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Cross-site comparison of variability of DOC and nitrate *c–q* hysteresis during the autumn–winter period in three Mediterranean headwater streams: a synthetic approach

BUTTURINI ANDREA[1,*], GALLART FRANCESC[2], LATRON JÉRÔME[3], VAZQUEZ EUSEBI[4] and SABATER FRANCESC[4]
*[1]Estudis Avancats Blanes (CSIC) Blanes, Girona, Spain; [2]Institute of Earth Sciences Jaume Almera (CSIC) Barcelona, Spain; [3]Pyrenean Institute of Ecology (CSIC) Zaragoza, Spain; [4]Department of Ecology, University of Barcelona, Barcelona, Spain; *Author for correspondence (e-mail: abutturini@ceab.csic.es)*

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Abstract. The forms, rotational patterns and trends of hysteretic loops of dissolved organic carbon (DOC) and nitrate (NO_3) were investigated in three headwater Mediterranean streams during one autumn–winter period using two biogeochemical descriptors summarizing the changes in solute concentrations (ΔC) and the overall dynamics of each hysteretic loop (ΔR). The study had two aims: (1) to examine whether the variability of solute hysteretic loops monitored in different streams during cold seasons followed a consistent and recurring pattern, (2) to identify hydrological parameters which could potentially influence features of the DOC and NO_3 hysteresis. Relationships between hysteresis features and hydrological parameters in the studied streams were explored using multivariate redundancy analysis (RDA). Both DOC and NO_3 typically increased in concentration during storm events, although hysteretic loops did not obey any consistent pattern across the three streams. The rotational patterns of DOC and NO_3 hysteresis ranged widely, from clockwise to counterclockwise. Storm hydrographs and also the magnitude of antecedent storm events were explanatory of the DOC and NO_3 concentration changes across the study sites. However, the detailed hydrological information did not offer a satisfactory explanation of the entire DOC and NO_3 concentration dynamics during the storm events.

Introduction

A complete understanding of stream-catchment biogeochemical interactions and of solute origin in stream waters requires an analysis of the variability in solute concentrations during storm events. Several authors have observed that the relationship between discharge and solute concentrations during storm events (i.e. the concentration (*c*)–discharge (*q*) hysteresis) follows cyclic trajectories (Walling and Foster 1975; Bond 1979; McDiffett et al. 1989; Swistock et al. 1989; Hill 1993). Bond (1979) hypothesized that the slope, direction and width of the *c–q* hysteresis are regular and recurrent properties of a solute and of the catchment. Evans and Davies (1998) demonstrated that the patterns of the *c–q* hysteresis could be explained using a mass balance mixing model with two or three-input components (ground water, hillslope water and eventually sub-surface soil water) and proposed a classification of types of *c–q* hysteresis according to their rotational pattern (clockwise/anticlockwise), curvature (convex/concave) and trend (positive/negative/null). However, it has recently been emphasized that some assumptions of this mixing model are arbitrary and that the interpretations made of the *c–q* hystereses may be doubtful (Duffy and Cusumano 1998; Hornberger et al. 2001; Scalon et al. 2001; Chanat et al. 2002; Joerin et al. 2002; Duffy and Cusumano 1998).

In most watersheds, the occurrence, intensity, duration and frequency of storm events cannot be easily predicted. Therefore, planning an accurate long-term solute sampling strategy with an aim to monitor a large number of storms is extremely demanding. Consequently, most field hydrological-biogeochemical studies are based on data collected from few storm events (Mulholland et al. 1990; Brown et al. 1999; Buffam et al. 2001; Avila et al. 2002). Despite these difficulties, recent field studies have focused on Mediterranean (Butturini and Sabater 2000, 2002; Bernal et al. 2002) and humid systems (Hinton et al. 1997), analyzing the variability of dissolved organic carbon (DOC) and nitrate (NO_3) concentrations during a small number of storm events. Similarly, several studies have focused on responses of DOC, nitrate and dissolved organic nitrogen concentrations to snowmelt in continental and alpine streams Carey 2003; Sickman et al. 2003; Creed et al. 1996; Hornberger et al. 1994). However, none of these studies have analyzed the main features of *c–q* hystereses. Moreover, no cross-site comparative studies have been done which analyze the variability of the main properties of the *c–q* hystereses.

The present study illustrates and analyzes *c–q* hysteresis of DOC and NO_3 in three Mediterranean headwater streams (Riera Major, Fuirosos and Can Vila) during the autumn–winter period. DOC and NO_3 typically increased in concentration at high discharges due to the mobilization of reactive solutes stored in forest and riparian topsoils during rains Fiebig et al. 1990; McGlynn and McDonnell 2003; Sickman et al. 2003). However, discharge explains only a small fraction of the temporal variability in solute concentrations in these Mediterranean streams (Bernal et al. 2002, 2004). In addition, bio-geochemical catchment scale models have so far been unable to capture satisfactorily this variability in solute response Bernal et al. 2004).

Based upon these assessments, the first objective of this study was to examine whether the variability of the hysteresis forms of DOC and NO_3, monitored in streams of the same climatic region but draining catchments with different characteristics, could be clustered following a general scheme. Our second objective was to explore the influence on main features of DOC and NO_3 hystereses, in the three study catchments, of storm hydrology and antecedent hydrological conditions. General features of DOC and NO_3-q hystereses were described using two simple descriptors that summarized their changes in concentration, global trends, rotational patterns and hysteresis areas. In addition, DOC and NO_3-q hystereses were compared with those of chloride and sodium. The latter indicate the hydrological mixing of water flow components during storm events (Evans and Davies 1998; Hooper 2003).

In this research, the study sites were intensively monitored during the cold and humid seasons, under high basal discharge conditions and when there was a relatively high probability of capturing storm events in the sampling series. In addition, the relatively narrow time window in our study means seasonal changes were not a primary source of variability of the solute responses (Butturini and Sabater 2000, 2002), facilitating the comparison between sites.

Study sites

Biogeochemical data were collected from three Mediterranean headwater catchments in North-East Spain called Riera Major, Fuirosos, and Can Vila.

Riera Major is a 15.8 km^2 forested, granitic catchment north of the Montseny mountain range (41°55′ N; 2°27′ E; 460–960 m a.s.l). The catchment area is entirely forested, predominantly by holm oak. Climate is typically humid Mediterranean, with annual mean rainfall ranging between 855 and 1660 mm Butturini and Sabater 2002). The stream flow is perennial and the baseflow discharge fluctuated during the study period between 40 and 63 $l\ s^{-1}$. Six storms were monitored in Riera Major between October 1997 and January 1998.

Fuirosos is a 10.5 km^2 forested, granitic catchment north of the Montnegre mountains (41°42′ N; 2° 34′ E; 50–700 m a.s.l.). The forest (oak holm, coniferous and deciduous) covers 90% of the total catchment area. Climate is typically Mediterranean, with annual rainfall ranging between 477 and 871 mm. Hydrology is intermittent, typically with a dry period from July to end of September, when the stream bed is dry, and a period in autumn–winter with high basal discharge (Butturini et al. 2003). However, the entire year 2002 was relatively wet and the stream did not dry up during the summer dry period. During the study period, the stream basal flow discharge ranged between 5 and 20 $l\ s^{-1}$. Five storm events were sampled in Fuirosos, occurring between October 2002 and January 2003.

