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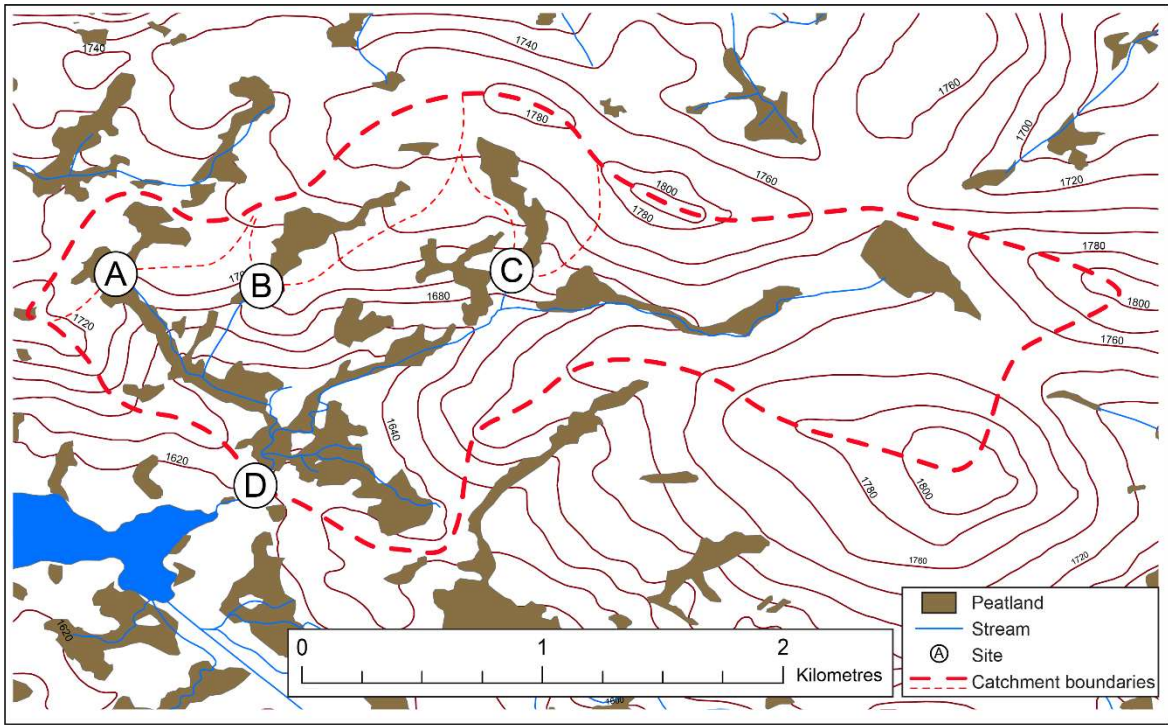
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40 of fit (R^2) scores of *a posteriori* fitted environmental variables fitted to the biofilm community nMDS ordination
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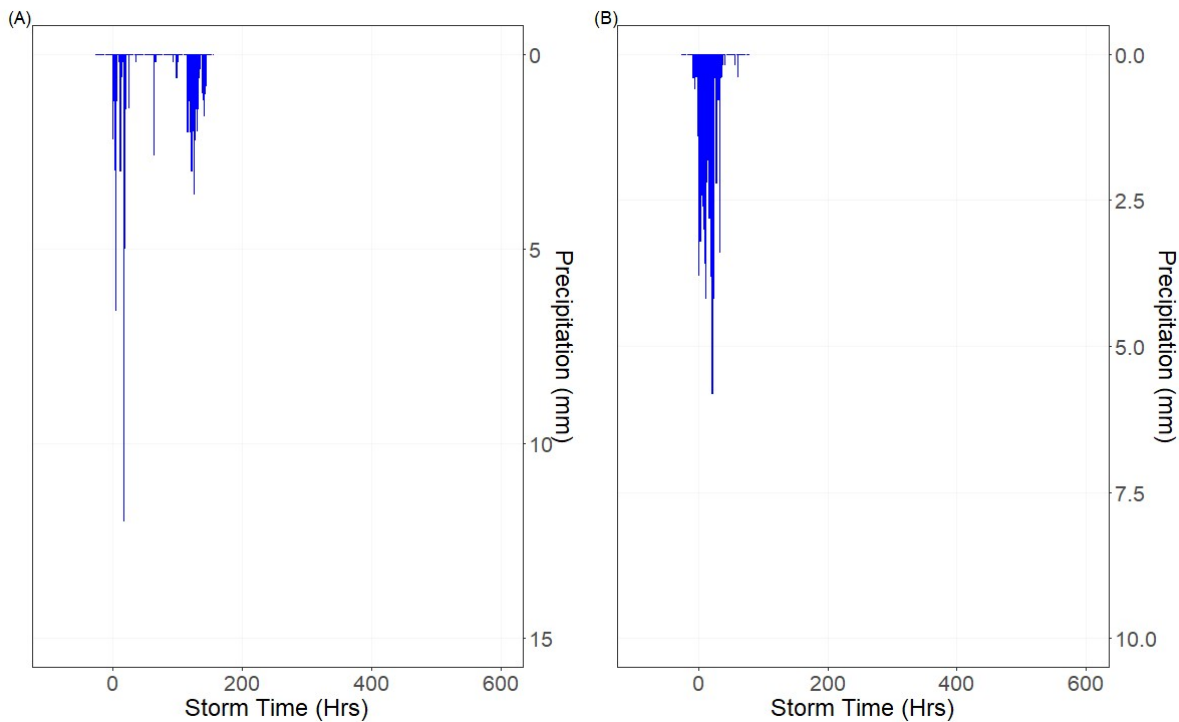
42 **S3. List of Detailed methods**

43 **Biofilm chl- a :** detailed description of chl- a measurement procedure.

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47 **Figure S1:** Map of the Watchbed Creek study location, showing catchment boundaries (red dashed lines), peatland dominated
48 areas (brown) and stream sampling site locations. Adapted from Karis et al. (2016).



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50 **Figure S2:** Half-hourly precipitation depth (mm) totals for (A) Storm Event 1 and (B) Storm Event 2 over storm time.

