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Seasonal variability of dissolved organic carbon in a Mediterranean stream

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Abstract. The seasonal variability of dissolved organic carbon (DOC) flux in a Mediterranean stream subjected to discharges of wide range of intensities and variable dry period was studied as a function of the hydrologic conditions, and the relationship between surface and subsurface (hyporheic and groundwater) DOC concentration. DOC concentration in stream water (2.6 mg l^{-1} ±1.5 SD) was higher than groundwater (1.3 mg l^{-1} ± 1.2 SD) and lower than hyporheic water (3.8 mg l^{-1} ±1.7 SD), suggesting that, at baseflow, stream DOC concentration increases when groundwater discharges through the hyporheic zone. Storms contributed to 39% of annual water export and to 52% of the total annual DOC export (220 kg km^{-2}). A positive relationship was observed between Discharge (Q) and stream DOC concentration. Discharge explained only 40% of the annual variance in stream DOC, but explained up to 93% of the variance within floods. The rate of stream DOC changes with discharge change during storms (dDOC/dQ), ranged between 0 and 0.0045 C mg l^{-1} s l^{-1}, with minimum values during Spring and Summer, and maxima values in Fall and Winter. These dynamics suggest that storm inputs of terrigenous DOC vary between seasons. During floods in the dormant season, DOC recession curves were always steeper than discharge decline, suggesting short flushing of DOC from the leaching of fresh detritus stored in the riparian zone.

Introduction

The recognition that terrestrial-aquatic linkages control stream biogeochemistry has focused attention on the identification of the origin of dissolved organic carbon (DOC) in lotic ecosystems. Generally, DOC concentration in stream water tends to be higher than in groundwater (Kaplan et al. 1980; Meyer and Tate 1983), and lower than the water leachate from forest floor, riparian and streamside soils (McDowell and Likens 1988; Fiebig et al. 1990; Qualls and Haines 1992). In addition, the increase of the stream DOC concentration observed during storms (Mulholland et al. 1990; Newbold et al. 1995; Hinton et al. 1997; Kao and Liu 1997; Tipping et al. 1997) or snowmelt

(Hornberger et al. 1994) suggests that DOC leaching from riparian soils makes a considerable contribution to the stream DOC flux (Meyer 1990). Other important sources of DOC in stream water are the leaching of organic matter stored in channel (Meyer etl al. 1998), hyporheic sediments (Crocker and Meyer 1987), streamside swamp lands (Mulholland 1981; Dosskey and Bertsch 1994) or excretion by benthic algae (Kaplan and Bott 1982). DOC concentrations appear to be more variable than other nutrients (Mulholland and Hill 1997), and discharge variations explain only a small proportion of the annual variability of DOC in streams (Hinton et al. 1997). The seasonal variability of DOC concentration and fluxes throughout the annual discharge regime has been analyzed in streams located in humid (Kaplan et al. 1980; Newbold et al. 1997; Mulholland and Hill 1997; Wehr et al. 1997), alpine (Baron et al. 1991; Boyer et al. 1997), subarctic (Wetzel et al. 1977; Eckhardt and Moore 1990; Ivarsson and Jansson. 1994; Hudon et al. 1996; Hope et al. 1997), arctic (Peterson et al. 1986) and tropical regions (Newbold et al. 1995). In contrast, the dynamics of DOC in Mediterranean streams have received little attention (see the review of Webster and Meyer 1997).

The Mediterranean climate is characterized by precipitation of a wide range of intensities followed by variable dry periods (Sabater et al. 1995) Therefore, we hypothesize that in Mediterranean streams, the variability of the magnitude of storms, their temporal sequence and frequency (i.e. the duration of the baseflow periods) can increase the variability of the relationship between DOC and discharge, and complicate the prediction of the response of the DOC concentration during the storms.

This paper, therefore, focuses on the dynamics of stream DOC concentration and fluxes in a Mediterranean stream (Riera Major) during baseflow and during storm conditions, and the relationship between surface and subsurface (hyporheic and groundwater) DOC concentrations in order to establish the relative contribution of DOC sources.

Study site

Riera Major is a second-order stream located 90 km north of Barcelona (NE Spain). The climate is typically humid-Mediterranean (Piñol et al. 1992). Annual precipitation ranged between 855 mm (1994) and 1660 mm (1996) during this study. The stream is 6 km long, and drains a forested siliceous area of 15.5 km^2 dominated by igneous rocks (granodiorite). The stream channel is $\sim$2.5 m wide and is characterized by step-pools with large pebbles and boulders. The total area of the stream bed is approximately 15,000 m^2, and sand sediments cover $\sim$ 30% of the total bottom area. The hyporheic zone ranges in depth from a few cm to 80–100 cm. The proportion of surface water in the hyporheic zone ranged between 33% and 95% at 25 cm depth, and 78% to 100% at 10 cm depth (Butturini and Sabater 1999). Stream flow is perennial; median stream discharge, considered to be the baseflow regime, fluctuates between 30 l s^{-1} in summer and 62 l s^{-1} in fall and winter. During storms, stream discharge can increase to as much as 1,600 l s^{-1} (December 1996). Alders (*Alnus glutinosa*) dominate riparian vegetation. Leaf fall is concentrated into a 20–30 day period in October when the transported particulate organic matter can increase up to 8–10 mg l^{-1} (Romaní et al. 1998). The epilithic community is dominated by an encrusting red algae (*Hildenbrandia rivularis*) and diatoms (in fall and winter) and patches of Cyanobacteria and filamentous Chlorophycaeae (in spring and summer) (Guash and Sabater 1994). The primary production of the stream epilithic community followed a seasonal pattern, with low activity (nearly null) during the fall period and high activity during spring (Guash and Sabater 1994).

Methods

Field methodology

Dissolved organic carbon in stream water (DOC_S) was sampled every 7–14 days for two years (February 1994–March 1996). From February 1997 to April 1998, daily water samples were collected (at 12:00 noon) with an automatic sampler (mod. Sigma 900 Max). From October 1997 to April 1998 all storms were sampled intensively (0.5–2 hours sampling time). The DOC in hyporheic waters (DOC_H) was sampled between February 1994 and July 1995 every 10–20 days from eight wells (PVC pipes of 4 mm diameter) placed in the sediment at between 10 cm and 50 cm depth. The wells were located in the middle of the stream channel along a 200 m stream reach. We only collected small amounts of water (30 ml) from these hyporheic wells to avoid drawing stream water into the hyporheic zone. From August 1995 to February 1998, DOC in groundwater (DOC_G) was sampled from a permanent spring located on the bank side of the riparian zone. Water samples stored in the automatic sampler were collected every 5–8 days during inter-storm periods, and every 2–3 days during storm periods, and were preserved in the sampler with 5 ml of 1 mM NaN_3 added to a final concentration of $\sim$20 μM (Kaplan 1994).