Can Vila is a 0.56 km^2 catchment on sedimentary clayey rocks located in the headwaters of the Llobregat river in the Pre-Pyrenean region (42°12′ N; 1° 49′ E; 1115–1458 m a.s.l). Climate is sub-Mediterranean with annual rainfall ranging between 503 and 1336 mm. The mean annual temperature is 7.3 °C. The catchment is mainly covered by pasture, and coniferous forest covers c.a. 34% of the total area. The stream flow is intermittent, with a variable dry period generally between July and early September. During the study period, baseflow discharge ranged from 1 to 7 l s^{-1}. Five storms were sampled here between October 2003 and March 2004.

Additional information on the hydrology and DOC/NO_3biogeochemistry of the study areas are available in Butturini and Sabater (2000, 2002), Butturini et al. (2002, 2003), Bernal et al. (2002), Gallart et al. (2002), Latron (2003), Latrón et al. (2004).

Material and methods

Field methodology

Stream water was intensively sampled during storm events (every 0.5–2 h), using automatic water samplers (Sigma 900 max at Fuirosos and Riera Major, and ISCO 2700 at Can Vila).

Stream discharges were estimated on each sampling date by mass balance calculation by the ''slug'' chloride addition method (Gordon et al. 1992). The stream level was continuously recorded using a water pressure transducer connected to an automatic sampler. At the Can Vila catchment, a stream gauging station equipped with a water pressure transducer connected to a logger (Datataker 50) was used. Continuous stream discharge was estimated for all sites, using an empirical relationship between the sampled discharge and stream level (Butturini and Sabater 2000; Butturini et al. 2002; Latron 2003).

Chemical analyses of DOC, NO_3 and conservative tracers

All water samples were filtered through pre-ashed glass microfibre filters (Whatman GF/F, nominal pore size 0.7 μm) and stored in the cold for DOC and nitrate analyses. DOC from all sites was analyzed using a Skalar 12 SK TOC analyzer with UV-promoted persulfate oxidation. Nitrate in Riera Major was analyzed by capillary electrophoresis (Waters, CIA-Quanta 5000), while samples from Fuirosos and from Can Vila were analyzed colorimetrically with a Technicon autoanalyser after reduction of the solute on a copper-doped cadmium column. At Riera Major, chloride concentration was measured, while at Can Vila, sodium was used because of the low chloride concentrations in this stream (1–2 ppm, unpublished data). At Fuirosos, both chloride and sodium were measured. These two conservative ions strongly covaried during the study period in Fuirosos ($r^2 = 0.8$, d.f. $= 67$, $p < 0.001$) and only chloride data are presented in the results section. Chloride was analyzed by capillary electrophoresis (Waters, CIA-Quanta 5000), while sodium was measured with an inducted coupled plasma-atomic emission spectrometer (Thermo Jarrell Ash Iris Advantage ER/S).

Data analysis

Hydrological and biogeochemical parameters.
For each storm event, three parameters were estimated describing the hydrological characteristics of the storm hydrographs: (i) the magnitude of the storm event relative to the basal discharge (ΔQ_t, %):

$$\Delta Q_t = (Q_P - Q_{\mathrm{Bas})}/Q_{\mathrm{Bas}}{}^{*}100, \tag{1}$$

where Q_P and Q_{Bas} are the storm peak and basal discharges (l/s), respectively. (ii) The slope of the initial phase of the hydrograph recession limb (k, 1/day). This slope was assumed to fit an exponential model (Singh 1988). (iii) the relative length of the rising limb (RL, %):

$$RL = R_D/S_D{}^{*}100, \tag{2}$$

where R_D and S_D are the length (days) of the rising limb of the hydrograph and of the entire hydrograph, respectively. The end of each hydrograph was marked by a rate of discharge change smaller than 10% d^{-1} (Butturini and Sabater 2002). Low values of RL indicate a short and abrupt rising limb. Δt and ΔQ_{t-1} describe the hydrological conditions antecedent to storm events. Δt (days) describes the interval between two consecutive storm events, while ΔQ_{t-1}(%) gives the magnitude of the preceding storm event (Table 1, Figure 1).

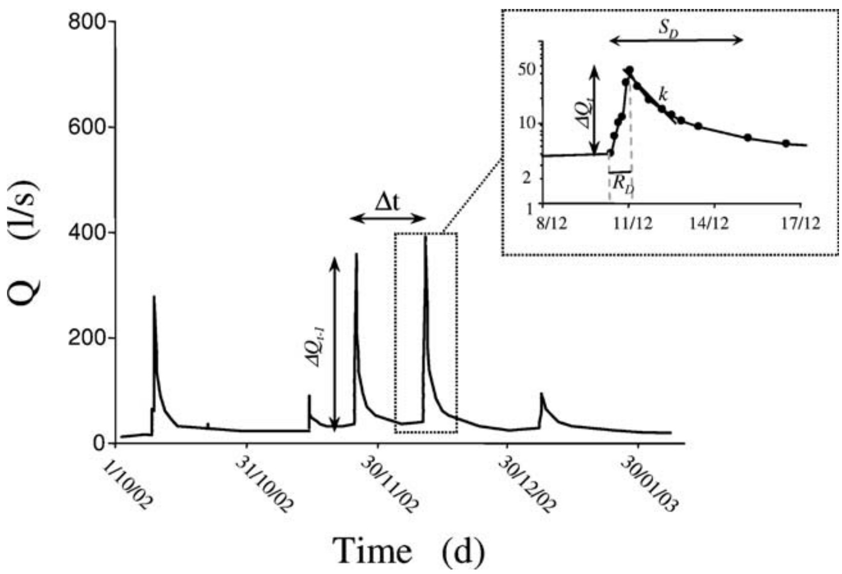

Figure 1. Schematic representation of the hydrologic parameters estimated for each monitored storm event. For symbols, see Table 1 (see text for additional information).

Table 1. Synthetic description of the hydrological parameters and *c–q* hysteresis descriptors estimated for each storm event in the three study catchments (Riera Major, Fuirosos and Can Vila, North-East Spain).

Description	Symbol
Hydrological parameters	
Magnitude of the storm event	ΔQ_t (Eq. 1)
Slope of the initial phase of the hydrograph recession limb	k
Relative length of the rising limb	RL(Eq. 2)
Duration of the dry period	Δt
Magnitude of the preceding storm event	ΔQ_{t-1}
c–q hysteresis descriptors	
Relative solute concentration changes	ΔC (Eq. 3)
Hysteresis area and rotational pattern	ΔR (Eq. 4)

For more details see the text.

