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

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**Abstract.** Seasonal variations of dissolved inorganic nitrogen (DIN) ($NO_3$–N and $NH_4$–N) and dissolved organic nitrogen (DON) were determined in Fuirosos, an intermittent stream draining an unpolluted Mediterranean forested catchment (10.5 $km^2$) in Catalonia (Spain). The influence of flow on streamwater concentrations and seasonal differences in quality and origin of dissolved organic matter, inferred from dissolved organic carbon to nitrogen ratios (DOC:DON ratios), were examined. During baseflow conditions, nitrate and ammonium had opposite behaviour, probably controlled by biological processes such as vegetation uptake and mineralization activity. DON concentrations did not have a seasonal trend. During storms, nitrate and DON increased by several times but discharge was not a good predictor of nutrient concentrations. DOC:DON ratios in streamwater were around 26, except during the months following drought when DOC:DON ratios ranged between 42 and 20 during baseflow and stormflow conditions, respectively. Annual N export during 2000–2001 was 70 kg $km^{-1}$ $year^{-1}$, of which 75% was delivered during stormflow. 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.

## 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 dissolved organic carbon to nitrogen ratio (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 DOC may show a similar pattern because both nutrients are likely to have the same origin. Michalzik et al. (2001) reported a high correlation between DOC and DON fluxes in a study of 42 soils in forested ecosystems. Several studies have reported 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 DON 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 streamwater 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.

## Study site

### *Climate*

Fuirosos is an intermittent third order stream located in a forested catchment (10.5 km$^2$) near Barcelona, in northeastern Spain (latitude 41°42′ N, longitude 2°34′ E, altitude range 50–770 m.a.s.l.). The climate is typically Mediterranean, with temperatures ranging from a monthly mean of 3 °C in January to 24 °C in August. Winter air temperatures below 0 °C are infrequent. Average annual precipitation is 750 mm (Ninyerola et al. 2000). The number of days with rain does not usually exceed 70 per year. Only occasional storms occur in summer. Throughfall plus stemflow fluxes of N in the Montseny Mountains (latitude 41°46′ N, longitude 2°21′ E), 20 km from Fuirosos, range between 6.8 and 11.4 kg N ha$^{-1}$ year$^{-1}$. Variation depends on the level of exposure to the polluted atmosphere of the urban and industrial areas around Barcelona (Rodà et al. 2002). In a previous 1-year study, N bulk deposition in Fuirosos catchment was estimated as 4.1 kg N ha$^{-1}$ year$^{-1}$ (Bernal et al. 2003).

### *The catchment*

The main rock type in the catchment is granite (Sala 1983) and the major tree species are perennial cork oak (*Quercus suber*) and pines (*Pinus halepensis* and *Pinus pinaster*). In the hillslope zone there is a mixed deciduous woodland of chestnut (*Castanea sativa*), hazel (*Corylus avellana*), and oak (*Quercus* *pubescens*) (Figure 1). The soils are poorly developed, with an A horizon of less than 5-cm, and dominated by sand (46%) and fine sand (24%), with smaller amounts of silt and clay (15% each, Sala 1983). Agricultural fields occupy less than 10% of the catchment. The 3–5 m wide stream channel is flanked by a well-developed riparian area which is 10–20 m in width and consists mainly of alder (*Alnus glutinosa*) and the exotic plane tree (*Platanus acerifolia*). The riparian soil is poorly developed and plane tree leaf litter tends to accumulate on the forest floor because of the low decomposition rates (Bernal et al. 2003).

### *Hydrology*

Hydrological data for the Fuirosos stream is available beginning in 1999 (Butturini et al. 2002, 2003). The present study includes data for three consecutive hydrological cycles (1999–2000, 2000–2001, 2001–2002), each running from streamwater recovery in September to June, when the stream dries again until the beginning of next cycle (Table 1). Baseflow was characterized by a long dry period from June to late September–October, when the first storms occur. During these events the stream fed the riparian groundwater compartment via subsurface water fluxes (Butturini et al. 2003). When such reverse