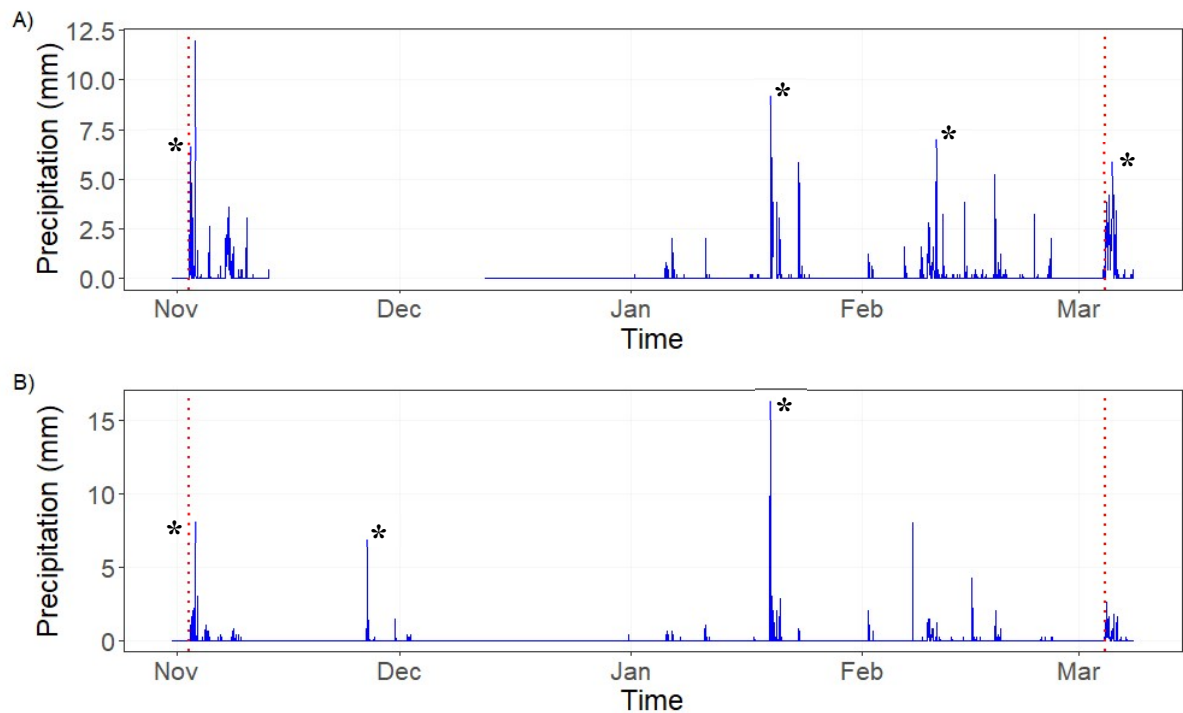


Figure S3: Precipitation depth (mm) recorded at (A) Falls Creek (BOM site: 083084) and (B) Omeo (BOM site: 083090) between 10:00am 31st October 2019 to 10:00am 8th March 2020. The vertical red dashed lines indicate zero time for Storm Event 1 and Storm Event 2. The asterisk ‘*’ indicate high intensity storms where >20mm precipitation fell within the first 24hrs of the storm starting. Precipitation totals are binned into 30-minute intervals. The missing data in the Falls Creek timeseries is due no observational data being available. The Omeo weather station is located approximately 40 km Southeast of the Falls Creek weather station.

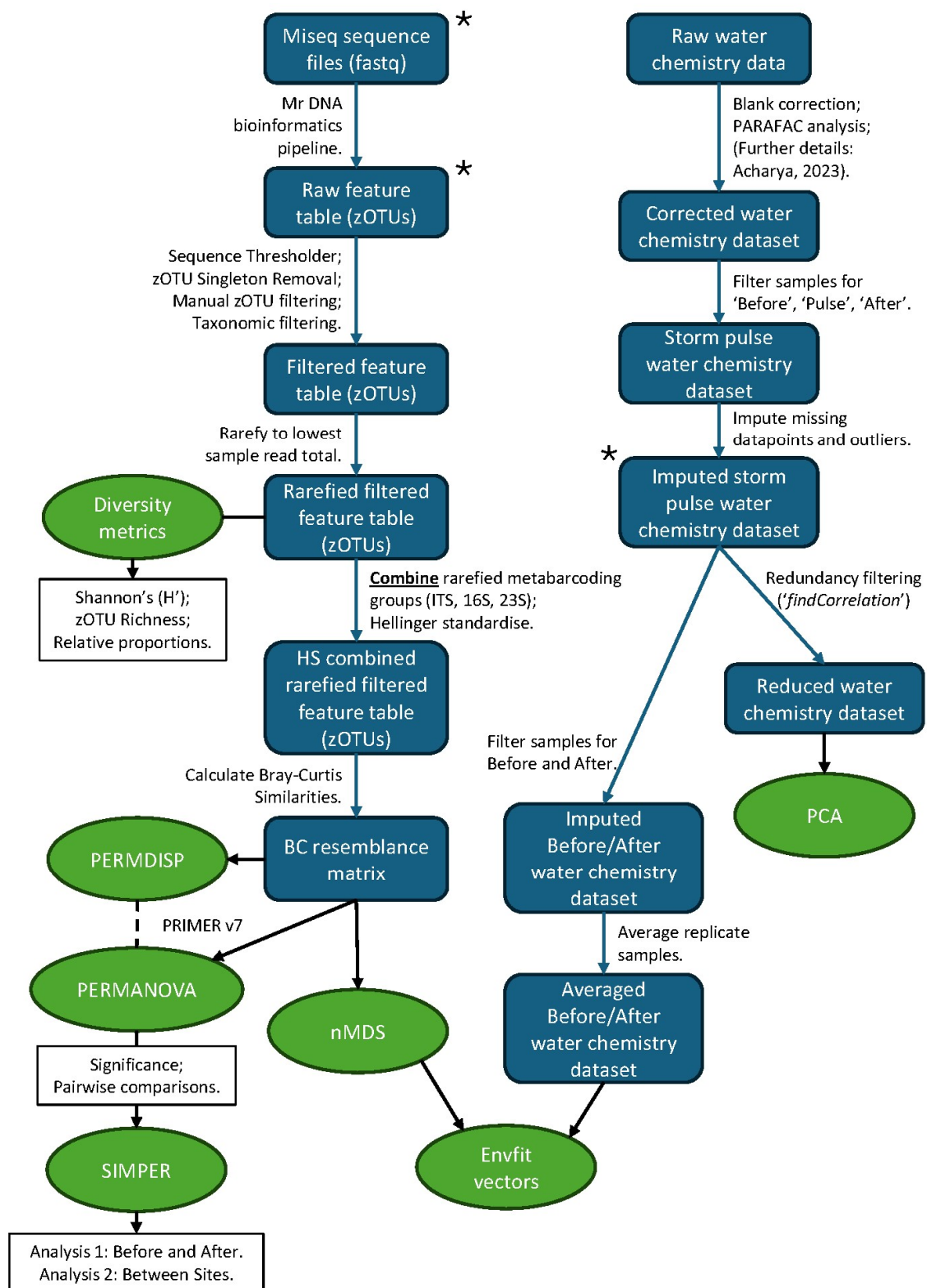


Figure S4: Workflow diagram for the processing and analysis of the water chemistry and biofilm community DNA sequence data for the study. Blue boxes indicate a processing step, and the green ovals indicate an analysis/output (see methods for details). Asterisks (*) indicate available/provided datasets for the study (see data availability statement).