For each *c–q* hysteresis we defined two simple descriptors of solute behaviour: ΔC and ΔR Table 1). ΔC (%) describes the relative changes in solute concentration and hysteresis trend, by the following formulae:

$$\Delta C = (C_s - C_b)/C_{\max} * 100, \tag{3}$$

where C_b and C_s are the solute concentrations at base flow and during peak storm flow, respectively. $C_{\max}$ is the highest concentration observed in the stream during a storm. ΔC ranged between -100 and 100. Negative ΔC values indicate *c–q* hystereses which follow a negative trend with respect to the discharge (i.e. solute dilution). Positive ΔC values indicate the opposite case (i.e. solute flushing) (Figure 2a). The ΔR (%) descriptor integrates information about the area and rotational pattern of the *c–q* hysteresis. Thus, it summarizes the entire dynamics of the solute during the storm event:

$$\Delta R = R^* A_h^* 100, \tag{4}$$

where A_h is the area of the *c–q* hysteresis. The area was estimated after standardizing discharges and concentrations to a unity scale. Therefore, A_h will be lower than the unity (Figure 2a). The term R summarizes the rotational pattern of the *c–q* hysteresis. If the *c–q* hysteresis is clockwise, then $R = 1$; if counterclockwise, then $R = -1$. For unclear or non-existent hystereses, $R = 0$. Therefore, ΔR ranges between -100 and 100.

The variability of the *c–q* hysteresis descriptors for the different solutes was explored in the unity plane ΔR vs. ΔC. In this plane, four regions (*A*, *B*, *C* and *D*) can be identified (Figure 2b). For the purpose of this study, *c-q* hystereses having ΔR values from -20 to 20% were considered to have a small area. In the classic mixing model with two input components (groundwater and hillslope water), a *c–q* hysteresis of a conservative tracer with a small hysteresis area or/an unclear rotational pattern indicate the near co-occurrence of the hydrological inputs components generating the storm water in the stream.

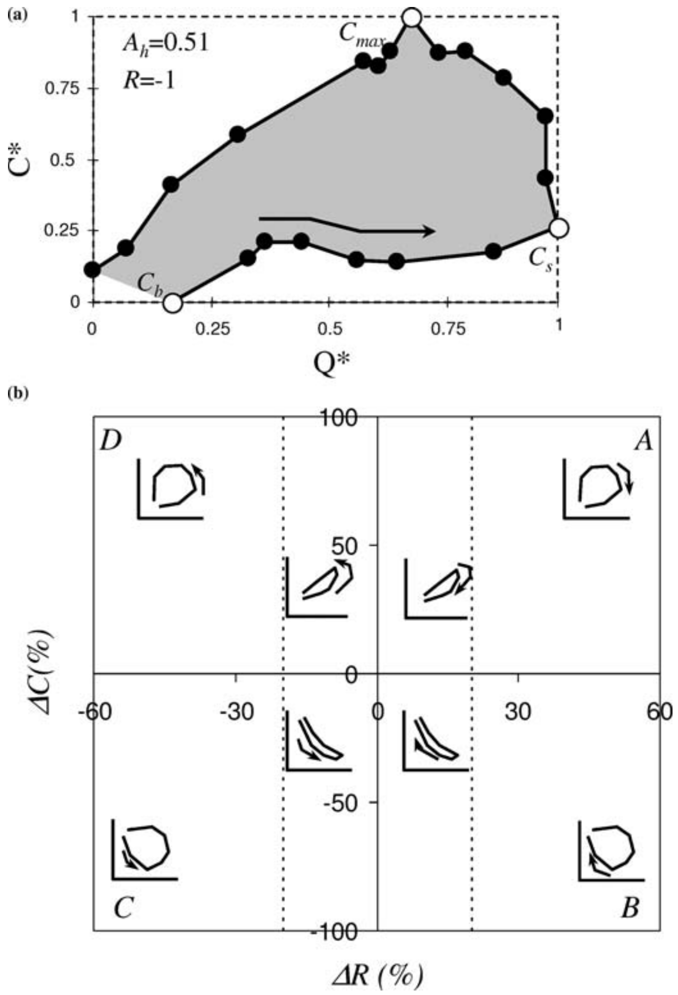

Figure 2. ((a) Schematic example of *c–q* hysteresis, illustrating the ΔC and ΔR descriptor estimation (example NO_3-*q* hysteresis from the storm on 20 December 1997 in Riera Major). C^* and Q^* are concentration and discharge standardized to unity. The area in grey corresponds to the value of A_h; Arrows indicate the direction of rotation of the *c–q* hysteresis. C_b, C_s, (open circles) represent the solute concentration at basal and peak discharges and $C_{\max}$ is the peak solute concentration measured during the storm event. (b) Schematic representation of the unity plane ΔR vs. ΔC. In this plane, four regions can be identified. In region *A* ($\Delta C > 0$, $\Delta R > 0$), are located the *c–q* hystereses with clockwise rotational pattern and with a general positive trend (i.e. solute flushing during the discharge rising limb). Region *B* ($\Delta C < 0$, $\Delta R > 0$) describes *c–q* hystereses with a clockwise rotational pattern but with a general negative trend (i.e. solute dilution during the recession discharge limb). Region *C* ($\Delta C < 0$, $\Delta R < 0$) describes the *c–q* hystereses with a counterclockwise rotational pattern and with a general negative trend (i.e. solute dilution during the discharge rising limb). Region *D* ($\Delta C > 0$, $\Delta R < 0$) describes *c–q* hystereses with a counterclockwise rotational pattern but with a general positive trend (i.e. solute flushing during the recession discharge limb).

Statistical analysis

The solute concentration vs. discharge relationships of the three study sites were plotted in a semi-logarithmic plot in which discharge had been log-transformed (Newbold et al. (1997). Regression fittings were considered significant at $p < 0.05$.

In our study sites, DOC and NO_3 concentrations typically increased during storms (Butturini and Sabater 2000, 2002; Bernal et al. 2002, 2004). This behaviour suggests that these patterns are driven by similar hydro-chemical mechanisms. Therefore, the hysteresis descriptors (ΔC and ΔR) can not be considered strictly independent from one another. Hence, to preserve this information, the relationships between the DOC and NO_3-q hysteresis descriptors (ΔC_{DOC}, ΔR_{DOC}, $\Delta C_{\mathrm{NO_3}}$ and $\Delta R_{\mathrm{NO_3}}$; the response variables) and the hydrological parameters (ΔQ_t, ΔQ_{t-1} R_L, Δt, and k; the explanatory variables), were explored using the multivariate gradient redundancy analysis (RDA). RDA is the extension of linear multiple regression to multivariate response data through a set of explanatory variables (Legend and Legendre 1998). This technique summarizes all the variance of response variables which is related to the explanatory variables and, at the same time, provides a synthetic and simple interpretation of the relationships between response and explanatory variables. In our study, the significant hydrological parameters ($p < 0.05$) were selected after forward selection using a Monte Carlo permutation test. In this test, the significance of an hydrological parameter is tested after eliminating possible effects of covariability of other hydrological variables (Manly 1997). The RDA analysis was performed using the program CANOCO 4. The ΔQ_t, and ΔQ_{t-1} parameters were log-transformed prior to analysis. In the RDA triplot, the correlation between hydrological parameters and the hysteresis descriptors is given by the cosine of the angle between the two vectors. Vectors pointing in roughly the same direction indicate a positive correlation, vectors crossing at right angles indicate a near zero correlation, while vectors pointing in opposite directions show a high negative correlation (ter Braak and Prentice 1988).

