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# Nitrogen storm responses in an intermittent Mediterranean stream

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# Nitrogen storm responses in an intermittent Mediterranean stream

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# Part II

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# The role of lithology, catchment size, and the alluvial zone on the hydrogeochemistry of the Fuirosos Stream Watershed in the Montnegre-Corredor Natural Park (Catalonia, NE Spain)

**Key words**

Alluvial zone, catchment size, hydrology, lithology, stoiquiometry of streamwater

## Introduction

Stream chemistry in undisturbed catchments is determined by the nature of the atmospheric inputs, by biogeochemical processes within the catchment (e.g., mineral weathering, ion exchange and plant uptake), and by runoff generation processes occurring in the catchment (e.g., Vitousek 1977). Several studies have investigated the variability of such processes through the year by focusing on the seasonal dynamics of base cation and anion concentrations on streamwater chemistry in both, intermittent (e.g., Piñol et al. 1992) and perennial streams (e.g., Krám et al. 1997; Peters et al. 1999). In particular, Mediterranean catchments often show a marked seasonal pattern due to the alternance of dry and wetting periods with high solute concentrations at the beginning of the water year and low concentrations during winter (Àvila et al. 1995; Biron et al. 1999; Holloway and Dahlgren 2001). However, although lithology might have a strong influence on the chemistry of drainage waters due to differences in weathering reactions, only few studies have compared streamwater chemistry from catchments underlained by different bedrock types and results are still inconclusive. Krám et al. (1997) showed that streamwater in areas underlained by granites and schists exhibited lower concentrations of basic cations and higher acidity than drainage water in areas underlained by more reactive rock types (e.g., serpentine, carbonates and mafic rocks), whereas Holloway and Dahlgren (2001) concluded that stream chemistry was similar in four catchments with contrasting bedrock lithologies in the Sierra Nevada (CA, USA). In both studies absolute concentrations were used as a measure of comparison among catchments. In contrast, Hooper (2003) has recently stressed that the relationship among solutes (i.e., stoiquiometry) might be the key point when comparing stream chemistry among catchments rather than solute concentrations or temporal dynamics.

Another relevant issue to address is whether hydrology and streamwater chemistry are similar at different catchment sizes (e.g., Blöschl 2001; Sivalapan 2003). In that sense, Shaman et al. (2004) showed that upon a critical basin size (in between 8 and 21 km$^2$) streamflow reflected a similar hydrological catchment response in the Neversink River Watershed (NY, USA) that was attributed to similar deep groundwater contributions and to a well-developed riparian area. Concerning streamwater chemistry, Wolock et al. (1997) pointed out that stream chemistry was invariable at the Neversink River Watershed for basins larger than 3 km$^2$ that had uniformly bedrock composition.

In its turn, some studies have shown that the chemical signal of drainage waters from uplands is lost once in the riparian or alluvial zone (e.g., Burns et al. 2001). For example, Hooper et al. 1998 suggested that hydrological flowpaths in the Panola Mountain Watershed (Georgia, USA) could not be inferred from the streamwater chemical signature because the riparian zone was modulating the chemical signal from upland groundwater. Recently, Shaman et al. (2004) pointed out that sand and gravel alluvial zones are capable of storing and releasing water which could exert some control on streamflow as well as on stream chemistry, masking the chemical influence of drainage waters from uplands on stream runoff.

In the present study, two intermittent streams draining pristine forested catchments, Fuirosos and Grimola, were chosen in the Montnegre-Corredor Natural Park (Catalonia, NE Spain). Fuirosos (10.5 km$^2$) had an alluvial zone with a well-developed riparian area, whereas no alluvial aquifer, nor a well developed riparian zone existed at Grimola (3 km$^2$). Both catchments were mainly underlained by igneous metamorphic rocks, though different types of granite and schists predominated in each site. The purpose of the present study was to investigate whether hydrology and geochemical processes regulating solute concentrations in the Fuirosos Stream Watershed were affected by differences in bedrock lithology, catchment size and/or by the presence of an alluvial zone. In particular, the objectives of the study were to elucidate (i) whether the hydrological response during storms was similar in both catchments and, (ii) whether solute concentrations, seasonal dynamics and streamwater stoiquiometry were similar between Fuirosos and Grimola.

## Geology at the Fuirosos Stream Watershed

The Fuirosos Stream Watershed in mainly underlained by granitoid rocks. The Fuirosos subcatchment drains about 10.5 km$^2$ and is underlained by leucogranite (51 % of the area), followed by granodiorite and biotitic granodiorite (21 % of the area) (IGME 1983) (Figure 5.1). The CaO and MgO content of the leucogranite is 1.07 and 0.36 % of the rock weight, respectively. In its turn, the content of the granodiorite and biotitic granodiorite ranges between 2.79 and 2.08 for CaO and 1.05 and 0.72 for MgO, respectively (IGME 1983). The proportion of $Na_2O$ is similar in the three types of rocks: 2.77 % for leucogranite, 3.01 % for granodiorite and 2.66 % for biotitic granodiorite (IGME 1983). At the top of the ridge there is a monotone formation of sericitic schists composed by muscovite and biotite (IGME 1983) that finishes at its West part with a formation of silicic slates, lidites and limestones. The weathering of limestones may provide greater amounts of Ca to drainage waters than the weathering of the plagioclases in granitoid rocks. In its turn, Mg may originate in part from weathering of biotite and also from the dissolution of limestones (Davis and DeWiest 1991). Sodium may be originated from sea-salt aerosols and weathering of plagioclases (Davis and DeWiest 1991). At the valley bottom there is an identifiable alluvial zone (2 % of the catchment area) characterized mainly by gravel (IGME 1983) and a well developed riparian area 10 to 20 m in width that flanks the stream channel (3-5 m width).

In the present study hydrological and chemical data of the Fuirosos stream were discussed in relation to data from one of its effluents, Grimola stream, with a 3.5 km$^2$ drainage area. Grimola was located at the East part of the Fuirosos Stream Watershed (Figure 5.1). In contrast to Fuirosos, Grimola did not have alluvial zone. Grimola was dominated by leucogranite (70 % of the area) and by sericitic schists that occupied the remaining part of the area (Figure 5.1).

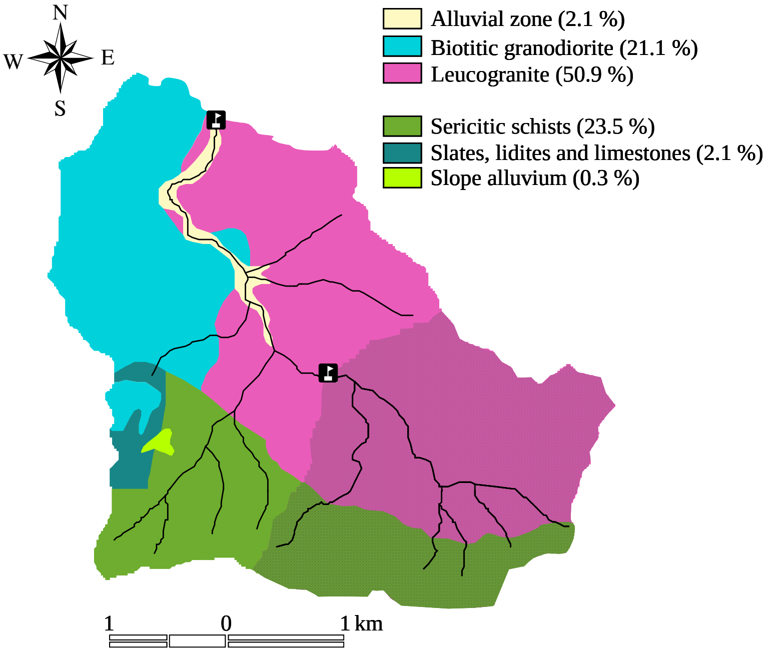

**Figure 5.1**. Lithological units in the Fuirosos and Grimola subcatchments located at the Fuirosos Stream Watershed (Catalonia, NE Spain) are shown in different colours (*sensu* IGME 1983). The Fuirosos Stream Watershed is mainly underlained by granitoid rocks (leucogranite and biotitic granodiorite). At the top of the ridge there is a monotone formation of sericitic schists that finishes at its West part with a mineral assemblage composed by slates, lidites and limestones. At the valley bottom there is an identifiable alluvial zone. The percent of area occupied by each type of rock in the Fuirosos subcatchment is indicated in parentheses. The dashed area indicates the Grimola subcatchment, which is mainly underlained by leucogranite (70 %) and sericitic schists (30 %). ■: Fuirosos and Grimola field stations.

**Table 5.1**. Relative bedrock composition (%) in both Fuirosos and Grimola subcatchments, which are located in the Montnegre-Corredor Natural Park (Catalonia, NE Spain). The drainage area is shown in parentheses (km$^2$). Groundwater springs and wells located on a specific bedrock area are also shown in parentheses. The W1 well was located in the hillslope zone at 250 m from the Fuirosos stream channel. Springs: SM, Santa Maria; CP, Can Preses; BR, Brinxa; MM, Sant Martí del Montnegre.

| | FUIROSOS | GRIMOLA | Springs |
|---|---|---|---|
| Lithology (% of the total area) | 10.5 (km$^2$) | 3.5 (km$^2$) | |
| Granodiorite and biotitic granodiorite | 21.11 | 0 | (W1) |
| Leucogranite | 50.94 | 70.04 | |
| Sericitic schists | 23.51 | 29.96 | (SM, BR, CP) |
| Slates, lidites and limestones | 2.12 | 0 | (MM) |
| Alluvial zone | 2.05 | 0 | |
| Slope alluvium | 0.28 | 0 | |

## Material and Methods

### Field measurements and chemical analysis

Precipitation data were recorded at 15 min intervals with a tipping bucket rain gage at the meteorological station commissioned in April 1999 at the study site. Streamwater level at Fuirosos has been monitored continuously beginning on 1 July 1999 until March 2002 using a water pressure sensor connected to an automatic sampler (Sigma$^©$ 900 Max). Since September 2000, a similar automatic sampler was used to monitor streamwater level at Grimola. An empirical relationship between discharge and streamwater level was obtained in each site using the “slug” chloride addition method in the field (Gordon et al. 1992). Runoff coefficient (RC) was estimated for each storm event monitored in Fuirosos and Grimola streams during the study period.

Streamwater samples were taken at least once every ten days (except during the cessation of flow in summer) from September 1999 to March 2002 at Fuirosos, and from September 2000 to March 2002 at Grimola. At both sites, the automatic sampler was programmed to start sampling at an increment in streamwater level of 2-3 cm, and water samples were taken during the rising and the recession limb of the hydrograph.

In order to know the water chemical composition of different mineral assemblages present at the Fuirosos Stream Watershed, water from springs and groundwater wells was sampled when possible. During the period of study, water from 4 springs was sampled several times a year at the point of discharge: Brinxa (BR), Santa Maria (SM), Can Preses (CP) and Sant Martí del Montnegre (MM). All the springs were located at the top of the ridge, coinciding with the geological boundary between granite and slates (Figure 6, pp 59). The BR, CP and SM spring were located in the area underlained by sericitic schists, while the MM spring was draining a silicic slates area accompanied by lidites and limestones (Table 5.1). Groundwater from the granodiorite and biotitic granodiorite area was also sampled from a well (W1) located upland at 250 m from the Fuirosos riparian zone (Figure 6, pp 59).

All water samples were filtered through pre-ashed GF/F glass fibre filters and stored at 4 ºC until analysed. Chloride ($Cl^-$) and sulfate ($SO_4^{2-}$) were analysed by capillary electrophoresis (Waters$^©$, CIA-Quanta 5000 (Romano and Krol 1993). Sodium ($Na^+$), calcium ($Ca^{2+}$) and magnesium ($Mg^{2+}$) were analysed using a Thermo Jarrell Ash ICAP61E inductively coupled plasma optical emission spectroscopy (ICP-OES) (Thermo Jarrell Ash Corporation, Franklin. MA, USA). Potassium concentrations were undetectable at the precision level used for detection of the other cations (i.e., 1 mg $l^{-1}$) (Technical Service of the University of Barcelona, personal communication) and thus, this element was not included in the present study. Carbonate ($CO_3^{2-}$) and bicarbonate ($HCO_3^-$) concentrations were estimated by subtracting the sum of anions to the sum of base cations.

## Data analysis

Statistical analyses were conducted to explore whether a significant difference existed in runoff coefficients and in stream solute concentrations between Fuirosos and Grimola. Differences in solute concentrations along different seasons (i.e., autumn, winter and spring) were also examined. Non-parametric tests were used when comparing data sets because concentrations showed a scattered and skewed distribution (i.e., Wilcoxon rank-sum test for non-paired data, and Wilcoxon signed-rank test for paired data). A difference between two groups was considered significant if $p < 0.01$. The 75th percentile minus the 25th percentile (i.e., the interquartile range) was considered a measure of dispersion of data. Correlation between pairs of solutes was calculated as the Spearman Rank Correlation Coefficient ($r_s$) (Helsel and Hirsch 1992).

To investigate whether the temporal variability for a given solute was similar between the two sites, Fuirosos stream daily concentrations were plotted against those measured at Grimola. Correlation between concentrations measured in each site was calculated as $r_s$. A positive and strong correlation was understood as an indication of a similar temporal pattern in both sites, whereas different temporal dynamics would be indicated by a weak or a nil correlation.

A classical Piper diagram was used to visualize differences in water chemistry among streams and groundwater (Piper 1944). Quantitative measures of similarity between Fuirosos and Grimola were performed by means of a multilinear approach as described by Hooper (2003). A mixing space was defined by means of a Principal Component Analysis (PCA) using the ions data set from Fuirosos stream. Fuirosos was considered the reference site because (i) was the most well characterized stream and (ii) the Grimola drainage area was integrated in the Fuirosos watershed. Chemical data from the Grimola stream were compared against chemistry at Fuirosos by projecting the former into the mixing space defined by the eigenvectors of the later. In this way, differences in stoiquiometry were visualized, similarly to a classical Piper plot. In addition, the residuals between projected and original values were examined in order to measure the degree of similarity between the reference site (i.e., Fuirosos) and the other catchment of interest (i.e., Grimola) by means of two measures of fit: the relative root mean square error (RRMSE) and the relative bias (RB). For each solute *j*, RRMSE is defined as:

$$RRMSE_j = \frac{\sqrt{\sum_{i=1}^{n}(\hat{x}_{ij} - x_{ij})^2}}{n \cdot \bar{x}_j} \cdot 100, \tag{5.1}$$

being *n* the number of samples, $\bar{x}$ the average concentrations for the solute *j*, and $\hat{x}$ and $x$ the expected and measured concentrations, respectively. In its turn, the RB (%) for solute *j* is defined as:

$$RB_j = \frac{\sum_{i=1}^{n}(\hat{x}_{ij} - x_{ij})}{n \cdot \bar{x}_j} \cdot 100. \tag{5.2}$$

The bias will always be zero for a site projected into a subspace defined by its own eigenvectors, as for the reference site. Positive biases (RB > 0) indicate that the model overestimates solute concentrations, while negative biases (RB < 0) indicate that the model underestimates solute concentrations. If a given stream has a similar stoiquiometry to that observed in the reference site, the RRMSE of both sites would be similar and the bias between observed and simulated values will be close to zero. In such a case, differences in solute concentrations could be attributed just to differences in the water residence time. By contrary, as RB and RRMSE differ from values estimated at the reference site, differences in stream chemistry between both catchments might be attributed to other factors than the residence time of water, for example to differences in lithology or in rock weathering processes.

