| = 11 \pm 1\%$ ) than for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ( $|F_{\text{sw}}/F_{\text{in}}| = 27 \pm 2\%$  and  $29.5 \pm 2\%$ , respectively). Yet, the frequency of sampling dates for which in-stream  $\text{NO}_3^-$  uptake and release did not counterbalance each other ( $F_{\text{sw}} \sim 0 \mu\text{g N m}^{-1} \text{s}^{-1}$ ) increase along the reach (Fig. 6a), especially during the vegetative period ( $\ln.\text{reg}$ ,  $r^2 = 0.71$ ,  $df = 13$ ,  $F = 28.8$ ,  $p < 0.001$ ). This longitudinal pattern was accompanied by an increase in the frequency of dates for which in-stream  $\text{NO}_3^-$  release prevailed over uptake ( $F_{\text{sw}} < 0 \mu\text{g N m}^{-1} \text{s}^{-1}$ ) ( $\ln.\text{reg}$ ,  $r^2 = 0.55$ ,  $df = 13$ ,  $F = 14.6$ ,  $p < 0.01$ ). For  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$ , the frequency of dates for which in-stream uptake or release predominated did not show any consistent longitudinal pattern (for the two nutrients,  $\ln.\text{reg}$ ,  $p > 0.05$  for both, the dormant and vegetative period) (Fig. 6b and c).

## 5 Discussion

The aim of this study was to gain understanding on the potential of biogeochemical processes at the riparian-stream interface (including the riparian zone, the riparian-stream edge, and the stream channel) to modify stream nutrient concentrations. To approach this objective, we adopted a longitudinal approach along a headwater forested stream to investigate whether biogeochemical processes at the riparian-stream interface were capable of controlling stream nutrient chemistry at the ecosystem level. We chose a 3.7 km stream reach that covered a 300 m elevation gradient within a headwater forested catchment showing remarkable changes in riparian characteristics compared to hillslope physiographic features, which remained fairly similar with increasing catchment size. One of the novelties of this study is that we analyzed longitudinal patterns of stream water together with changes in riparian groundwater to chase the influence of biogeochemical transformation at the riparian-stream edge on stream nutrient chemistry. Another keen aspect of the study is that we explored the influence of changes in riparian size and composition on stream nutrient concentration. Despite the inherent limitations of performing empirical studies at relatively large spatial scales, our results shed light on the spatial variation of biogeochemical processes at the riparian-stream interface from headwaters to the valley bottom, and further, on their potential to regulate stream nutrient chemistry at the ecosystem level.

We found that gradual increases in stream width (2-fold), riparian width (5-fold), riparian tree basal area (12-fold), and in the abundance of  $N_2$ -fixing riparian trees (from 0 to 60 % of the total basal area) along the reach were accompanied by changes in stream nutrient concentrations, which could vary from 27–51 % on a single date. Moreover, variability in nutrient concentrations was not random but followed gradual longitudinal patterns, though only during the dormant period for  $NO_3^-$  and  $NH_4^+$ . Longitudinal patterns in stream chemistry can result solely from hydrological mixing of different solute concentrations discharging from hillslopes, which is usually accompanied by a reduction in the variability of solute concentrations as catchment size increases (e.g., Asano

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longitudinal decrease in  $\text{NO}_3^-$  concentrations was mainly controlled by riparian groundwater inputs, as also reported for other headwater streams (Bernhardt et al., 2002; Asano et al., 2009; Scanlon et al., 2010).

