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Inferring nitrate sources through end member mixing analysis in an intermittent Mediterranean stream

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Abstract We monitored 24 storms during the period 1998–2002 in order to elucidate whether the origin of nitrate could be inferred from water sources in the catchment. The study was performed in the Fuirosos catchment (10.5 km^2) drained by an intermittent stream. Water sources were estimated through end member mixing analysis (EMMA) using chloride, sulfate and dissolved organic carbon as tracers. Three end members were identified in the catchment: event water, hillslope groundwater and riparian groundwater. Streamwater data encompassed the mixing space defined by the end members only during the 12 storms occurred during the wet period (from December to May). Water sources were related to stream nitrate concentrations during 6 of the 12 storms indicating a linkage between hydrological and nitrate sources. However, there was not a consistent pattern of a particular end member being a source of nitrate. EMMA was used to determine expected nitrate concentrations in stream water based on conservative mixing of the different water sources. The effect of the near- and in- stream zones on stream nitrate was inferred by comparing predicted nitrate concentrations to measured stream nitrate concentration. At discharges below 80 l s^{-1} stream nitrate concentrations were lower than expected from catchment sources in 82% of the cases suggesting nitrate retention in the near stream zones. The trend was the opposite at higher discharges.

Keywords EMMA · Intermittent stream · Mediterranean regions · Nitrate sources · Streamwater nitrate · Stormflow generation

Introduction

During the past 15 years, the mixing model or end member mixing approach (Christophersen and Neal 1990; Christophersen et al. 1990; Hooper et al. 1990; Christophersen and Hooper 1992) has been widely used to better understand runoff generation in a number of catchments (e.g. Burns et al. 2001; Soulsby et al. 2003). Generally, these studies have identified pre-event water as the main source of stormflow in a wide number of catchments (Buttle 1994; Hornberger et al. 1998). In contrast, event water usually represents a minor percentage of stormflow, although it is the

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dominant water source at peak flow in some cases (Rice and Hornberger 1998; Brown et al. 1999; Soulsby et al. 2003). Other workers have focused on the interaction between mobile waters on the upslope groundwater and groundwater stored in the valley-bottom area (e.g. McGlynn et al. 1999; Seibert et al. 2003). For example, Burns et al. (2001) concluded that riparian groundwater runoff dominated storm runoff during a storm event at the Panola, Georgia Research Watershed and that hillslope runoff was a minor but significant component of stream runoff at peak flow. These studies have been mainly performed in humid temperate forested catchments. In semiarid catchments, several authors have suggested that the size of runoff contributing areas is highly dependent on soil moisture (e.g. Piñol et al. 1991; Bernal et al. 2004). Stieglitz et al. (2003) recently proposed that for much of the year water draining through a catchment is spatially isolated (i.e., hydrological connectivity is low) and near-saturation from ridge to valley only occurs during storm and snow-melt events when antecedent soil moisture is high. Therefore, in semiarid catchments such as those in Mediterranean regions, hydrological connectivity might be low and hillslope and riparian groundwater might be disconnected for long periods of time.

While some workers have focused only on elucidating hydrological processes governing the generation of runoff in catchments, others have used mixing models to establish links between hydrological and biogeochemical aspects. For example, McHale et al. (2002) proposed a conceptual model of streamflow generation and nitrate release in the Archer Creek (NY, USA) watershed based on results obtained with EMMA models. Other studies performed in agricultural catchments have used nitrate as a tracer when applying mixing models to elucidate where water originated (e.g. Durand and Torres 1996; Soulsby et al. 2003). Flow paths and the spatial distribution of water in the catchment has a role in determining nutrient export, and since water is the medium in which nutrients are transported there should be a relationship between nutrient and water flowpaths. Nevertheless, many studies have shown that, at least during base flow conditions, such a relationship could be altered by processes occurring in the riparian area such as denitrification or uptake by vegetation (Hill 1996; Konohira et al. 2001; Schade et al. 2005), and/or by in-stream and hyporheic processes (e.g. Triska et al. 1989; Martí et al. 1997; Peterson et al. 2001; Mulholland 2004). Indeed, still much can be learned about the hydrological and biogeochemical controls of nitrate transport in near-stream zones (see Cirmo and McDonnell 1997 for a review).

The purpose of the present study was to elucidate whether the route of nitrate could be inferred from the water flowpaths in the catchment, which were estimated through end member mixing analysis (EMMA). The study was performed in a Mediterranean catchment drained by a stream (Fuirosos) with intermittent streamflow and was based on 24 storms monitored during a wide range of climatic and hydrological conditions. The high number of storms used in this study would help us to gain insights into which water and nitrate sources are relevant in this intermittent stream through the year. In particular, the objectives were: (i) to identify the potential hydrological end members contributing to runoff, (ii) to quantify the relative contribution of each end member to stormflow and to highlight whether this contribution was affected by the climatic conditions occurring in the catchment, (iii) to identify the sources of stream water nitrate by comparing the temporal evolution of measured nitrate concentrations with the temporal evolution of stormflow coming from each runoff source during different storms throughout the year. Finally, measured stream nitrate concentrations were compared to concentrations predicted by EMMA to infer the possible effects of near- and in-stream processes on nitrate concentrations arriving from the catchment to the stream.

Study site

Climate

Fuirosos is an intermittent third order stream located in a forested catchment (10.5 km^2) near Barcelona, in northeastern Spain (latitude 41°42′ N, longitude 2°34′, altitude range

50–770 m a.s.l.). The climate is typically Mediterranean, with temperatures ranging from a monthly mean of 3°C in January to 24°C in August. Winter air temperatures below 0°C are infrequent. Average annual precipitation is 750 mm (Ninyerola et al. 2000). The number of days with rain does not usually exceed 70 per year. Only occasional storms occur in summer.

The catchment

Fuirosos (10.5 km^2) is mainly underlain by granite with minor areas of sericitic schists. Leucogranite is the dominant rock type (51% of the area), followed by biotitic granodiorite (21% of the area) (IGME 1983). The catchment is mainly covered by perennial cork oak (*Quercus suber*), evergreen oak (*Quercus ilex* ssp. *ilex*) and pine tree (*Pinus pinea*, *Pinus pinaster* and *Pinus halepensis*) (Fig. 1). In the valley head there is mixed deciduous woodland of chestnut (*Castanea sativa*), hazel (*Corylus avellana*), and oak (*Quercus pubescens*). In Fuirosos, the soils are poorly developed, with a very thin organic O horizon, or more frequently an Ao horizon, that becomes rapidly (in less than 5 cm depth) a B horizon (Bech and Garrigó 1996). The pH is slightly acidic (usually lower than 5.5) and the organic matter content is low, and ranges from 4% at the soil surface to 2% at 10 cm below grounds (Bech et al. 2001). In the granodioritic area, soils are dominated by sand (46%) and fine sand (24%), with smaller amounts of silt and clay (15% each, Sala 1983). Because of the high percentage of sand and gravels, soil humidity is lower in the granitic area than in the sericitic area, especially in summer (Bech and Garrigó 1996). Because of all this features, soils at the Fuirosos Stream Watershed from the hillslope to the valley bottom are usually classified as Entisols (Great Group Xerorthents), Alfisols (Great Group Haploxeralfs), and less frequently as Inceptisols (Great Group Xerochrepts) (USDA 1975–1992) (Bech and Garrigó 1996). Agricultural fields occupy less than 2% of

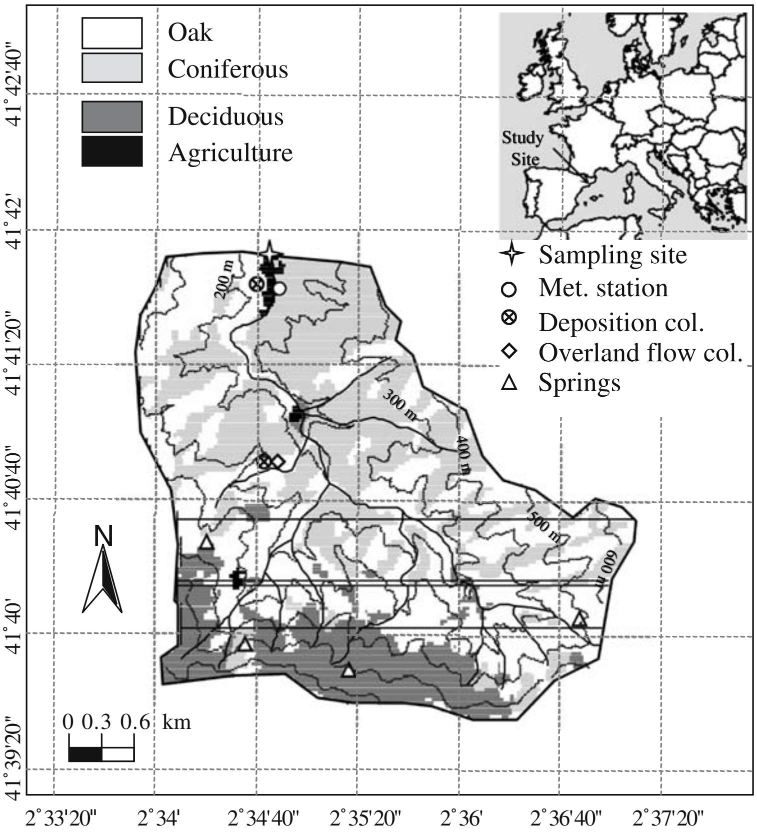

Fig. 1 Geographical location of the Fuirosos catchment (Catalonia, Spain). Main land uses (oak forest, coniferous forest, deciduous forest and agricultural fields) are shown by different shadings. The location of the sampling site, the meteorological station, groundwater springs and the deposition and overland flow collectors is indicated by different symbols

the catchment area and many of them are semi-abandoned. Agricultural practices are traditional and scarce (i.e., production is solely for self-consumption). A well-developed riparian area 10–20 m in width flanks the stream channel (3–5 m width). The riparian soil is poorly developed and the organic matter content in the first 10 cm is low (from 3% to 6%) (Bernal et al. 2003). The Fuirosos riparian soils are classified as sandy soils, Typic Xerochrepts (Bernal, unpublished data).