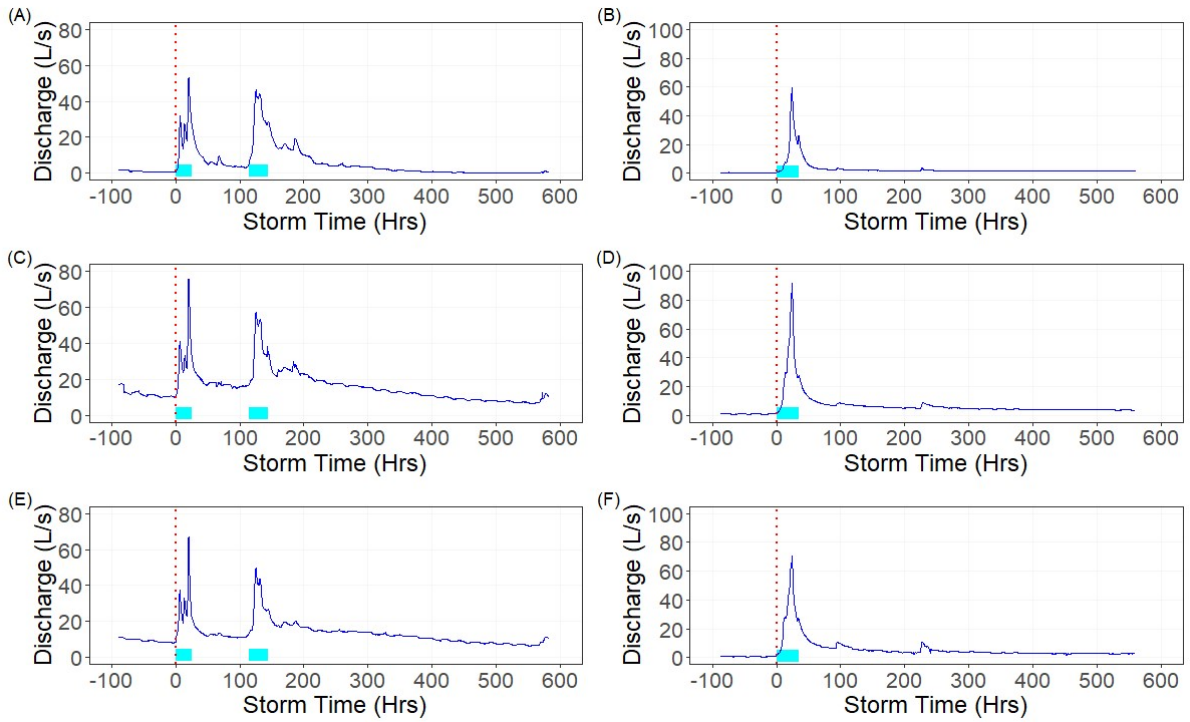


Figure S5: Discharge (L/s) hydrographs over storm time (hours since zero time) of Storm Event 1 (LHS; A, C, E) and Storm Event 2 (RHS; B, D, F) at Site A (A, B), Site B (C, D) and Site C (E, F). The red dashed lines indicate zero time for Storm Event 1 and Storm Event 2, blue marker indicates period of rainfall. Site D had no discharge data available.

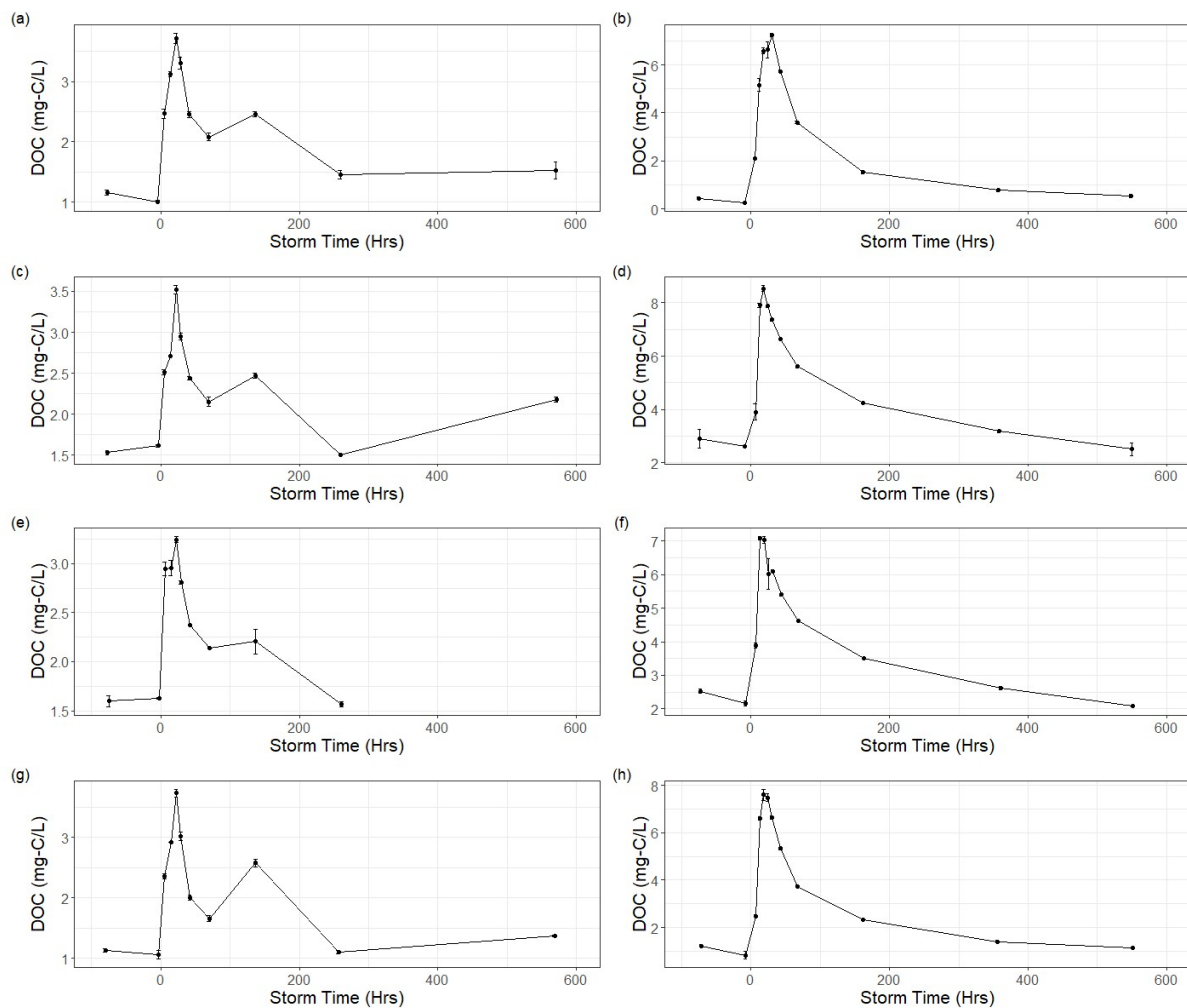


Figure S6: Dissolved organic carbon (DOC) concentration (mg-C/L) over storm time (hours since zero time) of Storm Event 1 (lefthand side; a, c, e, g) and Storm Event 2 (righthand side; b, d, f, h) at sites A (a, b), site B (c, d) site C (e, f) and site D (g, h). All error bars are $\pm 2SE$. Note different scales for DOC. No data available for Storm Event 1 Site C final sample.

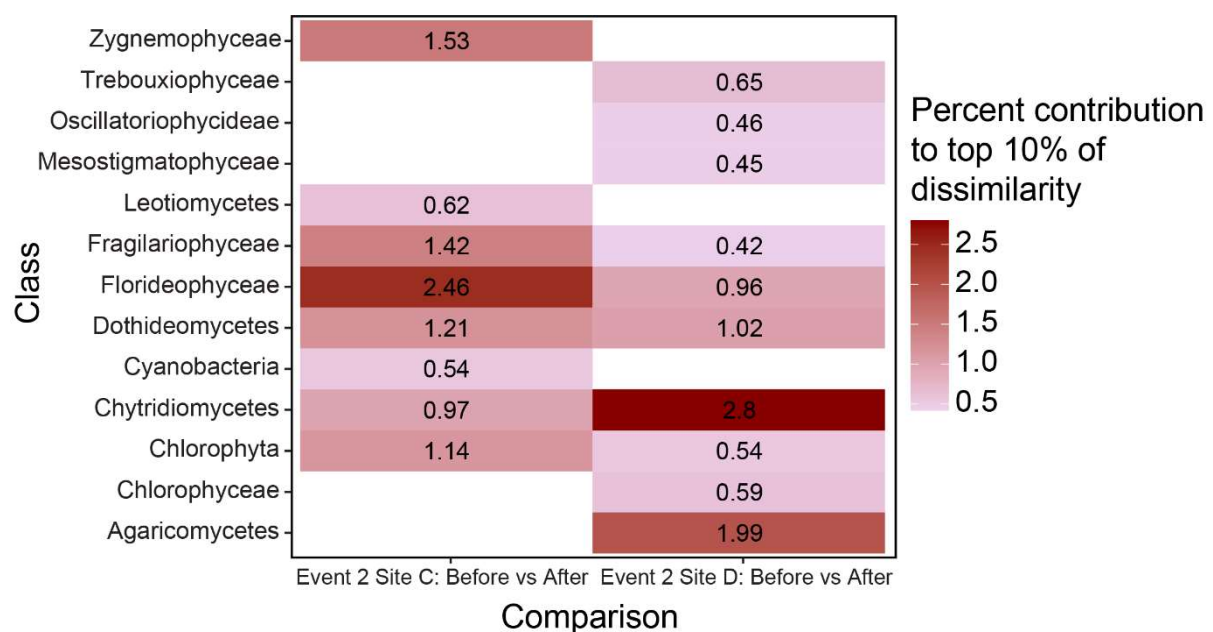


Figure S7: Heatmap of zOTUs contributing to the top 10% of dissimilarity, between biofilm communities at sites C and D before and after Storm Event 2, summed by class. Only statistically significant pairwise comparisons (sites C and D Before and After Event 2), are shown (see Table S9).