During the vegetative period, stream  $\text{NO}_3^-$  concentration increased along the down-  
5 iest part of the reach where both, the basal area of riparian trees and the proportion of  $\text{N}_2$ -fixing species were the highest. Previous studies in temperate and boreal forests have pointed out that  $\text{N}_2$ -fixing species such *Alder sp.* can increase N availability in riparian ecosystems (Helfield and Naiman, 2002), or even control hydrological N export at the whole catchment scale (Compton et al., 2003). In Mediterranean regions,  
10 the invasive  $\text{N}_2$ -fixing *Acacia sp.* can have a dramatic impact on soil nutrient cycling, by increasing N availability and decreasing C:N ratios which accelerates both, N and P soil mineralization (Stock et al., 1995). The impact of this species on stream nutrient export can become larger when invasion occurs in near-stream areas because soil available nutrients can be quickly leached to the stream (Ross et al., 2012). Support-  
15 ing this hypothesis, Lupon et al. (2014) reported immediate increases in stream  $\text{NO}_3^-$  concentration at the downiest part of the catchment after periods of high nitrification in these riparian soils, which usually occur in spring and summer. However, we could not establish any positive relationship between the proportion of  $\text{N}_2$ -fixing tree species and stream  $\text{NO}_3^-$  concentrations along the reach. The simplest explanation for the in-  
20 crease in stream  $\text{NO}_3^-$  concentrations at the valley bottom was the prevalence of in-stream  $\text{NO}_3^-$  release during the vegetative period (64% of the sampling dates showed  $F_{\text{sw}} < 0 \mu\text{g N m}^{-1} \text{s}^{-1}$ ). This finding together with the significant decrease of dates with  $F_{\text{sw}} \sim 0 \mu\text{g N m}^{-1} \text{s}^{-1}$  (< 6%) suggest that in-stream nutrient cycling in general, and nitrification in particular, was enhanced at the valley bottom during the vegetative pe-  
25 riod likely because of warming-induced mineralization (Strauss and Lamberti, 2000; Bernhardt et al., 2002). Further studies would be needed for a better understanding of environmental controls favoring in-stream  $\text{NO}_3^-$  release at the valley bottom in this headwater stream.

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tions, this relationship was from moderate to weak for  $\text{NO}_3^-$  and  $\text{PO}_4^-$ , and nil for  $\text{NH}_4^+$ . Our findings support the well-established idea that biogeochemical processing at the riparian-stream edge and within the stream channel can be high enough to modify nutrient concentrations from riparian sources (McClain et al., 2003; Harms and Grimm, 2008).

This pattern was especially noticeable for streamwater  $\text{NH}_4^+$  that showed no correlation with  $\text{NH}_4^+$  concentration in riparian groundwater or with any of the available variables related to the riparian forest. Nitrogen transformations at the riparian-stream edge may be favored by the strong change in redox conditions between groundwater and stream water that were more reduced in the former than in the later, as typically reported in the literature (Hill et al., 1998; Dent et al., 2007). Concordantly,  $\text{NH}_4^+$  concentrations were higher in riparian groundwater than in the stream while the opposite occurred for  $\text{NO}_3^-$  (especially during the vegetative period). Our results suggest fast  $\text{NH}_4^+$  nitrification at the riparian-stream edge and within the stream as environmental conditions become well oxygenated (Jones et al., 1995). Supporting this idea, we found that in-stream uptake prevailed over release along the reach for  $\text{NH}_4^+$  (mean  $F_{\text{sw}} \sim 0.6 \mu\text{g N m}^{-1} \text{s}^{-1}$ ) while the opposite occurred for  $\text{NO}_3^-$  (mean  $F_{\text{sw}} \sim -0.5 \mu\text{g N m}^{-1} \text{s}^{-1}$ ).

Our results highlight that the contribution of in-stream biogeochemical cycling to change input stream fluxes was 2- to 3-folds higher for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  ( $|F_{\text{sw}}/F_{\text{in}}| = 26$  and 29 %, respectively) than for  $\text{NO}_3^-$  ( $|F_{\text{sw}}/F_{\text{in}}| = 11$  %). These results support previous evidence that the former nutrients are cycled more efficiently than the latter in headwater streams (Peterson et al., 2001; Ensign and Doyle, 2006) and thus, that the contribution of in-stream processes to regulate stream nutrient dynamics may be higher for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  than for  $\text{NO}_3^-$ . However, we found that longitudinal trends in stream nutrient concentration were not consistent with the predominant in-stream processes, likely because in-stream biogeochemical cycling did not systematically lead to net uptake or release along the reach for a given nutrient. Moreover, our generalized linear model approach indicated that the best candidate models matching  $\text{NO}_3^-$  and