Results

Solute dynamics: an overview of biogeochemical responses

The overall temporal patterns of solutes were similar among the study sites: the conservative solutes generally were diluted at high discharges, while DOC and NO_3 were generally flushed at high discharges (Figure 3). DOC and the conservative solutes showed the clearer relationships with discharge. DOC concentrations were similar in the three study sites, while NO_3 concentrations in Can Vila were generally lower that in Riera Major and Fuirosos.

In Riera Major, chloride concentration ranged from 3 to 7 ppm and was inversely related to discharge ($r^2 = 0.38$, d.f. = 100, $p < 0.001$, Figure 4a), while DOC concentrations (from 0.8 to 8 ppm) and NO_3 (from 1.1 to 9.2 ppm) were positively correlated to discharge ($r^2 = 0.37$, d.f. = 111, $p < 0.001$, Figure 4b, and $r^2 = 0.21$, d.f. = 111, $p < 0.001$, Figure 4c, respectively). In Fuirosos, chloride concentration ranged from 7.4 to 22 ppm and was inversely correlated to discharge ($r^2 = 0.26$, d.f. = 66, $p < 0.001$, Figure 4a). By contrast, DOC (from 1.6 to 9.22 ppm) and NO_3 (from 0.05 to 6.6 ppm) concentrations were directly related to discharge ($r^2 = 0.48$, d.f. = 68, $p < 0.001$, Figure 4b, and $r^2 = 0.059$, d.f. = 68, $p < 0.05$, Figure 4c, respectively). In Can Vila, sodium concentrations ranged from 1 to 5.2 ppm and were inversely related to discharge ($r^2 = 0.58$, d.f. = 82, $p < 0.001$, Figure 4a), while DOC (from 1.9 to 6 ppm) and NO_3 (from 0.03 to 1 ppm) concentrations were directly related to discharge ($r^2 = 0.63$, d.f. = 82, $p < 0.001$, Figure 4b and $r^2 = 0.25$, d.f. = 82, $p < 0.001$, Figure 4c, respectively).

DOC and NO_3 hysteresis variability

Figure 5 shows an example of DOC and NO_3-q hystereses observed for each study site. Table 2 shows the values obtained for the c–q hysteresis descriptors during all storm events. Significant correlations were detected between ΔR_{DOC} and ΔR_{NO_3} ($r = 0.74$, d.f. = 15, $p < 0.01$) and between ΔR_{NO_3} and ΔC_{NO_3} ($r = 0.63$, d.f. = 15, $p < 0.01$). Specifically, the unity plane ΔR vs. ΔC (Figure 6) gave insight into the differences between c–q hystereses of different solutes and across study sites. The DOC concentration increased in all storm events ($\Delta C_{DOC} > 0$) and therefore data points of the DOC-q hysteresis were located exclusively in the regions *A* and *D* of the unity plane ΔR vs. ΔC. The rotational patterns of the DOC-q hysteresis ranged from clockwise ($\Delta R_{DOC} > 0$) to counterclockwise ($\Delta R_{DOC} < 0$). The DOC-q hystereses of Riera Major and of Fuirosos were clearly different. Most DOC-q hystereses from Riera Major followed a counterclockwise pattern and had large areas ($\Delta R_{DOC} < -30\%$, region *D*). In contrast, most DOC-q hystereses from Fuirosos were either clockwise or counterclockwise (regions *A* and *D*) and had a small area ($-20\% < \Delta R_{DOC} < 20\%$). Similarly, the DOC-$q$ hystereses from Can Vila were both clockwise and counterclockwise, although the range of variation along the ΔR_{DOC} axes ($-15\% < \Delta R_{DOC} < 56.1\%$) was more pronounced than that of Fuirosos (Figure 6a).

Similarly to DOC, NO_3 was usually flushed during storm events ($\Delta C_{NO_3} > 0$) and most of the NO_3-q hystereses were located in region *D of* the plane ΔR vs. ΔC. However, the dispersion of NO_3-q hystereses was markedly larger than that of the DOC–q hystereses. Weak NO_3 dilution (i.e. $\Delta C_{NO_3} < 0$) was observed in one storm episode in Riera Major and in one in Fuirosos (Table 2). The NO_3-q hystereses from Riera Major were somewhat different in form to those observed for the other two studied streams, and showed a

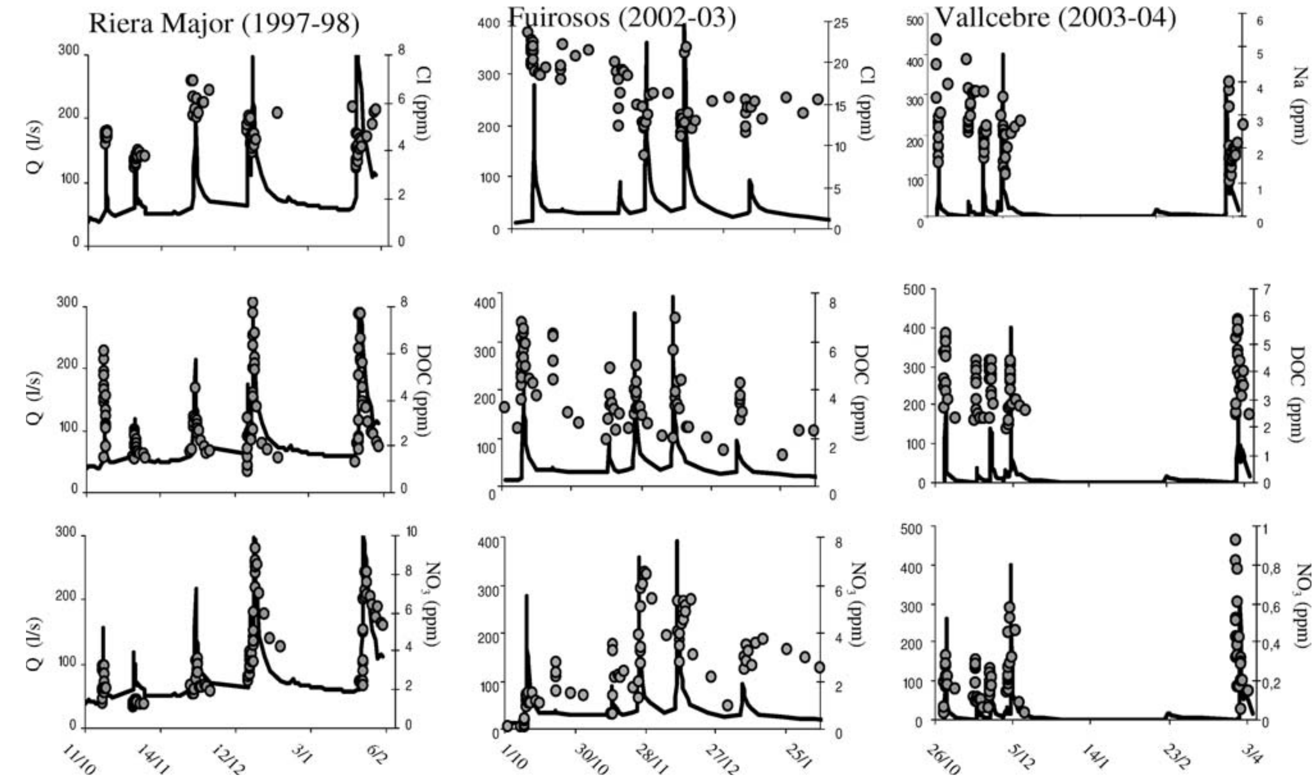

Figure 3. Discharge (*l*/*s*) and solute concentrations (ppm) at the three study sites (Riera Major, Fuirosos and Can Vila). Solid lines show the discharge and grey dots the solute (Cl^{-} or Na^{+}, DOC and NO_3) concentrations.

