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EUROLIMPACS EU project
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Deliverable 42 from UB:

Report on first results from the short-term solute additions along a Mediterranean aridity gradient emphasizing temporal variation.

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Introduction

Streams are sites of intense biogeochemical processing – unlike large rivers, where transport prevails. These ecosystems and their adjacent catchments are very sensitive to environmental change. Therefore, we should expect that climate change will not simply affect streams through changes in their catchment, but will also influence in-stream ecosystem processes affecting element cycling and transport.

Climate change in the Mediterranean region is expected to result in an increase in temperature. Precipitation will probably decrease but, most importantly, the seasonality of precipitation will be puzzled by more rain and more episodic events during the rainy seasons and more intense droughts in the summer. These changes in climate will have clear effects on stream hydrology, altering the flooding regime (probably with more spiky hydrographs) and increasing the number of intermittent streams associated with increases in water deficit in the catchment. In the Mediterranean region, fluvial ecosystems are prominent among aquatic ecosystems and most of them are currently subjected to intermittency, which provides a good opportunity to explore stream biogeochemical responses to future climate change scenarios of more humid regions in Europe.

Even though impacts of climate change on stream community structure are relatively well understood, our knowledge about impacts on stream ecosystem function is much poorer. Specifically, it is important to increase our knowledge of how environmental factors, such as hydrology and water temperature, influence stream biogeochemistry (e.g., nutrient retention, organic matter processing, metabolism) to be able to predict the effects of climate change on ecosystem function. Our hypothesis is that the relevance of these factors controlling ecosystem function may vary depending on the local climate conditions.

The overall aim of our study is to assess the variability in stream response in terms of nutrient retention and examine the role of stream hydrology and water temperature on this variability. For this purpose we have selected several streams within the Mediterranean region that cover a temperature and aridity gradient. In these streams, we will examine spatial variability in nutrient retention across streams for a given period of the year and temporal variability (i.e., over more than a year) in nutrient retention in streams located at different altitudes. Here we report the first results on the temporal variation in stream nutrient retention efficiency for ammonium and phosphate from two Mediterranean streams located at different altitudes within the same catchment. With these results we examined the temporal variation of hydrological and chemical parameters and compared it to that observed for nutrient retention parameters for each stream and between streams.

Study site description

This study was conducted in the Tordera catchment (50 km N of Barcelona, Fig. 1). The area of the catchment is 800 km^2 and covers an altitudinal gradient of 1706 m a.s.l. in ca. 35 km from headwaters to river mouth. This catchment is dominated by siliceous geology. The entire catchment is influenced by Mediterranean climate; however, due to the dramatic altitudinal range there are distinct sub-climate conditions along the gradient. In this catchment, we initially selected 3 streams located at 1300 (Sta. Fe stream), 800 (Font del Regàs streams) and 300 (Fuirosos stream) m a.s.l. in areas where anthropogenic influence is almost non-existent (Fig. 1). Dominant forest vegetation in the selected sub-catchments covers a gradient from *Fagus sylvatica* at the higher elevation, to a mixed forest with *Quercus pubescens* and *Pinus sylvestris* at mid elevation, and *Quercus ilex* and *Quercus suber* at the lower elevation.

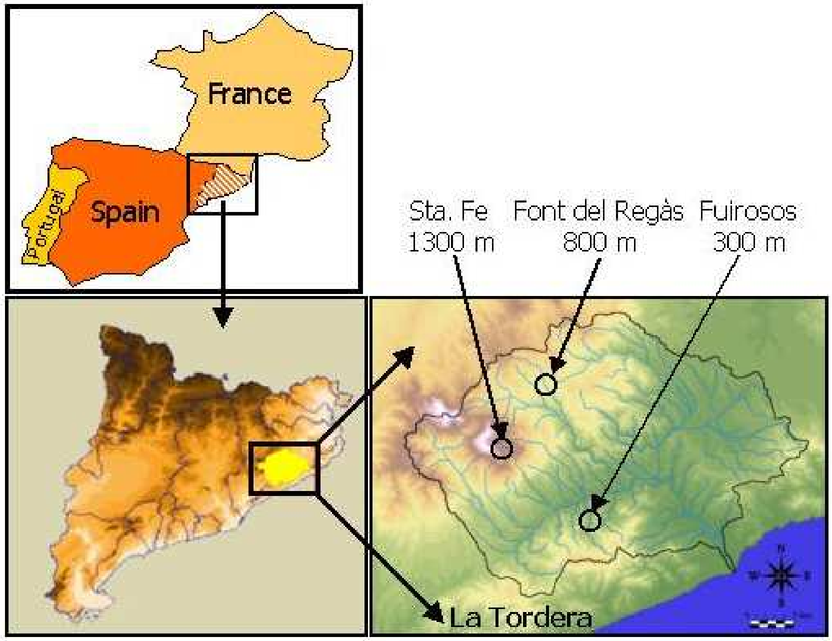

Figure 1. Location of the Tordera catchment and the study streams within the catchment.

