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Small-scale topography explains patterns and dynamics of dissolved organic carbon exports from the riparian zone of a temperate, forested catchment

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S1: Estimating variability of FT-ICR-MS samples across measurement days

To ensure that the molecular composition variance between riparian and stream water samples (n = 142, including three extra samples from further upstream, which were sample together with the samples from the study site) from different dates was not artificially induced due to systematic instrumental shifts in FT-ICR-MS measurements, a simulation of errors for molecular formulas (MF) peak intensities was conducted based on 15 SRFA (Suwannee River Fulvic Acid, an aquatic DOM reference) samples measured at the four measurement days. From this, a general error was derived for every MF intensity in the data matrix.

In this approach, we first calculated the mean coefficient of variance for the normalized peak intensities of every common MF detected in the 15 SRFA reference samples (n = 422) according to Eq. (A1):

$$CV_{ref,j} = \frac{SD_{ref,j}}{mean_{ref,j}}, \quad \text{(A1)}$$

Where $CV_{ref,i}$ is the coefficient of variance of every common MF j in the references, $SD_{ref,j}$ is the according standard deviation and $mean_{ref,j}$ is the according mean peak intensity of these MFs. These $CV_{ref,j}$ were found to scale with the normalized peak intensity I (r^2 = 0.43, p < 0.0001) within the reference sample set (Fig. S3) and thus were considered transferable to the actual water samples to determine the according standard deviation of every measured MF intensity. We subsequently assigned each common MF intensity j (1 to 471) of each sample i (1 to 142) its own standard deviation based on the scaling of $CV_{ref,j}$ by setting the actual measured sample intensities as new mean. Equation (A1) then transposes into Eq. (A2):

$$SD_{i,j} = CV_{mean,ref} \cdot I_{i,j}, \quad \text{(A2)}$$

Where $SD_{i,j}$ is the standard deviation of common MF j in sample i, $CV_{mean,ref}$ the mean coefficient of variation of all common MFs in the references and $I_{i,j}$ the actual measured intensity of common MF j in sample i. This resulted in the common MF sample intensity-matrix m ($i{\cdot}j$) and a SD-matrix k of a SD for every value in the intensity-matrix m also with the dimension ($i{\cdot}j$).

In a next step we randomly picked a value out of every normal distribution around the intensities $I_{i,j}$, where the mean was defined by the values in the sample intensity-matrix m and the SD by corresponding value in the SD-matrix k. Accordingly we get a modified common MF sample matrix accounting for analytical uncertainty. To check the robustness of clustering with bootstrapping, this step was repeated 300 times. The 300 matrices were then combined into one matrix with still 471 variables (MF) but 142·300 = 42900 samples (so every sample in the matrix now is present 300 times with slightly different intensities). For this dataset we performed k-means clustering (for two clusters) and analyzed in which cluster the 300 different versions of each sample occurred. The probability of a sample to be assigned to one cluster was then calculated for every sample (for all 300 variations), thus quantifying the stability of the cluster affinity. Our bootstrapping approach revealed that 12 out of 142 samples changed cluster affiliation (Fig. S4) in 1 to 141 times out of 300 cases, with 6 samples (4 % of the samples) having a probability of p > 0.05 to switch between clusters. These 6 samples did not seem to have systematic similarities.

We thus conclude that the analytical uncertainty from the FT-ICR-MS measurements between the different measurement dates does only little affect the overall variance (here clustering) of the samples, which allows a comparison of all samples against each other.

S2: Objective function of the HydroGeoSphere model calibration (Eq. (A3))

$$\text{Multi} - \text{Objective function } = \sum_{i=1}^{i=nq} w_q(O_q^i - S_q^i)^2 + \sum_{i=1}^{i=nl} w_l(O_l^i - S_l^i)^2 \quad \text{(A3)}$$

Where O_q^i and S_q^i are the observed and simulated discharge. nq is the number of number of the discharge observations (611). O_l^i and $S_l^i$are the observed and simulated groundwater level. nl is the number of groundwater level observations (110140). w_q and $w_l$are the weights for the two observation groups, both being assigned with the value of 1 in the calibration. Because the observation number of groundwater level was significantly larger than that of the discharge, this multi-objective function highlight the importance of the groundwater levels, such that the 94% of the multi-objective function for the calibrated best-fit was attributed to groundwater levels.

S3: Overview of FT-ICR MS results from stream and riparian samples

The formula assignment and blank filtering resulted in 3693 ± 960 MF (range: 1292 – 5625, *n* = 142) assigned to 16797 ± 2835 peaks (range: 9251 – 21511) in the mass range 150 – 1000 m/z. The assigned MF represented on average (24 ± 5) % of the total intensity in the mass spectra. In 93 spectra, multiple assignments (for 1 – 13 peaks, with m/z > 650) were present and these peaks represented < 0.12 % of the total intensity of all assigned MF.

Overall, 18910 unique MF were detected in all samples (*n* = 142), 6650 (3164) of them were present in at least 10 % (50 %) of the samples (Fig. S9). Shared among all 142 samples were 471 MF representing on average (40 ± 4) % of the summed intensity of all assigned MF in each sample. The 471 MF were distributed to 315 CHO, 150 CHNO and 6 CHOS formulas.

The riparian and stream samples were considerably different in terms of their average molecular composition (Table S5, Fig. S10). Note that in contrast to the PCA, here all 142 samples were considered (i.e. also the extra upstream samples, cf. Table S1). The PCA was run with all common MF found in 139 samples (i.e. 66 riparian, 68 event and 5 base flow samples), resulting in 482 common MF.

Table S1: Overview on sampling in the Rappbode stream and its adjacent riparian zone. GW: groundwater, SW: surface water. DOC concentration and DOC properties (see section 2.3 – FTICRMS measurements) was determined for all samples except the routine stream samples, where only DOC concentration was determined.

	Time of the Year	Interval [h]	All Samples $n = 253$	Samples FT-ICR MS $n = 142$	
Event 1	20 May 2017	1	24	11	68 event samples
Event 2	13 Sep 2017	1.5	24	8	
Event 3	05 Oct 2017	1	48	35	
Event 4	29 Oct 2017	2	24	9	
Event 5	09 Dec 2018	0.75	24	5	
Routine stream sampling	Oct 2017 - Oct 2018	Every second week with gaps in winter	38	-	
Riparian zone GW and SW routine sampling +1 Stream water sample per date (RB_dn)	24 Apr 2018 04 Dec 2018 11 Dec 2018 09 Apr 2019 23 Jul 2019	-	71 (3-24 per date)	19 24 20 5 3	66 riparian + 5 base flow samples
Grab sampling at the Rappbode source (RB_up)	24 Apr 2018 04 Dec 2018 23 Jul 2019	-	3	3	3 upstream samples

Table S2: The main parameters and their values used in this study. Asterisked parameters were subject to model calibration.

Parameter	**Process**	**Spatial distribution**	**Value of best fit**
Hydraulic conductivity*	Subsurface	Distributed	Elemental values from *K* field
Porosity	Subsurface	Uniform	0.56 [-]
Residual saturation	Subsurface	Uniform	0.08 [-]
Manning roughness coefficient*	Surface	Uniform	$6.34 \cdot 10^{-6}$ day $m^{-1/3}$
Manning roughness coefficient*	Channel	Uniform	$1.69 \cdot 10^{-6}$ day $m^{-1/3}$
Evaporation/root depth	ET	Uniform	0.5 m
van Genuchten functions (Therrien et al., 2010):			
α	Subsurface	Uniform	3.6 m^{-1}
β	Subsurface	Uniform	2.0 [-]
Residual saturation	Subsurface	Uniform	0.08 [-]
Fluxes from side boundaries:			
Q_{left},*	Subsurface	Uniform	0.88 $m^3 s^{-1}$ per unit length
Q_{right}*	Subsurface	Uniform	0.35 $m^3 s^{-1}$ per unit length

Table S3: Mean FT-ICR-MS derived molecular formula properties of the samples of the two DOC classes and the event samples.