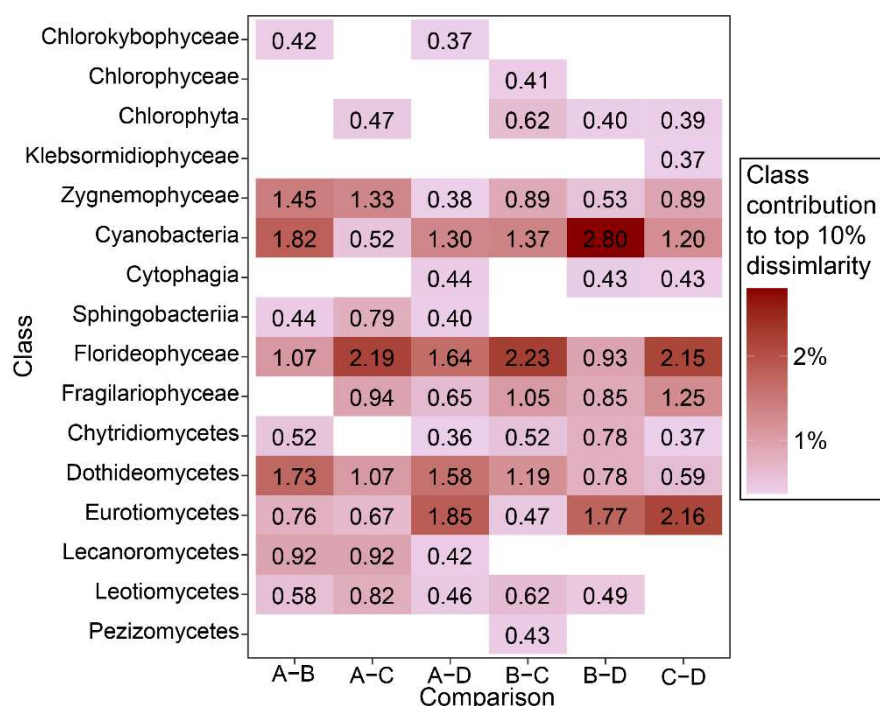


Figure S8: Heatmap of biofilm community zOTUs contributing to the top 10% of dissimilarity between sites only, summed by class.

S5: Supplementary Tables

Table S1: Latitude and longitude of stream sampling locations within the Watchbed Creek catchment used in this study. Also shown are site altitude (m), estimated (sub)catchment areas (km²) and estimated peatland cover (%). Note: Site D corresponds to the total Watchbed Creek catchment area (Lawrence, 1995; Karis et al., 2016).

Site	Latitude	Longitude	Altitude (m)	Catchment Area (km ²)	Peatland Cover (%)
A	-36.86332	147.31402	1701	0.149	16.1
B	-36.86378	147.31833	1700	0.258	17.4
C	-36.8639	147.32818	1685	0.308	16.2
D	-36.870833	147.31875	1625	3.35	17.0

Table S2: DOC sample PARAFAC components, component maximum excitation and emission wavelength, description of component and number of matches in OpenFluor database (www.openfluor.com; Murphy et al., 2014). Superscripts are studies describing that component.

Components	Excitation maximum (nm)	Emission maximum (nm)	Description	OpenFluor matches
C1	<250	425	Fulvic-like ^a	106
C2	250	500	Terrestrial humic-like ^a	83

C3	265	450	Humic-like ^b	8
C4	265	325	Protein-like ^c	66

^a(Santín et al., 2009), ^b(Lu et al., 2022), ^c(Acharya, 2023).

Table S3: Definitions and key references for optical metrics and LC-OCD components measured in this study.

Measurement	Description	Reference
SUVA ₂₅₄	Specific ultra-violet absorbance at 254 nm divided by the concentration of DOC; higher values indicate higher DOC aromaticity.	Weishaar et al. (2003)
S _R	Spectral slope ratio; inversely related to relative molecular weight; lower values indicate higher molecular weight DOC.	Helms et al. (2009)
FI	Fluorescence index; indicates relative source of DOC (microbial or terrestrial); higher values suggest microbially derived DOC (potentially from in-stream sources) and lower values indicate terrestrially derived DOC.	Cory and Mcknight (2005)
HOC	Hydrophobic component	Huber et al. (2011)
BP	Biopolymers ≥10 kDa; consisting of polysaccharides, proteins and/or amino-saccharides	Huber et al. (2011)
HS	Humic substances; consisting of humic and fulvic acids	Huber et al. (2011)
BB	Building blocks between 300 – 500 Da; generally characterised as derivatives/ breakdown products of humic substances	Huber et al. (2011)
LMWA	Low molecular weight acids ≤ 350 Da; consisting of organic acids	Huber et al. (2011)
LMWN	Low molecular weight neutrals; consisting of alcohols, aldehydes, ketones, saccharides and amino acids.	Huber et al. (2011)
Mn	Nominal molecular weight of the HS component, determined by elution time	Huber et al. (2011)

Table S4: Metabarcoding region, target community, forward and reverse primer sequences (5' to 3') and expected DNA fragment base pair (bp) length.

Metabarcoding region	Target Community	Forward Primer Sequence (5' → 3')	Reverse Primer Sequence (5' → 3')	Length (bp)
16S rRNA V4 variable gene region	Bacteria	GTG YCA GCM GCC GCG GTA A ¹	GGA CTA CNV GGG TWT CTA AT ²	~250
23S rRNA	Algae	GGA CAG AAA GAC CCT ATG AA ³	TCA GCC TGT TAT CCC TAG AG ³	~370
ITS1 region	Fungi	CTT GGT CAT TTA GAG GAA GTA A ⁴	GCT GCG TTC TTC ATC GAT GC ⁵	~230

¹(Parada et al., 2016), ²(Apprill et al., 2015), ³(Sherwood and Presting, 2007), ⁴(Gardes and Bruns, 1993), ⁵(White et al., 1990).

96 **Table S5:** Average water quality and DOC characteristic metric values collected at each site (A, B, C, D), before, during the peak of the storm pulse (coinciding with highest DOC concentration)
97 and after Storm Event 1 and Storm Event 2. Error represents $\pm 2SE$.