Hydrology

Streamflow data in Fuirosos are available from 1998 to the present. The present study includes data for four consecutive hydrological cycles (1998–1999, 1999–2000, 2000–2001, 2001–2002), each beginning with the initiation of streamflow in September and continuing through June, when streamflow ceases again until the beginning of the next cycle (Fig. 2). The basal discharge showed a marked seasonal pattern characterized by a long dry period season from June to late September-October, when the first storms occur. During these first events, stream water infiltrates into the riparian zone to a maximum distance of 10 m due to high conductivity sediments in the stream edge zone (Butturini et al. 2003). Average water discharge during the wet period ranged from less than 7 l s^{-1} in spring to 20 l s^{-1} in winter.

Material and methods

Field measurements

Precipitation data were recorded at 15-min intervals at a meteorological station commissioned in April 1999 near the catchment outlet (Fig. 1). Previous precipitation data were provided by the Catalan Meteorological Service for a meteorological station located 5 km from the study site. Two deposition collectors were located in the catchment: one in an open area (bulk deposition collector) and another one in an area cover by oak (throughfall collector). The

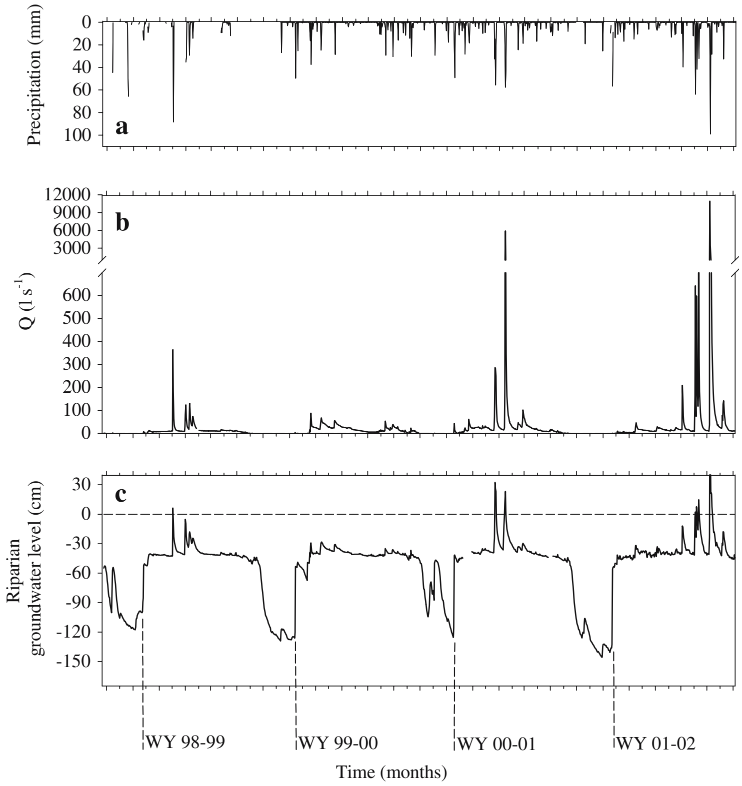

Fig. 2 Temporal dynamics of (**a**) precipitation (mm), (**b**) discharge (Q, l s^{-1}) and (**c**) riparian groundwater level (cm) in the Fuirosos catchment (Catalonia, Spain) during the study period (September 1998–August 2002). The dashed line indicates the soil surface

collectors were constructed of plastic funnels attached to 2 l glass bottles with 2 cm diameter plastic tubing. Samples were collected after each storm event.

Stream water level was monitored continuously since June 1998 using a water pressure sensor connected to an automatic sampler (Sigma© 900 Max). An empirical relationship between discharge and stream water level was obtained using a "slug" chloride addition method in the field (Gordon et al. 1992). Basal streamwater samples were collected from September 1998 to March 2002 at least once every ten days. The automatic sampler was programmed to start sampling at an increment in streamwater level of 2–3 cm. In this way, water samples were taken during the rising and the recession limb of the hydrograph.

Since January 2001, free-flowing soilwater from the upper 5 cm of the soil profile (that corresponded to a very thin O horizon and an Ao horizon) was collected after each storm event. Free-flowing soilwater (thereafter, overland flow) was collected using a 5 m long plastic pipe installed at a depth of 5 cm that drained to a 25 l receptacle. The trench was located close to the throughfall collector in a forest area covered by oak (Fig. 1).

Many studies have suggested that stormflow is generated mainly in the valley bottom while hillslope groundwater may only contribute to runoff generation during high moisture conditions in both, Mediterranean (Piñol et al. 1991; Durand and Torres 1996; Gallart et al. 2002) and temperate catchments (Bazemore et al. 1994; Seibert et al. 2003). Because of that, research in the Fuirosos catchment was focused on two areas, the riparian and the hillslope area to evaluate when these two areas become hydrologically connected. From May 1998 to September 2000 riparian groundwater was collected approximately once a week from a set of 3 wells along a transect parallel to the stream and located at 5.5 m from the stream channel. Wells were made by installing PVC tubes (15 cm) to depths of about 5 m. Wells were uniformly perforated along their entire length. Groundwater was sampled with a peristaltic pump. Prior to groundwater sampling, at least a volume of standing water in the well was removed. Since May 1998, riparian groundwater levels were continuously recorded every 30 min using a water pressure sensor connected to a data logger (Campbell© CR10X) in one of the wells (Butturini et al. 2003). Groundwater representative of the hillslope zone was collected several times a year from headwater springs (550–700 m a.s.l.) at the point of discharge from the ground. The riparian zone was the alluvial deposit in the valley bottom, whereas the area from 500 to 700 m a.s.l. was assumed to be the hillslope zone.

Chemical water analysis

All water samples were filtered through pre-ashed GF/F glass fibre filters and stored at 4°C until analyzed. Chloride (Cl^-) and sulfate (SO_4^{2-}) were analyzed by capillary electrophoresis (Waters©, CIA-Quanta 5000) (Romano and Krol, 1993). Nitrate (NO_3^-) was analyzed colorimetrically with a Technicon Autoanalyser® (Technicon 1976) by the Griess-Ilosvay method (Keeney and Nelson 1982) after reduction by percolation through a copperized cadmium column. All samples except bulk deposition samples were analyzed for dissolved organic carbon (DOC) using a high-temperature catalytic oxidation method (Shimadzu® TOC analyser). Analytical precision for chemical constituents was 0.5 mg l^{-1} for Cl^-, 0.6 mg l^{-1} for SO_4^{2-}, 0.085 mg l^{-1} for DOC and 0.007 mg l^{-1} for NO_3^-. The coefficient of variation for replicates was 3%, 4%, 4.9% and 4.3% for Cl^-, SO_4^{2-}, DOC and NO_3^-, respectively. These values were based on triplicate measurements of a set of 60 samples in the case of Cl^- and SO_4^{2-} and 32 samples in the case of DOC and NO_3^-.