Sample Group	n	wa_{mz}		wa_{HC}		wa_{OC}		wa_{NC} ($x10^3$)		wa_{SC} ($x10^3$)		wa_{AI}		wa_{NOSC}	
		mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd	mean	sd
DOC_I	19	432	5	1.223	0.029	0.404	0.020	18.8	2.4	7.2	1.6	0.115	0.018	-0.345	0.062
DOC_{II}	47	437	8	1.296	0.036	0.395	0.010	17.9	2.7	9.2	2.2	0.082	0.012	-0.434	0.043
Events	76	429	12	1.170	0.048	0.433	0.025	20.7	2.2	5.0	1.2	0.122	0.021	-0.231	0.092

Table S4: Hydro climatic overview (average (minimum/maximum)) of the preceding 5 days of sampling in the stream and the riparian zone. Bold dates mark event sampling in the stream. Others are riparian zone sampling dates. Note that sampling on 24.04.2018 happened right after a data gap. Thus the statistic values only represent rough estimations of the prevailing conditions. NA means no data available.

Sampling	Temp [°C]	Rain [mm $30min^{-1}$]	ET [mm h^{-1}]	Q [L s^{-1}]
20.05.2017	15.12 (6.1/25.8)	0.15 (0/8.2)	0.06 (0/0.253)	58.87 (18.39/411.52)
13.09.2017	11.09 (7.1/15.5)	0.12 (0/3.8)	0.025 (0/0.163)	11.36 (5.67/60.40)
05.10.2017	9.85 (5.5/16.6)	0.15 (0/2)	0.02 (0/0.166)	29.7 (13.31/94.37)
29.10.2017	9.03 (4.6/13.7)	0.12 (0/2.8)	0.01 (0/0.08)	40.49 (16.61/338.30)
09.12.2018	-0.29 (-4.6/3.7)	0.08 (0/2)	0.005 (0/0.073)	166.7 (107.0/453.1)
24.04.2018*	10.26*	NA*	0.02	49.54
04.12.2018	4.74 (0.6/9.8)	0.20 (0/4)	0.005 (0/0.037)	65.36 (32.24/160.19)
11.12.2018	3.84 (0.3/8.7)	0.27 (0/3.6)	0.003 (0/0.029)	132.09 (48.50/349.22)
09.04.2019	7.49 (-1.2/18.4)	0 (0/0)	0.042(0/0.21)	57.76(43.03/83.77)
23.07.2019	17.24 (9.6/27.1)	0.037 (0/3.8)	0.060 (0/0.23)	16.02 (8.87/23.84)

*There was a data gap for the preceding 20 days. The depicted values thus depict only mean values of 1 day before the data gap (04.04.2018), measurement date and one day after the sampling in order to get a rough approximation of the prevalent hydro climatic situation.

Table S5: Sample details, FT-ICR-MS derived molecular formula class distribution, and mean values of molecular formula descriptors for all 142 samples. Bold sample names denoted "BW_" are event samplings and "RB_" denote routine samplings in the stream. Cluster affiliation only refers to riparian water samples. MF: molecular formulas; wa: weighted average of wa_{mz} (mass to charge ratio), wa_{HC} (hydrogen to carbon ratio), wa_{OC} (oxygen to carbon ratio), wa_{SC} (sulfur to carbon ratio), wa_{AI} (aromaticity index), wa_{NOSC} (nominal oxidation state of carbon).

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
BW_05		Stream event sample	10.05.2017 19:30	3.47	6	4565	2102	1611	311	540	1	457	1.142	0.487	0.019	0.005	0.1	-0.1
BW_10		Stream event sample	11.05.2017 00:30	3.38	5	4496	2058	1609	322	504	3	454	1.15	0.482	0.02	0.005	0.1	-0.12
BW_15		Stream event sample	11.05.2017 05:30	3.92	5	4498	2063	1580	306	546	3	454	1.142	0.484	0.02	0.006	0.1	-0.1
BW_20		Stream event sample	11.05.2017 10:30	5.07	6	4615	2132	1662	284	536	1	449	1.144	0.48	0.021	0.006	0.1	-0.11
BW_49		Stream event sample	18.05.2017 15:00	4.61	6	4190	2011	1485	211	483	0	450	1.108	0.49	0.02	0.004	0.11	-0.06
BW_26		Stream event sample	20.05.2017 08:00	18.16	21	4166	2121	1426	151	467	1	451	1.104	0.485	0.02	0.004	0.12	-0.06
BW_28		Stream event sample	20.05.2017 10:00	17.96	17	4005	2033	1356	178	434	4	453	1.102	0.491	0.021	0.005	0.11	-0.05
BW_40		Stream event sample	20.05.2017 12:00	12.51	9	3838	1947	1311	149	429	2	446	1.11	0.473	0.021	0.004	0.12	-0.09
BW_31		Stream event sample	20.05.2017 13:00	16.82	13	3991	1966	1388	194	438	5	442	1.117	0.463	0.021	0.004	0.13	-0.12
BW_35		Stream event sample	20.05.2017 17:00	14.2	11	3930	1977	1362	162	426	3	437	1.106	0.472	0.022	0.005	0.13	-0.09
BW_48		Stream event sample	21.05.2017 06:00	11.28	9	3801	1858	1335	156	452	0	439	1.145	0.448	0.022	0.005	0.12	-0.17
BW_50		Stream event sample	13.09.2017 10:15	9.59	14	3400	1760	1154	65	416	5	438	1.185	0.452	0.02	0.005	0.09	-0.21
BW_52		Stream event sample	13.09.2017 13:15	8.48	14	3164	1635	1087	50	385	7	440	1.185	0.453	0.02	0.005	0.09	-0.21
BW_55		Stream event sample	13.09.2017 17:45	7.69	8	3861	1932	1352	91	482	4	443	1.187	0.452	0.02	0.005	0.09	-0.21
BW_60		Stream event sample	14.09.2017 01:15	6.77	6	3276	1699	1117	51	404	5	439	1.188	0.452	0.02	0.005	0.09	-0.21
BW_62		Stream event sample	14.09.2017 04:15	7.43	5	3437	1730	1207	75	421	4	437	1.18	0.448	0.021	0.005	0.1	-0.21
BW_65		Stream event sample	14.09.2017 08:45	9.2	4	3169	1637	1083	53	393	3	436	1.184	0.449	0.021	0.005	0.1	-0.21
BW_68		Stream event sample	14.09.2017 13:15	12.73	4	3157	1657	1083	57	359	1	432	1.186	0.447	0.021	0.005	0.1	-0.22
BW_73		Stream event sample	14.09.2017 20:45	12.29	6	2762	1483	919	52	302	6	435	1.183	0.451	0.02	0.005	0.1	-0.21

