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Changes in discharge and solute dynamics between a hillslope and a valley-bottom intermittent streams

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Abstract

We investigated differences on stream water flux as well as on chloride, carbon and nitrogen dynamics between two semiarid nested catchments, one at the hillslope and the other one at the valley-bottom. The two streams were intermittent, yet only the valley-bottom stream was embraced by a riparian forest and a well-developed alluvium with highly conductive coarse sediments. We found that stream water flux decreased by more than 40 % from the hillslope to the valley-bottom during hydrological transition periods (from dry-to-wet and from wet-to-dry conditions), coinciding with periods when stream-to-aquifer fluxes prevailed. During the hydrological transition period, stream export of chloride, nitrate, and dissolved organic carbon decreased 34–97 % between the hillslope and the valley-bottom catchments. There was a strong correlation between monthly differences in stream discharge and in stream Cl^- export between the two catchments. In contrast, monthly differences in stream export for bioreactive solutes were only partially explained by stream discharge. In annual terms, stream nitrate export from the valley-bottom catchment (0.32 ± 0.12 kg N ha^{-1} yr^{-1} – average ± standard deviation) was 30–50 % lower than from the hillslope catchment (0.56 ± 0.32 kg N ha^{-1} yr^{-1}). Although the riparian forest could be an extra source of organic matter to the valley-bottom stream, the annual export of dissolved organic carbon was similar between the two catchments (1.8 ± 1 kg C ha^{-1} yr^{-1}). Our results suggested that stream hydrology was a strong driver of stream solute export during the hydrological transition period, and that hydrological retention in the alluvial zone could contribute to reduce stream water and solute export under semiarid conditions in the valley-bottom stream.

1 Introduction

Dense riparian forests and well-developed alluvial zones are two of the main contrasting landscape features between hillslope and valley bottom areas in mountainous

HESSD

8, 9505–9536, 2011

Discharge and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

regions. The riparian zone is a critical ecotone in the interface between terrestrial and fluvial ecosystems with high potential for biogeochemical processing (Cirmo and McDonnell, 1997; Hedin et al., 1998; Hill, 2000). Riparian vegetation can supply large amounts of fresh particulate organic matter to aquatic ecosystems (Fiebig et al., 1990; Meyer et al., 1998). There is a large flux of dissolved organic carbon (DOC) from riparian soils to stream ecosystems (e.g. Bishop et al., 1994; Hornberger et al., 1994), and this source of organic matter can be relevant at the catchment scale (Inamdar and Mitchell, 2006; Pacific et al., 2010). At the same time, riparian zones can act as important sinks of essential nutrients such as nitrate via plant uptake and denitrification that can substantially reduce nitrate export from catchments (Peterjohn et al., 1984; Hill, 1996; Vidon et al., 2004a).

In its turn,the alluvial zone strongly affects the near-stream subsurface hydrology, and thus the ability of riparian zones to regulate solute fluxes (Pinay et al., 1995; Hill et al., 2004). When the river and the riparian zone are embraced by an alluvium with a large fraction of coarse material (hereafter, the alluvial-riparian zone), hydraulic conductivity is high favouring the mixing of surface-subsurface water bodies, which can exert control on stream flow as well as on stream chemistry in many different ways (e.g. Hooper et al., 1998; Hill, 2000; Burns et al., 2001). Some studies have shown that highly conductive coarse sediments enhance the retention of nutrients from stream ecosystems because the alluvium enlarges water storage zones, increasing hydrological retention and thus, attenuating the advective transport of streamwater (e.g. Valett et al., 1996; Morrice et al., 1997; Martí et al., 1997; Sobczak and Findlay, 2002). When the aquifer-to-stream fluxes prevail, however, conductive coarse sediments in the alluvium can favour that hillslope groundwater passes through the riparian area, thus lowering the mean residence time of groundwater in this compartment and limiting the removal of nutrients by biota (Vidon et al., 2004b). Therefore, coarse sediments in the alluvial zone could either impair (sensu Vidon et al., 2004b) or enhance (sensu Valett et al., 1996) the retention of nutrients, depending on the prevalent subsurface flow direction: from the upland aquifer to the stream (when the stream gains water) or otherwise, from the stream to the aquifer zone (when the stream loses water). Such surface-subsurface interactions could change spatially (D'Angelo et al., 1993; Covino and McGlynn, 2007), as well as temporally in response to changes in hydrological conditions (highly linked to local climate) (Dahm et al., 1998; Butturini et al., 2003; Vidon and Smith, 2007; Jencso et al., 2010). If surface-subsurface water interactions influence the removal of nutrients in the alluvial-riparian zone, changes in hydrological flow paths over time may thus affect stream nutrient concentration and catchment nutrient export. This may be specially noticeable in arid or semiarid regions where stream-to-aquifer water fluxes usually occur in the so called losing streams or temporary losing streams (only losing water during some periods) (Martí et al., 2000; Butturini et al., 2003).

The objective of this study was to explore differences on stream water flux as well as on carbon and nitrogen dynamics between two semiarid nested catchments, one located at the hillslope and the other located downstream at the valley-bottom. In addition to bio-reactive solutes, we analyzed a passive solute (chloride) to discern whether changes in water chemistry between the two catchments resulted solely from hydrological processes or were also affected by biogeochemical processes. The two catchments were drained by intermittent streams, though only the valley-bottom stream with an alluvial-riparian zone lost water toward the aquifer during hydrological transitions (from dry-to-wet and from wet-to-dry conditions) (Butturini et al., 2003). At the hillslope stream, outside the influence of the alluvial-riparian zone, hillslope groundwater flowed directly into the stream all the year around (Bernal and Sabater, 2008). We expected (i) that the local supply of organic matter by the riparian vegetation will lead to higher stream DOC and dissolved organic nitrogen (DON) concentrations and fluxes at the valley-bottom catchment than at the hillslope one, and (ii) that stream-to aquifer fluxes during hydrological transitions at the valley-bottom stream will lead to reduced water and solute fluxes compared to the hillslope stream.