In each stream, we selected a 200 m reach to conduct the measurements of this study. The three reaches were representative of each area and were comparable in terms of substrata type and canopy cover from riparian vegetation. All reaches are riffle-pool dominated and substrata type is basically composed of cobbles and pebbles with patches of sand. Riparian vegetation is well developed along the reaches and is dominated by riparian deciduous trees that completely shade the reach channel during spring and summer. Dominant tree species in each reach vary encompassing altitudinal changes. At the higher elevation, riparian vegetation is dominated by *Fagus sylvatica* with some stems of *Sambucus nigra*. At middle elevation, riparian vegetation is dominated by *Alnus glutinosa*, *Platanus hispanica* and *Robinia pseudoacacia*. Finally, riparian vegetation at lower elevation is dominated by *Alnus glutinosa*, *Fraxinus angustifolia*, and *Platanus hispanica*. In this report we only provide results from the streams located at 1300 and 300 m for which we have a complete data set for a year. Data from the site at 800 m are very scarce and inconsistent because we had several methodological problems that made us change the selected stream twice.

Methodology

Physical and chemical characterization of the study streams

On each stream reach we conducted regular samplings every two weeks since September 2004 for water chemistry (concentration of NO_3^--N, NO_2^--N, NH_4^+-N, PO_4^{3-}-P), water temperature, conductivity and stream discharge. Water temperature and conductivity were measured with a WTW® conductivity meter (model LF 340). Stream discharge was estimated from transect measurements of water velocity, water depth and channel width done at a single station. Water samples for chemical analyses were filtered *in situ* using Whatman® GF/F fiberglass filters (0.7 µm pore diameter). Water samples were ice-stored and transported to the laboratory where they were kept in the refrigerator until analysis. Nutrient concentrations were analyzed following standard colorimetric methods (APHA 1998) using Bran+Luebbe® autoanalyzers (TRAACS for NO_3^--N, NO_2^--N, and PO_4^{3-}-P, and Technicon for NH_4^+-N). All concentrations are reported as mg of the element/L.

Measurement of nutrient retention efficiency

To measure nutrient retention efficiency in each stream we used the method of short-term solute addition at constant rate (Webster and Ehrman 1996). At each stream we conducted solute additions monthly since September 2004 until August 2005. All additions were conducted under baseflow conditions. Each solute addition consists of adding a solution made of NH_4^+-N (as $NaNH_4$), PO_4^{3-}-P (as $Na(H_2PO_4)2{\cdot}H_2O$), and NaCl (used as a hydrologic tracer) at a constant rate for ca. 3 h (depending on the stream discharge) at the head of the reach. Water samples were collected at 8 locations along the reach before the addition (i.e., ambient concentration) and once the addition reached plateau at the bottom of the reach (i.e., the added solution has completely mixed along the entire reach). At each sampling station we also measured conductivity before the addition and at plateau conditions. During the addition we recorded the variation of conductivity over the course of the experiment at the bottom of the reach using a WTW® conductivity meter (model LF 340) connected to a data logger (Campbell®). We also measured complementary parameters such as photosynthetic active radiation (PAR), water temperature, wet channel width and depth. PAR and water temperature were measured several times over the course of the addition and values were averaged. Reach width and depth were estimated as the average of measurements done at transects located at each of the 8 sampling stations. At each transect, depth was measured at 20 cm intervals.

Water samples for concentration of NO_3^--N, NH_4^+-N, and PO_4^{3-}-P from the addition experiments were processed and analyzed as described for the regular sampling. Concentrations of NH_4^+-N and PO_4^{3-}-P and conductivity at ambient levels and at plateau were used to estimate nutrient uptake length for NH_4^+-N and PO_4^{3-}-P. Nutrient uptake length (S_w, m) is defined as the average distance that a nutrient atom travels until is removed from the water column and it is an indicator of the stream nutrient retention efficiency (Stream Solute Workshop 1990). Shorter distances indicate higher retention efficiency than longer distances. S_w was calculated based on the variation along the reach of nutrient concentration at plateau corrected by ambient concentration and by the variation in conductivity using the equation:

$$N_x = N_0 \, e^{-bx}$$

Where N is the corrected nutrient concentration at the first sampling station (N_0) and at the sampling station located x m downstream (N_x) and b is the nutrient retention coefficient in units of m^{-1}. S_w is the inverse of this coefficient (-1/b).

Time-curve conductivity data were used to estimate hydrologic parameters. Reach average velocity was computed as the reach length divided by the time needed for conductivity to reach one half of the plateau value. Stream discharge was estimated based on a mass balance between the added salt (NaCl) and the resulting concentration at the bottom of the reach using the following equations:

$$Qr = Qs + qa$$
$$Qr \times Cr = (qa \times Ca) + (Qs \times Cs)$$

Where Qr is discharge at the bottom of the reach, Qs is stream discharge, qa is addition flow and C is conductivity at ambient level (s), at plateau at the bottom of the reach (r), and at the added solution (a).

Results and discussion

Temporal variation of physical and chemical parameters

Water temperature showed a seasonal pattern in the two streams, with low temperatures in winter and high temperatures in summer (Fig. 2). However, in the stream located at the lower altitude (i.e., Fuirosos) the annual temperature range was wider and the average annual temperature was higher (T-test for independent samples, t-value= 3.282, df= 40, *p*=0.002) than in the stream located at the higher altitude (i.e., Sta. Fe, Table 1).