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$\text{PO}_4^{3-}$  concentrations included variables not only related to stream geomorphology but also variables more directly related to the riparian zone such as riparian groundwater and total tree basal area (for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ ), riparian width (for  $\text{PO}_4^{3-}$ ), or the proportion of  $\text{N}_2$ -fixing species (for  $\text{NO}_3^-$ ). Similar to previous studies, our results suggest that groundwater inputs as well as riparian forest features are strong controls of stream water chemistry, and can override the effect of in-stream biogeochemical processing on the longitudinal variation of stream nutrient concentrations (Acuña and Dahm, 2007; Brookshire et al., 2009; Scanlon et al., 2010).

## 6 Conclusions

The longitudinal approach adopted at the Font del Regàs stream highlights that the potential for biogeochemical transformations at the riparian-stream edge and within the stream was high from the headwaters to the valley bottom. Our study indicates that stream nutrient concentrations along the reach did not mimic riparian groundwater inputs, but that dissolved nutrients underwent through profound biogeochemical transformation while travelling throughout the riparian-stream edge and along the stream channel, especially for  $\text{NH}_4^+$ , but also for  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$ . Our results support previous studies performed at smaller spatial scales showing that the influence of in-stream biogeochemical processing on stream nutrient concentrations is more important for  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  than for  $\text{NO}_3^-$  which shows a more conservative behavior. These results add to the growing evidence that in-stream biogeochemical processes may be taken into consideration in either empirical or modeling approaches in we are to understand drivers of stream nutrient chemistry within landscapes.

Although the influence of in-stream biogeochemical processes on stream nutrient fluxes was remarkable, longitudinal trends in stream nutrient concentration were not consistent with the predominant in-stream processes, likely because the latters did not systematically lead to net uptake or release along the reach for a given nutrient.

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Moreover, we found that groundwater inputs and riparian forest features were important drivers of the spatial variation of  $\text{NO}_3^-$  and  $\text{PO}_4^{3-}$  concentrations along the stream. Despite the capacity of in-stream processes to transform nutrients, our study shows that the influence of terrestrial sources on the longitudinal variation of stream nutrient concentrations can offset the effect of in-stream nutrient cycling on stream water chemistry.

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

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**Table 1.** Average  $\pm$  SE of stream and riparian groundwater solute concentrations and chemical index ( $CI = \ln[DO] / [NH_4]$ ) for both, the dormant and vegetative period. The number of cases is shown in parenthesis for each group. For each variable, the asterisk indicated statistically significant differences between the two water bodies (Wilcoxon paired rank sum test,  $p < 0.01$ ).

		Stream	Riparian groundwater
Dormant	$Cl^-$ ( $mg L^{-1}$ )	$7.4 \pm 0.1$ (58)	$7.9 \pm 0.2$ (57)*
	$N-NO_3^-$ ( $\mu g N L^{-1}$ )	$211 \pm 9$ (58)	$214 \pm 19$ (56)
	$N-NH_4^+$ ( $\mu g N L^{-1}$ )	$8.7 \pm 0.4$ (60)	$24.4 \pm 1.9$ (56)*
	$P-PO_4^{3-}$ ( $\mu g P L^{-1}$ )	$9.1 \pm 5.1$ (60)	$14.9 \pm 2.2$ (57)
	Chemical Index	$0.4 \pm 0.5$ (69)	$-2.3 \pm 1.3$ (66)*
Vegetative	$Cl^-$ ( $mg L^{-1}$ )	$10.6 \pm 0.4$ (100)	$12.1 \pm 0.5$ (98)*
	$N-NO_3^-$ ( $\mu g N L^{-1}$ )	$249 \pm 12$ (102)	$200 \pm 16$ (98)*
	$N-NH_4^+$ ( $\mu g N L^{-1}$ )	$11.2 \pm 0.5$ (103)	$30.6 \pm 1.9$ (101)
	$P-PO_4^{3-}$ ( $\mu g P L^{-1}$ )	$16.2 \pm 0.7$ (103)	$16.5 \pm 0.9$ (97)
	Chemical Index	$0.002 \pm 0.3$ (60)	$-2.8 \pm 1.2$ (84)*