2 Study site

2.1 Climate

The Fuirosos Stream Watershed (FSW) is located in the Natural Park of Montnegre-Corredor at 60 km from Barcelona, in northeastern Spain (latitude 41°42′ N, longitude 2°34′, altitude range 50–770 m a.s.l.). The climate is typically Mediterranean, with temperatures ranging from a monthly mean of 3 °C in January to 24 °C in August. Average annual precipitation is 750 mm yr^{-1} and thus the climate is Mediterranean subhumid (sensu Strahler and Strahler, 1989). Nonetheless, the distribution of rainfall through the year is irregular – the number of days with rain does not usually exceed 70 per year, so that climatic conditions at the FSW can be semiarid rather than subhumid during some periods.

2.2 The catchment

The FSW has a drainage area of 16 km^2 and is mainly underlain by granite with minor areas of sericitic schists. Leucogranite is the dominant rock type (48 % of the area), followed by biotitic granodiorite (27 % of the area) (IGME, 1983). There is an identifiable alluvial zone at the valley bottom embracing the stream and the riparian zone, which resulted from the transport and deposition of coarse material from the catchment (mainly sands and gravels). The alluvial zone is 50–130 m width and it extends for almost 4 km along the stream (Fig. 1). The soils at the FSW are poorly developed, with a very thin organic O horizon, or more frequently an Ao horizon, that becomes rapidly (in less than 5-cm depth) a B horizon (Bech and Garrigó, 1996). Soils at the FSW (from the top to the valley bottom) are usually classified as Entisols (Great Group Xerorthents), Alfisols (Great Group Haploxeralfs), and less frequently as Inceptisols (Great Group Xerochrepts) (USDA 1975–1992) (Bech and Garrigó, 1996). The riparian soils are sandy soils, Typic Xerochrepts (60 % sand, 34 % silt and 5.3 % clay) with low organic matter content (3–6 % in the first 10 cm) (Bernal et al., 2003). The catchment is mainly

HESSD
8, 9505–9536, 2011

covered by perennial cork oak (*Quercus suber*), evergreen oak (*Quercus ilex ssp. ilex*) and pine trees (*Pinus pinea*, *Pinus pinaster* and *Pinus halepensis*). In the valley head there is mixed deciduous woodland of chestnut (*Castanea sativa*), hazel (*Corylus avellana*), and oak (*Quercus pubescens*). The riparian forest is conformed by alder (*Alnus glutinosa*) and plane (*Platanus acerifolia*). Agricultural fields occupy less than 2 % of the catchment area and most of them are semi-abandoned.

For the present study, we monitored intensively two third-order streams draining nested catchments: Fuirosos (10.5 km^2) and Grimola (3.5 km^2). The Grimola sampling station was located 1.5 km upstream of the alluvial-riparian zone while the Fuirosos sampling station was located 3 km after the beginning of the alluvial-riparian zone (Fig. 1). The alluvial zone occupies 2.1 % of the Fuirosos catchment area, and embraces a well-developed riparian forest (10–20 m width) and the stream channel (3–5 m width). In the Grimola catchment, the streambed is mainly formed by bedrock, and the hillslope groundwater flows directly into the stream channel. The Fuirosos stream has four main effluents (Ef-1, Ef-2, Ef-3, and Ef-4). The Ef-1 and Ef-2 effluents ran dry during the period of study. The Ef-3 and Ef-4 catchments are outside the influence of the alluvial zone and their lithology and vegetation are similar to Grimola (Fig. 1).

Streamflow at the Fuirosos stream and all its effluents is intermittent. The cessation of flow occurs in summer and it lasts for several weeks or even months depending on the dryness of the year. For the two water years included in this study, the duration of the summer drought was of similar magnitude (11 and 14 weeks of drought, respectively). Only occasionally, during the wettest years (rain >800 mm yr^{-1}) the stream does not run dry in summer. At the FSW, the water year starts in September when the stream flow is recovered due to autumn storm events. During the hydrological transition from dry-to-wet conditions, stream water at the Fuirosos site infiltrates into the riparian zone due to the high conductivity of the sediments in the alluvial zone (5–20 m day^{-1}, Butturini et al.,2003). The Fuirosos stream loses water until November and after that, the aquifer-to-stream groundwater flux predominates until early summer (Butturini et al., 2003). Stream water loses has been detected at the end of the water year during

HESSD
8, 9505–9536, 2011

the transition from wet-to-dry conditions (Bernal and Sabater, 2008). At the Grimola stream, aquifer-to-stream fluxes prevail all the year long and no stream-to-aquifer water flux has been observed (Bernal and Sabater, 2008).

3 Material and methods

3.1 Field measurements and chemical water analysis

Air temperature and precipitation (collected with a tipping bucket rain gage) data were recorded at 15 min intervals at the meteorological station commissioned in April 1999 at the FSW. Streamwater level at Fuirosos was monitored continuously from September 1998 until May 2002 using a water pressure sensor connected to an automatic streamwater sampler (Sigma© 900 Max) (Fig. 2). From September 2000, similar equipment was used to monitor streamwater level at Grimola (Fig. 2). An empirical relationship between discharge and streamwater level was obtained at each site using the "slug" chloride addition method in the field (Gordon et al., 1992).

Streamwater samples were taken manually at least once every ten days (except during the cessation of flow in summer) from September 2000 to March 2002 at the Fuirosos, the Grimola and the Ef-4 sampling stations. Stream water samples were collected on the same day within 2 to 5 h. The automatic samplers at the Fuirosos and Grimola sites were programmed to start sampling at an increment in streamwater level of 2–3 cm and water samples were collected at hourly and sub-hourly intervals during stormflow conditions. At the Ef-4 site, we installed an automatic sampler (without water pressure sensor) that collected water samples at different time intervals depending on the weather forecasting (hourly when the probability of storms was high and daily when storms were not expected). To assess whether water samples were collected during baseflow or stormflow conditions, we installed a water pressure sensor connected to a data logger (Campbell© CR10X). Although Ef-4 was not sampled as intensively as

Discussion Paper | Discussion Paper | Discussion Paper | Discussion Paper |
HESSD
8, 9505–9536, 2011

the other two sites, the data collected was useful to characterize water chemistry at the hillslope effluents and to strengthen some of the patterns observed at the Grimola site.