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
BW_76		Stream event sample	05.10.2017 10:30	10.23	11	3094	1595	1065	53	376	5	415	1.149	0.419	0.024	0.005	0.15	-0.23
BW_77		Stream event sample	05.10.2017 11:30	12.21	16	3011	1562	1031	51	361	6	414	1.146	0.426	0.024	0.005	0.15	-0.21
BW_78		Stream event sample	05.10.2017 12:30	14.07	19	2853	1499	961	48	340	5	415	1.144	0.422	0.023	0.005	0.15	-0.22
BW_88		Stream event sample	05.10.2017 12:30	16.82	26	2622	1434	845	39	296	8	415	1.136	0.427	0.024	0.005	0.15	-0.2
BW_79		Stream event sample	05.10.2017 13:30	14.37	22	3013	1558	1038	63	351	3	417	1.159	0.421	0.023	0.005	0.14	-0.24
BW_80		Stream event sample	05.10.2017 14:30	14.1	26	3090	1631	1018	73	366	2	417	1.155	0.419	0.022	0.004	0.14	-0.24
BW_81		Stream event sample	05.10.2017 15:30	14.8	31	2829	1525	934	47	319	4	418	1.161	0.419	0.022	0.004	0.14	-0.25
BW_82		Stream event sample	05.10.2017 16:30	15.41	36	2734	1495	908	39	287	5	427	1.129	0.449	0.022	0.004	0.13	-0.16
BW_83		Stream event sample	05.10.2017 17:30	14.76	41	3171	1734	1067	64	302	4	422	1.164	0.424	0.021	0.004	0.13	-0.24
BW_84		Stream event sample	05.10.2017 18:30	15.77	40	2674	1471	874	51	275	3	419	1.154	0.422	0.021	0.004	0.14	-0.24
BW_85		Stream event sample	05.10.2017 19:30	15.2	37	2788	1529	898	53	302	6	415	1.156	0.42	0.022	0.005	0.14	-0.24
BW_86		Stream event sample	05.10.2017 20:30	16.37	34	2709	1457	891	45	309	7	420	1.149	0.424	0.021	0.005	0.14	-0.23
BW_87		Stream event sample	05.10.2017 21:30	15.84	30	2814	1518	922	44	328	2	419	1.153	0.423	0.021	0.005	0.14	-0.23
BW_89		Stream event sample	05.10.2017 23:30	16.05	23	2643	1415	869	53	302	4	418	1.15	0.423	0.021	0.005	0.14	-0.23
BW_90		Stream event sample	06.10.2017 00:30	14.84	21	2764	1474	911	47	329	3	420	1.156	0.424	0.021	0.005	0.14	-0.23
BW_91		Stream event sample	06.10.2017 01:30	14.09	18	2731	1433	905	52	334	7	418	1.142	0.426	0.022	0.005	0.14	-0.21
BW_92		Stream event sample	06.10.2017 02:30	13.69	17	2647	1400	866	49	329	3	417	1.166	0.424	0.022	0.005	0.14	-0.24
BW_93		Stream event sample	06.10.2017 03:30	12.98	15	2830	1483	948	42	357	0	419	1.157	0.426	0.022	0.005	0.14	-0.23
BW_94		Stream event sample	06.10.2017 04:30	12.23	14	2632	1386	887	31	321	7	417	1.154	0.422	0.022	0.005	0.14	-0.23
BW_96		Stream event sample	06.10.2017 06:30	12.66	13	2541	1347	839	48	301	6	416	1.147	0.425	0.023	0.005	0.14	-0.22
BW_97		Stream event sample	06.10.2017 07:30	12.65	13	2719	1459	907	54	296	3	417	1.137	0.433	0.023	0.005	0.14	-0.19
BW_98		Stream event sample	06.10.2017 08:30	12.98	13	2871	1536	968	56	309	2	419	1.151	0.427	0.022	0.004	0.14	-0.22
BW_99		Stream event sample	06.10.2017 09:30	13.03	14	2979	1542	1032	61	338	6	418	1.151	0.421	0.023	0.005	0.14	-0.23
BW_100		Stream event sample	06.10.2017 10:30	13.74	14	2973	1585	1004	46	332	6	419	1.161	0.423	0.022	0.005	0.14	-0.24
BW_101		Stream event sample	06.10.2017 11:30	14.27	15	2927	1560	990	41	333	3	420	1.147	0.426	0.023	0.004	0.14	-0.22

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
BW_102		Stream event sample	06.10.2017 12:30	12.74	16	2966	1561	995	52	354	4	420	1.152	0.425	0.022	0.005	0.14	-0.23
BW_103		Stream event sample	06.10.2017 13:30	13.71	17	2786	1476	919	58	325	8	417	1.157	0.42	0.023	0.005	0.14	-0.24
BW_104		Stream event sample	06.10.2017 14:30	12.86	18	2771	1468	917	58	322	6	417	1.159	0.412	0.023	0.005	0.15	-0.26
BW_105		Stream event sample	06.10.2017 15:30	13.55	19	3078	1645	1031	63	333	6	420	1.154	0.426	0.022	0.004	0.14	-0.23
BW_106		Stream event sample	06.10.2017 16:30	13.52	20	2715	1446	921	54	291	3	418	1.156	0.428	0.022	0.004	0.14	-0.23
BW_107		Stream event sample	06.10.2017 17:30	13.6	20	2683	1419	916	35	310	3	417	1.144	0.43	0.023	0.005	0.14	-0.21
BW_108		Stream event sample	06.10.2017 18:30	13.05	21	2876	1509	991	35	336	5	420	1.152	0.43	0.022	0.005	0.14	-0.22
BW_110		Stream event sample	06.10.2017 20:30	12.32	22	2701	1402	946	41	309	3	417	1.149	0.426	0.023	0.005	0.14	-0.22
BW_111		Stream event sample	06.10.2017 21:30	12.69	21	2738	1446	915	52	320	5	419	1.148	0.424	0.022	0.005	0.14	-0.22
BW_113		Stream event sample	06.10.2017 23:30	10.99	18	2873	1473	981	41	375	3	419	1.15	0.427	0.022	0.005	0.14	-0.22
BW_115		Stream event sample	29.10.2017	13.63	NA	2528	1409	839	34	239	7	423	1.158	0.44	0.021	0.004	0.12	-0.21
BW_116		Stream event sample	29.10.2017	14.77	NA	2593	1407	901	46	237	2	425	1.157	0.444	0.022	0.004	0.12	-0.2
BW_117		Stream event sample	29.10.2017	15.06	NA	2326	1315	749	52	207	3	426	1.149	0.447	0.021	0.004	0.12	-0.18
BW_118		Stream event sample	29.10.2017	15.52	NA	2693	1481	912	44	250	6	427	1.143	0.446	0.021	0.004	0.12	-0.18
BW_119		Stream event sample	29.10.2017	15.1	NA	2184	1225	717	38	200	4	425	1.146	0.442	0.02	0.004	0.13	-0.19
BW_120		Stream event sample	29.10.2017	14.36	NA	2242	1268	732	25	213	4	422	1.137	0.454	0.021	0.004	0.12	-0.16
BW_121		Stream event sample	29.10.2017	13.55	NA	2236	1294	708	32	195	7	428	1.159	0.443	0.019	0.003	0.12	-0.21
BW_122		Stream event sample	29.10.2017	7.98	NA	2319	1277	761	34	243	4	429	1.171	0.439	0.019	0.004	0.11	-0.23
BW_123		Stream event sample	29.10.2017	7.76	NA	2573	1393	858	41	271	10	431	1.17	0.439	0.02	0.004	0.11	-0.23
BW_125		Stream event sample	09.12.2018 10:15	7.11	34	5092	2266	1700	280	840	6	441	1.262	0.409	0.016	0.007	0.09	-0.38
BW_128		Stream event sample	09.12.2018 12:30	7.73	35	4940	2206	1682	249	798	5	437	1.262	0.398	0.016	0.007	0.1	-0.4
BW_136		Stream event sample	09.12.2018 18:30	7.38	29	4911	2205	1636	266	800	4	437	1.261	0.398	0.016	0.007	0.1	-0.4
BW_141		Stream event sample	09.12.2018 22:15	6.38	25	5323	2363	1791	305	862	2	443	1.26	0.409	0.016	0.007	0.09	-0.38
BW_146		Stream event sample	10.12.2018 02:00	7.58	21	5334	2343	1804	298	886	3	444	1.259	0.412	0.016	0.007	0.09	-0.37

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
A5-1	II	Low groundwater sample	24.04.2018	2.05	NA	3419	1165	1305	309	634	6	434	1.413	0.39	0.027	0.011	0.05	-0.53
B1-1	I	Low groundwater sample	24.04.2018	5.37	-3	3036	1366	1112	107	447	4	423	1.233	0.433	0.024	0.008	0.1	-0.28
B2-1	II	Low groundwater sample	24.04.2018	2.5	-26	4006	1752	1581	175	497	1	440	1.287	0.397	0.021	0.006	0.09	-0.42
B3-1	II	Low groundwater sample	24.04.2018	0.85	-34	3316	1276	1269	237	530	4	450	1.316	0.401	0.02	0.008	0.06	-0.44
B4-1	I	Low groundwater sample	24.04.2018	7.4	0	3290	1518	1149	103	511	9	433	1.212	0.425	0.021	0.007	0.1	-0.29
B5-1	II	Low groundwater sample	24.04.2018	2.74	2	3263	1251	1215	242	549	6	453	1.355	0.396	0.021	0.008	0.05	-0.49
C1-1	I	Low groundwater sample	24.04.2018	6.18	1	3386	1609	1239	149	388	1	440	1.215	0.412	0.019	0.005	0.11	-0.33
C2-1	II	Low groundwater sample	24.04.2018	0.86	-23	3427	1403	1380	230	405	9	452	1.292	0.401	0.022	0.007	0.07	-0.41
C3-1	II	Low groundwater sample	24.04.2018	2.14	-28	3525	1553	1190	218	557	7	439	1.343	0.377	0.02	0.01	0.09	-0.51
C4-1	II	Low groundwater sample	24.04.2018	2.61	-5	3939	1736	1392	216	592	3	446	1.292	0.388	0.016	0.006	0.08	-0.46
C5-1	II	Low groundwater sample	24.04.2018	1.69	-2	3503	1382	1246	263	609	3	453	1.36	0.402	0.021	0.01	0.06	-0.47
D1-1	I	Low groundwater sample	24.04.2018	5.91	-3	3850	1810	1317	170	548	5	440	1.243	0.418	0.02	0.007	0.09	-0.33
D2-1	II	Low groundwater sample	24.04.2018	2.36	-33	3702	1667	1291	185	557	2	442	1.284	0.392	0.019	0.008	0.09	-0.43
D3-1	II	Low groundwater sample	24.04.2018	2.69	-34	3841	1548	1372	271	646	4	448	1.334	0.384	0.021	0.01	0.08	-0.48
D4-1	II	Low groundwater sample	24.04.2018	1	-4	3243	1234	1186	253	564	6	442	1.358	0.384	0.023	0.01	0.07	-0.5
D5-1	II	Low groundwater sample	24.04.2018	0.73	NA	3341	1354	1326	214	443	4	451	1.292	0.401	0.022	0.007	0.07	-0.41
A5O-1	II	Surface pond sample	24.04.2018	1.88	0	3673	1640	1423	169	433	8	443	1.275	0.419	0.022	0.006	0.07	-0.36