Event	Event 1											
Site	A			B			C			D		
Storm-time	Before	Pulse	After	Before	Pulse	After	Before	Pulse	After	Before	Pulse	After
pH	5.74 ± 0.00	5.50 ± 0.00	5.02 ± 0.00	5.96 ± 0.00	5.63 ± 0.00	5.40 ± 0.00	6.22 ± 0.00	5.92 ± 0.00	5.83 ± 0.00	6.37 ± 0.00	5.88 ± 0.00	6.19 ± 0.00
EC ($\mu S/cm$)	6.26 ± 0.00	7.85 ± 0.00	6.20 ± 0.00	6.26 ± 0.00	8.23 ± 0.00	5.90 ± 0.00	5.44 ± 0.00	6.70 ± 0.00	5.00 ± 0.00	5.80 ± 0.00	7.48 ± 0.00	5.60 ± 0.00
DOC (mg-C/L)	1.00 ± 0.02	3.72 ± 0.08	1.45 ± 0.07	1.61 ± 0.01	3.52 ± 0.04	1.50 ± 0.01	1.63 ± 0.01	3.24 ± 0.03	1.57 ± 0.03	1.06 ± 0.07	3.73 ± 0.06	1.11 ± 0.03
C:N	34.1 ± 1.39	46.7 ± 1.46	41.8 ± 2.78	47.6 ± 2.72	59.9 ± 4.08	56.1 ± 7.17	48.5 ± 1.94	56.8 ± 1.27	77.5 ± 0.00	39.9 ± 1.80	47.5 ± 2.16	60.5 ± 17.6
Acetic acid (ppm)	3.30E-02 $\pm 4.21E-04$	8.24E-02 $\pm 3.45E-03$	3.34E-02 $\pm 4.50E-03$	2.90E-02 $\pm 1.63E-03$	5.28E-02 $\pm 5.88E-03$	2.79E-02 $\pm 1.76E-03$	3.39E-02 $\pm 5.28E-03$	4.96E-02 $\pm 4.68E-03$	2.68E-02 $\pm 1.42E-03$	2.32E-02 $\pm 2.01E-03$	7.13E-02 $\pm 4.84E-03$	1.95E-02 $\pm 1.86E-03$
Fumaric acid (ppm)	9.38E-04 $\pm 2.16E-04$	2.44E-03 $\pm 6.61E-05$	7.42E-04 $\pm 2.98E-04$	1.35E-03 $\pm 7.95E-05$	2.26E-03 $\pm 4.56E-04$	1.16E-03 $\pm 3.63E-05$	1.06E-03 $\pm 7.95E-05$	1.78E-03 $\pm 1.76E-04$	9.00E-04 $\pm 1.13E-04$	8.00E-04 $\pm 3.82E-05$	1.98E-03 $\pm 1.80E-04$	5.79E-04 $\pm 4.64E-05$
Glycolic acid (ppm)	1.05E-02 $\pm 1.02E-03$	3.06E-02 $\pm 1.37E-03$	9.30E-03 $\pm 3.02E-03$	1.39E-02 $\pm 3.01E-04$	2.77E-02 $\pm 3.78E-03$	1.14E-02 $\pm 9.73E-04$	1.45E-02 $\pm 1.47E-04$	2.32E-02 $\pm 1.53E-03$	1.21E-02 $\pm 4.45E-04$	8.94E-03 $\pm 2.50E-04$	2.59E-02 $\pm 2.30E-03$	7.08E-03 $\pm 1.64E-04$
Glyoxylic acid (ppm)	1.13E-03 $\pm 1.88E-04$	3.18E-03 $\pm 5.19E-04$	1.01E-03 $\pm 2.04E-04$	1.30E-03 $\pm 1.34E-04$	3.05E-03 $\pm 6.50E-04$	1.24E-03 $\pm 5.83E-05$	1.69E-03 $\pm 2.35E-04$	2.74E-03 $\pm 8.33E-06$	1.49E-03 $\pm 8.33E-06$	1.23E-03 $\pm 4.17E-05$	3.56E-03 $\pm 3.32E-04$	1.08E-03 $\pm 1.64E-04$
Malic acid (ppm)	4.86E-03 $\pm 7.37E-04$	1.44E-02 $\pm 4.02E-04$	4.47E-03 $\pm 1.42E-03$	6.30E-03 $\pm 1.01E-04$	1.14E-02 $\pm 1.77E-03$	5.36E-03 $\pm 4.43E-04$	6.45E-03 $\pm 2.84E-04$	9.83E-03 $\pm 1.04E-04$	5.45E-03 $\pm 3.86E-04$	4.44E-03 $\pm 1.66E-04$	1.22E-02 $\pm 1.12E-03$	3.41E-03 $\pm 1.95E-04$
Malonic acid (ppm)	6.40E-03 $\pm 1.23E-03$	1.28E-02 $\pm 1.32E-04$	5.63E-03 $\pm 1.67E-03$	9.87E-03 $\pm 3.38E-04$	1.24E-02 $\pm 2.22E-03$	8.30E-03 $\pm 1.02E-03$	8.93E-03 $\pm 4.59E-04$	1.00E-02 $\pm 1.44E-04$	8.02E-03 $\pm 3.98E-04$	6.06E-03 $\pm 1.91E-04$	1.06E-02 $\pm 1.34E-03$	5.23E-03 $\pm 4.38E-04$
Pyruvic acid (ppm)	3.71E-04 $\pm 2.50E-05$	8.33E-04 $\pm 1.01E-04$	2.75E-04 $\pm 1.01E-04$	3.08E-04 ± 0.00	6.12E-04 $\pm 1.10E-04$	2.46E-04 $\pm 3.82E-05$	5.92E-04 $\pm 7.26E-05$	7.79E-04 $\pm 8.46E-05$	3.83E-04 $\pm 5.77E-05$	2.54E-04 $\pm 4.41E-05$	7.42E-04 $\pm 5.07E-05$	2.04E-04 $\pm 3.00E-05$
Succinic acid (ppm)	2.79E-03 $\pm 5.91E-04$	7.45E-03 $\pm 5.86E-04$	2.79E-03 $\pm 8.55E-04$	4.46E-03 $\pm 7.41E-05$	6.41E-03 $\pm 1.23E-03$	3.65E-03 $\pm 4.44E-04$	4.49E-03 $\pm 7.95E-05$	5.35E-03 $\pm 1.17E-04$	3.73E-03 $\pm 3.15E-04$	3.59E-03 $\pm 1.83E-04$	7.22E-03 $\pm 7.81E-04$	2.65E-03 $\pm 2.83E-04$