All water samples were filtered through pre-ashed GF/F glass fibre filters and stored at 4 °C until analysed (usually in <7 days). Chloride (Cl^-) was analyzed by capillary electrophoresis (Waters®, CIA-Quanta 5000) (Romano and Krol, 1993). Dissolved nitrogen was measured colorimetrically with a Technicon-Autoanalyser® (Technicon, 1976). Nitrate (NO_3^-) was measured by the Griess-Ilosvay method (Keeney and Nelson, 1982) after reduction by percolation through a copperized cadmium column; ammonium (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. For measuring TDN, the sample was previously digested with UV light and potassium persulfate (Valderrama, 1981; Walsh, 1989) and then analyzed as NO_3^- DON concentration was calculated by subtracting NO_3^- and NH_4^+ from TDN. DOC samples were analyzed using a high-temperature catalytic oxidation (Shimadzu® TOC analyzer).

3.2 Data analysis

Hydrological stream-aquifer interactions at the Fuirosos stream have been intensively analyzed (Butturini et al., 2002, 2003; Bernal and Sabater, 2008). These previous studies showed that stream-to-aquifer water fluxes occur in the FSW valley-bottom during hydrological transition periods (from dry-to-wet and from wet-to-dry conditions) due to highly conductive alluvial sediments. Based on these previous knowledge, we considered two hydrological periods in the present study: the transition period (from June to October) when there is a high likelihood that stream-to-aquifer water fluxes occur, and the wet period (from November to May) when the aquifer-to-stream water fluxes prevail. Accordingly, all the environmental variables included in this study as well as water and solute fluxes from the hillslope and valley-bottom catchments were calculated separately for each hydrological period.

HESSD
8, 9505–9536, 2011

3.2.1 Environmental variables

From the meteorological data set, we calculated monthly precipitation (in mm month^{-1}), and average monthly air temperature (in °C). We calculated daily potential evapotranspiration (PET, in mm day^{-1}) with the Penman-Monteith method (Campbell and Norman, 1998). To characterize the environmental conditions for each water year and for each hydrological period, we calculated the UNEP Aridity Index (AI) that is P/PET. Values of AI = 1, 0.65 < AI < 1, 0.5 < AI < 0.65, 0.2 < AI < 0.5, 0.05 < AI < 0.2, AI = 0.05 indicate humid, dry land, dry sub-humid, semi-arid, arid and hyper-arid conditions, respectively (UNEP, 1992).

3.2.2 Stream water export

We estimated monthly stream water export (Q, in mm month^{-1}) from the Grimola and the Fuirosos catchment by linearly interpolating instantaneous discharge between sampling dates and summing up values for each month. To investigate changes in stream discharge between the hillslope and the valley-bottom catchments, we calculated the relative difference in Q (ΔQ, in %) between the two sites with $100 \times (Q_{fui} - Q_{gri})/Q_{gri}$, for each month and for each hydrological period. When $\Delta Q \approx 0$ %, stream water export from the two catchments was similar. Negative ΔQ values indicated that stream water export from the valley-bottom catchment was lower than from the hillslope catchment; positive ΔQ values indicated the opposite.

3.2.3 Stream solute concentrations and fluxes

We calculated monthly volume-weighted solute concentrations (in mg l^{-1}) for each of the two catchments. For each solute i, we calculated monthly stream solute export (E_i, in g ha^{-1}) from the hillslope and from the valley-bottom catchments by multiplying instantaneous concentration by daily discharge. Volume-weighted daily concentrations were used when more than one stream water sample per day was

HESSD
8, 9505–9536, 2011

available. Continuous solute concentrations were estimated by linear interpolation of measured solute concentrations (Hinton et al., 1997). We calculated the relative difference in stream solute export between the two catchments (ΔE_i, in %) with $100 \times (E_{\text{fui},i} - E_{\text{gri},i})/E_{\text{gri},i}$ for each month and for each hydrological period. To investigate whether ΔE_i was related to hydrological processes and/or also affected by biogeochemical processes, we explored the relationship between ΔQ and ΔE_i. We expected a strong correlation between ΔQ and ΔE_i for passive solutes such as chloride little affected by biogeochemical processing.

To explore how consistent water chemistry was from different hillslope streams, we compared instantaneous streamwater solute concentration for samples collected within the same day at the Grimola and Ef-4 streams.

3.2.4 Statistical analysis

We used a Wilcoxon/Kruskal-Wallis test to examine whether significant differences existed in stream solute concentrations between (i) the transition and the wet periods for each catchment, and (ii) the hillslope and the valley-bottom catchments for a given hydrological period. We explored the correlation between different environmental variables using a Spearman rank correlation coefficient (ρ). To examine the relationship between ΔQ and ΔE_i we applied a linear regression. The best fit line was determined by least squares and the significance of the regression was tested by analysis of variance (Zar, 2010). We used a Student's t-test to explore whether a given slope was significantly different from 1 (Zar, 2010). We used a Wilcoxon signed rank test for analyzing whether instantaneous solute concentrations for stream water samples collected within the same day from different streams differed significantly between each other. Non-parametric tests were chosen because concentrations showed a scattered and skewed distribution (Helsel and Hirsch, 1992). In all cases differences were considered significant when $p < 0.01$.

HESSD
8, 9505–9536, 2011

4 Results

4.1 Environmental variables

Annual P was 711 and 804 mm yr^{-1} during 2000–2001 and 2001–2002, respectively. Annual PET was similar for the two water years (1050 mm yr^{-1} for 2000–2001 and 931 mm yr^{-1} for 2001–2002). Annual AI ranged between 0.67 and 0.86. When analyzing each hydrological period separately, we found that the AI was particularly low during the transition period and it exhibited typical values of semiarid conditions (Table 1). In contrast, during the wet period P and PET were similar, so that the AI was close to 1.

4.2 Stream water export

During the transition period, stream runoff was lower from the valley-bottom than from the hillslope catchment (i.e. $\Delta Q < 0\,\%$), while the opposite trend was observed during the wet period (Table 2). Figure 2a shows that differences in stream runoff were particularly large during the transition period months. We found a significant and negative relationship between ΔQ and T ($\rho = -0.63$; $n = 24$; $p < 0.01$), indicating that the difference in stream water export between the two catchment was related to climatic conditions (Fig. 2b).

4.3 Stream solute concentrations

Monthly volume-weighted stream Cl^- concentrations were similar between the hillslope and the valley-bottom catchments (Wilcoxon/Kruskal-Wallis test, $p > 0.05$) (Fig. 3a). Although stream Cl^- concentration at the valley-bottom tended to be higher during the transition period (24.9 ± 5.3 mg l^{-1}) than during the wet period (19.9 ± 4.5 mg l^{-1}), the difference was only marginally significant (Wilcoxon/Kruskal-Wallis test, $p = 0.06$).

