Supplementary Information

Table S1. Maxima location($\lambda_{EX}/\lambda_{EM}$) of the components identified in the PARAFAC model, classification, and description including potential origin and processing status according to the literature and the OpenFluor on-line data base.

	$\lambda_{EX}/\lambda_{EM}$	*Classification*	*Description*
*F1**	270 / 300	Protein-like peak, tyrosine[a]	Indicator of biologic activity both fast turnover[a] or persistent DOM pools[b]
F2	300/410	Humic-like, ubiquitous[d]. Corresponding to peaks A and C as in Coble[c]	Related with fulvic acids and materials of terrestrial origin[e]. Potentially bioavailable or re-processed[f]
F3	380/460	Humic-like[g]	Terrestrial origin[h] Likely sensitive to photodegradation
*F4**	280 (430)/330	Protein-like peak, tryptophan[c]	Potentially less degraded protein material[a]

*not found in OpenFluor; [a]Fellman et al. 2010; [b] Kothawala et al. 2014; [c]Coble 1996; [d]Amaral et al. 2016; [e]Osburn et al. 2011;[f]Shutova et al. 2014; [g] Stedmon et al. 2011; [h]Yamashita et al. 2011

Table S2. Excitation and emission loadings of the fluorescence components identified from the PARAFAC model for stream water and riparian GW samples (n = 284) at the Font del Regàs catchment during the period 2010-2011.

Excitation					*Emission*				
λ (nm)	*F1*	*F2*	*F3*	*F4*	*λ (nm)*	*F1*	*F2*	*F3*	*F4*
250	0.479	0.498	0.384	0.386	*290*	0.501	0	0	0
260	0.552	0.380	0.354	0.287	*300*	0.577	0.011	0	0
270	0.683	0.307	0.305	0.318	*310*	0.551	0	0.001	0.136
280	0.015	0.236	0.265	0.736	*320*	0.314	0	0	0.444
290	0	0.261	0.193	0.349	*330*	0.106	0	0	0.660
300	0	0.263	0.157	0.060	*340*	0.044	0.044	0	0.468
310	0	0.259	0.138	0.010	*350*	0.023	0.093	0	0.285
320	0	0.257	0.131	0.004	*360*	0.011	0.149	0	0.175
330	0	0.252	0.147	0	*370*	0.004	0.209	0	0.106
340	0	0.236	0.173	0	*380*	0.001	0.270	0	0.063
350	0	0.202	0.205	0	*390*	0	0.314	0	0.028
360	0	0.137	0.245	0	*400*	0	0.336	0.022	0.008
370	0	0.084	0.271	0	*410*	0	0.365	0.081	0
380	0	0.036	0.283	0	*420*	0	0.365	0.161	0
390	0	0	0.265	0	*430*	0	0.342	0.240	0
400	0	0	0.207	0	*440*	0	0.299	0.318	0
410	0	0	0.150	0.001	*450*	0.002	0.250	0.370	0
420	0	0	0.110	0.002	*460*	0.002	0.200	0.391	0.007
430	0	0	0.084	0.002	*470*	0.004	0.157	0.385	0.013
440	0	0	0.059	0.002	*480*	0.006	0.127	0.352	0.018
					490	0.007	0.103	0.309	0.018
					500	0.005	0.083	0.264	0.018
					510	0	0.064	0.219	0.015
					520	0	0.041	0.180	0.005

Table S3. Discharge (Q) and chloride (Cl^-), dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) concentrations at the top, bottom (*bot*), tributaries (*tr*), and riparian groundwater (*gw*) of the study reach for each sampling date. Values for tributaries and riparian groundwater are means for the whole reach. Note that for Eq. (1), we used values measured at each tributary and at each riparian groundwater well along the reach.

	Q ($L\ s^{-1}$)				Cl^- ($mg\ L^{-1}$)				DOC ($\mu g\ C\ L^{-1}$)				DON ($\mu g\ N\ L^{-1}$)			
	top	*bot*	*tr*	*gw*	*top*	*bot*	*tr*	*gw*	*top*	*bot*	*tr*	*gw*	*top*	*bot*	*tr*	*gw*
27/10/2010	28.6	106	14.8	2.3	9.7	15.3	13.6	14.9	535.6	860.3	703.4	686.2	*bdl*	32.3	66.9	39.5
22/11/2010	14.9	65.4	13.4	0.7	6.2	8.3	8	8.2	894.7	750.2	3546.3	2650.5	47.9	1521	77.8	161.1
19/01/2011	17.5	76.4	10.1	2.0	5.9	7.8	7.3	7.5	466.6	1375.3	423.6	503.7	125.7	43.6	77.4	79.6
01/03/2011	15.2	31.7	9	-0.7	5.8	7.8	7.3	7.6	277.1	252.3	305.2	293.9	33.6	76.9	49.3	49.6
12/04/2011	36.5	197.7	32.2	4.3	5.9	8.9	8.05	10.4	581.5	415.1	543.2	535.6	67.3	21.2	52.6	49.8
26/05/2011	24.3	103.3	21.3	1.1	5.8	8.6	7.8	8.7	265.1	361.8	349.3	327.9	25.8	137.2	34.8	40.5
09/08/2011	14.3	67.8	12.9	1.1	10.9	16.2	17.6	18.3	590.3	663	678.8	638.9	125.9	460	65.9	90.3
13/09/2011	10.2	44.9	7.5	0.8	7.5	9.2	9.1	10.7	267.3	361.6	267.9	276.3	80.05	56.7	57.6	49.5
26/10/2011	9.58	28.3	9.3	-0.7	9.9	13.5	13.2	12.5	555.9	1144.9	1107.9	1025.6	38	*bdl*	19.7	9.5
15/12/2011	38	213.6	39.7	4	6.3	9.2	7.9	8.4	468.7	794.1	752.3	708.8	63.6	78.1	45.5	44.6