%C1	40.4 ±2.24	46.1 ±1.05	46.8 ±1.31	40.1 ±3.82	47.0 ±0.258	46.4 ±0.685	40.7 ±1.19	45.9 ±0.367	46.4 ±0.116	42.5 ±1.68	46.2 ±0.487	46.0 ±0.209
%C2	26.5 ±1.79	28.1 ±0.760	29.8 ±1.58	30.2 ±3.14	29.8 ±0.106	32.3 ±0.958	31.1 ±1.21	30.5 ±0.376	32.4 ±0.198	30.0 ±1.26	29.4 ±0.315	30.3 ±0.279
%C3	13.0 ±0.969	14.3 ±0.289	14.6 ±0.942	13.4 ±1.27	15.6 ±0.0643	14.7 ±0.627	13.8 ±0.428	16.0 ±0.250	14.9 ±0.102	14.3 ±0.579	15.9 ±0.192	15.4 ±0.0778
%C4	20.1 ±4.96	11.5 ±2.10	8.85 ±3.83	16.4 ±8.24	7.67 ±0.368	6.65 ±2.24	14.4 ±2.81	7.56 ±0.968	6.23 ±0.332	13.2 ±3.51	8.41 ±0.968	8.21 ±0.532
Mn	642 ±45.2	846 ±33.8	682 ±26.7	708 ±32.5	882 ±24.7	757 ±27.9	750 ±5.93	862 ±46.5	724 ±0.00	701 ±28.8	765 ±7.69	691 ±11.8
BB	10.3 ±3.34	9.18 ±0.851	11.7 ±0.679	11.4 ±2.07	9.52 ±0.564	11.1 ±0.617	11.4 ±0.615	9.49 ±1.46	11.2 ±0.00	9.81 ±1.94	9.58 ±0.239	11.5 ±0.843
BP	7.38 ±0.838	5.42 ±0.372	5.60 ±2.23	2.50 ±1.59	2.49 ±0.722	1.34 ±0.401	2.75 ±0.267	2.82 ±0.261	1.87 ±0.00	2.73 ±0.879	4.29 ±0.984	2.60 ±0.513
HOC	20.7 ±11.5	20.5 ±1.46	13.1 ±2.40	12.3 ±0.807	20.6 ±0.552	14.8 ±10.9	14.3 ±2.81	19.6 ±0.322	12.8 ±0.00	23.1 ±4.72	15.3 ±0.106	13.9 ±3.24
HS	54.4 ±2.01	60.3 ±2.13	61.7 ±3.24	65.2 ±1.16	63.5 ±0.349	63.2 ±6.21	63.7 ±2.69	64.2 ±1.15	67.4 ±0.00	58.2 ±2.59	66.4 ±0.866	63.1 ±3.66
LMWN	7.28 ±7.42	4.59 ±0.306	7.96 ±1.28	12.0 ±5.15	3.89 ±0.763	9.62 ±4.60	7.83 ±1.51	3.82 ±0.158	6.76 ±0.00	6.13 ±2.98	4.49 ±0.372	8.90 ±0.812
FI	1.47 ±4.28E-02	1.47 ±3.72E-02	1.43 ±3.55E-02	1.38 ±6.05E-02	1.46 ±2.46E-02	1.36 ±3.58E-02	1.40 ±1.24E-02	1.46 ±5.44E-03	1.36 ±0.00	1.42 ±1.37E-02	1.47 ±1.81E-02	1.41 ±1.59E-02
S _R	0.686 ±2.77E-02	0.679 ±6.31E-03	0.762 ±1.88E-02	0.633 ±2.22E-02	0.641 ±4.71E-03	0.698 ±1.72E-02	0.668 ±4.58E-02	0.661 ±4.83E-03	0.718 ±2.72E-02	0.711 ±4.93E-02	0.671 ±4.50E-03	0.759 ±2.03E-02
SUVA ₂₅₄	4.72 ±0.0897	4.42 ±0.183	4.73 ±0.254	4.85 ±0.468	4.58 ±0.114	4.75 ±0.0757	4.79 ±0.0481	4.36 ±0.0872	4.36 ±0.00	4.85 ±0.129	4.43 ±0.147	4.52 ±0.250

98

99 *Table S5 continued:*

Event	Event 2											
Site	A			B			C			D		
Storm-time	Before	Pulse	After	Before	Pulse	After	Before	Pulse	After	Before	Pulse	After
pH	5.27 ±0.00	5.24 ±0.00	5.72 ±0.01	5.65 ±0.00	5.39 ±0.01	6.03 ±0.01	5.63 ±0.00	5.64 ±0.01	6.20 ±0.01	5.99 ±0.00	5.66 ±0.00	6.54 ±0.01

EC (μ S/cm)	6.73 ± 0.00	9.44 ± 0.00	6.16 ± 0.01	7.22 ± 0.00	10.7 ± 0.01	5.57 ± 0.01	4.73 ± 0.00	7.76 ± 0.00	3.90 ± 0.01	7.31 ± 0.00	8.68 ± 0.01	5.35 ± 0.02
DOC (mg-C/L)	0.248 ± 0.01	7.26 ± 0.07	0.775 ± 0.06	2.63 ± 0.02	8.54 ± 0.11	3.18 ± 0.05	2.16 ± 0.08	7.08 ± 0.04	2.62 ± 0.05	0.83 ± 0.17	7.59 ± 0.24	1.40 ± 0.06
C:N	37.0 ± 15.5	53.8 ± 0.50	39.4 ± 0.00	52.5 ± 5.02	67.4 ± 3.39	62.8 ± 1.65	45.9 ± 1.29	60.0 ± 2.52	52.4 ± 5.48	36.7 ± 2.68	53.6 ± 0.60	46.3 ± 2.22
Acetic acid (ppm)	2.36E-02 ± 1.41 E-03	6.52E-02 ± 2.15 E-02	1.57E-02 ± 8.72 E-03	1.42E-02 ± 8.44 E-03	2.56E-02 ± 1.66 E-02	4.88E-02 ± 1.03 E-02	3.02E-02 ± 7.88 E-03	5.77E-02 ± 3.76 E-03	1.85E-02 ± 1.82 E-02	3.41E-02 ± 9.30 E-03	7.05E-02 ± 1.20 E-02	1.74E-02 ± 6.48 E-03
Fumaric acid (ppm)	1.92E-04 ± 1.76 E-04	1.42E-03 ± 6.37 E-04	3.13E-04 ± 9.28 E-05	2.08E-04 ± 1.40 E-04	9.42E-04 ± 3.69 E-04	1.08E-03 ± 1.17 E-04	4.54E-04 ± 1.61 E-04	8.96E-04 ± 1.88 E-04	3.21E-04 ± 4.49 E-04	3.83E-04 ± 6.51 E-05	1.32E-03 ± 2.25 E-04	2.71E-04 ± 1.16 E-04
Glycolic acid (ppm)	1.78E-03 ± 6.75 E-04	2.51E-02 ± 8.07 E-03	2.76E-03 ± 9.31 E-04	3.98E-03 ± 1.60 E-03	2.14E-02 ± 5.21 E-03	1.21E-02 ± 2.16 E-03	7.64E-03 ± 1.83 E-03	2.05E-02 ± 3.18 E-03	4.06E-03 ± 1.25 E-03	5.12E-03 ± 1.41 E-03	2.67E-02 ± 4.86 E-03	2.78E-03 ± 6.71 E-04
Glyoxylic acid (ppm)	1.21E-04 ± 8.33 E-06	5.47E-03 ± 5.56 E-04	6.04E-04 ± 2.67 E-04	1.52E-03 ± 2.81 E-04	7.74E-03 ± 4.50 E-04	3.93E-03 ± 5.09 E-04	2.34E-03 ± 4.05 E-04	8.38E-03 ± 8.22 E-04	3.26E-03 ± 3.22 E-03	8.71E-04 ± 1.44 E-05	6.57E-03 ± 7.40 E-04	1.01E-03 ± 1.80 E-04
Malic acid (ppm)	1.69E-03 ± 6.00 E-04	9.58E-03 ± 3.76 E-03	2.21E-03 ± 7.78 E-04	2.36E-03 ± 7.73 E-04	8.04E-03 ± 2.03 E-03	6.52E-03 ± 4.01 E-04	3.73E-03 ± 1.59 E-03	7.29E-03 ± 1.50 E-03	1.57E-03 ± 2.75 E-03	3.24E-03 ± 9.34 E-04	9.13E-03 ± 1.87 E-03	1.73E-03 ± 4.23 E-04
Malonic acid (ppm)	1.05E-03 ± 3.15 E-04	1.12E-02 ± 4.50 E-03	1.91E-03 ± 7.89 E-04	2.83E-03 ± 6.93 E-04	9.64E-03 ± 2.20 E-03	7.41E-03 ± 1.59 E-03	4.86E-03 ± 1.10 E-03	8.18E-03 ± 1.13 E-03	2.66E-03 ± 9.90 E-04	3.40E-03 ± 1.11 E-03	1.19E-02 ± 2.25 E-03	1.88E-03 ± 3.69 E-04
Pyruvic acid (ppm)	1.14E-04 ± 1.15 E-04	1.51E-03 ± 1.31 E-04	2.50E-04 ± 1.80 E-04	4.54E-04 ± 1.42 E-04	1.87E-03 ± 1.30 E-04	9.42E-04 ± 1.52 E-04	5.13E-04 ± 3.47 E-04	1.54E-03 ± 2.21 E-04	2.38E-04 ± 2.05 E-04	4.33E-04 ± 1.13 E-04	2.71E-03 ± 3.06 E-04	3.04E-04 ± 6.51 E-05
Succinic acid (ppm)	0.00 ± 0.00	5.42E-03 ± 3.90 E-03	1.19E-03 ± 1.75 E-03	4.58E-04 ± 6.11 E-04	3.67E-03 ± 1.43 E-03	3.62E-03 ± 6.91 E-04	1.51E-03 ± 1.78 E-03	3.45E-03 ± 2.24 E-04	0.00 ± 0.00	1.74E-03 ± 1.29 E-03	5.23E-03 ± 1.13 E-03	3.25E-04 ± 6.50 E-04
%C1	41.6 ± 3.85	47.2 ± 1.46	44.1 ± 1.19	46.7 ± 0.131	51.0 ± 0.0678	46.2 ± 0.301	44.3 ± 0.838	48.3 ± 0.149	44.3 ± 1.20	42.9 ± 1.83	47.0 ± 2.78	45.2 ± 0.774
%C2	15.6 ± 1.99	25.9 ± 0.935	25.8 ± 0.925	31.8 ± 0.0896	26.0 ± 0.0364	32.4 ± 0.213	31.7 ± 1.01	26.2 ± 0.118	31.2 ± 1.24	24.0 ± 1.56	25.1 ± 1.43	29.8 ± 0.537
%C3	11.0 ± 1.33	15.6 ± 0.508	14.8 ± 0.598	15.6 ± 0.0842	17.0 ± 0.0202	15.9 ± 0.166	15.2 ± 0.584	17.1 ± 0.0564	13.7 ± 2.23	13.5 ± 0.921	16.4 ± 1.02	15.5 ± 0.244
%C4	31.8 ± 7.04	11.3 ± 2.90	15.3 ± 2.71	5.94 ± 0.305	5.92 ± 0.0443	5.52 ± 0.680	8.82 ± 2.43	8.41 ± 0.282	10.8 ± 4.32	19.6 ± 4.30	11.4 ± 5.23	9.48 ± 1.51