At the valley-bottom, monthly volume-weighted stream NO_3^- concentration followed a clear seasonal pattern with maximum in winter and minimum in summer (Fig. 3b). The

HESSD
8, 9505–9536, 2011

hillslope stream did not exhibited such a marked seasonality because high NO_3^- concentration was measured during winter as well as during the transition period (Fig. 3b).

There were not significant differences in stream DON concentrations between the two catchments nor between the two hydrological periods (in the two cases, Wilcoxon/Kruskal-Wallis test, $p > 0.05$). Monthly volume-weighted DON concentration ranged from 0.04 to 1.8 mg N l^{-1} and did not showed any seasonal pattern (Fig. 3c).

Monthly volume-weighted stream DOC concentration peaked in September at both, the hillslope and the valley-bottom sites (Fig. 3d). High stream DOC concentrations were also measured in winter and spring, so that differences in stream DOC concentration between the two hydrological periods were not statistically significant.

Stream water chemistry was similar between the Ef-4 and the Grimola streams. In particular, stream water samples collected within the same day had similar Cl^-, DOC and DON concentrations at these two hillslope streams (Fig. 4). The only exception was higher NO_3^- concentration at Grimola than at Ef-4 during the wet period (Fig. 4b). Instantaneous stream NO_3^- concentration during the transition period tended to be higher at the two hillslope streams than at the valley-bottom stream (Fig. 4b). In contrast, instantaneous DOC concentration tended to be higher at the valley-bottom stream than at the two hillslope streams (Fig. 4d).

4.4 Catchment solute export

During the transition period, monthly stream solute export from the valley-bottom catchment was consistently lower than from the hillslope catchment ($\Delta E_i < 0$ %, Fig. 5) (except one case for DON, Fig. 5c). In contrast, ΔE_i varied greatly during the wet period, especially for NO_3^- and DOC that exhibited extremely high ΔE_i values (i.e. >200 %) (Fig. 5b and d). There was a strong linear relationship between ΔQ and ΔE_{Cl} (Fig. 5a) whereas the relationship between ΔQ and ΔE_i was only moderate for bio-reactive solutes (NO_3^-, DON and DOC) (Fig. 5b–d). The ΔQ vs. ΔE_i slope was not significantly

HESSD
8, 9505–9536, 2011

different from 1 for Cl^- (t-test, d.f. – degrees of freedom – = 21, $t = 0.47$, $p < 0.001$), NO_3^- (t-test, d.f. = 21, $t = 1.71$, $p < 0.01$), and DON (t-test, d.f. = 21, $t = 1.89$, $p < 0.05$).

Relative changes in stream Cl^- export between the hillslope and the valley-bottom catchment (ΔE_{Cl}) were in agreement with those observed for stream discharge during both, the transition and the wet periods (Table 2). During the transition period, not only Cl^-, but also DOC and NO_3^-, showed decreased stream export from the valley-bottom catchment compared to the hillslope catchment ($\Delta E < 0\,\%$) (Table 2). Values of ΔE_{NO_3} were below 0 % also during the wet period, and in annual terms the stream export of NO_3^- was ~30–50 % lower from the valley-bottom catchment than from the hillslope catchment (Table 2). Although ΔE_{DOC} was below 0 % during the transition period, the annual export of DOC was similar between the two catchments (<2 % of difference, Table 2). The annual ΔE_{DON} did not showed a consistent pattern between the two studied water years (Table 2).

5 Discussion

There is an increasing body of knowledge showing that major hydrological and biogeochemical processes change as streams flow from the hillslope to the valley bottom (Covino and McGlynn, 2007; Jencso et al., 2010). In this sense, previous studies have shown that alluvial zones (usually present at the catchment's valley bottom) can impact strongly on stream hydrology and nutrient cycles (e.g. Triska et al., 1993; Cirmo and McDonnell, 1997; Ranalli and Macalady, 2010). Other studies have shown that such impact can be relevant at the catchment scale and it can modify water and solute export from catchments (Creed et al., 2008; Jencso et al., 2009; Pacific et al., 2010). We compared water and solute dynamics between two small nested catchments with similar geology, soil type, and vegetation cover. They mainly differed in that the one located upstream drained water only from the hillslope while the other one, located at the valley-bottom, included a well-developed alluvial zone and a riparian forest. Supporting previous studies, our results showed substantial differences in water flux as well as on

C and N flux between these two streams. Differences were specially noticeable during hydrological transition periods when the valley-bottom stream was more likely to lose water toward the aquifer. Based on the results presented here and on previous studies performed at the FSW we discuss the potential effect that the alluvial-zone could have on stream hydrology and water chemistry in this intermittent stream.

5.1 Potential effect of the alluvial-riparian zone on stream water export

We showed that stream water export consistently decreased (by >40 %) between the hillslope and the valley-bottom catchments during the hydrological transition periods. These results are in agreement with previous studies at the FSW showing that surface water at the valley-bottom stream penetrated up to 10 m into the riparian zone during hydrological transitions (Butturini et al., 2003; Vázquez et al., 2007). The valley-bottom stream lost water toward the aquifer due to the difference between the aquifer and stream water hydraulic heads. Such stream-to-aquifer flow was favoured by the high hydraulic conductivity of the alluvial sediments (5–20 m day^{-1}, Butturini et al., 2003). Similar results have been reported for other alluvial streams in semiarid regions world-wide (Triska et al., 1993; Morrice et al., 1997). In contrast to the valley-bottom stream, previous studies at the FSW showed that upstream of the alluvial zone the stream did not lose water (Bernal and Sabater, 2008). This difference in stream-aquifer hydrological interactions could explain why stream discharge during hydrological transition periods was several times larger at the hillslope site than at the valley-bottom site. Another feasible mechanism that could explain such a drop in stream discharge and that could contribute to exacerbate the difference between the aquifer and stream water hydraulic heads, is a disproportionate lower contribution of hillslope groundwater to stream discharge downstream the Grimola sampling station. In that sense, Detty and McGuire (2010) showed that most of the catchment was hydrologically disconnected from the channel network during summer at an experimental catchment in the Hubbard Brook Experimental Forest. In contrast, nearly the entire catchment was hydrologically connected during the largest storm events occurring in the wet period. McGuire and

HESSD
8, 9505–9536, 2011
Discharge and water chemistry in hillslope and valley-bottom streams
S. Bernal and F. Sabater

McDonnell (2010) reported that changes in hillslope-stream hydrological connectivity between dry and wet periods were complex and followed non linear patterns at the HJ Andrews Experimental Forest (OR, USA). Likely, hillslope-stream hydrological connection may change seasonally at the FSW, which could partially explain the observed variation of ΔQ. Unfortunately, we have no hydrometric data to explore how this mechanism contributes to drop stream water export at the valley-bottom catchment during the transition period.