Linear regression was used to explore the relationship between pairs of variables (e.g., residual concentrations and measured concentration). The best fit line through the data was determined by least squares and the significance of the regression was tested by analysis of variance (Zar 1984). To test the equality of two regression coefficients or slopes a Student's t-test was used (Zar 1984).

## Results

### Hydrology

The amount of precipitation (P) during the water year (WY) 1999-2000 in the Fuirosos stream subcatchment was equal to 525 mm. The median discharge at Fuirosos stream was 16 l $s^{-1}$ and there was a summer drought period with no streamwater flow. During the WY 2000-2001, the amount of P was 753 mm. Because discharge at Fuirosos was in average 7.5 times higher than at Grimola, specific discharge (l $s^{-1}$ $km^{-2}$) was used for comparison purposes rather than discharge (l $s^{-1}$). During 2000-2001, the median specific discharge was 1.8 and 0.5 l $s^{-1}$ $km^{-2}$ at Fuirosos and Grimola, respectively. There was not streamwater flow during the summer period at Fuirosos, nor at Grimola. Occasionally, summer storms produced a sustained water outflow (i.e., for several days) only in the Grimola subcatchment. In both cases stream flow was recovered after September storms. Finally, annual P during the WY 2001-2002 was 871 mm, 44 % of which fall during May and April. Likely because of such a wet spring none of the two streams dried up during the summer months in 2002. Median specific discharges during 2001-2002 were 1.2 and 1.1 l $s^{-1}$ $km^{-2}$ at Fuirosos and Grimola respectively.

During the study period, runoff coefficients (RC) from 54 and 21 storm events were recorded at the Fuirosos and Grimola catchments respectively. Median RC ± interquartile range (IQR) was similar at the two sites (1.3 % ± 4.8 at Fuirosos and 2 % ± 6.6 at Grimola; Wilcoxon test, $p > 0.05$). Highest values were recorded during severe storm events ($P > 100$ mm) at the largest catchment (i.e., Fuirosos). For example, RC was 71.3 % during a storm in January 2001 ($P = 130$ mm) and 76.2 % during one recorded in May 2002 ($P= 150$ mm). However, the RC during January 2001 at Grimola was only 18.6 %. Aside from such extreme cases, RCs estimated at Fuirosos were similar to those estimated at Grimola (Wilxocon signed-rank test, signed rank = -24.5, d.f. = 18, $p > 0.01$).

In general, rainfall *vs.* runoff data fall well below the 1:1 line (Figure 5.2). During the main part of the hydrological year, Fuirosos and Grimola showed a significant and positive relationship between rainfall and runoff (Figure 5.2, white symbols). Further, the slope of both regressions was similar (t-test, $t = 0.49$, $p > 0.05$). However, September storm cases at Fuirosos (Figure 5.2, black circles) fall far from the consistent trend showed by the other measurements.

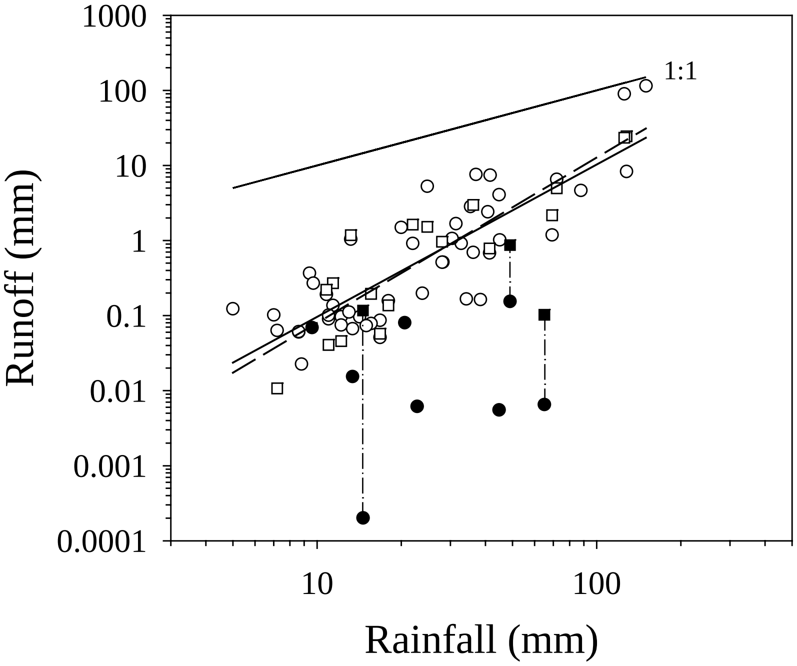

**Figure 5.2**. Relationship between rainfall (mm) and runoff (mm) for 54 events monitored in the Fuirosos catchment (circles) during 1998-2002 and 21 events monitored in the Grimola catchment (squares) during 2000-2002 in the Montnegre-Corredor Natural Park (Catalonia, NE Spain). Black symbols correspond to September events in Fuirosos (circles) and Grimola (squares) respectively. The dash-dot lines connect September storm events monitored in the same day in each of the two catchments. The lineal regression between the amount of rainfall and runoff (only white symbols) is shown for Fuirosos and Grimola data (solid and dashed lines, respectively) (for Fuirosos: $r^2 = 0.7$, $p < 0.0001$; for Grimola $r^2 = 0.78$, $p < 0.0001$). The 1:1 line is also shown.

Daily specific discharge in Fuirosos and Grimola streams showed a positive and significant, though moderate, relationship ($r_s = 0.49$, $p < 0.0001$) (Figure 5.3, black crosses). Divergences from this relationship were mainly detected during September 2000 (Figure 5.3, white circles) and in particular, during September 2001 (Figure 5.3, grey circles) when specific discharge at Grimola was in average 56 times higher than at Fuirosos stream. Differences between both sites were also detected in June 2001 during the drying up period (Figure 5.3, white squares), when the ratio between Grimola and Fuirosos specific discharge increased from 0.3 (the 26th of May) to 6.7 (the 14th of June). In contrast, during June 2002, when the Fuirosos and Grimola streambeds did not dry up, specific discharges were similar at the two sites (Figure 5.3, grey squares).

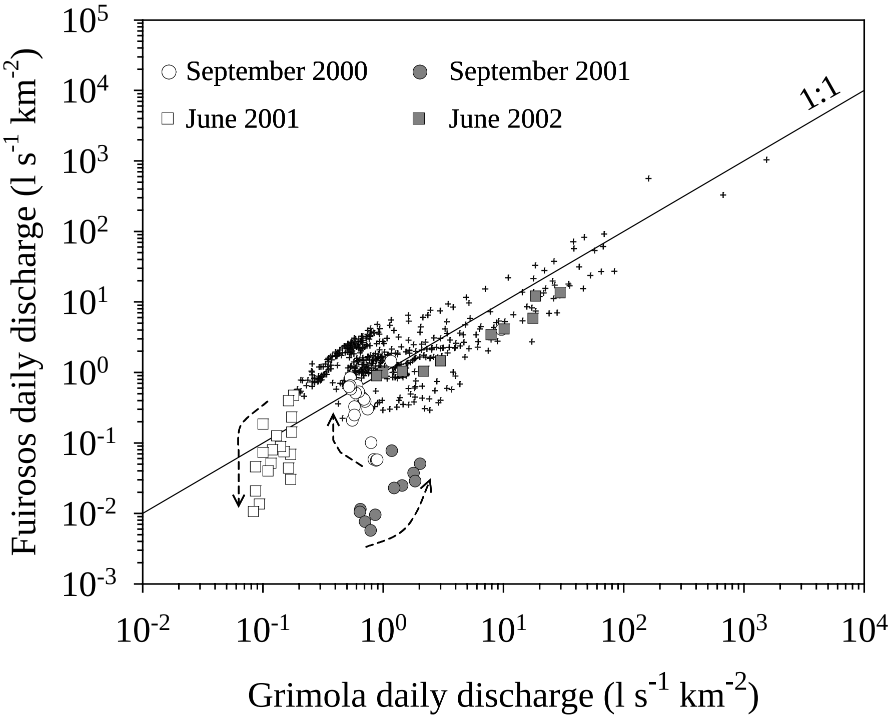

**Figure 5.3**. Relationship between Grimola and Fuirosos average daily specific discharges ($l\ s^{-1}\ km^{-2}$) during the period (2000-2002) in the Montnegre-Corredor Natural Park (Catalonia, NE Spain). September and June samples are indicated with different symbols: September 2000, white circles; June 2001, white squares; September 2001, grey circles; June 2001, grey squares. Arrows indicate the temporal evolution of samples. The 1:1 line is also shown.

### Solute chemistry in streamwater

Solute concentrations were not significantly different between winter and spring (for all cases, Wilcoxon test, $p > 0.05$). Thus, in alias of simplicity winter and spring were considered a unique period, hereafter the *wet period*. In all cases, solute concentrations were higher in autumn than in the wet period in both Fuirosos and

Grimola streams (Table 5.2). During the wet period, $Ca^{2+}$ and $Mg^{2+}$ concentrations were higher in Fuirosos than in Grimola, while $Cl^-$ and $Na^+$ were similar (Table 5.2). Only $SO_4^{2-}$ streamwater concentrations were higher at Grimola than at Fuirosos (Table 5.2).

The degree of correlation between daily solute concentrations was used as a measure of comparison of solute temporal dynamics between Fuirosos and Grimola. During the wet period, daily concentrations at Fuirosos showed a moderate or strong relationship against those measured at Grimola in all cases. (Figure 5.4, $Ca^{2+}$ not shown). High solute concentrations occurred in September with the first autumn rain in both sites (data not shown). However, correlation between daily solute concentrations during autumn was nil in all cases (Figure 5.4).

**Table 5.2**. Median concentration ± interquartile range (IQR) (μequiv $l^{-1}$) for the major ions ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) in both Fuirosos and Grimola streams, in autumn and in the wet period during the period of study. The number of cases is shown in parentheses in each case. Different letters indicate significant differences for each solute between autumn and the wet period and between catchments (Wilcoxon rank-test, $p < 0.01$).

| Solutes | FUIROSOS | | GRIMOLA | |
|---|---|---|---|---|
| | AUTUMN | WET | AUTUMN | WET |
| $Cl^-$ | $^a$811 ± 211 (220) | $^b$549 ± 264 (335) | $^c$701± 352 (196) | $^b$551 ± 113 (189) |
| $SO_4^{2-}$ | $^a$687 ± 296 (220) | $^b$375 ± 222 (374) | $^a$741 ± 569 (196) | $^c$422 ± 165 (188) |
| $Na^+$ | $^a$1056 ± 247 (55) | $^b$876 ± 166 (99) | $^a$1066 ± 100 (56) | $^b$817 ± 192 (79) |
| $Ca^{2+}$ | $^a$1166 ± 396 (55) | $^b$987 ± 249 (99) | $^c$922 ± 259 (57) | $^d$652 ± 210 (79) |
| $Mg^{2+}$ | $^a$588 ± 159 (55) | $^b$476 ± 159 (99) | $^c$521± 144 (57) | $^d$349 ± 98 (79) |

In general, the dominant anion in groundwater samples and in streamwater at Fuirosos and Grimola was $HCO_3^-$ + $CO_3^{2-}$, followed by $SO_4^{2-}$ (Figure 5.5). In its turn, $Na^+$ and $Ca^{2+}$ codominated in streamwater and in groundwater collected at the Can Preses spring (CP) and in the W1 groundwater well (Figure 5.5 and Table 5.3). At Brinxa spring (BR) and at Santa Maria del Montnegre spring (SM), $Mg^{2+}$ concentrations were as high as those measured for $Na^+$ or $Ca^{2+}$ (Table 5.3), and thus the proportion of $Mg^{2+}$ was relevant at these two sites (Figure 5.5). In contrast to all other groundwater springs and streamwater samples, the proportion of $Na^+$ at San Martí del Montnegre spring (MM) was low (< 10 %) while the median proportion of $Ca^{2+}$ was 70 % (Figure 5.5).

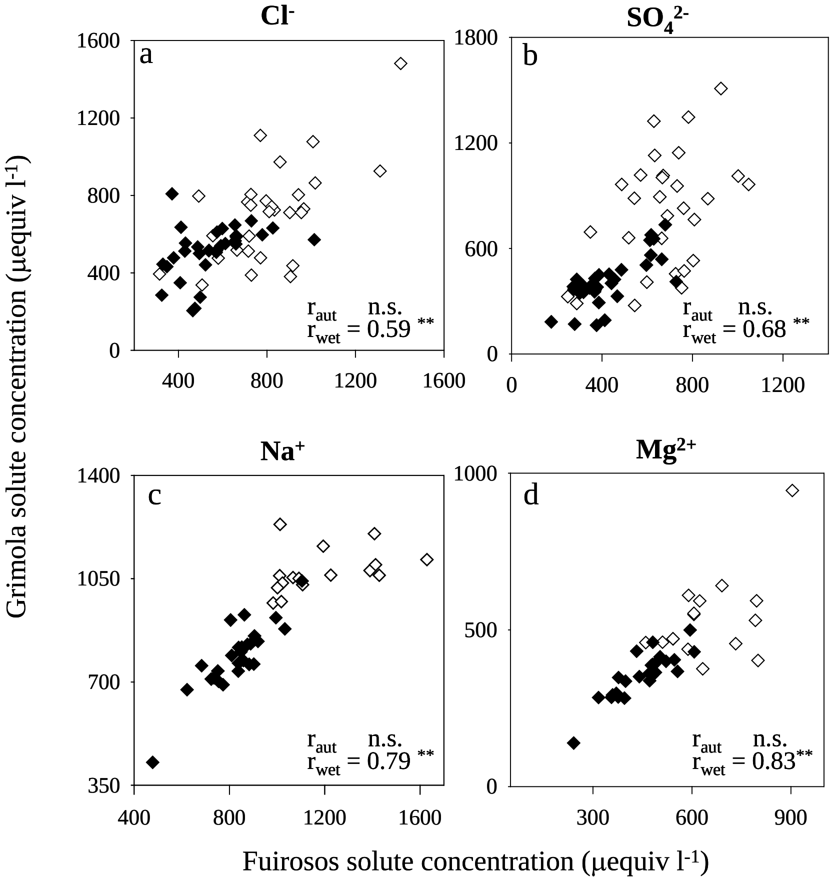

**Figure 5.4**. Relationship between daily concentrations (μequiv $l^{-1}$) in Fuirosos and Grimola streams during autumn (white diamonds) and the wet period (black diamonds) for (a) $Cl^-$, (b) $SO_4^{2-}$, (c) $Na^+$ and (d) $Mg^{2+}$. The $r_s$ is indicated for each solute and for each period. Note that values vary with solutes. n.s. non significant. ** $p < 0.001$.