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
S3O-1	I	Surface pond sample	24.04.2018	15.77	0	3108	1491	1126	103	381	7	431	1.148	0.451	0.024	0.005	0.12	-0.16
RB_up-1		Rappbode streamwater sample	24.04.2018 14:15	6.83	22	3223	1556	1170	86	409	2	439	1.183	0.445	0.02	0.005	0.1	-0.22
RB_dn-1		Rappbode streamwater sample	24.04.2018 15:45	6.72	11	3065	1497	1071	83	411	3	437	1.171	0.448	0.02	0.005	0.11	-0.2
C1-2	II	High groundwater sample	04.12.2018	3.43	-8	5012	2105	1697	308	898	4	436	1.271	0.397	0.015	0.009	0.09	-0.41
D2-2	II	High groundwater sample	04.12.2018	1.97	-31	5143	2262	1778	295	806	2	440	1.243	0.39	0.017	0.007	0.11	-0.4
E2-2	II	High groundwater sample	04.12.2018	2.4	-25	4911	1965	1941	368	634	3	446	1.274	0.4	0.017	0.007	0.08	-0.41
C3b-2	II	High groundwater sample	04.12.2018	2.4	NA	5625	2258	2050	444	870	3	440	1.277	0.396	0.018	0.009	0.09	-0.41
RB_up-2		Rappbode streamwater sample	04.12.2018	5.47	22	1906	916	583	51	355	1	426	1.28	0.404	0.016	0.008	0.08	-0.41
RB_dn-2		Rappbode streamwater sample	04.12.2018	5.42	22	5231	2168	1724	369	966	4	433	1.269	0.403	0.017	0.009	0.09	-0.39
A2-2	II	High groundwater sample	04.12.2018	2.76	-11	3924	1603	1315	208	793	5	436	1.271	0.41	0.017	0.01	0.08	-0.38
A4-2	II	High groundwater sample	04.12.2018	2.51	-11	1474	830	340	34	263	7	428	1.265	0.381	0.011	0.007	0.1	-0.46
B1-2	II	High groundwater sample	04.12.2018	3.45	-13	4222	1602	1418	325	873	4	428	1.311	0.411	0.016	0.016	0.07	-0.41
B3-2	II	High groundwater sample	04.12.2018	3.01	-20	5204	1931	2087	421	760	5	442	1.273	0.409	0.018	0.01	0.07	-0.38
B4-2	II	High groundwater sample	04.12.2018	3.25	-6	5072	1844	1791	466	969	2	436	1.285	0.403	0.016	0.012	0.08	-0.41
C4-2	II	High groundwater sample	04.12.2018	2.08	-16	4965	1846	1718	489	910	2	438	1.305	0.401	0.014	0.012	0.07	-0.44
D1-2	II	High groundwater sample	04.12.2018	6.08	-17	4427	1782	1505	254	880	6	435	1.269	0.408	0.015	0.01	0.08	-0.39
D4-2	II	High groundwater sample	04.12.2018	1.55	-32	5074	1846	1828	504	892	4	439	1.301	0.393	0.016	0.01	0.07	-0.45

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
E1-2	I	High groundwater sample	04.12.2018	7	-14	5027	2066	1790	310	854	7	440	1.251	0.401	0.017	0.008	0.1	-0.38
E4-2	II	High groundwater sample	04.12.2018	0.69	-13	5165	2313	1763	312	765	12	434	1.293	0.364	0.014	0.007	0.1	-0.51
E5-2	II	High groundwater sample	04.12.2018	3.68	-38	4059	1512	1401	322	820	4	441	1.361	0.393	0.018	0.014	0.07	-0.49
B2b-2	II	High groundwater sample	04.12.2018	1.72	NA	4921	1965	1960	343	650	3	442	1.257	0.4	0.019	0.007	0.09	-0.38
S2-2	II	High groundwater sample	04.12.2018	2.61	-16	4511	1735	1500	349	923	4	432	1.292	0.399	0.016	0.011	0.08	-0.42
T2-2	II	High groundwater sample	04.12.2018	1.81	-8	5361	2003	1872	434	1048	4	424	1.328	0.397	0.018	0.013	0.08	-0.46
MO-2	I	Surface pond sample	04.12.2018	7.37	0	4244	1876	1293	181	891	3	435	1.243	0.418	0.016	0.01	0.1	-0.34
B4O-2	I	Surface pond sample	04.12.2018	12.94	0	4217	1857	1415	171	770	4	427	1.223	0.404	0.019	0.009	0.12	-0.34
B5O-2	II	Surface pond sample	04.12.2018	4.69	0	1292	670	423	33	158	8	428	1.297	0.4	0.019	0.006	0.07	-0.43
T2O-2	I	Surface pond sample	04.12.2018	5.22	0	5117	2102	1702	354	956	3	435	1.25	0.408	0.018	0.009	0.1	-0.36
A2O-2	II	Surface pond sample	04.12.2018	4.81		4069	1671	1332	232	829	5	428	1.28	0.4	0.017	0.011	0.09	-0.41
B2-3	II	High groundwater sample	11.12.2018	2.11	-25	4548	1835	1691	343	674	5	430	1.28	0.379	0.019	0.007	0.1	-0.45
T2-3	II	High groundwater sample	11.12.2018	2.14	-9	4892	1924	1652	408	906	2	429	1.292	0.386	0.017	0.01	0.09	-0.45
S1-3	I	High groundwater sample	11.12.2018	6.33	NA	4331	1970	1482	200	676	3	437	1.217	0.407	0.018	0.006	0.11	-0.33
S3-3	II	High groundwater sample	11.12.2018	4.08	NA	4857	2020	1585	338	910	4	439	1.259	0.398	0.015	0.008	0.09	-0.4
C1-3	I	High groundwater sample	11.12.2018	4.36	-9	4332	1955	1427	233	714	3	432	1.256	0.38	0.016	0.008	0.11	-0.43
T2O-3	I	Surface pond sample	11.12.2018	9.68	0	4391	1931	1518	193	746	3	433	1.22	0.407	0.019	0.007	0.11	-0.33
B2O-3	II	Surface pond sample	11.12.2018	4.65	0	4724	2036	1611	269	801	7	439	1.258	0.4	0.016	0.008	0.09	-0.4
RB_dn-3		Rappbode streamwater sample	11.12.2018	5.67	13	1919	989	578	37	311	4	432	1.279	0.402	0.014	0.006	0.08	-0.42