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**Table 2.** Spearman  $\rho$  coefficient between stream water and riparian groundwater solute concentrations for each season and for the whole data set collected at the Font del Regàs during the period of study. The relative root mean square error (RRMSE) indicates divergences from the 1 : 1 line. The number of cases is shown in parenthesis for each variable. ns, no significant.

	Dormant			Vegetative			All data		
	$\rho$	RRMSE (%)	n	$\rho$	RRMSE (%)	n	$\rho$	RRMSE (%)	n
Cl <sup>-</sup>	0.78*	2.1	53	0.8*	2.9	98	0.84*	2.8	151
N-NO <sub>3</sub> <sup>-</sup>	0.48*	8.1	57	0.34*	8.3	101	0.37*	6	158
N-NH <sub>4</sub> <sup>+</sup>	ns	11.7	57	ns	9.1	101	ns	7.3	158
P-PO <sub>4</sub> <sup>3-</sup>	ns	17.9	57	0.43*	5.5	101	0.41*	7.3	158

\*  $p < 0.001$

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**Table 3.** Best  $AIC_c$  models ( $\Delta_i < 4$ ) predicting stream nutrient concentration for each season. Variables available for the model selection were: distance to the upper most site (D), specific discharge ( $Q_{spf}$ ), riparian forest width (RW), total basal area (BA), relative contribution of  $N_2$ -fixing trees to BA (NBA), riparian groundwater nutrient concentration (RC), stream velocity (V), mean wet width (WW), percentage of sand in the stream bed (S). The sign of the relationship is shown for each variable. The null model is included as a reference in each case. The model likelihood, the Akaike weight ( $w_i$ ), and the df are indicated in each case. The  $p$  value of the ANOVA test between each model and the best available model ( $AIC_{min}$ ) is included.

		Rank	Model covariates	$AIC_c$	$\Delta_i$	Model likelihood	$w_i$	df	ANOVA $p$ value	
N-NO <sub>3</sub> <sup>-</sup>	Dormant	1	-V, +BA, -NBA	139.76	0	1	0.796	11		
		2	-V, +BA	142.48	2.72	0.26	0.204	12	0.044	
		null	-	161.45	21.69	0.00	0.000	14	< 0.0001	
	Vegetative	1	+Q <sub>spf</sub> , -WW, -NBA, +BA, +D, +RC	149.68	0	1	0.478	8		
		2	+Q <sub>spf</sub> , -WW, -NBA, +BA, +D	150.27	0.59	0.74	0.356	9	0.22	
		3	+Q <sub>spf</sub> , -WW, -NBA, +BA	151.81	2.13	0.34	0.165	10	0.13	
		null	-	163.87	14.19	0.00	0.000	14	< 0.0001	
	N-NH <sub>4</sub> <sup>+</sup>	Dormant	1	+D	50.59	0	1	0.959	13	
			null	-	56.87	6.28	0.04	0.041	14	< 0.0001
Vegetative		1	-NBA, +RW	63.71	0	1	0.431	12		
		2	-NBA	63.99	0.28	0.87	0.375	13	0.16	
		null	-	65.3	1.59	0.45	0.195	14	0.066	
P-PO <sub>4</sub> <sup>3-</sup>	Dormant	1	+BA, +RC, -WW	78.87	0	1	0.755	11		
		2	+BA, +RC	81.4	2.53	0.28	0.213	12	0.048	
		null	-	94.93	16.06	0.00	0.000	14	< 0.0001	
	Vegetative	1	-WW, +RC, +V, -D, +RW, -BA	58.79	0	1	0.957	8		
		null	-	85.97	27.18	0.00	0.000	14	< 0.0001	