Climatic and hydrological data analysis

During the 1998–2002 period, climatic and hydrological data for 54 storm events in Fuirosos were available. Each storm event was characterized by the following hydrological and climatic variables (see Table 1): the amount of precipitation (P) and the maximum rainfall intensity (PI_{Max}); the time to reach the peak of the event (T_{peak}); the runoff coefficient, that is the proportion of precipitation that appears in the stream after each storm event (RC); the amount of precipitation during 1 day

Table 1 Storms monitored from 1998 to 2002 in the Fuirosos catchment (Catalonia, Spain). Rainfall amount (P) and maximum rainfall intensity (PI_{Max}) are indicated for each storm. The antecedent moisture conditions are indicated for each storm by the antecedent precipitation index (API) and by the rainfall amount during 24 h (Σ1d), 4 days (Σ4d), 8 days (Σ8d) and 32 days (Σ32d) before the start of the precipitation event. The hydrograph shape is characterized in each case by the time to reach the peak of the hydrograph (T_{peak}) and the runoff coefficient (RC). * Indicates chemical data were available

Case	Date	P (mm)	PI_{Max} (mm/h)	API (mm)	Σ1d (mm)	Σ4d (mm)	Σ8d (mm)	Σ32d (mm)	T_{peak} (h)	RC (%)
1[a]	23/09/1998	40	6.8	21	0.2	22.4	22.6	81.7	2	0.39
2[a]	05/10/1998	32	4.8	17.3	2.2	5.2	7	62.4	7.7	0.49
3[a]	03/12/1998	112	11	8.3	4	8.2	8.8	14	17.5	5.28
4	30/12/1998	34	21.2	33.7	3.4	3.4	3.4	95.2	9.5	0.42
5	31/12/1999	31	10.6	33.2	11	42.8	42.8	134.6	10.5	5.34
6	09/01/1999	40.6	6.8	65.8	0.2	0.2	38.2	70	31.3	9.09
7	18/01/1999	20	3.8	69.3	0	0	45.2	115.2	24.3	7.45
8	14/09/1999	44.8	23.2	1.6	7.4	7.4	11.4	14.4	1.5	0.012
9[a]	19/09/1999	25	9.8	31.7	2.6	4.6	55.2	62.2	6	0.027
10	17/10/1999	23.8	14.8	4.1	0.2	0.8	0.8	27.8	5.5	0.83
11[a]	20/10/1999	45	12.6	21.3	0	24.2	24.6	51.2	12.2	2.26
12[a]	12/11/1999	40.8	5.8	19.8	0.2	0.6	1	89.8	12.9	5.91
13[a]	15/12/1999	28.2	2.8	9.8	0	0	0.4	19.4	7	1.82
14	31/03/2000	11	3.4	8.7	0	12.4	18.4	19.8	10	0.92
15	10/04/2000	32.8	4	7.4	1.2	3.4	11.2	41.6	7.8	2.79
16	27/04/2000	30.4	6	9.9	0.2	1.2	8.2	83.4	8	3.49
17	06/06/2000	14.2	8.2	4	0	0	0.6	40.8	4	0.68
18	10/06/2000	30	8	10.9	0	14.4	14.4	55.2	11	0.49
19[a]	19/09/2000	49	30	24.1	22.2	22.4	22.6	49.6	2.5	0.31
20[a]	20/09/2000	9.6	6	68.7	49	71.4	71.6	98.6	7	0.72
21[a]	29/09/2000	13.4	5.8	34.3	0.2	0.4	0.6	107.6	2	0.11
22[a]	13/10/2000	28	4.8	19.5	3	8.4	16.4	115	21.5	1.83
23[a]	21/10/2000	37	8.6	27.2	0.2	0.2	1.4	11.8	8	1.65
24	22/11/2000	9.4	3.8	11.1	0	0.2	0.6	47.4	12	3.9
25	29/11/2000	9.7	9.5	13.4	0	0	9.8	22.6	4.5	2.78
26[a]	21/12/2000	127.6	13	7.2	0.2	0.6	1	3.8	56	6.48
27[a]	12/01/2001	131.6	15.2	42.7	5.6	5.6	6	135.4	44	71.3
28[a]	13/02/2001	15.8	4	27.1	0	0.4	0.4	133.2	8	0.87
29[a]	15/02/2001	9.6	7.6	27.4	18	18.4	18.4	145.6	3.5	1.2
30[a]	24/02/2001	24.2	2.4	23.8	0	0.4	1.6	34.35	37.5	21.23
31	07/03/2001	7	2.8	19.5	0	1.2	4.4	61.2	3	1.45
32	29/03/2001	16.8	10.2	4.6	0	3.2	3.2	40.4	5.5	0.51
33[a]	30/04/2001	8.6	6.6	1.6	0	0	0	29.8	5.5	0.7
34	04/05/2001	12.2	4.2	8	8.6	8.6	8.6	21.4	5.5	0.79
35	18/05/2001	7.2	4.8	4.6	1.6	1.6	2.4	50.4	2	0.88
36	09/06/2001	8.8	2.4	0.3	0	0	0	11	0.7	0.26
37[a]	22/09/2001	65.4	32.8	15.7	0	0	12.4	38	0.5	0.007
38	28/09/2001	14.6	6.8	59.2	0.8	0.8	66.2	104.2	1.7	0.001
39[a]	03/10/2001	10.8	6.6	44.5	0	1.8	15.6	93.4	10.7	1.76
40	09/10/2001	8.6	4	31.8	4.2	4.4	15.2	110.97	4	0.71
41	17/10/2001	16.8	13.4	21.3	0	1.2	10	118.4	1.7	0.3
42	10/11/2001	15.6	9	7.9	0	0.4	0.8	37.2	3.2	0.5
43	15/11/2001	69.3	8.4	16.4	0	16	16.4	42.79	11.7	1.7
44	3/1/2002	22	1.8	6	7.4	7.8	7.8	20	16.5	4.14
45	7/1/2002	5	3	13.4	0.2	6.5	21.7	41.11	1.2	2.46
46	5/2/2002	13.4	7	3.4	0.2	0.4	0.6	22.1	2.7	0.5
47	13/02/2002	11	3.2	9.3	0	0.4	14.2	19.6	2.7	0.82
48	15/02/2002	13.2	1.6	17	2.4	13	13.4	31.6	2.7	7.89

Table 1 continued

Case	Date	P (mm)	PI_{Max} (mm/h)	API (mm)	Σ1d (mm)	Σ4d (mm)	Σ8d (mm)	Σ32d (mm)	T_{peak} (h)	RC (%)
49	1/3/2002	13	3	2.1	0	0	0.2	41.4	4.2	0.86
50[a]	4/3/2002	36.2	8.4	14.3	0	13.2	13.3	54.3	5.2	1.92
51	29/03/2002	12.2	2.8	5.1	0	0.2	0.4	52.08	2	0.61
52[a]	2/4/2002	72	10.6	10.3	0	12.4	12.6	52.02	10.2	9.06
53[a]	6/4/2002	41.6	7.4	59	0	72.4	84.8	122.64	11.2	17.82
54[a]	11/4/2002	37	8.4	66.5	14.2	26.8	109.4	145.56	5.2	20.5

(Σ1d), 4 days (Σ4d), 8 days (Σ8d) and 32 days (Σ32d) before each storm event; and the antecedent hydrological precipitation index (API). The API was calculated for rainstorms to determine the antecedent moisture conditions prior to each storm. The API on a given day (API_i) was calculated as described by Gregory and Walling (1973) and Foster (1978):

$$API_i = K(API_{i-1}) + (P_i - 2\,mm)$$

Where $API_{i\text{-}1}$ is the antecedent precipitation index on the previous day and P_i is the total daily precipitation (mm). To account for interception, 2 mm were subtracted from P_i on each rainy day (Helvey and Patric 1956). K is a recession constant normally reported in the range 0.85–0.95 (Viessman et al. 1989). To account for the marked seasonality of the soil moisture deficit (maximum in summer and minimum in winter) a sinusoidal function was applied:

$$K = 0.9 - (0.05\cos((2\pi/365)d_i - 2.96))$$

Where d_i is the Julian day. In this way, K values ranged from 0.85 on the 21th of June to 0.95 on the 21th of December.

Factor analysis was used to classify the climatic and hydrologic data of the 54 monitored storm events. This method allowed the complexity of the large dataset to be reduced by assuming that a linear relationship exists among the set of variables and a smaller number of underlying "factors". Factors, which are not correlated with each other, are obtained through an eigenvalue analysis of the correlation matrix of the set of variables (Davis 1973; Evans et al. 1996). Each factor explains a percentage of the variance of the full dataset and usually the first few factors explain the bulk of the total variance. Here, we have considered those factors explaining at least as much of the total variance as one of the original variables could explain. The factors selected were then "rotated" using the Varimax method, described by Johnston (1978). The rotated factors explain exactly the same amount of covariance among the descriptors as the initial factors, but certain factor loadings are maximized while others are minimized (Legendre and Legendre 1998, pp 478).

Mixing model analysis and procedures

The mixing model was developed according to the procedure outlined by Christophersen and Hooper (1992), using Cl^-, SO_4^{2-} and DOC as tracers. DOC was used as an indicator of shallow flowpaths, an assumption supported by several studies (e.g. McGlynn et al. 1999; Brown et al. 1999). In particular, a recent study performed in the Fuirosos stream showed that DOC was not available to biota during the winter period (BDOC $<$ 5% of DOC; Romaní et al. 2004), which reinforces the idea that DOC can be used as a conservative tracer in the present study.

