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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 I

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Seasonal variations of dissolved nitrogen and DOC:DON ratios in an intermittent Mediterranean stream*

Key words

Dissolved inorganic nitrogen, dissolved organic nitrogen, DOC:DON ratio, intermittent stream, Mediterranean

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* Bernal S., Butturini A. and Sabater F. 2005. Biogeochemistry 75: 351-372.

Introduction

Recent studies have shown that dissolved organic nitrogen (DON) could be a major part of nitrogen losses from unpolluted forests (e.g., Kortelainen et al. 1997; Perakis and Hedin 2002). However, there are few studies focused on elucidating the causes of natural variability and the role of biological processes on stream organic nitrogen. Several authors have reported an inverse pattern for nitrate and DON in runoff with highest nitrate concentrations in late winter and highest DON concentrations in summer and early fall (e.g., Triska et al. 1984; Arheimer et al. 1996; Vanderbilt et al. 2003). Nitrate is likely to increase in winter due to low biological demand, while DON would increase in summer and fall due to the higher activity of decomposers on recent litterfall (e.g., Hedin et al. 1995) or because of a higher production in the stream (Chapman et al. 2001). Other studies have not found a clear seasonal trend of DON concentrations (Lovett et al. 2000; Goodale et al. 2001). These studies were based on baseflow streamwater samples. The few studies which have considered DON concentrations during stormflows have reported that both DON and nitrate concentrations increase by several times during high flow (McHale et al. 2000; Hagedorn et al. 2001) and that stormflows could be responsible for up to 58 % of the total annual DON flux (Buffam et al. 2001). Variations during episodic high flows may be caused by different flowpaths of water through the catchment in relation to baseflow conditions (e.g., Bormann and Likens 1979).

Qualls and Haines (1992) and Hedin et al. (1995) suggest that DON may be largely unavailable to organisms in the stream because it is composed of refractory fulvic acids from soil organic matter. For example, Buffam et al. (2001) reported for Paine Run, a small stream in Virginia (USA), a DOC:DON ratio of approximately 45:1 which was similar at baseflow and at high flow conditions, indicating that the bioavailability of dissolved organic matter was the same under both conditions. DON and dissolved organic carbon (DOC) may show a similar pattern because both nutrients are likely to have the same origin. Michalzik et al. (2001) found out a high correlation between DOC and DON fluxes in a study of 42 soils in forested ecosystems. Several studies have shown a positive correlation between DOC and DON concentrations in streamwater (e.g., Harriman et al. 1998; Goodale et al. 2001). However, differences in the dynamics and rates of release of DOC and DON have also been reported, suggesting that different mechanisms may apply to each solute in some cases (Solinger et al. 2001).

There are no previous published data on dissolved organic nitrogen in unpolluted Mediterranean catchments. Regions with Mediterranean climate (Gasith and Resh 1999) are characterized by a marked seasonality and typically large differences in the precipitation between years. Annual potential evapotranspiration is large and greater than precipitation (Piñol et al. 1991). The alternating dry and humid conditions stimulate microbial activity and lead to nutrient pulses following precipitation because it takes a period of days to weeks for biota to deplete the nutrient pool (Mummey et al. 1994; Cui and Caldwell 1997; Rey et al. 2002). Recent studies in Mediterranean catchments suggest that the seasonal pattern of nitrate concentrations in stream water indicates a temporal decoupling between when nitrate is available to plants and when those plants are able to use mineral N (Holloway and Dahlgren 2001; Meixner and Fenn 2004). Several studies in Mediterranean catchments have shown that nutrient dynamics in streamwater after a drought period are different from the rest of the year. For example, in several Mediterranean streams the highest spikes of nitrate concentration occurred following the summer drought (e.g., Àvila et al. 1992; Biron et al. 1999). A previous study in Fuirosos showed that changes in DOC concentration occurred during storm events following a drought. These changes coincided with the mobilization of litter accumulated on the streambed and the stream edge (Bernal et al. 2002).

If DON and DOC have a same origin, then we should expect a similar behaviour of both solutes throughout the annual hydrological cycle in the intermittent stream in our study (Fuirosos). The relationship among concentrations of DON and DOC and dissolved inorganic nitrogen (DIN) together with the variability of DOC:DON ratios through the year may help us to elucidate the origin and quality of organic nitrogen in this Mediterranean catchment. The intensive monitoring during baseflow and stormflow conditions conducted in the Fuirosos stream allowed us to examine, throughout the year, the influence of discharge on streamwater concentrations and whether DOC:DON ratios were different during baseflow and stormflow conditions.

The objectives of the present study were: (i) to determine the seasonal patterns of DIN (NO_3-N and NH_4-N) and DON concentrations, and DOC:DON ratios during baseflow and stormflow conditions, (ii) to infer the quality of organic matter by means of DOC:DON ratios and to identify the possible sources of dissolved organic matter throughout the year, (iii) to determine the influence of discharge on the variations in streamwater concentration of the solutes and, (iv) to establish the importance of DON *vs.* DIN in the annual total nitrogen export in a Mediterranean intermittent stream. Finally, N fluxes in Fuirosos are compared with those reported for forested catchments in Mediterranean and other bioclimatic regions.

Material and Methods

Hydrological monitoring

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.

Stream water level has been monitored continuously beginning on 1 July 1999 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 the "slug" chloride addition method in the field (Gordon et al. 1992). The end of each storm period was marked by a change in discharge smaller than 10 %.

Chemical water analyses

Streamwater samples were taken from September 1999 to March 2002 at least once every ten days (except during the cessation of flow in summer). 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. All water samples were filtered through pre-ashed GF/F glass fibre filters and stored at 4 ºC until analysed. Both NO_3^- and NH_4^+ were analysed colorimetrically with a Technicon Autoanalyser® (Technicon 1976); NO_3^- was measured by the Griess-Ilosvay method (Keeney and Nelson 1982) after reduction by percolation through a copperised cadmium column; NH_4^+ was measured after oxidation with salicilate using sodium nitroprusside as a catalyst (Hach 1992).

Total dissolved nitrogen (TDN) was analysed from March 2000 to March 2002 colorimetrically as nitrate with a Technicon Autoanalyser® (Technicon 1976) by the Griess-Ilosvay method (Keeney and Nelson 1982) after a combined digestion with UV light and potassium persulfate (Valderrama 1981; Walsh 1989). The efficiency of the digestion process ranged between 87 % and 100 % and was established each time by analysis of EDTA samples of known concentration and molecular composition. For each sample, DON concentration was calculated subtracting nitrate and ammonium concentrations from TDN. DOC samples were analysed using a high-temperature catalytic oxidation (Shimadzu® TOC analyser).

DON, NO_3-N and NH_4-N stream fluxes were calculated both for baseflow and during storms. During baseflow, the daily solute fluxes were calculated by multiplying the mean daily discharges by the solute concentrations. During stormflow, solute fluxes were estimated by integrating the instantaneous concentrations by the instantaneous discharge. The continuous solute concentrations were estimated by linear interpolation of the measured solute concentrations (Hinton et al. 1997).

Data analysis

To estimate the influence of flow on concentrations, the data were analysed to determine whether a significant difference existed between concentrations measured during stormflow and during baseflow. Further, to estimate the influence of seasonality, the two subsets of data (i.e., stormflow and baseflow data) were further divided into seasons, under two assumptions. First, it was assumed that vegetative activity followed a cycle of growing and dormant periods, which could affect nitrogen concentrations in streamwater. Second, the assumption was made that stream intermittence exerted a noticeable influence on both hydrology and stream chemistry during the months following the summer drought (see Bernal et al. 2002; Butturini et al. 2002). Thus, the data subsets were analysed to determine whether there were significant differences in concentrations measured during: (1) September to November (the transition from dry to wet conditions, or *transition period*), (2) December to February (the wet and dormant period, or *wet period*), and (3) March to May (i.e., the *vegetative period*).

Statistical analyses were conducted to examine whether a significant difference existed in concentrations during each flow period and/or season. A non-parametric test (Wilcoxon test) was used when comparing data sets because concentrations showed a scattered and skewed distribution. A difference between two groups was considered significant if $p < 0.01$. Correlations between each of two sets of samples were calculated as the Spearman Rank Correlation Coefficient (r_s) (Helsel and Hirsch 1992).

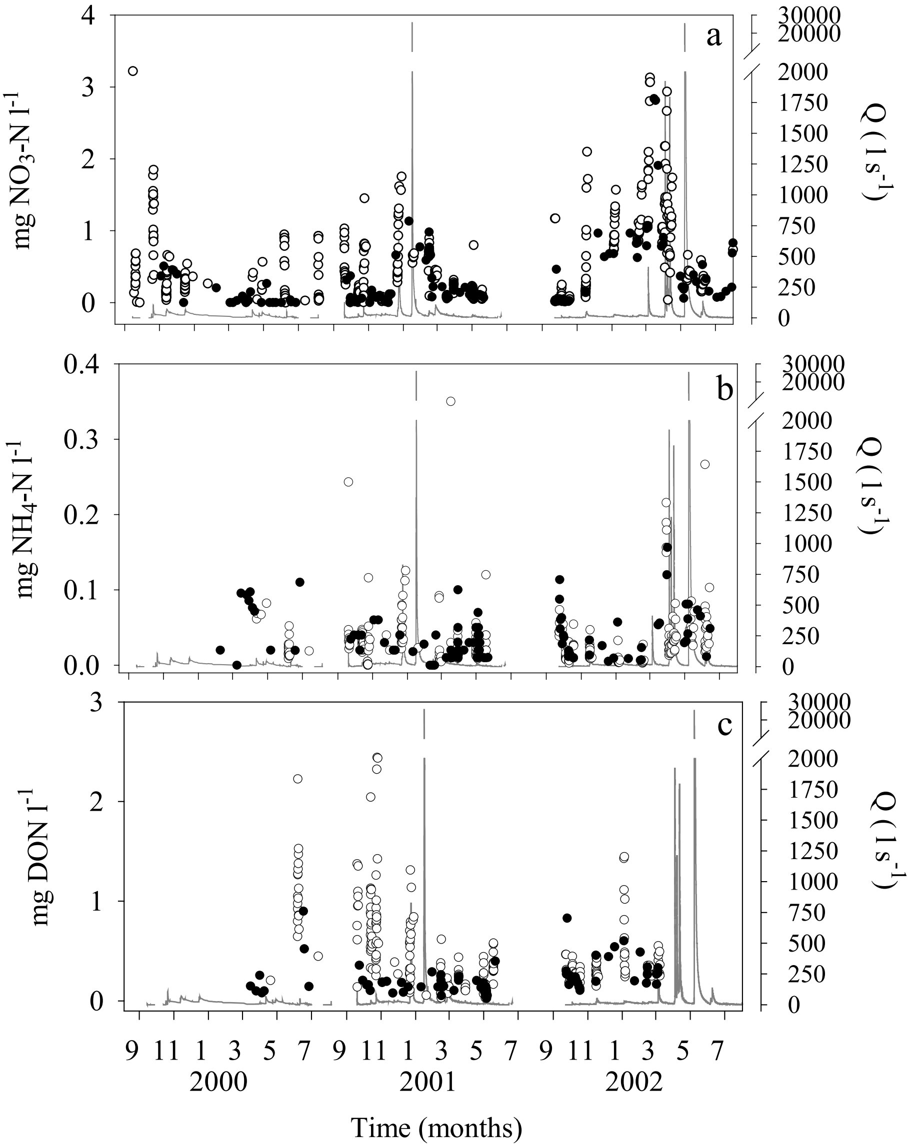

Figure 1.1. Temporal dynamics of discharge (Q, l s^{-1}) (solid line) and (a) NO_3-N (mg l^{-1}); (b) NH_4-N (mg l^{-1}); and (c) DON (mg l^{-1}) in Fuirosos (Catalonia, NE Spain) during the study period (September 1999 - August 2002). Solid circles are baseflow concentrations and open circles are stormflow concentrations.

Results

Seasonal patterns of DIN and DON concentration

Figure 1.1 shows the temporal dynamics of nutrient concentrations during baseflow and stormflow conditions, while mean concentrations for each solute are compiled in Table 1.1. Commonly, the mean was larger than the median due to a positive skewness of data. The difference between mean and median was more pronounced when more extreme values of concentration were recorded, in particular during stormflow conditions (Figure 1.2e, f, g and h).

During baseflow, nitrate and ammonium concentrations had different seasonal patterns. Nitrate was consistently low during both the transition and vegetative periods, while baseflow concentrations increased during the wet season ($p < 0.0001$) (Figure 1.2a). In contrast, ammonium baseflow concentrations were higher after the summer drought than during the wet season ($p < 0.002$) (Figure 1.2b). Baseflow DON concentrations did not have a clear seasonal pattern (Figure 1.2c). In contrast, baseflow DOC concentrations were significantly higher during the transition period than during the remainder of the year ($p < 0.0001$) (Figure 1.2d).

Table 1.1. Mean concentration* (mg l^{-1}) and standard error* during baseflow and stormflow conditions for each solute (NO_3-N, NH_4-N, DON and DOC) separately shown for each season (transition, wet and vegetative) in Fuirosos (Catalonia, NE Spain). In parentheses, number of cases.* Not flow-weighted.

	Baseflow			Stormflow		
	Transition	Wet	Vegetative	Transition	Wet	Vegetative
NO_3-N	0.11 ± 0.02 (87)	0.57 ± 0.1 (22)	0.21 ± 0.05 (38)	0.4 ± 0.04 (158)	0.68 ± 0.04 (113)	0.43 ± 0.09 (74)
NH_4-N	0.044 ± 0.004 (33)	0.019 ± 0.004 (15)	0.037 ± 0.01 (25)	0.033 ± 0.006 (101)	0.026 ± 0.004 (69)	0.033 ± 0.006 (62)
DON	0.31 ± 0.03 (34)	0.29 ± 0.05 (13)	0.17 ± 0.02 (24)	0.61 ± 0.05 (97)	0.4 ± 0.04 (77)	0.26 ± 0.03 (67)
DOC	5.9 ± 0.37 (85)	3.78 ± 0.53 (12)	3.35 ± 0.13 (31)	7.77 ± 0.24 (156)	4.9± 0.2 (95)	4.21± 0.17 (45)

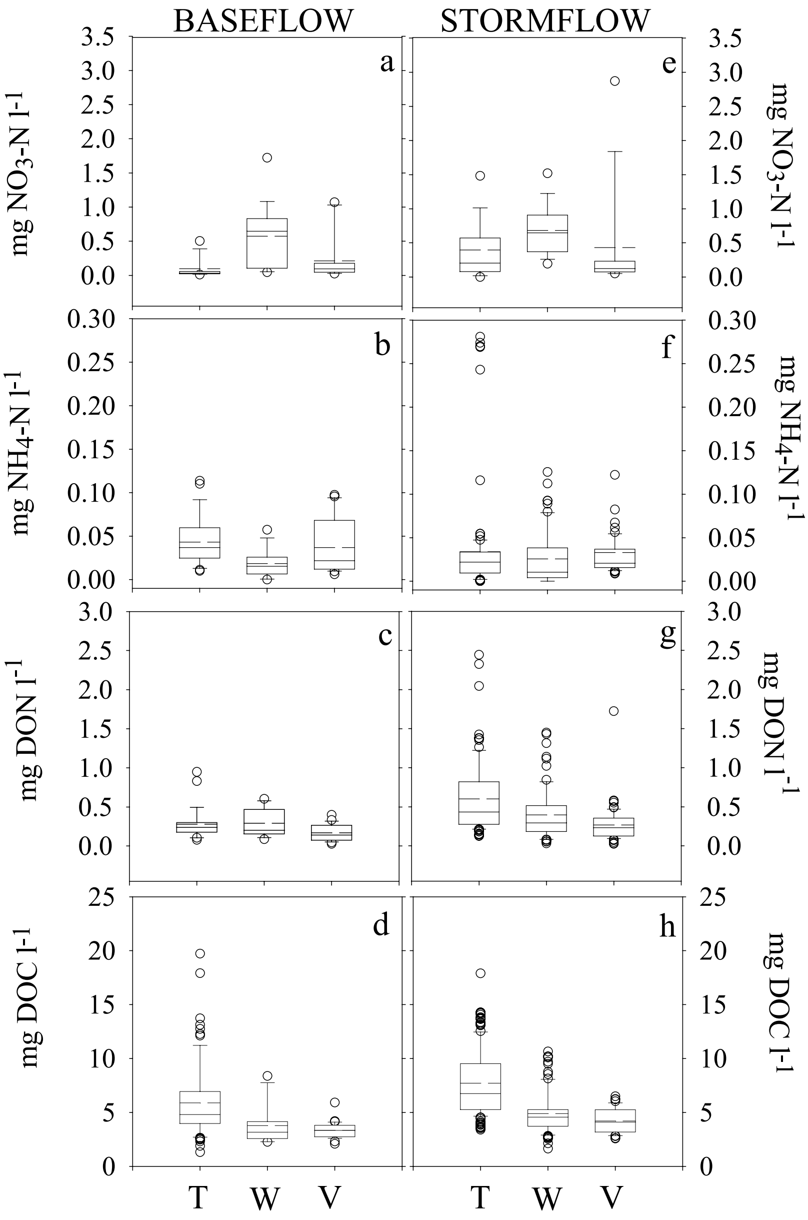

Figure 1.2. Box plots summarising concentration data (mg l^{-1}) in streamwater at Fuirosos (Catalonia, NE Spain) during baseflow (left panels) and stormflow (right panels) conditions. (a and e) NO$_3$-N; (b and f) NH$_4$-N; (c and g) DON; and (d and h) DOC. The centre horizontal line in each box is the median value of concentration. The dashed line is the mean 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. Circles are outliers. T: transition period; W: wet period; V: vegetative period.

During storms, nitrate and DON concentrations tended to increase. The highest nitrate concentrations were recorded during the wet season ($p < 0.0001$, Figure 1.2e), although the most significant changes in relation to baseflow concentrations were recorded during the transition period ($p < 0.0001$). In contrast to nitrate, highest DON and DOC concentrations occurred during the transition period (in both cases $p < 0.0001$) (Figure 1.2g and h). Stormflow concentrations of ammonium did not have a seasonal pattern (Figure 1.2f).

Table 1.2. Spearman rho correlation coefficients (r_s) between pairs of solutes (NO_3-N, NH_4-N, DON, DOC) under baseflow and stormflow conditions. Coefficients are shown for each season (transition, wet and vegetative). * $p < 0.01$, ** $p < 0.001$; *** $p < 0.0001$; ns: not significant ($p > 0.01$).

	Baseflow			Stormflow		
	Transition	Wet	Vegetative	Transition	Wet	Vegetative
NH_4-N *vs* NO_3-N	ns	ns	ns	ns	ns	ns
DON *vs* NO_3-N	ns	ns	ns	0.29^{*}	0.37^{**}	ns
DOC *vs* NO_3-N	ns	ns	-0.6^{**}	0.69^{***}	ns	0.45^{*}
DON *vs* NH_4-N	ns	ns	ns	0.3^{*}	ns	ns
DOC *vs* NH_4-N	0.63^{**}	ns	ns	ns	ns	ns
DOC *vs* DON	0.81^{***}	ns	ns	ns	0.36^{*}	ns

Relationships among nutrients

During the baseflow period, nutrients had a nil or weak relationship among each other, while some seasonal relationships were strong (Table 1.2). During the transition from dry to wet conditions, DON covaried with DOC under baseflow conditions (Figure 1.3a). Ammonium was positively correlated to baseflow DOC concentrations (Figure 1.3b).

During stormflow conditions, covariation of nutrients was nil or weak during the wet and vegetative periods (Table 1.2). During the transition period, all nutrients had a positive, albeit not always significant, relationship. The strongest relationship was between nitrate and DOC (Table 1.2).

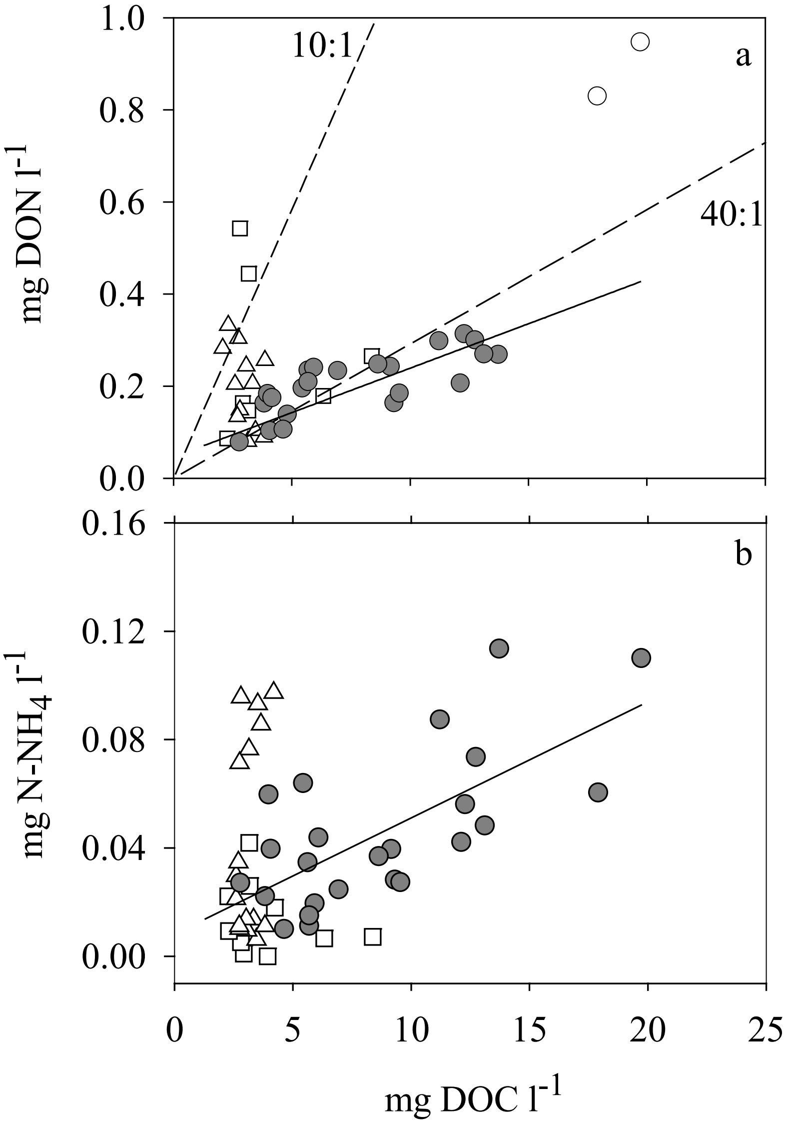

Figure 1.3. Relationships between baseflow concentrations of solutes. (a) DOC *vs.* DON, and (b) DOC *vs.* NH_4-N. Circles are data points from the transition period, squares are from the wet period and triangles from the vegetative period. Solid lines are the linear regressions between solute concentrations during the transition period (only shaded circles) (DOC *vs.* DON, $r^2 = 0.63$, d.f. = 21, $p < 0.0001$; DOC *vs.* NH_4-N, $r^2 = 0.42$, d.f. = 23, $p < 0.0006$). Dashed lines indicate the DOC:DON molar ratios shown.