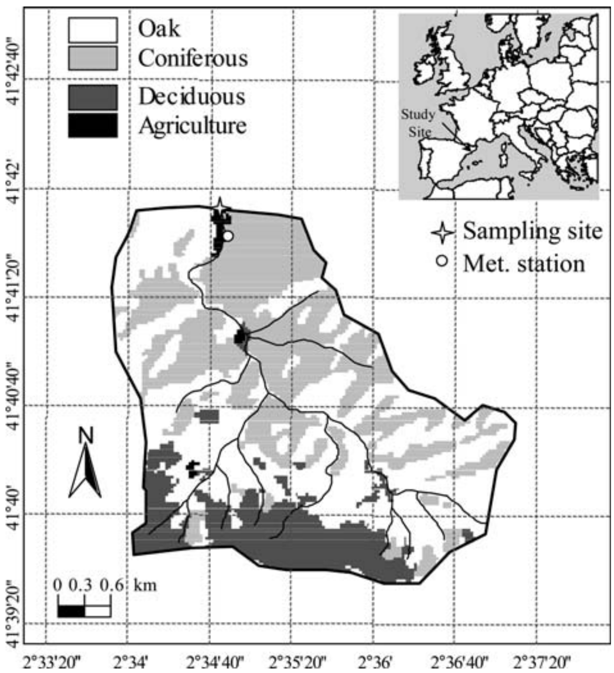


*Figure 1.* Geographical location of Fuirosos (Catalonia, Spain). Main land uses (agricultural fields, coniferous forest, oak forest, deciduous forest) are shown as different shadings.

*Table 1.* Annual precipitation (*P*), annual runoff, annual runoff coefficient (RC) and days that the streambed was dry for each hydrological year included in this study (1999–2002) in Fuirosos (Catalonia, Spain) (from Bernal et al. 2004).

| | 1999–2000 | 2000–2001 | 2001–2002 |
|---|---|---|---|
| *P* (mm) | 525 | 752.6 | 871 |
| Runoff (mm) | 38.4 | 105.3 | 226.5 |
| RC (%) | $<8$ | 14 | 26 |
| Drought period (days) | 103 | 75 | 72 |

fluxes occur, streamwater could infiltrate into the riparian zone to a maximum depth of 10 m. Average discharge during the wet period ranged from 7 l $s^{-1}$ in spring to 20 l $s^{-1}$ in winter. The annual hydrological budget in Fuirosos was driven by the occurrence of large precipitation events ($P > 100$ mm). For example, in January 2001 a precipitation event of 132 mm (equivalent to the 17% of the total annual precipitation) was responsible for approximately 70% of the total annual runoff (Bernal et al. 2004).

## 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.

Streamwater 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 streamwater 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 10 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 °C until analyzed. Both $NO_3^-$ and $NH_4^+$ were analyzed 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 copperized cadmium column; $NH_4^+$ was measured after oxidation with salicilate using sodium nitroprusside as a catalyst (Hach 1992).

Total dissolved nitrogen (TDN) was analyzed 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 analyzed using a high-temperature catalytic oxidation (Shimadzu® TOC analyzer).

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*

#### *Seasonal patterns*

To estimate the influence of flow on concentrations, the data were analyzed 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 analyzed 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 $p < 0.01$. The correlations between each of two sets of samples was calculated as the Spearman Rank Correlation Coefficient ($r_s$) (Helsel and Hirsch 1992).

## Results

### *Seasonal patterns of DIN and DON concentration*

Figure 2 shows the temporal dynamics of nutrient concentrations during baseflow and stormflow conditions, while mean concentrations for each solute are compiled in Table 2. 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 3e–h).