Stream discharge was on average low and comparable between the two streams (Table 1). Unlike temperature, temporal variation in discharge did not follow any seasonal pattern in any stream, and it differed between the two streams (Fig. 2). Conductivity was on average 4 times higher in the lower than in the higher elevation stream (T-test for independent samples, t-value= 23.402, df= 40, *p*<0.0001; Table 1). Conductivity was negatively correlated with discharge (Pearson correlation, n=20, r=-0.761, *p*<0.001) and positively correlated with temperature (Pearson correlation, n=20, r=-0.612, *p*=0.004) in Sta. Fe stream. In Fuirosos, we did not find any significant correlation between conductivity and discharge or temperature.

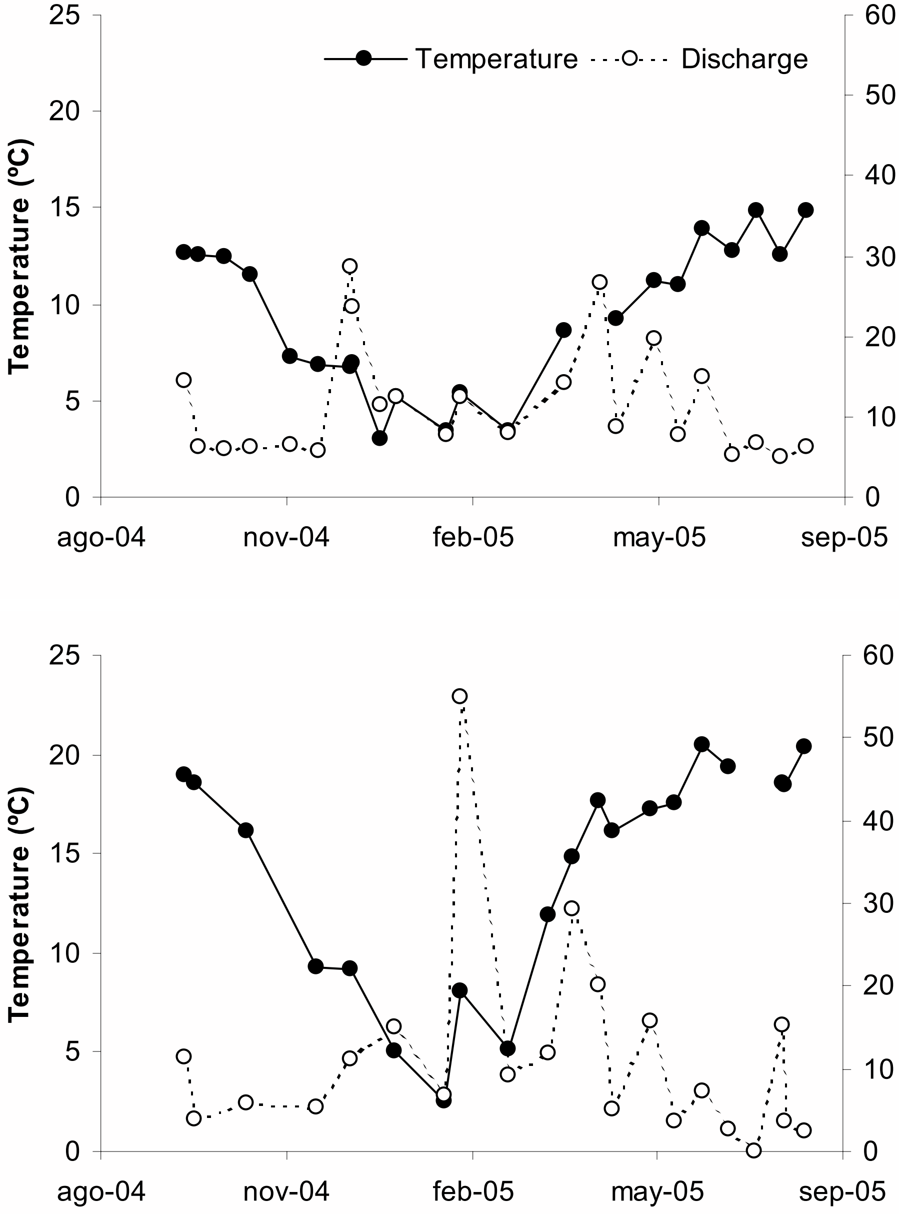

Figure 2. Temporal variation of water temperature and stream discharge in Sta. Fe (top graph) and Fuirosos (bottom graph) streams during the study period.