Seasonal patterns of DOC:DON ratios

DOC:DON ratios during baseflow were higher than during stormflow, 33 ± 2.5 (n=43) *vs.* 24 ± 1.7 (n=177) ($p < 0.0001$). During the wet and vegetative periods, the DOC:DON ratios during baseflow conditions were similar to those during stormflow conditions. The averaged value for both periods was 26 ± 2.2 (n=115). During the transition period, the DOC:DON ratios at baseflow conditions were significantly higher than during the rest of the year ($p < 0.005$) and averaged 42 ± 2.8 (n=24). In contrast to the wet and vegetative periods, the DOC:DON ratios during the transition period storms were lower than those measured at baseflow conditions ($p < 0.0001$) (Figure 1.4).

DOC:DON ratios during high flow had a higher dispersion than during baseflow conditions. DOC:DON ratios below 10 were common, in particular during the transition and vegetative periods. The organic matter with highest DOC:DON ratios was flushed during winter storms, though outliers were detected during all seasons (Figure 1.4b).

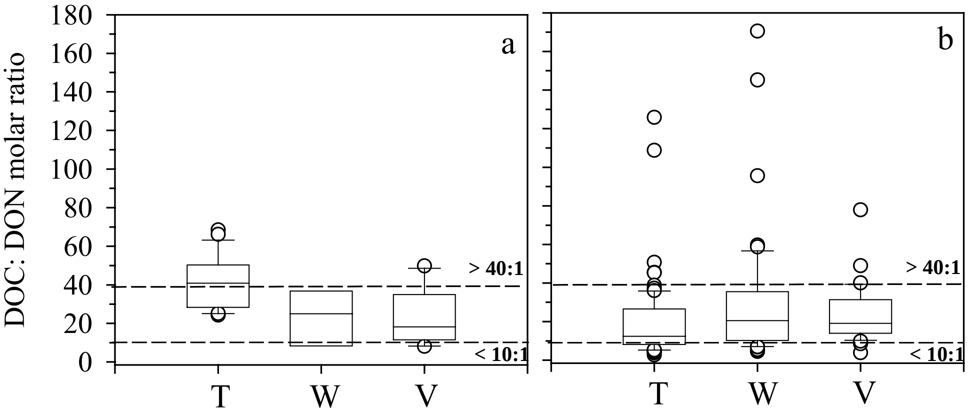

Figure 1.4. Box plots showing the DOC:DON molar ratios for each season during baseflow (panel a) and stormflow (panel b) conditions in Fuirosos (Catalonia, NE Spain). The centre horizontal line in each box is the median value of concentration. Fifty percent of the data points lie within each box. Boxes indicate the upper and lower quartiles of data. The whiskers above and below each box indicate the 90 and 10 percentiles, respectively. Circles are outliers. Dashed lines indicate a DOC:DON ratio of 10 and of 40. T: transition period; W: wet period; V: vegetative period.

Table 1.3. Spearman rho correlation coefficients (r_s) between discharge and concentration for each solute (NO_3-N, NH_4-N, DON, DOC) under baseflow and stormflow conditions. Coefficients are shown for all the data set and for the transition, wet and vegetative periods separately. All: all measurements; * $p < 0.01$, ** $p < 0.001$; ns: not significant ($p > 0.01$). Sample sizes are shown in parentheses for each case.

	Baseflow				Stormflow			
	All	Transition	Wet	Vegetative	All	Transition	Wet	Vegetative
NO_3-N	0.22* (143)	ns	-0.54* (22)	ns	0.47** (349)	0.42** (163)	ns	0.51** (73)
NH_4-N	-0.32* (69)	ns	ns	ns	ns	ns	ns	ns
DON	-0.3* (67)	ns	-0.8** (13)	ns	ns	0.44** (102)	ns	ns
DOC	-0.60** (121)	-0.64** (78)	ns	ns	ns	ns	0.45** (95)	ns

Influence of water flow on nutrient concentrations and annual N export

Discharge was generally not a good predictor of nutrient concentrations in streamwater (Table 1.3). When all measurements were considered, nitrate concentrations had a weak positive relationship with discharge at baseflow conditions, while DON, ammonium, and specially DOC, were significantly lower at greater discharges (Table 1.3). In contrast, during stormflow conditions, nitrate had a positive relationship against discharge, while changes in ammonium, DON and DOC concentrations were not related to discharge variations.

The annual nitrogen export during the period 2000-2001 was 70 kg km^{-2} $year^{-1}$, 26 % delivered during baseflow and 74 % occurring during stormflow. Intense rain episodes strongly influenced the flush of solutes: 82 % of the total nitrogen export during stormflow was delivered during the two single events that occurred in December 2000 and January 2001. During baseflow conditions, the contribution of nitrogen forms was 49 %, 44 % and 7 % as DON, NO_3-N and NH_4-N, respectively. During stormflow conditions, NO_3-N was responsible for 61 % of the nitrogen delivered, while the remaining 30 % and 9 % were delivered as DON and NH_4-N, respectively. In annual terms, 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.

Discussion

Seasonal patterns of organic and inorganic nitrogen

Baseflow conditions

Hedin et al. (1995) hypothesised that dissolved inorganic nitrogen (DIN) availability exerts a stronger biological control than DON. To date, all published studies point in this direction. In many cases, low nitrate concentrations during the growing season were ascribed to a higher biological demand during this time, both in temperate (e.g., Chapman et al. 2001) and Mediterranean catchments (Butturini and Sabater 2002). Accordingly, in Fuirosos, nitrate concentrations were higher during winter months (wet period) than during the rest of the year. Also, high stream nitrate concentrations during the wet period could have been partly due to the elevation of the groundwater level during the growing season. Ohte et al. (2003) proposed that during the wet period, the elevation of the groundwater level could lead to the mixing of deep groundwater with a shallower layer, which would be relatively enriched in nitrate because of little uptake by plants.

Ammonium had a seasonal pattern of change, which was opposite to nitrate, suggesting that mineralization activity by decomposers existed in the mineral soil and/or in the stream channel, particularly during the transition period. This observation coincides with that made by previous studies performed in the soil of the riparian area of Fuirosos reporting highest mineralization rates in autumn (Bernal et al. 2003).

Several studies have shown that DON concentrations are generally larger in summer and autumn. Triska et al. (1984) found that peak litterfall coincided with peak DON concentrations in streamwater, suggesting that autumnal increases in DON concentration were related to the litter inputs. Chapman et al. (2001) attributed summer increases in DON concentrations to an increment in stream primary production. In Fuirosos, DON baseflow concentrations did not follow an identifiable seasonal pattern. This lack of pattern was also reported for a catchment in the Adirondack Mountains (McHale et al. 2000) and for a set of catchments in New England (Campbell et al. 2000). In contrast, DOC had highest concentrations during the transition period. Further, DOC and DON concentrations did not covary (except during the transition period). These results are in contrast with those in previous studies, where DON and DOC concentrations were significantly related to each other (e.g., Campbell et al. 2000) and were, therefore, thought to have a similar origin. In cases in which DOC and DON are not correlated this could be due to both solutes having different sources or sinks.

Although allochthonous inputs (i.e., from terrestrial systems) are the major source of organic matter into streams, autochthonous production within the stream and bank erosion are also possible sources of DON (Arheimer et al. 1996; Chapman et al. 2001). In addition, adsorption and release of DON and DOC from forest floor and mineral soil could be occurring (Solinger et al. 2001) or the stream microbial community could have a preference for consuming either C or N compounds (Sun et al. 1997). Baseflow concentrations of both DON and NH_4 during the transition period, but not during the wet and vegetative periods, showed a positive relationship with DOC, suggesting both DON and NH_4 had come from decomposing litter which had accumulated on the streambed and stream edge zones. The negative relationship between DOC and discharge during baseflow conditions also suggests that during the beginning of the transition period there is an important mobilization of the organic matter accumulated during the period without water flow.

Stormflow conditions

DON and nitrate concentrations in Fuirosos tended to increase during storms as reported by other studies (e.g., Buffam et al. 2001). In Fuirosos, the highest nitrate concentrations were recorded during winter storms. This flushing of nitrate could have been caused by the decoupling of soil nitrification and nitrogen demand by plants (Holloway and Dahlgren 2001). The decoupling could have brought about the increase in nitrate concentrations in subsoil and/or groundwater, both of which may have a major role in the generation of runoff during this period. In contrast to nitrate, the most substantial increases in DON, and particularly in DOC concentrations, occurred during storms in the transition period. The hydrographs during this period were flashy and with low runoff coefficients indicating that the generation of runoff likely occurred primarily at the stream edge zone. Therefore, the "wash out" of solutes probably occurred from areas close to the stream channel. Nutrient concentrations were positively correlated, suggesting that the soil nutrient pool buildup over the drought period in near stream zones might be flushed during the transition period storms. Other studies in Mediterranean streams have reported that the highest nitrate peaks occurred following the summer drought (Àvila et al. 1992; Biron et al. 1999). In Fuirosos, a nitrate release in the stream edge zone in early autumn due to the elevation of the groundwater table into the unsaturated riparian soil layer adjacent to the stream channel has already been described (Butturini et al. 2003).

Sources and quality of organic matter based on DOC:DON ratios

In Fuirosos, the highest DOC:DON ratios (≈ 64) were recorded during baseflow conditions during the transition period, indicating that the organic matter transported by the stream in autumn has a terrestrial origin rather than an in-stream origin (Meybeck 1982). Such high DOC:DON ratios suggest that this organic matter, likely leaf litter accumulated during the drought period, with a low N content and in an early stage of processing, is little available for mineralization. A “critical” C/N of 30:1 for mineralization was proposed by Lutz and Chandler (1946). In contrast, during the transition period storms, the DOC:DON ratio decreased by 3 with respect to baseflow conditions. Such a large decrease could indicate that, during storms, water flowpaths go through organic-rich compartments containing organic matter with a high N content, such as throughfall or shallow subsurface riparian soil. However, humified organic matter composed mainly by recalcitrant N with low C/N (below 10) has been described in deep soils (depths of 50 cm or below) (Àvila et al. 1995). Hence, another reasonable explanation for low DOC:DON ratios could be the mobilization of soluble compounds from the deep soil of the riparian area due to the elevation of the groundwater table. During the wet and vegetative periods, the average DOC:DON ratio was approximately 26 during both baseflow and stormflow conditions, indicating a shift in the dominant source of DOC and DON between the transition and wet periods. Likely, once the groundwater table has recovered from the summer drought there might be a gradual solubilization of the organic matter contained in the subsoil compartment. The pattern observed in Fuirosos during the wet and during the vegetative periods is close to the one reported in temperate regions where changes in C/N ratios between baseflow and stormflow conditions were almost nil (e.g., Campbell et al. 2000; Buffam et al. 2001).

During storms, DOC:DON ratios in Fuirosos had a wide range of variation, in particular during the wet period. Mediterranean catchments are characterized by high temporal and spatial variability of soil moisture, which implies high variability in the size of saturated areas contributing to the generation of runoff (Castillo et al. 2003). As a consequence, organic matter at different stages of decomposition and from different pools of the catchment that are unconnected from each other for long spans of time, may only be leachated during the wettest periods. In Fuirosos, DOC:DON ratios below 10 were recorded mainly during storms. Hagedorn et al. (2000) observed during summer storms narrow DOC:DON ratios (of approximately 6), indicating a source of organic matter that was not coming from soil or throughfall, where DOC:DON ratios were approximately 25. Chapman et al. (2001) reported the lowest DOC:DON ratios occurring in summer, coinciding with peak production in the stream channel. In Fuirosos, high rates of primary production reported in spring immediately before leaf emergence (Acuña et al. 2004) could explain the low DOC:DON ratios observed in some cases during the vegetative period. Bonin et al. (2000) found that the reduction of the C:N ratio in streamwater following an October storm was accompanied by increases in microbial respiration and enzyme activity, which were attributed to large inputs of fresh organic matter following the storm. Acuña et al. (2004) reported that the highest respiration rates in Fuirosos stream occurred in autumn, when accumulation of organic matter on the streambed was high, suggesting that the organic matter was suitable for microbial biodegradation.

Influence of water flow

Discharge explained little of DIN and DON dynamics in Fuirosos, indicating that other factors must be in operation accounting for concentration changes in this Mediterranean stream. Nitrate had a positive relationship with discharge, especially during stormflow conditions, suggesting a “wash out” effect, although the amount of total variance explained by discharge was almost nil. Other studies have also reported low correlation coefficients between nitrate and discharge (McHale et al. 2000; Vanderbilt et al. 2003), generally attributed by authors to a high biological control on nitrate concentrations. These same studies reported higher correlations between DON and discharge because of less biological control. For example, discharge explained 26 % of the variation in DON streamwater concentrations in a forested catchment in the Adirondack Mountains (McHale et al. 2000) and 53 % in a headwater catchment in Switzerland (Hagedorn et al. 2000). By contrast, in Fuirosos the relationship between discharge and DON concentrations was weak or nil, suggesting that the supply of DON from the catchment to the stream was heterogeneous and variable.

Nutrient annual output in Fuirosos and comparison with other catchments

In order to compare the DIN and DON export in Fuirosos with other unpolluted forested catchments, a set of study sites from both Mediterranean and temperate regions was selected (Table 1.4). Dise and Wright (1995) proposed a threshold for throughfall flux of 25 kg N ha^{-1} year^{-1} upon with catchments could be considered N saturated. Based on this criteria none of the catchments selected was N saturated since bulk N deposition ranged from 1.6 to 18 kg N ha^{-1} year^{-1}.

The annual DIN export *vs.* the annual runoff was compared for the set of Mediterranean catchments (Figure 1.5a, capital letters). Levels of annual DIN export in Fuirosos, ranging from 0.1 to 0.46 kg ha^{-1} year^{-1} (present study; Bernal et al. 2002), were in the same range than those reported in other forested Mediterranean catchments with similar annual runoff (e.g., 0.04 kg ha^{-1} year^{-1} in San Dimas Forests, CA (USA) (Riggan et al. 1985), 0.19 – 0.39 kg ha^{-1} year^{-1} in Santa Barbara catchments, CA (USA) (Leydecker, personal communication) or 0.66 kg ha^{-1} year^{-1} in Riera Major, Spain (Butturini and Sabater 2002).

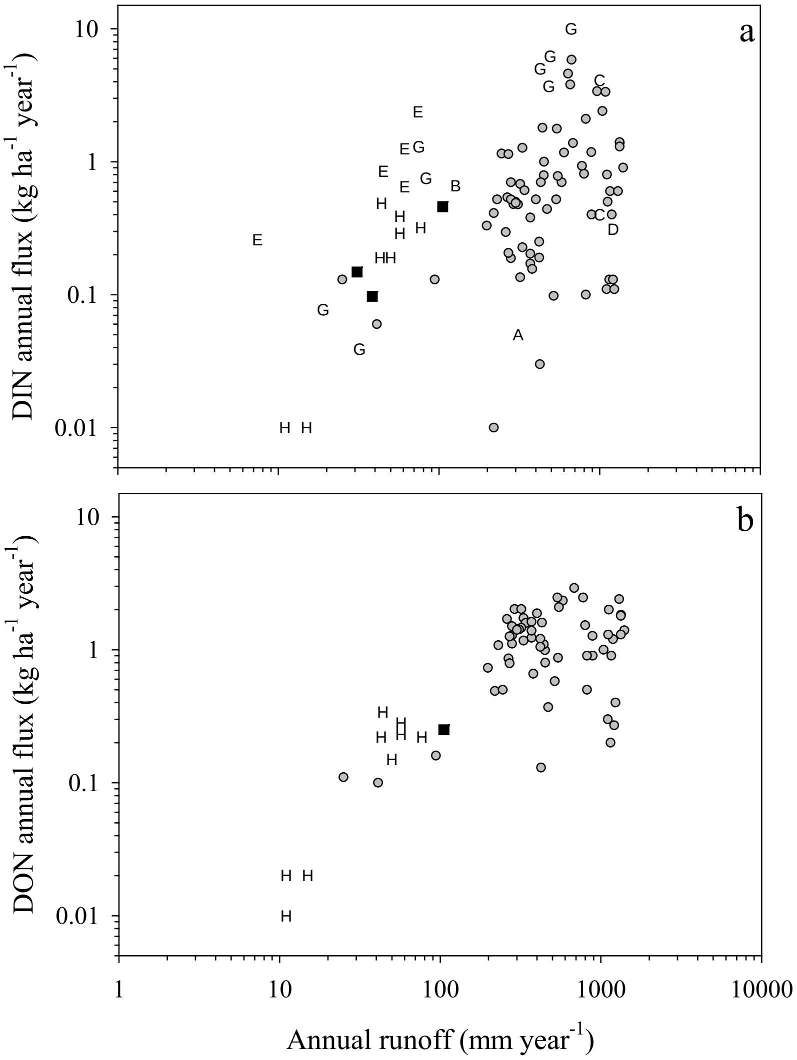

Figure 1.5. Log-log relationship between annual runoff (mm year^{-1}) and annual export (kg ha^{-1} year^{-1}) of: DIN (panel a) and DON (panel b) in Fuirosos (Catalonia, NE Spain) (black squares) and in a set of temperate (grey circles) and Mediterranean catchments (different letters). Data have been extracted from the published studies summarised in Table 1.4. Letters relate to the following studies: (A) Àvila et al. (2002); (B) Butturini and Sabater (2002); (C) Durand et al. (1992); (D) Britton (1991); (E) Meixner and Fenn (2004); (G) Riggan et al. (1985); (H) Leydecker (personal communication).

By contrast, DIN export in Fuirosos was low when compared to those catchments with higher annual runoff (Figure 1.5a) (e.g., 6 kg ha^{-1} year^{-1} in San Dimas Forests, CA (USA) (Table 1.4, Riggan et al. 1985)). The strong relationship generally found between stream discharge and N fluxes (e.g., Lewis et al. 1999) is consistent with the low N export estimated in an undisturbed Mediterranean catchment with low annual runoff such as Fuirosos. In spite of the differences in the annual runoff, annual DIN fluxes in Fuirosos were similar to those in humid Mediterranean catchments (Britton 1991; Durand et al. 1992; Àvila et al. 2002) where the climate is wetter (annual precipitation > 1000 mm) and colder than in semiarid Mediterranean regions (Gasith and Resh 1999). This suggests that in humid Mediterranean regions the leaching of DIN is lower than in semiarid ones.

Table 1.4. Summary of runoff (mm year^{-1}) and annual output (kg ha^{-1} year^{-1}) of DIN (NO_3-N + NH_4-N) and DON for the set of Mediterranean, temperate and tropical catchments included in Figure 1.5. Ref: References to the published studies from where data have been gleaned. WY: water year. [a]References from *Mediterranean catchments*: (F) present study; (f) Bernal et al. 2002; (A) Àvila et al. 2002; (B) Butturini and Sabater 2002; (C) Durand et al. (1992); (D) Britton (1991); (E) Meixner and Fenn (2004); (G) Riggan et al. (1985); (H) Leydecker (personal communication), and from *temperate catchments:* (j) Lewis 2002; (k) Campbell et al. 2000; (m) Vanderbilt et al. 2003; (n) Lovett et al. 2000; (p) Kortelainen et al. 1997; (q) Williams and Melack (1997); (r) Adams et al. 1997; (s) Sickman et al. (2001); (t) Coats and Goldman (2001). [b] only NO_3-N; [c] DON + PON (particulate organic nitrogen); [d] estimated.