**Table 5.3**. Median concentration ± interquartile range (IQR) (μequiv $l^{-1}$) for the major ions ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) in springwater collected at the point of discharge of several springs in the Fuirosos Stream Watershed and groundwater collected at the W1 well (located in the hillslope zone, 250 m from the Fuirosos stream channel). The number of samples is shown in parentheses in each case.

| Solute | BR | SM | CP | MM | W1 |
|---|---|---|---|---|---|
| $Cl^-$ | 444 ± 53 (4) | 460 ± 75 (3) | 456± 37 (14) | 723 ± 66 (4) | 782 ± 108 (5) |
| $SO_4^{2-}$ | 169 ± 37 (4) | 171 ± 20 (3) | 255 ± 49 (14) | 1049± 116 (4) | 300± 20 (5) |
| $Na^+$ | 579 ± 22 (4) | 531 ± 13 (3) | 595 ± 30 (14) | 533 ± 13 (4) | 1502 ± 292 (5) |
| $Ca^{2+}$ | 435 ± 10 (4) | 364± 15 (3) | 476 ± 46 (14) | 4744 ± 302 (4) | 2047 ± 230 (5) |
| $Mg^{2+}$ | 595 ± 16 (4) | 393 ± 20 (3) | 292± 31 (14) | 1554 ± 114 (4) | 663 ± 126 (5) |

**Table 5.4**. Spearman-rho coefficient ($r_s$) between each pair of solutes in Fuirosos and the Grimola streams (Catalonia, NE Spain).$^{**}$ $p < 0.001$.

| FUIROSOS | $Cl^-$ | $SO_4^{2-}$ | $Na^+$ | $Ca^{2+}$ | GRIMOLA | $Cl^-$ | $SO_4^{2-}$ | $Na^+$ | $Ca^{2+}$ |
|---|---|---|---|---|---|---|---|---|---|
| $Cl^-$ | -- | -- | -- | -- | $Cl^-$ | -- | -- | -- | -- |
| $SO_4^{2-}$ | $0.69^{**}$ | -- | -- | -- | $SO_4^{2-}$ | $0.84^{**}$ | -- | -- | -- |
| $Na^+$ | 0.21 | 0.21 | -- | -- | $Na^+$ | $0.4^{**}$ | $0.5^{**}$ | -- | -- |
| $Ca^{2+}$ | 0.26 | 0.27 | $0.75^{**}$ | -- | $Ca^{2+}$ | $0.56^{**}$ | $0.78^{**}$ | $0.74^{**}$ | -- |
| $Mg^{2+}$ | 0.22 | 0.25 | $0.9^{**}$ | $0.85^{**}$ | $Mg^{2+}$ | $0.44^{**}$ | $0.65^{**}$ | $0.75^{**}$ | $0.85^{**}$ |

## Streamwater stoiquiometry

In both Fuirosos and Grimola streams, there was a positive and strong relationship between $Cl^-$ and $SO_4^{2-}$, and between $Ca^{2+}$ and $Mg^{2+}$ concentrations (Table 5.4). In both streams, $Na^+$ showed a strong correlation against $Ca^{2+}$ and $Mg^{2+}$. Anions and cations showed a moderate relationship among them in Grimola stream, whereas the correlation between anions and cations was nil at Fuirosos (Table 5.4).

To further investigate differences in stoiquiometry between Fuirosos and Grimola, a multivariant approach was performed. A mixing space was defined by means of a PCA using the correlation matrix obtained with the data set of major solute concentrations from Fuirosos stream. Fuirosos was considered the reference site against which observed concentrations at Grimola were compared. A good model fit was obtained for the reference site (i.e., Fuirosos) using the first three principal components, which accounted for 97 % of the total variance (Table 5.5). This was so because (i) simulated values were similar to observed ones (for all ions, Wilcoxon paired-sample test, $p > 0.02$), (ii) the slope between simulated and observed data was closed to 1 (for all ions, t-test, $p > 0.05$) and (iii) residuals showed no trend (Figure 5.6, left panels). Data from Grimola stream were projected into the reference mixing space defined by the first three eigenvectors of the PCA and the differences between simulated and measured concentrations for each solute were explored (Figure 5.6, right panels). For all major ions but $Mg^{2+}$, the RRMSE was from 1.8 to 2 times higher at Grimola than at Fuirosos (Table 5.5). Biases between simulated values and measured concentrations at the Grimola stream were low (< 15 %). Nevertheless, $Ca^{2+}$ was overestimated (RB > 0)

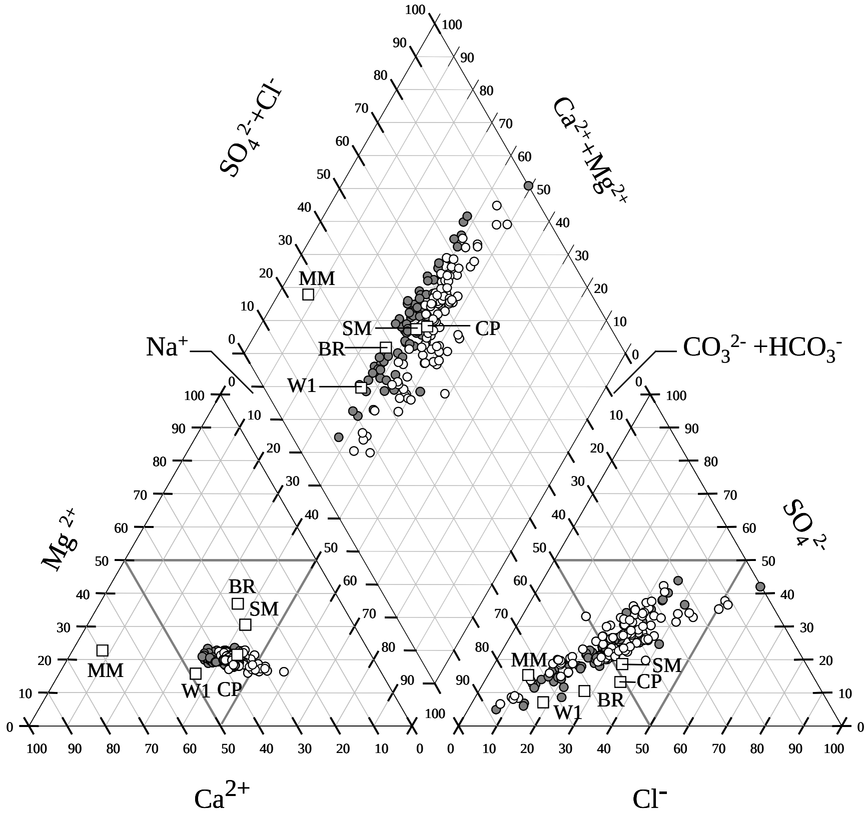

**Figure 5.5**. Piper plot of streamwater major ion concentrations in Fuirosos (grey circles) and Grimola (white circles) during the study period. Squares indicate the median relative proportion of major ions in groundwater (W1) and different springwaters. BR, Brinxa spring; CP, Can Preses spring; SM, Santa Maria spring and MM, San Martí del Montnegre spring.

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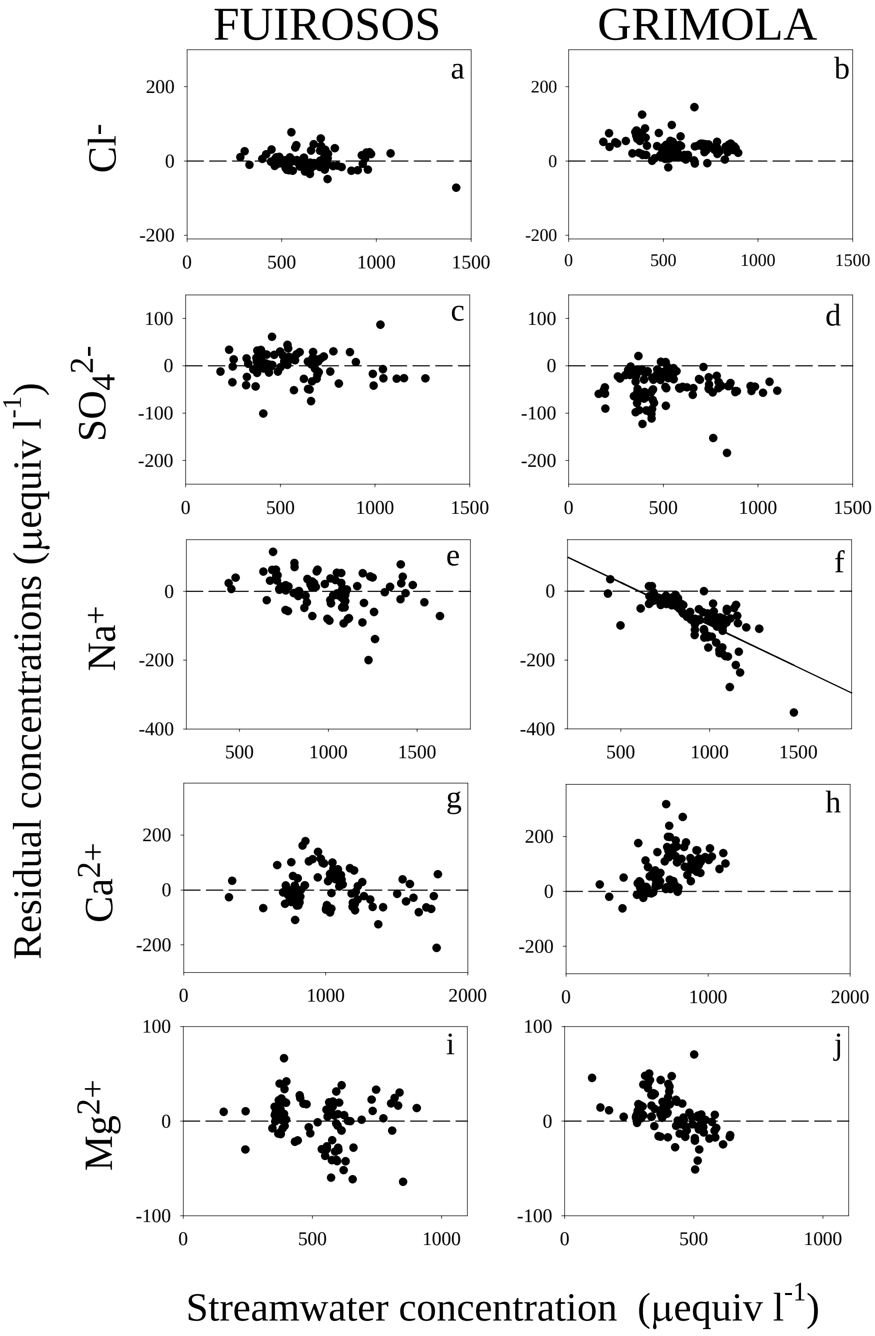

**Figure 5.6**. Residual plots for the Fuirosos (left panels) and Grimola (right panels) catchments after comparison of measured streamwater concentrations (μequiv $l^{-1}$) with those estimated from the model defined by the Fuirosos eigenvectors (see text for details). (a) and (b) for $Cl^-$; (c) and (d) for $SO_4^{2-}$; (e) and (f) for $Na^+$; (g) and (h) for $Ca^{2+}$ and, (i) and (j) for $Mg^{2+}$. Dashed lines show the zero-line. The solid line in panel (f) shows the linear trend between $Na^+$ residual concentration and $Na^+$ concentration for the Grimola stream ($r^2 = 0.53$, $p < 0.001$).

while $SO_4^{2-}$ and $Na^+$ were underestimated (RB < 0) (Table 5.5 and Figure 5.6, right panels). Further, $Na^+$ residuals showed a significant negative slope against Grimola streamwater concentrations ($r^2 = 0.53$, $p < 0.001$) (Figure 5.6f).

**Table 5.5**. Loadings for each solute in the first three principal components obtained by means of a PCA with the data set of major solute concentrations from the Fuirosos stream. The total variance in the data set explained by each factor (%) is shown in parentheses. The relative root mean square error (RRMSE, %) and the relative bias (RB, %) between measured streamwater concentration and values obtained from the PCA model are also shown for each solute ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) and for each stream (Fuirosos and Grimola).

| Solute | PCA results | | | RRMSE (%) | | RB (%) | |
|---|---|---|---|---|---|---|---|
| | U1 (64 %) | U2 (30.6 %) | U3 (2.5 %) | Fuirosos | Grimola | Fuirosos | Grimola |
| $Cl^-$ | 0.35 | 0.6 | -0.6 | 0.38 | 0.72 | 0 | 5.49 |
| $SO_4^{2-}$ | 0.3 | 0.65 | 0.57 | 0.52 | 0.96 | 0 | -7.29 |
| $Na^+$ | 0.5 | -0.28 | -0.43 | 0.55 | 1.04 | 0 | -7.86 |
| $Ca^{2+}$ | 0.51 | -0.28 | 0.33 | 0.67 | 1.34 | 0 | 10.11 |
| $Mg^{2+}$ | 0.53 | -0.23 | 0.16 | 0.5 | 0.5 | 0 | 1.22 |

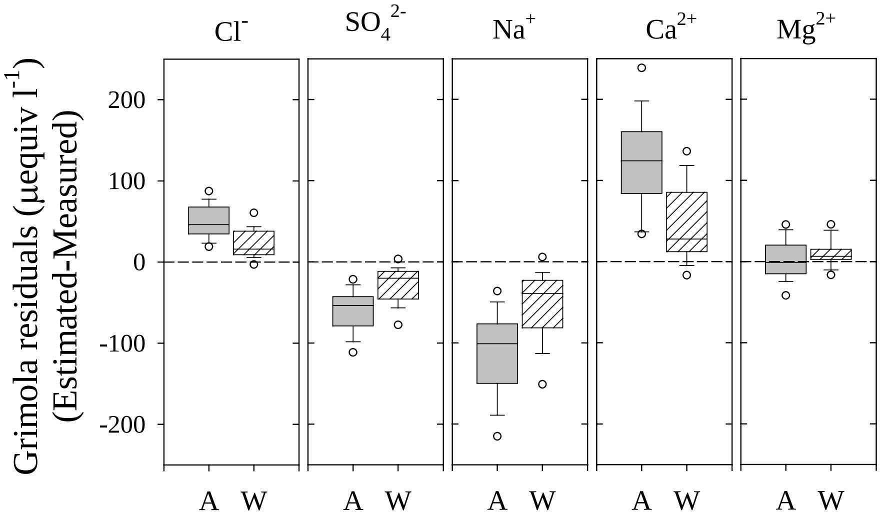

**Figure 5.7**. Box plots of residual concentrations (μequiv $l^{-1}$) measured at Grimola for each solute ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) and for each period after using Fuirosos stream stoiquiometry as a reference. A, autumn and W, wet period.

Because differences in hydrology and solute concentrations were detected in Fuirosos and Grimola catchments between autumn and the wet period, residuals from each period were explored separately to investigate whether differences in stoiquiometry existed between autumn and the wet period. For all solutes, but $Mg^{2+}$, Grimola residual concentrations differed from those estimated at Fuirosos during autumn and also during the wet period (for all cases, Wilcoxon test, $p < 0.0001$) (Figure 5.7). Furthermore, the difference between estimated and measured concentrations at Grimola was larger in autumn than in the wet period (Wilcoxon test for $Cl^-$, $SO_4^{2-}$, $Na^+$ and $Ca^{2+}$, $p < 0.0001$) (Figure 5.7).

## Discussion

### Hydrology

During the wet period, both Fuirosos and Grimola subcatchments exhibited a similar rainfall-runoff relationship and similar runoff coefficients (RC). The rainfall-runoff relationship fall well below the 1:1 line and the median RC at both Fuirosos and Grimola streams was below the 2 %, an indication of an important water deficit in the Fuirosos Stream Watershed. The most significant differences on hydrological behaviour between Fuirosos and Grimola streams were detected during the wetting up (September 2000 and September 2001) and drying up (June 2001) periods. At those moments, specific discharge at Fuirosos was several times lower than that estimated at Grimola, though during the main part of the year specific discharge at Fuirosos was in average 1.3 times higher than at Grimola. Also, the RC during September storms at Fuirosos fall well below the general trend exhibited by the main part of the data. The hydrological behaviour observed at the Fuirosos stream during the wetting and drying up periods, suggests that there might be, in deed, a loss of water, which could be attributed to reverse fluxes (i.e., the stream feeds the near-stream groundwater zone) (Butturini et al. 2002) and/or to a high evapotranspiration demand by riparian vegetation (in particular during spring). In that sense, Bond et al. (2002) have recently shown that in early summer water used by riparian vegetation within only 0.3 % of the basin area, accounted for the flow diel variations observed in streamflow in the Andrews Experimental Forest (OR, USA). In concordance to our results, Shaman et al. (2004) suggested that sand and gravel alluvial zones are capable to store and release water, thus exerting some control on stream flow dynamics. In contrast to Fuirosos, water output during September storm events in the Grimola subcatchment was similar to that expected during the main part of the year (Figure 5.2, black squares). This result together with the fact that at Grimola stream (i) bedrock was visible at some points of the streambed, (ii) there was not an alluvium zone nor a significant riparian area and,

(iii) there was a sustained streamflow during few days after some summer rainfall events, reinforce the idea that the near-stream groundwater compartment at Grimola either may be small or either may have a small influence on regulating streamflow dynamics. Our results also suggest that reverse fluxes do not occur at the Grimola stream.