Table 1. Statistics for physical and chemical parameters measured on a biweekly basis in the two study streams from September 2004 to August 2005. DIN = dissolved inorganic nitrogen.

	n	Mean±SEM	median	range
Sta. Fe stream (1300 m a.s.l.)				
Temperature (ºC)	22	9.4±0.8	10.1	3.1 – 14.8
Discharge (L/s)	23	11.5±1.5	7.9	5.0 – 28.7
Conductivity (µS/cm)	22	57±1	58	40 – 64
NO_3^--N (µg/L)	23	123±16	118	21 – 249
NO_2^--N (µg/L)	23	2.9±0.6	2.3	0.7 – 14.7
NH_4^+-N (µg/L)	22	8.2±1.1	7.3	1.8 – 25.9
PO_4^{3-}-P (µg/L)	22	15.1±1.9	13.8	3.7 – 33.6
DIN:P (molar)	21	23±2	23	7 – 47
Furiosos stream (300 m a.s.l.)				
Temperature (ºC)	20	14.3±1.3	16.7	2.5 – 20.5
Discharge (L/s)	21	11.4±2.7	7.2	0 – 55.0
Conductivity (µS/cm)	20	225.7±7.4	219.3	152.0 – 282.0
NO_3^--N (µg/L)	20	475±139	124	15 – 2137
NO_2^--N (µg/L)	20	5.1±0.9	3.9	1.1 – 17.2
NH_4^+-N (µg/L)	21	38.0±16.7	13.1	5.1 – 317.0
PO_4^{3-}-P (µg/L)	19	9.4±5.0	3.0	0.4 – 97.0
DIN:P (molar)	19	632±204	311	8 – 2853

Concentrations of all nutrients, except NO_3^--N, were relatively low in the two streams, as expected for small streams draining undisturbed catchments (Table 1). Major differences in nutrient concentration between the two streams were found for NO_3^--N. On average, the stream at higher elevation (i.e., Sta. Fe) showed significant lower NO_3^--N concentration than the stream at the lower elevation (T-test for independent samples, t-value= 2.699, df= 41, *p*=0.010; Table 1). In addition, temporal variation of NO_3^--N concentration also differed between the two streams (Fig. 3). In Sta. Fe stream, NO_3^--N concentration showed a clear seasonal pattern that was positively correlated with water temperature (Pearson correlation, n=20, r=0.796, *p*<0.001). In this stream, temporal variation in PO_4^{3-}-P concentration was coupled to that of NO_3^--N concentration (Pearson correlation, n=20, r=0.572, *p*=0.008; Fig 3). In Fuirosos stream, NO_3^--N concentration also showed a seasonal pattern, but it was inversely related to temperature (Pearson correlation, n=18, r=-0.508, *p*=0.032). Temporal variation of PO_4^{3-}-P concentration in this stream was not coupled to that of NO_3^--N concentration and was positively related to temperature (Pearson correlation, n=18, r=0.656, *p*=0.014). In the two streams, concentration of NH_4^+-N was in general low and mostly accounted for <10% of dissolved inorganic nitrogen (DIN, Table 1). Only in Fuirosos during summer dates, when stream water was almost stagnant, NH_4^+-N concentration was high and even exceeded NO_3^--N concentration (Table 1). Besides of these dramatic increases, in general temporal variation of this nitrogen form did not follow any clear temporal pattern in any of the streams. On all dates and for the two streams, NO_2^--N concentration was very low, and accounted only for <3 % of the DIN (Table 1).