Name	Latitude	Longitude	Runoff	Annual output (kg ha^{-1} year^{-1})		Ref[a]
	(°)	(°)	(mm yr^{-1})	DIN	DON	
MEDITERRANEAN CATCHMENTS						
Fuirosos (Catalonia, Spain) (WY00-01)	41N	2E	105.3	0.46	0.25	F
Fuirosos (Catalonia, Spain) (WY98-99)	41N	2E	30.8	0.15[b]	--	f
Fuirosos (Catalonia, Spain) (WY00-01)	41N	2E	38.4	0.097[b]	--	f
La Castanya (Catalonia, Spain)	41N	2E	311	0.05[b]	--	A
Riera Major (Catalonia, Spain)	41N	2E	126.9	0.66[b]	--	B
Mont-Lozere, beech forest (France)	44N	3E	1000[d]	0.40	--	C
Mont-Lozere, spruce forest (France)	44N	3E	1000[d]	4.08	--	C
Swartboskloof (South Africa)	34S	18E	1215	0.31	--	D
Devil Canyon Cat 2, CA (USA)	34N	118W	74	2.37	--	E
Devil Canyon Cat 6, CA (USA)	34N	118W	7.4	0.26	--	E
Devil Canyon Cat 7, CA (USA)	34N	118W	45	0.85	--	E
Devil Canyon Cat 8, CA (USA)	34N	118W	61	1.25	--	E
Devil Canyon Cat 2-trib, CA (USA)	34N	118W	61	0.65	--	E
San Dimas 0803 (WY79-80), CA (USA)	34N	117W	665	10[b]	--	G
San Dimas 0803 (WY80-81), CA (USA)	34N	117W	32	0.04[b]	--	G
San Dimas 0803 (WY81-82), CA (USA)	34N	117W	83	0.75[b]	--	G
San Dimas 0803 (WY82-83), CA (USA)	34N	117W	483	3.7[b]	--	G
San Dimas 0804 (WY79-80), CA(USA)	34N	117W	491	6.2[b]	--	G
San Dimas 0804 (WY80-81), CA (USA)	34N	117W	19	0.08[b]	--	G
San Dimas 0804 (WY81-82), CA (USA)	34N	117W	75	1.3[b]	--	G
San Dimas 0804 (WY82-83), CA (USA)	34N	117W	426	5.0[b]	--	G
Gobernador Creek (WY01-02), CA (USA)	34N	117W	11	0	0.01	H
Gobernador Creek (WY02-03), CA (USA)	34N	117W	57	0.29	0.23	H
Gaviota Creek, CA (WY02-03), (USA)	34N	117W	43	0.19	0.22	H
Upper Mission Creek (WY01-02), CA (USA)	34N	117W	11	0.01	0.02	H
Upper Mission Creek (WY02-03), CA (USA)	34N	117W	57	0.39	0.28	H
Upper Refugio Creek (WY02-03), CA (USA)	34N	117W	77	0.32	0.22	H
Rattlesnake (WY01-02), CA (USA)	34N	117W	15	0.01	0.02	H
Rattlesnake (WY02-03), CA (USA)	34N	117W	50	0.19	0.15	H
San Roque Creek (WY01-02), CA (USA)	34N	117W	1	0	0	H
San Roque Creek (WY02-03), CA (USA)	34N	117W	44	0.49	0.34	H

Table 1.4. *(cont)*

Name	Latitude	Longitude	Runoff	Annual output (kg ha^{-1} year^{-1})		Ref[a]
	(°)	(°)	(mm yr^{-1})	DIN	DON	
TEMPERATE CATCHMENTS						
Young Womans Creek, PA (USA)	41N	77W	541	1.77	0.87	j
Scape Ore Swamp, SC (USA)	34N	80W	266	0.54	0.86	j
Falling Creek, GA (USA)	33N	83W	219	0.41	0.49	j
Sopchoppy, FL (USA)	30N	84W	580	0.7	2.34	j
Sipsey Fork, AL (USA)	34N	87W	470	0.44	0.37	j
Upper Twin Creek, OH (USA)	38N	83W	245	1.15	0.5	j
Popple River, WI (USA)	45N	88W	299	0.5	1.43	j
Rock Creek, MT (USA)	48N	106W	25	0.13	0.11	j
Castle Creek, SD (USA)	44N	103W	41	0.06	0.1	j
Encampment River, WY (USA)	49N	106W	548	0.78	2.09	j
Kiamichi River, OK (USA)	34N	94W	775	0.93	2.47	j
Vallecito Creek, CO (USA)	37N	107W	682	1.38	2.91	j
Wet Bottom Creek, AZ (USA)	34N	111W	94	0.13	0.16	j
Red Butte Creek, UT (USA)	40N	111W	198	0.33	0.73	j
Merced River, CA (USA)	37N	119W	886	1.18	1.27	j
Elder Creek, CA (USA)	39N	123W	1333	1.39	1.83	j
Andrews Creek, WA (USA)	48N	120W	536	0.52	2.47	j
Cache Creek, WY (USA)	43N	110W	449	0.79	0.99	j
Minam River, OR (USA)	45N	117W	799	0.81	1.53	j
Hubbard Brook 6 (WY 95-96), NH (USA)	43N	71W	1400	0.9	1.4	k
Hubbard Brook 6 (WY 96-97), NH (USA)	43N	71W	1190	0.4	1.2	k
Hubbard Brook 7 (WY 95-96), NH (USA)	43N	71W	1330	1.4	1.3	k
Hubbard Brook 7 (WY 96-97), NH (USA)	43N	71W	1160	0.6	0.9	k
Hubbard Brook 8 (WY 95-96), NH (USA)	43N	71W	1330	1.3	1.8	k
Hubbard Brook 8 (WY 96-97), NH (USA)	43N	71W	1110	0.8	1.3	k
Hubbard Brook 9 (WY 95-96), NH (USA)	43N	71W	1300	0.6	2.4	k
Hubbard Brook 9 (WY 96-97), NH (USA)	43N	71W	1120	0.5	2	k
Cone Pond (WY 95-96), NH (USA)	43N	71W	890	0.4	0.9	k
Cone Pond (WY 96-97), NH (USA)	43N	71W	820	0.1	0.9	k
Sleepers River (WY 95-96), VT (USA)	44N	72W	1040	2.4	1	k
Sleepers River (WY 96-97), VT (USA)	44N	72W	820	2.1	0.5	k
Lye Brook 4 (WY 94-95), VT (USA)	43N	73W	450	1	0.8	k
Lye Brook 6 (WY 94-95), VT (USA)	43N	73W	440	1.8	1.1	k
Lye Brook 8 (WY 94-95), VT (USA)	43N	73W	430	0.7	1.6	k
WS2, OR (USA)	45N	121W	1103.5	0.11	0.3	m
WS9, OR (USA)	45N	121W	1231.6	0.11	0.4	m
WS10, OR (USA)	45N	121W	1148.3	0.13	0.2	m
Biscuit, NY (USA)	42N	74W	963.2	3.39 b	--	n
Winnisook, NY (USA)	42N	74W	1084.9	3.35 b	--	n
Huhtisuonoja, Finland	60-69N	20-31E	230	0.52	1.08 c	p
Katajaluoma, Finland	60-69N	20-31E	330	1.27	1.73 c	p
Heinästönluoma, Finland	60-69N	20-31E	290	0.48	2.02 c	p
Sydänmaanoja, Finland	60-69N	20-31E	280	0.7	1.5 c	p
Kruunuoja, Finland	60-69N	20-31E	280	0.19	1.11 c	p
Töllinoja, Finland	60-69N	20-31E	280	0.52	1.28 c	p
Kesselinpuro, Finland	60-69N	20-31E	260	0.29	1.7 c	p
Vertailualue, Finland	60-69N	20-31E	320	0.68	2.02 c	p
Pahkaoja, Finland	60-69N	20-31E	340	0.61	1.59 c	p
Joutenpuro, Finland	60-69N	20-31E	320	0.13	1.46 c	p
Kirsioja, Finland	60-69N	20-31E	370	0.17	1.23 c	p
Kotioja, Finland	60-69N	20-31E	370	0.38	1.62 c	p
Ylijoki, Finland	60-69N	20-31E	400	0.52	1.88 c	p
Teeressuonoja, Finland	60-69N	20-31E	270	1.14	1.26 c	p
Paunulanpuro, Finland	60-69N	20-31E	310	0.48	1.42 c	p
Heinäjoki, Finland	60-69N	20-31E	300	0.49	1.41 c	p
Kellojoki, Finland	60-69N	20-31E	330	0.23	1.17 c	p
Myllypuro, Finland	60-69N	20-31E	370	0.2	1.39 c	p
Vääräjoki, Finland	60-69N	20-31E	420	0.19	1.21 c	p
Vähä-Askanjoki, Finland	60-69N	20-31E	420	0.25	1.05 c	p
Kuusivaaranpuro, Finland	60-69N	20-31E	270	0.21	0.79 c	p
Myllyoja, Finland	60-69N	20-31E	380	0.16	0.66 c	p
Log Creek, Sierra Nevada, CA (USA)	37N	119W	219	0.00	--	q
Tharp' s Creek, Sierra Nevada, CA (USA)	37N	119W	219	0.01	--	q
Fernow Experimental Forest WS3, PE (USA)	39N	79W	656	3.81	--	r
Fernow Experimental Forest WS4, PE (USA)	39N	79W	636	4.60	--	r
Fernow Experimental Forest WS4control, PE (USA)	39N	79W	669	5.85	--	r
Crystal, Sierra Nevada, CA (USA)	37N	119W	424	0.03	0.13	s
Lost, Sierra Nevada, CA (USA)	38N	120W	1210	0.13	0.27	s
Tahoe, Sierra Nevada, CA (USA)	38N	120W	516	0.1	0.58	t

The range of annual DIN fluxes in Mediterranean catchments was compared to that in unpolluted forested catchments from temperate regions in North America and Europe (Table 1.4 and Figure 1.5a, grey circles). Because runoff has a strong influence on total nitrogen load, only temperate catchments with similar annual runoff to the mentioned Mediterranean studies were gleaned. Annual DIN export in Mediterranean streams ranged between 0 and 10 kg N ha^{-1} year^{-1} (e.g., Riggan et al. 1985; Meixner and Fenn 2004) (Table 1.4). For a similar range of annual runoff, annual DIN fluxes in temperate and subalpine catchments were lower than in the Mediterranean ones (e.g., Campbell et al. 2000; Sickman et al. 2001; Lewis 2002) (Table 1.4 and Figure 1.5). This observation suggests that inorganic N might be leached more easily in forested Mediterranean catchments than in temperate ones. Indeed, recent studies performed in Mediterranean regions in CA (USA) suggest an asynchrony between the availability of mineral N and the ability of vegetation to use it (Holloway and Dahlgren 2001; Meixner and Fenn 2004). Accordingly, the simulation approach proposed by Vitousek and Field (2001) pointed out that a highly variable precipitation regime, which is one of the main characteristics of Mediterranean regions, enhances the loss of inorganic N thereby limiting substantially production and biomass in terrestrial ecosystems. The fact that in semiarid Mediterranean regions such as Fuirosos, soil microbial activity and mobilization of DIN are so linked to precipitation events (Cui and Caldwell 1997; Rey et al. 2002) might explain why DON was responsible for only a moderate fraction (35 %) of the total annual N export. This figure is far from those reported by several studies conducted in temperate (Kortelainen et al. 1997; Lewis 2002; Vanderbilt et al. 2003) and tropical catchments (Lewis et al. 1999, Perakis and Hedin 2002), where up to 80 % of the annual N flux was in the form of DON. Nonetheless, annual DON export in Fuirosos (0.25 kg N ha^{-1} year^{-1}) was in the range of those reported for forested catchments from other regions with similar annual runoff (from 30 to 100 mm year^{-1}): 0.16 kg N ha^{-1} year^{-1} in Wet Bottom Creek, AZ (USA), 0.73 kg N ha^{-1} year^{-1} in Red Buttle Creek, UT (USA) (Lewis 2002) or 0.15 – 0.28 kg N ha^{-1} year^{-1} in Santa Barbara catchments (Leydecker, personal communication) (Figure 1.5b, Table 1.4). Further studies in Mediterranean catchments would clarify whether annual DON export is similar to that in temperate catchments with similar annual discharge and, thereby, whether a low fraction of DON is due to a high annual release of DIN.

Concluding remarks

Nutrient dynamics in streamwater during the months following the period without water flow were different than during the rest of the year. Likely, the mobilization of litter and products from decomposition and mineralization processes, accumulated in the streambed and near-stream zones during the drought period may explain the observed relationships among nutrients. During the remainder part of the year (winter and spring), nutrient dynamics in Fuirosos were closer to those reported in temperate catchments. Studies are needed on the level of biodegradability of organic matter and microbial activity helping clarify which is the likely origin and expected availability of organic matter during the transition and wet periods.

Although Fuirosos can not be considered a N-saturated catchment, this relatively undisturbed Mediterranean ecosystem leaks to the stream most of the nitrogen loss in the form of nitrate (57 %). This figure is far from those reported by several studies conducted in temperate and tropical catchments (e.g., Kortelainen et al. 1997; Perakis and Hedin 2002), where up to 80 % of the annual N flux was in the form of DON. In Mediterranean systems, which are water-limited, soil processes occur in pulses enhanced by storm events. Such dynamics may lead to the decoupling between soil nitrification and nutrient uptake by biota, bringing about the leaking of nitrate to the stream. Studies in forested Mediterranean catchments are still few when compared with those in temperate or tropical catchments, and further investigations are needed to gain insights into processes governing organic *vs.* inorganic N fluxes in Mediterranean regions.

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2

Variability of DOC and nitrate responses during storms in a small Mediterranean forested catchment[*]

Key words

Dissolved organic carbon, drought, Factor Analysis, Mediterranean, nitrate, storm responses

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Introduction

Studies in small forested catchments in both Mediterranean and humid regions have shown abrupt changes during storm events (see Meyer et al. 1988 for a thorough review; Mulholland et al. 1990; Àvila et al. 1992; Arheimer et al. 1996; Biron et al. 1999; Brown et al. 1999; Butturini and Sabater 2000; Hagedorn et al. 2000). These short-term variations may be of major importance when solute output fluxes from a catchment have to be estimated because solute concentrations do not vary linearly with discharge (Arheimer et al. 1996). Changes in concentration of DOC and nitrate are often erratic and depend on the intensity of rainfall and on antecedent soil moisture conditions (Àvila et al. 1992; Britton et al. 1993; Biron et al. 1999; Brown et al. 1999), catchment characteristics (i.e., soil type, land use, altitude, topography) and seasonality of biological processes (Arheimer et al. 1996).

Knowledge of the processes affecting solute concentration changes during storms is important for understanding both short and long term variations in solute cycling in catchments and for accurate modelling of solute mass-balances. Dissolved organic carbon (DOC) and nitrogen are two of the most studied nutrients in biogeochemistry. DOC is a primary component in the organic energy budget of running waters (Mulholland 1981; Schlesinger 2001). The flushing of interstitial and soil water DOC into the stream channel during high flow is presumably one of the main surges in DOC (Allan 1995). In Mediterranean forested catchments, in particular, soils are poorly developed (Serrasolses et al. 1999). This might limit DOC inputs into the stream channel and consequently, DOC dynamics might be erratic. In its turn, nitrogen usually limits vegetation growth in arid and semi-arid regions (Terrades 2001). Nitrate is the most abundant and mobile form of nitrogen within stream waters (Schlesinger 2001) and is a limiting nutrient in pristine streams in Mediterranean (Martí and Sabater 1996) and arid regions (Grimm and Fisher 1986).

Studies of solute responses during storms have generally been based on a limited number of events (Britton et al. 1993; Hagedorn et al. 2000) or at different times in the hydrological cycle (Brown et al. 1999; Ribolzi et al. 2000). These studies involve a detailed description of the solute dynamics during stormflow and in the separation of the hydrograph components. Also, the within-year variability in the response of solute concentrations to storms has been examined and a positive relationship has been established between DOC concentration and discharge (Meyer et al. 1988; Brown et al.

1999; Butturini and Sabater 2000) and a large variability in the relationship between nitrate concentrations and discharge has been observed, both among and within catchments (Meyer et al. 1988; Àvila et al. 1992; Arheimer et al. 1996; Hagedorn et al. 2000; Butturini and Sabater 2002). However, the potential seasonality of solute short-term variations induced by storms has not been studied widely. Furthermore, several studies have suggested a relationship between the antecedent moisture conditions and changes in DOC concentration during storms (Biron et al. 1999; Brown et al. 1999). Butturini and Sabater (2000), for example, reported a seasonality of DOC concentrations during storms not related to the duration of the inter-storm period. On the other hand, several authors have noted that the largest changes in nitrate concentration were induced by storms following warm (Roberts et al. 1984) or dry periods (Àvila et al. 1992; Biron et al. 1999).

In this study, factorial analysis is used to separate the different influences of biogeochemical processes and the hydrological cycle on the response of solutes in Fuirosos, a small Mediterranean catchment. This multivariate analysis method has been applied in other hydrogeochemical studies (Reid et al. 1981; Williams et al. 1983; Davies et al. 1993; Evans et al. 1996). The aims of this study were to identify the most relevant factors controlling the hydrological responses of a small intermittent Mediterranean stream during storms and to find general links between those factors and DOC and nitrate concentrations, particularly during storm events. This was undertaken to gain understanding of the variability of DOC and nitrate concentrations during storms in Mediterranean catchments subjected to severe summer drought.

Material and Methods

Stream runoff, precipitation and soil moisture monitoring

The stream water level was monitored continuously from September 1, 1998 to July 1, 2001 using a water pressure sensor connected to an automatic sampler (Sigma$^{©}$ 900 Max). To estimate stream discharge from measurements of stage, the “slug” chloride addition method (Gordon et al. 1992) was used to derive and empirical relationship between discharge and stage. Precipitation data were recorded continuously at 15-min intervals from the meteorological station commissioned in April 1999 on the study site. Before that time, precipitation data were provided by the Catalan Meteorological Service from a meteorological station located at 5 km from the study site. PI_{Max} (mm h^{-1}) is the highest value of precipitation intensity recorded during a precipitation event; the average precipitation intensity (PI_{Avg}, mm h^{-1}) is the ratio between the total precipitation of an event (mm) and its duration (Dt, h). Soil moisture content in the catchment area was monitored continuously from December 1998 to June 2001 by using time domain reflectometry (TDR). Two probes (Campbell CS615) were placed below the soil surface, one just below the organic horizon (i.e., 5-cm depth) and the other at 15-cm depth. Soil moisture (θ) is expressed as percent of the volumetric water content.

Estimation of the Potential Evapotranspiration (PET) and the Soil Moisture Deficit (SMD)

The *in situ* potential evapotranspiration (PET, mm) was calculated on a daily basis from meteorological data using the Pennan-Monteith equation (Campbell and Norman 1998). The soil moisture deficit on a daily basis (SMD of day x, SMD_x, mm) is, for the x^{th} day,

$$SMD_x = SMD_{x-1} - P_x + AET_x \text{, if } \quad SMD_{x-1} > P_x - AET_x . \qquad (2.1)$$

$$SMD_x = 0 \text{,} \qquad\qquad \text{if } \quad SMD_{x-1} < P_x - AET_x \text{,} \qquad (2.2)$$

where P_x is observed daily rainfall on day x and AET_x is the estimated actual evapotranspiration on day x.

Streamwater monitoring during storm events and chemical analyses

The automatic sampler was programmed to start sampling at an increment of the streamwater level of 2-3 cm. During the rising limb of the hydrograph, samples were collected at intervals of 30-60 min; during the recession limb the sampling intervals were 2-5 hours. All water samples were filtered through pre-ashed GF/F fibreglass filters and cold-stored for subsequent analysis. DOC samples were analysed using a high-temperature catalytic oxidation (Shimadzu® TOC analyser). Nitrate in samples was analysed colorimetrically with a Technicon Autoanalyser® (Technicon 1976) using the Griess-Ilosvay method (Keeney and Nelson 1982) after reduction by percolation on a copper doped cadmium column.

Statistical analyses

Factor Analysis classified the climatic and hydrologic data of 26 storm events monitored during three hydrological years (1998-2001). This method reduces the complexity of a large dataset by assuming that a linear relationship exists among the set of variables and a smaller number of underlying "factors". Factors, which are uncorrelated 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, so the remaining factors can be excluded from the analysis, although this implies some loss of the information in the full dataset. Here, only those factors explaining at least as much of the total variance as one of the original variables have been considered. The factors selected were then "rotated" using the Varimax method (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). In the present study, the variables included in the Factorial Analysis (Table 2.1) were the amount of rainfall (P) and the duration of the rainfall events (Dt); the maximum rainfall intensity (PI_{Max}) and the average rainfall intensity (PI_{Avg}); the stream peakflow value minus the baseflow prior to the storm event (ΔQ); the mean soil moisture (θ_{Avg}), the mean potential evapotranspiration (PET_{Avg}) and the mean soil moisture deficit (SMD_{Avg}). Means are for periods between storm events. SMD_{Avg} is the mean soil moisture deficit calculated for the five days before each storm (or less, if two storms were less than five days apart).

Dissolved organic carbon and NO_3-N stream fluxes were calculated both at baseflow and during storm conditions. During baseflow conditions, the daily solute fluxes were calculated by multiplying the mean daily discharges by the instantaneous solute concentrations. During stormflow conditions, solute fluxes were estimated by integrating the instantaneous concentrations by the instantaneous discharges. Continuous solute concentrations were estimated by linear interpolation of measured solute concentrations (Hinton et al. 1997). The end of each storm period was marked by a rate of discharge change lower than 10 % day^{-1}. The change in solute concentrations (Δ DOC (mg-C l^{-1}) and Δ NO_3-N (mg-N l^{-1})) during storms was defined as the difference between peak values measured during the event and the solute concentration in streamwater immediately before the event. Solute concentration during stormflow was regressed against discharge. The analyses were performed with logarithmic transformation of flow, since concentration-discharge relationship rarely changes linearly over time (Arheimer et al. 1996). Changes in solute concentrations were also regressed against variables included in the Factor Analysis and against each factor extracted after the Varimax rotation. A multiple regression analysis was performed between the factors extracted, which are independent of each other, and one dependent variable (i.e., DOC or NO_3-N concentration change). Regression techniques are empirical and, therefore, any statistically significant relationship does not imply causality.

Table 2.1. Precipitation amount (P) and rainfall duration (Dt), rain maximum intensity (PI_{Max}), rain average intensity (PI_{Avg}), soil moisture average (θ_{Avg}), potential evapotranspiration average (PET_{Avg}) and soil moisture deficit average (SMD_{Avg}), in the small forested catchment of Fuirosos (Catalonia, NE Spain). Also shown are magnitude of the flow change (Δ Q) and changes in NO_3-N and DOC concentrations in streamwater during the indicated storm events in the intermittent Fuirosos stream. na, no data available. [a] Positive values indicate that the solute concentration has increased during the storm and negative values indicate that the solute concentration has decreased.* Cases not included in the Factorial Analysis.