Temperature and specific electric conductivity were measured for stream, hyporheic waters and groundwater using a WTW® conductimeter.

Stream discharge was measured on each sampling date by mass balance calculation using chloride as a conservative tracer (Stream Solute Workshop 1990). From February 1997 to April 1998, the stream water level was continuously recorded (every 15 min) by a water pressure transducer connected to the automatic sampler. The discharge was then estimated using an empirical relationship between the discharge measured by the conservative tracer and the water level.

Chemical analysis

All water samples were filtered through pre-ashed fiberglass filters (Whatman® GF/F) and cold-stored for DOC analyses. DOC samples collected during the period February 1994–March 1996 were analyzed using a high-temperature catalytic oxidation Shimadzu® TOC analyzer. DOC samples collected between February 1997 and April 1998 were analyzed using a Skalar® 12 SK TOC analyzer with UV-promoted persulfate oxidation. Intercalibration results between Shimadzu and Skalar showed that DOC samples analyzed by Shimadzu were 0.38 mg l^{-1} (0.16 SD, n = 25) higher than samples analyzed by Skalar. All DOC data from Skalar were then adjusted to correspond to the Shimadzu results.

Data analyses

(1) DOC stream fluxes
Stream DOC fluxes were calculated in two ways depending on hydrologic conditions. During baseflow, daily DOC fluxes were calculated by multiplying average daily discharges by DOC concentrations. During floods (when $\mathrm{Discharge}_{\mathrm{peak}}/\mathrm{Discharge}_{\mathrm{pre\text{-}event}} > 1.5$), DOC fluxes were estimated by assuming a linear relationship between storm discharge and DOC concentrations. This linear relationship was obtained from samples collected at 12:00 noon (±2 h) during the decreasing limb of the discharge (Q) curve. The slope of this relationship will be referred to $d\mathrm{DOC}_S/d\mathrm{Q}$ (Figure 1(b)) and it describes the rate of DOC concentration change per unit of discharge change (mg C l^{-1} s l^{-1}). The detailed DOC concentration monitoring during storms of the period October 1997–April 1998 allowed us to calculate detailed DOC exports by using the linear interpolation method (Hinton et al. 1997). The DOC fluxes estimated with the linear relationship method match DOC fluxes estimated with the method of the linear interpolation (the slope of the correlation is 1.05, r^2 = 0.99, df = 5, $P < 0.001$).

Volume-weighted stream DOC concentrations (the ratio between DOC export and water export) were calculated for each storm and for baseflow conditions, in order to observe a seasonal tendency without discharge influence. Average DOC stream exports were also calculated for the growing (April–September 1997) and the dormant (October 1997–March 1998) periods.

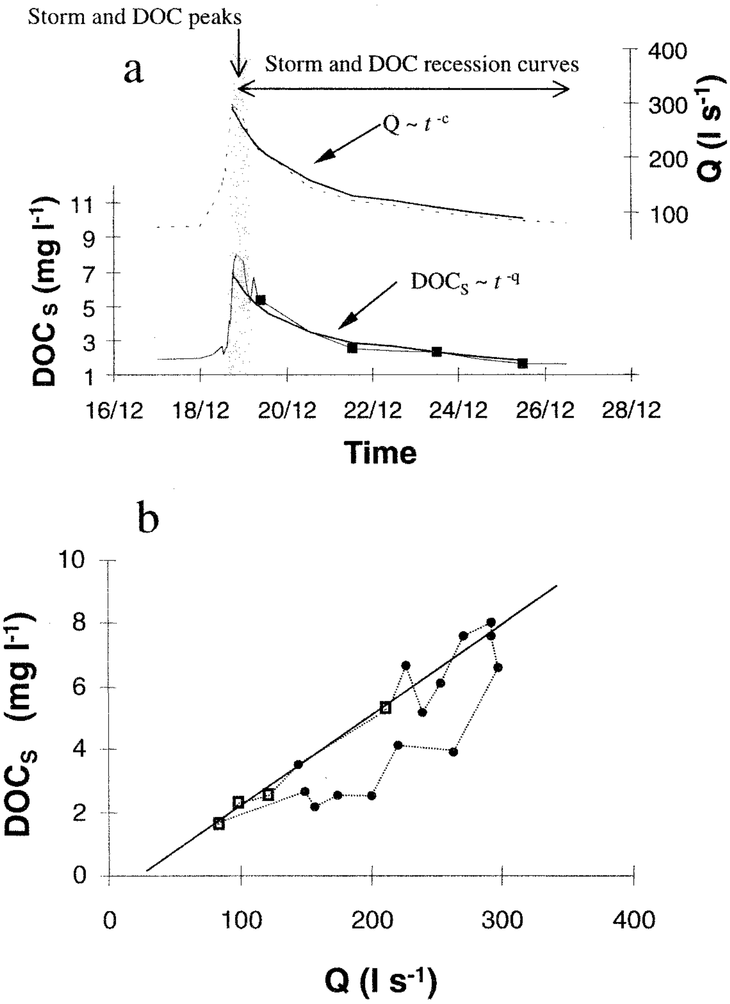

Figure 1. Example of the temporal dynamics of discharge and Disolved Organic Carbon in surface waters (DOC_S during a storm in December 1997. In (a), solid lines show the power model interpolating the decreasing limb of the discharge and DOC_S. In (b), the dotted line shows the corresponding DOC_S vs discharge loop graph with all the data collected during the storm (closed circles). The open square points correspond to the daily DOC_S data (samples obtained at 12:00 noon) used to calculate the power exponent of the DOC_S *vs* time relationship (referred to as the exponent "c") and DOC_S *vs* discharge slope (the solid line, referred to as $dDOC_S/dQ$).