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
A1-3	II	High groundwater sample	11.12.2018	2.25	-12	4385	1802	1416	272	883	12	421	1.317	0.379	0.015	0.011	0.09	-0.49
A2-3	II	High groundwater sample	11.12.2018	3.65	-10	4813	1881	1642	367	920	3	434	1.272	0.397	0.017	0.01	0.09	-0.41
A3-3	II	High groundwater sample	11.12.2018	0.88	-48	4293	1799	1546	303	640	5	434	1.301	0.392	0.017	0.008	0.08	-0.45
A4-3	I	High groundwater sample	11.12.2018	3.65	-11	4220	1859	1240	204	916	1	427	1.232	0.392	0.015	0.01	0.12	-0.38
B1-3	II	High groundwater sample	11.12.2018	2.85	-15	4692	1791	1645	345	909	2	426	1.275	0.402	0.018	0.012	0.09	-0.39
B3-3	II	High groundwater sample	11.12.2018	3.27	-27	5102	1951	1763	390	995	3	432	1.279	0.395	0.017	0.01	0.09	-0.42
B4-3	II	High groundwater sample	11.12.2018	4.07	-5	4197	1641	1624	281	649	2	432	1.27	0.397	0.019	0.009	0.09	-0.4
B5-3	II	High groundwater sample	11.12.2018	1.1	-7	4288	1816	1449	310	700	13	424	1.371	0.375	0.017	0.011	0.07	-0.55
B2b-3	II	High groundwater sample	11.12.2018	2.67	NA	4034	1637	1564	263	566	4	431	1.26	0.393	0.02	0.008	0.09	-0.4
S2-3	II	High groundwater sample	11.12.2018	3.29	-16	4941	1963	1670	377	929	2	437	1.267	0.403	0.017	0.009	0.09	-0.39
A2O-3	II	Surface pond sample	11.12.2018	3.78	0	4842	2061	1629	285	866	1	445	1.266	0.398	0.015	0.008	0.09	-0.41
B5O-3	I	Surface pond sample	11.12.2018	2.53	0	4521	2046	1643	193	633	6	434	1.245	0.399	0.02	0.006	0.1	-0.37
S2O-4	I	Surface pond sample	09.04.2019	5.66	0	4754	2270	1614	164	703	3	436	1.18	0.391	0.018	0.005	0.15	-0.33
RB_dn-4		Rappbode streamwater sample	09.04.2019	3.29	10	4532	2219	1476	132	702	3	438	1.192	0.385	0.015	0.005	0.14	-0.37
A2-4	I	High groundwater sample	09.04.2019	4.74	-11	3820	1939	1338	85	453	5	430	1.187	0.381	0.018	0.005	0.15	-0.36
B4-4	I	High groundwater sample	09.04.2019	10.44	-3	3964	1969	1308	115	566	6	420	1.214	0.392	0.02	0.009	0.14	-0.35
B5-4	I	High groundwater sample	09.04.2019	3.21	-3	4948	2246	1666	254	777	5	431	1.212	0.389	0.018	0.007	0.13	-0.37

Sample Name	Cluster affiliation	Sample Type	Date and Time of Sampling	DOC [mg/L]	Water Level / Depth to GW [cm]	Total MF	CHO	CHNO	CHNOS	CHOS	other	wa_{mz}	wa_{HC}	wa_{OC}	wa_{NC}	wa_{SC}	wa_{AI}	wa_{NOSC}
RB_dn-5		Rappbode streamwater sample	23.07.2019	1.3	5	3862	1549	1544	251	507	11	441	1.363	0.374	0.018	0.006	0.07	-0.55
RB_up-5		Rappbode streamwater sample	23.07.2019	9.54	10	4228	1821	1459	249	687	12	416	1.292	0.365	0.02	0.011	0.12	-0.48
B5-5	I	High groundwater sample	23.07.2019	2.76	-53	4463	2145	1554	199	555	10	427	1.261	0.365	0.018	0.006	0.12	-0.46
B_C1-5	II	High groundwater sample	23.07.2019	4.13	-48	3741	1676	1225	137	700	3	433	1.296	0.394	0.016	0.008	0.08	-0.44

Table S6: Overview of model results. Absolute values and comparison of the water fluxes in the study site for a dry (29 Aug 2018) and wet (13 Dec 2017) situation. Negative fluxes indicate exit out of the system.

	Dry [mm d^{-1}]	Wet [mm d^{-1}]	Absolute change [mm d^{-1}]	Rel. change factor [-]
Channel in	45.04	1315.08	1270.04	29.2
Channel out	-45.71	-1321.10	1275.39	28.9
Channel gain total	0.67	6.06	5.39	9.1
Channel gain from subsurface	0.60	5.83	5.23	9.7
Channel gain from surface	0.07	0.23	0.17	3.4
Channel loss total	0.00	0.00	0.00	NA
Subsurface in	0.10	0.17	0.07	1.7
Subsurface out	-0.20	-0.29	0.10	1.5
Subsurface gain	0.10	0.13	0.03	1.3
Outflow exit through surface	-0.47	-14.75	14.28	31.4
Total runoff gain	1.23	20.94	19.71	17.0

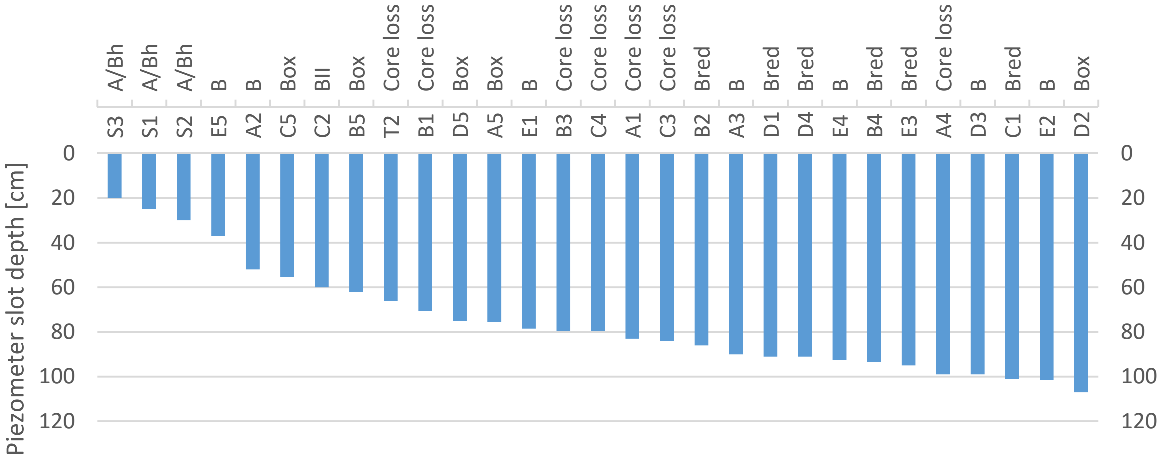

Figure S1: Overview of depth of slots and soil types of the piezometer network.

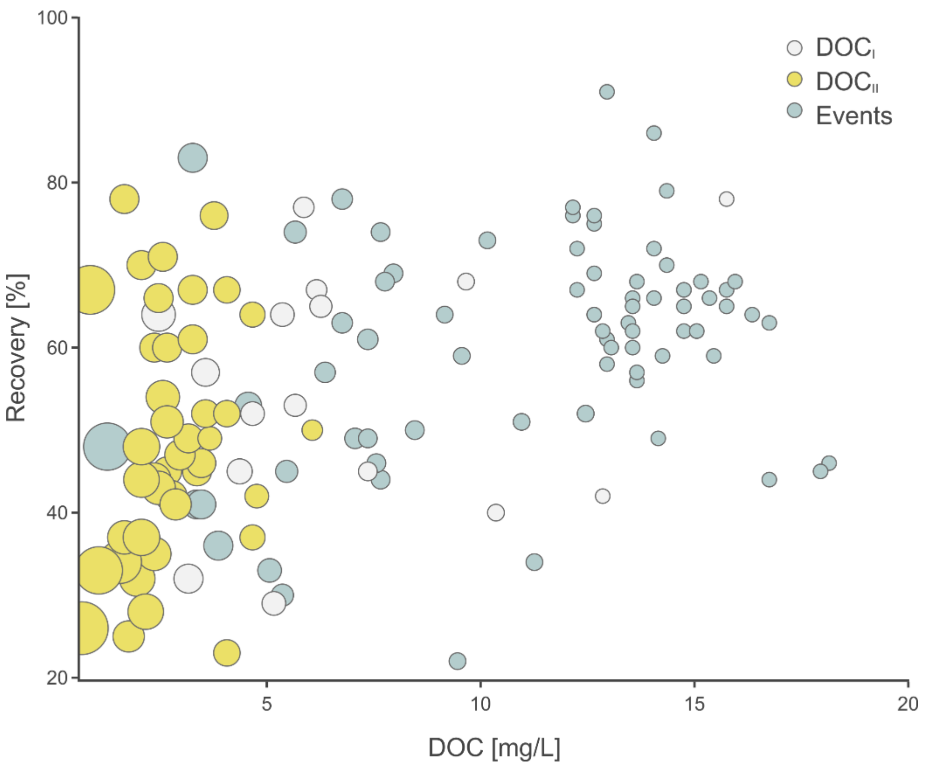

Figure S2: Quality control of solid phase extraction for DOC samples. SPE recovery vs sample DOC concentration for stream samples (blue) and riparian samples of type DOC$_I$ (grey) and DOC$_{II}$ (yellow) with dot size corresponding to the sample volume used for the extraction (range: 15-200 mL, *n* = 133).