## Streamwater chemistry

Solute concentrations (volume-weighted) measured at both Fuirosos and Grimola streams were compared to concentrations measured at other small catchments underlained by igneous rocks. Regarding $Ca^{2+}$ and $Mg^{2+}$, concentrations (volume-weighted) measured at Fuirosos (1512 μequiv $Ca^{2+}$ $l^{-1}$ and 733 μequiv $Mg^{2+}$ $l^{-1}$) and at Grimola (624 μequiv $Ca^{2+}$ $l^{-1}$ and 341 μequiv $Mg^{2+}$ $l^{-1}$) were higher than those reported for a small stream draining a 4.3 ha catchment in the Montseny Mountains (Catalonia, NE Spain) (299 μequiv $Ca^{2+}$ $l^{-1}$ and 192 μequiv $Mg^{2+}$ $l^{-1}$) (Piñol et al. 1992) or in the Lysina River (179 μequiv $Ca^{2+}$ $l^{-1}$ and 56 μequiv $Mg^{2+}$ $l^{-1}$) which drained a leucogranite area of 28 ha in the Czech Republic (Krám et al. 1997). In contrast, $Ca^{2+}$ streamwater concentrations in Fuirosos were in the range of those measured at a set of granitic catchments (from 3 to 5 ha) at the Neversink River watershed (NY, USA) (from 973 to 1880 μequiv $Ca^{2+}$ $l^{-1}$) but lower than those reported for $Mg^{2+}$ (from 730 to 1130 μequiv $Mg^{2+}$ $l^{-1}$) (Holloway and Dahlgren 2001). In its turn, $Cl^-$ and $Na^+$ streamwater concentrations (volume-weighted) at Fuirosos (698 μequiv $Cl^-$ $l^{-1}$ and 1350 μequiv $Na^+$ $l^{-1}$) and Grimola (519 μequiv $Cl^-$ $l^{-1}$ and 761 μequiv $Na^+$ $l^{-1}$) were higher than values reported at any of the catchments mentioned before, where $Na^+$ ranged from 90 to 730 μequiv $l^{-1}$ and $Cl^-$ ranged from 39 to 340 μequiv $l^{-1}$. A possible explanation of such high $Cl^-$ and $Na^+$ concentrations may be the proximity of the Fuirosos Stream Watershed to the Mediterranean Sea (about 10 km). Since bulk deposition may be the main source of $Cl^-$ in Fuirosos, this ion can be considered as a tracer of the marine influence in the study site. Na:Cl ratios close to 0.86 would indicate a maritime nature of the $Na^+$ and $Cl^-$ in streamwater. Despite of high concentrations of both solutes at Fuirosos and Grimola streams, only at high $Cl^-$ concentrations Na:Cl fall close to the sea-salt ratio (Figure 5.8), an indication that the relative proportion of ions coming from weathering processes in relation to those with an atmospheric origin might be lower at those moments. Thus, the marine influence in the Fuirosos Stream Watershed was difficult to identify because $Na^+$ measured in streamwater could have either an atmospheric or a weathering origin (mainly dissolution of plagioclases). In deed, $Na^+$ exhibited a strong correlation against $Ca^{2+}$ and $Mg^{2+}$ in both streams (Table 5.3) reflecting that an important fraction of this solute was a weathering product.

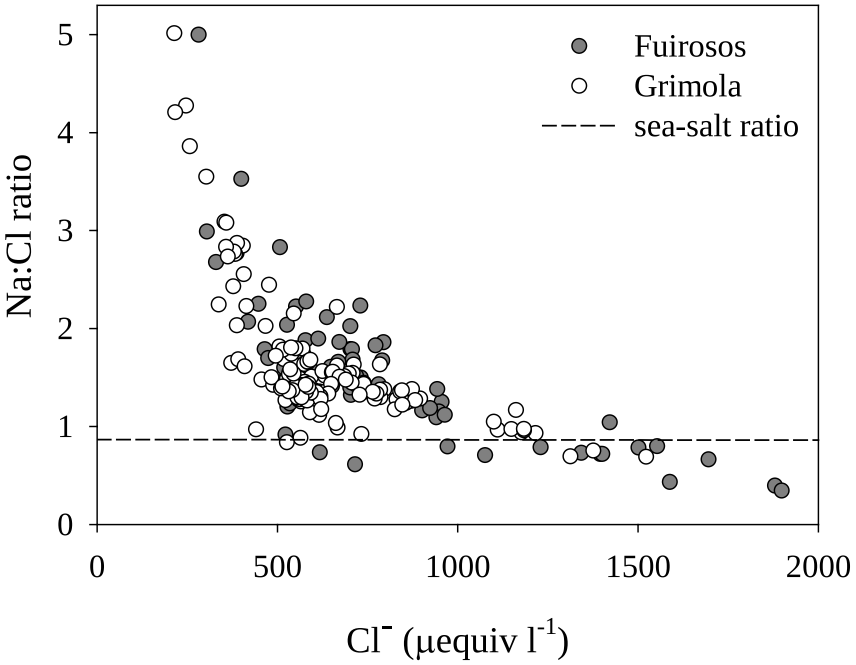

**Figure 5.8**. Relationship between $Cl^-$ concentrations (μequiv $l^{-1}$) and Na:Cl ratios in streamwater at Fuirosos (grey circles) and at Grimola (white circles) in the Montnegre-Corredor Natural Park (Catalonia, NE Spain). The dashed line shows the Na:Cl sea-salt ratio.

Our results showed that chemistry at both Fuirosos and Grimola streams, had a pronounced seasonal pattern. In all cases, water was more ionized during autumn than during the remaining part of the water year. Other studies performed in Mediterranean streams have also reported higher solute concentrations at the beginning of the water year, which could be partially explained by the high concentrating effect of evapotranspiration during the vegetative period (Àvila et al. 1995; Biron et al. 1999; Holloway and Dahlgren 2001). In addition, soil water and groundwater might be enriched in rock weathering products during the drought period because of longer residence time of water in soil micropores (White and Brantley 1995). The temporal evolution of stream solute concentrations during autumn was different between Fuirosos and Grimola, though absolute concentrations were not statistically different in some cases (i.e., $SO_4^{2-}$ and $Na^+$, Table 5.2). Nevertheless, high solute concentrations occurred in September with the first autumn rain in both sites, which may respond to the leaching of solutes accumulated in the streambed and the near-stream zone during the drought period. Such a rapid flushing response has also been reported in other studies performed in Mediterranean regions (Piñol et al. 1992; Àvila et al. 1995; Biron et al. 1999; Holloway and Dahlgren 2001).

During the wet period, the correlation between $Ca^{2+}$ and $Mg^{2+}$ was positive and strong indicating that both solutes came mainly from weathering processes. Results showed that concentrations of both solutes were higher in Fuirosos than in Grimola. Similarly, Wolock et al. (1997) reported that base cation concentration increased with basin size in the Neversink River Watershed in NY (USA). This was attributed to a higher contact time between subsurface water and bedrock as basin size increases. In contrast to the other solutes, $SO_4^{2-}$ was higher at Grimola than at Fuirosos. In addition, this solute showed a strong correlation against $Mg^{2+}$, and in particular against $Ca^{2+}$ in Grimola streamwater samples. Sulfate has predominantly an atmospheric origin, however it can be associated to local sulfide deposits within schists and slates (Rosen and Jones 1998; Holloway and Dahlgren 2001). Thus, such results could be attributed to the leaching of sulfate originated from oxidation of sulfide deposits within the schists, which may enhance depletation of cations from the soil exchange pool. The oxidation of sulfide deposits may have a relative major influence in Grimola than in Fuirosos streamwater chemistry because the outlet of the former was closer to the area underlained by sericitic schists. If so, it could be argued that the potential importance of this bedrock type may be limited to small geographical scales within the Fuirosos Stream Watershed and that its influence on drainage waters might decrease with increases in catchment size. Also, other studies have pointed out that particular hydrogeochemical processes occurring at small catchments may be substituted by key processes at larger scales (e.g., Sivalapan 2003; Shaman et al. 2004).

At Grimola stream, anions and cations showed a moderate or strong relationship among each other, whereas the correlation among them was nil at Fuirosos (Table 5.4). In that sense, some studies have pointed out that alluvial zones can decouple the linkage between the drainage waters from uplands and stream runoff (e.g., Hooper et al. 1998; Hill 2000; Burns et al. 2001). If so, the Fuirosos alluvial zone could be responsible for the lack of correlation observed among anions and cations. To gain some insights on that, we sampled Fuirosos streamwater, alluvial groundwater and groundwater from the W1 well (located at the hillslope, 250 m from the Fuirosos stream channel) several times from October 2003 to January 2004. Groundwater at W1 was considered to be representative of the upland chemical signal at the Fuirosos catchment. Alluvial groundwater was collected from two piezometers located at 5 m and 25 m from the stream channel. Further description of the piezometers setting can be found elsewhere (Butturini et al. 2003). Despite of the few number of samples, this subset of data showed that the relationship between anions and cations observed at the W1 groundwater disappeared once in the alluvial zone (Figure 5.9), thus decoupling the linkage between upland groundwaters and the Fuirosos streamwater.

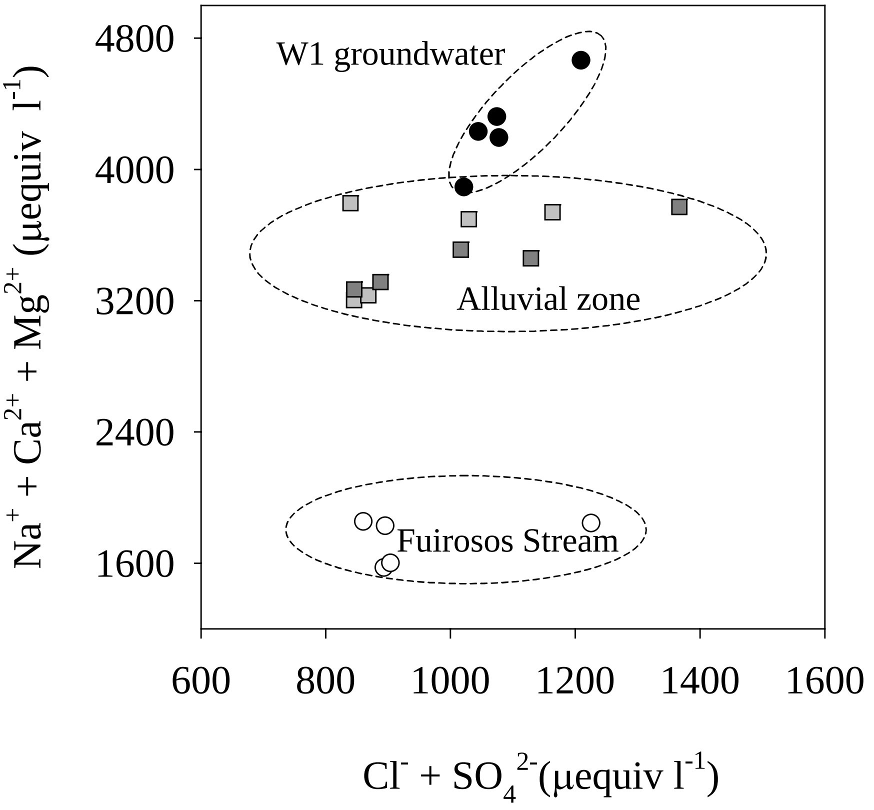

**Figure 5.9**. Scatterplot of anion ($Cl^-$ + $SO_4^{2-}$) *vs.* cation ($Na^+$ + $Ca^{2+}$ + $Mg^{2+}$) concentrations (μequiv $l^{-1}$) measured at the W1 well (250 m from the Fuirosos stream channel) (black circles), at piezometers located in the Fuirosos alluvial zone at 25 m and 5 m from the stream channel (dark grey and light grey squares, respectively) and at the Fuirosos stream (white circles) from October 2003 to January 2004.

### Streamwater stoiquiometry in Fuirosos and Grimola

Holloway and Dahlgren (2001) concluded that streamwater chemistry was similar in four catchments with contrasting bedrock lithologies in the Sierra Nevada (CA, USA) based only on solute concentrations. In contrast, Hooper (2003) proposed that streamwater chemistry is similar when the ratio among solutes is preserved rather than absolute concentrations. In this section we show that stoiquiometry is more useful than absolute concentrations if the goal is to gain insights on the influence of different lithologies on streamwater chemistry.

Overall, the multivariant model showed that for most of the solutes there were little differences on its proportion between Fuirosos and Grimola streamwater samples, as also shown qualitatively by the Piper plot (Figure 5.5). However, $Na^+$ concentrations at Grimola stream were underestimated, while $Ca^{2+}$ was overestimated when using Fuirosos stoiquiometry as a reference (Figure 5.6, Table 5.5). These differences could be mainly attributed to (i) different mineral assemblages or (ii) different weathering rates. Regarding $Na^+$, an additional source would be needed to explain the major proportion of this solute in the Grimola streamwater. This fact would have been difficult to elucidate from the Piper plot (Figure 5.5) or from absolute concentrations since $Na^{2+}$ concentrations were similar in Fuirosos and Grimola streams (Table 5.2). The Grimola watershed was mainly underlained by leucogranite, which has a greater proportion of felsic minerals (i.e., sodium and calcium plagioclases) than granodioritic rocks (which have a major proportion of mafic minerals) (e.g., Hess 1989). Thus, weathering of sodium plagioclases contained in the leucogranite bedrock could be an additional source of sodium to Grimola stream in relation to Fuirosos stream.

In its turn, a major supply of $Ca^{2+}$ in Fuirosos, and consequently a systematic overestimation of $Ca^{2+}$ concentrations at Grimola, could respond to the dissolution of limestones in Fuirosos. Reinforcing this idea, water samples from Sant Martí del Montnegre (MM), a spring draining water from the limestones area, had the highest $Ca^{2+}$ concentrations (Table 5.3) and the highest proportion of this solute (Figure 5.5). In addition, granodiorite and biotitic granodiorite, only present at the Fuirosos catchment (Figure 5.1), had a higher proportion of CaO than leucogranite (IGME 1983). This was reflected in groundwater samples from the W1 well (located at the biotitic granodiorite area), which had a higher proportion of $Ca^{2+}$ than springwater samples from the area underlained by sericitic schists (i.e., BR, SM and CP springs) (Figure 5.5). Several studies have pointed out that calcite ($CaCO_3$) is ubiquitous in granitoid rocks (e.g., Mast et al. 1990; Rosen and Jones 1998) and that its reactivity brings about significant amounts of $Ca^{2+}$ to drainage waters, eventhough tracer amounts of calcite in bedrock. The origin of $Ca^{2+}$ may not be attributed to a specific source and this might well be the reason why $Ca^{2+}$ residual concentrations did not show any pattern against Grimola stream concentrations (Figure 5.6h), which contrasts with the negative trend exhibited by residuals of $Na^+$ (Figure 5.6f ).