Day	P	Dt	PI_{Max}	PI_{Avg}	Δ Q	θ_{Avg}	PET_{Avg}	SMD_{Avg}	Δ NO_3-N	Δ DOC
	(mm)	(h)	(mm $15min^{-1}$)	(mm $15min^{-1}$)	($l\ s^{-1}$)	(%)	(mm)	(mm)	(mg l^{-1})[a]	(mg l^{-1})[a]
Drought period										
23/09/1998	40	68	4.4	0.1	9.55	0.125	3.23	23.91	+ 0.474	+ 16.271
05/10/1998	32	10	4.7	0.8	17.41	0.129	2.83	2.19	+ 0.027	+ 3.528
03/12/1998	112	23	3	1.2	1303.7	0.163	1.11	11.98	+ 1.427	+ 3.169
30/12/1998	34	15	3	0.6	43.64	0.164	0.64	5.85	+ 1.516	-0.249
31/12/1998	31	20	3.4	0.4	165.57	0.175	0.87	0.00	+ 0.96	+ 1.5
09/01/1999	40.6	36	1.5	0.3	117.39	0.167	0.46	0.45	+ 0.067	na
18/01/1999	20	38	2.2	0.1	30.77	0.163	0.75	0.69	-0.032	na
Drought period										
19/09/1999	25	14	3.4	0.4	14.16	0.127	2.90	24.19	+ 0.548	+ 8.9
20/10/1999	45	13	7.8	0.9	102.55	0.147	1.81	0.63	+ 1.444	+ 7.4
12/11/1999	40.8	40	3.6	0.3	55.72	0.155	1.24	1.33	+ 0.56	+ 2.58
15/12/1999	38.6	19	1.6	0.4	23.42	0.164	0.70	3.43	+ 0.439	+ 2.61
31/03/2000	16	53	2	0.1	9.52	0.124	3.30	19.39	+ 0.24	+ 2.25
06/06/2000	14.2	3	3.6	1.2	4.28	0.088	5.48	19.43	+ 0.895	+ 3.98
10/06/2000	30	19	6.6	0.4	52.44	0.092	5.36	14.90	+ 0.08	+ 4.77
Drought period										
19/09/2000	58.6	22	11.8	0.7	127.42	0.139	2.15	47.00	+ 0.99	+ 9.7
29/09/2000	13.4	10	2	0.3	7.38	0.129	2.33	5.46	+ 0.365	+ 2.45
13/10/2000	28	12	1.4	0.6	29.49	0.136	1.29	0.00	+ 0.21	+ 1.884
21/10/2000	37	48	5.2	0.2	79.29	0.149	1.68	1.38	+ 0.731	+ 7.8
21/12/2000	127.6	92	6.4	0.3	816.52	0.168	0.40	1.76	+ 1.471	+ 3.843
12/01/2001*	131.6	54	5.2	0.6	26054	0.165	0.59	3.09	-0.356	+ 5.946
14/02/2001	15.8	9	1.6	0.4	28.04	0.195	1.04	7.06	+ 0.281	+ 0.594
15/02/2001	9.6	3	3.6	0.8	35.17	0.195	0.88	0.00	+ 0.262	+ 0.732
24/02/2001	24.2	29	1	0.2	81.14	0.178	1.57	2.06	+ 0.121	+ 0.31
29/03/2001	16.8	5	6	0.8	20.79	0.162	3.03	11.05	+ 0.245	+ 1.73
30/04/2001	8.6	5	2.8	0.4	22.94	0.109	4.69	26.79	+ 0.09	+ 1.085
04/05/2001	18.9	29	3	0.2	10.35	0.105	3.97	20.24	+ 0.054	na
18/05/2001	7.2	2	8.8	3.6	10	0.124	4.22	13.24	+ 0.131	na

Results

Precipitation and catchment runoff

Annual precipitation during the three hydrological years monitored (1998-2001) averaged 613 mm year^{-1}. Precipitation occurred 2.5 % of the time and rain intensities ranged between 0.02 and 1.45 mm min^{-1}. The highest values of PI_{Max} were recorded in September 1999 (1.29 mm min^{-1}) and September 2000 (0.78 and 1.45 mm min^{-1}). During the study period, 66 precipitation events were recorded (spring (24), summer (12), autumn (15) and winter (15)) with rainfall levels between 5 and 131.6 mm. Precipitation events were generally < 65 mm, except for three cases, when precipitation exceeded 100 mm. On 50 % of occasions, total precipitation was less than 15 mm (Table 2.2). Twenty-six storm events were selected for this study, for which complete climatic, hydrologic and chemical data were available.

Table 2.2. Precipitation (P, mm) events occurred in Fuirosos (Catalonia, NE Spain) during three hydrological periods (1998-2001) grouped by rainfall level classes. In parentheses, occasions in each rainfall class which have been included in analyses.

P (mm)	# cases
5-15	33 (5)
15-25	15 (7)
25-35	10 (6)
35-45	5 (5)
45-55	1 (0)
55-65	1 (1)
> 65	3 (2)
TOTAL	66 (26)

Stream discharge was low during the dry period, from the end of May each year and the channel was completely dry from July to September, until the first autumn rains in late September. During baseflow conditions, discharge ranged between 0.1 l s^{-1} in autumn to 25 l s^{-1} in winter. Precipitations (P) of between 5 and 65 mm induced peak discharges between 4.3 l s^{-1} and 200 l s^{-1}. The rainiest episodes (i.e., P > 100 mm) produced the highest peak discharges, i.e., December 1998 (P =112 mm, Q_{peak} = 1315 l s^{-1}), December 2000 (P = 128 mm, Q_{peak} = 829 l s^{-1}) and January 2001 (P = 132 mm, Q_{peak} = 26000 l s^{-1}) (Figure 2.1).

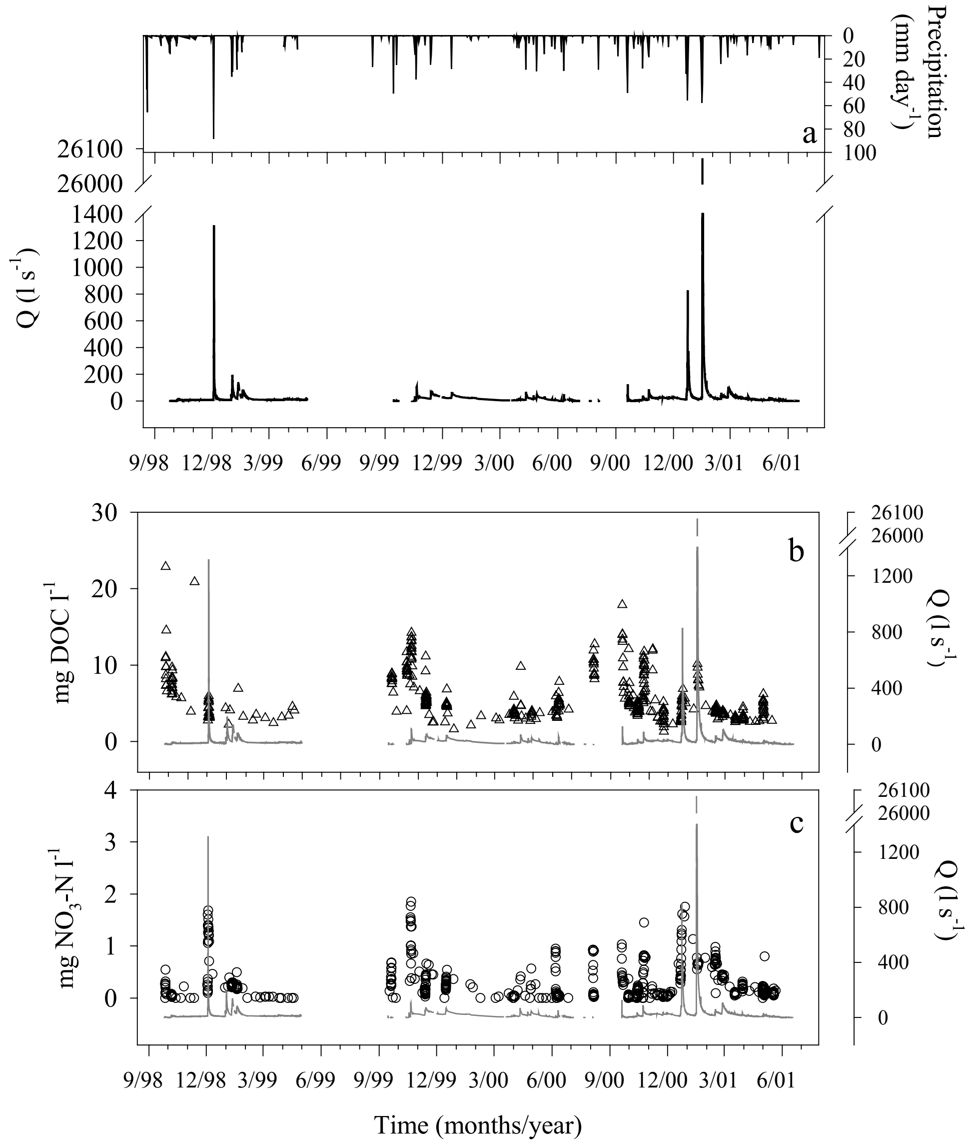

Figure 2.1. Temporal dynamics of: (a) discharge (Q, l s^{-1}), and associated daily precipitation (mm day^{-1}), (b) DOC concentration (mg l^{-1}) and (c) nitrate concentration (mg NO_3-N l^{-1}), in Fuirosos (Catalonia, NE Spain) during the study period (September 1998-July 2001).

The relative contribution of stormflow to the total annual water flux during the three hydrological cycles studied was 41 % in 1998/1999, 35.5 % in 1999/2000, and 72.5 % during 2000/2001. The larger contribution of stormflows in 2000/2001 resulted from the large peak flow in January 2001. Further information about the hydrological regime of Fuirosos stream can be found in Butturini et al. (2002).

Table 2.3. Varimax-rotated factor loadings for the indicated climatic and hydrological variables in 26 storm events in Fuirosos (Catalonia, NE Spain) measured during three hydrological years (1998-2001). Loadings in the range 0 - 0.50 are given in parentheses. The total variance in the data set explained by each factor (%) is also shown.

Variable	Factor		
	1	2	3
P	(-0.12)	0.97	(-0.028)
Dt	(0.05)	0.65	-0.58
PI_{Max}	(0.45)	(0.36)	0.57
PI_{Avg}	(0.08)	(-0.03)	0.93
ΔQ	(-0.18)	0.85	(0.13)
θ_{Avg}	-0.88	(0.19)	(-0.01)
PET_{Avg}	0.86	(-0.33)	(0.18)
SMD_{Avg}	0.82	(0.08)	(0.08)
Variance explained (%)	38.23	25.21	16.78

Factors controlling the hydrological responses during the storm events

The results of the Factor Analysis after Varimax rotation for the 26 selected storm cases are shown in Table 2.3. For the purpose of interpretation, a “high” loading was defined as greater than 0.75, and a “moderate” loading as 0.40 to 0.75. The categories are arbitrary, although Puckett and Bricker (1992), and Evans et al. (1996) have used the same classification. Factor 1 and Factor 2 explained 38.2 % and 25.2 % respectively of the total variance; together they account for 63.4 % of the total variance. In Factor 1, both PET_{Avg} and SMD_{Avg} were inversely related to soil moisture (θ_{Avg}) (Figure 2.2) and consequently Factor 1 may be regarded as representing the moisture conditions prior to the storm event; the storm cases are organized to show a gradient from wet to dry antecedent conditions. In Factor 2, the amount of precipitation (P), the duration of the event (Dt) and the Δ Q were variables with high positive loadings, and consequently this factor is interpreted as the magnitude of the storm event. Factor 3 explained 16.7 % of the total variance and the variables related to rain intensity (i.e., PI_{Max} and PI_{Avg}) had high positive loadings. In contrast, the duration of the precipitation event showed a moderate negative loading (Table 2.3).

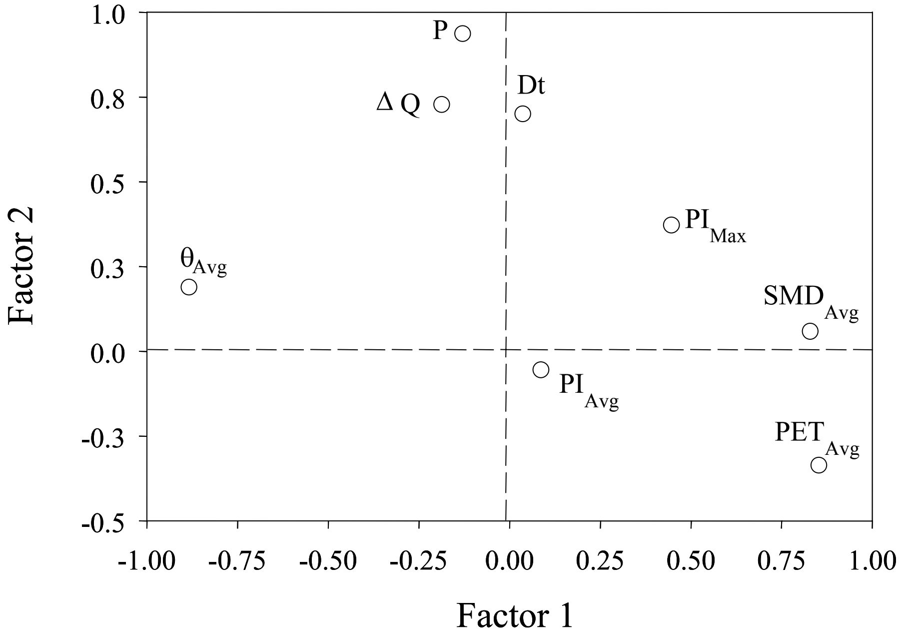

Figure 2.2. Plot of the factor loadings 1 and 2 from the Factor Analysis for the indicated variables (amount of rainfall (P), duration of the rainfall event (Dt), maximum rainfall intensity (PI_{Max}) average rainfall intensity (PI_{Avg}), peak flow value minus the base flow value prior to the storm event (ΔQ), mean soil moisture (θ_{Avg}), mean potential evapotranspiration (PET_{Avg}) and mean soil moisture deficit (SMD_{Avg}). Factor 1 is related to the antecedent moisture conditions, Factor 2 is related to the magnitude of the event.

Annual DOC export and storm DOC responses

Annual DOC export was 180.7 ± 43.8 (standard error) kg C km^{-2} $year^{-1}$. The contribution of storms ranged from 30 to 60 % of the total annual DOC export (Table 2.4). The three largest storms (i.e., P > 100 mm) contributed most to the annual DOC (i.e., 22 % each), owing to the large volume of water in these storm flows. Stream DOC concentration during baseflow conditions averaged 3 mg l^{-1} in winter and spring, while in summer and autumn, DOC concentration ranged from 4 to 8 mg l^{-1}. The DOC concentration during stormflow conditions increased by 1.1 to 3.5 times pre-storm DOC concentrations. The most pronounced concentration changes in DOC concentration occurred during stormflow conditions following droughts (Table 2.1). The variability in DOC concentration explained by the logarithm of discharge during stormflow conditions generated by rainfall up to 65 mm was not significant ($r^2 = 0.004$, d.f. = 308, $p > 0.05$). The overall relationship Δ DOC *vs.* Δ Q for all selected storms was not significant either ($r^2 = 0.09$, d.f. = 21, $p > 0.05$). In contrast, during high flow following the three largest precipitation events (i.e., P >100 mm), there was a strong positive semilog-relationship between discharge and DOC concentration (Figure 2.3, $r^2 = 0.65$, d.f. = 57, $p < 0.001$).

Table 2.4. Summary of annual stream DOC and NO_3-N exports (in kg m^{-2}) in Fuirosos (Catalonia, NE Spain) during three hydrological cycles (1998/1999, 1999/2000, 2000/2001). Export values are shown separately for baseflow and stormflow conditions in each hydrological year. The relative contribution to the total annual export is shown in parentheses in each case.

		1998/1999	1999/2000	2000/2001
DOC	Baseflow	82.42 (70 %)	107.91 (67 %)	106.57 (40 %)
(kg km^{-2})	Stormflow	35.31 (30 %)	51.68 (33 %)	158.34 (60%)
	TOTAL	117.73	159.59	264.91
NO_3-N	Baseflow	1.86 (12.6 %)	4.69 (48.2 %)	7.94 (19.9 %)
(kg N km^{-2})	Stormflow	12.94 (87.4 %)	5.03 (51.8 %)	31.95 (80.1 %)
	TOTAL	14.8	9.72	39.89

The results of the Factorial Analysis showed that the antecedent moisture conditions (i.e., Factor 1) explained 22.7 % of the total variability in DOC concentration during stormflow conditions (Table 2.5). The scores of Factor 1 for spring cases were similar to those of summer ones, indicating that the antecedent moisture conditions in spring and summer were comparable. Nevertheless, DOC concentration changes in streamwater were more pronounced during the late summer storm events (Figure 2.4). The two first factors extracted from the Factorial Analysis (F1+F2 in Table 2.5) and Δ DOC were related significantly ($p < 0.05$). In this case, the variance explained (R^2 = 37.9 %) was larger than that explained by the antecedent moisture conditions only (i.e., Factor 1), suggesting that the changes in DOC concentration during storms were also influenced by the magnitude of the event (i.e., Factor 2).

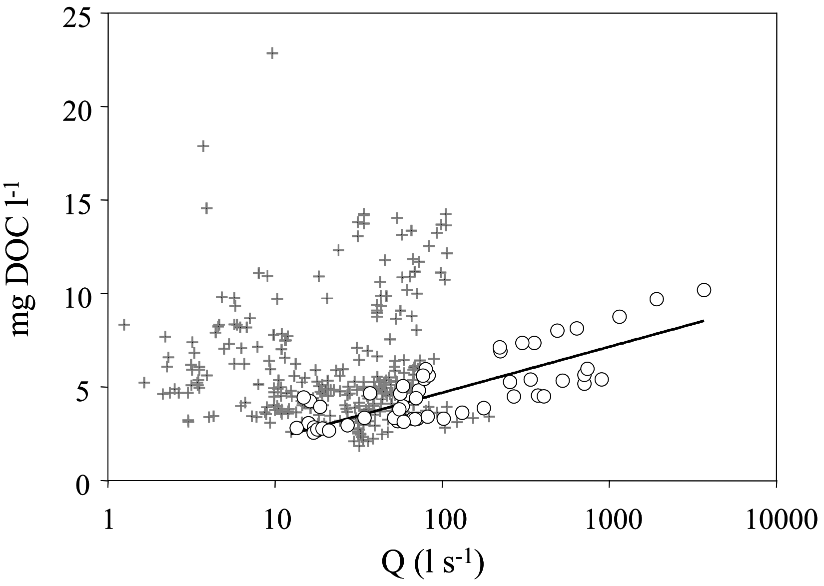

Figure 2.3. Relationship between stream DOC concentrations (mg l^{-1}) and logarithm of the discharge (log Δ Q, l s^{-1}) during stormflow conditions for the entire selected storm events. Crosses correspond to high flow generated by rainfalls smaller than 100 mm. Circles correspond to rainfalls higher than 100 mm. The solid line is the fitted logarithm curve (r^2= 0.65, d.f. = 57, $p < 0.001$).

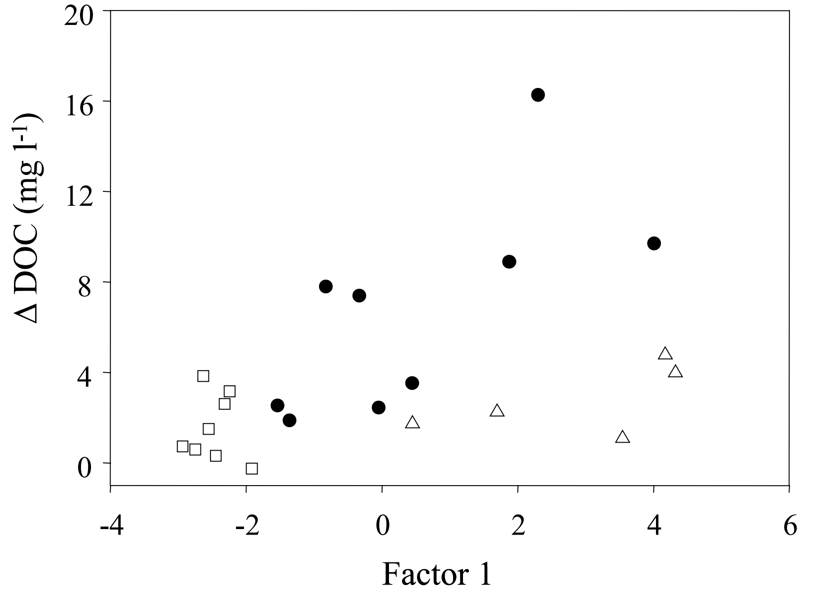

Figure 2.4. Relationship between Factor 1 extracted from the Factor Analysis, representing the antecedent moisture conditions and Δ DOC during high flow for each selected storm event. Squares are winter and autumn cases, filled circles are late summer cases and empty triangles are spring cases.

Annual nitrate export and storm nitrate responses

The calculated annual nitrate (NO_3-N) export was 21.4 ± 9.3 kg N $km^{-2}year^{-1}$. The contribution of storms to the total nitrate-N export was 16.64 ± 7.9 kg N $km^{-2}year^{-1}$, ranging between 52 % and 87 % of the total annual export (Table 2.4). The contribution to the total export of the three largest storms (i.e., P >100 mm) ranged between 34 % (December 1998) and 45 % (December 2000 and January 2001). Stream NO_3-N concentration at baseflow conditions mean 0.04 mg N l^{-1} during spring and summer, while in autumn and winter, baseflow concentrations ranged between 0.15 and 0.8 mg N l^{-1}. The changes in NO_3-N concentration during storms were variable. Nitrate concentrations increased during storms by 1.3 to 9 times those prior to the event. During some storms in late summer, nitrate concentrations increased by one to two orders of magnitude due to the low baseflow concentrations. By contrast, on two occasions (January 18, 1999 and January 12, 2001), NO_3-N concentrations during the high flow decreased in relation to pre-storm concentrations.

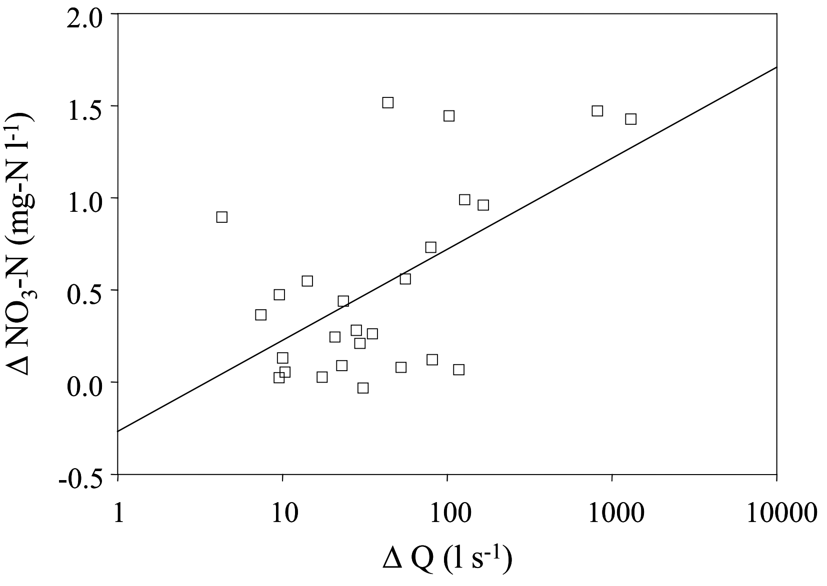

Figure 2.5. Relationship between the nitrate concentration changes during stormflow conditions (Δ NO_3-N, mg-N l^{-1}) and the logarithm of the discharge increment (Δ Q, l s^{-1}) for the 26 selected storms (r^2= 0.33, d.f. = 25, $p < 0.01$).