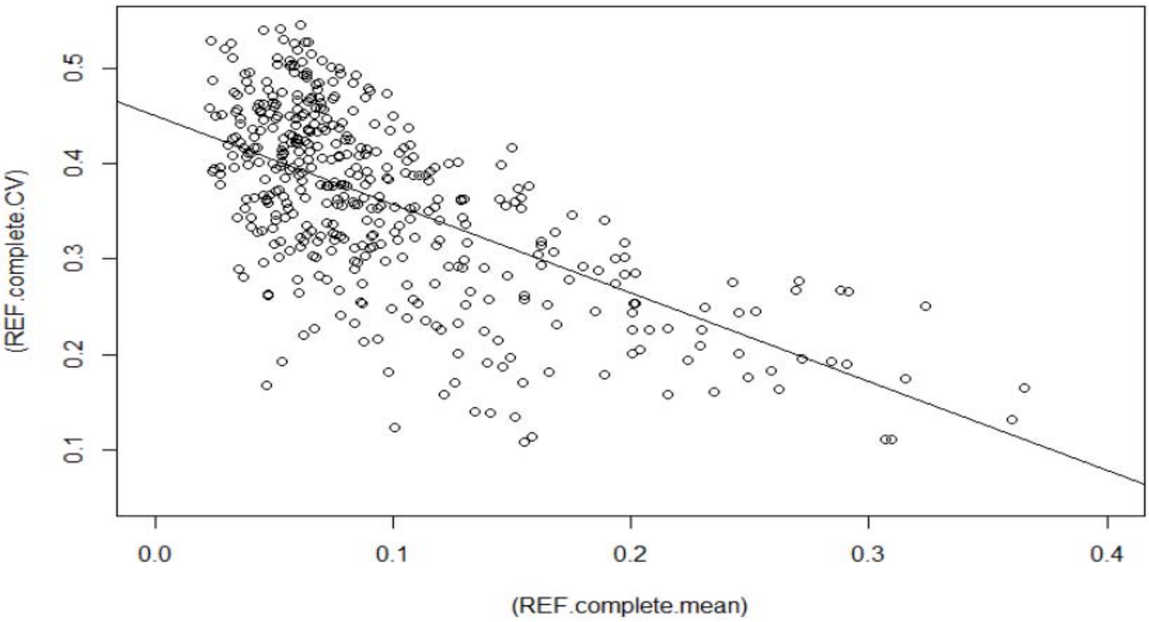

Figure S3: Coefficient of variation (*REF.complete.CV*) versus the mean normalized intensities (*REF.complete.mean*) of the common FT-ICR-MS reference samples compounds (*n* = 422). Black line indicates linear regression. Mean *REF.complete.CV* was 0.36.

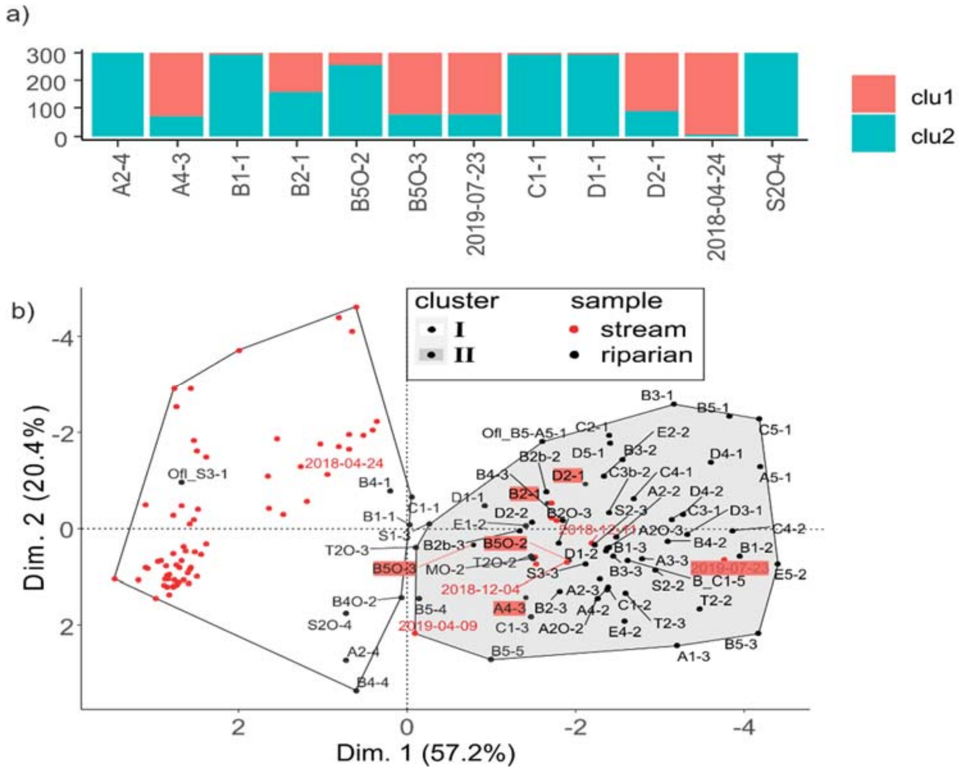

Figure S4: a) Bootstrapping of cluster analysis. Only samples are depicted where the random deviation made samples switch between the two clusters. Overall there are 142 samples. b) Visualization of k-means clustering results of all samples. Highlighted samples in red indicate samples with a probability of *p* > 0.05 to switch between clusters (see (a)). Samples marked with red dates indicate stream water samples of riparian sampling dates.

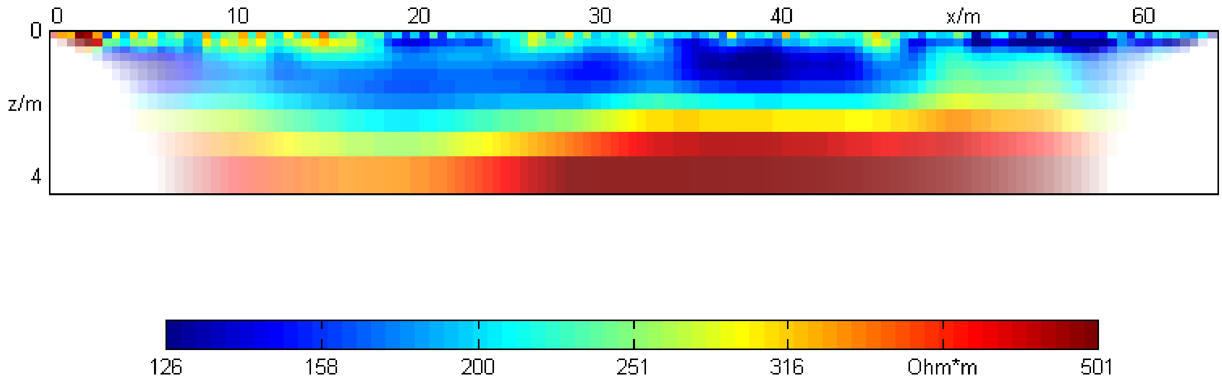

Figure S5: Electrical resistivity plot of the transect AB derived from geoelectrics.