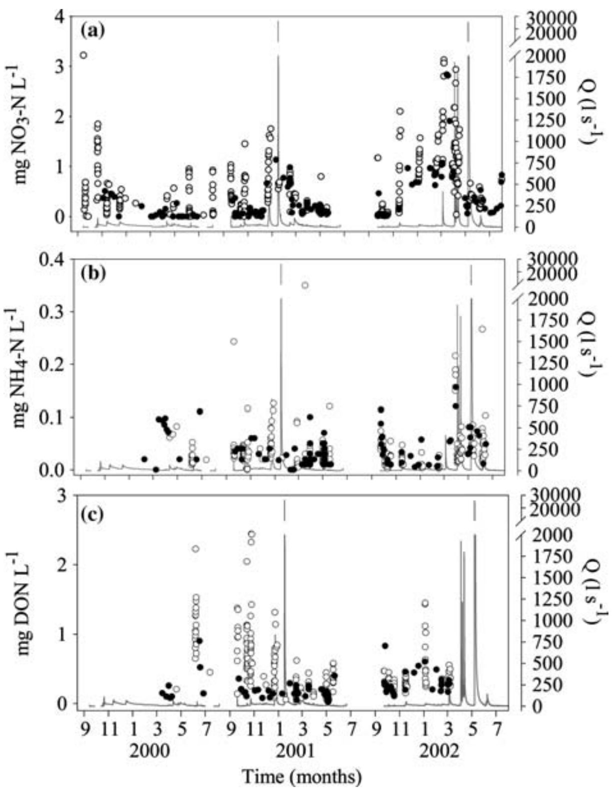


*Figure 2.* Temporal dynamics of discharge ($Q$, $l\ s^{-1}$) (solid line) and (a) $NO_3$–N ($mg\ l^{-1}$); (b) $NH_4$–N ($mg\ l^{-1}$); and (c) DON ($mg\ l^{-1}$) in Fuirosos (Catalonia, Spain) during the study period (September 1999–August 2002). Solid circles are baseflow concentrations and open circles are stormflow concentrations.

*Table 2.* Mean concentration[a] ($mg\ l^{-1}$) and standard error[a] 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, Spain).

| | 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) |

In parentheses, number of cases.
[a]Not flow-weighted.

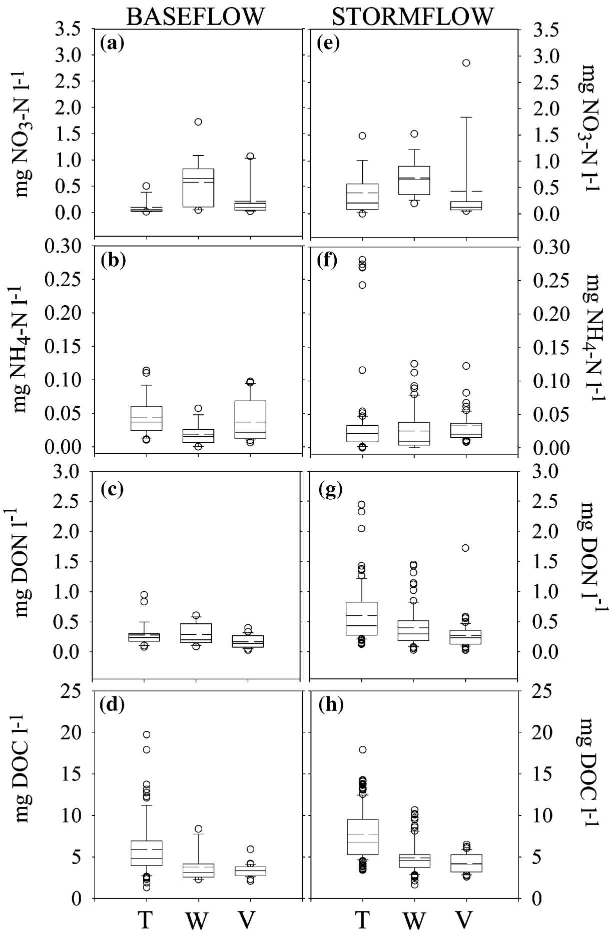


*Figure 3*. Box plots summarizing concentration data (mg $l^{-1}$) in streamwater at Fuirosos (Catalonia, Spain) during baseflow (left panels) and stormflow (right panels) conditions. (a and e) $NO_3$–N; (b and f) $NH_4$–N; (c and g) DON; and (d and h) DOC. The centre horizontal line in each box is the median value of concentration. The dashed line is the mean concentration. Fifty percent of the datapoints lie within each box. The whiskers above and below the box indicate the $10^{th}$ and $90^{th}$ limits of the distribution. Circles are outliers. T: transition period; W: wet period; V: vegetative period.

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 3a). In contrast, ammonium baseflow concentrations were higher after the summer drought than during the wet season ($p < 0.002$) (Figure 3b). Baseflow DON concentrations did not have a clear seasonal pattern (Figure 3c). In contrast, baseflow DOC concentrations were significantly higher during the transition period than during the remainder of the year ($p < 0.0001$) (Figure 3d).

During storms, nitrate and DON concentrations tended to increase. The highest nitrate concentrations were recorded during the wet season ($p < 0.0001$, Figure 3e), 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 3g and h). Stormflow concentrations of ammonium did not have a seasonal pattern (Figure 3f).

## *Relationships among nutrients*

During the baseflow period, nutrients had a nil or weak relationship among each other, while some seasonal relationships were strong (Table 3). During the transition from dry to wet conditions, DON covaried with DOC under baseflow conditions (Figure 4a). Ammonium was positively correlated to baseflow DOC concentrations (Figure 4b).