(2) Stream DOC concentration vs *discharge relationship*

The relationship between stream DOC (DOC_S) and discharge was studied over one year (i) fitting their respective data in a semilogarithmic model (Newbold et al. 1997), and (ii) analyzing single $dDOC_S/dQ$ slope variations between storms. The objective of the use of the $dDOC/dQ$ slopes is to detect anomalies in changes of DOC concentration per unit of discharge change and, therefore, to compare DOC changes under storms with different magnitude. Since, in Riera Major, discharge and DOC peaks nearly coincide in time, and both temporal recession curves fitted a power regression model (Figure 1(a)), we used the ratio between the slopes of the two power models in order to detect small differences in their temporal dynamics. DOC and discharge slopes will be indicated in this paper as "c" and "q" respectively. The ratio between the two slopes (c/q) indicate whether DOC_S concentrations fall more slowly or more rapidly than discharge. Thus, ratio values of c/q > 1 indicates a short pulse of DOC during storms since DOC decrease is faster than the discharge recession limb. On the other hand, c/q < 1 indicate that change in DOC concentration is slower than change in discharge. In the latter case, DOC_S concentrations showed a long-tailed recession curve. We focused on the analysis of the DOC_S recession curve because during floods the discharge recession limb is slower than the rising limb; thus, more samples were collected. Linear and logarithmic regression fittings will be considered significant at $P < 0.05$.

Results

Water temperature and electrical conductivity in stream and subsurface waters (hyporheic and groundwater)

The stream water temperature averaged 11.2 ±4.4 °C with maxima in summer (between 15 and 25 °C) and minima in winter (between 7 and 2.5 °C). In the hyporheic zone, water temperature followed the same pattern and showed the same values observed for the stream water (*t*-paired test $t = 1.5$, df = 30, $P > 0.05$). Groundwater temperature averaged 12.2 ± 1.5 °C with a smaller range of variation than stream water, (10–11 °C in winter, and 12.5–13 °C in summer, Figure 3).

Electrical Conductivity in surface, hyporheic and groundwater averaged 195 μS cm^{-1}(±31 SD), 207 μS cm^{-1}(±36 SD) and 227 μS cm^{-1}(±32 SD), respectively. Conductivity in surface and hyporheic waters was strongly correlated ($r^2 = 0.96$, df = 24, $P < 0.01$) and decreased gradually when discharge increased ($r^2 = 0.82$, df = 59, $P < 0.01$ for surface waters and $r^2 = 0.81$, df = 24, $P < 0.01$ for hyporheic waters, Figure 2). Conductivity in

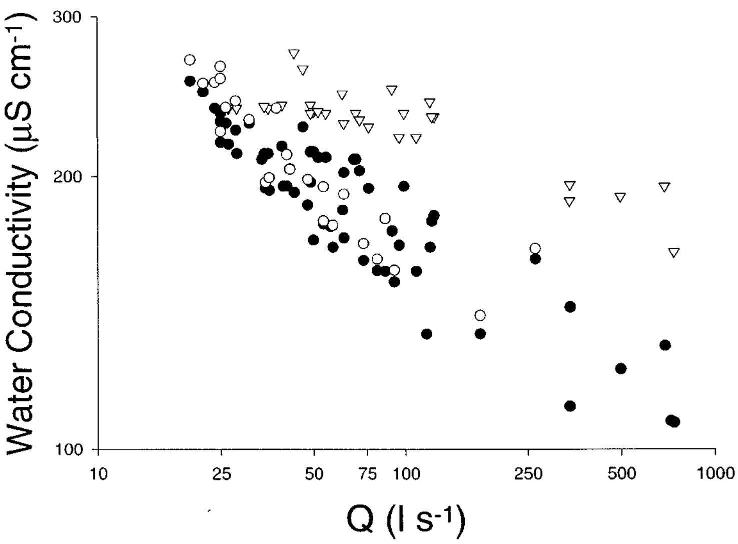

Figure 2. Relationship between stream discharge and water electrical conductivity in stream water (closed circles), hyporheic water (open circles) and groundwater (open triangles).

hyporheic waters was slightly higher than in stream water in 92% of samples (*t*-test for paired samples, t = 6.7, df = 25, $P < 0.01$). In groundwater the conductivity values were more steady than stream water (Figure 2) and decreased significantly only during intense storms (Q > 300 ls^{-1}, Figure 2). The conductivity in groundwater was always higher than stream water, and the ratio between surface water and groundwater was inversely related to discharge (r^2 = 0.48, df = 27, $P < 0.01$) and it approached 0.89 ± 0.06SD (n = 10) at baseflow conditions.

Seasonal stream DOC concentrations with respect to discharge variability (April 1997–March 1998)

Stream DOC_S concentrations ranged between 0.65 mg l^{-1} (mainly in summer) and 7.3 mg l^{-1} (in fall and winter, Figure 3), and discharge accounted for 37% of the annual variance (r^2 = 0.37, df = 240, $P <$ 0.001). During this period, we monitored 16 storms (10 storms in the growing period, and 6 in the dormant period). In all storms (except that on 11/8/97) we observed a significant increase in DOC_S concentration over pre-storm DOC_S concentrations (Table 1). When each flood was analyzed separately, we observed, in the 76% of the events, a positive linear relationship beween DOC_S and discharge (Table 1). The slopes of these relationships (i.e. $dDOC_S/dQ$) were significantly lower during the growing season than the