Table 2.5. r^2 statistic (%) for the regressions between each variable included in the Factorial Analysis (i.e., precipitation amount (P) and rainfall duration (Dt), rain maximum intensity (PI_{Max}), rain average intensity (PI_{Avg}), magnitude of the flow change (Δ Q), soil moisture average (θ_{Avg}), potential evapotranspiration average (PET_{Avg}) and soil moisture deficit average (SMD_{Avg})) and changes in DOC (Δ DOC) and NO_3-N (Δ NO_3-N) concentrations in streamwater during stormflow conditions in Fuirosos (Catalonia, NE Spain). Also shown are r^2 statistic (%) for simple and multiple regressions of the factors extracted from the factorial analysis (Factor 1 (F1), Factor 2 (F2), Factor 3 (F3)) against changes in DOC (Δ DOC) and NO_3-N (Δ NO_3-N) concentrations in streamwater.(* $p < 0.05$, ** $p < 0.01$, ***$p < 0.001$).

	Δ DOC	Δ NO_3-N
P	5.12	12.26
Dt	17.06	0.8
PI_{Max}	27.07*	7.86
PI_{Avg}	1.78	0.37
Δ Q	0.09	32.67**
θ_{Avg}	12.52	2.2
PET_{Avg}	4.92	5.85
SMD_{Avg}	22.16*	0.1
Factor 1	22.71*	3.75
Factor 2	4.11	39.68***
Factor 3	0.31	0.6
F1+F2	37.92*	39.9**
F1+F3	26.1	7.95
F2+F3	4.98	44.83**

A positive weak semilog-relationship between discharge and NO_3-N concentration was found with rainfall levels less than 65 mm, ($r^2 = 0.08$, d.f. = 384, $p < 0.001$). For the largest rain episodes (i.e., P >100 mm) the logarithm of discharge and NO_3-N concentration were weakly related, too ($r^2 = 0.12$, d.f. = 57, $p < 0.01$). However, there was a significant relationship between Δ NO_3-N and Δ Q ($r^2 = 0.32$, d.f. = 26, $p < 0.01$) (Figure 2.5). On the other hand, NO_3-N changes (i.e., Δ NO_3-N) could not be explained by the antecedent moisture conditions (i.e., Factor 1, $r^2 = 0.03$, d.f. = 25, $p > 0.05$), and NO_3-N concentration changes during storms did not show any seasonal trend along the hydrological cycle. Thus, although a statistically significant relationship was found between Δ NO_3-N and the two first factors extracted from the factorial analysis (F1+F2 in Table 2.5, $R^2 = 0.39$, $p < 0.01$), the variance explained (39.9 %) was equal to that explained by the magnitude of the event (i.e., Factor 2).

Discussion

Annual DOC export and storm DOC responses

The annual DOC export estimated for Fuirosos is similar to that estimated by Butturini and Sabater (2000) in another Mediterranean forested catchment (Riera Major: 220 kg C km^{-2} $year^{-1}$). However, these estimates are one to two orders of magnitude lower than the annual DOC export documented for small humid and forested catchments (e.g., 185 x 10^2 kg C km^{-2} $year^{-1}$ in the Pre Alps of central Switzerland, Hagedorn et al. 2000; or 15 x 10^2 kg C km^{-2} $year^{-1}$ in North Carolina, USA. Meyer and Tate 1983). The small value for the annual DOC export in Fuirosos suggests that the productivity in this catchment is low, as has already been observed in other Mediterranean systems (Schlesinger and Hasey 1981).

Hinton et al. (1997), establishing the importance of individual storms for DOC export in humid regions, found that storms were responsible for some 60 % of the total annual DOC export during autumn and 35 % in spring. Also, Butturini and Sabater (2000) estimated that 52 % of the total annual DOC export from Riera Major, a Mediterranean catchment, occurred during storms. In Fuirosos, a maximum of 30 % of the annual DOC export was due to mobilization of dissolved organic matter during storm events, although most of the DOC export occurred during baseflow conditions. Large rain episodes strongly influenced the flush of solutes. For example, a single large storm was found to be responsible for 20 % of the total annual DOC export. The strong positive relationship found between DOC concentrations and discharge for the largest rainfall episodes ($r^2 = 0.65$, $p < 0.001$), suggests that a reservoir of DOC in the soil may be leached only during the largest storms, when pathways other than the usual hydrological pathways are established between the catchment and the stream.

In Fuirosos, discharge was not a good predictor of DOC concentrations during stormflow conditions except for the largest storm cases. In upland catchments and humid climates, a direct relationship between DOC concentration and stream discharge has frequently been observed (Mulholland and Watts 1982; Meyer and Tate 1983; Thurman 1985; Hornberger et al. 1994; Hinton et al. 1997). In other Mediterranean catchments, a moderate relationship between DOC concentrations and stream discharge has been reported (e.g., 40 % of the total DOC variance is explained by discharge in Butturini and Sabater 2000). However, in the Fuirosos case, DOC concentrations were unrelated to stream discharge, suggesting the importance of the biogeochemical processes in the response of solutes. In Fuirosos, the largest changes in DOC concentration during stormflow conditions occurred in late summer, when antecedent conditions following the seasonal drought period were very dry. In contrast, spring storms occurring after similarly dry antecedent conditions did not produce DOC concentration changes as pronounced as during summer. Also, DOC concentration changes in spring were small and comparable to those during winter episodes. Hence, DOC responses in late summer were affected by biogeochemical processes other than antecedent moisture conditions. For instance, the leaching of fresh organic matter accumulated during the drought period in the streambed and in the riparian zone could explain late summer surges in DOC. In fact, previous studies in Fuirosos have estimated that all the leaf litter accumulated on the dry streambed during the period without water flow (0.45 kg DW m^{-2}) was removed and transported downstream with the first rains after the summer drought (Sabater et al. 2001). Baseflow DOC concentrations during September and October were two to four times higher than during the rest of the year. Thus, the influence of the recently fallen litter on DOC concentration may extend also to the baseflow conditions during late summer and early autumn. The influence of litter fall on stormflow DOC concentrations has been observed in other intermittent streams (Biron et al. 1999) and also in perennial streams (Hinton et al. 1997; Butturini and Sabater 2000).

Annual NO_3-N export and storm NO_3-N responses

In Fuirosos, the contribution of storms to the total annual NO_3-N export was larger than that estimated for DOC: the export of NO_3-N during stormflow conditions ranged between 52 % and 87 % of the total annual export, depending on the occurrence of large storm events, while the corresponding figure for DOC was between 30 % and 60 %. The largest storms (i.e., P >100 mm) produced a disproportionally large contribution to the annual nitrate export. A moderately positive relationship was observed between discharge and NO_3-N concentration changes during stormflow conditions ($r^2 = 0.12$, $p < 0.001$). Likewise, studies in humid regions have found that discharge is not a good predictor of nitrate concentrations during stormflow conditions (Arheimer et al. 1996; Hagedorn et al. 2001). However, in Fuirosos, a better relationship was found when the magnitude of the storm event was considered simultaneously (i.e., Factor 2 *vs.* Δ NO_3-N; $r^2 = 0.39$, $p < 0.001$). In Riera Major, a perennial Mediterranean stream, storm magnitude was the key to explaining nitrate concentrations and discharge could account for 47 % of the annual variability in nitrate concentrations (Butturini and Sabater 2002). Thus, in Fuirosos, processes other than hydrological seem to govern the behaviour of nitrate dynamics during stormflow conditions, as has also been found for DOC. Studies focused on the response of solutes during the transition from dry to wet antecedent conditions have observed a marked peak in nitrate concentration after the first storm event ending the drought period, followed by slighter increases during the subsequent events (Àvila et al. 1992; Biron et al. 1999). The increases in nitrate on the first large storm event probably relate to the contribution of rapid runoff through the organic-rich surface horizons. From these near-surface zones, the products of organic matter decomposition and nitrification accumulated during the inter-storm periods are leached during precipitation events (Biron et al. 1999). In Fuirosos, however, nitrate did not behave in this way even though peaks occurred after the drought period. In addition, it was not possible to distinguish any seasonal trend in relation to the antecedent moisture conditions because important nitrate peaks were also detected during winter precipitation events.

Conclusions

This study shows that the hydrochemistry in this Mediterranean intermittent stream is highly variable and unpredictable. However, antecedent moisture conditions, and the magnitude of storm events had significant effects on the hydrochemical responses during storms. DOC showed a moderate relationship with the antecedent moisture conditions, while NO_3-N was significantly related to the magnitude of the storm events.

In perennial streams belonging to both humid (Mulholland and Watt 1982; Meyer and Tate 1983; Thurman et al. 1985; Hornberger et al. 1994; Hinton et al. 1997) and Mediterranean regions (Butturini and Sabater 2000), a direct relationship has been observed between DOC concentrations and stream discharge. In contrast, in the intermittent Fuirosos, DOC concentrations were unrelated to discharge. The suggestion is that DOC dynamics in Fuirosos are related to the abrupt changes occurring between drought and humid periods. For both nitrate and DOC, additional research is necessary to understand the processes that may be altered by these drastic changes, and to evaluate the links between surface and groundwater during and after spates. Catchments such as Fuirosos are particularly susceptible to varying global weather conditions and should become “hot-spots” for future studies on the effects of climatic change on catchment functioning.

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3

Inferring nitrate sources through End Member Mixing Analysis in an intermittent Mediterranean stream*

Key words

EMMA, intermittent stream, Mediterranean regions, nitrate sources, streamwater nitrate, stormflow generation

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* Bernal S., Butturini A. and Sabater F. 2006. Biogeochemistry (in revision).

Introduction

During the past 15 years, the mixing model or end member mixing approach (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 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). Flowpaths 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 baseflow 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). In deed, 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.

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. 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 covered by vegetation (throughfall collector). The collectors were constructed of plastic funnels attached to 2 l and 5 l glass bottles respectively, with 2 cm diameter plastic tubing. Samples were collected after each storm event, but only on a few occasions.

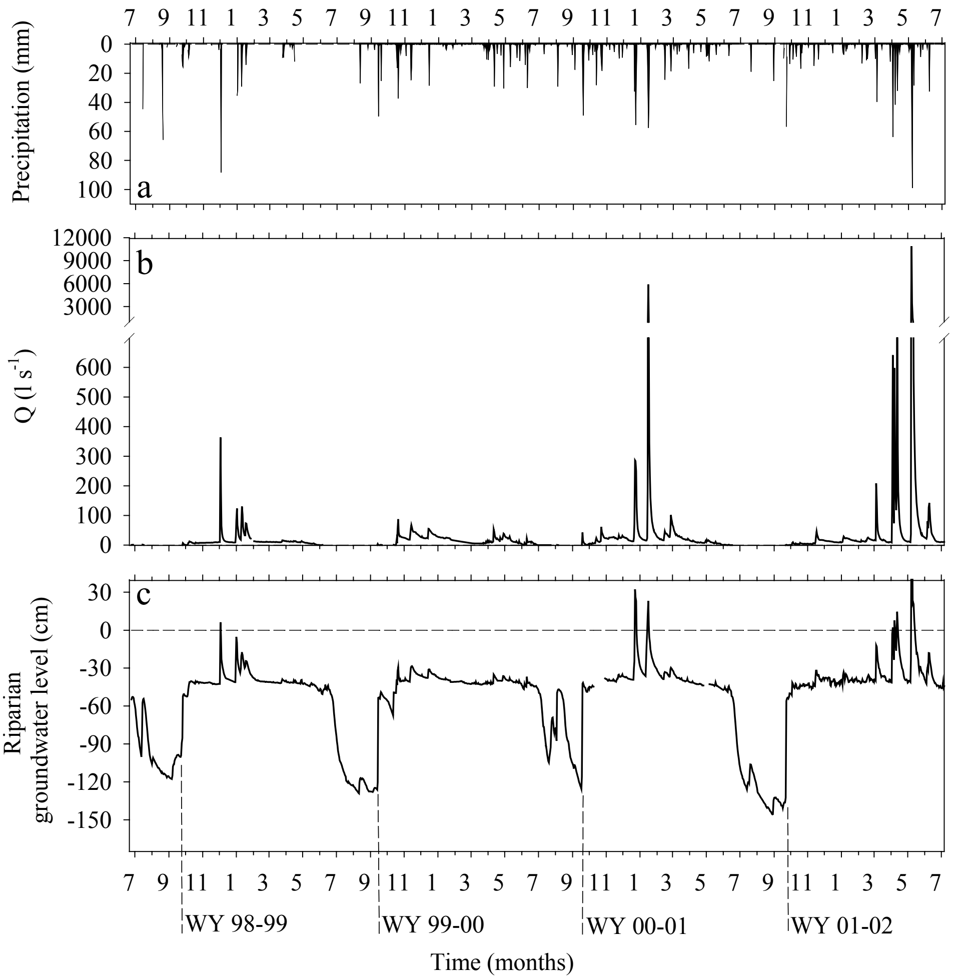

Figure 3.1. Temporal dynamics of (a) precipitation (mm), (b) discharge (Q, l s^{-1}) and (c) riparian groundwater level (cm) in the Fuirosos catchment (Catalonia, NE Spain) during the study period (September 1998 - August 2002). The horizontal dashed line indicates the soil surface. The vertical dashed lines indicate the beginning of the hydrological years.

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 leachate from the upper soil organic layers was collected after each storm event. Overland flow from a trench of 20 m^2 was collected using a 5 m long plastic pipe installed at a depth of 5 cm that drained to a 25 l carboy.

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 located 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. 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) (Figure 3.1). Groundwater representative of the hillslope zone was collected several times a year from headwater springs located at ca. 500 m a.s.l. at the point of discharge from the ground. The riparian area was considered to be the valley-bottom zone that was underlained by an alluvial zone, whereas the area from 500 m a.s.l. to the top of the ridge (770 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 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. 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: the amount of precipitation (P), the maximum rainfall intensity (PI_{Max}), the time to reach the peak of the event (T_{peak}), the runoff coefficient (RC), the amount of precipitation during 1 day (Σ1d), 4 days (Σ 4d), 8 days (Σ 8d) and 32 days (Σ 32d) before each storm event; and the antecedent hydrological precipitation index (API) (see Table 3.1). 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):

$$API_i = K(API_{i-1}) + (P_i - 2), \tag{3.1}$$

where API_{i-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,

$$K = 0.9 - (0.05\cos((2\pi/365)d_i - 2.96)), \tag{3.2}$$

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).

Table 3.1. Storms monitored from 1998 to 2002 in the Fuirosos catchment (Catalonia, NE 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 hours (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	PI_{Max}	API	Σ 1d	Σ 4d	Σ 8d	Σ 32d	T_{peak}	RC
		(mm)	(mm h^{-1})	(mm)	(mm)	(mm)	(mm)	(mm)	(h)	(%)
1*	23/09/1998	40	6.8	21	0.2	22.4	22.6	81.7	2	0.39
2*	05/10/1998	32	4.8	17.3	2.2	5.2	7	62.4	7.7	0.49
3*	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*	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*	20/10/1999	45	12.6	21.3	0	24.2	24.6	51.2	12.2	2.26
12*	12/11/1999	40.8	5.8	19.8	0.2	0.6	1	89.8	12.9	5.91
13*	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*	19/09/2000	49	30	24.1	22.2	22.4	22.6	49.6	2.5	0.31
20*	20/09/2000	9.6	6	68.7	49	71.4	71.6	98.6	7	0.72
21*	29/09/2000	13.4	5.8	34.3	0.2	0.4	0.6	107.6	2	0.11
22*	13/10/2000	28	4.8	19.5	3	8.4	16.4	115	21.5	1.83
23*	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*	21/12/2000	127.6	13	7.2	0.2	0.6	1	3.8	56	6.48
27*	12/01/2001	131.6	15.2	42.7	5.6	5.6	6	135.4	44	71.3
28*	14/02/2001	15.8	4	27.1	0	0.4	0.4	133.2	8	0.87
29*	15/02/2001	9.6	7.6	27.4	18	18.4	18.4	145.6	3.5	1.2
30*	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*	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*	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*	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	1.71
44	03/01/2002	22	1.8	6	7.4	7.8	7.8	20	16.5	4.14
45	07/01/2002	5	3	13.4	0.2	6.5	21.7	41.11	1.2	2.46
46	05/02/2002	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
49	01/03/2002	13	3	2.1	0	0	0.2	41.4	4.2	0.86
50*	04/03/2002	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*	02/04/2002	72	10.6	10.3	0	12.4	12.6	52.02	10.2	9.06
53*	06/04/2002	41.6	7.4	59	0	72.4	84.8	122.64	11.2	17.82
54*	11/04/2002	37	8.4	66.5	14.2	26.8	109.4	145.56	5.2	20.5

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 that has been demonstrated in 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 on 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. For example, in the case of three end members the mass balance equation follows the form:

$$Q_{st} = Q_{em1} + Q_{em2} + Q_{em3}, \tag{3.3}$$

$$U1_{st} Q_{st} = U1_{em1} Q_{em1} + U1_{em2} Q_{em2} + U1_{em3} Q_{em3}, \tag{3.4}$$

$$U2_{st} Q_{st} = U2_{em1} Q_{em1} + U2_{em2} Q_{em2} + U2_{em3} Q_{em3}. \tag{3.5}$$

Where Q is the discharge, $U1$ and $U2$ are the first and second principal component of the PCA, and the subscripts *st* and *em* related to *stream* and *end member* respectively. 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. 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 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_s). 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 3.1). 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 PI_{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 (Figure 3.2). Factor 1 explained the largest proportion of the total variance (35 %). The API, Σ1d, Σ4d, Σ8d and Σ32d exhibited a high positive loading (Table 3.2). Thus, Factor 1 may be regarded as 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.

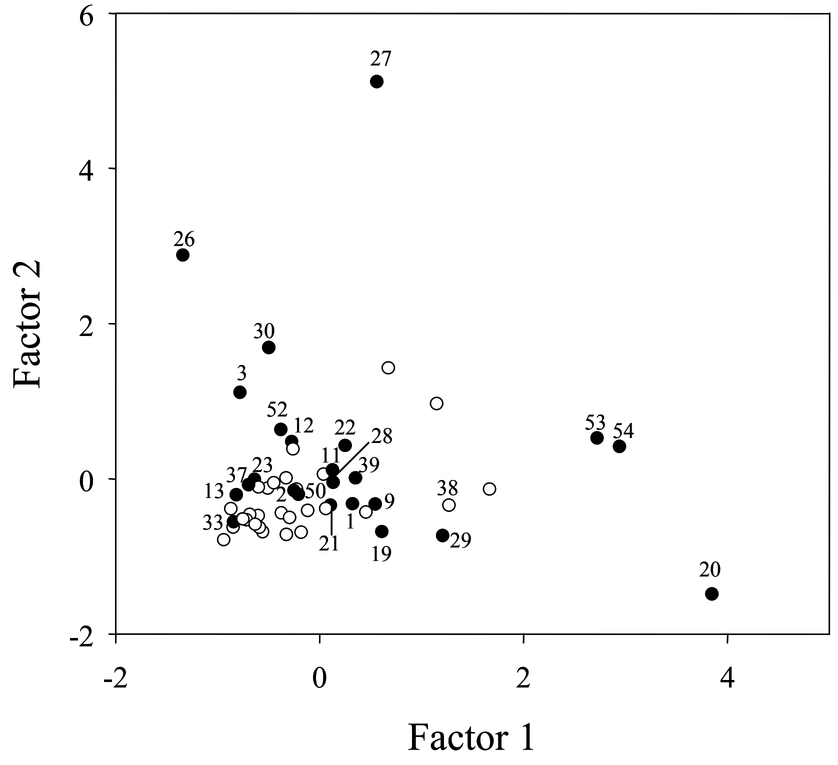

Figure 3.2. Plot of the factor scores 1 and 2 from the Factor Analysis for the 54 storms indicated in Table 3.1. Factor 1 is related to the antecedent moisture conditions, Factor 2 is related to the magnitude of the event. Black circles represent storms in which chemical data were available. To follow results and discussion some storms are indicated as in Table 3.1.

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 3.2). 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 3.2 shows that these 24 storms (black circles) were of different magnitude and covered a wide range of moisture conditions in the catchment.

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 (Figure 3.1c). The water level rose above the soil surface only during 6 of the storm events (storms 3, 26, 27, 52, 53 and 54).