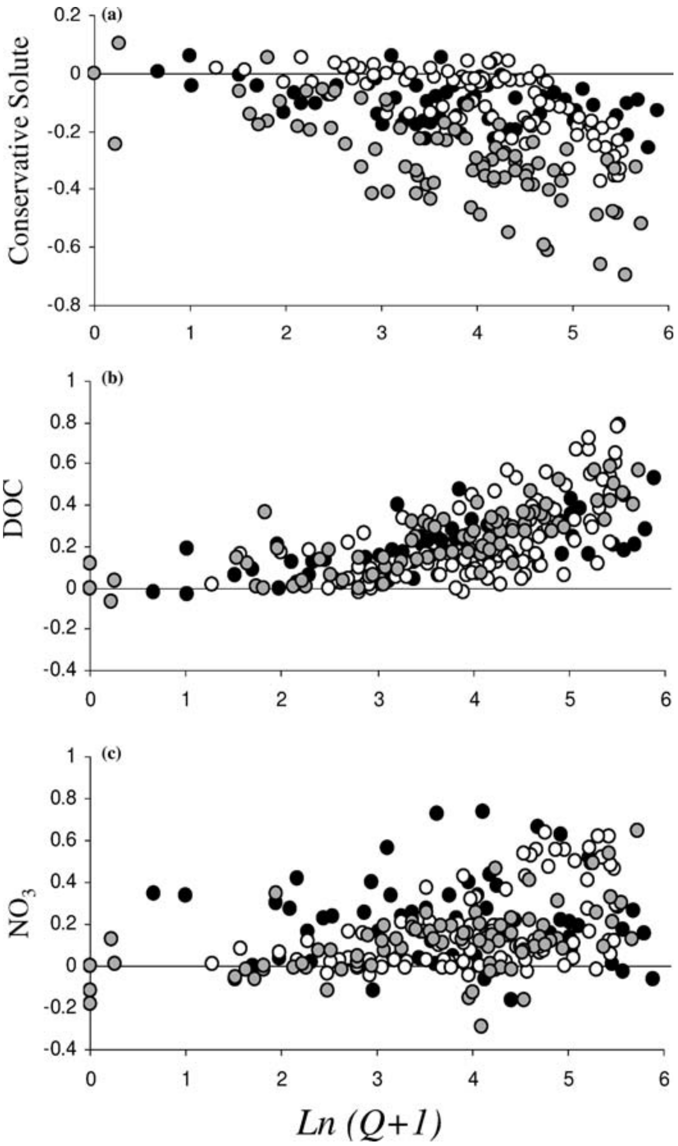

Figure 4. Semilogarithmic dispersion plots of solute concentration vs. discharge of conservative solutes (a), DOC (b) and NO_3 (c) in Fuirosos (black circles), Riera Major (white circles) and Can Vila (grey circles) during the study period. To compare data from different streams, the discharge values were standardized to the basal discharge. To facilitate the visual comparison of the general trends, concentrations were standardized to the concentration at basal discharge and then normalized to values between −1 and 1. Positive values indicate solute flushing and negative values indicate dilution.

consistent counterclockwise rotational pattern and a large area ($\Delta R_{NO_3} < -31\%$). On the other hand, in Fuirosos the values of the ΔR_{NO_3} descriptor ranged widely, from a large and marked counterclockwise rotational pattern together with a weakly negative trend (region *C*), to an ambiguous rotational pattern ($\Delta R_{NO_3} = 0$) and a strongly positive trend. Similarly, the NO_3-*q* hysteresis from Can Vila ranged from a marked counterclockwise rotational pattern and weakly positive trend (region *D*), to a clockwise rotational pattern (region *A*) and a clearly positive trend (Figure 6b).

The hystereses of the conservative solutes were located exclusively in region *C* ($\Delta C_C < 0$). In Riera Major and in Fuirosos they were predominantly counterclockwise ($\Delta R_C < 0$), while in Can Vila the rotational pattern was generally unclear ($\Delta R_C = 0$).

Cross-site comparison: the relevance of the hydrological parameters

The response to storm episodes differed widely among the three study sites. The most severe storm events, with abrupt recession curves, were observed in Can Vila ($8600\% < \Delta Q_t < 1913\%$; $-6.3 d^{-1} < k < -1.4\ d^{-1}$), and the mildest at Riera Major ($429\% < \Delta Q_t < 95\%$; $-1.8^{-1} < k < -0.2\ d^{-1}$). At Fuirosos, the ΔQ_t showed intermediate values, ranging from 217 to 1793%, while *k* was in the same range than in Riera Major (Table 2). On the other hand, the relative duration of the rising limb (*RL*) and the duration of the dry period (Δt) were comparable in the three sites (Table 2). Significant covariance among the hydrological variables was only observed between ΔQ_t and *k* ($r = -0.68$, d.f. $= 14$, $P < 0.05$).

These differences in hydrology had substantial effects on the magnitude of the relative dilution of the conservative solutes: ΔC_C values showed a strong inverse relation to ΔQ_t, following the semilogaritmic model ($r^2 = 0.66$, d.f. $= 14$, $p < 0.001$). The more substantial dilutions were observed at Can Vila, while the wider oscillations of ΔC_C values among the three streams were observed in Fuirosos (Figure 7a; Table 2). These clear response patterns to storm magnitude of the conservative solutes were not apparent with DOC ($r^2 = 0.03$, d.f. $= 14$, n.s. Figure 7b) nor with NO_3 ($r^2 = 0.18$, d.f. $= 14$, n.s.; Figure 7c).