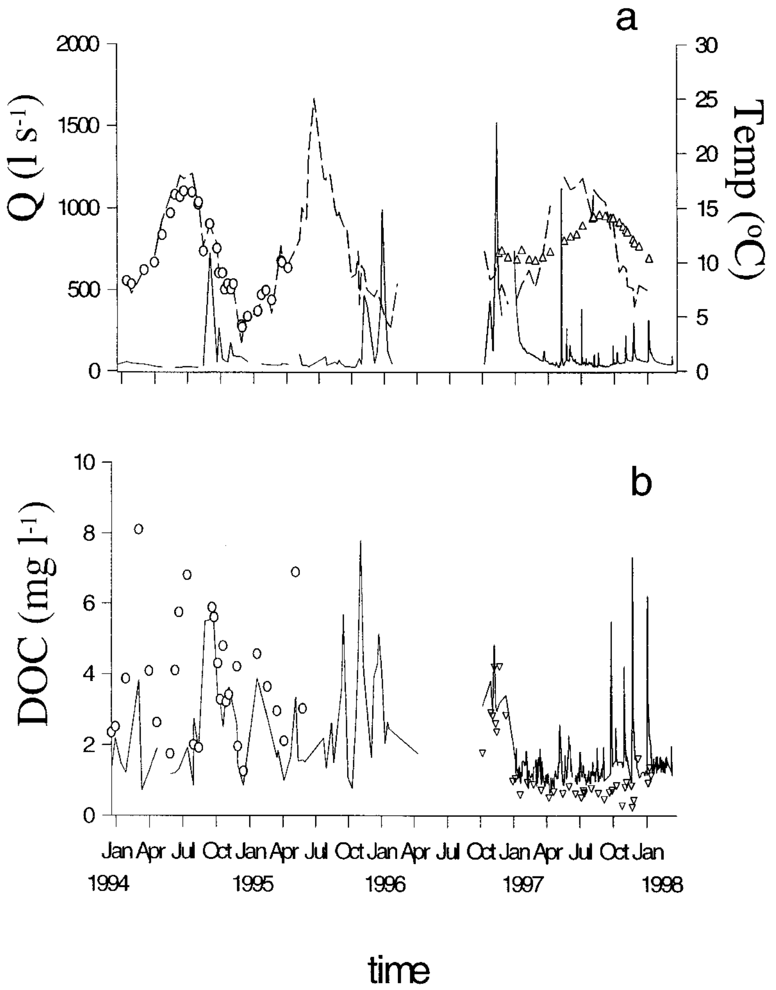

Figure 3. (a) Seasonal variation of stream discharge (solid line) and temperature in stream water (dotted line), hyporheic water (open circles) and groundwater (open triangles). (b) Seasonal viriation of dissolved organic carbon in stream water (solid line), in hyporheic water (open circles), groundwater (open triangles) over the study period. Mean values from DOC_H and hyporheic water temperature were calculated from eight samples. DOC_S and DOC_G mean values were calculated from 3–6 samples.

dormant season (t = 3.75, df = 14, $P < 0.01$, Figure 4). The highest slope (0.0445 C mg l^{-1} s l^{-1}) was measured during the first storm in the autumn leaf fall period (Figure 4). $d\mathrm{DOC}_S/d\mathrm{Q}$ values did not correlate with the length of the previous inter-storm period (r^2 = 0.0045, df = 13, $P > 0.05$).

Table 1. Summary of the differences in DOC in stream water before ($DOC_{S\ pre\text{-}event}$) and during the storm event ($DOC_{S\ event}$), the slopes of the linear relationship between DOC_S and discharge ($d\ DOC_S/dQ$) with the regression coefficients (r^2), the exponents of the power model relating the temporal decay of the stream DOC after the discharge peak (c) with the regression coefficients (r^2), the exponents of the power model relating the temporal decay of the discharge recession limb (q, all $r^2 > 0.9$), the ratio a/b, stream water and DOC exports during the storm period, and volume-weighted stream DOC concentration (DOC_{Sw}) during the storm events of the period April 1997–April 1998.

Storm period	$DOC_{S\ pre\text{-}event}$ (mg 1^{-1})#	$DOC_{S\ pre\text{-}event}$ (mg 1^{-1})#	$d\ DOC_S/dQ$ 10^{-3}	r^2	c	r^2	q	c/d	Water flux ($10^2 m^3$	DOC_S flux (kg)	DOC_{Sw} (mg 1^{-1})
18–25/04/97	0.95	1.6**	4.3	0.82(**)	–0.26	0.95**	–0.37	0.69	430	52	1.1
22–28/05/97	0.80	1.3**	0	0.33 (n.s.)	0	0.32 n.s.	–0.5	0	233	25	1.13
31/05–1/06/97	1	1.4*	0	0.58 (n.s.)	0	0.6 n.s.	–0.32	0	118	18	1.5
3–11/06/97	1.3	2.6**	1.8	0.5 (**)	–0.37	0.82**	–0.81	0.24	1175	330	2.8
18–24/06/97	0.95	1.8**	8.6	0.85 (**)	–0.25	0.87**	0.76	0.35	438	73	1.32
26/06–7/07/97	1.1	2.3**	11.3	0.67 (**)	–0.26	0.69**	–0.58	0.55	1067	192	1.8
26/07–4/08/97	1.1	1.9**	7.8	0.71 (*)	–0.28	0.97**	–0.87	0.44	336	55	1.62
11–17/08/97	1.1	1.2 n.s.	0	0.35 (n.s.)	0	0.4 n.s.	–0.44	0	298	31	1.04
2–5/09/97	1.15	1.55**	0	0.74 (n.s.)	0	0.75 n.s.	–0.73	0	128	15	1.17
14–18/09/97	1.35	2**	19.8	0.8 (*)	–0.53	0.93**	–0.51	1.03	254	48	1.88
23–28/10/97	1.4	2.7**	44.5	0.8 (*)	–0.87	0.94**	–0.61	1.42	208	52	2.51
3–9/11/97	1.5	2.02**	11.9	0.87 (*)	–0.37	0.82**	–0.21	1.80	274	46	1.68
25/11–2/12/97	1.6	3.1**	20.2	0.9 (**)	–0.58	0.95**	–0.50	1.17	518	104	2
16–17/12/97	0.96	2.3**	n.m.	n.m.	n.m.	n.m.	n.m.	n.m.	109	28	2.4
17–30/12/97	2.5	5.5**	25.9	0.93 (**)	–0.66	0.96**	–0.57	1.25	1124	312	2.78
27/01–3/02/98	1	3.5**	16	0.9 (**)	–0.59	0.97**	–0.55	1.28	1112	379	3.41
1–5/04/98	1.2	1.6**	11.9	0.84 (*)	–0.42	0.91**	–0.69	0.61	107	18	1.66

Differences between $DOC_{S\ pre\text{-}event}$ and $DOC_{S\ event}$ were tested with *t*-test (df = 4)
* $p < 0.05$; ** $p < 0.01$; n.s. not significant; n.m.: not measured
# daily data collected at 12:00 p.m.