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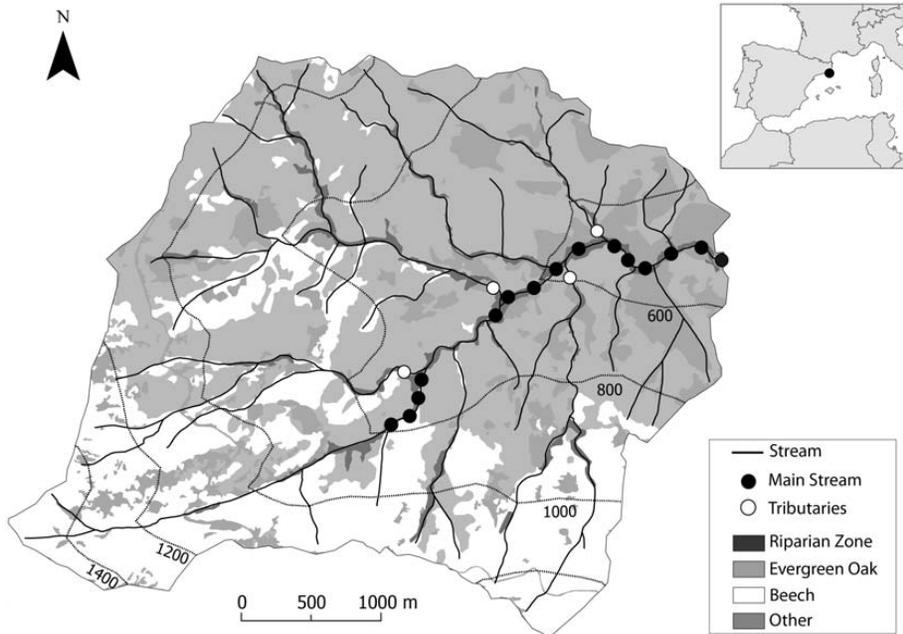
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**Figure 1.** Map of the Font del Regàs catchment within the Montseny Natural Park (NE, Spain). The vegetation cover and the main stem and tributaries sampling stations along the 3.7 km stream reach are indicated.