Negative ΔQ occurred mainly during hydrological transition periods when the environmental conditions were semiarid as indicated by AIs < 0.5. In contrast to the transition period, ΔQ was usually >0 % during the wet period which could respond to increased hydrological connectivity between different landscape units through the catchment (Detty and McGuire, 2010). These findings point toward contrasting hydrological processes between these two semiarid nested catchments during the transition and the wet periods. Moreover, the negative relationship between ΔQ and temperature suggests that differences in stream water flux between the hillslope and the valley-bottom catchments were linked to climatic conditions. This result implies that future warming could exacerbated the observed differences in stream water flux between these two catchments.

5.2 Riparian vegetation as a potential source of dissolved organic matter to stream ecosystems

Most of the DOC entering to the stream from groundwater sources is supposed to be recalcitrant and a little source of energy for microorganisms (Schiff et al., 1997). Contrastingly, riparian forests typically composed by deciduous species provide fresh leaf litter to streams as well as to riparian forest floors so that, riparian soils are often considered an important source of particulate and dissolved organic matter to streams (Fiebig et al., 1990; Hinton et al., 1997; Acuña et al., 2004). Supporting our expectation that the riparian forest at the FSW is an extra source of organic matter for the valley-bottom stream, we found higher instantaneous DOC concentration at the valley-bottom

HESSD
8, 9505–9536, 2011

Discharge and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

stream than at the other two hillslope streams during both, the transition and the wet periods. Similarly, other studies have reported higher stream DOC concentrations for catchments with wetlands and riparian zones than for catchments without them (Hinton et al., 1998; Inamdar and Mitchell, 2006; Creed et al., 2008). Other parts of the catchment could act as DOC sources to the main stream. However, the fact that the two hillslope streams (Grimola and Ef-4) had similar DOC concentrations suggests consistent DOC concentrations through the FSW hillslopes.

Following the idea that the FSW riparian forest may act as an extra source of DOC to the stream, we expected higher stream DOC and DON fluxes at the valley-bottom stream than at the hillslope stream. Nevertheless, and despite the large amount of riparian leaf litter accumulated on the valley-bottom streambed during the period with no stream flow (Acuña et al., 2004), the DOC flux was 45–64 % lower at the valley-bottom stream than at the hillslope stream during the transition period. This finding is not surprising when taking into account that the valley-bottom stream loses water toward the aquifer during hydrological transition, reducing stream water export as well as stream nutrient flux. In fact, the correlation between ΔQ and ΔE_{DOC} was high during the transition period and all values fall close to the 1:1 line (Fig. 5d) suggesting that hydrology was a strong driver of stream DOC fluxes during this period. During the wet period, we did measure a ~15 % increase in stream DOC fluxes between the valley-bottom and the hillslope catchment. Yet, the difference in the annual hydrological export of DOC between the two locations was small ($\Delta E_{\mathrm{DOC}} < 2$ %). These results suggest that (i) the hydrological retention of DOC during the transition period minimized the potential of the riparian forest as a source of DOC to the stream, and (ii) the capacity of this riparian forest to supply DOC to the stream was limited. Recently, Pacific et al. (2010) concluded that a significant riparian-to-hillslope area ratio is needed (at least 5 %) for a riparian system to impact substantially on annual stream DOC export. According to Pacific et al. (2010), the FSW riparian forest (that occupied only 2 % of the catchment area) migth be too small to modify annual stream DOC export.

HESSD

8, 9505–9536, 2011

In contrast to DOC, the flux of DON between the hillslope and the valley-bottom streams did increase during the transition period, though the magnitude of change was extremely different between the two water years (3 % vs. 170 %). Moreover, the ΔE_{DON} during the wet period was not consistent between the two water years (–35 % vs. 29 %). This lack of pattern complicates drawing any conclusion about factors driving in stream DON dynamics between the two catchments. The DON pool in stream ecosystems is still poorly understood, yet previous research acknowledges that it may be composed by a varying proportion of refractory and labile internally recycled DON over time and space (Brookshire et al., 2005). The most recalcitrant terrestrial fraction of DON it may be intrinsically linked to DOC, so that C and N organic solutes may showed similar patterns. That we did not find any clear pattern for DOC and DON concentrations and fluxes between the hillslope and the valley-bottom catchments suggest that labile DON could account for a relevant proportion of the organic N pool at the FSW. Alternatively, differences between DOC and DON could respond to different terrestrial sources and different biogeochemical cycling in forest soils (Inamdar et al., 2008). Studies on degradability of DON compounds at the FSW over different periods of the year would be needed to further test these hypothesis.

5.3 Hydrological and biogeochemical solute retention in the alluvial-riparian zone

We expected that stream-to-aquifer water flux during hydrological transitions at the alluvial-riparian zone will increase hydrological retention, leading to lower solute fluxes at the valley-bottom stream compared to the hillslope stream. Concordantly, we found that the difference in stream water flux between the two catchments was accompanied by concomitant differences in stream solute export. In particular, changes in Cl^- flux between the hillslope and the valley-bottom streams were strongly correlated to changes in discharge. That we observed a decrease in stream export with decreasing stream water flux for a passive solute such as Cl^- suggests that hydrological retention in the alluvial zone is an important mechanism governing solute fluxes during the transition period in this semiarid catchment. Other studies in semiarid regions have reported increased water residence time in the alluvial zone when the hydraulic conductivity of sediments is high which can have important implications on nutrient cycling and retention (e.g. Valett et al., 1996, 1997; Morrice et al., 1997; Martí et al., 1997).