Finally, the multivariant approach showed that differences in stoiquiometry between Fuirosos and Grimola were more pronounced during autumn than during the wet period. The fact that Grimola residual concentrations fall closer to zero in the wet period than in autumn indicates that in autumn other processes in addition to lithology might be considered when explaining residual concentrations, otherwise deviations from the reference model would be similar in both periods. As mentioned before, the alluvial zone may be affecting the hydrology and chemistry at the Fuirosos stream, in particular during autumn, which in its turn might be affecting water stoiquiometry too. In particular, differences in stoiquiometry between the two catchments at the beginning of the water year could be attributed to different mineral dissolution rates or soil exchange reactions at the Fuirosos alluvial zone. However, further studies focused on weathering processes and groundwater chemistry during autumn in the Fuirosos alluvial zone would be needed to gain insights on this topic.

## Acknowledgements

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# 6

# Hydrobiogeochemical insights on Mediterranean catchments from the spectral analysis of discharge and chemical time series

**Key words**

Hydrology, Mediterranean regions, nitrate, passive solutes, spectral analysis, time series

## Introduction

Nowadays, water flow and chemical automatic monitoring are more and more common on field studies. These technological developments allow obtaining not only long-term records but also high-frequency (at hourly or sub-hourly intervals) hydrochemical data series. As recent studies have stressed, statistical methods such as cross-correlation and spectral analysis of such data series can help us to elucidate the internal dynamics of catchments across a wide range of timescales (e.g., Feng et al. 2004a; Kirchner et al. 2004).

Several studies have shown that rainfall is highly variable in time, and that its variance between consecutive days is as much as between months or seasons (e.g., Duarte et al. 1999). Because rainfall time series contain a similar amount of variance across time scales, its power spectra (S(f)) usually fluctuates around a horizontal line through the whole range of frequencies (f) (Duarte et al. 1999). In other words, rainfall exhibits a “white noise” pattern (Schroeder 1991). In its turn, stream discharge usually responds rapidly to rainfall inputs, an indication that hydrological signals are transmitted rapidly through the catchment. In concordance, the spectra of streamwater fluxes are flat or almost flat, in particular at low frequencies (i.e., at timescales of several months or more) (Kirchner et al. 2001; Zhang and Schilling 2005). However, the same studies reported that at timescales lower than ca. 3 weeks streamflow spectra show a more or less pronounced attenuation in relation to the rainfall signal. Zhang and Schilling (2005) attributed this observation to a persistent behaviour of stream discharge for hours or days after a rainfall event superimposed on cycles of flow related to seasonal or annual variations of rainfall.

Regarding stream solutes, Kirchner et al. (2000) observed that the temporal evolution of chloride ($Cl^-$) concentrations, a natural passive tracer, was highly damped compared with the rainfall time series in the Hafren stream (Plynlimon, Wales, UK), which was attributed to the authors to the mixing of recent rainfall water with preexisting water stored in the catchment. In contrast to the white noise exhibited by $Cl^-$ concentrations in rainfall, the spectra of stream $Cl^-$ concentrations at the Hafren stream showed strong attenuation (that is, the power S(f) was lower) in relation to the one of rainfall on all wavelengths lower than 5-10 years. The spectral power of fluctuations of stream chloride concentrations showed 1/f noise, or in other words, the relationship between the power S(f) and the frequency (f) followed the scaling law S(f) ~ 1/f. Time series where fluctuations at each frequency scale according to a power law, lack a characteristic timescale (i.e., are scale invariant) and are proper of self-affine processes (Korvin 1992). In light of these results, Kirchner et al. (2000) claimed that catchments act as fractal filters for conservative solutes converting white noise in fractal noise (or 1/f noise). They proposed that simple advection-dispersion processes could give arise to such a phenomenon, based on the idea that solutes landing at the top of the ridge will experience a big dispersion before arriving to the stream channel, while solutes that land near the stream would suffer of little dispersion (Kirchner et al. 2001). Further, Kirchner et al. (2001) demonstrated that as a consequence of that, the travel-time distribution (that is the distribution of times that a population of solute particles took to arrive to the stream) would be a power law, characterized by a long tail, indicating a low-level of solute delivery to streams for a long period of time. Such distributions generate temporal signals that when analyzed in the frequency domain (spectral analysis) show fractal noise (or 1/f noise). Feng et al. (2004b) showed that the power scaling of sodium in the Hafren stream (Wales, UK) also followed a scaling law S(f) ~ 1/f. Recently, Zhang and Schilling (2005) have reported that nitrate concentrations in the Raccoon river (Iowa, USA) also exhibited 1/f scaling.

So far, the phenomenon explained above has been observed in a wide range of humid catchments at Wales (UK), Scandinavia and North America, regardless of lithology or catchment size (Kirchner et al. 2001). However, no one has yet investigated the usefulness of this powerful statistical tool to gain insights on whether processes occurring at particular geomorphological catchment units (e.g., alluvial and/or riparian zones, ponds, wetlands, etc.) are transferred to the stream. The characterization of spectral signals due to particular compartments or landscape units in the catchment may help to discriminate which compartments might be considered when modelling catchment hydrobiogeochemical processes. Such discrimination may be especially relevant in Mediterranean catchments. In contrast to more mesic regions, in Mediterranean zones rainfall is irregularly distributed through the year (e.g., Duarte et al. 1999), soil moisture deficit in the catchment is high during the main part of the year and streamflow is highly variable through the year and in-between years (e.g., Bernal et al. 2004). Hydrological processes governing runoff generation in Mediterranean catchments are not so well understood as in more mesic regions, and as a consequence of that deterministic hydrochemical models developed in regions where water is not limiting as for example the semi-lumped INCA model (Wade et al. 2002) or the semi-distributed TOPMODEL (Ambroise et al. 1996) usually failed when applied to Mediterranean regions (e.g., Piñol et al. 1997; Bernal et al. 2004). Likely, in Mediterranean regions, different catchment areas might be disconnected for long periods of time, that is, hydrological connectivity might be low in Mediterranean catchments, which might decrease flowpath lengths and might affect advection and dispersion of water particles and dissolved solutes in the catchment. Ephemeral and intermittent streams, which are, common in Mediterranean regions, are the paradigm of low hydrological connectivity.

The main goal of the present study was to investigate whether Mediterranean catchments were acting as fractal filters for water and solutes. Streamwater flux and solute concentrations (chloride, sulfate and nitrate) power spectra were explored at Fuirosos and Grimola, two intermittent streams draining a 10.5 km$^2$ and 3.5 km$^2$ area, respectively at the Fuirosos Stream Watershed (Natural Park of Montnegre-Corredor, Catalonia, NE Spain). Both catchments were mainly underlained by granitoid rocks, though only Fuirosos stream had an alluvial zone and a well developed riparian area. In particular our objectives were (i) to investigate whether rainfall and streamflow showed a similar spectral signal for water fluxes and solute concentrations, and (ii) to explore differences between the spectral signals exhibited by passive tracers (chloride and sulfate) and by a highly reactive tracer as nitrate, during both baseflow and stormflow conditions. Finally, spectra obtained at Fuirosos were compared to those measured at Grimola stream in order to elucidate whether hydrological and biogeochemical processes occurring at the Fuirosos alluvial zone might be modifying the spectral signature of streamwater fluxes and solute concentrations.

## Material and Methods

### Field measurements and chemical water analysis

Precipitation data were recorded at 15 min intervals with a tipping bucket rain gage at the meteorological station commissioned in April 1999 at the study site. Hydrological data for the Fuirosos stream is available from 1998 to 2002. Streamwater level at Fuirosos has been monitored continuously using a water pressure sensor connected to an automatic sampler (Sigma$^©$ 900 Max). Since September 2000, a similar automatic sampler was used to monitor streamwater level at Grimola. An empirical relationship between discharge and streamwater level was obtained in each site using the “slug” chloride addition method in the field (Gordon et al. 1992).

Streamwater samples were taken at least once every ten days (except during the cessation of flow in summer) from September 1999 to March 2002 at Fuirosos, and from September 2000 to March 2002 at Grimola. Moreover, the automatic samplers were programmed to start sampling at an increment in streamwater level of 2-3 cm, and water samples were taken during the rising and the recession limb of the hydrograph. All water samples were filtered through pre-ashed GF/F glass fibre filters and stored at 4 ºC until analysed. Chloride ($Cl^-$) and sulfate ($SO_4^{2-}$) were analysed by capillary electrophoresis (Waters©, CIA-Quanta 5000) (Romano and Krol 1993). Nitrate ($NO_3^-$) was analysed colorimetrically with a Technicon Autoanalyser® (Technicon 1976) by the Griess-Ilosvay method (Keeney and Nelson 1982) after reduction by percolation through a copperised cadmium column.

### Spectral analysis of unevenly distributed series and interpretation of power spectra

The Fuirosos chemical data sets include 4 years of measurements taken more or less regularly (ca. each 10 days), with higher-frequency sampling during storm events. The spectral analysis of such unevenly distributed series was made by using the Lomb-Scargle method (Scargle 1982; Press and Rybicki 1989), which has statistical properties similar to those of the conventional Fast Fourier method applied to evenly spaced data (Scargle 1982). Briefly, the Lomb-Scargle method is computed by performing a general linear least squares regression of the unevenly spaced data to a sine/cosine series of different frequencies (Scargle 1982). The appealing feature of the Lomb-Scargle power spectra is that it does not require interpolation of missing data avoiding undesirable bizarre results. The Lomb-Scargle method has been already used to describe fluctuations of natural phenomena as, for example, the natural variability of atmospheric temperature for the last 220 kyears (Pelletier 1997).

The results of a Lomb-Scargle analysis are often portrayed in the form of a power spectrum or Power Spectrum Density (PSD). The spectrum of a signal shows how much power (which is equal to the square of the amplitude) is contained in each of its sinusoidal components of the signal. The total power is equivalent to the total variance of the series and thus, the PSD refers to the partitioning of variation of the time series. The larger the power S(f) at a particular frequency (f), the large its contribution to the total variance in a series. Thus, the obtained power spectra allow the identification of peaks or characteristic frequencies that are responsible for an important part of the total variance in the data series. Furthermore, when dealing with complex time series as those from natural phenomena, the PSD allow us to see the scaling of the power in relation to a range of frequencies that give us information about how fluctuations of the time series (at a given frequency or at a given time scale), are embedded on fluctuations at higher and lower frequencies.

The power spectra of series where successive values are independent (series that do not present short-range, nor long-range correlations) are more or less flat, i.e., the power is independent of frequency and follows the function $S(f) \sim 1/f^{0} \sim 1$. Since all frequencies contribute equally to the variance in the series, “white noise” gets its name from an analogy to white light (Schroeder 1991). In the other hand, “brown noise” represents a series where successive values are correlated, but the directions and magnitudes of change between successive values are not (Schroeder 1991; Middleton et al. 1995). These series show a certain degree of persistence, but have short-memory because there is not a propagation of persistence at larger scales (i.e., there are not long-range correlations). The spectral analysis of such series shows a strong negative relationship between power and frequency, proportional to $1/f^{2}$, with higher frequencies contributing proportionally less to the total variance. An intermediate case is the $1/f^{\beta}$ noise or simply, 1/f noise or “pink noise” that characterizes scale invariant processes. Time series that lack a characteristic timescale are very common in nature from discharge in rivers to seismic waves (e.g., Mandelbrot and Wallis 1969; Feder 1988; Korvin 1992). The 1/f noises are a power law phenomenon and are thus fractal, i.e., the amplitude of the waveform scales in a self-similar way with frequency (Middleton et al. 1995). Power law implies long-tail distributions and thus, fractal time series are an indication of high-memory processes with short-range correlations embedded in correlations at longer scales. In synthesis, for white noises the value of the scaling exponent (or β slope) of the relationship between power S(f) and frequency (f) is $\beta \sim 0$. Power spectra with a scaling exponent $\beta \sim 2$ (i.e., brown noise) indicate a certain degree of persistence or short-range correlations. Power spectra that exhibit a 1/f scaling with $0 \leq \beta \leq 1$ (i.e., fractal noise) are an indication of long-memory processes.

Power spectra can be substantially distorted by spectral aliasing (Feng et al. 2004a). Aliasing artifacts appear when the sampling frequency is lower than needed to represent the maximum period of a data series. In order to avoid aliasing artefacts it is assumed that sampling must be at least more than 1/2 times such maximum period, which is know as the Nyquist criterion. Aliasing introduces artefactual noise by increasing or inflating the measure of the power (or the variance) at the Nyquist limit but also well below it, thus distorting the scaling exponent β of a given power spectrum (Kirchner 2005). Recently, Kirchner (2005) presented a spectral filtering method that corrects the distortions introduced by spectral aliasing, thus recovering the original spectrum and the original $1/f^{\beta}$ noise. In the present study, power spectrum obtained with the Lomb-Scargle method was filtered for aliasing by such method. Finally, power spectra were smoothed using LOWESS (Locally Weighted Scatterplot Smoothing) (Cleveland 1979).

### Data analysis

The short-wavelength (or high-frequency) of the spectra of data series taken more or less regularly with higher-frequency sampling during storm events, such as those chemical series recorded at the Fuirosos Stream Watershed, would be biased towards the catchment behaviour during storm events (Feng et al. 2004a). In order to determine biases caused by storm samples and to be able to discern the spectral signal of hydrobiogeochemical processes occurring either during baseflow or stormflow conditions, spectral analysis of hydrological and chemical data series were performed using (i) the all data set, (ii) only data corresponding to baseflow conditions and (iii) only data corresponding to stormflow conditions. In each case it was estimated the scaling exponent or the $\beta$ slope of the power spectra by a least squares fit and the coefficient of determination ($r^2$) was used as a measure of the strength of the relationship. In the present study, the $\beta$ exponent and the ordinate position of the power spectrum (hereafter, the level of the power), were used for comparison purposes among different periods (baseflow *vs.* stormflow) and catchments (Fuirosos *vs.* Grimola). Calculation of the PSD, the filtered PSD and LOWESS were performed with MATLAB software.

## Results and Discussion

### Discharge temporal dynamics and power spectral signal

During the period of study, rainfall inputs in the Fuirosos Stream Watershed showed an erratic pattern (Figure 6.1, grey lines) and accordingly, its spectrum exhibited a white noise, that is, it was almost flat through the whole range of frequencies (Figure 6.2, grey line). In its turn, streamflow respond rapidly to rainfall inputs in both Fuirosos and Grimola streams (Figure 6.1, black line) and thus, showed a flattened power spectra for a large range of low frequencies (i.e., $0.001 < f < 0.1$ day$^{-1}$, or what is the same, at wavelengths from years to weeks) (Figure 6.2, thick black line). However, at $f > 0.2$ day$^{-1}$ ($t < 5$ days) a break point in the temporal scaling of the Fuirosos discharge appeared and its power started to be attenuated, being proportional to $1/f^2$ ($\beta = 1.9$, $r^2 = 0.96$, $p < 0.0001$) (Figure 6.2a). Such a pattern was clearly related to the duration of the influence of storm events, since the power spectra obtained when analyzing Fuirosos streamflow during baseflow conditions showed a scaling exponent $\beta = 1.4$ ($r^2 = 0.93$, $p < 0.0001$) rather than $\beta \sim 2$ through the whole range of frequencies (Figure 6.2a, blue line).