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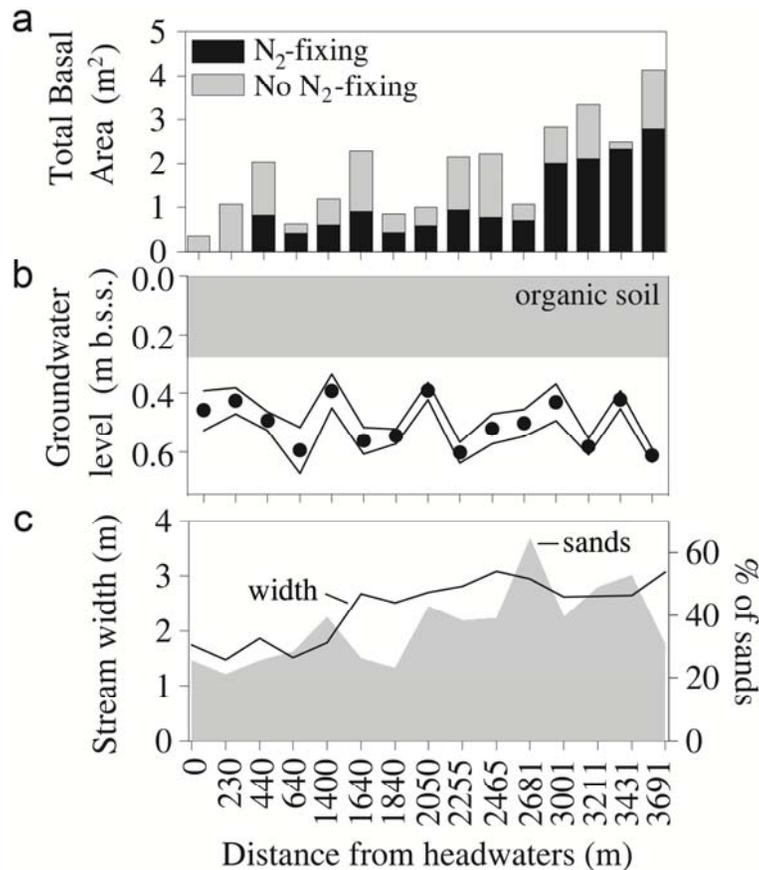
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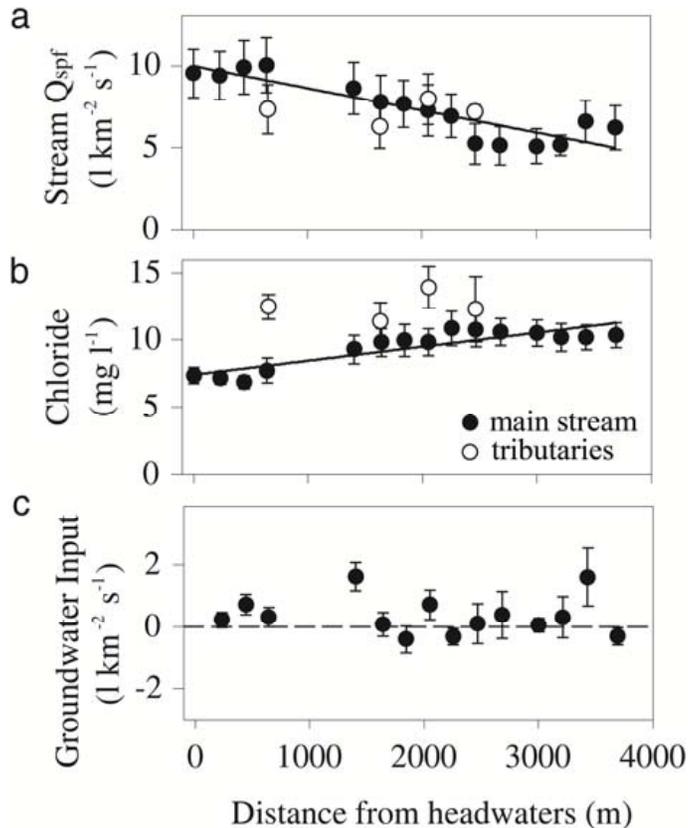


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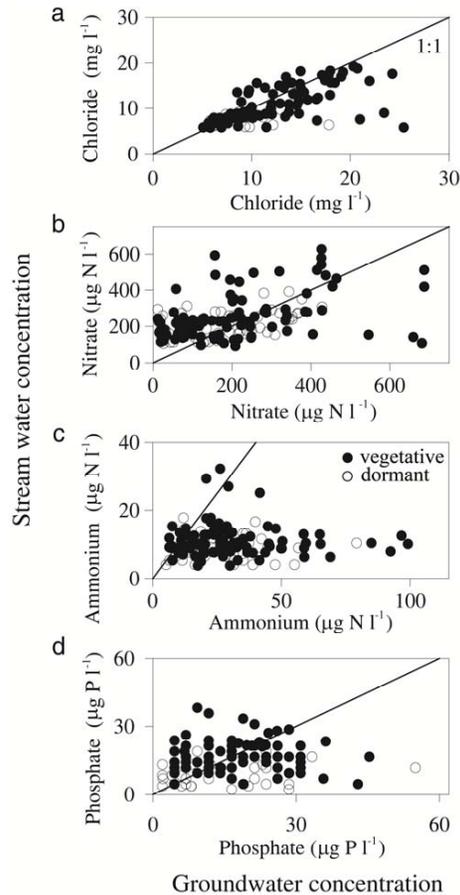
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**Figure 2.** (a) Total basal area of riparian trees, (b) mean riparian groundwater level (in m below the soil surface), and (c) stream width and percentage of sands in streambed for the different sampling sites from the top to the bottom of the Font del Regàs stream reach. Different colors in (a) indicate the basal area of N<sub>2</sub>- and no N<sub>2</sub>-fixing trees. The solid lines in (b) are the 95% lower and upper values of the riparian groundwater level.