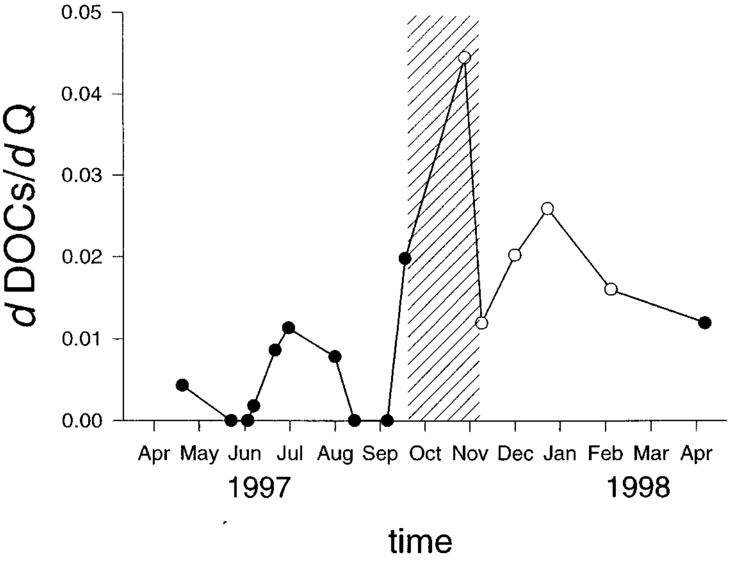

Figure 4. Temporal dynamics of the $d\mathrm{DOC_S}/d\mathrm{Q}$ slopes for the storms between April 1997–April 1998 for the dormant period (open circles) and for the growing period (closed circles). Shaded area represents the leaf fall period.

The values of slopes of $\mathrm{DOC_S}$ recession curves after the storm peaks (exponent "c") ranged widely between 0 and –0.87. During the growing season, the "c" values were not related to the slope discharge recession curves (exponent "q") (r = 0.36, df = 9, $P > 0.05$), and the c/q ratio values ranged bteween 0 to 1.1. However, during the dormant season, DOC_S and discharge exponents did correlate (r = 0.94, df = 3, $P < 0.05$), "c" being higher than "q", with an averaged ratio of 1.38 (Figure 5).

Annual stream DOC export (April 1997–March 1998)

The estimated annual $\mathrm{DOC_S}$ export was 3,414 kg C (220 C kg km^{-2} y^{-1}) with an annual $\mathrm{DOC_S}$ volume-weighted concentration ($\mathrm{DOC_{Sw}}$) of 1.58 mg C l^{-1}. Monthly $\mathrm{DOC_{Sw}}$ concentrations followed a seasonal trend with minimum values during the growing season and maximum values during the dormant season (Table 2). Average $\mathrm{DOC_{Sw}}$ concentrations in storms and baseflow conditions were 1.9 mg l^{-1} and 1 mg l^{-1}, respectively, during the growing season, and 2.7 mg l^{-1} and 1.7 mg l^{-1} during the dormant season. Thus, $\mathrm{DOC_S}$ export during the dormant season was 55% higher than in the growing season (2,080 kg *vs* 1,334 kg Table 2). Neverthless, storms contributed to 52% of the total annual DOC (921 kg during the dormant season and 839 kg

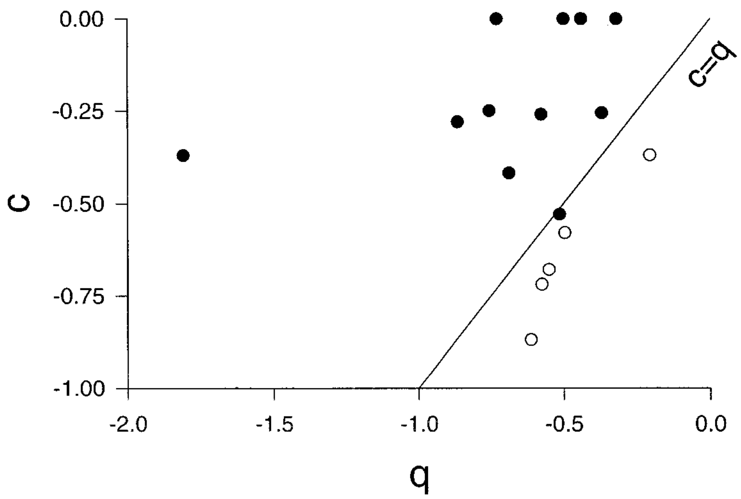

Figure 5. Relationships between the exponent of the empirical power model relating the decreasing limb of the discharge with time (exponent "q"), and the corresponding exponent of power model relating DOC_S temporal decay (exponent "c") for the dormant period (open circles) and for the growing period (closed circles). The solid line shows the c = q line.

during the growing season), although floods accounted only for 39% of the annual water flux.

Relationship between DOC concentration in surface and subsurface waters (hyporheic and groundwater)

Hyporheic waters were sampled at the same time as surface waters from February 1994 to July 1996. During this period, DOC_S and DOC_H concentrations averaged 2.6 mg l^{-1} (1.5 SD) and 3.8 mg l^{-1} (1.7 SD), respectively. DOC_H content was higher than DOC_S at 90% of the sampling dates (paired *t*-test, $t = 5.29$, df = 27, $P < 0.001$) (Figure 6).

During the period when stream and hyporheic waters were sampled simultaneously, DOC_S concentration was significantly related to discharge by a semilogarithmic model ($r^2 = 0.4$, df = 26, $P < 0.001$), whereas DOC_H was not ($r^2 = 0.035$, df = 26, $P > 0.05$). However, the residual values of the relationship DOC_S versus discharge were significantly related to DOC_H data using the same empirical semilogarithmic model ($r^2 = 0.38$, df = 26, $P < 0.001$). Both semilogarithmic models enabled a new empirical model relating DOC_S to discharge (Q) and DOC_H:

$$DOC_S = -4.4 + 1n(Q^{1.32} DOC_H{}^{1.34}) \quad (1)$$

$(r^2 = 0.65, \text{df} = 26, P < 0.001)$.

Table 2. Summary of monthly stream water flux, stream DOC flux (DOC_S) and volume weighted stream DOC concentration (DOC_{Sw}) during the April 1997–March 1998.

Month	Water flux (10^5 m^3)	DOC_S flux (kg)	DOC_{Sw} (ppm)
Apr 1997[g]	1.83	222	1.23
May[g]	1.10	105	0.95
Jun[g]	2.73	506	1.85
Jul[g]	1.70	237	1.39
Aug[g]	1.24	142	1.15
Sep[g]	0.97	123	1.27
Oct[d]	1.01	160	1.58
Nov[d]	1.59	340	2.14
Dec[d]	2.43	595	2.45
Jan 1998[d]	2.14	530	2.48
Feb[d]	1.74	288	1.66
Mar[d]	1.14	167	1.46