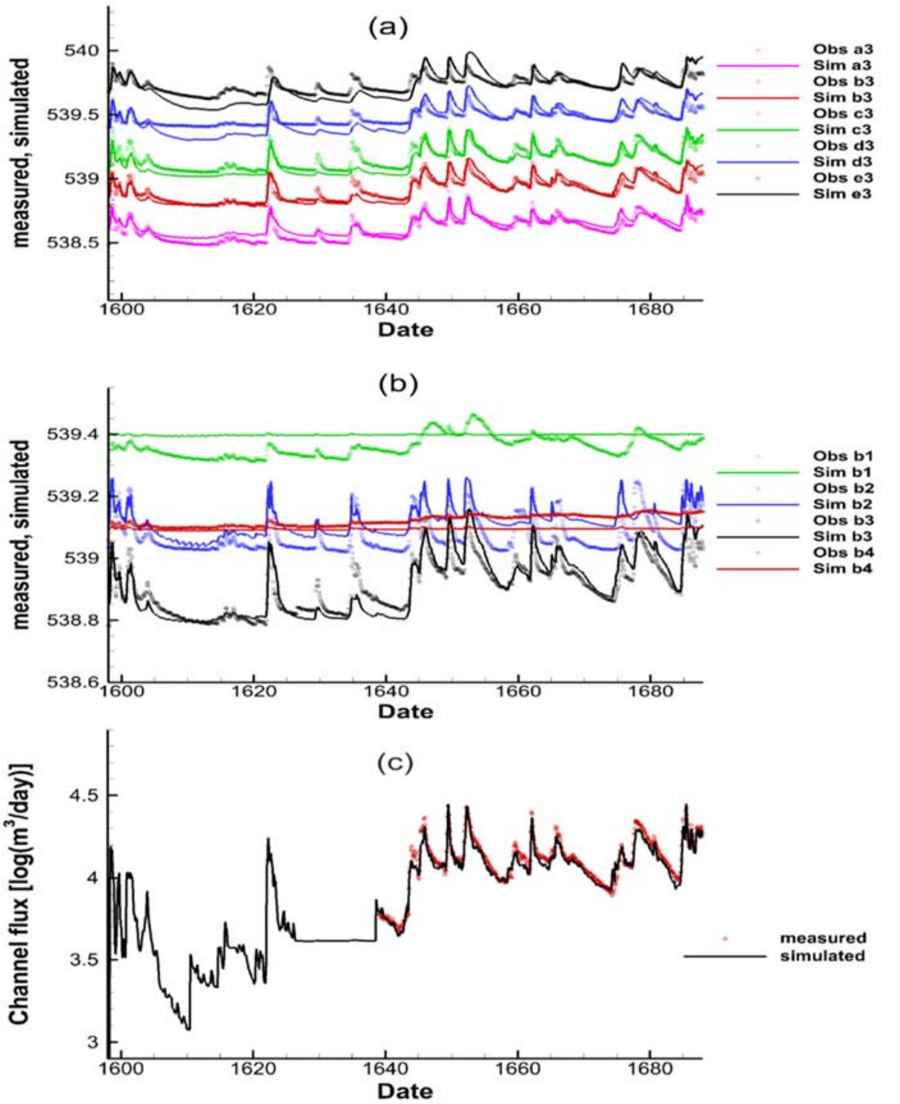

Figure S6: Comparison between the simulated groundwater levels and the measured ones for (a) five wells close to the channel, and for (b) wells along cross-section B, with the well b2 and b3 closer to channel, and b1 and b4 close to side boundaries. (c) Comparison between the simulated and the measured channel fluxes at the outlet.

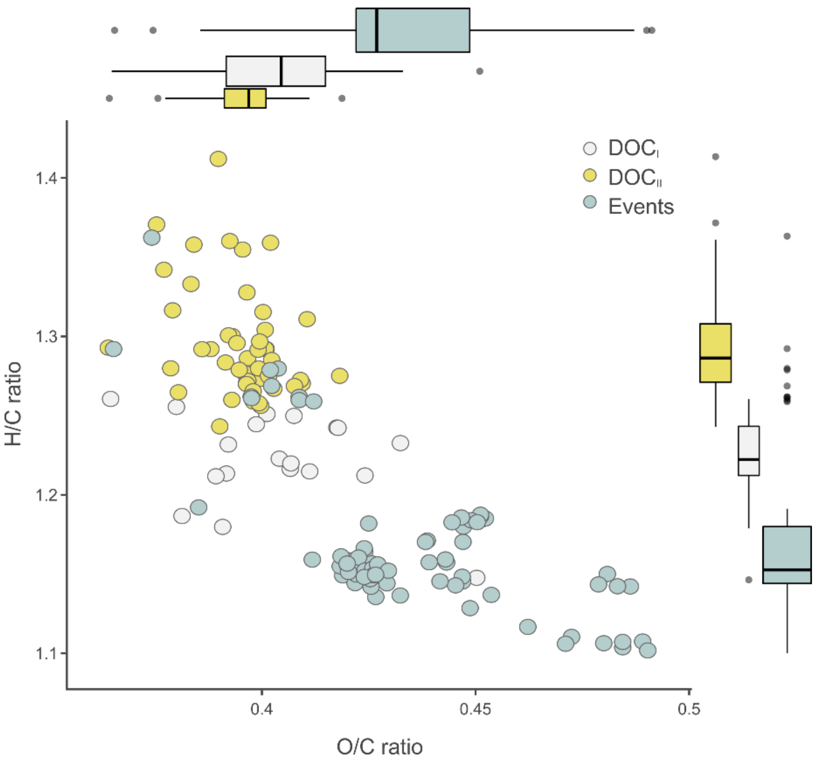

Figure S7: Aggregated van Krevelen plot of all FT-ICR-MS sample of stream (blue) and riparian origin with type DOCI (grey) and DOCII (yellow). Data represent the intensity weighted average (wa) of the molecular H/C and O/C ratios considering all valid MF in these samples (*n* = 142). See also Table S5 for individual values.

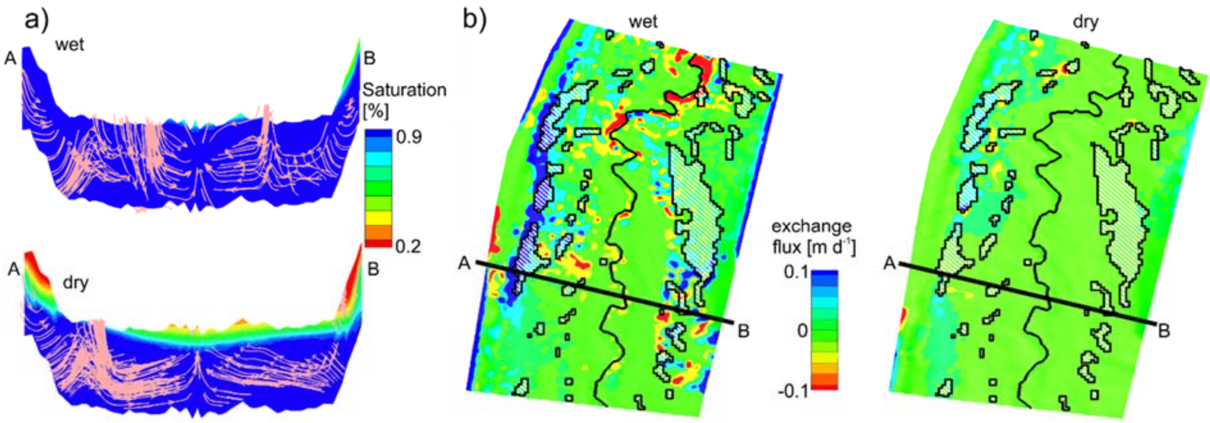

Figure S8: Panels a) & b) show the hydrological condition in the riparian zone for a wet situation on 13 Dec 2017, right after an event and at dry conditions and on 29 Aug 2018, amidst of a longer dry period in summer. a) Subsurface flow paths (pink arrows) along a vertical cross-section along a transect in the modeled riparian zone (indicated by black lines from A to B in (b)). b) Exchange flux (positive values = groundwater exfiltration).