If hydrological retention in the alluvial-riparian zone would have been the only mechanism responsible for decreased stream nutrient fluxes at the valley-bottom during the transition period, we might expect no changes in nutrient concentration between the hillslope and the valley-bottom streams. However, stream NO_3^- concentration drop significantly between the hillslope and the valley-bottom during the transition period. Several mechanisms operating at the valley-bottom stream and/or at the alluvial-riparian zone could explain this decrease in NO_3^- concentrations. First, increased immobilization of inorganic N by microorganisms colonizing large amounts of fresh leaf litter stored in the streambed during summer and autumn (Mulholland et al., 1992). At the FSW, the riparian forest supplies about 0.15–0.49 kg C m^{-2} yr^{-1} to the adjacent stream mainly as leaf litter (Bernal et al., 2003; Acuña et al., 2007). Such a large supply of organic substrate enhances extremely high peaks of heterotrophic activity in the stream during autumn (Acuña et al., 2004), supporting the idea that leaf litter from the riparian forest can promote the immobilization of inorganic N by the microbial stream community. Second, NO_3^- uptake by riparian vegetation and/or microbial denitrification in riparian soils could also contribute to decreased NO_3^- concentrations in the valley-bottom stream (Peterjohn et al., 1984; Vidon et al., 2004a). However, Butturini et al. (2003) reported a marked increase, rather than a decrease, of NO_3^- concentrations at the FSW riparian groundwater during hydrological transitions due to the dissolution of salts build up in the riparian soil during the dry period. This phenomenon has also been documented in other arid and semiarid regions (Heffernan et al., 2004; Meixner et al., 2007). That we observed consistently lower NO_3^- concentrations in the valley-bottom stream than in the two hillslope streams (Ef-4 and Grimola), even when release of NO_3^- from riparian soils is significant, suggests that the stream-to-aquifer water flux

HESSD
8, 9505–9536, 2011

enhances the retention of NO_3^- available in the riparian soil which otherwise would be flushed to the stream.

Although stream NO_3^- export was higher from the valley-bottom catchment than from the hillslope catchment during some months, annual stream NO_3^- export from the former was 30–50 % lower than from the later. A dilution effect due to some other water sources seems unlikely since the drop in stream NO_3^- flux was not accompanied by a decrease in Cl^- flux. Retention of NO_3^- in the alluvial-riparian zone during the wet period could partially explain the decrease of stream NO_3^- flux from the hillslope to the valley-bottom since significant reductions (from 9–100 %) of groundwater NO_3^- concentrations through the riparian zone have been reported at the FSW (Butturini et al., 2003). Although previous studies indicated that soil denitrification is small in this semiarid catchment (Bernal et al., 2003), other hot spots/hot moments of NO_3^- removal can not be ruled out. More detailed studies exploring the spatial-temporal variation of NO_3^- retention at different compartments through the FSW would be needed to test this hypothesis.

Overall, our results showed that stream water and solute export changed substantially between the hillslope and the valley bottom at the FSW. In particular, stream water and solute fluxes from the hillslope catchment were higher than from the valley-bottom catchment during hydrological transitions under semiarid conditions. These results are in line with previous studies performed at the FSW showing that the alluvial sediments favour stream-to-aquifer water flux increasing hydrological retention during transition periods. The influence of hydrological retention on stream nutrient export at this alluvial-riparian zone may increase in the future since climate change models predict more frequent drought periods (IPCC, 2007), which could increase stream losing water episodes. Our study contributes to the urgent need of understanding the links between hydrology and nutrient cycling in ecosystems with limited water availability for forecasting how ecosystems in semiarid and in other regions of the world could respond to global warming in the future.

HESSD
8, 9505–9536, 2011

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HESSD

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Discharge and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

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HESSD

8, 9505–9536, 2011

Discharge and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

HESSD

8, 9505–9536, 2011

Discussion and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

Table 1. Cumulative precipitation (ΣP), cumulative potential evapotranspiration (ΣPET), aridity index (AI), and average air temperature (T) for the transition and the wet periods during two consecutive water years at the FWS in the Montnegre-Corredor Natural Park (NE, Spain). The range of monthly temperature for each period is shown in brackets.

	ΣP (mm)	ΣPET (mm)	AI	T (°C)
WY 2000–2001				
Transition	263	614	0.43	19.6 [13.9, 23.5]
Wet	448	436	1.03	10.8 [7.5, 17.1]
WY 2001–2002				
Transition	256	566	0.45	20.4 [(17.3, 22.8]
Wet	548	365	1.5	9.8 [5.28, 15.6]

Table 2. Cumulative water (Q) and solute export (E_i) from the hillslope (gri) and the valley-bottom (fui) catchments during the transition and the wet periods for two consecutive water years. The relative difference of water (ΔQ) and solute (ΔE_i) fluxes between the two catchments is shown in each case.

	Q			Cl^-			NO_3^-			DON			DOC		
	Q_{gri} mm	Q_{fui} mm	ΔQ %	E_{gri} g ha^{-1}	E_{fui} g ha^{-1}	ΔE %	E_{gri} g ha^{-1}	E_{fui} g ha^{-1}	ΔE %	E_{gri} g ha^{-1}	E_{fui} g ha^{-1}	ΔE %	E_{gri} g ha^{-1}	E_{fui} g ha^{-1}	ΔE %
WY 2000–2001															
Transition	9	5	−44	2154	1416	−34	93	19	−80	35	36	3	521	288	−45
Wet	76	127	68	12 375	20 881	69	698	385	−45	350	226	−35	2179	2454	13
Total	84	132	57	14 529	22 298	53	791	404	−49	385	262	−32	2700	2742	2
WY 2001–2002															
Transition	16	8	−48	1061[a]	303[a]	−71	26[a]	0.8[a]	−97	10[a]	27[a]	176	159[a]	57[a]	−64
Wet	164	197	20	4683[b]	5129[b]	10	313[b]	245[b]	−22	71[b]	91[b]	29	751[b]	865[b]	15
Total	180	206	14	5744	5432	−5	339	246	−27	81	118	46	910	922	1