g: Growing period
d: Dormant period

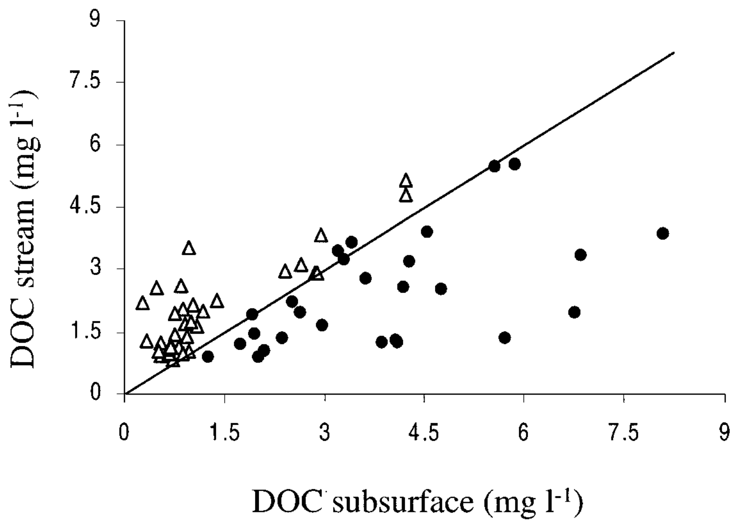

Figure 6. Relationships between DOC in hyporheic and in stream water (closed circles) and between DOC in groundwater and stream water (open triangles). Solid line shows the y = x line.

This empirical model increased the proportion of the annual DOC variance explained from 44% (using only discharge) to 65% (using discharge and DOC_H).

Groundwater was sampled from November 1996 to February 1998 (Figure 3). Throughout the study period, DOC_G was always lower than DOC_S ($t = 7.7$, df = 37, $P < 0.001$) with a mean DOC_G concentration of 1.3 mg l^{-1} (1.2 SD) and an average ratio DOC_G/DOC_S of 0.62 (0.22 SD). The higher DOC_G concentrations (between 1.8 and 4.4) were only measured over an unusual period of high water conditions observed during November 1996–January 1997 (Figure 3).

Discussion

Dynamics of dissolved organic carbon concentration in Riera Major can be explained basically by the combination of processes occurring during baseflow conditions and floods.

Baseflow periods

The similar values in conductivity observed in stream water and groundwater at low discharges (Figure 2) suggested that at baseflow conditions the stream flow is supplied mainly by the groundwater input. In addition, the strong correlation of electrical conductivity between surface and hyporheic waters indicated a rapid water exchange through the two water compartments (Butturini and Sabater 1999). The role of the hyporheic zone as source or sink of dissolved organic carbon has often been discussed in the literature (Crocker and Meyer 1987; Kaplan and Newbold 1993; Findlay et al. 1993; Schindler and Krabbenhoft 1998). Equation (1) suggestes that hyporheic sources can explain a critical portion of the DOC in surface waters. On the other hand, the content of DOC_S can also be due to groundwater sources. Although the direct comparison between DOC content in the hyporheic and groundwater is difficult because samples were collected during different periods, we observed that: (a) DOC in hyporheic zone ranged widely (Figure 3), but never dropped below 1.3 ppm; (b) DOC in groundwater is quite steady around 0.8 ppm (Figure 3), except for the period of unusual high discharges observed between November 1996 and January 1997. Figure 6 shows a lack of overlap between DOC_G and DOC_H (i.e. $DOC_H \geq DOC_S \geq DOC_G$), suggesting that the observed differences between DOC in stream and groundwater might be due to the leaching of organic matter stored in stream sediments during baseflow conditions, as well as groundwater discharge through the hyporheic zone. The Riera Major stream bed is characterized by a step-pool morphology dominated by boulders and cobbles and permeable sediments. This morphology facilitates the accumulation of organic matter in the stream bed (Romaní et al. 1998). Moreover, we measured a rapid water exchange between hyporheic and stream waters (Butturini and Sabater 1999), which explained small differences in water conductivity and the similar temperature values observed between stream and the hyporheic waters. We hypothesize that rapid water exchange facilitates the perfusion of fine particulate organic matter (FPOM) into the sediments (Thibodeaux and Boyle 1987, Huettel et al. 1996) with dissolved organic matter leaching. On the other hand, assuming that DOC from groundwater is not retained in hyporheic sediment, (i.e. not taken up by microbial organisms, Wallis 1981; Kaplan and Newbold 1993), and that 62% of the total dissolved carbon export measured at baseflow conditions might come from groundwater (i.e. the average value of $DOC_G/DOC_S = 0.62$), we estimated that 719 kg (i.e. 0.26 g C d^{-1} m^{-2} on the basis of stream bottom area) came from groundwater input and the remaining 440 kg from the hyporheic zone (i.e. 0.16 gC d^{-1} m^{-2}) during the dormant season 1997–98. On the other hand, during the growing season we estimated a groundwater DOC flux of 307 kg (0.11 g C d^{-1} m^{-2}) and a DOC hyporheic release of 188 kg (i.e. 0.07 gC d^{-1} m^{-2}). Obviously, these DOC in stream production rates require careful interpretation, since they were obtained only by comparing DOC content from groundwater, hyporheic and stream water, and we did not test the bioavailability of the DOC from groundwater. However, these DOC production rates are close to other estimates: 0.12 g C d^{-1} m^{-2} for White Clay Creek (Kaplan and Newbold 1993); 0.07 g C d^{-1} m^{-2} for Creeping Swamp (Mulholland 1981); between 0.07 and 0.4 g C d^{-1} m^{-2} for two small first-order streams in North Carolina (Meyer et al. 1998); but much lower than 74 g C d^{-1} m^{-2} for a temperate forested stream (Schindler and Krabbenhoft 1998).

Flood conditions

During the dormant season, floods exported 10% more DOC than in the growing season, despite a 40% reduction in the storm water export. This change of DOC export during the storms reflected the observed variability in $dDOC_S/dQ$ rates between storms. High variability in annual DOC concentration/discharge regressions is widely reported in the literature (Eckhardt and Moore 1990; Hudon et al. 1996; Newbold et al. 1997; Shiff et al. 1997). Hinton et al. (1997) observed that the variability of the annual stream DOC concentration/discharge relationship is due to changes in the slope of DOC concentration *vs* discharge relationship of individual storms (i.e. the $dDOC_S/dQ$ rates). Our results confirm this observation, yet discharge explained only between 37% and 40% of annual DOC variance, but explained up to 93% of DOC variance in individual storms (Table 1).