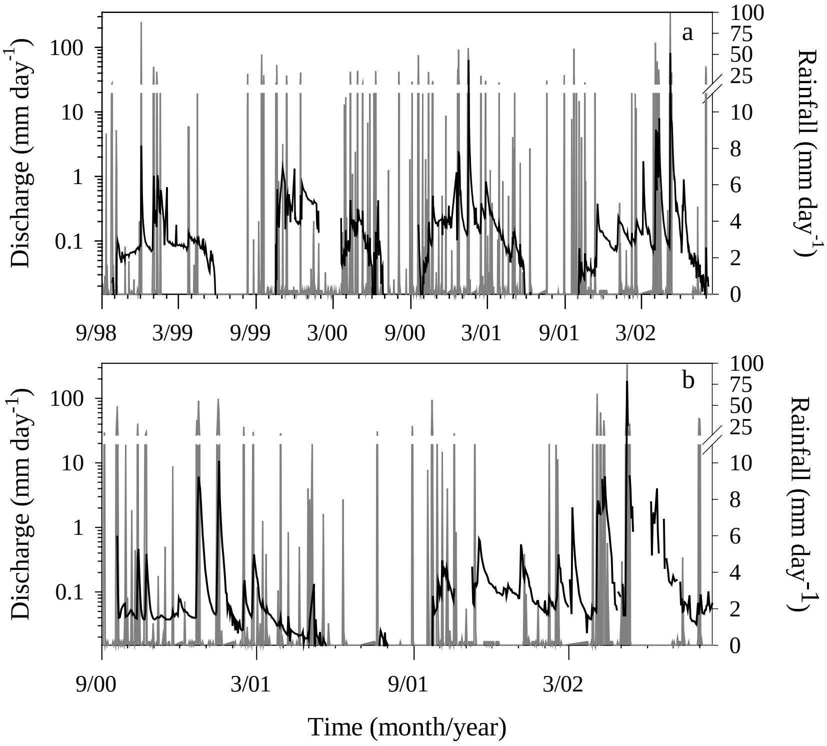

**Figure 6.1**. Temporal dynamics of rainfall (mm day$^{-1}$) (grey line) and discharge (mm day$^{-1}$) (black line) in Fuirosos stream (panel a) and Grimola stream (panel b) at the Montnegre-Corredor Natural Park (Catalonia, NE Spain) during the period of study.

Thus, the influence of storm events provided a certain degree of persistence over short-time periods or short-range correlations (from hours to days) in the Fuirosos streamflow. Similarly to Fuirosos, Zhang and Schilling 2005 have also reported that the Raccoon River, which drains a 8909 km$^2$ in Iowa (USA) (a watershed three orders of magnitude higher than Fuirosos), had a short-medium memory of the storm events spanning from hours to weeks with a slope $2 < \beta < 2.2$. By contrary, at long periods of time (from years to weeks), the pattern of temporal variations of the Fuirosos streamflow exhibited little memory, likely due to an irregular distribution of rainfall through the year and in-between years.

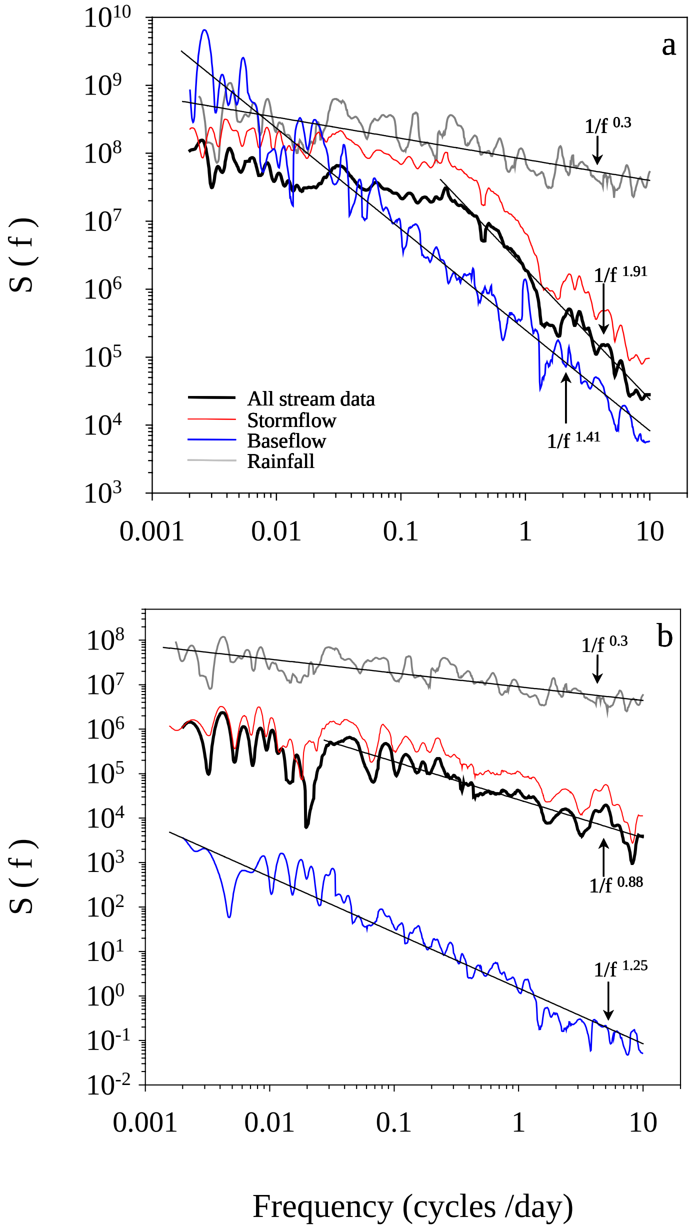

**Figure 6.2**. Power spectra of water fluxes at Fuirosos stream (a), and Grimola stream (b). The power spectra of rainfall was almost flat and had a $\beta = 0.3$ ($r^2 = 0.79$; $p < 0.001$) (grey line). The power spectra of streamwater fluxes (thick black line) at the Fuirosos and at the Grimola streams were attenuated at high frequencies. The blue and red lines in each panel are the power spectra for streamwater fluxes at baseflow and stormflow conditions, respectively. The regression fit and the $1/f^{\beta}$ slope are indicated in each case. In all cases $p < 0.001$.

As observed in Fuirosos, the power spectrum of the Grimola streamflow was almost flat at low frequencies (i.e., $0.0014 < f < 0.03$ day$^{-1}$) indicating that the stream discharge fluctuations were related to rainfall fluctuations over long time periods (from years to months) (Figure 6.2b, thick black line). The Grimola stream discharge had long-range correlations, and contrary to Fuirosos, the noise showed by its spectrum was fractal ($\beta = 0.87$, $r^2 = 0.9$, $p < 0.0001$) at $f > 0.03$ day$^{-1}$ ($t < 33$ days) rather than brown (i.e., $\beta \sim 2$). Kirchner et al. (2001) proposed that fractal scaling in streams could be generated simply by an integration of advection and dispersion processes of spatially distributed rainfall inputs from upslope to near-stream zones. If so, the pattern showed by stream discharge at Grimola would be close to that expected from a system dominated by advection-dispersion processes, whereas at Fuirosos other hydrological processes might be superimposed to the advection-dispersion ones. This could not be directly attributed to differences in the size of the drainage area, since previous studies have reported that catchment size do not affect the stream hydrochemical signal in the frequency domain (Kirchner et al. 2000). Both subcatchments, Fuirosos and Grimola are underlained mainly by granitoid rocks. However, a significant fraction of the Fuirosos catchment is underlained by biotitic granodiorite (21 %), while leucogranite dominates at the Grimola catchment (70 %). Weathering of biotitic granodiorite is more rapid than that of leucogranite (White and Brantley 1995). The presence of biotite in granitoid rocks increases its weathering rate because biotite forms alteration products that occupy a greater volume than the original biotite did. This process causes many localized points of stress within the rock because of the mineral expansion (Birkeland 1999). As a consequence of that, biotitic granodiorite breaks up to form gravel, a phenomenon that is easily observable in Fuirosos by visual inspection. Furthermore, because of such high erodability and regolith desestructuration the average hydraulic conductivity may be higher in Fuirosos than in Grimola. In addition, the Fuirosos alluvial zone may act as an intermediate water storage zone between the hillslope zone and the stream, screening the hydrological signal from the hillslope groundwater. During storms, high hydraulic conductivity at the near-stream alluvial zone (from 4.8 m day$^{-1}$ to 19 m day$^{-1}$, Butturini et al. 2003) may favour the transmission of the pressure pulse generated by a rainfall event. Overall, higher hydraulic conductivy at the biotitic granodiorite hillslopes and at the alluvial zone in Fuirosos may decrease the time needed to transfer the pulse of water through the catchment during storm events in relation to that in the Grimola subcatchment. This might well be the reason why only short-range correlations spanning only from hours to days were observed in the Fuirosos streamwater flux spectral signature (Figure 6.2a, red line).

## Solute temporal dynamics and power spectral signal for passive tracers

For the period of study, $Cl^-$ and $SO_4^{2-}$ concentrations were high at the beginning of the hydrological cycle (i.e., September) and then decreased through the year (Figure 6.3). This annual cycle was well represented in the spectra of both solutes by a very high power at f ~ 0.0027 $day^{-1}$ (i.e., 1 year) (Figure 6.4). Further, the spectral power of stream solute concentrations was above that one of rainfall, contrasting with results obtained at the Hafren stream in Plynlimon (Wales, UK) where the level of the power of rainfall concentrations was always above that one of stream concentrations (Kirchner et al. 2000). At Plynlimon, rainfall $Cl^-$ concentrations ranged between 0 and 30 mg $l^{-1}$, while the average $Cl^-$ concentration at the Hafren

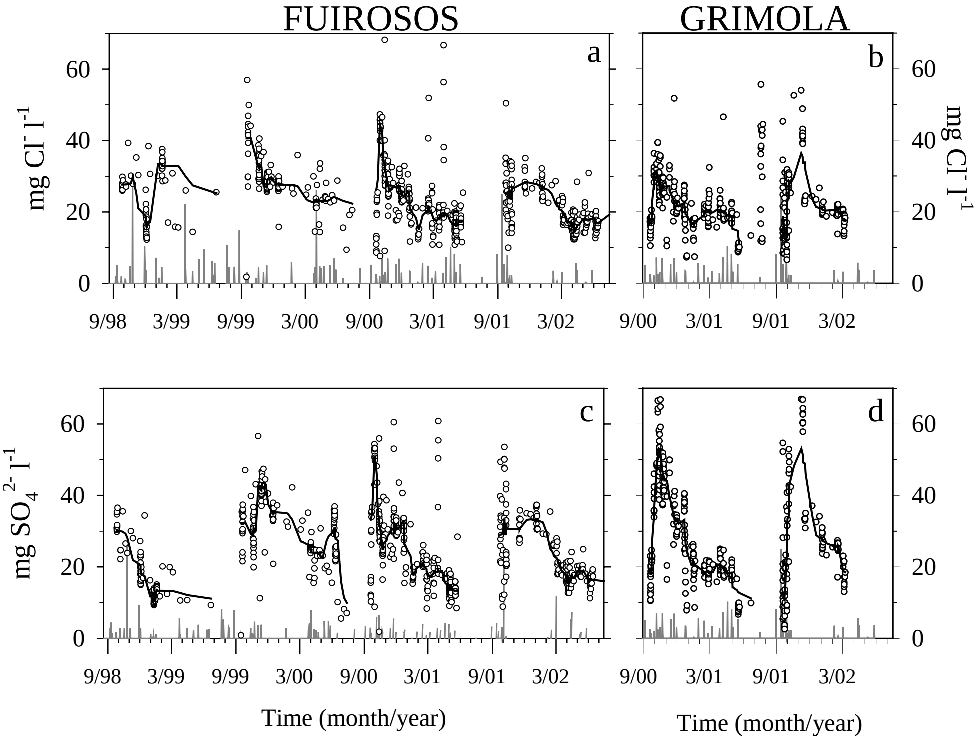

**Figure 6.3**. Temporal dynamics of chloride and sulfate concentrations (mg $l^{-1}$) (white circles) in the Fuirosos stream (panels a and c, respectively), and in the Grimola stream (panels b and d, respectively). Concentrations in rainfall are indicated with a grey line in each panel. The black line is the LOWESS of solute concentrations in each case.

at the Hafren stream was about 6.5 mg l$^{-1}$ (Kirchner et al. 2000). In contrast, at the Fuirosos Stream Watershed, average Cl$^{-}$ concentration in streamwater was up to 22 mg l$^{-1}$, though Cl$^{-}$ concentrations in rainfall ranged between 0 and 29 mg l$^{-1}$ (Figure 6.3). Such a difference in streamwater concentrations between Hafren stream and, Fuirosos and Grimola streams could be explained by the fact that at the Fuirosos Stream Watershed evapotranspiration is the major driver of the water balance (accounting for about the 90 % of the annual precipitation, Bernal et al. 2004), which give arise to the reconcentration of solutes arriving to the catchment by atmospheric deposition.

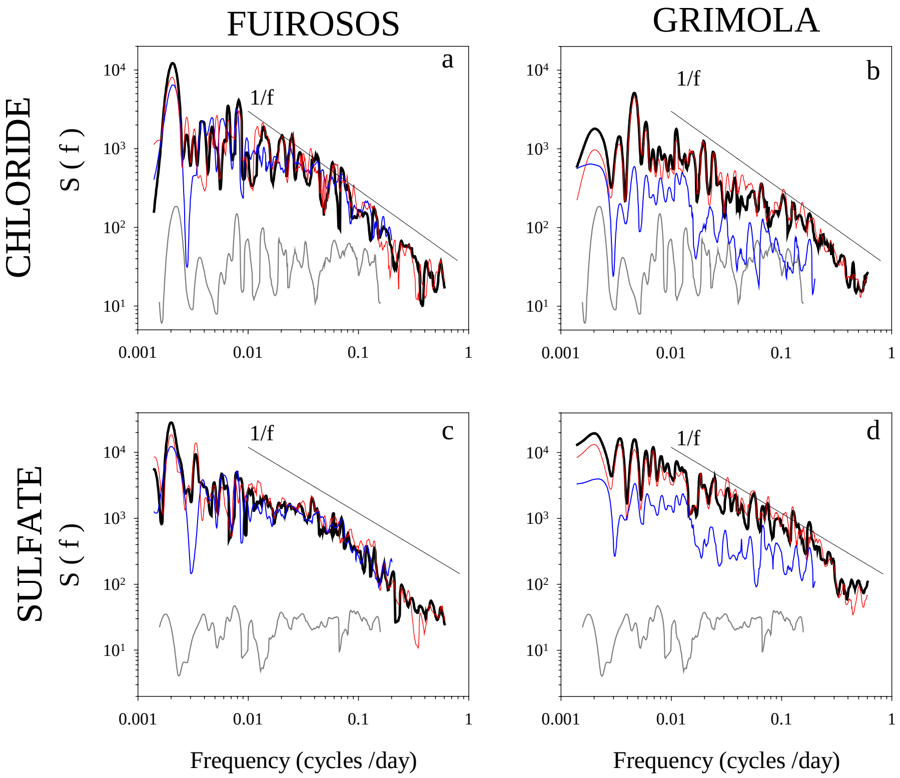

**Figure 6.4**. Power spectra of Cl$^{-}$ and SO$_4^{2-}$ concentrations in the Fuirosos stream (panels a and c, respectively) and the Grimola stream (panels b and d, respectively). Power spectra of rainfall concentrations are indicated in each panel with a grey line. The thick black line in each panel is the power spectra measured for all available data. The blue and red lines are the power spectra measured for data corresponding to baseflow and stormflow conditions, respectively. The 1/f line is shown in each case as a reference. The β slope and the coefficient of determination in each case are shown in Table 6.1.