Mn	495 ±26.2	693 ±22.7	565 ±0.00	739 ±7.51	694 ±14.3	702 ±12.3	811 ±6.77	718 ±11.0	744 ±39.3	708 ±4.00	704 ±14.2	672 ±18.9
BB	10.4 ±1.07	8.30 ±0.783	8.81 ±0.00	10.5 ±0.401	8.56 ±0.219	9.12 ±0.333	11.1 ±0.278	9.31 ±0.337	8.44 ±0.660	11.5 ±0.234	9.17 ±0.254	9.44 ±0.825
BP	11.9 ±0.801	3.85 ±0.317	9.43 ±0.00	2.31 ±1.26	2.22 ±0.688	1.80 ±1.77	2.58 ±0.0994	3.19 ±0.669	0.853 ±0.603	6.61 ±0.354	3.72 ±0.528	3.27 ±0.420
HOC	29.0 ±4.41	20.5 ±0.192	26.2 ±0.00	15.0 ±3.30	17.7 ±0.688	21.4 ±1.51	14.2 ±1.62	16.6 ±0.530	24.6 ±3.71	14.3 ±1.84	19.2 ±0.361	24.0 ±1.43
HS	34.3 ±3.04	63.2 ±0.296	49.6 ±0.00	66.2 ±4.10	67.3 ±0.242	63.6 ±1.36	66.8 ±1.27	66.3 ±0.802	63.4 ±0.296	58.4 ±2.24	63.8 ±0.721	58.0 ±0.714
LMWN	14.4 ±1.36	4.17 ±0.133	5.97 ±0.00	5.94 ±1.38	4.20 ±0.210	4.02 ±0.306	5.37 ±0.0714	4.60 ±0.303	2.69 ±2.15	9.22 ±0.507	4.13 ±0.0314	5.25 ±1.15
FI	1.35 ±3.25E-02	1.52 ±3.16E-02	1.56 ±0.00	1.41 ±1.71E-02	1.56 ±1.95E-02	1.44 ±1.37E-03	1.41 ±1.27E-02	1.54 ±2.20E-02	1.41 ±1.94E-02	1.43 ±3.93E-02	1.53 ±1.38E-02	1.47 ±3.61E-02
S _R	0.793 ±1.73E-01	0.680 ±1.86E-02	0.785 ±2.70E-03	0.618 ±1.09E-02	0.656 ±1.92E-02	0.683 ±4.51E-02	0.706 ±2.21E-02	0.645 ±3.05E-03	0.717 ±2.74E-02	0.685 ±2.33E-02	0.662 ±2.70E-02	0.731 ±4.05E-02
SUVA ₂₅₄	3.95 ±0.307	4.03 ±0.0757	4.21 ±0.00	4.31 ±0.209	3.98 ±0.0636	4.45 ±0.103	4.27 ±0.194	3.85 ±0.0611	4.52 ±0.127	3.86 ±0.0529	3.92 ±0.0371	4.42 ±0.416

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Table S6: List of water quality (WQ) and dissolved organic carbon (DOC) characteristic parameters identified by the function ‘findCorrelation’ with high ($r \geq 0.7$) linear correlation in the WQ and DOC dataset and excluded from the principal component analysis (PCA). For each redundant (and subsequently excluded) parameter, the name, linear correlation and direction of relationship of the most correlated parameter retained in PCA analysis to the redundant parameter is listed. In total, 13 parameters were identified by ‘findCorrelation’ at a cut off value of 0.7 and were excluded from the PCA.

Redundant Parameter	Correlated parameter in PCA	Pearson’s correlation coefficient (r)	Correlation relationship
Glycolic acid	Acetic acid	0.857	Positive
Malonic acid	Acetic acid	0.768	Positive
Glyoxylic acid	Conductivity	0.622	Positive
Malic acid	Acetic acid	0.847	Positive
Pyruvic acid	Conductivity	0.703	Positive
Succinic acid	Acetic acid	0.794	Positive
Fumaric acid	Acetic acid	0.776	Positive
DOC	Conductivity	0.760	Positive
%C1	C:N	0.597	Positive
%C3	C:N	0.563	Positive
%C4	%C2	-0.786	Negative
HS	%C2	0.711	Positive
BP	%C2	-0.760	Negative

Table S7: Baseflow and maximum discharge (L/s), dissolved organic carbon (DOC) concentration (mg-C/L) and DOC loads (mg-C/s) measured at sites A, B, C and D during Storm Event 1 and Storm Event 2. Baseflow discharge was measured within 30 minutes prior to storm zero time (zero storm time taken as the commencement of rainfall). Stream DOC loads (mg-C/s) have been calculated using linear interpolated stream discharge values and average DOC concentration (mg-C/L). Uncertainties in discharge and in DOC loads (upper, lower) are based on a nominal error of ± 5 mm in stage readings. All other error ranges are $\pm 2SE$. No (*n.d.*) discharge and DOC load data was available for Site D.