As mentioned in the method section, the *d*DOC/*d*Q ratio allowed us to compare DOC changes between storms with different magnitude. Therefore, *d*DOC/*d*Q is not directly related to the DOC concentration, nor to the discharge. In fact, peak DOC concentration was not observed during the storm of 24/10/97, but rather, occurred from December to January (Figure 3 and Table 1). However, direct comparison of the DOC peaks is not appropriate, because it does not take into account the storm magnitude: the storms of December '97 and January '98 were much more severe than the storm of October 97. Nonetheless, the small storm of 24/10/97 determined a relative change of DOC (i.e. *d*DOC/*d*Q) higher than the storms of December '97 and January '98 (Figure 4). We consider this $dDOC_S/dQ$ peak the result of leaching of fresh organic detritus stored in the riparian zone during the leaf fall period (Figure 4). In addition, $dDOC_S/dQ$ pattern showed lower values during spring and summer (Figure 4). Theoretically, soil leaching has high DOC concentrations throughout the year (Qualls and Haines 1991), with small increases during the summer (McDowell and Wood 1984; Currie et al. 1996). Therefore, the low *d*DOC/*d*Q values observed during the growing period suggested that soil leaching did not contribute to the DOC stream export.

On the other hand, we were surprised that the duration of inter-storm periods did not appear to influence the *d*DOC/*d*Q values. We expected higher *d*DOC/*d*Q values after long inter-storm periods due to accumulation of leachable organic matter in the watershed. However, our results did not confirm this hypothesis. For instance, the last storm of winter (i.e. on 01/29/1998, 42 days after the previous storm) and the first storm of spring (i.e. on 04/01/1998, 62 days after the previous storm) had lower slopes than storms preceded by shorter inter-storm periods.

The temporal pattern of the recession curves of DOC_S after storms helps to elucidate DOC sources during floods. Kaplan and Newbold (1993) suggested that slow and continuous input of DOC from the catchment area can retard the DOC recession curve in a stream and therefore result in a c/q ratio < 1. In Riera Major, we found c/q < 1 during the growing season; however, during the dormant season, DOC concentration decreased faster than discharge (i.e. c/q > 1). Therefore, the observed values of c/q in the dormant season indicate that the input of allochthonous DOC from detritus in the riparian zone occurred in a short pulse. Several authors consider that fresh detritus leaching from the riparian zone contributes considerably to the stream DOC fluxes (Meyer 1990; Qualls and Haines 1992). On the other hand, the long DOC tails observed in the growing season (i.e. c/q < 1) can be explained by groundwater discharge through the hyporheic zone. Long tails were not observed during the dormant season because the high terrigenous inputs during the storm peaks probably mask the effect of the groundwater perfusion through the hyporheic zone.

Our data provide the first evidence that the variability of storm intensity and the seasonal change of terrigenous DOC inputs can be an important source of variability of DOC concentration in Mediterranean streams. In general, seasonal change of DOC concentration has been observed in streams characterized by simple hydrologic regimes such as in alpine regions (Boyer et al. 1997), or in wetlands subjected to dry conditions (Schiff et al. 1998). However, it is more difficult to find clear patterns in streams located in humid and subartic areas (Wetzel et al. 1977; Eckhardt and Moore 1990; Ivarsson and Jansson 1994; Mulholland and Hill 1997). The high inter- and intra-annual variability of the hydrological regime of the Mediterranean streams complicates the identification of clear patterns of stream DOC concentration, and therefore the prediction of its dynamics. Although storms can contribute greatly to the total DOC export in streams, few studies focused on the variability of the DOC response during storms (Hinton et al. 1997), and no information is available on the causes of this variability. We suggest that the analysis of DOC/discharge relationship, between storms, over an annual hydrologic period, is useful to understand DOC dynamics in streams with abrupt changes of discharge such as Mediterranean streams.

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References

Baron J, Mcknight D & Denning AS (1991) Sources of dissolved and particulate organic material in Loch vale watershed, Rocky mountain national park, Colorado, USA. Biogeochemistry 15: 89–110

Boyer EW, Horneberger GM, Bencala KE & McKnight DM (1997) Response characteristics of DOC flushing in an alpine catchment. Hydrol. Process. 11: 1635–1647

Butturini A (1999) Contribution of the boundary zones on nutrient dynamics in a stream with Mediterranean regime. PhD Thesis, Departament d'Ecologia, Universitat de Barcelona

Butturini A & Sabater F (1998) Ammonium and phosphate retention in a Mediterranean stream: hydrological versus temperature control. Can. J. Fish. Aquat. Sci. 55: 1–8

Butturini A & Sabater F (1999) Importance of transient storage zones for ammonium and phosphate retention in a sandy-bottom Mediterranean stream. Freshwater. Biol., 41: 593–603

Crocker MT & Meyer JL (1987) Interstitial dissolved organic carbon in sediments of a southern Appalachain headwater stream. J. N. Am. Benthol. Soc. 6: 159–167

Currie WS, Aber JD, McDowell WH, Boone RD & Magill AH (1996) Vertical transport of dissolved organic C and N under long-term N amendments in pine and hardwood forests. Biogeochemistry 35: 471–505

Dosskey MG & Bertsch PM (1994) Forest sources and pathways of organic matter transport to a blackwater stream: a hydrologic approach. Biogeochemistry 24: 1–19

Eckhardt BW & Moore TR (1990) Controls on dissolved organic carbon concentrations in streams, Southern Quebec. Can. J. Fish. Aquatic. Sci. 47: 1537–1544

Fiebig DM, Lock MA & Neal C (1990) Soil water in the riparian zone as a source of carbon for a headwater stream. J. Hydrol. 116: 217–237

Findlay S, Strayer D, Goumbala C & Gould K (1993) Metabolism of stream water dissolved organic carbon in the shallow hyporheic water. Limnol. Oceanogr. 38. 1493–1499

Guash H & Sabater S (1994) Primary production of epilithic communities in undisturbed Mediterranean streams. Verh. Internat. Verein. Limnol., 25: 1761–1764

Heikkinen K (1989) Organic carbon transport in an undisturbed boreal humic river in northern Finland. Arch. Hydrobiol. 117: 1–19

Hinton MJ, Schiff SL & English MC (1997) The significance of storms for the concentration and export of dissolved organic carbon from two Precambrian Shield catchments. Biogeochem. 36: 67–88

Hope D, Billett M F & Cresser MS (1997) Exports of organic carbon in two river in NE Scotland. J. Hydrol. 193: 61–82

Hornberger GM, Bencala KE & McKnight DM (1994) Hydrological controls on dissolved organic carbon during snowmelt in the Snake River near Montezuma, Colorado. Biogeochem. 25: 147–165