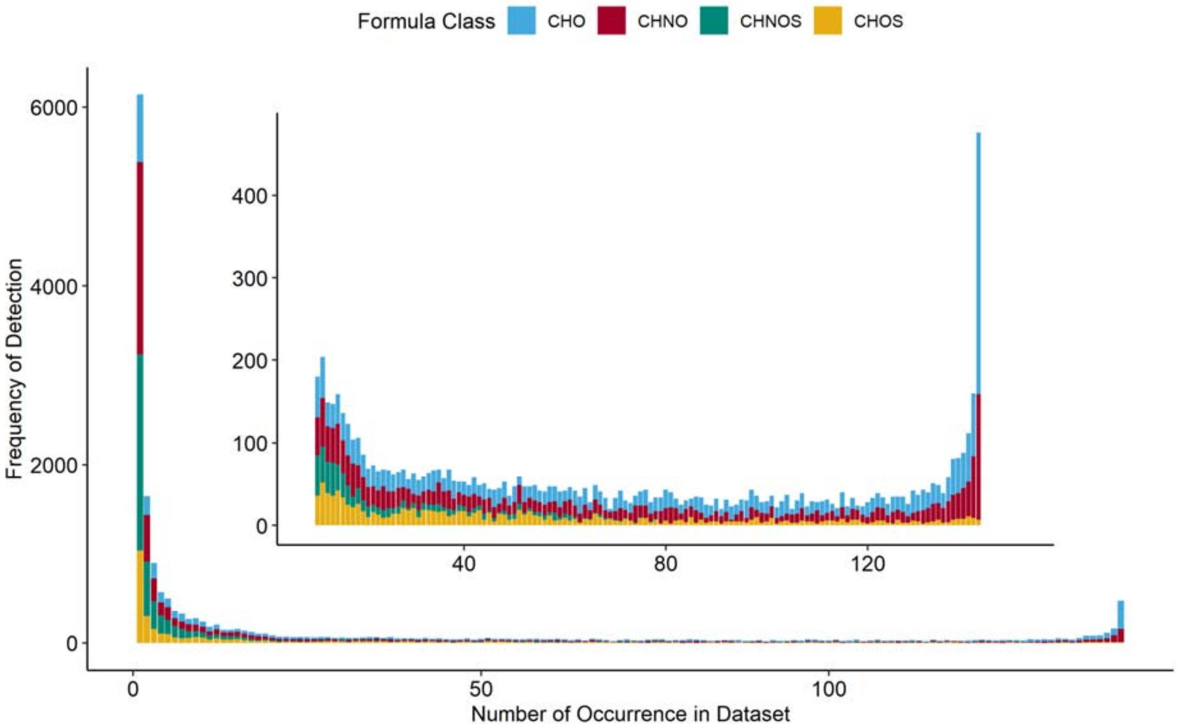

Figure S9: Frequency of detection of molecular formulas in the entire data set (*n* = 142). Formulas classes are represented as CHO (blue), CHNO (red), CHNOS (cyan), and CHOS (yellow) and the inset shows only MF occurring in at least 10 samples.

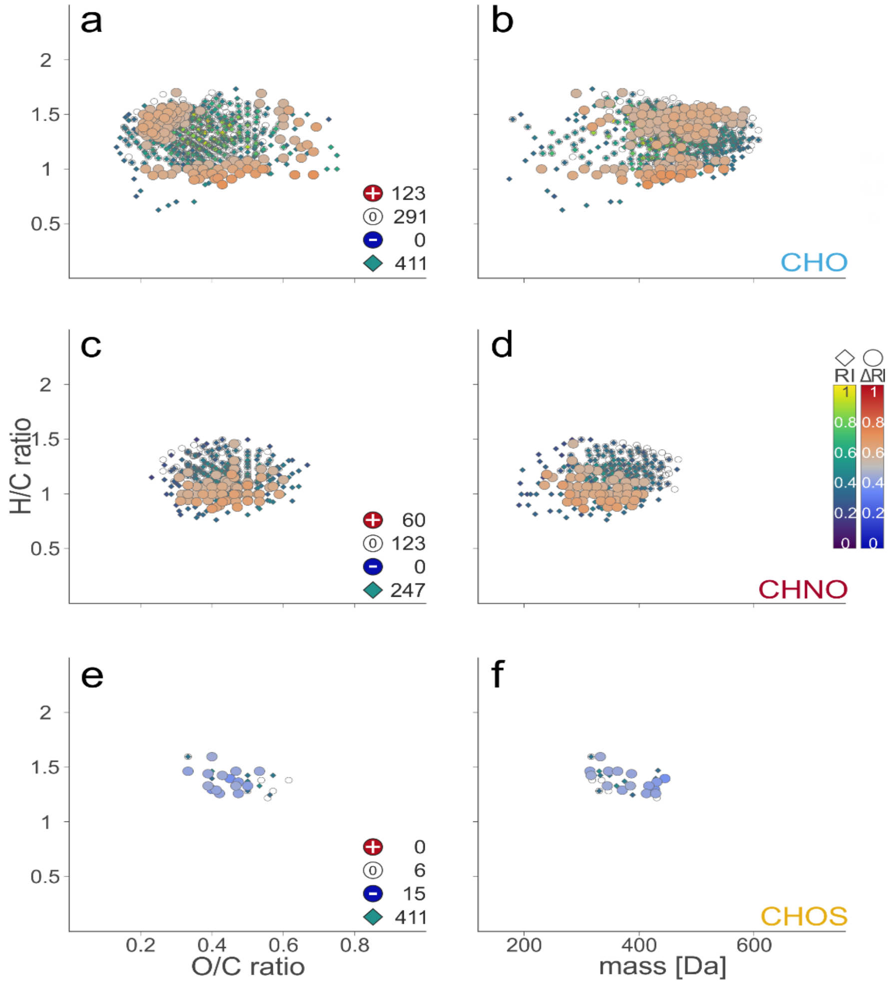

Figure S10: Molecular H/C vs O/C (a, c, e) and H/C vs mass (b, d, f) plot of averaged stream (*n* = 76), DOCI (*n* = 19) and DOCII (*n* = 47) sample groups. Group averages were calculated based on those molecular formulas (MF) which occur in all samples of the respective groups and the normalized peak intensities (reference to the base peak: RI) were used. The data are displayed based on the scaled normalized intensity difference between DOCI and DOCII (circles, ΔRI = RI(DOCI)/[RI(DOCI) + RI(DOCII)], red (+) indicates higher intensity in DOCI, blue (-) higher intensity in DOCII) and split according to formula classes (CHO: a, b; CHNO: c, d; CHOS: e, f). Only those MF are considered, which occur in both group averages (*n* = 618) and MF which were not significantly different between both group averages are displayed as open circles (0). Underlying is distribution of normalized intensity values (RI, diamonds) of the stream group average. See also Table S3 for aggregated values.

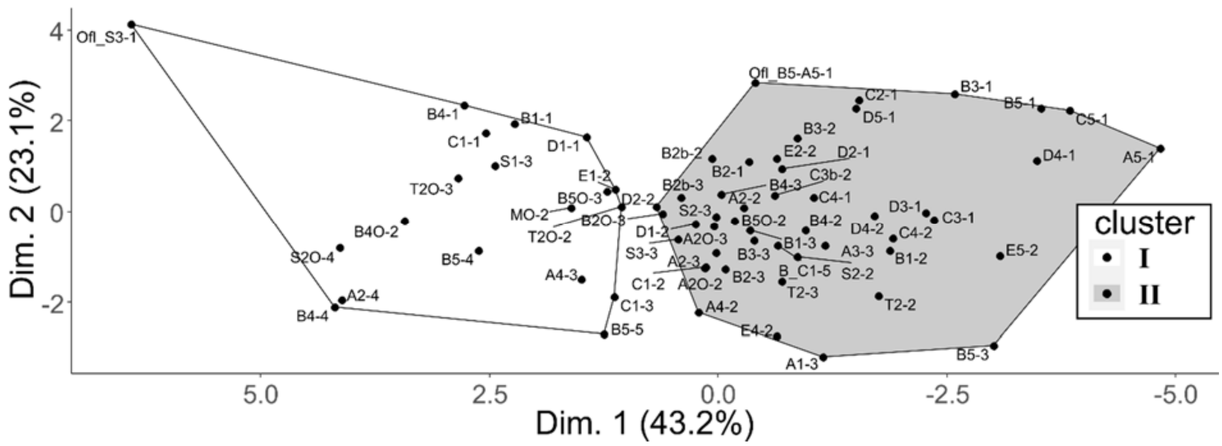

Figure S11: Visualization of the k-means cluster analysis on principal components for riparian samples only.

Additional Reference:

Therrien, R., McLaren, R., Sudicky, E., and Panday, S.: HydroGeoSphere: A three-dimensional numerical model describing fully-integrated subsurface and surface flow and solute transport, Groundwater Simulations Group, University of Waterloo, Waterloo, ON, 2010.