During stormflow conditions, covariation of nutrients was nil or weak during the wet and vegetative periods (Table 3). During the transition period, all nutrients had a positive, albeit not always significant, relationship. The strongest relationship was between nitrate and DOC (Table 3).

## *Seasonal patterns of DOC:DON ratios*

DOC:DON ratios during baseflow were higher than during stormflow, $33 \pm 2.5$ ($n = 43$) vs. $24 \pm 1.7$ ($n = 177$) ($p < 0.0001$). During the wet and vegetative periods, the DOC:DON ratios during baseflow conditions were similar to those

*Table 3.* Spearman $\rho$ correlation coefficients ($r_s$) between pairs of solutes ($NO_3$–N, $NH_4$–N, DON, DOC) under baseflow and stormflow conditions.

| | 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 |

Coefficients are shown for each season (transition, wet and vegetative). ns: Not significant ($p > 0.01$).
$^{*}p < 0.01$.
$^{**}p < 0.001$.
$^{***}p < 0.0001$.

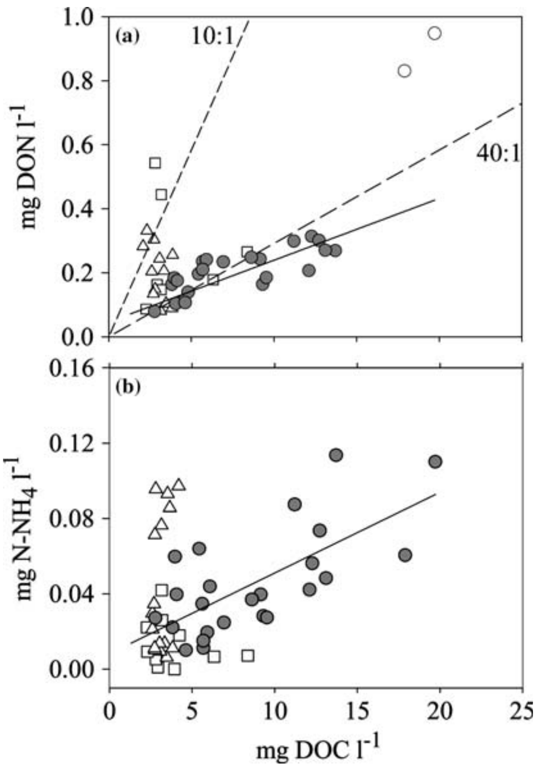


*Figure 4*. Relationships between baseflow concentration of solutes. (a) DOC vs. DON, (b) DOC vs. $NH_4$–N. Circles are datapoints from the transition period, squares are from the wet period and triangles from the vegetative period. Solid lines are the linear regressions between solute concentrations 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.

during stormflow conditions. The averaged value for both periods was $26 \pm 2.2$ ($n = 115$). 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 $42 \pm 2.8$ ($n = 24$). 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 5).

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 5b).

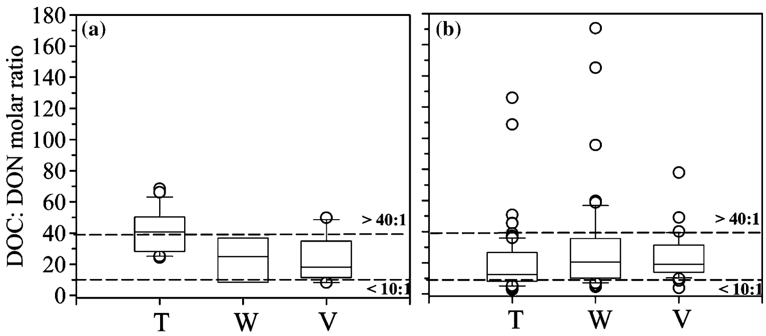


*Figure 5.* Box plots showing the DOC:DON molar ratios for each season during baseflow (panel a) and stormflow (panel b) conditions in Fuirosos (Catalonia, Spain). The centre horizontal line in each box is the median value of concentration. Fifty percent of the datapoints lie within each box. Boxes indicate the upper and lower quartiles of data. The whiskers above and below each box indicate the 10th and 90th limits of the distribution, 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.

## *Influence of water flow on nutrient concentrations and annual N export*

Discharge was generally not a good predictor of nutrient concentrations in streamwater (Table 4). 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 4). 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.

*Table 4.* 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.

| | 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 |

Coefficients are shown for all the data set and for the transition, wet and vegetative periods separately. All: all measurements; ns: not significant ($p > 0.01$). Sample sizes are shown in parentheses for each case.