The ordinate position of the power spectra (i.e., the level of the power) during baseflow and stormflow conditions at Fuirosos stream was fairly similar (Figure 6.4a and c, blue and red lines). By contrast, the level of the power at the Grimola stream was lower during baseflow than during stormflow conditions, an indication that the amount variance related to $Cl^-$ and $SO_4^{2-}$ concentrations during baseflow conditions was lower than during storms (Figure 6.4b and d, blue and red lines). On the other hand, the level of the power spectra was fairly similar between the Fuirosos and Grimola streams (Figure 6.4, note that plots have similar values) suggesting that the amount of variance was equivalent in both cases. This could be an indication that hydrobiogeochemical processes affecting the advection and dispersion of conservative solutes through the catchment may be similar at both sites.

**Table 6.1**. The scaling exponent $\beta$ and the coefficient of determination ($r^2$) of the best-least squares fit of the regression $S(f) \sim 1/f^{\beta}$ for $Cl^-$, $SO_4^{2-}$ and $NO_3$-N in Fuirosos and Grimola streams for baseflow and stormflow conditions. The range of frequencies considered for fitting the regression was $^{(a)}$ $0.01 < f < 1$ and $^{(b)}$ $0.001 < f < 1$. For all cases $p < 0.001$.

| | | FUIROSOS | | GRIMOLA | |
|---|---|---|---|---|---|
| | | $\beta$ | $r^2$ | $\beta$ | $r^2$ |
| $^{(a)}Cl^-$ | Baseflow | 0.81 | 0.81 | 0.71 | 0.58 |
| | Stormflow | 1.09 | 0.85 | 0.88 | 0.86 |
| $^{(a)}SO_4^{2-}$ | Baseflow | 0.81 | 0.77 | 0.64 | 0.51 |
| | Stormflow | 1.28 | 0.9 | 1.05 | 0.83 |
| $^{(b)}NO_3$-N | Baseflow | 0.6 | 0.6 | 1.12 | 0.92 |
| | Stormflow | 1.09 | 0.92 | 1.02 | 0.78 |

The streamflow signal at $0.3 < f < 1$ day$^{-1}$ coincided with the signature measured at stormflow conditions and, in fact, fluctuations at all frequencies were biased towards fluctuations measured for the stormflow data set (Figure 6.4, black and red lines). This is an evidence that the spectral signal of stream data sets containing high frequency sampling during storm events such as those obtained in the Fuirosos Stream Watershed are biased towards the catchment response during stormflow, and thus can not be considered as representative of the average catchment behaviour (Feng et al. 2004a).

The spectra of $Cl^-$ and $SO_4^{2-}$ rainfall concentrations were flat, whereas fluctuations of $Cl^-$ and $SO_4^{2-}$ streamwater concentrations at high frequencies were attenuated in relation to those at low frequencies (Figure 6.4). Further, the temporal scaling of $Cl^-$ and $SO_4^{2-}$ stream concentrations followed the scaling law $S(f) \sim 1/f^{\beta}$, in other words, it was proportional to a 1/f noise (i.e., $0 < \beta < 1$) at Fuirosos and at Grimola during both, baseflow and stormflow conditions at $f > 0.01$ day$^{-1}$ ($t < 100$ days) (Table 6.1). In particular, the scaling exponent $\beta$ measured for passive tracers at Fuirosos was closer to a fractal power law scaling (i.e., $\beta \sim 1$) and showed a stronger least square fit ($r^2 > 0.8$) than the exponent $\beta$ measured at Grimola (Table 6.1). Likely, the fact that at Grimola there was only available a 2-year data set might give arise a more noisy signal than at Fuirosos since there were less cycles, especially at low frequencies. The spectrum of short data sets is more variable than the one obtained from longer data sets because the average spectral signature cannot be measured so accurately (Feng et al. 2004a). Nevertheless, results show that, in general, both catchments were acting as fractal filters for $Cl^-$ and $SO_4^{2-}$ stream concentrations, converting the rainfall white noise in a 1/f signal over time scales ranging from days to months. This result is similar to that obtained from data sets recorded at small humid catchments of different size (from 0.05 to 3.5 km$^2$) and different lithology, from fractured shale at Plynlimon (Wales, UK) to granitic and metamorphic rocks in Scandinavian and North American catchments (Kirchner et al. 2000), which was attributed to the authors to advection-dispersion processes affecting the travel of solutes through the catchment (Kirchner et al. 2001). On the other hand, Haggerty et al. (2002) showed that the residence time distribution at the alluvial zone of a 2nd-order stream at the H.J. Experimental Forest (Oregon, USA) followed a power law suggesting that fractal scaling in streams at short-time scales (that is, at high frequency cycles) could be due to the transport of water throughout the alluvial zone.

Overall, the present study indicates that the property of converting a white noise input signal of a given solute in a fractal output signature also occurs in Mediterranean catchments, though the hydrological connectivity in such catchments is low for long spans of time and the variability through the year and in-between years is very high. Further, this phenomenon was observed at both streams, Fuirosos and Grimola, though the hydrological signal indicated a lack of long-range correlations in the discharge time series, in particular at Fuirosos stream (Figure 6.2). These results suggest that a long-time delivery of solutes occurs, despite of different hydrological processes or preferential water flowpaths in catchments during storms. The essential meaning of such, until now, “ubiquitous” 1/f temporal scaling of solutes in catchments may be that old water dominates the stream hydrograph during storms, regardless of the dominant hydrological processes in the catchment.

### Temporal dynamics and power spectral signal for nitrate

During baseflow conditions, nitrate ($NO_3$-N) described a clear seasonal pattern at Fuirosos: concentrations were higher at the end of autumn and winter and decreased in spring, when biological activity was maximum (Bernal et al. 2005) (Figure 6.5). In concordance, its power spectra for baseflow conditions was high at f = 0.0023 day $^{-1}$ (about 1 year) and f = 0.005 day $^{-1}$ (about half year) (Figure 6.6a, blue line). This was also observed in the Grimola stream power spectrum, that in addition showed a high peak at f = 0.011 day $^{-1}$ (about 3 months).

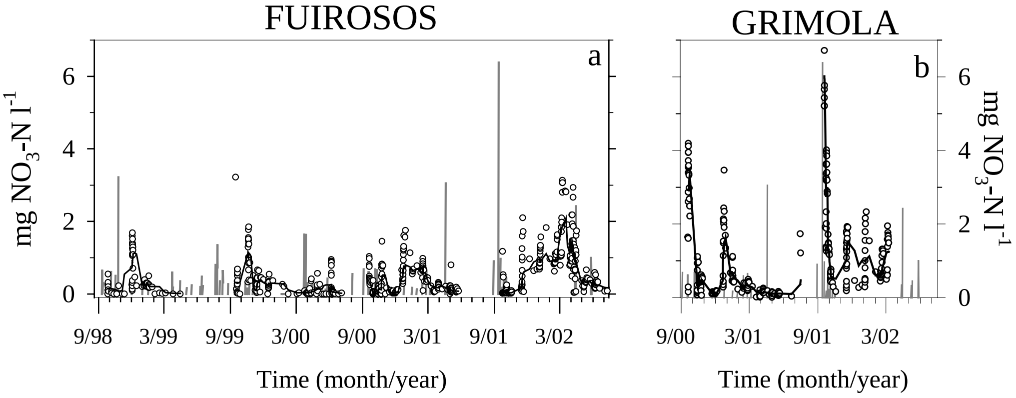

**Figure 6.5**. Temporal dynamics of nitrate concentrations (mg $NO_3$-N $l^{-1}$) (white circles) in Fuirosos stream (panel a) and in Grimola stream (panel b). Nitrate concentrations in rainfall are indicated with a grey line in each panel. The black line is the LOWESS of nitrate concentrations.

Besides, the temporal scaling of $NO_3$-N stream concentrations lacked a characteristic frequency, giving rise to 1/f noises over a range of time scales spanning from days to years. Thus, the $NO_3$-N signature in Fuirosos and Grimola streams was containing long-range correlations, which could be understood as a short-term memory of $NO_3$-N inputs and a long-term memory of $NO_3$-N inputs in the past. In other words, the retention of $NO_3$-N by biota was translated in a more persistent signal of this solute in relation to more passive solutes as $Cl^-$ and $SO_4^{2-}$, which only scaled as a power law over timescales of days to months. This result implies that reactive tracers would be retained in the catchment for longer timescales than passive tracers. Similarly, Zhang and Schilling (2005) have recently showed that stream $NO_3$-N concentrations in the Raccoon River, Iowa (USA) showed fractal scaling and long-tail travel time distributions.

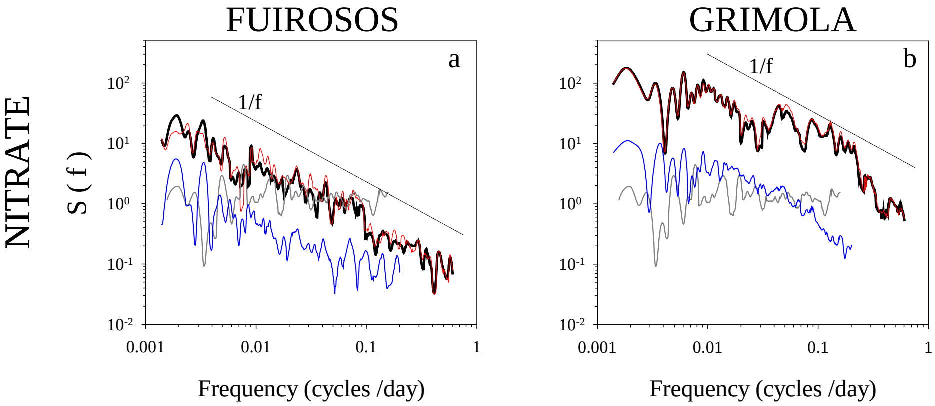

**Figure 6.6**. Power spectra of $NO_3$-N concentrations in Fuirosos stream (a), and Grimola streams (b). Power spectra of rainfall concentrations are indicated in each panel with a grey line. The thick black line in each panel is the power spectra measured for all available data. The blue and red lines are the power spectra measured for data corresponding to baseflow and stormflow conditions, respectively. The 1/f line is shown in each case as a reference. The β slopes and the coefficients of determination are shown in Table 6.1.

In contrast to passive solutes, the level of the $NO_3$-N spectral signal at baseflow conditions was lower than that obtained at stormflow (Figure 6.6, red and blue lines). This was particularly obvious at Fuirosos because the $Cl^-$ and $SO_4^{2-}$ spectra had exactly the same level of power at baseflow than at stormflow conditions (Figure 6.4a and c). This result might be an indication of $NO_3$-N control by biological activity in the catchment, which may hold concentration of this nutrient down damping its variability and retarding its delivery, except during storm events. During storms, water flowpaths may vary in relation to those at baseflow conditions and leaching of nitrate accumulated in the vadose zones might occur. Further, nitrification pulses in soil and groundwater could occur during storms enhanced by the impact of water on soil moisture (Rey et al. 2002) and increasing $NO_3$-N concentrations in the stream.

Finally, although the spatial distribution of bulk deposition of $NO_3$-N at the Fuirosos Stream Watershed might be fairly similar, the level of the spectrum was higher at Grimola than at Fuirosos (Figure 6.6, note that plots have similar units). This result contrasts with what was observed for passive solutes: the level of the spectra was fairly similar between Fuirosos and Grimola for $Cl^-$ (Figure 6.4a *vs.* b) and $SO_4^{2-}$ (Figure 6.4c *vs.* d). This result indicates that fluctuations of $NO_3$-N concentrations were lower at Fuirosos than at Grimola subcatchment, in other words, that the delivery on nitrate was more damped in Fuirosos than in Grimola.

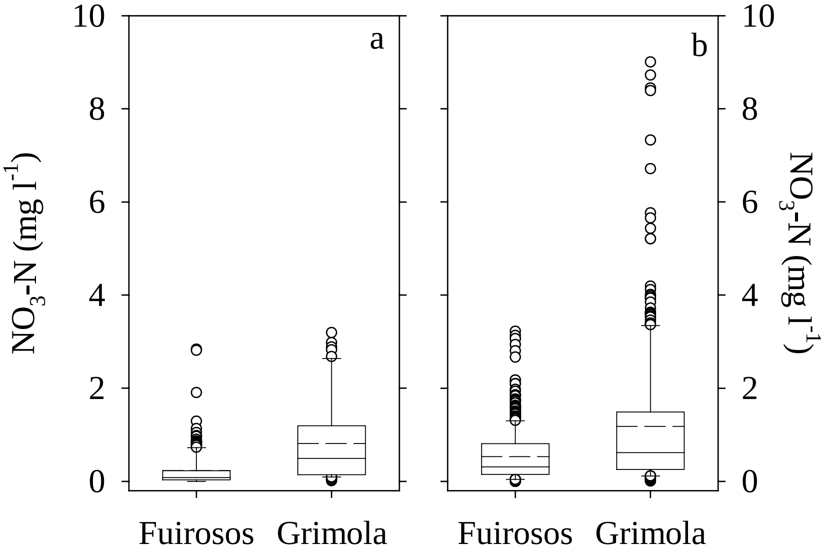

**Figure 6.7**. Box-plots showing nitrate concentrations (mg $NO_3$-N $l^{-1}$) at Fuirosos and Grimola streams during (a) baseflow and (b) stormflow conditions. The centre horizontal line and the dashed line in each box are the median and the average value of concentration, respectively. Fifty percent of the datapoints lie within each box. Boxes indicate the upper and lower quartiles data. The whiskers above and below each box indicate the 10th and 90th limits of the distribution, respectively. Circles are outliers.

However, both catchments were almost totally forested by pine and oak species, though only a Fuirosos stream had an alluvial zone and was flanked by a well developed riparian forest. In that sense, many studies have pointed out riparian zones as nitrate buffering zones in catchments (e.g., Hill 1996). In particular, a previous study performed in the Fuirosos riparian zone showed that nitrate was efficiently removed from the deep groundwater flowing into the riparian zone from hillslope groundwater through sediments with low hydraulic conductivity (Butturini et al. 2003) (though the same study showed that in September, that is, at the beginning of the hydrological year, the riparian zone was a source of nitrate for the stream). Also, many studies performed at the reach-scale have demonstrated that in-stream processes do decrease nitrate concentrations, in particular at low flows (e.g., Martí et al. 1997; Mulholland 2004). The effect of in-stream processes on nitrate concentrations could be enhanced by the near-stream alluvium characteristics. Morrice et al. (1997) showed that the transient storage zone increased with hydraulic conductivity in the near-stream alluvium of three headwaters streams in New Mexico (USA). Larger storage zones implied a higher hydrological retention, attenuating the advective transport of streamwater and thus, favouring the retention of nutrients (Morrice et al. 1997). In light of these studies, the “retarded” delivery of nitrate in Fuirosos in relation to Grimola could be understood as evidence, at the catchment scale, of the effect of the alluvial and riparian zones on buffering nitrate concentrations.