A data set was obtained that consisted of the concentrations of the three solutes in 292 samples of streamwater collected at the catchment during 1998–2002. The data were standardized into a correlation matrix and a principal component analysis (PCA) was performed on the correlation matrix. The concentrations of the potential end members were standardized and projected into the mixing space defined by the stream PCA by multiplying the standardized values by the matrix of the eigenvectors. The extent to which the potential end members encompassed the streamwater observations for the monitored rainstorms was examined in the mixing space. When data from a given rainstorm fit on to the space defined by the end members, the contribution of each end member was calculated by solving a mass balance equation. The goodness of fit between solute concentrations predicted by EMMA and measured streamwater concentrations was determined through least-squares linear regression.

Statistical analysis

A Mann–Whitney test was used to examine whether a significant difference existed in stream solute concentrations between baseflow and stormflow conditions. Differences among bulk deposition, throughfall, overland flow and groundwater solute concentrations were determined with a Wilcoxon paired *t* test. For the Wilcoxon paired *t* test only samples collected the same day were used. In both cases, non-parametric tests were chosen because data sets showed a scattered and skewed distribution (Helsel and Hirsch 1992). The difference between two groups was considered significant if $p < 0.05$.

Smoothed curves were used to highlight the pattern and the possible breakpoints between pairs of variables (e.g. between the contribution of an end member and discharge). A moving median was chosen because it is more resistant to outliers than a moving average (Helsel and Hirsch 1992). Breakpoints were estimated by adjusting a bilinear equation following the method described by Muggeo (2003) and using the library segmented within the R package software (Version 1.8.1., R foundation, http://www.r-project.org/).

In order to determine whether or not climatic conditions were affecting the relative contribution to runoff of different water sources, the proportion of each end member predicted by EMMA was correlated against hydrological and climatic variables included in the factor analysis and against each factor extracted after the Varimax rotation. Finally, the estimated proportion of water coming from each source of runoff was used to infer the possible sources of nitrate in the catchment during each storm event. The hypothesis is that if nitrate during a given event originates from one particular source in the catchment, there might be a positive relationship between the proportion of water from this source and the observed streamwater nitrate concentrations. In contrast, a negative relationship between stream nitrate and the proportion of water from a particular source may indicate that it is not a source of nitrate to the stream but has a diluting effect on nitrate concentrations. A weak relationship may indicate that the origin of nitrate is not clearly related to any of the considered sources. The strength of the relationship between the proportion of water from each source of runoff and both climatic variables and measured stream nitrate concentrations was determined by the Spearman's Rho coefficient (*r*). The correlation was regarded as statistically significant if $p < 0.05$. Non-parametric tests were chosen because non-linear relationships could exist among variables.

Results

Hydrological characterization of storm events and groundwater level dynamics

From 1998 to 2002, 54 precipitation events were monitored (Table 1). Precipitation (P) ranged from 5 to 128 mm, although in 50% of the storms, the total amount of rainfall was lower than 20 mm. Only on three occasions was P greater than 100 mm (storm events 3, 26 and 27). The $\mathrm{PI}_{\mathrm{Max}}$ was lower than 10 mm h^{-1} in 74% of the cases. The API index during the study period ranged from 0.3 to 69.3 mm indicating a wide range of antecedent hydrological conditions in the catchment. The RC was lower than 1% in half of the storms suggesting that water deficit was relevant during extended periods of the water year.

The results of the factor analysis showed that the 54 storms were distributed along the axes representing the first two factors of the analysis, which explained 60% of the total variance (Fig. 3). Factor 1 explained the largest proportion of the total variance (35%). The API, Σ1d, Σ4d, Σ8d and Σ32d exhibited a high positive loading (Table 2). Thus, Factor 1 may be regarded as

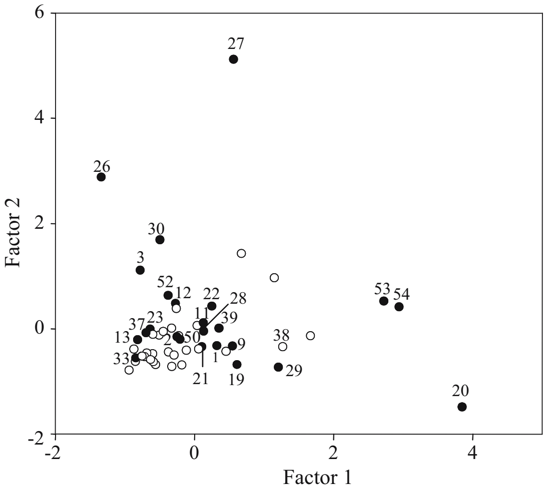

Fig. 3 Plot of the factor scores 1 and 2 from the factor analysis for the 54 storms indicated in Table 1. Factor 1 is related to the antecedent moisture conditions, Factor 2 is related to the magnitude of the event. Black circles represent storms in which chemical data were available. To follow results and discussion some storms are indicated as in Table 1

representing the moisture conditions prior to the storm event, and the storms were organized along a gradient from dry to wet antecedent hydrological conditions. Factor 2 explained 25% of the total variance. The amount of precipitation (P), the time to reach the peak of discharge (T_{peak}) and the runoff coefficient (RC) had a high positive loading (Table 2). Consequently, Factor 2 was interpreted as reflecting the magnitude of the storm event. During the study period, chemical data from 24 out of the 54 storms were obtained. Figure 3 shows that these 24 storms (black circles) were of different magnitude and covered a wide range of moisture conditions in the catchment.

Table 2 Varimax-rotated factor loadings for the indicated climatological and hydrological variables in 54 storm events in the Fuirosos catchment (Catalonia, Spain) measured during four hydrological years (1998–2002). Loadings in the range 0–0.5 are given in parentheses. The total variance in the data set explained by each factor (%) is also shown

	Factor 1	Factor 2	Factor 3
P	(– 40.07)	0.77	– 40.53
PI_{Max}	(0.01)	(0.11)	– 0.86
API	0.85	(0.27)	(0.17)
$\Sigma 1d$	0.67	(– 0.18)	(– 0.4)
Σ 4d	0.79	(– 0.09)	(– 0.28)
Σ 8d	0.88	(0.01)	(0)
Σ 32d	0.72	(0.20)	(0.26)
T_{peak}	(– 0.03)	0.88	(0.01)
RC	(0.22)	0.83	(0.03)
Variance explained (%)	34.8	24.8	15.1

Groundwater levels in the riparian zone were constant from late October until June (between 40 and 50 cm below soil surface) and increased during storm events (Fig. 2c). The water level rose above the soil surface only during 6 of the storm events (storms 3, 26, 27, 52, 53 and 54).

Chemical characterization of streamwater and end members

During the months following the dry period, Cl^- and SO_4^{2-} concentrations were greatest at baseflow conditions (up to 40 mg l^{-1} for both solutes). Chloride concentrations during baseflow decreased from 43 to 26 mg l^{-1} from September to December-January and then remained constant at a value of 23 mg l^{-1} until March (Mann–Whitney test, $p > 0.05$) when concentration decreased to 18 mg l^{-1} (Mann–Whitney test, $p < 0.01$) (Fig. 4a). Sulfate concentrations followed a similar pattern decreasing from 50 to 30 mg l^{-1} from September to December-January and then remaining constant until April (Mann–Whitney test, $p > 0.05$) and decreasing again in May to 16 mg l^{-1} (Mann–Whitney test, $p < 0.01$) (Fig. 4b). The median concentration of DOC during September and October was above 5 mg l^{-1}, whereas the median decreased to 3.2 mg l^{-1} during the rest of the year (Fig. 4c). Nitrate concentrations showed a seasonal pattern with maximum concentrations during the winter months (Fig. 4d).