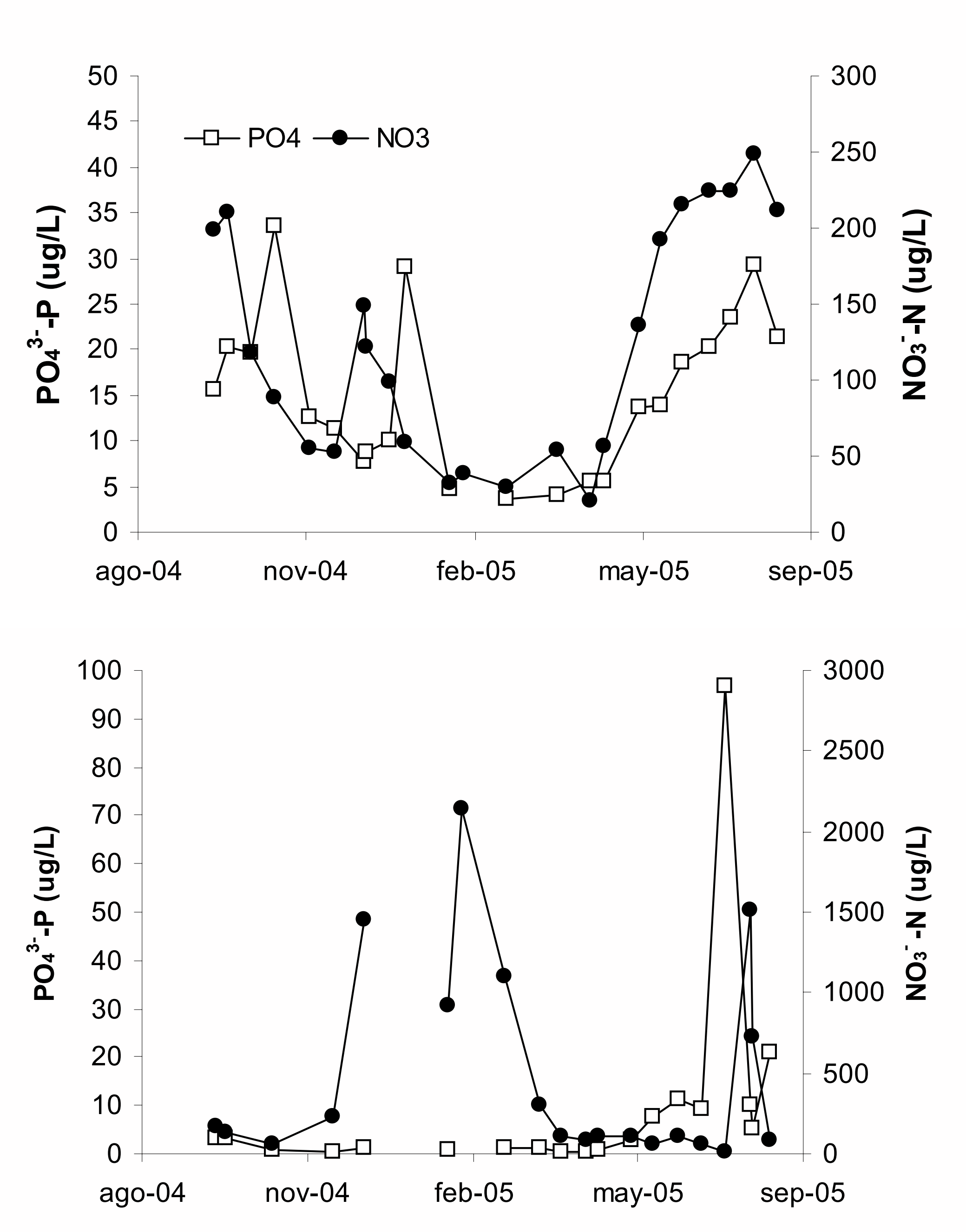

Figure 3. Temporal variation of phosphate (PO_4^{3-}-P) and nitrate (NO_3^--N) concentrations in Sta. Fe (top graph) and Fuirosos (bottom graph) streams during the study period.

As a result of the difference between the two streams in NO_3^--N concentration and its temporal variation, the DIN:P molar ratio was much higher (T-test for independent samples, t-value= 3.140, df= 38, *p*=0.003) and more variable in Fuirosos stream than in Sta. Fe stream (Table 1). Median DIN:P molar ratio was close to 16 in Sta. Fe stream, whereas in Fuirosos was much higher than 16, which suggest a potential P limitation in this stream (Grimm and Fisher 1986).

Finally, results from a principal component analysis (PCA) taking data from the two streams together and considering all the physical and chemical parameters measured in the regular sampling, including molar DIN:P ratio and NO_3:NH_4 ratio, showed larger variability in Fuirosos stream than in Sta. Fe stream (Fig. 4). The highest variance among data was associated to NO_3^--N concentration and the DIN:P and NO_3:NH_4 ratios, which were correlated to the first factor of the PCA (36 % of the total variance). Factor 2 accounted for 20.5 % of the total variance and concentration of NH_4^+-N and PO_4^{3-}-P were the two parameters correlated to this factor. Finally, temperature and conductivity were correlated to factor 3 (15.7 % of the total variance). The loading of discharge on the first 3 PCA factors was not significant.

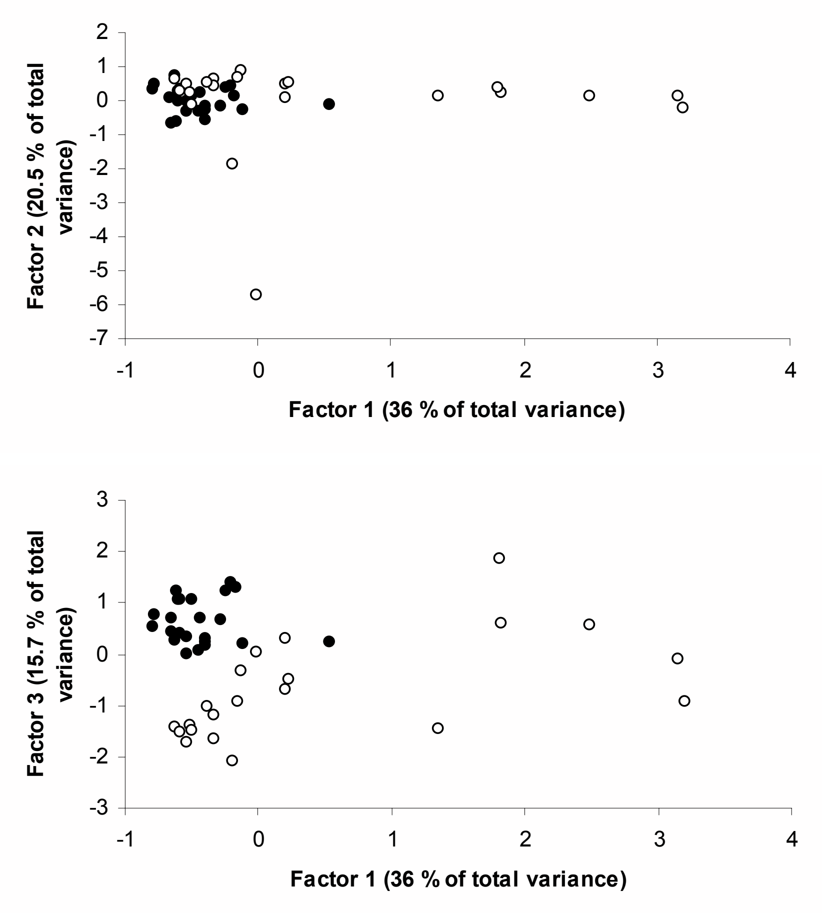

Figure 4. Ordination of sampling dates for Sta. Fe stream (closed circles) and Fuirosos (open circles) according to factors 1 and 2 (top graph) and factors 1 and 3 (bottom graph) of the principal component analysis done using physical and chemical parameters measured on the regular samplings. Data are from the September 2004 - August 2005 period.