$^{*}p < 0.01$.

$^{**}p < 0.001$.

The annual nitrogen export during the period 2000–2001 was 70 kg $km^{-1}$ $year^{-1}$, 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, nitrate 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) hypothesized that 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) have 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 which 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*

Annual DON export in Fuirosos was 0.25 kg N $ha^{-1}$ $year^{-1}$. As far as we are aware, the present study is the first one reporting annual DON fluxes in a Mediterranean experimental catchment. The annual DON flux in Fuirosos 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) or 0.73 kg N $ha^{-1}$ $year^{-1}$ in Red Buttle Creek, UT (USA) (Lewis 2002).

In order to compare the DIN export in Fuirosos with other unpolluted forested catchments, a set of study sites from both Mediterranean and temperate regions was selected. Dise and Wright (1995) proposed a threshold for throughfall flux of 25 kg N $ha^{-1}$ $year^{-1}$ upon with catchments could be consider 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 $ha^{-1}$ $year^{-1}$.

Figure 6 compares the annual DIN export vs. the annual runoff for the set of Mediterranean catchments. Levels of annual DIN export in Fuirosos, ranging

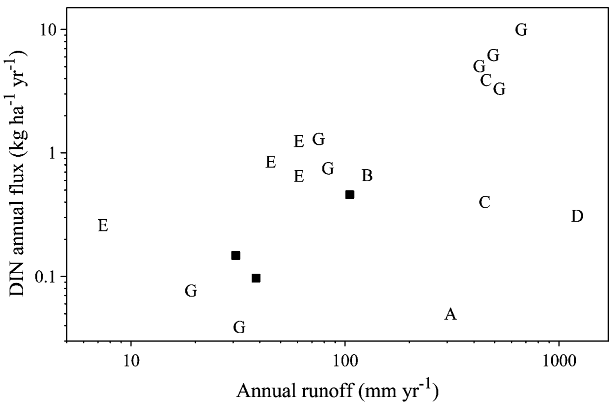


*Figure 6*. Log–log relationship between annual runoff (mm $year^{-1}$) and annual export (kg $ha^{-1}$ $year^{-1}$) of DIN in Fuirosos (Catalonia, Spain) (black squares) and in a set of Mediterranean catchments. Data have been extracted from the following published studies: (A) Àvila et al. (2002); (B) Butturini and Sabater (2002); (C) Durand et al. (1992); (D) Britton (1991); (E) Meixner and Fenn (in press); (G) Riggan et al. (1985).

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) or 0.66 kg $ha^{-1}$ $year^{-1}$ in Riera Major, Spain (Butturini and Sabater 2002). By contrast, DIN export in Fuirosos was low when compared to those catchments with higher annual runoff (e.g., 6 kg $ha^{-1}$ $year^{-1}$ in San Dimas Forests, CA (USA) (Riggan et al. 1985)) (Figure 6). 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.

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 5). 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 in press). 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 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 in press). 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. 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

*Table 5.* Annual runoff (mm year$^{-1}$), annual deposition and annual yield (kg ha$^{-1}$ year$^{-1}$) of DIN (nitrate-N + ammonium-N) in Fuirosos and in other streams draining forested catchments in Mediterranean and temperate regions in North America, Europe and South Africa.

| | Runoff (mm year$^{-1}$) | DIN load (kg ha$^{-1}$ year$^{-1}$) | DIN yield (kg ha$^{-1}$ year$^{-1}$) | Source |
|---|---|---|---|---|
| Mediterranean | 7–1220 | 5.5–18 | 0.04–10 (21) | Present study A B C D E F G |
| Temperate and subalpine | 25–1400 | 1–14 | 0–5.9 (70) | H I J K L M N O P Q |

In brackets, total number of catchments included.
Source: (A) Àvila et al. (2002), (B) Butturini and Sabater (2002), (C) Durand et al. (1992), (D) Britton (1991), (E) Meixner and Fenn (in press), (F) Bernal et al. (2002), (G) Riggan et al. (1985), (H) Adams et al. (1997), (I) Dow and DeWalle (1997), (J) Kortelainen et al. (1997), (K) Williams and Melack (1997), (L) Campbell et al. (2000), (M) Lovett et al. (2000), (N) Coats and Goldman (2001), (O) Sickman et al. (2001), (P) Lewis (2002) and (Q) Vanderbilt et al. (2003).

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 cannot 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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