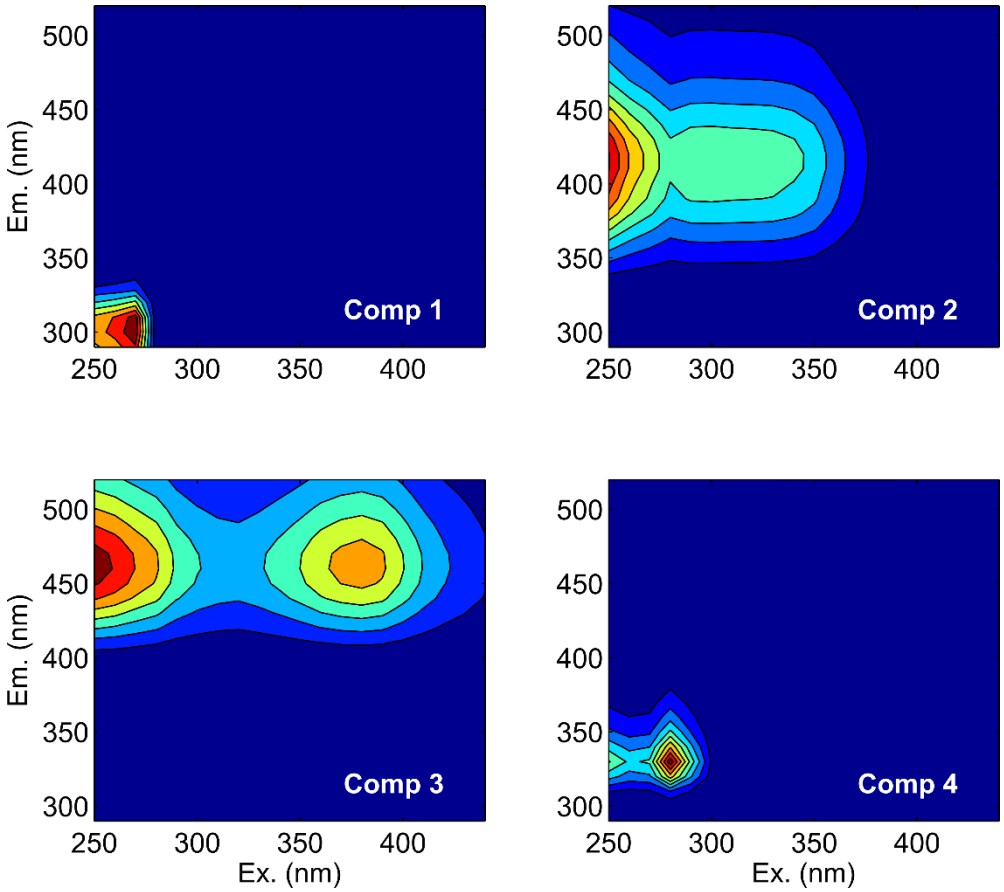


Figure S1. Excitation-emission plots of the fluorescence components identified from the PARAFAC model for stream water and riparian GW samples (n = 284) at the Font del Regàs catchment during the period 2010-2011.