Temporal variation in stream nutrient retention efficiency

The two streams showed relatively short uptake lengths (i.e., in the order of few hundred meters) for the two nutrients on most of the dates, indicating that they have a high efficiency retaining these two nutrients. These values are similar to values published elsewhere for streams of similar size draining unperturbed catchments (Marti and Sabater 1996, Peterson et al. 2001, and references therein). However, the most interesting result is that the temporal variation in nutrient uptake lengths clearly differed between streams, which suggests that different factors control dynamics of these nutrients in the two streams. In Sta. Fe stream (i.e., the stream located at the higher altitude), temporal variation of S_w for the two nutrients was coupled (Pearson correlation, n=12, r=0.984, $p<0.001$), but S_w-NH_4 was consistently shorter than S_w-PO_4 for the entire study period (Fig. 5). In this stream, temporal variation of S_w for the two nutrients did not follow any clear seasonal pattern and was basically associated to variation in stream discharge (Fig. 6 a and b). Increases in discharge resulted in longer S_w (i.e., lower retention efficiency). The influence of discharge on nutrient retention efficiency has been widely described in previous studies and evidences that this factor plays a key role on stream nutrient dynamics at an inter-biome scale (Butturini and Sabater 1998, Peterson et al. 2001). A decrease of the contact between the streambed, where most of the biogeochemical process take place, and the water column as discharge increases is the most plausible mechanism explaining this hydrological effect.

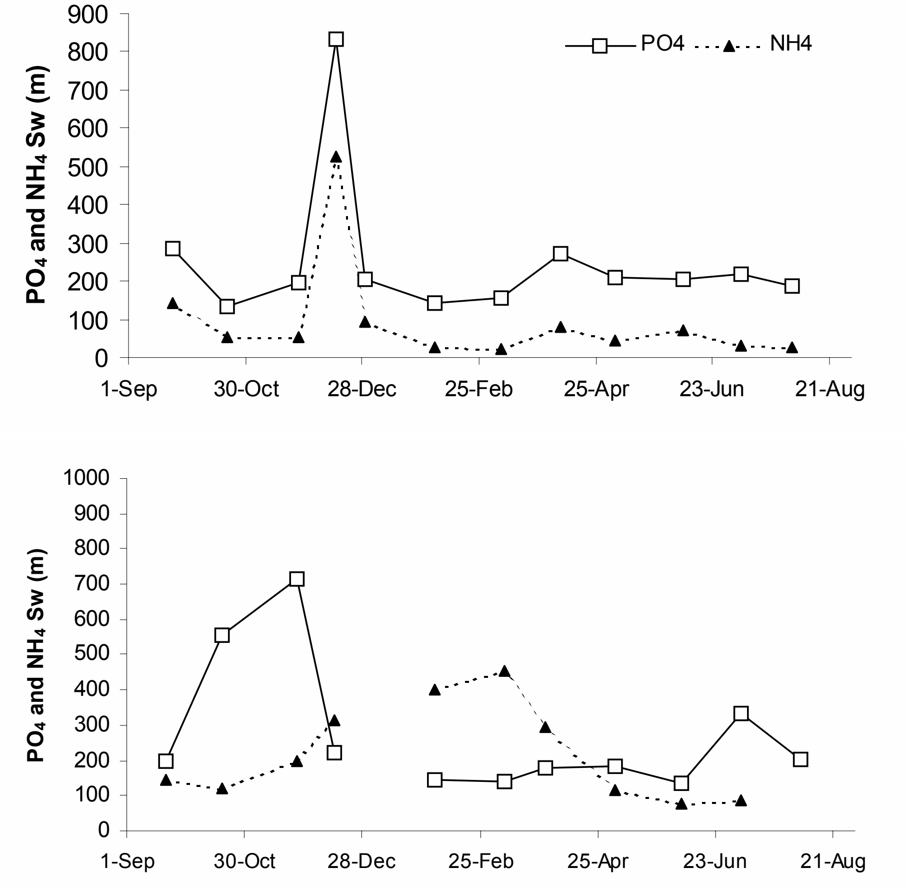

Figure 5. Temporal variation of ammonium and phosphate uptake length (S_w) in Sta. Fe (top graph) and Fuirosos (bottom graph) streams during the study period.