During storms, Cl^- concentrations were similar to those measured at baseflow conditions, except during September and April when concentrations decreased significantly during storms (Mann–Whitney test, $p_{Sep} < 0.01$ and $p_{Apr} < 0.001$). Sulfate concentrations decreased during stormflow conditions only during September, October and April (Mann–Whitney test, $p_{Sep} < 0.01$, p_{Oct} and $p_{Apr} < 0.001$). In contrast, DOC and nitrate concentrations tended to increase during storms (Fig. 4g, h) (Mann–Whitney test, $p_{DOC} < 0.0001$

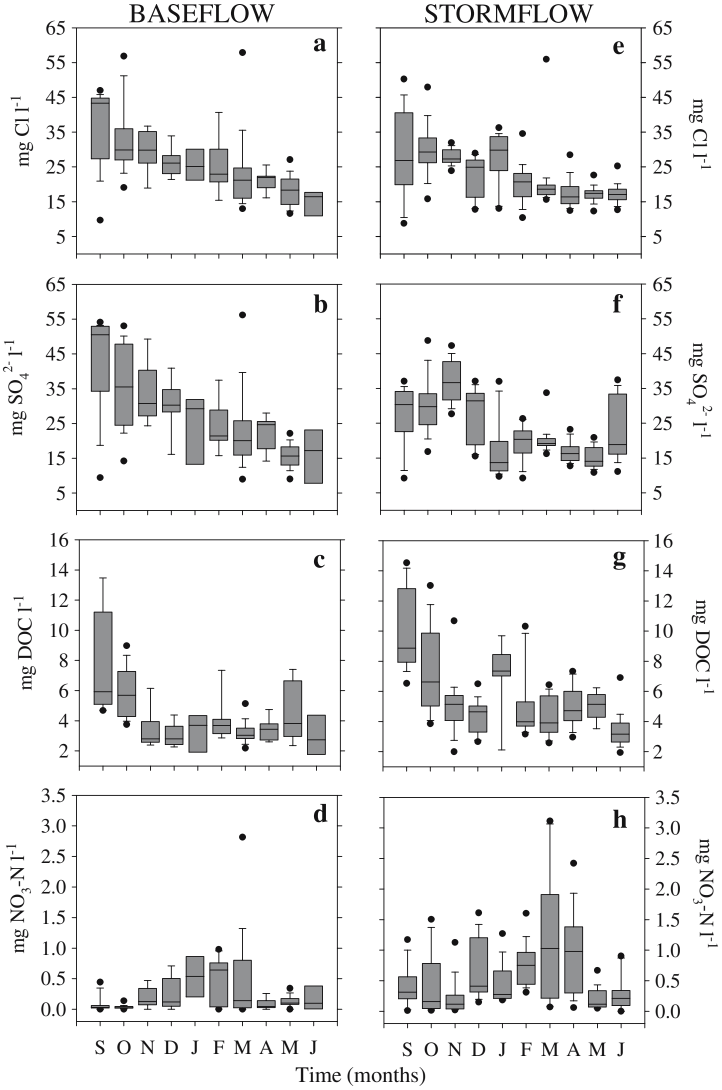

Fig. 4 Box plots summarizing concentration data (mg l^{-1}) in streamwater at Fuirosos (Catalonia, Spain) during baseflow (left panels) and stormflow (right panels) conditions. (**a** & **e**) Cl$^-$; (**b** & **f**) SO$_4^{2-}$; (**c** & **g**) DOC; and (**d** & **h**) NO$_3$-N. The centre horizontal line in each box is the median value of concentration. Fifty percent of the data points lie within each box. The whiskers above and below the box indicate the 90% and the 10% percentiles, and circles indicate outliers

and $p_{\mathrm{NO_3\text{-}N}}<0.0001$), albeit that differences in monthly concentrations between baseflow and stormflow were not significant in some cases.

Bulk deposition (BD) and throughfall (TF) had similar Cl$^-$ and NO$_3$-N concentrations, whilst the concentration of both solutes was higher in the superficial overland flow samples (OF) (Wilcoxon paired *t* test, for BD vs. OF: $n_{\mathrm{CL}} = 22$, $p_{\mathrm{CL}} < 0.02$ and $n_{\mathrm{NO_3\text{-}N}} = 18$, $p_{\mathrm{NO_3\text{-}N}}<0.02$; for TF vs. OF: $n_{\mathrm{CL}} = 16$, $p_{\mathrm{CL}} < 0.03$ and $n_{\mathrm{NO_3\text{-}N}} = 22$, $p_{\mathrm{NO_3\text{-}N}}<0.01$). Sulfate concentrations increased as precipitation passed through the canopy (Wilcoxon paired *t* test, $n_{\mathrm{SO_4^{2-}}} = 22$, $p_{\mathrm{SO_4^{2-}}}<0.01$), and DOC concentrations were higher in OF than in TF samples (Wilcoxon paired *t* test, $n_{\mathrm{DOC}} = 11$, $p_{\mathrm{DOC}} < 0.01$) (Table 3). The differences in Cl$^-$ and SO$_4^{2-}$ concentrations among BD, TF and OF could be considered negligible when compared to groundwater concentrations because in both cases concentrations were 3-folds lower in BD, TF and OF than in hillslope groundwater (HGW) and 12-folds lower than in riparian groundwater (RGW). Additionally, DOC concentrations in HGW and RGW were from 7 to 66 times lower than in BD, TF or OF. Thus, in the present study BD, TF and OF were considered a unique end member labelled event water (EW) which refers to the mixture of waters contributing to the generation

Table 3 The median concentration (mg l^{-1}) and the 25th and 75th percentile of Cl^-, SO_4^{2-}, DOC and NO_3-N for bulk deposition (BD), throughfall (TF), superficial overland flow (OF), hillslope groundwater (HGW), riparian groundwater (RGW) and streamwater (SW) in the Fuirosos catchment (Catalonia, Spain) are shown. In the present study event water (EW) was considered a mixture of BD, TF and OF. The median and percentile concentrations for EW are also shown. *n*: number of cases, na: not available

	Cl^-				SO_4^{2-}				DOC				NO_3-N			
	25th	Med	75th	*n*	25th	Med	75th	*n*	25th	Med	75th	*n*	25th	Med	75th	*n*
BD	1.75	3.61^a	5.4	94	1.54	2.41^a	3.78	97	na				0.17	0.30^a	0.64	88
TF	1.39	3.88^a	4.98	20	2.18	3.12^b	4.71	25	8.27	10.25^a	13.55	15	0.39	0.54^a	1.18	24
OF	3.38	5.02^b	10.21	24	2.14	4.12^b	7.73	24	22.65	36.23^b	48.01	22	0.39	1.32^b	1.97	25
EW	2	3.85	5.7	138	1.57	3.59	4.26	146	12.34	21.7	31.9	37	0.21	0.39	1.16	137
HGW	15.27	16.09	16.69	24	7.89	10.46	12.63	24	0.25	0.55	0.78	19	0.14	0.23	0.32	19
RGW	20.9	31.63	39.42	98	21.33	28.15	35.15	111	0.99	1.41	1.3	59	0.06	0.36	1.3	150
SW	16.47	20.14	26.38	292	17.21	20.42	32.89	292	3.29	4.24	5.36	292	0.16	0.37	0.83	282

^{a} and ^{b} are used to indicate different groups of samples after performing a Wilcoxon paired-sample test ($\alpha = 0.05$) on samples collected the same day

of runoff that resided for a short time in the catchment. There were a higher number of samples of BD than of TF and OF, which slightly biased EW towards BD solute concentrations. However, these differences in EW solute concentrations did not affect results obtained with EMMA (result not shown). The concentrations of Cl^-, SO_4^{2-} and DOC in streamwater (SW) ranged among those concentrations measured for EW, HGW and RGW (Table 3).

The principal components analysis (PCA) that included all the available streamwater samples exhibited a wide range of values, in particular during the months following the dry period (i.e., September–November period) (Fig. 5). Results showed that 94.6% of the chemical variability in these samples could be explained by two principal components, implying that at least three end members were required to explain the streamwater response (Christophersen and Hooper 1992). However, the three selected end members EW, HGW and RGW encompassed the variability in streamwater samples only during December to June (Fig. 5).

Relative contribution of each end member during the wet period

An end member mixing analysis (EMMA) was performed considering only streamwater data for the December to June period, which included 12 storms. The first two axes of the sub-space defined by the eigenvectors of the EMMA model explained 96.9% of the variability of these data. The fit between predicted and measured concentrations for each solute was significant (Wilcoxon paired-test $p < 0.005$) and slopes ranged from 0.78 to 1, indicating that the EMMA model was a strong predictor of stream solute concentrations.

The contribution of EW was low until a discharge value of 57 ± 1 l s^{-1} was reached, whilst at higher discharges the proportion of EW ranged from 16 to 45% and increased with increasing discharge (Fig. 6). The groundwater source (HGW + RGW) was the major contributor to runoff, mainly at discharges lower than 57 l s^{-1} when the median contribution was 86%. The average relative contribution of each end member during each storm event was used to compare the contribution of each runoff source among individual storms (Table 4). The relative contribution of EW to stormflow was always lower than 25%, except during the storm of highest magnitude (13/01/2001, case number 27) when EW provided up to 40% of the stream runoff. During the water year 2000–2001, the relative contribution of HGW increased from the 7% to the 62% from December (storm case 26) to April (storm case 33) (Table 4). In the same way, the percent contribution of HGW increased from the 37% to the 53% throughout the wet period in 2001–2002 (Table 4).