Table 3.2. Varimax-rotated factor loadings for the indicated climatic and hydrological variables in 54 storm events in the Fuirosos catchment (Catalonia, NE 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	(-0.07)	0.77	-0.53
PI_{Max}	(0.01)	(0.11)	-0.86
API	0.85	(0.27)	(0.17)
$\Sigma 1d$	0.67	(-0.18)	(-0.4)
$\Sigma 4d$	0.79	(-0.09)	(-0.28)
$\Sigma 8d$	0.88	(0.01)	(0)
$\Sigma 32d$	0.72	(0.2)	(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

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, $p < 0.01$) (Figure 3.3a). 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

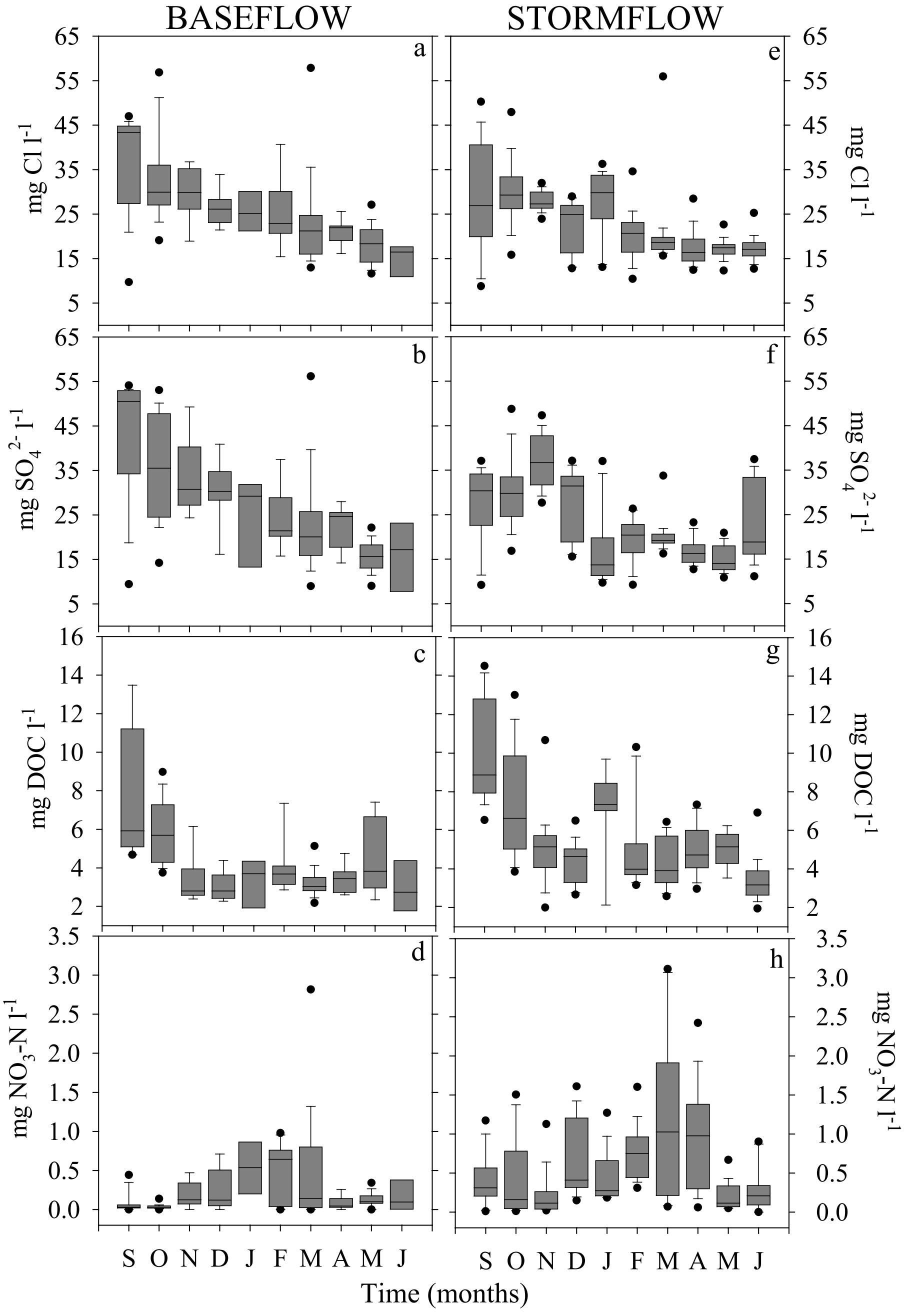

Figure 3.3. Box plots summarizing concentration data (mg l^{-1}) in streamwater at Fuirosos (Catalonia, NE Spain) during baseflow (left panels) and stormflow (right panels) conditions. (a and e) Cl^-; (b and f) SO_4^{2-}; (c and g) DOC; and (d and h) NO_3-N. The centre horizontal line in each box is 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.

(Mann-Whitney test, $p > 0.05$) and decreasing again in May to 16 mg l^{-1} (Mann-Whitney test, $p < 0.01$) (Figure 3.3b). 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 (Figure 3.3c). Nitrate concentrations showed a seasonal pattern with maximum concentrations during the winter months (Figure 3.3d).

During storms, Cl^- concentrations were similar to those measured at baseflow conditions (Figure 3.3a and e), 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 $p_{Abr}< 0.001$). In contrast, DOC and nitrate concentrations tended to increase during storms (Figure 3.3g and h) (Mann-Whitney test, $p_{DOC} < 0.0001$ and $p_{NO3\text{-}N} < 0.0001$), albeit differences between baseflow and stormflow monthly concentrations 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: $n_{CL} = 22$, $p_{CL} < 0.02$ and $n_{NO3\text{-}N} = 18$, $p_{NO3\text{-}N} < 0.02$; for TF *vs.* OF: $n_{CL} = 16$, $p_{CL} < 0.03$ and $n_{NO3\text{-}N} = 22$, $p_{NO3\text{-}N} < 0.01$). Sulfate concentrations increased as precipitation passed through the canopy (Wilcoxon paired t-test, $n_{SO42} =22$, $p_{SO42} < 0.01$), and DOC concentrations were higher in OF than in TF samples (Wilcoxon paired t-test, $n_{DOC} = 11$, $p_{DOC} < 0.01$) (Table 3.3). 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 of runoff that resided for a short time in the catchment. The concentrations of Cl^-, SO_4^{2-} and DOC in streamwater (SW) ranged among those of EW, HGW and RGW (Table 3.3).

The Principal Component 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) (Figure 3.4). 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

Table 3.3. 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: no data 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 (α=0.05).

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 (Figure 3.4).

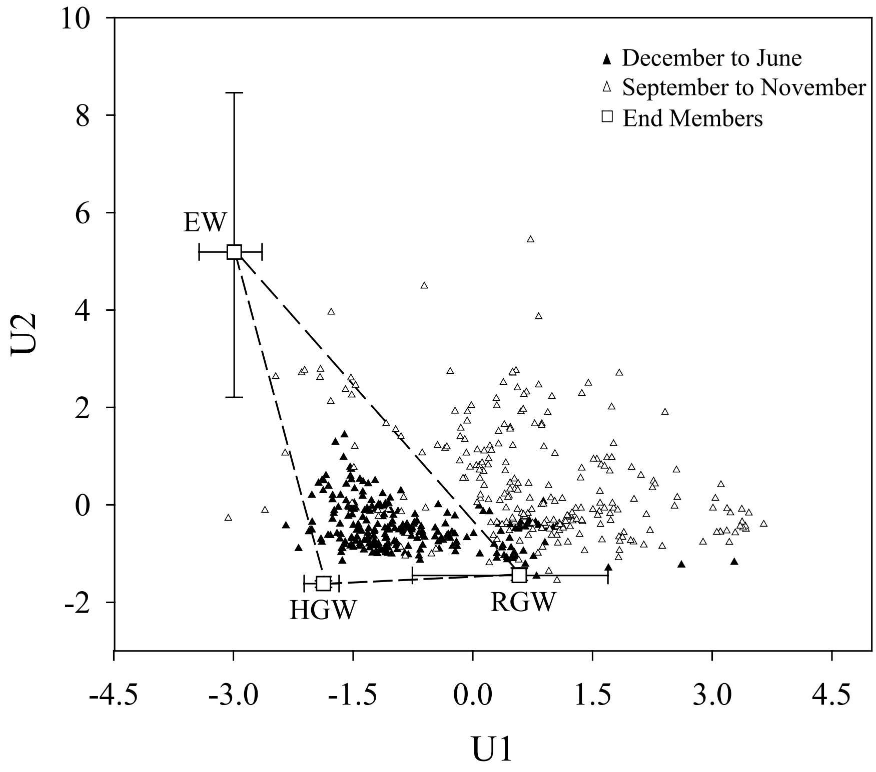

Figure 3.4. Ordination plot of the scores 1 and 2 obtained from the principal component analysis (PCA) of the streamwater data from the Fuirosos catchment (Catalonia, NE Spain). White triangles are streamwater data from September to November. Black triangles are streamwater data from December to June. 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.

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 0.78-1.0, 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 (Figure 3.5). 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 3.4). 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 3.4). In the same way, the percent contribution of HGW increased from the 37 % to the 53 % throughout the wet period in 2001-2002 (Table 3.4).

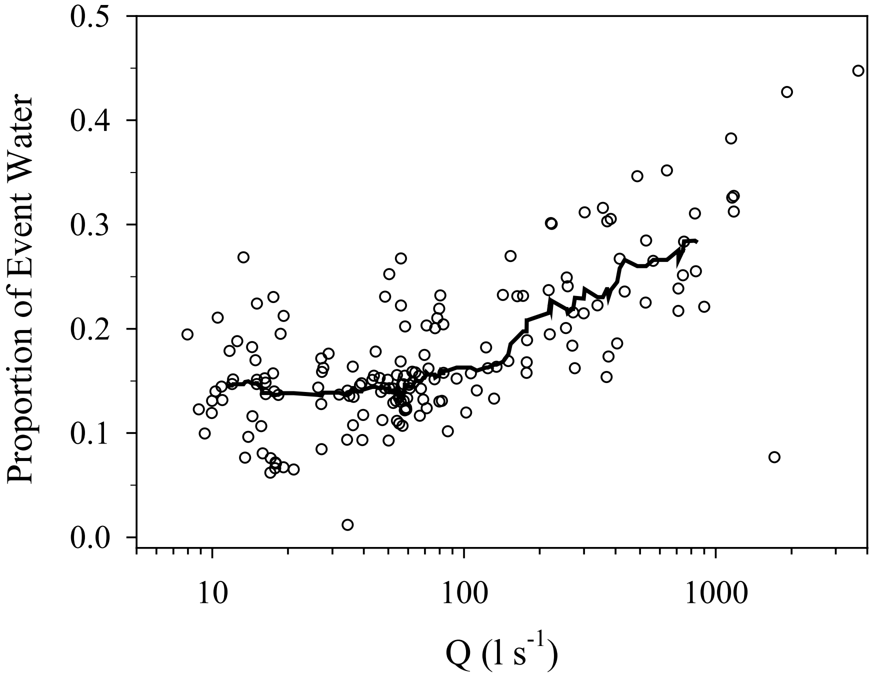

Figure 3.5. Scatterplot of the relative contribution of Event Water estimated with EMMA against discharge during the wet period in the Fuirosos catchment (Catalonia, NE Spain). The solid line is the 20-point moving median. The breakpoint of the relationship (Q = 57 ± 1 l s^{-1}) was estimated by adjusting a bilinear equation (Muggeo 2003).

Table 3.4. 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_s) 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: no data available.

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

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.* Σ 4d; $r_s = 0.59$, $p < 0.05$). 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 ($r_s = 0.67$, $p < 0.05$) and also to the Σ 8d ($r_s = 0.63$, $p < 0.05$) and to the antecedent moisture conditions in the catchment (EW *vs.* Factor 1; $r_s = 0.64$, $p < 0.05$). On the other hand, the proportion of HGW was positively related to the RC ($r_s = 0.62$, $p < 0.05$), whereas the contribution of RGW tended to decrease as the RC increased ($r_s = -0.75$, $p < 0.01$).

Sources of nitrogen during storm events in the wet period

We used the Spearman's coefficient (r_s) 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 3.4). 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 ($r_{HGW} > 0$). 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 ($r_{EW} > 0$) 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 3.4).

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 litter decomposition and root exudates of terrestrial vegetation were the likely sources of organic matter in the catchment, and that these sources decreased with soil depth as in many studies (e.g., McGlynn et al. 1999). 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*). In deed, during the transition period the stream water chemistry was different than during 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 reconcentrated 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, because the highest DOC concentrations in streamwater were observed during this transition period, this DOC may be largely mobilized riparian organic matter (derived mainly from leaf litter) that accumulated in the streambed and near-stream zones during summer (Sabater et al. 2001; Bernal et al. 2005). Tracer concentrations likely changed during the transition period because of the gradual flushing of solutes built up over the dry period, thus violating one of the main assumptions of the mixing model approach, that of constant composition of source waters (Christophersen and Hooper 1992). Such a flushing response would explain why storm episodes that occurred during similar climatic 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 Factor Analysis (Figure 3.2) 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 (Figure 3.2). If only hydrological and/or climatic conditions would be responsible for the chemical differences between storms then we would expect storms with similar hydrological and climatic 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 showed 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 low (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 (14/02/01) and 29 (15/02/01), though the former occurred under drier moisture conditions than the later (Figure 3.2). 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 (Figure 3.2). 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 would be probably 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 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} day^{-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 later 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 (about 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 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 meter from the stream channel averaged 0.5 mg N l^{-1} (Bernal, unpublished data). Since the groundwater body was similar and contiguous at both points (Butturini et al. 2003), such a decrease in nitrate concentrations could not be attributed to a dilution effect. 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 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 (Figure 3.6). 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 at the reach scale 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

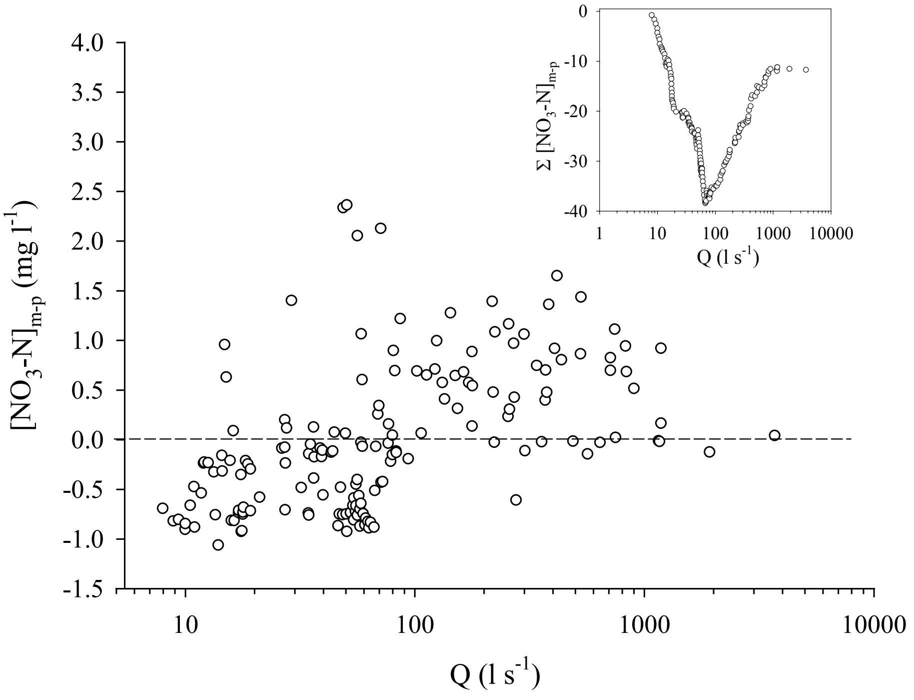

Figure 3.6. Relationship between the difference of measured and predicted NO_3-N concentrations ($[NO_3\text{-}N]_{m\text{-}p}$, mg N l^{-1}) and stream discharge (Q, l s^{-1}). The dashed line indicates equal measured and predicted NO_3-N concentrations. The inset is the sum of $[NO_3\text{-}N]_{m\text{-}p}$ while increasing discharge. At discharges lower than 80 l s^{-1} the slope of the accumulative difference between measured and predicted concentrations (Σ $[NO_3\text{-}N]_{m\text{-}p}$) is negative because predicted concentrations are higher than measured ones (i.e., $[NO_3\text{-}N]_{m\text{-}p} < 0$ predominates over $[NO_3\text{-}N]_{m\text{-}p} > 0$). The opposite trend occurs at discharges higher than 80 l s^{-1}.

inorganic 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, Figure 3.6 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 (Figure 3.6 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 (about 3 ha) at the top of the ridge. 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 resulted not appropriate to highlight water sources contributing to runoff in this intermittent stream during the months following the dry period. In that sense, Butturini et al. (2005) have recently pointed out that a mixing model accounting for the stream catchment interface could explain better than a conventional mixing model the variability of DOC and nitrate during the low flow period following summer drought.

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, in deed, 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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4

Calibration of the INCA model in a Mediterranean forested catchment: the effect of hydrological inter-annual variability in an intermittent stream[*]

Key words

Ammonium, environmental modelling, hydrology, INCA, intermittent stream, Mediterranean climate, nitrate

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[*] Bernal S., Butturini A., Riera J.L., Vázquez E. and Sabater F. 2004. Hydrology and Earth System Sciences 8 (4): 729-741.

Introduction

In recent decades, nitrate export has become a major concern in river systems because of increases in both atmospheric deposition of nitrogen and diffuse transport from agricultural land uses (Vitousek et al. 1979). The Integrated Nitrogen in Catchments model (INCA) (Wade et al. 2002) is one of the first models to simulate the integrated effects of both point and diffuse N sources of streamwater nitrogen and to estimate N loads resulting from microbial processes in the plant/soil system (Whitehead et al. 1998). To develop INCA as a means for improving understanding of the functioning river system and as a tool for integrated catchment management, INCA has been applied to a variety of river systems throughout Europe (Wade et al. 2002). Within this European framework, Mediterranean catchments contrast with the temperate-humid catchments to which INCA has been applied historically, Mediterranean regions are subjected to severe drought periods, which are followed by intense rainfall events. The annual variability in the amount and distribution of precipitation is high, and so is the variability in the annual water balance (Piñol et al. 1991; Ceballos and Schnabel 1998). This precipitation regime results in complex stream hydrology, with high inter-annual variability and a characteristic seasonal pattern in hydrological behaviour. This consists mainly of a long summer dry period that lasts until the first rains in autumn, when the water table recovers, and is followed by a wet period that extends through the autumn and winter months (Butturini et al. 2002; Gallart et al. 2002). Although hydrological stream responses are highly variable, a gradual change from dry to wet periods can be established, from flashy to more damped hydrographs with relevant recession limbs, and from low to high runoff coefficients (Àvila et al. 2002; Butturini et al. 2002; Gallart et al. 2002). Accordingly, Butturini et al. (2002) have suggested the near-stream zone as a key compartment in regulating the hydrological stream response during the transition from the dry to the wet period. Their study, in Fuirosos (Spain) (the catchment studied here), demonstrated that stream runoff and rainfall input were well correlated only after this riparian near-stream compartment was refilled with streamwater. This suggests that, in Mediterranean catchments the upland and the drainage network become disconnected for some periods of the year, or even for some years. Another characteristic of Mediterranean zones is the occurrence of intense precipitation events, resulting in overland flow when rainfall exceeds the soil infiltration rate (Castillo et al. 2003) and leads to extreme flood events, with stream discharge rates orders of magnitude higher than baseflow (Butturini et al. 2002).

Regarding inorganic nitrogen, previous studies in arid and semiarid regions have stressed the importance of alternating dry and humid conditions on soil microbial activity. Soil processes occur in pulses stimulated by the re-wetting of soil after rains (Mummey et al. 1994; Terrades 1996). Moreover, N mineralization in Mediterranean soils exhibits a marked seasonality, with the highest rates occurring in spring and autumn when temperature is favourable and enough water available (Read and Mitchell 1983; Serrasolses et al. 1999). Nitrate leaching is one of the major pathways for N loss in terrestrial ecosystems because nitrate is relatively mobile in soils (Schlesinger 2001). In Mediterranean catchments, nitrate leaching has also a marked seasonal pattern determined by rainfall and almost coincident with the N mineralization pattern (Serrasolses et al. 1999). This is consistent with studies on nitrate dynamics during stormflow periods in Mediterranean and semiarid regions that have described important peaks of nitrate concentrations during the first rains after the drought period (Àvila 1995; Biron et al. 1999). Nevertheless, the relationship between discharge and nitrate concentration in Mediterranean catchments remains unclear: a study conducted in a sub-humid Mediterramean catchment, Riera Major, concluded that discharge was a key control on nitrogen dynamics (Butturini and Sabater 2002), while recent work in Fuirosos showed that discharge was not a good predictor of nitrate concentrations (Bernal et al. 2002).

Within this hydrological and biogeochemical framework, the aim of this study was to test the ability of the INCA model (Wade et al. 2002) to simulate streamflow and streamwater nitrate and ammonium dynamics and loads in a Mediterranean catchment and thereby to test whether the model structure was an appropriate representation of the hydrologic and nutrient dynamics. The model was applied to the Fuirosos Stream Watershed, an almost "pristine", undisturbed forested catchment, with little agricultural activity and no urban areas. Therefore, validating the capacity of INCA to simulate discharge and N loads can be accomplished without interference of any significant point or diffuse agricultural N sources. Because stream hydrology in Fuirosos shows a high inter-annual variability, the model calibration may be affected by the period selected. Thus, in addition to the three year period, the model was calibrated for two years with contrasting precipitation regimes. This calibration process is an essential step before the INCA model can be used to investigate climate, deposition or land-use change scenarios in Mediterranean catchments.

Material and Methods

Hydrological monitoring, sampling and water analysis

Stream water level was monitored continuously from 1 July 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 the "slug" chloride addition method in the field (Gordon et al. 1992).

Baseflow stream water samples were taken at least once every ten days. To monitor nutrient dynamics during stormflow, the automatic sampler was programmed to start sampling at an increment in the streamwater level of 2-3 cm. In this way, water samples were taken during the rising and the recession limb of the hydrograph. A daily average of nitrogen concentrations during stormflow conditions was used in order to compare simulated daily nitrogen concentration with measured concentration. All water samples were filtered through pre-ashed fibreglass filters (Whatman® GF/F) and cold-stored until analysed. Both nitrate and ammonium were analysed colorimetrically with a Technicon Autoanalyser® (Technicon 1976); nitrate with the Griess-Ilosvay method (Keeney and Nelson 1982) after reduction by percolation on a copperised cadmium column, and ammonium after oxidation with salicilate using sodium nitroprusside as a catalyser (Hach 1992). To compare the estimations of export of inorganic nitrogen derived from the measurements with those derived from INCA N estimations, NO_3-N and NH_4-N stream fluxes were calculated by multiplying average daily discharges by solute instantaneous concentrations. At basal conditions, daily continuous solute concentration was estimated by linear interpolation of the measured solute concentration.

INCA model description

On the basis of earlier work by Whitehead et al. (1998), a new version of the process-based INCA model has been developed (Wade et al. 2002). This model integrates hydrology, catchment and river N processes, and simulates daily NO_3-N and NH_4-N concentrations. Sources of nitrogen include atmospheric deposition, terrestrial environment, urban areas and direct discharges. The hydrological model is based on a simple two-compartment system, i.e., the soil zone and the groundwater compartment. Daily stream flow is derived from the output of the two compartments as follows (Whitehead et al. 1998):

Soil zone: $$dx_1/dt = (HER - x_1)/T_1 \,. \qquad (4.1)$$

Groundwater: $$dx_2/dt = (BFIx_1 - x_2)/T_2 \,, \qquad (4.2)$$

where x_1 and x_2 are output flows from the soil and groundwater stores (m^3 s^{-1} km^{-2}), T_1 and T_2 are residence times in days in each compartment, HER is the hydrologically effective rainfall (mm), and BFI is the base flow index, i.e. the proportion of water being transferred from the soil zone to the groundwater zone.

Model input data

The input data for INCA are daily data series of precipitation, air temperature, soil moisture deficit and hydrological effective rainfall (Figure 4.1).