Temporal patterns observed in Fuirosos stream (i.e., the stream at the lower elevation) clearly contrasted with those from Sta. Fe (Fig. 5). S_w of NH_4^+-N and PO_4^{3-}-P were not correlated (Pearson correlation, n=10, r=-0.310, *p*=0.382). However, longer S_w-PO_4 tended to coincide with short S_w-NH_4. Temporal variation of S_w-PO_4 did not show any clear seasonal pattern and we did not find any significant relationship between this parameter and discharge or water temperature (Fig 6. c and d). In contrast, S_w-NH_4 was related to both discharge (positive relationship) and water temperature (negative relationship; Fig. 6 c and d) and showed a seasonal pattern with longer values during the coldest months (Fig. 5). Unlike with the effect of discharge, few studies have explored the effect of temperature on stream nutrient retention efficiency. No clear temperature effect has been found taking data from different streams (Webster et al. 2003), but studies done at single streams over time revealed similar results as those from our study (Butturini and Sabater 1998, Simon et al. 2005). The influence of water temperature on variation in S_w suggests that nutrient retention efficiency is most likely controlled by biological mechanisms.

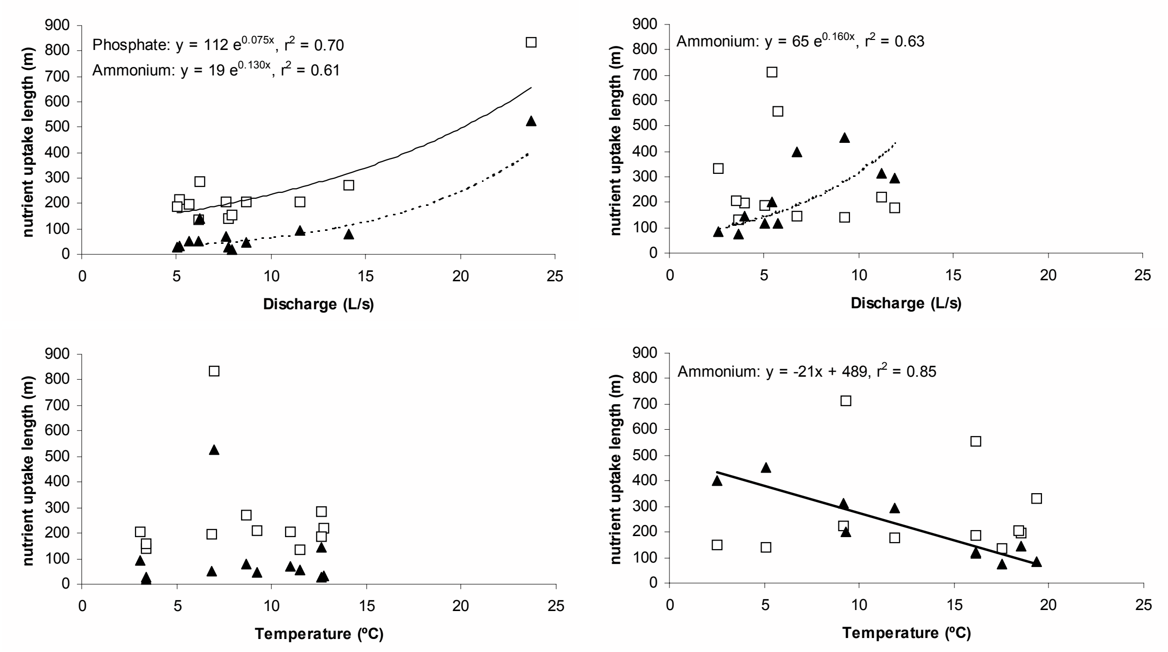

Figure 6. Relationships between nutrient uptake length and discharge (a and c graphs) and water temperature (b and d graphs) in Sta. Fe stream (left panel) and Fuirosos (right panel). The graphs show data for phosphate (open squares) and ammonium (closed triangles) uptake lengths, highlight the regressions that are significant (solid lines for PO_4 and dotted lines for NH_4), and include the equations of significant regressions.

Comparison of nutrient retention response between the two streams

Results from this study show that within-stream variability in nutrient retention efficiency can be large (Table 2) and even comparable to that measured across streams from the same region for a given period (Hall et al. 2002). Similar findings have been reported in the few studies addressed to examine in-stream temporal variation in nutrient retention (Marti and Sabater 1996, Butturini and Sabater 1998, Simon et al. 2005). Together, these results highlight the need to consider within-stream variation when comparing nutrient retention responses among streams. In this sense, our results show that despite Fuirosos stream exhibited larger variability in physical and chemical conditions than Sta. Fe stream (Fig. 4), its variability in nutrient retention response (expressed in terms of the coefficient of variance, Table 2) was smaller than in Sta. Fe stream.

Taking all data together, major differences in retention efficiency between the two streams were associated to NH_4^+-N. Sta. Fe stream showed a significantly higher NH_4^+-N retention efficiency than Fuirosos (ANOVA, F-= 4.296, df= 20, *p*=0.050; Table 2). Retention efficiency for PO_4^{3-}-P was similar in the two streams, and in Sta. Fe stream was lower than that for NH_4^+-N (paired T-test, *p*<0.0001). These results are consistent with the differences in nutrient concentrations between the two streams described in previous sections, and evidence a certain control of in-stream processes on stream nutrient availability, at least on its temporal regime.

Table 2. Comparison of mean±SEM and median nutrient uptake lengths (S_w) for the study period between the two streams. Significance level from one-way ANOVA considering stream as a factor is also shown.