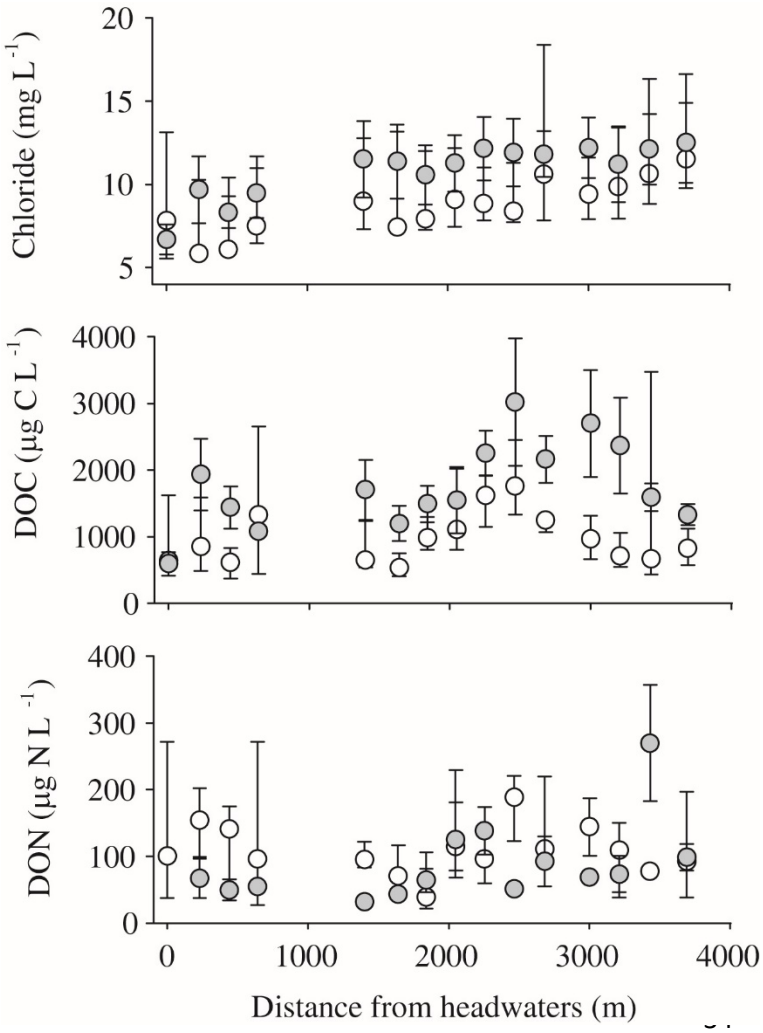
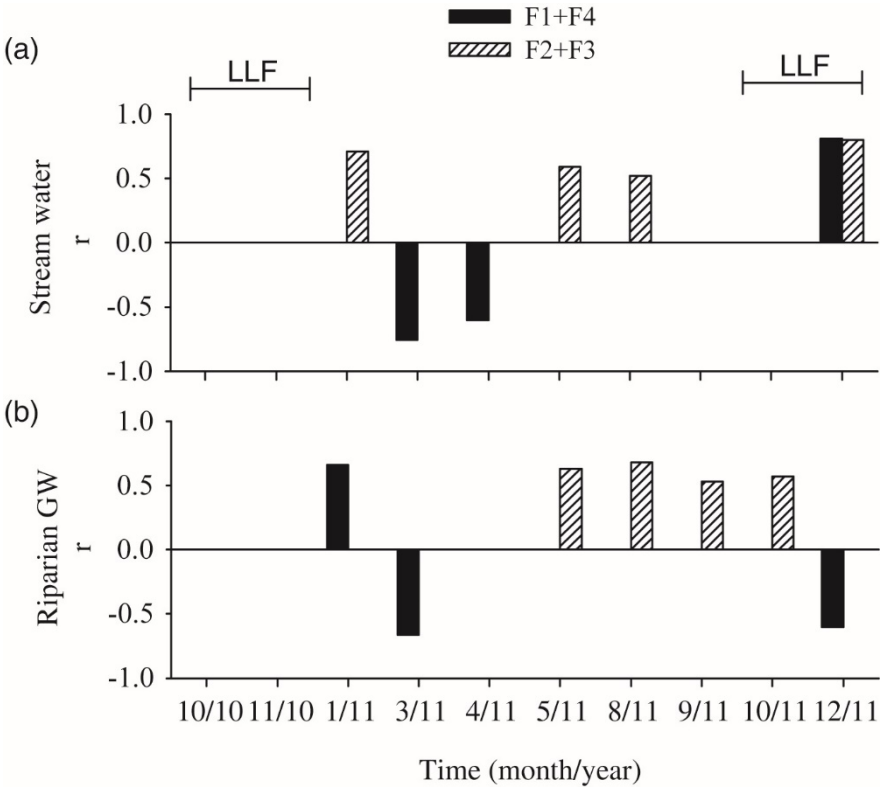


Figure S2. Longitudinal patterns of chloride, dissolved organic carbon (DOC), and dissolved organic nitrogen (DON) concentrations in riparian groundwater along the reach. Symbols are median values and whiskers are the interquartile range (25^{th}, 75^{th} percentiles). Concentrations are shown separately for the LLF (grey) and non-LLF period (white).



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53 **Figure S3.** Temporal pattern of the standardized regression coefficient (*r*) obtained by
54 fitting linear regression models to values of the PARAFAC components measured along
55 the 4km reach at Font del Regàs for (a) stream water, and (b) riparian groundwater
56 (GW). The *r* is shown for the components F1+F4 (associated with protein-like
57 compounds) and F2+F3 (associated to humic-like compounds). For each pair of
58 PARAFAC components, $r > 0$ indicates that values increased significantly along the
59 reach in a particular sampling date, while $r < 0$ indicates the opposite. Bars are shown
60 only when the model was significant ($p < 0.05$). The leaf litter fall (LLF) period is
61 indicated.

62

References for Supplementary Information

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