Precipitation and air temperature

Precipitation and air temperature data were recorded continuously at 15 min intervals at a meteorological station commissioned in April 1999 at the study site. Previous precipitation data were provided by the Catalan Meteorological service for a meteorological station located 5 km away. On-site daily meteorological measurements facilitated estimation of daily potential evapotranspiration (PET, mm) using the Penman-Monteith equation (Campbell and Norman 1998).

Soil moisture deficit (SMD)

Daily soil moisture deficit (SMD, mm) was estimated for the xth day as:

$$SMD_x = SMD_{x-1} - (P_x - I_x) + AET_x, \quad \text{if} \quad SMD_{x-1} > (P_x - I_x) - AET_x \,. \qquad (4.3)$$

$$SMD_x = 0\,, \quad \text{if} \quad SMD_{x-1} < (P_x - I_x) - AET_x \,, \qquad (4.4)$$

where P is the observed daily rainfall (mm), AET is the estimated actual evapotranspiration (mm) and I is the rainfall interception by tree canopies (mm).

Based on previous studies in Mediterranean catchments, rainfall interception by tree canopies at event scale was assumed to be 15 % of the total bulk precipitation, except for events occurring during very dry atmospheric conditions when rainfall interception can be up to 49 % of the total bulk precipitation (Llorens et al. 1997).

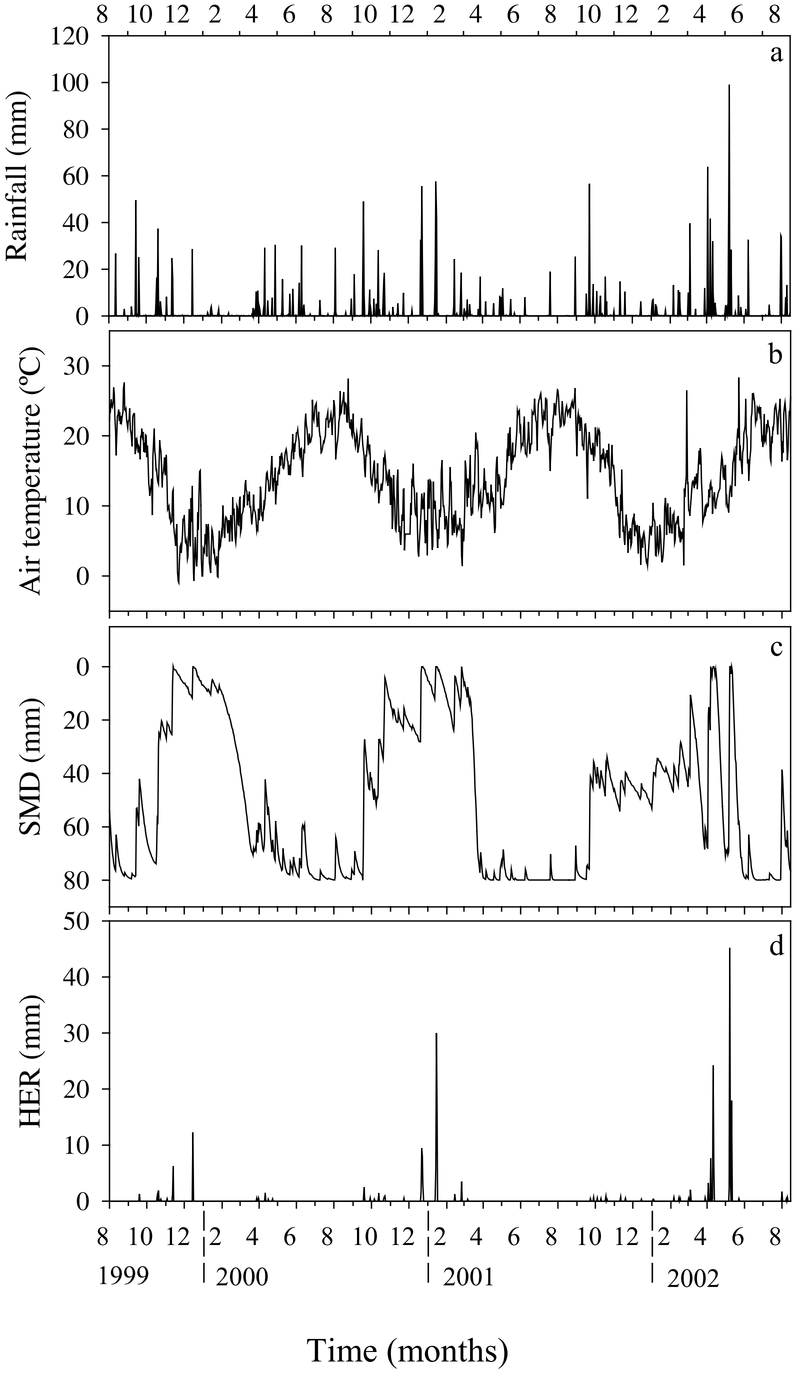

Figure 4.1. Bulk rainfall, air temperature, soil moisture deficit (SMD) and hydrologically effective rainfall (HER) at Fuirosos for the period 1999-2002.

Actual evapotranspiration (AET)

Regarding tree transpiration (T), previous work showed a strong dependency of transpiration on PET when soil water was not limiting (Levitt et al. 1995). Several studies have reported a ratio T/PET ranging from 0.7 to 0.8 (Bréda et al. 1993). In the present work a value of 0.8 has been used. Further, Mediterranean vegetation can limit transpiration when soil becomes dry by mechanisms related to stomatal closure (Terrades 2001). Bréda and Granier (1996) showed that under conditions of water stress, the ratio T/PET decreases linearly as soon as extractable water falls below a threshold, when regulation of transpiration occurs because of stomatal closure. This critical value was around 0.4 and was found to be constant for both coniferous and broad-leaved species, regardless of the technique used to estimate transpiration (Granier et al. 1999). Thus, actual evapotranspiration for the xth day was estimated here as follows:

$$AET_x = k_c PET_x , \qquad \text{if} \qquad SMD_{x-1} < SMD_{THR} . \tag{4.5}$$

$$AET_x = k_c PET_x (SMD_{x-1} SMD_{MAX}) / (SMD_{THR} - SMD_{MAX}) , \qquad \text{if} \qquad SMD_{x-1} > SMD_{THR} , \tag{4.6}$$

where AET is actual evapotranspiration (mm), PET is potential evapotranspiration (mm) and SMD is soil moisture deficit (mm). k_c is the ratio T/PET when soil water is not limiting transpiration. SMD_{MAX} is the maximum soil water deficit and SMD_{THR} is the value of SMD at which transpiration begins to decrease due to water stress.

Hydrologically effective rainfall (HER)

In the INCA model the Hydrologically Effective Rainfall (HER) is used to drive the water flow and N fluxes through the catchment system. Generally, HER for the xth day is calculated as follows:

$$HER_x = (P_x - I_x) - SMD_{x-1} - AET_x , \text{if} \qquad (P_x - I_x) > SMD_{x-1} + AET_x . \tag{4.7}$$

$$HER_x = 0 , \qquad \text{if} \qquad (P_x - I_x) < SMD_{x-1} + AET_x , \tag{4.8}$$

where P is observed daily rainfall (mm), I is rainfall interception (mm), AET is estimated actual evapotranspiration (mm) and SMD is estimated soil moisture deficit (mm). Unfortunately, no standard method for the calculation of HER is yet available for

Mediterranean regions, and thus some additional points based on field observation are considered here. For instance, in Fuirosos small to medium peak discharges occur even when most of the soil moisture in the catchment is below field capacity, because some zones at the valley bottom and near the stream channel may be water-saturated. Those episodes imply the leaching of soluble compounds and although they may be negligible in terms of annual N fluxes, they may be relevant in terms of temporal dynamics. In Fuirosos, this riparian zone has been estimated to be 0.7 % of the total catchment area, and in this study it has been considered that the net precipitation falling on that area reaches the stream channel, except during the driest moments.

Land use and N deposition

Land use data were derived from the 1998 digital land use / land cover map of Catalonia, a raster dataset with 30 m cell size derived from Landsat TM satellite imagery.

Recently, Rodà et al. (2002) have estimated the atmospheric N deposition in a forest situated in Montseny Mountains, less than 30 km from Fuirosos. The wet deposition of inorganic N for this region was 5.7 kg N ha^{-1} year^{-1}, 52 % as ammonium and 48 % as nitrate. The dry deposition of inorganic N was 9.2 kg N ha^{-1} year^{-1}, 55 % as nitrate and the remaining 45 % as ammonium (Rodà et al. 2002).

Parameterization

The plant growth period was set to 190 days and plant uptake was adjusted to give the N demand estimated for other Mediterranean oak forests (Bonilla and Rodà 1992).

In INCA the following velocity-flow relationship is used to estimate residence times of water (Wade et al. 2002):

$$V = aQ^b, \tag{4.9}$$

where V and Q are mean daily velocity and flow respectively, and a and b are constants. In Fuirosos this relationship has been estimated empirically by tracer additions: a = 0.867 and b = 0.630 ($r^2 = 0.94$, d.f. =16, $p < 0.0001$).

Parameters such as the base flow index or time constants for the soil reactive zone and the groundwater zone were adjusted against the peaks of the hydrograph. Parameters related to soil N processes were adjusted to obtain: (i) simulated streamwater nitrate concentrations similar to those measured in the field, and (ii) simulated nitrogen annual rates similar to those reported in the literature.

Calibration of the INCA model for different hydrological periods

Climatic data was available for the period 1999-2002. These three hydrological years were characterized by a large variability in river flow and climatic conditions. A hydrological year was defined from the recovery of stream water with the first autumn rains until the stream bed dried out in early summer. During the first hydrological year 1999-2000, rainfall input was low (525 mm) and there was a prolonged drought period in the summer, with dry stream bed for 75 days. The total runoff for this period was 38.4 mm, less than 8 % of the total precipitation. During the second hydrological year (2000-2001), total precipitation (P) was 753 mm, of which 35 % was due to two single events: December 2000 (P = 128 mm, $Q_{peak} = 829\ l\ s^{-1}$) and January 2001 (P = 132 mm, $Q_{peak} = 26000\ l\ s^{-1}$). Annual runoff was 14 % of total precipitation, with ca. 71 % of it due to the severe storm event that occurred in January 2001. During this year the stream was dry for 72 days. The third period (2001-2002) was by far the wettest with a total precipitation of 871 mm. Annual runoff accounted for 26 % of total rainfall and the stream did not dry out in the summer. In May 2002, an extreme flood event (P = 150 mm, $Q_{peak} = 28000\ l\ s^{-1}$) was responsible for 40 % of the annual runoff. The events occurring in January 2001 and May 2002 were so severe that the field equipment was swept away by the flood waters, which implies a high uncertainty in the estimation of discharge. For this reason, these two extreme events were not considered when comparing simulated and observed data.

Model calibration was performed separately for three sets of data, i.e. the whole three-year period, the driest year and the wettest year. The aim was to determine whether in Fuirosos a single calibration set sufficed to simulate the observed discharge and nitrogen dynamics properly and to evaluate whether two parameter sets, i.e. one for dry years and one for wet years, improve model fit substantially. Unfortunately, with only three years of data it is not possible to perform an appropriate two-step calibration process, i.e. to divide the data into two parts and then adjust the parameters of the model with one part and “test” with the other (Oreskes et al. 1994). In the present study, the testing process refers to the runs made with INCA for each of the three hydrological years after calibrating the model separately for the dry year and the wet year. This was used as an indicator of how useful those two parameter sets could be for simulating different hydrological periods.

To test INCA, the goodness of fit was measured by the coefficient of determination (r^2) and by the slope of the linear regression between simulated and observed data series. Also, differences between water outputs and N loads estimated from observed and simulated data were quantified.

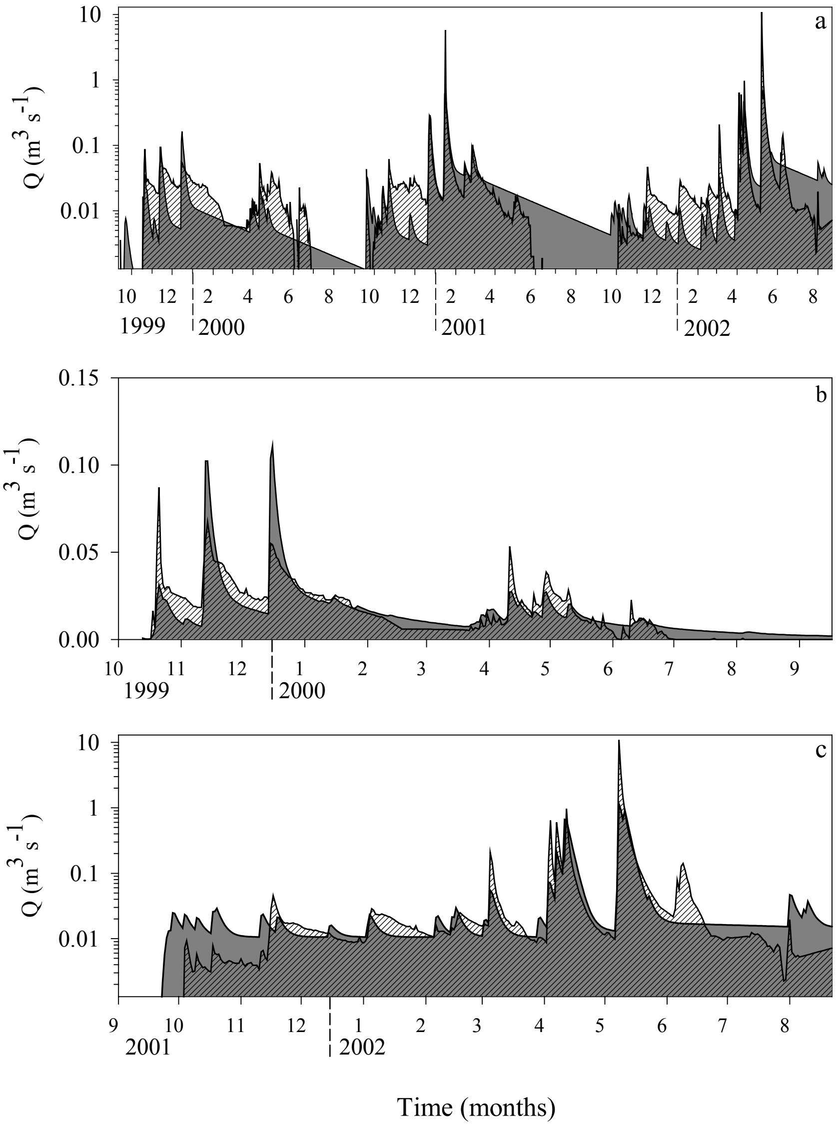

Figure 4.2. INCA outputs and mean daily discharge (m^3 s^{-1}): (a) for the three-year run (1999-2002), (b) for the period 1999-2000 (dry year), and (c) for the period 2001-2002 (wet year). The area filled in grey represents the simulated discharge in (a), (b) and (c), respectively. The area filled with coarse lines represents the observed streamwater discharge in (a), (b) and (c), respectively. Note that the discharge axis in (a) and (c) is logarithmic.

Results

Calibration of the hydrological component of the INCA model

Observed mean daily stream flow at Fuirosos from 1999 to 2002 and the corresponding simulated mean daily stream flow are shown in Figure 4.2a. In general, INCA reproduced the temporal pattern of flow to some extent ($r^2 = 0.54$, $p < 0.0001$). Nevertheless, when calibration was made for a single hydrological year, the simulated data reproduced the observations for that year. Figure 4.2b and c, show that the timing of peak flows was well simulated, though the absolute magnitude was not always matched. In the dry year (period 1999-2000) the drought period (June to September) was not well simulated (Figure 4.2b). In the wet year (period 2001-2002), the wetter months (December to June) were well simulated, although discharge was clearly overestimated during the transitions from dry to wet and from wet to dry conditions (Figure 4.2c). In both simulations, the coefficient of determination (r^2) was above 0.6 and the slope between simulated and observed data close to 0.9 (Figure 4.3a and f). Also, INCA reproduced the water fluxes observed in the wet and dry years (Table 4.1). The main differences in the parameter sets were related to the water residence time in the soil and groundwater compartments and to the base flow index (Table 4.2).

Table 4.1. Water fluxes (mm) and N loads (kg N km^{-2} year^{-1}) for each hydrological period at Fuirosos (Catalonia, NE Spain) calculated from observed values and INCA simulated values. DRY set, simulated values using the calibration of the hydrological period 1999-2000 (dry year); WET set, simulated values using the calibration of the hydrological period 2001-2002 (wet year). In parentheses, percentage of error for the simulated values in relation to observed values. * The two most severe floods (January 2001 and May 2002) have not been considered when estimating annual discharge and nitrate loads.

	Water flux (mm)			NO_3-N (kg N km^{-2} year^{-1}) *		
Hydrological period	Observed	DRY set	WET set	Observed	DRY set	WET set
1999-2000 (dry)	40.4	41.8 (+ 3.5%)	58.4 (+ 44.5%)	10.5	13.3 (+ 26%)	71.5 (> + 100%)
2000-2001	55.7	73.8 (+ 32.4%)	68 (+ 22%)	33.3	25.4 (- 24%)	131.6 (> + 100%)
2001-2002 (wet)	93.3	101.6 (+ 8.8%)	91.8 (+ 1.6%)	86.55	31 (- 64%)	86.3 (< - 1%)

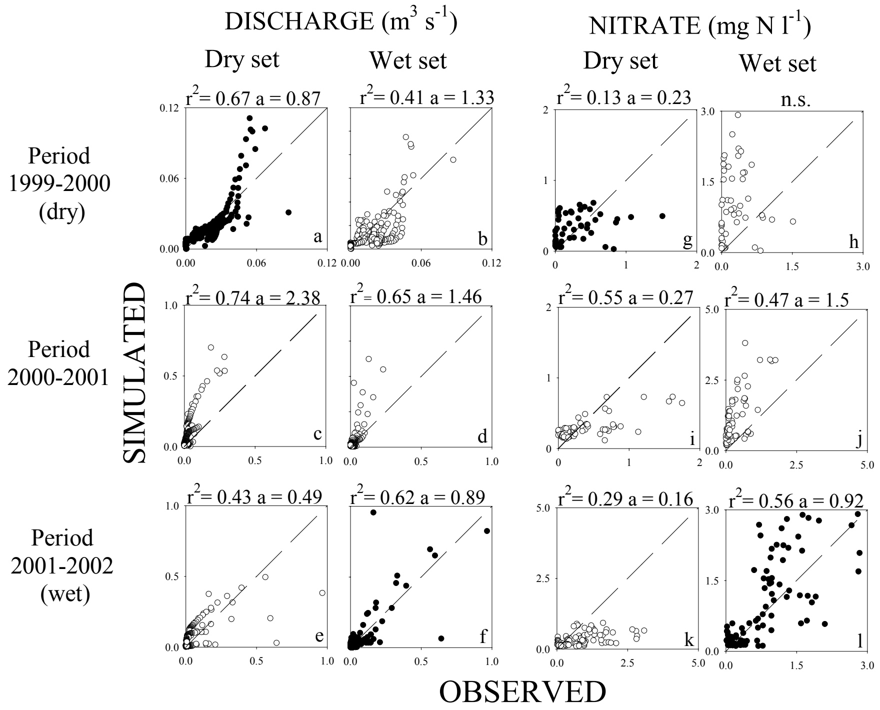

Figure 4.3. Relationship between observed and INCA simulated discharge (m^3 s^{-1}) for the 3 hydrological periods (1999-2000, 2000-2001 and 2001-2002) using: (a), (c) and (e) the dry parameter set, and (b), (d) and (f) the wet parameter set, for each period respectively. Relationship between measured and INCA simulated nitrate concentrations (mg N l^{-1}) for the 3 hydrological periods (1999-2000, 2000-2001 and 2001-2002) using: (g), (i) and (k) the dry parameter set, and (h), (j) and (l) the wet parameter set, for each period respectively. Note that (a), (f), (g) and (l) correspond to the model runs after the adjusting process (black circles) and (b), (c), (d), (e), (h), (i), (j) and (k) correspond to the runs of the testing process (white circles). In all cases, the dashed line is the 1:1 relationship; r^2 is the correlation coefficient between simulated and observed values; a is the slope for the fitted linear model, y = ax + b, between measured and simulated values when this model was significant at the $p < 0.01$ level; n.s.: not statistically significant.

N dynamics and N load in the stream

In general, the observed baseflow nitrate concentrations in Fuirosos during late autumn and winter ranged between 0.15 and 0.8 mg N l^{-1}, and between 0.01 and 0.46 mg N l^{-1} during spring and summer. However, no clear annual pattern was observed during the driest year (1999-2000) when basal nitrate concentrations were always lower than 0.5 mg N l^{-1}. During stormflow conditions, nitrate increased by 1.3 to 9 times the baseflow concentration, though the observed concentrations were not explained by variations in discharge ($r^2 = 0.04$, $p < 0.0001$). During the most extreme events, the nitrate concentration fell, which may be due to a dilution effect because of the high amount of water flow in those episodes.