The RDA analysis indicated that five hydrological parameters (ΔQ_t, ΔQ_{t-1} *RL*, Δt, and *k*) jointly explained 60.3% of the variation of the descriptors in the DOC and NO_3 *c–q* hystereses and that the first two axes in the analysis accounted for 99.3% of the total variance (both axes were significant, Monte Carlo test of significance, $p < 0.008$). The magnitude of the preceding storm event (ΔQ_{t-1}) loaded positively on axis 2, while the rest of the hydrological parameters (ΔQ_t, *RL*, Δt, and *k*) loaded on axis 1. Specifically, ΔQ_t and Δt loaded positively, while *RL* and *k* loaded negatively on axis 1. The Monte Carlo permutation test revealed that, of the five parameters, only ΔQ_{t-1} ($p < 0.008$, 24% of variance explained) and *RL* ($p < 0.012$, 19% of variance

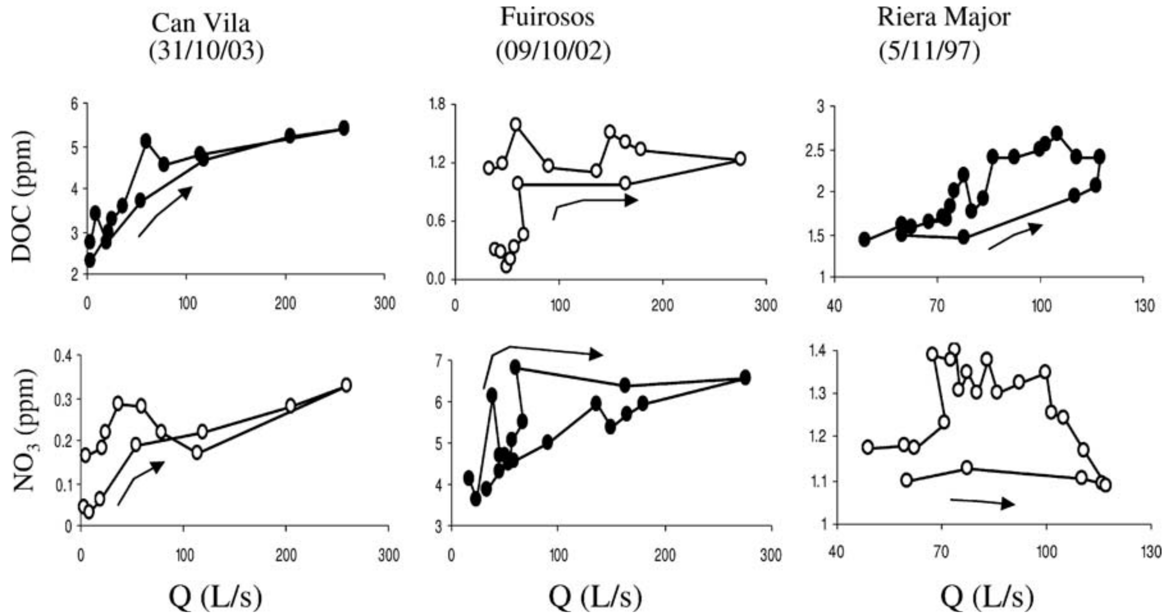

Figure 5. Selected examples of DOC and NO_3-q hystereses observed at the three study sites (Riera Major, Fuirosos and Can Vila) during the study period. Arrows indicate the direction of rotation. See Table 2 for the detailed results for each storm event in each study site.

Table 2. Values of the hydrological parameters and *c–q* hysteresis descriptors for each sampled storm event in the three study catchments.

	Δt (d)	RL (%)	K (d^{-1})	ΔQ_t (%)	ΔQ_{t-1} (%)	ΔR_C (%)	ΔC_C (%)	ΔR_{DOC} (%)	ΔC_{DOC} (%)	ΔR_{NO_3} (%)	ΔC_{NO_3} (%)
RM (25/10/97)	38.6	14.6	−1.8	135	319	0	−3.8	−32.0	75.9	−60.5	54.4
RM (5/11/97)	11.2	23.1	−1.0	95	135	−28.5	−3.9	−36.8	33.8	−47.8	−1.4
RM (27/11/97)	22.0	22.9	−0.8	258	95	0	−18.3	0.0	60.9	−43.7	10.0
RM 16/12/97)	19.6	22.5	−0.7	282	258	−33.9	−4.3	−28.1	69.0	−31.1	18.3
RM (20/12/97)	1.3	12.2	−0.6	167	282	−11.4	−28.5	−20.9	54.9	−51.4	16.7
RM (28/1/98)	39.7	9.6	−0.2	429	167	−26.4	−33.9	−19.3	84.5	−57.5	33.0
F (09/10/02)	32.7	17.5	−2.0	1793	208	0	−10.0	19.5	65.6	−23.6	64.1
F (14/11/02)	36.1	2.1	−2.4	267	1793	0	−27.0	8.7	59.2	0	81.2
F (25/11/02)	13.4	12.5	−1.3	984	267	−20.8	−40.9	13.3	49.5	−39.8	15.1
F (10/12/02)	15.3	15.6	−1.0	1030	984	−25.9	−18.7	−8.1	68.8	−26.0	−7.1
F (06/01/03)	26.2	14.6	−0.5	217	1030	−48.6	−0.8	28.0	51.1	0	56.5
CV (31/10/03)	9.7	8.3	−6.3	6149	393	0	−69.8	−15.1	49.8	0	86.7
CV (17/11/03)	16.7	18.8	−1.4	2159	6149	−13.3	−42.0	56.1	39.8	20.9	51.7
CV (24/11/03)	7.3	9.4	−3.4	2142	2159	0	−52.0	18.3	41.5	0	44.4
CV (4/12/03)	10	17.8	−4.8	1913	344	0	−56.1	−18.0	55.5	−40.9	20.3
CV (29/03/04)	116	4.2	−3.0	8604	753	0	−65.5	14.8	58.8	22.4	72.1

(RM = Riera Major; F = Fuirosos; CV = Can Vila).

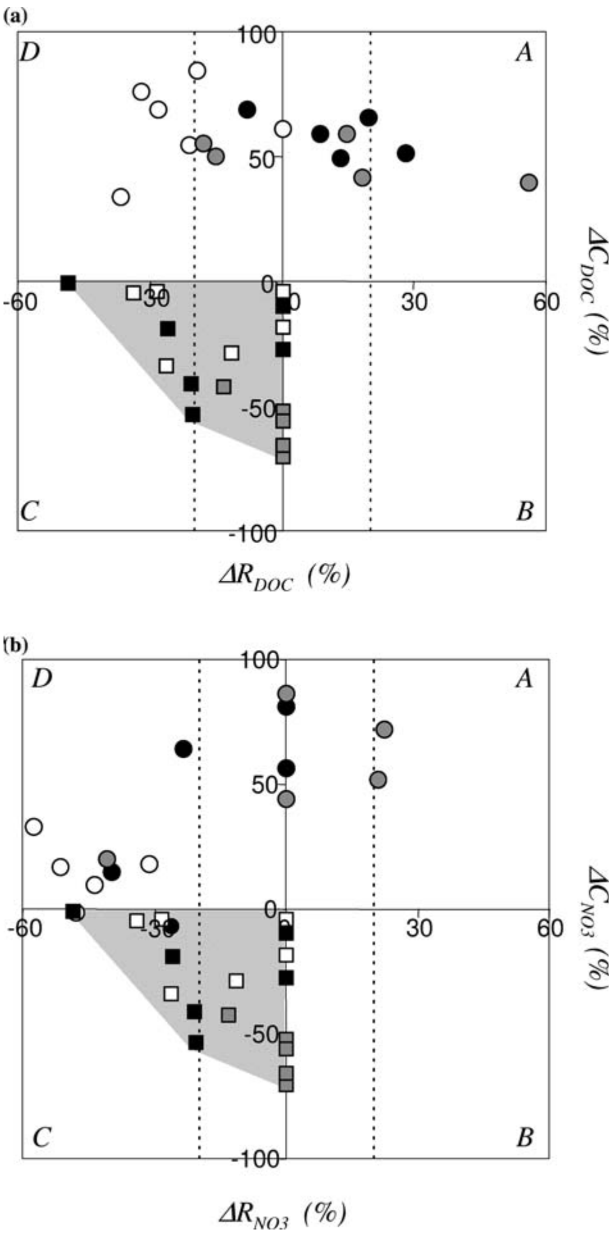

Figure 6. Representation of the *c–q* hysteresis characteristics of DOC (a) and NO_3 (b) in the unity plane ΔR vs. ΔC. Riera Major (white circles), Fuirosos (black circles), Can Vila (grey circles). Squares in the shaded area (region *C*) correspond to the conservative solute hysteresis.