	Mean ± SEM			Median		Coefficient of variance (%)	
	Sta. Fe	Fuirosos	*p*	Sta. Fe	Fuirosos	Sta. Fe	Fuirosos
S_w-NH_4 (m)	98±40	220±43	0.050	53	173	143	62
S_w-PO_4 (m)	253±54	274±57	0.799	204	196	74	69

Comparison of the temporal variation pattern in S_w between the two streams provides additional information, which can be useful to predict changes in stream nutrient retention response under future climate scenarios. Our results show that environmental factors susceptible to climate change, such as stream discharge and water temperature, can influence stream nutrient retention response. Moreover, results indicate that the relative importance of these factors depends on both the location of the stream (and, thus the local climate) and the nutrient under consideration. This latter case suggests that biogeochemical mechanisms controlling retention of each nutrient are not completely coupled. This is especially evident in Fuirosos stream.

Finally, we also compared responses in nutrient retention efficiency between the two streams from an stoichiometric approach by examining temporal variation of the uptake length ratio between the two nutrients (i.e., S_w-NH_4: S_w-PO_4). This ratio indicates the importance of in-stream processes controlling NH_4^+-N relative to PO_4^{3-} -P (Marti and Sabater 1996). Ratios <1 indicate a higher retention efficiency for NH_4^+-N than for PO_4^{3-} -P, and ratios >1 indicate the opposite.

The nutrient retention efficiency ratio clearly evidences the distinct dynamics of the two streams. In Sta. Fe, the range of temporal variation in this ratio is very narrow and is <1 throughout the year. In contrast, Fuirosos exhibits a broad range of variation in this ratio and more interestingly, it shows a shift in the importance of NH_4^+-N retention efficiency relative to PO_4^{3-}-P retention efficiency over the year. This shift coincides with seasonal changes. The ratio is >1 during winter months and >1 during the rest of the year. It is interesting to notice that when efficiency for the two nutrients is considered together, using this ratio, the range of variability of this functional integrated parameter is larger for the stream that showed also a larger variability in the combination of physical and chemical parameters.

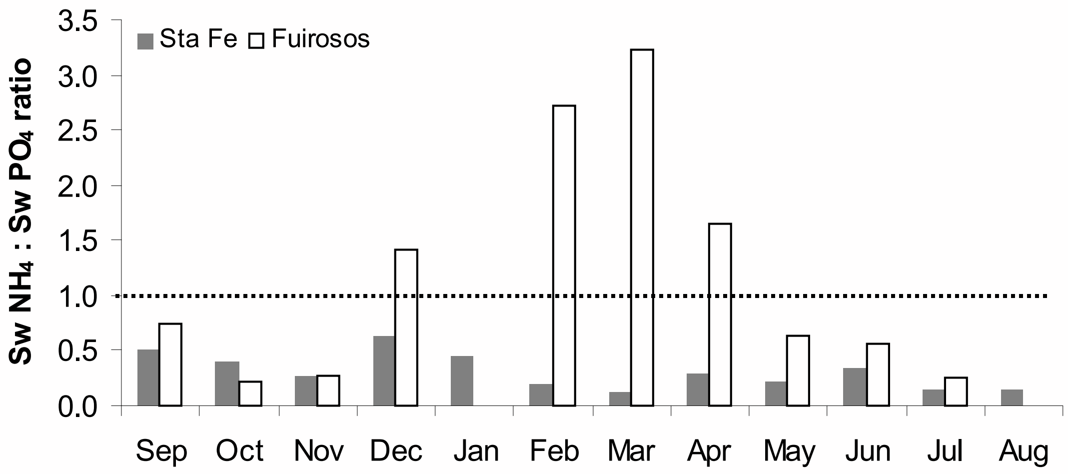

Figure 7. Temporal variation of the ratio between nutrient uptake lengths for ammonium and phosphate (S_w NH_4 : S_w PO_4) for the study period (Sep 2004 - Aug 2005). Values <1 indicate higher retention efficiency for ammonium than for phosphate and values >1 indicate higher retention efficiency for phosphate than for ammonium. The graph compares the temporal variation of S_w NH_4 : S_w PO_4 between the two streams.

Future research

Our results show that the study streams have a high efficiency to retain both NH_4^+-N and PO_4^{3-}-P. Most interestingly, results indicate that this capacity varies over time following patterns either associated to seasonal changes or to the hydrological regime. Previous to this study, few studies have addressed this question and their results are consistent with ours. Nevertheless, consistency of these results, especially those indicating seasonal patterns, is still pending on longer time series. The high interannual variation in environmental factors characteristic of the Mediterranean climate provides an excellent opportunity to examine in more detail the linkage between environmental factors and stream nutrient retention responses by expanding measurements beyond the annual scale. Results from this present study come from a particularly dry year where no major floods have occurred. Our aim is to continue the monthly measurements of nutrient retention efficiency in the two streams at least for another year. This will provide more consistency to our observed seasonal patterns. In addition, we have started conducting solute additions in a new selected stream located at 800 m a.s.l. We hope that for the next year we will have a complete data set for the three streams that will allow examining patterns in nutrient retention response along the altitudinal gradient. Together, this information will certainly contribute to expand our knowledge on potential effects of climate change on in-stream nutrient dynamics.

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