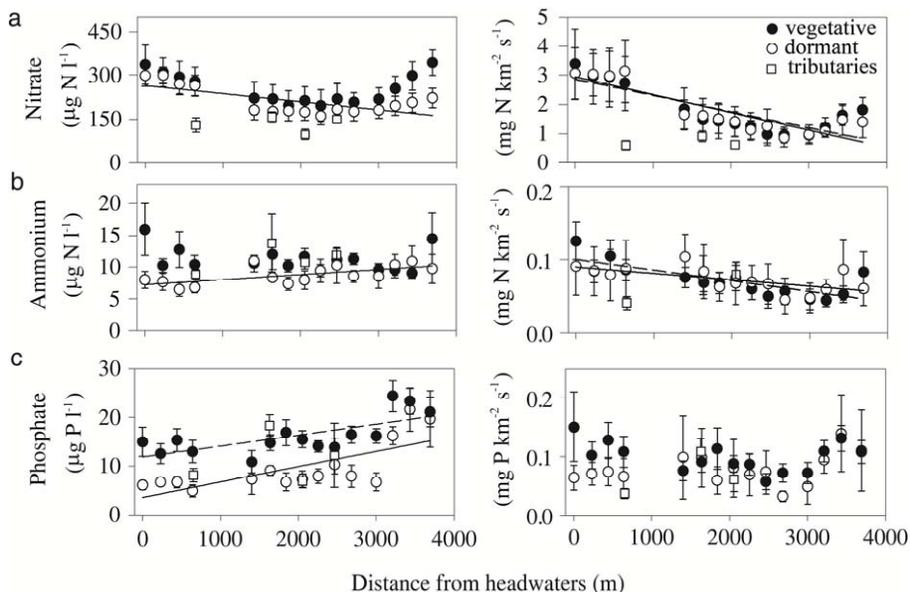
**Figure 3.** Longitudinal pattern of (a) catchment-specific stream discharge, (b) stream chloride concentration, and (c) net groundwater input to stream at the study reach. Symbols are average and standard error (whiskers) during the period of study for the main stream channel and tributaries. Linear regression is indicated with a solid line only when significant (tributaries not included in the model).



**Figure 4.** Relationship between riparian groundwater and stream water concentrations for **(a)** chloride, **(b)** nitrate, **(c)** ammonium, and **(d)** phosphate at each sampling site and for each sampling data at Font del Regàs. The 1 to 1 line is indicated in black.

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**Figure 5.** Longitudinal pattern of stream nutrient concentrations (left panels) and fluxes (right panels) for (a) nitrate, (b) ammonium, and (c) phosphate concentrations at Font del Regàs. Symbols are average and standard error (whiskers) for the dormant and vegetative period for the main channel. Lines indicate significant linear trends in either concentration or flux along the reach for the dormant (solid) and the vegetative (dashed) period (tributaries not included in the model).