explained) were statistically significant in the RDA analysis (Figure 8). With regard to the hysteresis descriptors, the vector ΔC_{NO_3} loaded positively on axis 1, and pointed in an opposite direction to *RL*, indicating an inverse relationship exists with this explanatory variable. On the other hand, the vector ΔC_{DOC} loaded negatively on both axes and pointed roughly in the opposite direction to the vector ΔQ_{t-1}, suggesting an inverse relationship exists

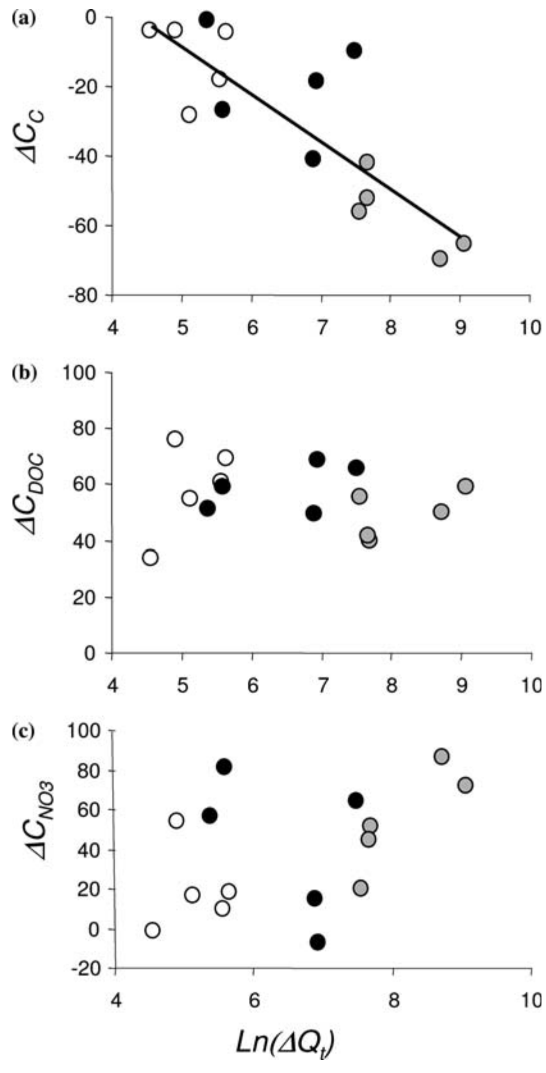

Figure 7. Relationships between storm discharge increase (ΔQ_t) and the relative solute concentration changes (ΔC) observed in the study sites for the conservative solutes (a), DOC (b) and NO_3 (c). In (a), the solid line is the regression line fitting the data ($r^2 = 0.74$, d.f. = 15, $p < 0.001$). Symbols as for Figure 4.

between these variables. Both ΔR_{DOC} and ΔR_{NO_3} were unrelated to the hydrological parameters (Figure 8). Regarding the analysis across study sites, axis 1 weakly separated Can Vila from Riera Major. Most data from Can Vila loaded positively on axis 1, while the data from Riera Major loaded negatively on this axis (Figure 8).

Discussion

Variability of DOC and NO_3-q hystereses

In this study, we have shown that a remarkable variability exists in the DOC and NO_3-*q* hysteresis forms and rotational patterns, both among and within the three studied Mediterranean streams. The Mediterranean climate is characterized by a marked within- and between-year variability (Gasith and Resh 1999), with a summer dry period which has strong effects on both the hydrology and the biogeochemistry of small streams, permanent and intermittent (Butturini et al. 2002; Bernal et al. 2004). In the present study, a

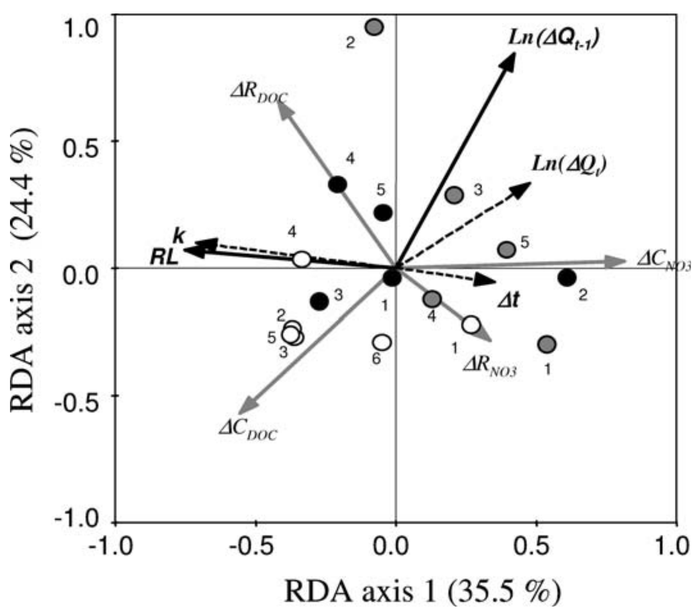

Figure 8. Graphical representation of the RDA performed on 16 storm events. The black arrows are the vectors of the hydrological parameters which were statistically significant ($p < 0.05$). The grey arrows are the vectors of the DOC and NO_3-*q* hystereses descriptors (ΔC_{DOC}, ΔR_{DOC}, ΔC_{NO_3}, ΔR_{NO_3}). Dotted arrows are the vectors of the hydrological parameters which were not significant ($p > 0.05$). Numbers indicate the time sequence of storm events in each study site (1 first, 6 last). Fuirosos (black circles), Riera Major (white circles) and Can Vila (grey circles).

cross-site comparison was performed using data obtained during the colder, humid and rainy season. Consequently, seasonality was not an important source of variability of the solute responses (Butturini and Sabater 2000, 2002). In addition, to reduce the relevance in our dataset of the antecedent summer period, the data were collected 1.5–2 months after the dry period. Based upon these assessments, we expected *c*–*q* hystereses to have more consistent and recurring features both within and across the study sites. DOC and NO_3-*q* hystereses lacked any consistent and recurrent pattern, hindering their classification into a general model. NO_3 concentrations in different sites showed a wide spectra of clearly different temporal patterns during storms, determining NO_3-*q* hystereses of varied form ($-60\% < \Delta R_{NO_3} < 22\%$) and a wide range of concentration changes ($-7\% < \Delta C_{NO_3} < 87\%$). The form of the DOC–*q* hystereses were also variable ($-37\% < \Delta R_{DOC} < 56\%$), although concentration changes for DOC ($33\% < \Delta C_{DOC} < 85\%$) were smaller than those observed for NO_3. Uncertainty associated with DOC and NO_3-*q* hystereses forms and rotational patterns in our study prevented our reaching a general hydrological and biogeochemical explanation for DOC and NO_3 temporal dynamics in Mediterranean streams during storms. This contrasts with the typically consistent clockwise DOC and NO_3-*q* hystereses observed in Alpine catchments in response to snowmelt (Hornberger et al. 1994; Carey 2003; Sickman et al. 2003), or in steep and wet small catchments (McGlynn and McDonnell 2003). The consistent DOC and NO_3 dynamics in these catchments has allowed to build up a solid, detailed understanding of the hydrological, biogeochemical and landscape processes typically underlying the nitrogen and organic carbon fluxes during storms.