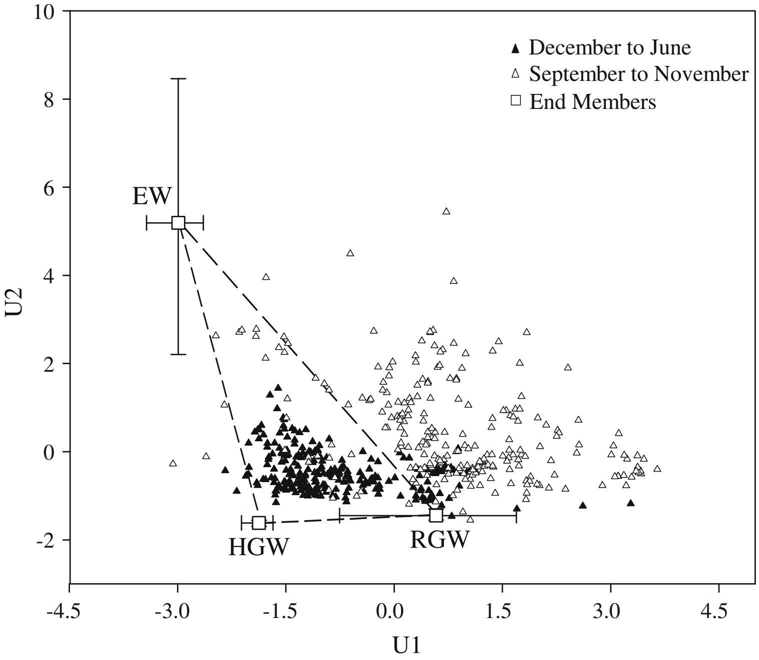

Fig. 5 Ordination plot of the scores 1 and 2 obtained from the principal component analysis (PCA) of the streamwater data (i.e., Cl^-, SO_4^{2-} and DOC concentrations) from the Fuirosos catchment (Catalonia, Spain). White triangles are streamwater data from September to November. Black triangles are streamwater data from December to June. Dashed lines are used to show the mixing diagram defined by the proposed end members. EW: event water, HGW: hillslope groundwater, RGW: riparian groundwater. The 25th and 75th percentile of the projected concentrations for the entire period of study are shown for each end member

Since different types of vegetation were present in the catchment, spatial variability of solute concentrations in the Fuirosos watershed could be relevant, especially for EW. A Monte Carlo like approach was used to quantify the uncertainty associated to the estimation of the contribution of water sources through EMMA due to the spatial variability of chemical tracer concentrations in the EW compartment. The variability of median solute concentrations (for Cl^-, SO_4^{2-} and DOC) of EW was assumed to be as much as ± 25% of those concentrations measured in the field. We run 10^2 times the EMMA mixing model using different combinations of EW solute concentrations in each simulation. The uncertainty associated to each water source was measured by means of the coefficient of variation (CV, %), which is a measure of relative variability. Results showed that the relative contribution of EW and RGW changed with a CV equal to the 13% (median value), whereas the CV for the HGW was about the 20%. For storms 26 and 27 (the ones of highest magnitude, Fig. 3) the CV of the percent contribution of HGW was higher than 50% indicating a high uncertainty

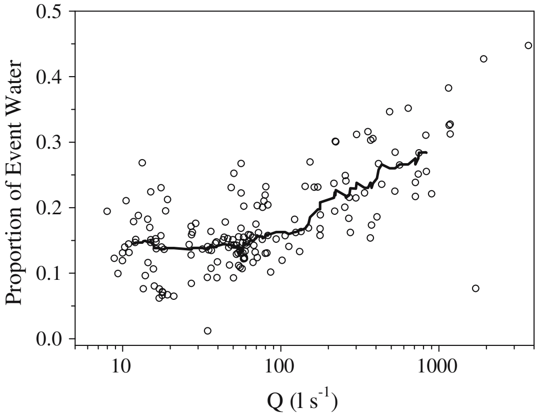

Fig. 6 Scatterplot of the relative contribution of Event Water estimated with EMMA against discharge during the wet period in the Fuirosos catchment (Catalonia, Spain). The solid line is the 20-point moving median. The breakpoint of the relationship (Q = 57 ± 1 l s^{-1}) was estimated by adjusting a bilinear equation (Muggeo 2003)

associated to the estimation of the contribution of this water source during these particular events.

In general, there was not any clear relationship among the contribution of different water sources and the hydrological and climatic variables considered in the present study, except for a positive relationship between the proportion of EW and the amount of rainfall during the days before the storm (i.e., EW vs. Σ4d: $r = 0.59$, $p < 0.05$). Only when the storm case 33 was not included in the data set, significant relationships arose among percent contribution of water sources and hydrologic and climatic variables. On the one hand, the proportion of EW was related to the Σ 4d ($r = 0.67$, $p < 0.05$) and also to the Σ 8d ($r = 0.63$, $p < 0.05$) and to the antecedent moisture conditions in the catchment (EW vs. Factor 1: $r = 0.64$, $p < 0.05$). On the other hand, the proportion of HGW was positively related to the RC ($r = 0.62, p < 0.05$), whereas the contribution of RGW tended to decrease as the RC increased ($r = -0.75, p < 0.01$).

Sources of nitrogen during storm events in the wet period

We used the Spearman's coefficient to determine whether there was a relation between stream NO_3-N concentration and the percentage of streamflow for each end member. In 6 out of 12 storms (storms 3, 13, 26, 29, 50 and 54) there was a strong positive correlation between stream NO_3-N concentration and percent contribution from one or more of the end members, suggesting that the correlated end members were the most likely sources of nitrate in the catchment. For 4 of those storms there was also a strong negative correlation between the contribution of the other end members and NO_3-N concentration. For example, in storm 26 EW and HGW were strongly correlated with NO_3-N concentration while RGW and NO_3-N had a negative correlation. In contrast, for storm 54 EW had a strong negative correlation with NO_3-N concentration and HGW had a strong positive correlation. Therefore, a consistent pattern of a particular end member being a source of nitrate was not observed.

The RGW level rose above the soil surface during at least part of storms 3, 26, 27, 52, 53 and 54 (RGW_{Max} in Table 4). However, only during storms 3 and 26 was EW the most likely source of nitrate ($r_{EW} > 0$), whilst groundwater was the most likely source during storm 54. In contrast, during storms 13, 29 and 50, the RGW level was well below soil surface. Event water was the most likely source of nitrate for storms 29 and 50

Table 4 The average relative contribution to runoff (± standard deviation) of each end-member (EM) is shown for 12 storm events in the Fuirosos catchment (Catalonia, Spain) during the wet period. The Spearman's Rho coefficient (r) between measured nitrate concentrations in streamwater and the proportion of water from each EM is also indicated. The maximum daily groundwater level (RGW_{Max}, cm) recorded at the riparian zone piezometer (located 5 m from the stream channel) and the inter-storm period (ISP, days) are also included. EW: event water, HGW: hillslope groundwater, RGW: riparian groundwater. $^{*}p < 0.05$, $^{**}p < 0.01$. In brackets when r was no significant, n: number of cases, na: not available

Water year	Case	Date	Contribution to runoff			$EM_{contribution}$ vs. $[NO_3\text{-}N]_{stream}$				RGW_{Max}	ISP
			% EW	% HGW	% RGW	r_{EW}	r_{HGW}	r_{RGW}	n	cm	days
1998–1999	3	03/12/98	16.2 ± 4.9	51.6 ± 14.4	32.2 ± 16.6	0.76^{**}	(0.29)	-0.51^{*}	22	6.3	59
1999–2000	13	15/12/99	14.1 ± 1.5	0	85.9 ± 1.5	-0.76^{**}	–	0.76^{**}	20	–30.9	33
2000–2001	26	21/12/00	13.8 ± 7	6.8 ± 14.8	79.4 ± 20.3	0.82^{**}	0.6^{**}	-0.83^{**}	23	32.4	21
	27	12/01/01	36 ± 5.4	33.4 ± 4.8	30.6 ± 4.9	(0.1)	(–0.3)	(0.4)	8	23.1	24
	28	13/02/01	14.6 ± 1.3	31 ± 5.8	54.4 ± 6.1	(0.14)	(0.31)	(–0.45)	10	–38.6	30
	29	15/02/01	16.1 ± 1.2	29.6 ± 6.4	54.3 ± 6.1	0.81^{*}	(–0.37)	(–0.14)	6	–33.1	2
	30	24/02/01	13.8 ± 1.7	56.6 ± 23.8	29.6 ± 25.1	(–0.01)	(–0.2)	(0.2)	11	–29.7	10
	33	30/04/01	17.8 ± 4.3	62.2 ± 17.1	20 ± 16.1	-0.6^{*}	(0.3)	(–0.02)	14	na	33
2001–2002	50	04/03/02	23.6 ± 3.2	36.7 ± 4.2	39.7 ± 4.5	0.86^{*}	(–0.3)	(–0.25)	7	–11.9	3
	52	02/04/02	22.9 ± 6.1	45.9 ± 11.6	31.2 ± 15.5	(0.3)	(0.3)	(–0.4)	11	2.2	4
	53	06/04/02	23.8 ± 7.4	53 ± 7.3	23.2 ± 12.2	(0.14)	(0.57)	(–0.54)	8	7.6	4
	54	11/04/02	20 ± 6.7	53.2 ± 10	26.8 ± 6	-0.88^{**}	0.61^{*}	(0.2)	14	14.7	5

($r_{EW} > 0$) while it was RGW for the storm 13 ($r_{RGW} > 0$). Hence, hydrometric measurements (i.e., the RGW level) indicated that the leaching of nitrate from the catchment was not related to the water table elevation. The inter-storm period (ISP) (i.e., the days between two storm events) was not a good indicator of the catchment nitrate sources (Table 4).