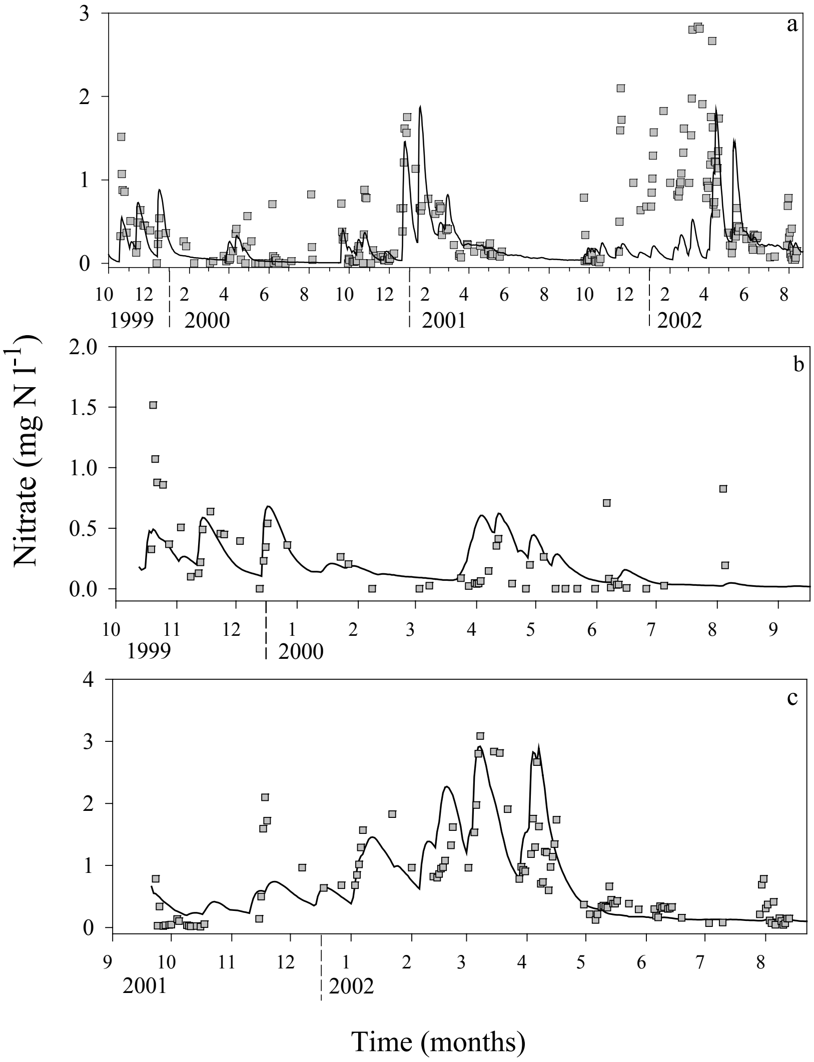

Figure 4.4. INCA outputs and measured nitrate concentrations (mg N l^{-1}): (a) for the three-year run (1999-2002), (b) for the period 1999-2000 (dry year), and (c) for the period 2001-2002 (wet year). The solid lines represent the simulated nitrate concentrations in (a), (b) and (c), respectively. The square symbols represent the measured streamwater nitrate concentrations in (a), (b) and (c), respectively.

Figure 4.4a shows the temporal dynamics of simulated and observed values of daily nitrate concentrations for the period 1999-2002. The INCA model was unable to match the seasonal pattern for the entire period (1999-2002): baseflow nitrate concentrations were well simulated from October 1999 to June 2001, while during the hydrological cycle 2001-2002 the observed seasonal pattern could not be simulated.

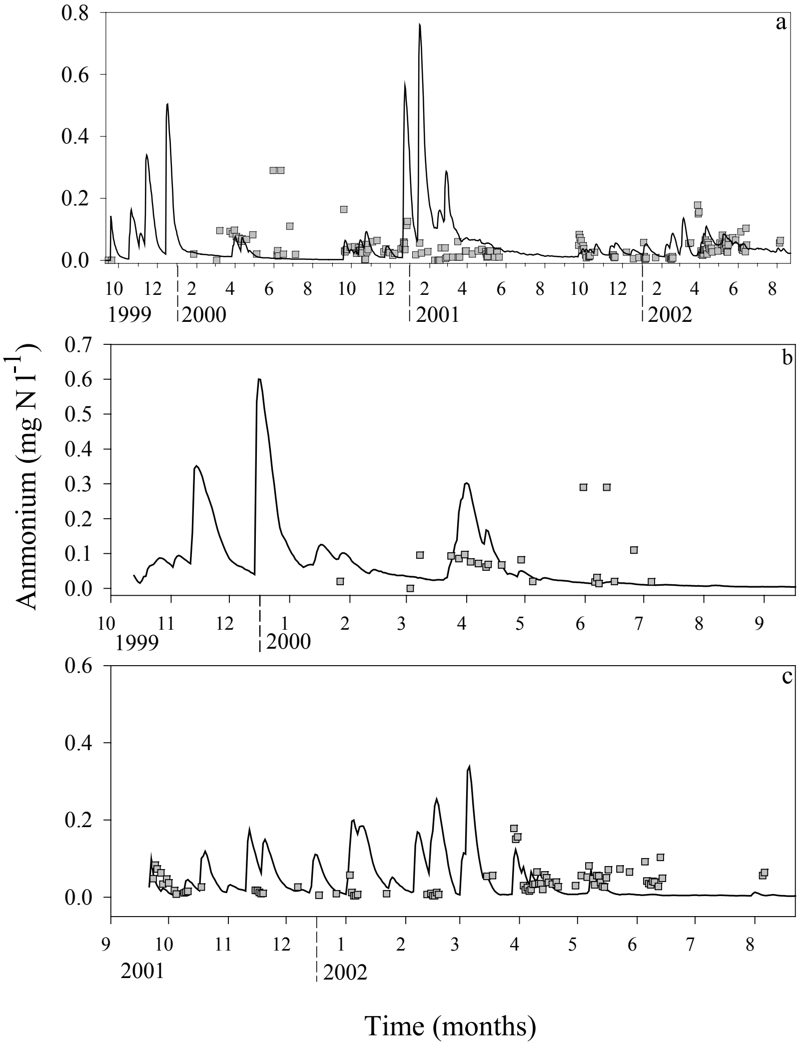

Figure 4.5. INCA outputs and measured ammonium concentrations (mg N l^{-1}): (a) for the three-year run (1999-2002), (b) for the period 1999-2000 (dry year), and (c) for the period 2001-2002 (wet year). The solid lines represent the simulated ammonium concentrations in (a), (b) and (c), respectively. The square symbols represent the measured streamwater ammonium concentrations in (a), (b) and (c), respectively.

The coefficient of determination for the correlation between the simulated data for this simulation was low ($r^2 = 0.11$, $p < 0.0001$). In general, peak concentrations were underestimated during the wetting-up period (Figure 4.4a). After separate calibrations for the dry and the wet year, INCA reproduced the seasonal pattern of stream nitrate concentrations successfully, although nitrate concentrations during peak discharges were not always matched (Figure 4.4b and c) and the coefficient of determination (r^2) was still poor for the dry period 1999-2000 (Figure 4.3g). During the wet year simulated and observed nitrate concentrations fitted better (Figure 4.3l). Annual nitrate loads were overestimated during the dry year, while during the wet year simulated and observed nitrate loads were similar (Table 4.1).

In Fuirosos, the observed baseflow ammonium concentrations ranged between 0.01 and 0.1 mg N l^{-1} and showed no clear seasonal pattern (Figure 4.5a). During stormflow conditions, ammonium concentration increased by 1.3 to 4 times in some cases, while in other cases the concentration decreased by up to 10 times. The observed ammonium concentrations were not related to discharge ($r^2 = 0.1$, $p < 0.0001$). In contrast, simulated ammonium concentrations tended to peak with discharge (Figure 4.5a, b and c). The coefficient of determination (r^2) between the observed and simulated ammonium concentrations was neither significant when the whole study period (1999-2002) was used for the calibration nor when the calibration was made separately for the dry and wet periods. Because of the poor fit between the observed and simulated ammonium concentrations, this solute was not considered for testing the model.

After calibration for both wet and dry periods, the values of the parameters related to soil N processes were generally higher for the wet than for the dry year (Table 4.2). The soil water residence time and the V_r (soil retention volume) appeared to be key parameters in the simulation of nitrogen streamwater concentrations.

The annual rates of net mineralization and nitrate uptake by vegetation estimated by INCA were in the range of values reported for Mediterranean oak forests. In contrast, ammonium uptake by vegetation was below the values found in the literature (Table 4.3).

Testing INCA calibrations

The testing process consisted of running the model for each of the three available hydrological years, with each of the two sets of parameters obtained after calibrating the model for the wet and the dry year separately. For 2000-2001, the coefficient of determination (r^2) between observed and simulated discharge was high

Table 4.2. Parameters of the INCA model used for modelling the hydrological period 1999-2000 (dry year) and 2001-2002 (wet year) at the Fuirosos catchment.

	1999-2000	2001-2002
SOIL N PROCESSES		
Denitrification m day^{-1}	0	0.002
Nitrogen fixation (kg N ha^{-1} day^{-1})	0	0
Nitrification m day^{-1}	0.015	0.04
Mineralisation (kg N ha^{-1} day^{-1})	0.3	0.5
Immobilisation m day^{-1}	0.005	0.01
Max soil moisture deficit (mm)	ç	80
Max temperature difference (ºC)	7	7
Stop denitrification at (ºC)	0	0
Stop nitrification at (ºC)	0	0
Plant growth start day	90	90
Plant growth period (days)	190	190
Nitrate uptake rate m day^{-1}	0.045	0.08
Ammonium uptake rate m day^{-1}	0.65	1
Maximum uptake rate kg N ha^{-1} year^{-1}	90	90
HYDROLOGICAL VALUES		
Sustain Surface flow (m^3 s^{-1})	0	0.0005
Sustain Sub-surface flow (m^3 s^{-1})	0	0
Vr_{max} (depth x porosity)	1.5	0.55
Soil water residence time (days)	4	2.5
Groundwater water residence time (days)	60	150
Base flow index	0.65	0.35
INITIAL VALUES		
Initial surface flow (m^3 s^{-1})	0	0
Initial surface nitrate (mg l^{-1})	0.6	0.6
Initial surface ammonium (mg l^{-1})	0.1	0.1
Initial surface Drainage volume (m^3)	1000	1000
Initial sub-surface flow (m^3 s^{-1})	0	0
Initial sub-surface nitrate (mg l^{-1})	0.1	0.1
Initial sub-surface ammonium (mg l^{-1})	0.06	0.06
Initial sub-surface Drainage volume (m^3)	105	105
IN-STREAM PROCESSES		
Instream Denitrification rate (day^{-1})	0.2	0.15
Instream Nitrification rate (day^{-1})	0.3	0.3

regardless of the parameter set used (Figure 4.3c and d). Nevertheless, the slope of the linear regression among observed and simulated values was higher than 1, especially whith the dry parameter set, and, therefore, annual discharges were overestimated (Table 4.1). For the same period, the coefficient of determination (r^2) for nitrate was moderately good using either the dry or the wet parameter set (Figure 4.3i and j), indicating that the concentration dynamics were captured by the model. However, nitrate concentrations were underestimated when using the dry set (Figure 4.3i), while they were overestimated when using the wet parameter set (Figure 4.3j). Also, nitrate concentrations during 1999-2000 were highly overestimated when using the parameter set obtained from the wet year (Figure 4.3h).

Table 4.3. Nitrogen annual process rates: a comparison of values from previous studies in forests of *Quercus ilex* in Catalonia (Spain) with simulated values for the periods 1999-2000 (dry year) and 2001-2002 (wet year).

N process	Measured values (kg N ha^{-1} $year^{-1}$)	Simulated values (kg N ha^{-1} $year^{-1}$)	
		DRY year	WET year
Net mineralization	32.4^a - 80.1^b	36.7	62.8
Net nitrification	4.4^a - 7.5^b	11.4	34.3
Immobilisation	0.08^c	5.7	8.6
Nitrate uptake by vegetation	10.3^c – 58^d	10.7	33.5
Ammonium uptake by vegetation	53^d - 80.5^c	30	33.6

References: [a] Serrasolses et al. (1999), [b] Bonilla and Rodà (1992), [c] Bonilla (1990), [d] Escarré et al. (1987).

Discussion

In general, adequate field measurements of hydrological and soil processes are difficult because these mechanisms are highly variable in space and time. Usually, the scale at which these processes are measured in the field is smaller than that of the model elements (Oreskes et al. 1994). In consequence, many of the parameters required by any given model cannot be fixed prior to the calibration process and are adjusted to achieve an acceptable fit. Commonly, there are multiple acceptable parameterizations and qualitative information may be used to constrain model uncertainties (Franks et al. 1998). Although the parameter sets obtained in the present study are not the only acceptable ones, the results obtained are adequate to discussion of the merits of the

INCA model structure as a representation of the hydrologic and nutrient dynamics in Mediterranean catchments.

Hydrological processes

Annual water yield in Fuirosos during the period 1999-2002 varied from 8 % to 26 % of total annual precipitation. However, if the two most severe storm events (P > 100 mm, January 2001 and May 2002) are excluded, the estimated annual discharges were 7.9 %, 7.5 % and 10.5 % of the total annual precipitation, for the three consecutive years. Thus, evapotranspiration is the key factor controlling annual water budgets in this catchment and changes in the water yield are related more to the distribution of rainfall throughout the year than to the annual volumes. Other studies in Mediterranean and semiarid catchments have also described a high variability in the amount of discharge from year to year and have reported similar ranges for annual yields (e.g., Piñol et al. 1991; Ceballos and Schnabel 1998). In contrast, in humid regions variations in annual water yields are more damped and the annual discharge is a higher fraction of total bulk rainfall (Hudson 1988; Wade et al. 2002). Indeed, the records at Fuirosos account for a wide range of climatic and stream hydrological conditions, although the monitoring period is still not very long. This circumstance has allowed testing the model's ability to simulate highly contrasting hydrologic conditions.

In general, INCA matched the general flow dynamics well and the coefficient of determination was above 0.54 in all cases. The timing of the storm events was well simulated, though the actual value of peak flows was not always captured. Nevertheless, INCA had difficulties simulating the most complex episodes of the Mediterranean hydrology, i.e. the wetting-up period, the transition from wet to dry conditions and the extreme floods. INCA splits the volume of water stored in the soil and in the groundwater by means of the base flow index. This index is based on observed river flows in the UK and purports to attribute the proportions of water in a stream derived from surface and deeper groundwater sources (Wade et al. 2002). So far, the baseflow index in INCA is a fixed value within and between years. There might be two underlying assumptions: (i) that the whole drainage area is contributing to the catchment runoff and, (ii) that the relative contribution of the two runoff mechanisms considered (i.e., saturation excess surface flow and groundwater flow) is constant over time. This approximation to catchment hydrology is not appropriate in Mediterranean catchments. Regarding the area contributing to the generation of runoff, Butturini et al. (2002) showed that, in Fuirosos, the stream-riparian system was totally or partially disconnected from the rest of the catchment during the drought and the wetting-up period. Moreover, Gallart et al. (1997) showed that in Vallcebre catchments (Catalonia, NE Spain) groundwater transfer, which frequently feeds saturated areas, was interrupted during dry periods (early autumn and late spring) and that the timing of the drought and wetting-up period showed a high inter-annual variability. Both studies suggest a common idea, i.e. that in Mediterranean catchments the area contributing to runoff generation contracts and expands within a year and between years. There have been attempts to reproduce the hydrological response of semiarid catchments during the wetting-up period by using TOPMODEL, a hydrologic model widely used in temperate catchments that is based on topographic indeces of hydrological similarity (e.g., Ambroise et al. 1996). Piñol et al. (1997) showed that simulated stream flow in Mediterranean catchments improved significantly provided an extra runoff generation process, i.e. from unsaturated areas to the stream (lateral unsaturated flow), as well as a variable effective upslope drainage area that was a function of soil saturation deficit. Recently, Castillo et al. (2003) reported a simulation approach showing that in Mediterranean semiarid catchments the hydrological response after high intensity storms ($P > 50$ mm h^{-1}) is independent of the initial soil water conditions. The authors suggest that, during these intense rainstorms, infiltration excess overland flow dominates over saturation excess overland flow and the whole catchment responds uniformly. Thus, it would be more appropriate in the INCA model structure: (i) to consider the area contributing to catchment runoff as a function of soil moisture and, (ii) to include a parameter related to the infiltration excess overland flow mechanism rather than an unique base flow index parameter. In this paper, some specific considerations have been made when estimating HER (Hydrological Effective Rainfall) at Fuirosos partially to solve the questions raised above. For example, at high soil moisture deficits only the riparian area has been considered responsible for runoff generation (see Material and Methods). Although this is an over-simplification, it allowed us to generate HER, and therefore stream flow, during periods when most of the catchment suffers an important soil moisture deficit. Another attempt to get some insights has been to perform different calibration processes for years with different hydrological conditions. In fact, the fit of simulated data with observations improved considerably when calibration was made for the dry and the wet period separately. Overall, differences between the two INCA parameter sets were in the residence time of water in the soil and in the groundwater compartment. In particular, the groundwater residence time was 2.5 times higher in the wet year than in the dry year. In this particular case study, this parameter seems to be related to the potential effective drainage area. If hydrological connectivity is higher during the wet year than during the dry year, the mean size of the groundwater storage might also be higher allowing a sustained transfer of water to the stream over a longer time period. Also, the base flow index differed in each case, suggesting that water flowpaths are not equivalent during wet and dry periods. The testing process also indicated the need for different parameterization depending on the precipitation regime.

N export, soil N processes and N dynamics in streamwater

The export of nutrients in catchments is linked strongly to hydrological processes. Particularly, soil studies in semiarid regions often conclude that leaching and mobilization of nutrients in these regions are closely linked to precipitation events (e.g., Mummey et al. 1994; Terrades 1996). In Fuirosos, the leaching of ammonium was not related to precipitation events, while a recent study has reported that nitrate export during wet years was from 1.5 to 4 times higher than the export during dry years (Bernal et al. 2002). Differences between years were mainly due to large rain episodes that strongly influenced the flush of solutes. To account for the influence of precipitation events on nutrient leaching, monitoring in Fuirosos has been intense during stormflow conditions, which is essential to test the model's ability to simulate nitrogen dynamics.

Water has not only a flushing effect but also an impact on soil microbial processes owing to an increase in soil moisture. In semiarid regions microbial soil processes, for instance denitrification, occur in pulses stimulated by the re-wetting of soil after rains (Mummey et al. 1994). Accordingly, soil N process rates in INCA were higher during the wet year than during the dry year. Yet, previous studies in Mediterranean oak forests have shown that nitrification is limited by soil moisture (Serrasolses et al. 1999) and that the ratio between mineralization and nitrification is roughly 10:1 (Table 4.3). This may well be the reason why nitrogen uptake by vegetation is mainly in the form of ammonium (Serrasolses et al. 1999). However, in the present INCA simulations, annual nitrification rates were only two to three times lower than mineralization rates, reflecting the fact that the model structure does not include a soil moisture threshold for nitrification.

In general, INCA simulations of flow and concentration led to annual nitrate loads roughly similar to observed values. However, even in the best cases, the model captured less than 56% of the variance in daily nitrate concentrations. During the wetting-up period and the transition from wet to dry conditions, nitrate peaks during stormflow were usually underestimated. Yet, at those moments the release of nutrients stored in the unsaturated riparian soil layers might be provoked by stream reverse fluxes (Butturini et al. 2003). Reverse fluxes are characteristic of arid and semiarid areas and this hydrological process may not be general enough to be included in a wide scope model such as INCA. However, there might be other hydrological mechanisms following storm events such as shallow subsurface flow generated in the vadose zone (or lateral unsaturated flow) that also occur in temperate catchments, which allow for flushing of soil nutrients from the near-surface zones (Stieglitz et al. 2003).

In Fuirosos, nitrate concentration dynamics showed strong inter-annual variation. During 2000-20001 and 2001-2002, baseflow nitrate concentrations were higher during the non-vegetative period than the vegetative period; this trend was not observed in the driest year, due possibly to a non-mobilization of nutrients or to a longer vegetative period. In any case, results showed that further work is needed if INCA is to capture all the observed inter-annual variability in nitrate dynamics. When the calibration was made for the dry and the wet year separately, INCA was more able to capture the seasonal pattern in both cases (especially in the wet year), though the coefficient of determination for the dry year was still very low. Differences between both parameter sets were in INCA parameters that had a major influence on nitrate dynamics, in particular the soil water residence time and the soil retention volume (V_r), which is related to the mobilization of solutes in the soil. This indicates that nitrate mobilization in Mediterranean catchments is highly variable from year to year depending on the precipitation regime and the soil moisture conditions. Thus, high nitrate concentrations during stormflow occurring in the wet year (2001-2002) might respond to an intense mobilization of nutrients (perhaps from soil areas which, during drier years, may be even isolated), which might well be accompanied by higher soil nitrification rates.

In Fuirosos ammonium concentrations were low even during precipitation events; INCA simulated ammonium leaching during stormflow. Further work is needed if INCA is to simulate the observed concentration dynamics of ammonium. Rapid ammonium uptake by vegetation together with non-biological uptake may explain the observed low ammonium mobilization. Non-biological uptake should be taken into account for an appropriate simulation of ammonium dynamics and the incorporation of ammonium adsorption into INCA is strongly recommended.

Concluding remarks

Overall, results show that, in Fuirosos, both hydrology and nitrate mobilization are strongly influenced by soil moisture, which is highly variable within and between years. INCA could be calibrated to simulate flow and nitrate dynamics in Fuirosos, but simulations were more successful in the wet year. A more stringent test of INCA's ability to simulate flow and N dynamics yielded poorer results. When the parameter set obtained from a particular hydrological year, dry or wet, was applied to another hydrological year, the model explained flow and nitrate dynamics only moderately well and the estimated annual loads were overestimated (except for nitrate loads that were underestimated when applying the dry parameter set). Thus, a single parameter set for several years fails to capture the intrinsic inter-annual variability of Mediterranean regions. However, really to test whether two or more parameter sets for contrasting hydrological conditions could be used to apply INCA in semiarid catchments, long data series (at least 10 years) including several dry and wet years would be needed.

The implementation of a variable effective drainage area and a lateral unsaturated flow may improve INCA's ability to simulate flow and nitrogen dynamics in semiarid catchments. It is also suggested that infiltration excess overland flow mechanisms are incorporated in to the INCA model structure, because in semiarid regions extreme storm events are responsible for the major part of water and nutrients annual export. Nevertheless, it has been shown that adding model components and parameters to reproduce specific aspects of catchment behaviour does not necessarily lead to better results or to easier parameter calibration (Hornberger et al. 1985).

Catchment size may also be important. Several authors have suggested that the effect of the heterogeneity of soil characteristics and water flowpaths on water quality is more apparent in small catchments (< 50 km^2) than in larger ones (e.g., Wade et al. 2001). Consequently, the detailed descriptions of hydrological and soil processes needed when modelling small catchments may shift to dominant or key processes that control water quality at larger scales (Sivapalan et al. 2003). Applying INCA to larger Mediterranean catchments than Fuirosos, preferably with permanent flow, may give fresh insights into the usefulness of INCA for semiarid systems.

INCA has shown widely its ability to simulate discharge and nitrate dynamics in humid catchments. However, further work is needed before INCA becomes a suitable management tool for semiarid catchments. Also, present results call for caution when running climatic scenarios, including drier conditions and more irregularly distributed rainfall patterns, in any catchment.

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