[a] only September and October,

[b] from November to March

HESSD
8, 9505–9536, 2011

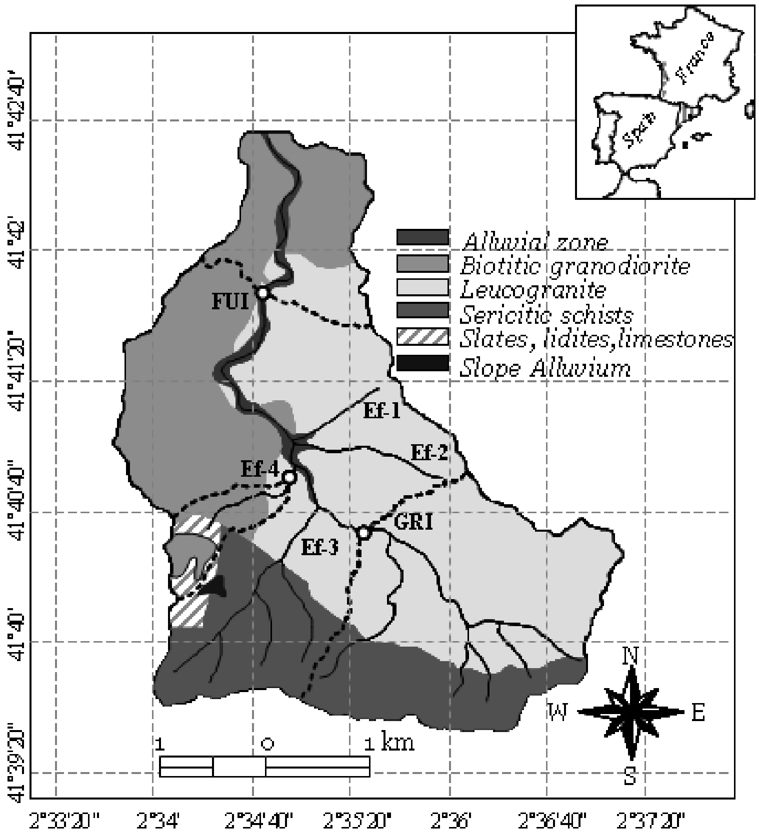

Fig. 1. Lithological units in the Fuirosos Stream Watershed (FWS) in the Montnegre-Corredor Natural Park are shown in different shades (sensu IGME, 1983). At the valley bottom there is an identifiable alluvial zone. The dashed lines indicate the drainage area of the catchments monitored during the study: Fuirosos (FUI, 10.5 km^2), Grimola (GRI, 3.5 km^2) and Ef-4 (0.3 km^2).

HESSD
8, 9505–9536, 2011

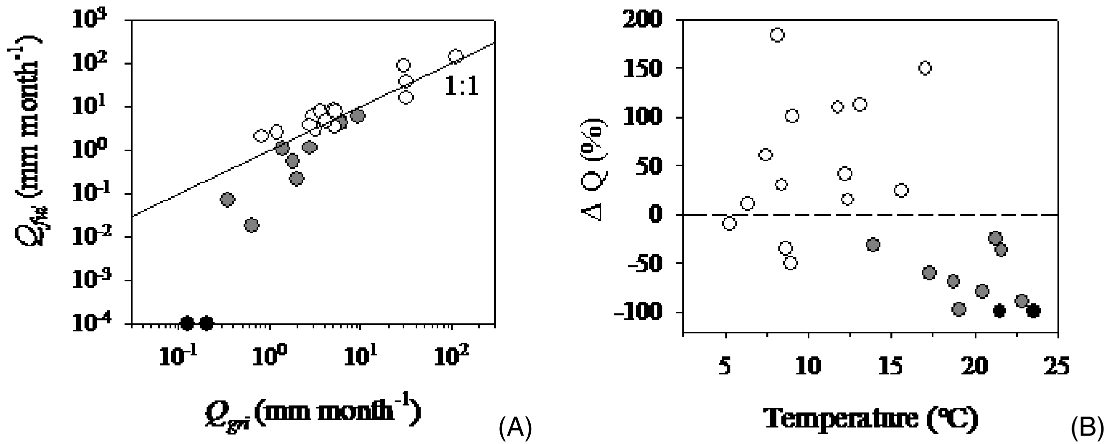

Fig. 2. (A) Relationship between monthly stream water export from the hillslope and the valley-bottom catchments. The 1:1 line is shown. **(B)** Relationship between monthly average air temperature and the relative difference in stream water export between the hillslope and the valley-bottom catchments. The dashed line shows no changes in stream runoff between the two catchments. The grey and the white circles indicate the transition and the wet period, respectively. The black circles correspond to months when the Fuirosos stream ran dry.

HESSD

8, 9505–9536, 2011

Discharge and water chemistry in hillslope and valley-bottom streams

S. Bernal and F. Sabater

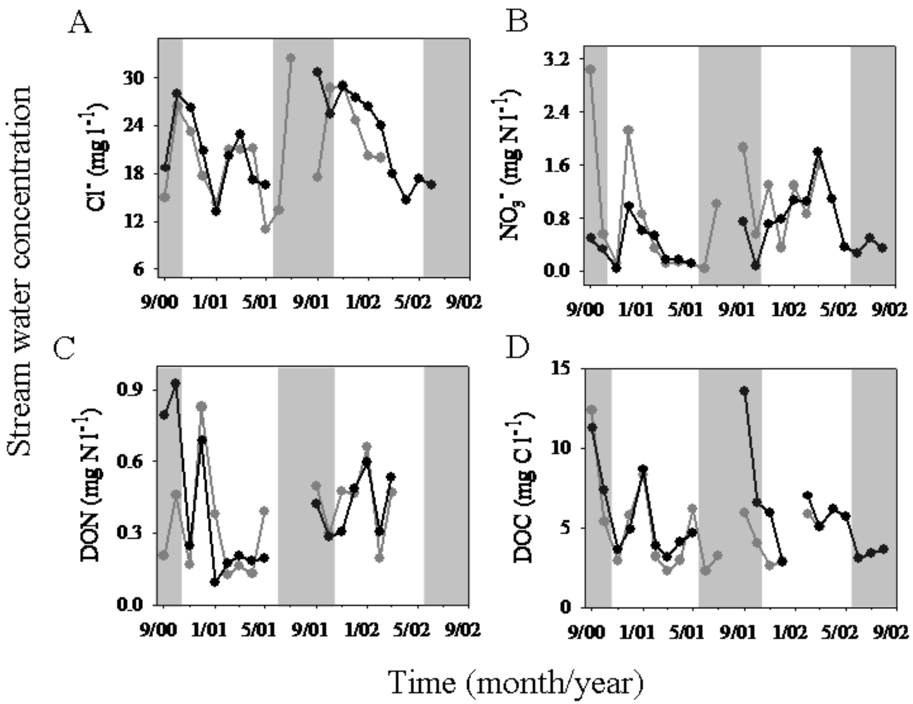

Fig. 3. Monthly volume-weighted stream water concentration for **(A)** Cl^-, **(B)** NO_3^-, **(C)** DON, and **(D)** DOC at the hillslope (grey) and the valley-bottom (black) catchments during the period of study. The shaded area shows the hydrological transition period.