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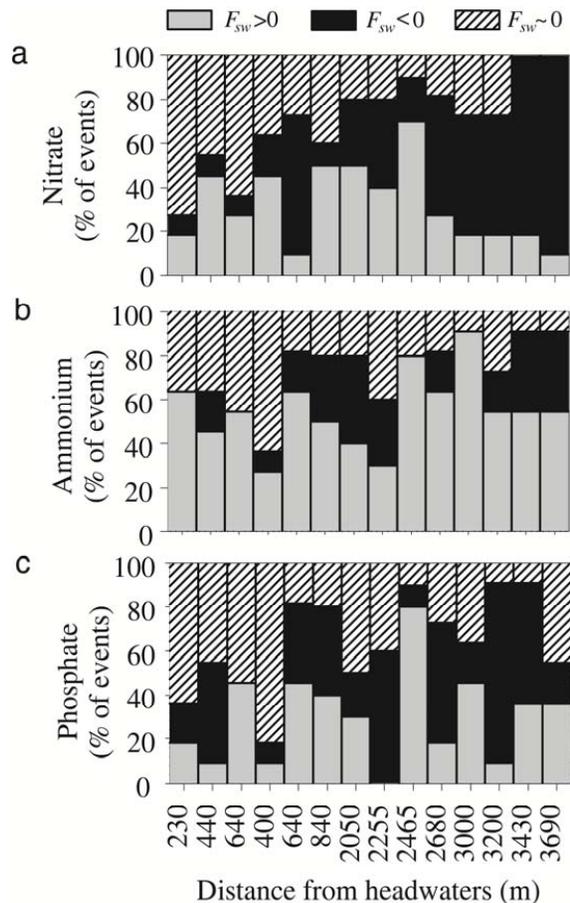
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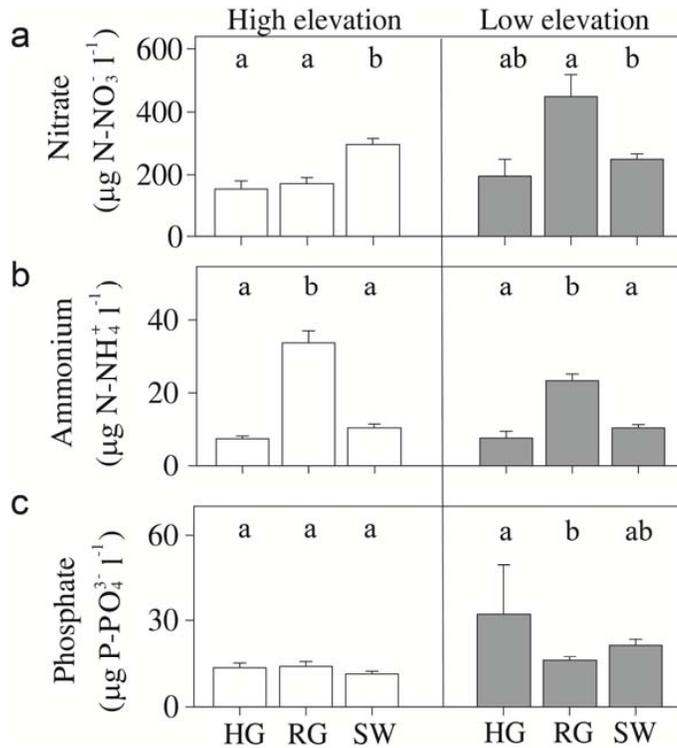


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**Figure 6.** Frequency of dates with  $F_{sw} > 0$ ,  $F_{sw} < 0$ , and  $F_{sw} \sim 0$  for (a) nitrate, (b) ammonium, and (c) phosphate for each stream segment along the Font del Regàs reach during the study period. The frequency is expressed as number of events in relative terms.



**Figure 7.** Solute concentrations measured in hillslope groundwater (HG), riparian groundwater (RG), and stream water (SW) at high (800–1200 m a.s.l.) and low (500–650 m a.s.l.) elevations at the Font del Regàs catchment. Hillslope groundwater corresponds to water samples collected from springs (10 and 4 for high and low elevations, respectively) during four field campaigns (May and November 2011, and January and July 2012). Bars are means and whiskers are standard errors. For each elevation, different letters indicate statistical differences between solute concentrations measured in the different water pools (Mann Whitney test with post-doc Tukey test,  $p < 0.05$ ).