Discussion

The end members considered in this study showed contrasting tracer concentrations. Chloride and sulfate concentration were low in event water indicating that the residence time of this water in the catchment was short. In contrast, these solutes had their highest concentrations in riparian groundwater, probably due to evaporative concentration. In contrast to anions, DOC concentrations were higher in event water than in any of the groundwater sources. This indicates that decomposition of organic material in the topsoil such as litter or root exudates was the likely source of dissolved organic carbon in the cathment, and that these sources decreased with soil depth as in many studies (e.g. McGlynn et al. 1999; Yano et al. 2004). We expected that the selected end members would bound the majority of stream water samples at Fuirosos, and while this was true for most of the year it was not the case from September to November (hereafter, the '*transition period*'). Indeed, during the transition period the stream water chemistry was different from the rest of the year with the highest concentrations of both, anions and DOC. Chloride and sulfate are predominantly of atmospheric origin and once in the catchment these anions are concentrated by evapotranspiration, in particular during the driest part of the year (i.e., summer). The high concentrations of both solutes measured in the stream during early autumn (up to 60 mg l^{-1} in some cases) could respond to the flush out of soluble salts built up during the summer period as described in other studies conducted at both semiarid and temperate catchments (e.g. Durand et al. 1991; Piñol et al. 1992). Additionally, the high DOC concentrations observed in streamwater during the transition period could respond to the leaching of organic matter accumulated on the streambed and on the near-stream zones during summer months (Acuña et al. 2005; Bernal et al. 2005). This organic matter corresponded mainly to an important peak of riparian leaf litter fall in midsummer (Sabater et al. 2001). Tracer concentrations likely changed during the transition period because of the gradual flushing of solutes built up over the dry period as also shown by Àvila et al. (1992) for a perennial Mediterranean stream, thus violating one of the main assumptions of the mixing model approach, that of constant composition of source waters (Christophersen and Hooper 1992). In that sense, Butturini et al. (2005) have recently pointed out that a mixing model accounting for the release of solutes from the hyporheic/riparian sediments into streamwater during storms could explain better than a conventional mixing model the variability of solute concentrations in Fuirosos during low flow periods following summer drought. Also, other studies have pointed out the inherent difficulty to apply classical mixing models in highly heterogeneous systems where there may not be end members of constant composition (Neal 1997; Neal et al. 1997).

In Fuirosos, the flushing response observed in the transition period would explain why storm episodes that occurred during similar climatological and hydrological conditions produced different streamwater chemistry depending upon the time of the year. For example, storms 29 and 38 fell close to each other in the factorial analysis (Fig. 3) indicating that (1) the antecedent hydrological conditions in the catchment and (2) the amount of precipitation and the shape of the hydrograph were similar. However, streamwater samples for event 38 that occurred in September 2001 fell in the upper right side of the U-space (out of the mixing triangle), while the samples for event 29 (February 2001) fell within the mixing triangle. A similar pattern was observed for the pair of events 2 and 50 (Fig. 3). If only hydrological and/or climatological conditions would be responsible for the chemical differences between storms then we would expect storms with similar hydrological and climatological conditions to have a similar chemical response.

Relative contribution of each end member and variation in the groundwater component during the wet period

Aside from the transition period, streamwater samples collected from December to June fell within the mixing space defined by the three selected end members: event water, hillslope groundwater and riparian groundwater. Therefore, the proportion of water contributed by each end member was calculated for every storm to determine the relative importance of the different stormflow sources during the wet period. In Fuirosos, the groundwater source (HGW + RGW) was the dominant contributor to stormflow. This result is coincident with many others performed in northern humid temperate catchments (e.g. Buttle 1994; Hornberger et al. 1998) and also those in Mediterranean catchments (e.g. Neal et al. 1992; Durand et al. 1993).

Results suggested that the percent contribution of hillslope groundwater (HGW) was increasing throughout the hydrological year. However, there was not any clear relationship between the contribution of HGW and the antecedent moisture conditions in the catchment. This result contrasts with other studies that reported a greater contribution of hillslope groundwater under wet antecedent moisture conditions (e.g. Hooper et al. 1990; Burns et al. 2001). Further, we found that the percent contribution of groundwater sources to runoff was fairly similar when the inter storm period was short (ISP $<$ 1 week), despite of differences in the climatic conditions. For instance, the contribution of HGW and RGW to stream runoff was similar for storms 28 (13/02/01) and 29 (15/02/01), though the former occurred under drier moisture conditions than the latter (Fig. 3). Further, the contribution of HGW during the storm 33 (30/04/01) was high, though it was an event of low magnitude that occurred under dry antecedent moisture conditions (Fig. 3). Overall, these results suggest an inertial response of groundwater sources in Fuirosos during storms and this might well be the reason why we did not found clear relationships among groundwater sources and climatic variables. Such a behaviour could be explained by a gradual increase of hydrologic connectivity between the riparian and the hillslope zone through the year (Stieglitz et al. 2003) that probably would be affected by the distribution of precipitation and evapotranspiration throughout each hydrological year (Devito et al. 2005).

Sources of nitrogen during storm events in the wet period

The main goal of mixing models has been to investigate water flowpaths in catchments (e.g. Hooper et al. 1990; Buttle 1994), which in turn helps us discern the possible links between water and solute flowpaths (e.g. McHale et al. 2002). If nitrate arriving from the catchment was not strongly transformed once in the riparian, the hyporheic and the in-stream zones, one might expect to find out a relationship between water sources and the sources of this nutrient in the catchment. However, nitrate is readily transformed by biological activity, which confounds an easy interpretation of its source and flowpath.

In Fuirosos, a positive and significant relationship between stream nitrate concentrations and the proportion of water coming from a given end member was found in 6 of the 12 storms studied. That is, a link between the water sources and the nitrate sources in the catchment could be established in 50% of the storms. In three of these 6 cases (storms 3, 26 and 54), the riparian groundwater level rose to the soil surface for at least part of the storm. During storms 3 and 26 the event water was apparently a source of nitrate suggesting that the flushing of nitrate could be attributed to the rise of the groundwater to shallow levels in Fuirosos (Creed and Band 1998; Ohte et al. 2003). However, stream nitrate concentrations showed a poor relationship with event water during the spring storm (number 54). During a storm, nitrate would be flushed from a given source if enough time passed between storms for nitrate to reaccumulate. This would depend on the frequency of storm events together with the net balance of processes affecting nitrate concentrations (i.e., nitrification–denitrification and uptake by vegetation). Many studies have shown that the net result of these processes changes over time (e.g. Creed and Band 1996): during the growing season, warm temperatures favour nitrification, while high demand for nitrate by the forest reduces its accumulation. This situation reverses during the dormant season. A study conducted in the Fuirosos riparian zone confirms this hypothesis; the mineralization rate in the organic soil layer (i.e., first 10 cm) was higher in spring than in winter (1.1 vs. 0.5 mg N kg^{-1} d^{-1}, respectively), whereas the mean soil nitrate concentration in spring (1.4 mg NO_3-N l^{-1}) was half of that measured in winter (Bernal et al. 2003). Therefore, the lack of correlation between stream nitrate concentrations and the proportion of event water during the April storms when the soil was water saturated (cases 52, 53 and 54) might be explained by (1) a short time between storms ($<$ 1 week), (2) a high demand for nitrate by vegetation and/or (3) low soil nitrification rates. On the other hand, event water was a source of nitrate even when groundwater level was well below the soil surface (storms 29 and 50). In those cases, the leaching of nitrate might be a consequence of either infiltration excess overland flow or subsurface flow from unsaturated areas. The latter explanation seems more feasible in both cases since the amount of precipitation (10 mm and 36 mm for storms 29 and 50, respectively) and the rain intensity (ca. 8 mm h^{-1} in each case) were too moderate to exceed the infiltration rate.

Sources of nitrate in the catchment were not always related to hydrological sources and thus, the knowledge of the dominant water sources in Fuirosos did not allow prediction of nitrate response to hydrological events. This result contrasts with that of many other studies that inferred predominant annual hydrological or nutrient sources in catchments from the analysis of one or a few storm events. Overall, the present study calls for caution when inferring general hydrological trends and biogeochemical processes at the catchment scale from the analysis of only a small number of storm events.