Hudon C, Morin R, Bunch J & Harland R (1996) Carbon and nutrient output from the Great Whale river (Hudson Bay) and a comparison with other rivers around Quebec. Can. J. Fish. Aquatic. Sci. 53: 1513–1525

Huettel M, Ziebis W, and Forster S. (1996) Flow-induced uptake of particulate matter in permeable sediments. Limnol. Oceanogr. 41: 309–322

Ivarsson H & Jansson M (1994) Temporal variations in the concentration and character of dissolved organic matter in a highly colored stream in the coastal zone of nothern Sweden. Arch. Hydrobiol. 132: 45–55

Kao SJ & Liu. KK (1997) Fluxes of dissolved and nonfossil particulate organic carbon from an Oceania small river (Lanyang Hsi) in Taiwan. Biogeochem. 39: 255–269

Kaplan LA (1994) A field and laboratory procedure to collect, process, and preserve freshwater samples for dissolved organic carbon analysis. Limnol. Oceanogr. 39: 1470–1476

Kaplan LA & Newbold DJ (1993) Biogeochemistry of dissolved organic carbon entering streams. In Ford TE (Ed) Aquatic Microbiology. An ecological approach (pp: 139–166) Blackwell

Kaplan LA & Bott TL (1982) Diel fluctuations of DOC generated by algae in a piedmont stream. Limnol. Oceanogr. 27: 1091–1100

Kaplan LA, Larson RA & Bott TL(1980) Patterns of dissolved organic carbon in transport. Limnol. Oceanogr. 15: 1034–1043
McDowell WH & Wood T (1984) Podzolization: soil processes control dissolved organic carbon concentrations in stream water. Soil Sci. 137: 23–32
McDowell WH & Likens GE (1988) Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook valley. Ecol. Mon. 58: 177–195
McDowell WH & Asbury CE (1994) Export of carbon, nitrogen, and major ions from three tropical mountain watersheds. Limnol. Oceanogr. 39: 111–125
Meyer JL (1990) Production and utilization of dissolved organic carbon in riverine ecosystems. In Perdue EM & Gjessing ET (Ed) Organic acids in aquatic ecosystems (pp. 281–299). John Wiley & Sons Ltd
Meyer JL & Tate CM (1983) The effects of watershed disturbance on dissolved organic carbon dynamics of a stream. Ecology 71: 668–677
Meyer JL, Wallace BJ & Eggert SL (1998) Leaf litter as a source of dissolved organic carbon in streams. Ecosystems 1: 240–249
Mulholland PJ (1981) Organic carbon in a swamp-stream ecosystem. Ecol. Mon. 51: 307–322
Mulholland PJ, Wilson GV & Jardine PM (1990) Hydrogeochemical response of a forested watershed to storms; effects of preferential flow along shallow and deep pathways. Water Resour. Res. 26: 3021–3036
Mulholland PJ & Hill WR (1997) Seasonal pattern in streamwater nutrient and dissolved organic carbon concentration: separating catchment flow path and in-stream effects. Water Resour. Res. 33: 1297–1306
Newbold DJ, Bott TL, Kaplan LA, Sweeney BW & Vannote RL (1997) Organic matter dynamics in White Clay Creek, Pennsylvania, USA. J. N. Am. Benthol. Soc. 16: 46–50
Newbold DJ, Sweeney BW, Jackson JK, & Kaplan LA (1995) Concentrations and export of solutes from six mountain streams in northwestern Costa Rica. J. N. Am. Benthol. Soc. 14: 21–37
Peterson BJ, Hobbie JE & Corliss TL (1986) Carbon flow in a tundra stream ecosystem. Can. J. Fisch. Aquatic. Sci. 43: 1259–1270
Piñol J, Avila A & Rodá F (1992) The seasonal variation of streamwater chemistry in three forested Mediterranean catchments. J. Hydrol. 140: 119–141
Qualls RG & Haines BL (1991) Geochemistry of dissolved organic nutrients in water percolating through a forest ecosystem. Soil Sci. Soc. Am. J. 55: 1112–1123
Qualls RG & Haines BL. (1992) Biodegradability of dissolved organic matter in forest throughfall, soil solution, and stream water. Soil Sci. Soc. Am. J. 56: 578–586
Romaní AM, Butturini A, Sabater F & Sabater S (1998) Heterotrophic metabolism in a forest stream sediment: surface versus subsurface zones. Aquat. Microb. Ecol. 16: 143–151
Sabater F, Guash E, Martí E, Armengol J. & Sabater S (1995) The Ter: a Mediterranean river case-study in Spain. In: Cushing CE, Cummins KW, & Minshall GW (Eds) Ecosystems of the World 22. River and Stream Ecosystems (pp 419–438) Elsevier, Amsterdam
Schiff S, Aravena R, Mewhinney E, Elgood R, Warner B, Dillon P & Trumbore S. (1998) Precambian shield wetlands: hydrologic control of the sources and export of dissolved organic matter. Climatic Change 40: 167–188
Schindler JE & Krabbenthoft DP (1998) The hyporheic zone as source of dissolved organic carbon and gases to a temperate forested stream. Biogeochemistry 43: 157–174
Stream Solute Workshop (1990) Concepts and methods for assessing solute dynamics in stream ecosystems. J. N. Am. Benthol. Soc. 9: 95–119
Thibodeaux LJ, and Boyle JD (1987) Bedform-generated convective transport in bottom sediments. Nature 325: 341–343

Tipping E, Marker AFH, Butterwick C, Collett GD, Cranwell PA,. Ingram JKG, Leach DV, Lishman JP, Pinder AC, Rigg E & Simon BM (1997) Organic carbon in the Humber rivers. Sci. Tot. Envir. 194/195: 345–355

Wallis PM (1981) The uptake of dissolved organic matter in groundwater by stream sediments-a case study. In: Lock MA & Williams DD (Eds) Perspectives in Running Waters Ecology (pp. 97–111) Plenum, New-York

Webster JR & Meyer JL (1997) Stream organic matter budget-introduction. In: Webster JR & Meyer JL (Eds) Stream Organic Matter Budget. J. N. Am. Benthol. Soc. 16: 13–161

Wehr JD, Loergan SP & Thorp JH (1997) Concentrations and controls of dissolved organic matter in a constricted-channel region of the Ohio River. Biogeochemistry 38: 41–65

Wetzel RG, Corners H & Manny BA (1977) Seasonal Changes in particulate and dissolved organic carbon and nitrogen in a hardwater stream. Arch. Hydrobiol. 80: 20–39