The differences between the *c*–*q* hystereses of conservative tracers in the three catchments reflect their differences in drainage size area and storm hydrology. Most of the sodium-*q* hystereses in the smallest catchment (Can Vila) were characterized by an unclear rotational pattern ($\Delta R_C = 0$) and a higher relative dilution ($\Delta C_C < -42\%$) than in the larger catchments (Riera Major and Fuirosos). This suggests that in Can Vila the hillslope and ground waters inputs co-occurred in time and that, the contribution of hillslope water, is more relevant in Can Vila than in Fuirosos and Riera Major.

By contrast, this effect on solute behaviour of site-specific hydrological properties was unclear for DOC and NO_3. For instance, DOC relative changes (ΔC_{DOC}) in Can Vila were identical to those estimated in Fuirosos and in Riera Major. The DOC–*q* hysteresis rotational patterns (ΔR_{DOC}) in the small Can Vila showed characteristics observed in the large Fuirosos (clockwise hysteresis) and Riera Major (counterclockwise hysteresis) catchments. Similarly, both ΔR_{NO_3} and ΔC_{NO_3} in Can Vila ranged widely and had similar values to those reported for Fuirosos.

DOC and NO_3 *c*–*q* hystereses for Riera Major were the most steady of the three study sites. This consistency of the hystereses facilitated reaching an hydrological and biogeochemical explanation for this stream. In Riera Major, nearly all DOC and NO_3-*q* hystereses were counterclockwise, with pronounced negative ΔR values. Furthermore, during storm events, NO_3 concentrations did not change during the rising limb, and highest NO_3 concentrations coincided with the tail of the recession curve. In contrast, the highest DOC concentrations coincided with the storm peak, or lagged just behind it, with a rapid decline to pre-storm levels during the discharge recession limb (Figure 5, right plots). This remarkable behaviour of NO_3 flushing suggests a time-delay in the entrance of NO_3-rich, DOC-poor groundwater into the stream ((Butturini and Sabater 2000, 2002). On the other hand, the interpretation of counterclockwise DOC hysteresis is more complex. It could be attributed to a delaed peak of event water. Katsuyama and Ohte (2002) and Brown et al. (1999), for instance, used the DOC as a hydrological tracer to evaluate the relevance and timing of hillslope water in runoff generation. In Riera Major, this conclusion appears unlikely, because the counterclockwise/ambiguous Cl-q hysteresis suggests that the hillslope water preceded or co-occurred with the ground water with no delay.

Effects of hydrology on DOC and NO_3-q hystereses

According to the RDA analysis, NO_3 and DOC concentrations were related to the duration of the storm rising limbs (*RL)* and to the magnitude of the antecedent storm event (ΔQ_{t-1}).

The inverse relationship found between ΔC_{NO_3} and RL was confirmed using a simple univariant linear model ($r^2 = 0.41$ g.l. $= 15$, $p < 0.01$). This suggests that storm events with short abrupt changes in discharge during the hydrograph rising limbs favour NO_3 flushing at the beginning of the storm event. On the other hand, the DOC responses (ΔC_{DOC}) were negatively related to the magnitude of the antecedent storm events (ΔQ_{t-1}). This suggests that severe antecedent storm events damped the DOC leaching occurring during future storm episodes. However, caution is required when emphasizing the strength of this relationship because the univariant regression was not significant ($r^2 = 0.12$, g.l. $= 15$, n.s.). Several field studies, running during at least 1 year, have attempted a qualitative analysis of the relevance of the antecedent hydrological conditions on NO_3 and DOC concentration responses during storms (Avila et al. 2002; Chapman et al. 1993; Evans et al. 1996; Biron et al. 1999; Butturini and Sabater 2000; Bernal et al. 2002; Carey 2003; McKee et al. 2000). For instance, long inter-storm periods should favour the build-up of leachable DOC and NO_3. However, it has been difficult to build a solid empirical model relating the solute responses to the antecedent hydrological conditions because a detailed dataset covering a long hydrological and biogeochemical series is needed.

Finally, the RDA results point to an unclear influence of the hydrological descriptive variables on DOC and NO_3-q hysteresis forms and rotational patterns (ΔR_{DOC} and ΔR_{NO_3}). Consequently, the multivariate analysis demonstrates the difficulties of correctly predicting the entire DOC and NO_3 temporal dynamics during storm events in our study sites.

Our results clearly show that the variability of DOC and NO_3 responses hinder the ability of catchment-scale biogeochemical models to reproduce satisfactorily their temporal dynamics. For instance, a remarkable effort has been made to assess the ability of a semi-distributed biogeochemical model (INCA) to reproduce stream nitrogen dynamics across European catchments (Wade et al. 2005). However, data calibration of their model in Fuirosos has shown the complexities of satisfactorily capturing the variability of nitrate concentrations (Bernal et al. 2004). In Fuirosos, the analysis of multiannual DOC and NO_3 data has shown that discharge explains little variability, and that DOC concentrations reached a maximum in late summer, after the typical drought period (Bernal et al. 2002). The DOC peaks are probably generated by leaching of abundant organic matter stored on the dry stream bed (max. of 80 gC/m^2, Acuña 2004; Butturini et al., in press). These results have lead to think that the riparian strip and the hyporheic-groundwater interface exert a control on DOC and NO_3 dynamics in Fuirosos, particularly in late summer. Consequently, the above multivariate analysis technique may be a more useful exploratory tool for analyzing *c–q* hystereses of reactive solutes when site-specific information is included in the analysis and larger storm event series across seasons are available.

Conclusions

The synthetic approach used in this study to describe the DOC and NO_3-q hysteresis features in three Mediterranean headwater streams during the autumn–winter period shows that the DOC and NO_3 dynamics are far from following consistent and recurring patterns. This variability in the forms and rotational patterns of the DOC and NO_3-q hystereses was only weakly related to the hydrological features of the study sites. Therefore, these results prevented our reaching a general hydrological and biogeochemical explanation for DOC and NO_3 dynamics in Mediterranean streams during storms. The exploratory multivariate analysis technique used indicates that specific characteristics of the storm hydrographs, particularly the relative duration of the storm rising limb, and the magnitude of the antecedent storm events, may be useful parameters for describing the DOC and NO_3 changes in concentration across these streams (ΔC_{DOC} and $\Delta C_{\mathrm{NO_3}}$). However, detailed hydrological information did not explain satisfactorily the entire of the DOC and NO_3 concentration dynamics (the ΔR descriptor) during storm events.

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