Effect of near- and in-stream zones on nitrate concentrations

In Fuirosos the source of nitrate to stream water was clearly related to a hydrological source water in 6 of 12 storms monitored during the wet period, whereas the source was unrecognizable for the remaining storms. During the wet period, groundwater nitrate concentrations at piezometers located 5 m from the streambed averaged 0.9 mg N l^{-1} whilst those located 1 m from the stream channel averaged 0.5 mg N l^{-1} (Bernal, unpublished data). Such a decrease in nitrate concentrations could not be attributed to a dilution effect because chloride concentrations were identical at both sites and covaried with time, evidence that the groundwater body was similar and contiguous at both points (Butturini et al. 2003). Thus, during the wet period (when no stream to groundwater fluxes occur) nitrate might be retained along the 5-m riparian area and processes occurring in the Fuirosos riparian zone might be changing the signature of nitrate sources in the catchment. Based on these observations and in order to infer whether or not those processes might be affecting stream nitrate concentrations in Fuirosos, end member mixing analysis of streamwater chemistry was used to determine expected nitrate concentrations in stream water based on conservative mixing of the different water sources. Predicted stream nitrate concentrations based on hydrologic sources were considered the expected stream concentrations if only hydrological and terrestrial biogeochemical processes regulate stream chemistry (Mulholland 2004). Concentrations were estimated from water proportions calculated with EMMA, and then compared to measured stream nitrate concentrations. At discharges below 80 l s^{-1}, stream nitrate concentrations were lower than expected from catchment sources in 82% of the stream samples, whilst the trend was the opposite at higher discharges (Fig. 7). Consistent with this observation, many studies show that at baseflow conditions nitrate is depleted in riparian areas due to uptake by vegetation and/or denitrification (e.g. Hill 1996; Konohira et al. 2001). Other studies conducted in headwater streams have shown that in-stream processes decrease stream nitrate concentrations at low flows (e.g. Triska et al. 1989; Martí et al. 1997; Burns 1998; Mulholland 2004) and that the efficiency of these processes tends to diminish while decreasing the surface to volume ratio (Peterson et al. 2001). Recently, Schade et al. (2005) showed that riparian trees of a sonoran desert stream assimilated stream inorganic

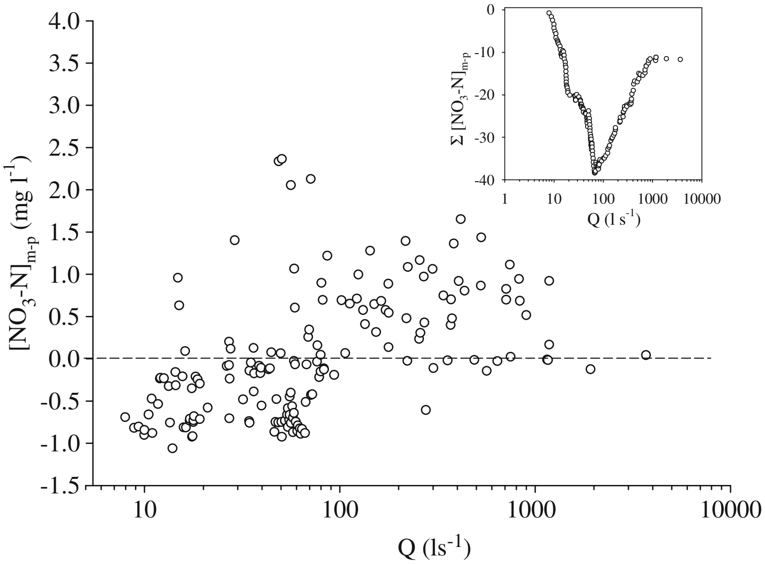

Fig. 7 Relationship between the difference of measured and predicted NO_3-N concentrations ($[NO_3\text{-}N]_{m\text{-}p}$, mg N l^{-1}) and stream discharge (Q, l s^{-1}). The dashed line indicates equal measured and predicted NO_3-N concentrations. The inset is the sum of $[NO_3\text{-}N]_{m\text{-}p}$ while increasing discharge. At discharges lower than 80 l s^{-1} the slope of the accumulative difference between measured and predicted concentrations (i.e., $\Sigma\,[NO_3\text{-}N]_{m\text{-}p}$) is negative because $[NO_3\text{-}N]_{m\text{-}p} < 0$ predominates over $[NO_3\text{-}N]_{m\text{-}p} > 0$. The opposite trend occurs at discharges higher than 80 l s^{-1}

nitrogen during baseflow conditions, thus acting as a filter of N from streamwater. In light of these studies, the result obtained in Fuirosos suggests that near-stream and/or in-stream zones retain nitrate arriving from the catchment during the wet period (winter and spring) at low discharges. In contrast, at discharges higher than 80 l s^{-1} the relative importance of processes such as denitrification or nitrate uptake by biota at the near-stream and/or in-stream zones might be small in Fuirosos since nitrate measured in the stream was similar or higher than predicted concentrations. Several workers have suggested that increased flow may decrease the role of near-stream zones in controlling nitrate transport (see Cirmo and McDonnell 1997 for a review). However, only a few studies have evaluated whether the effectiveness of riparian areas in retaining nitrate changes under different hydrological conditions. For example, Konohira et al. (2001) showed that only at baseflow conditions was a riparian zone in Japan effective in removing nitrate via denitrification, whereas during stormflow biota were not able to retain nitrate and consequently stream nitrate concentrations increased. In that sense, Fig. 7 suggests that regarding near and in-stream processes two contrasting behaviours emerged in Fuirosos depending on the amount of discharge. Further, our data indicate that the shift between these two patterns was abrupt rather than gradual (Fig. 7 inset).

In principle, one might expect that at high flow, measured and predicted concentrations would be fairly similar. Differences between these values could be attributed, for example, to nitrification pulses in the catchment during the evolution of storm events, especially in semiarid regions where the impact of water on soil moisture enhances microbial processes that are usually limited by soil moisture (Rey et al. 2002). If so, soil nitrate concentrations might be increasing during a given storm and nitrate concentrations of water arriving from the catchment might be underestimated. In Fuirosos, a metallic V-notch was installed in two microcatchments at the top of the ridge (ca. 3 ha). Water from both sites was drained only during storms occurring under wet conditions (i.e., precipitation of high magnitude or during sequential storms). Nitrate concentrations of this subsurface soil water, which has infiltrated roughly 75 cm through the soil profile, ranged between 0.1 and 0.16 mg N l^{-1} (Bernal, unpublished data). These concentrations were lower than those measured in the EW or the RGW compartments (0.36 mg N l^{-1} in both cases) and thus, this flowpath is not likely responsible for increasing nitrate concentrations measured in the stream. Despite this observation, the increase in hydrological connectivity during large storm events may imply the mobilization of nitrate from isolated areas where it has accumulated for long spans of time (Bazemore et al. 1994; Creed and Band 1998). Consequently, other regions in the catchment that were not considered in the present study could be responsible for those high stream nitrate concentrations. Further studies are needed in Fuirosos in order to establish the spatial heterogeneity of nitrate concentrations in the catchment and to highlight the possibility of nitrification pulses in groundwater during the evolution of storms.

Concluding remarks

Stream samples during the transition period (i.e., from September to November) were not encompassed by the mixing diagram defined by event water, hillslope and riparian groundwater. The reason might be that the composition of source waters was not constant and/or was masked by the gradual flushing of solutes built up over the dry period in the near- and in-stream zones. Therefore, a classical EMMA approach applied at the catchment scale was not appropriate to differentiate water sources contributing to runoff in this intermittent stream during the months following the dry period.

During the wet period, groundwater was the most important contributor to stormflow. Results suggested that two groundwater sources feed the stream: riparian groundwater and hillslope groundwater and that the relevance of the latter increased throughout the hydrological year. Hydrologic source contributions were strongly related to stream nitrate concentrations during 6 of the 12 storms studied indicating that in some cases there was, indeed, a link between hydrological and nitrate sources. However, there was not a consistent pattern of a particular end member being a source of nitrate and thus, nitrate response during hydrological events could not be predicted from water sources. Further work is needed in order to elucidate biogeochemical processes controlling nitrate responses during storms at Fuirosos.

The comparison between measured and predicted nitrate concentrations in Fuirosos indicated that only at flows lower than 80 l s^{-1} do near- and in-stream zones retain nitrate in this 10.5 km^2 catchment. Above this threshold, our results suggested that the system was not efficient in retaining nitrate arriving from the catchment. This might be considered when establishing the importance of near- and in-stream processes for regulating catchment nitrate loads since in many catchments a major fraction of the annual nitrate export occurs during stormflow conditions. For example, only 3 out of the 18 hydrological events monitored at Fuirosos during the water year 2000–2001 had discharges higher than 80 l s^{-1}. However, nitrate export at such moments (that comprised only 6% of the total time of the water year) was 50% of the total annual load.

Overall, this study emphasizes how stream water and nitrate sources vary throughout the year and points out the importance of sampling storms during all seasons to draw general conclusions about watershed processes.

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