HESSD
8, 9505–9536, 2011

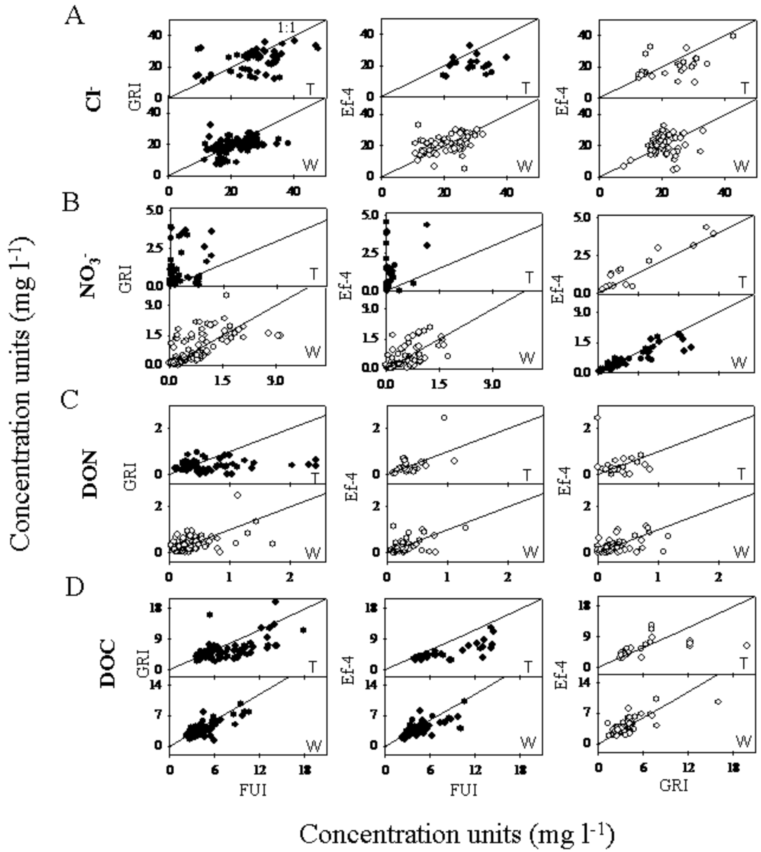

Fig. 4. Dispersion plots between **(A)** Cl^-, **(B)** NO_3^-, **(C)** DON and **(D)** DOC instantaneous concentration from stream water samples collected within the same day at the Fuirosos (FUI), the Grimola (GRI), and the Ef-4 streams. *T*, transition period; *W*, wet period. The 1:1 line is shown in black. Circles are black only when differences between instantaneous solute concentrations were statistically significant ($p < 0.01$).

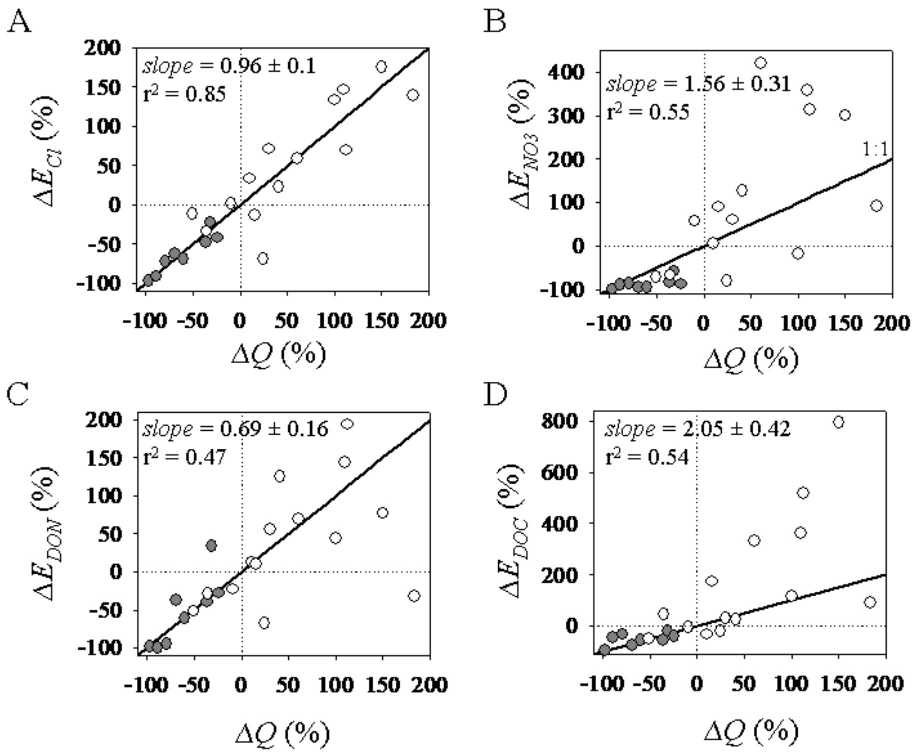

Fig. 5. Relationship between the relative difference in runoff and in solute export between the hillslope and the alluvial catchments for **(A)** Cl^-, **(B)** NO_3^-, **(C)** DON, and **(D)** DOC. The grey and the white circles indicate the transition and the wet period, respectively. The 1:1 line is shown in black. The r^2 and the slope ± standard error of the linear regression between ΔQ and ΔE_i is shown in each case.

HESSD
8, 9505–9536, 2011

Title Page
Abstract | Introduction
Conclusions | References
Tables | Figures
◀| |▶
◀ ▶
Back | Close
Full Screen / Esc
Printer-friendly Version
Interactive Discussion