Feng et al. (2004b) reported that the power signal of sodium ($Na^+$) was more damped (i.e., had a lower level) that the one of $Cl^-$ in the Plynlimon watersheds (Wales, UK) due to a chemical retardation of $Na^+$ by adsorption/desorption reactions within the catchments. The retardation factor of $Na^+$ was equal to 2.4-3 and it was estimated from the vertical offset between the $Cl^-$ power spectrum (only affected by advection/dispersion processes during subsurface transport and mixing) and the $Na^+$ power spectrum (affected by advection/dispersion and also by adsorption/desorption processes) (Feng et al. 2004b). Following this idea, we have estimated a “buffer retention factor” ($R_{buffer}$) for $NO_3$-N in the Fuirosos Stream Watershed. To do so, the power of the nitrate signature ($S_{NO3}(f)$) was integrated over the same range of frequencies at Fuirosos and Grimola. One has to keep on mind, that the total power obtained in this manner is equal to the total variance of the signal for the range of frequencies of interest. Then, for a given catchment *x*,

$$P_{NO3,x} = \int_i^j S_{NO3,x}(f)df. \qquad (6.1)$$

Taking into account the available data, the most reliable range of frequencies has been considered to be $0.0027 < f < 0.1$ $day^{-1}$ (that is, from 10 days to 1 year). The $R_{buffer}$ was defined as the ratio between the power for a catchment without buffer zones and the power for a catchment with buffer zones. In our particular case,

$$R_{buffer} = \frac{P_{NO3,Grimola}}{P_{NO3,Fuirosos}} . \qquad (6.2)$$

In the present study, the $R_{buffer}$ was 5.4 and 9 during baseflow and stormflow conditions, respectively. Essentially, this result means that the variance of stream nitrate concentrations was lower in Fuirosos than in Grimola, an observation that is easily visualized from a box-plot (Figure 6.7). However, aside from information on the temporal scaling and the memory of the system regarding the delivery of nitrate, the spectral analysis allowed us to obtain an integrated measure of the fluctuations of nitrate concentrations at different time scales and to quantify the difference between the two time series by means of the $R_{buffer}$. Merot et al. (2003) estimated that at the Fuirosos catchment there was about 3.5 % of potential saturated areas, which corresponded to the main river network and areas located nearly by. Therefore, the $R_{buffer}$ suggests that small portions of the catchment area could have a marked effect on the variance of time series of nutrients such as nitrate. Further research is needed in order to elucidate how different landscape structures shape the $R_{buffer}$. Nevertheless, taking into account that chemical automatic monitoring is each time more common on field studies, the $R_{buffer}$ presented in this study could be used in an immediate future as a measure of the effectiveness of buffer zones (i.e., wetland, ponds, riparian zones, etc.) on retaining nitrate concentrations at the catchment scale.

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# Conclusions

## Summary

**PART I**. The chapters included in this part of the thesis explored nitrogen dynamics in Fuirosos, an intermittent Mediterranean stream. Special emphasis was put on determining the variability of nitrogen dynamics during storms in relation to baseflow conditions and on elucidating climatic, hydrological and biogeochemical factors shaping nitrogen, and in particular nitrate, responses during storm events. In several occasions, the comparison of nitrogen responses against those of dissolved organic carbon (DOC) was used as a tool to gain a better understanding on hydrobio-geochemical processes involved on nitrogen variability.

### Chapter 1. Seasonal variations of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream

1. During baseflow conditions, nitrate ($NO_3$-N) concentrations in the Fuirosos stream were higher during winter months (0.57 mg N $l^{-1}$) than during the rest of the year (from 0.11 to 0.21 mg N $l^{-1}$). Ammonium ($NH_4$-N) concentrations ranged between 0.019 and 0.044 mg N $l^{-1}$ and had a seasonal pattern of change that was opposite to nitrate. Dissolved organic nitrogen (DON) baseflow concentrations did not follow an identifiable seasonal pattern (concentrations ranged from 0.17 to 0.31 mg N $l^{-1}$), while DOC had highest concentration during the months following drought (i.e., after summer) (5.9 mg $l^{-1}$ *vs.* 3.5 mg $l^{-1}$ during the remaining part of the year).

2. During stormflow conditions, DON and nitrate concentrations increased about 1.5 and 9 times in relation to baseflow conditions, but discharge was not a good predictor of nitrogen concentrations. The highest nitrate concentrations were recorded during winter storms (up to 3 mg N $l^{-1}$).

3. DON and $NH_4$ baseflow concentrations showed a positive relationship with DOC only during the months following drought. Also, nutrient concentrations during storms were positively correlated only during autumn. DOC:DON ratios were around 42 (baseflow) and 20 (stormflow) in autumn and then turned to a fairly constant value of 26 during the remaining part of the year. All these results

indicate that during autumn solutes have a similar origin, which is litter accumulated on the streambed and stream edge zones during summer drought.

4. Annual N export during 2000-2001 was 70 kg $km^{-2}$ $year^{-1}$, of which 75 % was delivered during stormflow conditions. The relative contribution of nitrogen forms to the total annual export was 57, 35 and 8 % as $NO_3$-N, DON and $NH_4$-N, respectively.

## Chapter 2. Variability of DOC and nitrate responses during storms in a small Mediterranean forested catchment

5. Nitrate ($NO_3$-N) was mainly mobilized during high flow (from 52 % to 80 % of the annual yield was delivered during storms), while most of the DOC export occurred during baseflow conditions (from 40 to 70 %). Both, $NO_3$-N and DOC concentrations showed a weak or nil relationship against discharge.

6. Factor Analysis showed that antecedent moisture conditions and the magnitude of the storm event were the most relevant factors shaping the hydrological response during storms in the Fuirosos stream (26 storm cases, total variance explained: 63 %). Although storm responses were highly variable, $NO_3$-N concentration changes showed a significant and moderate relationship with the magnitude of the storm event ($r^2$ = 39.7, $p < 0.001$), whereas DOC concentration changes showed a positive, though moderate, relationship with antecedent moisture conditions ($r^2$ = 22.7, $p < 0.05$).

## Chapter 3. Inferring nitrate sources through End Member Mixing Analysis in an intermittent stream

7. Event water, hillslope groundwater, and riparian groundwater were identified as three end members involved in the generation of runoff in the Fuirosos catchment. Chloride, $SO_4^{2-}$ and DOC were used as tracers. Event water had low $Cl^-$ and $SO_4^{2-}$ concentrations (about 4 mg $l^{-1}$ in both cases) and high DOC concentrations (22 mg $l^{-1}$). Hillslope and riparian groundwater had low DOC concentrations (0.5 and 1.4 mg $l^{-1}$, respectively). Chloride and $SO_4^{2-}$ concentrations were higher in the riparian groundwater than in the hillslope groundwater ($Cl^-$: 32 mg $l^{-1}$ *vs.* 16 mg $l^{-1}$ and $SO_4^{2-}$: 28 mg $l^{-1}$ *vs.* 10 mg $l^{-1}$).

8. Streamwater data encompassed the mixing space defined by the three end members only in those storm cases occurred during the wet period (from December to May) (12 out of 25 storm cases). Only in half of these 12 cases a

positive and significant relationship between the proportion of water from a particular water source and stream nitrate concentrations was found. Although, a linkage between hydrological and nitrate sources was established in 6 storm cases, there was not a consistent pattern of a particular end member being a source of nitrate.

9. The effect of near- and in- stream zones on stream nitrate was inferred by comparing predicted nitrate concentrations by EMMA with measured stream nitrate concentration. At discharges below 80 l $s^{-1}$ stream nitrate concentrations were lower than expected from conservative mixing of catchment water sources in 82 % of the cases, indicating nitrate retention in the near- and/or in-stream zones. The trend was the opposite at higher discharges.

## Chapter 4. Calibration of the INCA model in a Mediterranean forested catchment: the effect of hydrological inter-annual variability in an intermittent stream

10. After the calibration of the INCA model for a three-year period with a high inter-annual variability, the coefficients of determination ($r^2$) between simulated and observed data were 0.54 and 0.1 for discharge and $NO_3$-N temporal dynamics, respectively. Ammonium dynamics were simulated poorly and the linear regression between observed and simulated data was not significant statistically.

11. The calibration process was run separately for two contrasting hydrological years: a dry year (total precipitation 525 mm) and a wet year (total precipitation 871 mm). The coefficients of determination for the correlation between observed and simulated discharge for these two periods were 0.67 ($p < 0.0001$) and 0.62 ($p < 00001$), respectively. Nitrate temporal dynamics were not simulated as well as in the dry year ($r^2 = 0.13$, $p < 0.0001$) as in the wet year ($r^2 = 0.56$, $p < 0.0001$).

12. A single parameter set is insufficient to capture the inter-annual variability in the Fuirosos stream. Certain parameters currently fixed in INCA (such as the base flow index or the drainage area) must be treated as variables dependent on soil moisture deficit. This is an essential step before INCA becomes a suitable management tool for arid and semi-arid catchments where water is limiting during long spans of time.

**PART II**. Hydrology and solute concentrations in Fuirosos stream were compared with those observed in its major tributary, Grimola stream. There were three main differences between the two sites: (i) drainage area (10.5 $km^2$ *vs.* 3.5 $km^2$ at Fuirosos and Grimola, respectively) (ii) mineral assemblage and (iii) a well developed alluvial and riparian zone only at Fuirosos. The effect of these three factors on stream hydrobiogeochemistry was investigated.

## Chapter 5. The role of lithology, catchment size, and the alluvial zone on the hydrogeochemistry of the Fuirosos Stream Watershed in the Montnegre-Corredor Natural Park (Catalonia, NE Spain)

13. There was a similar positive and strong relationship between stream runoff and rainfall in Fuirosos and Grimola streams, except during September storms when Fuirosos runoff coefficients were several times below those measured at Grimola. Daily specific discharge during the months before and after the drought (i.e., June and September - October) was several times higher at Grimola than at Fuirosos stream, in particular in September when specific discharge was 56 times higher at the former than at the later. These results indicate that (i) reverse fluxes (i.e., from the stream to the alluvial zone) occur at Fuirosos and (ii) that the alluvial compartment at Grimola is small and has a small influence on regulating streamflow dynamics.

14. Streamwater concentrations ($Cl^-$, $SO_4^{2-}$, $Na^+$, $Ca^{2+}$ and $Mg^{2+}$) at both, Fuirosos and Grimola streams were higher during the months following summer drought than during the remaining part of the year. This result indicates a reconcentrating effect or/and higher weathering rates during summer. Only concentrations of cations originated mainly by bedrock dissolution (i.e., $Ca^{2+}$ and $Mg^{2+}$) showed a significant increase with increasing catchment size.

15. Differences in stoiquiometry between Fuirosos and Grimola streamwater were quantified by analysing residual concentrations obtained from a multivariate model based on Fuirosos stoiquiometry. The model showed that the proportion of both, $SO_4^{2-}$ and $Na^+$ was higher at Grimola than at Fuirosos stream. A higher proportion of $SO_4^{2-}$ is explained by the proximity of the schistic formation to the Grimola outlet. A higher proportion of $Na^+$ is explained by a major proportion of leucogranite (rich in sodium plagioclases) at the Grimola than at the Fuirosos catchment. The model highlighted that the proportion of $Ca^{2+}$ was higher at Fuirosos than at Grimola stream. This is attributed to the presence of limestones only at the Fuirosos catchment.

## Chapter 6. Hydrobiogeochemical insights on Mediterranean catchments from the spectral analysis of discharge and chemical time series

16. The spectral analysis of discharge time series showed certain degree of persistence during stormflow conditions in Fuirosos and Grimola streams, though substantial differences were observed between the two sites. The effect of storm events on Fuirosos stream discharge resulted on short-range correlations ($\beta = 1.9$) detectable from hours to days, whereas at Grimola longer range correlations were observed ($\beta = 0.88$) spanning from hours to weeks. Higher hydraulic conductivities at the alluvial zone and/or at the biotitic granodiorite regolith in Fuirosos decrease the time needed to transfer the pulse of water through the catchment during storms in relation to that in the Grimola catchment causing a lower persistence in the Fuirosos than in the Grimola discharge time series.

17. Time series of passive solutes (chloride and sulfate) exhibited long-range correlations ($\beta \sim 1$) and contained a similar amount of variance (as indicated by a similar level of the power spectra in the ordinate axis) during baseflow and stormflow conditions in both streams, Fuirosos and Grimola. This result indicates that a long-time delivery of solutes occurs in the Fuirosos Stream Watershed and points out that old water dominates the stream hydrograph during storms, regardless of differences on hydrological processes driving runoff generation in each of the two catchments.

18. In contrast to passive solutes, the level of the power spectra of nitrate ($NO_3$-N) in the ordinate axis were lower at baseflow than at stormflow conditions. This result is an indication of $NO_3$-N control by biological activity in the catchment and/or in the stream, which holds concentration of this nutrient down damping its variability and retarding its delivery. In addition, the level of the $NO_3$-N power spectrum at Fuirosos was from 5.4 to 9 times lower than at Grimola at baseflow and stormflow conditions, respectively. This difference is attributed to the buffer effect of the Fuirosos alluvial and riparian zone on $NO_3$-N concentrations. The ratio between the power of nitrate at Fuirosos and at Grimola streams is referred as the "buffer retention factor" ($R_{buffer}$). The $R_{buffer}$ is proposed as a measure of the effectiveness of buffer zones on retaining nitrate concentrations at the catchment scale.

## Concluding remarks

The Fuirosos Stream Watershed, a relatively undisturbed Mediterranean ecosystem that can not be considered a N-saturated catchment, leaks to the stream most of the nitrogen loss in the form of nitrate (57 %). This figure contrast with that reported for other pristine tropical and humid catchments where nitrogen export is mainly in the form of dissolved organic nitrogen. In particular, nitrate is mainly mobilized during stormflow conditions (from 52 % to 80 % of the annual yield). Contrastingly, most of the dissolved organic export of carbon occurs during baseflow conditions (from 40 to 70 % of the annual yield). These results point to a decoupling between soil nitrification and nutrient uptake by biota, which brings about the leaking of nitrate to the stream.

Hydrochemistry in this Mediterranean intermittent stream is highly variable within and in between years. The antecedent moisture conditions and, the magnitude of storm events are key factors on shaping the hydrological responses to storm events. However, storm episodes that occur during similar climatological and hydrological conditions produce different streamwater chemistry depending upon the time of the year. This is so, mainly because of the influence of the summer drought period on solute concentrations in streamwater that has, in deed, a marked effect on the seasonality of solute dynamics. On the one hand, concentrations of anions ($Cl^-$ and $SO_4^{2-}$) and cations ($Na^+$, $Ca^{2+}$ and $Mg^{2+}$) in streamwater are the highest during the months following summer drought (i.e., autumn), likely because of a reconcentrating effect or/and a higher weathering rates during summer. On the other hand, the mobilization in autumn of litter and products from decomposition, accumulated on the streambed and near-stream zones during summer drought lead to a positive relationship among nutrients and to high nutrient concentrations in streamwater (in particular of $NH_4$-N, DON and DOC). During the remainder part of the year (winter and spring), nutrient dynamics in Fuirosos are closer to those reported in temperate humid catchments.

Both the mixing model (EMMA) and the spectral analysis approaches, point out that groundwater is the most important contributor to stormflow in Fuirosos. Nonetheless, the EMMA approach emphasizes how stream water and nitrate sources vary throughout the year. Furthermore, there is not a consistent pattern of a particular end member being a source of nitrate. These results stress the importance of sampling storms during all seasons to draw general conclusions about watershed processes. Regarding nitrate, the mixing model shows that, in Fuirosos, this nutrient is retained by biota in the alluvial zone (either in the stream channel, either in the riparian area) only when streamflows is lower than 80 $l\ s^{-1}$. Above this threshold, the system is not efficient in retaining nitrate arriving from the catchment. This result might be keep on mind when establishing the importance of near- and in-stream processes for regulating catchment nitrate loads since a major fraction of the annual nitrate export usually occurs during stormflow conditions in many catchments. The spectral analysis approach also shows that stream nitrate concentrations in Fuirosos are holded down in relation to concentrations of this nutrient at Grimola stream (an effluent of Fuirosos without alluvial zone). This difference between Fuirosos and Grimola is attributed to the buffer effect that biota has on $NO_3$-N concentrations in the Fuirosos alluvial zone (including both in-stream and riparian processes), which damps the variability of this nutrient and retards its delivery in relation to the Grimola catchment.

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