Storm Event	Site	Discharge (L/s)		Discharge (L/s)		DOC (mg-C/L)		DOC load (mg-C/s)		DOC load (mg-C/s)	
		Baseflow		Maximum		Baseflow		Baseflow		Maximum	
1	A	0.639	(+0.186, -0.158)	53.1	(+2.47, -2.40)	1.00 $\pm$ 0.02	3.72 $\pm$ 0.08	0.651	(+0.188, -0.160)	155	(+7.96, -7.72)
	B	10.4	(+0.942, -0.894)	75.5	(+3.05, -2.97)	1.61 $\pm$ 0.01	3.52 $\pm$ 0.04	16.7	(+1.51, -1.43)	177	(+8.42, -8.19)
	C	8.37	(+0.827, -0.781)	66.9	(+2.83, -2.76)	1.63 $\pm$ 0.01	3.24 $\pm$ 0.03	13.3	(+1.33, -1.25)	110	(+5.89, -5.71)
	D	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	1.06 $\pm$ 0.07	3.73 $\pm$ 0.06	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>
2	A	0.528	(+0.167, -0.140)	59.5	(+2.64, -2.57)	0.248 $\pm$ 0.01	7.26 $\pm$ 0.07	0.111	(+0.038, -0.031)	393	(+17.5, -17.0)
	B	1.30	(+0.280, -0.248)	91.9	(+3.42, -3.35)	2.63 $\pm$ 0.02	8.54 $\pm$ 0.11	2.41	(+0.600, -0.522)	712	(+26.7, -26.1)
	C	1.19	(+0.265, -0.234)	70.7	(+2.93, -2.86)	2.16 $\pm$ 0.08	7.08 $\pm$ 0.04	1.38	(+0.402, -0.342)	362	(+16.0, -15.6)
	D	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	0.83 $\pm$ 0.17	7.59 $\pm$ 0.24	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

Table S8: Variable loading scores and percent contribution (%) to principal components (PCs). Principal component analysis (PCA) was conducted using water quality and DOC characteristics measured from water samples collected from sites A – D, before, during (at maximum DOC concentration – the pulse) and after Storm Events 1 and 2. Note PCA analysis was conducted on the reduced water quality and dissolved organic carbon dataset (see table S4). Variable contributions to PCs where the contribution was greater than the average expected contribution (8.33%), are bolded. Data for the first two PCs are shown.

Variable	PC1 (% contribution)	PC2 (% contribution)
pH	0.387 (4.36%)	0.236 (1.95%)
Conductivity	-0.803 (18.8%)	-0.019 (0.01%)
Acetic acid	-0.615 (11.0%)	0.321 (3.62%)
%C2	0.395 (4.54%)	0.817 (23.4%)
S _R	0.292 (2.48%)	-0.636 (14.2%)
HOC	-0.342 (3.40%)	-0.472 (7.82%)
BB	0.720 (15.1%)	0.011 (0.01%)
LMWN	0.564 (9.26%)	-0.487 (8.31%)
SUVA ₂₅₄	0.644 (12.1%)	0.333 (3.88%)
Mn	-0.074 (0.16%)	0.854 (25.5%)
C:N	-0.149 (0.65%)	0.569 (11.3%)
FI	-0.792 (18.2%)	0.009 (0.01%)

Table S9: Average Shannon diversity index (H') ±1SE of biofilm community groups (algae, bacteria and fungi) before and after Storm Event 1 and Storm Event 2 at each site.

Group	Event	Site	Before (H')		After (H')	
Algae	1	A	3.70	(±0.03)	3.77	(±0.09)
		B	2.97	(±0.20)	2.78	(±0.22)
		C	3.16	(±0.14)	2.90	(±0.24)
		D	3.93	(±0.03)	3.33	(±0.34)
	2	A	3.83	(±0.05)	3.24	(±0.17)
		B	2.54	(±0.25)	2.71	(±0.27)
		C	3.68	(±0.12)	3.13	(±0.05)
		D	3.94	(±0.11)	3.70	(±0.39)
Bacteria	1	A	4.55	(±0.04)	4.51	(±0.16)
		B	4.29	(±0.45)	4.50	(±0.08)
		C	3.75	(±0.25)	4.11	(±0.40)
		D	4.44	(±0.21)	4.14	(±0.21)
	2	A	4.74	(±0.13)	4.47	(±0.15)

		B	4.35	(±0.15)	4.23	(±0.08)
		C	4.89	(±0.21)	3.93	(±0.11)
		D	4.98	(±0.08)	4.77	(±0.23)
Fungi	1	A	2.38	(±0.19)	1.94	(±0.20)
		B	3.54	(±0.21)	3.31	(±0.74)
		C	3.36	(±0.66)	4.07	(±0.70)
		D	2.94	(±0.22)	2.88	(±0.77)
	2	A	2.54	(±0.07)	2.59	(±0.34)
		B	2.86	(±0.21)	2.97	(±0.34)
		C	3.20	(±0.37)	4.59	(±0.08)
		D	4.01	(±0.08)	4.00	(±0.33)

Table S10: Three-way fully factorial PERMANOVA results. Significant permutation (Perm) p-values are bolded; α cut-off score = 0.05. Type 1 sum of squares (sequential) was used to partition variation. Site was treated as a random factor (four levels), Event and Storm-time were treated as fixed factors (2 levels each). The order of fit did not change the statistical significance of terms within the model. Additionally, the square root of the estimates of the components of variation (ECV) in units of Bray-Curtis dissimilarity, are provided for each term in the model. The square root of ECV provides an estimate of the variation attributed to each term in the model in the units of the distance measure chosen for the PERMANOVA test.

Source of Variation	df	SS	Pseudo F score	P value (Perm)	Sq. root ECV
Storm-time	1	1674.7	1.21	0.3778	3.488
Site	3	34459	17.2	0.0001	30.03
Event	1	7132.2	2.72	0.0718	13.71
Storm-time *Site	3	4148.1	2.07	0.0001	10.92
Storm-time *Event	1	1920.3	1.76	0.2106	8.325
Site*Event	3	7869.5	3.93	0.0001	18.05
Storm-time *Site*Event	3	3266	1.63	0.0022	11.84
Residual	32	21373			25.84
Total	47	81843			

Table S11: PERMDISP results for the three factor PERMANOVA test. Non-significant results indicate that the groups displayed homoscedasticity (homogeneity of multivariate dispersion). P-value α cut off score = 0.05.

P-value	F-score
0.176	4.65

Table S12: PERMANOVA post-hoc pairwise comparison results between the Storm-time factor levels ‘Before’ and ‘After’, within the factors Site and Event following the significant three-way interaction in main PERMANOVA test. Monte Carlo (MC) p-value estimates and pseudo-t scores are shown. Significant p-values are bolded. P-value α cut-off score = 0.05.

Pairwise comparisons	Pseudo-t score	p-value (MC)
Site A Event 1: Before vs After	1.35	0.184
Site B Event 1: Before vs After	1.01	0.412
Site C Event 1: Before vs After	1.18	0.278
Site D Event 1: Before vs After	1.08	0.356
Site A Event 2: Before vs After	0.98	0.450
Site B Event 2: Before vs After	1.25	0.231
Site C Event 2: Before vs After	2.42	0.016
Site D Event 2: Before vs After	2.19	0.028

Table S13: Correlation (Pearson’s r) scaled vector cosines, permutational p-values of fitted vectors and goodness of fit (R^2) scores of *a posteriori* fitted environmental variables fitted to the biofilm community nMDS ordination using the *vegan* function ‘envfit’. Statistically significantly correlated variables (α cut-off = 0.05) to biofilm community nMDS ordination axes are bolded. Note Pyruvic acid displayed borderline statistical significance.

Variable	nMDS1	nMDS2	P value (perm)	R^2
pH	-0.359	-0.653	0.001	0.556
DOC (dissolved organic carbon)	0.389	-0.393	0.001	0.306
Conductivity	0.063	0.429	0.009	0.188
HOC (hydrophobic organic carbon)	-0.152	0.207	0.209	0.066
BP (biopolymer)	-0.117	0.618	0.001	0.396
HS (humic substance)	0.152	-0.513	0.001	0.286
BB (building block)	-0.014	0.063	0.911	0.004
LMWN (low molecular weight neutral)	0.054	0.340	0.060	0.119
SUVA ₂₅₄	0.176	-0.071	0.434	0.036
Mn (molecular weight)	0.087	-0.543	0.001	0.302
C:N (carbon to nitrogen ratio)	0.247	-0.412	0.003	0.230
FI (fluorescence index)	-0.243	0.214	0.080	0.105
C1 (PARAFAC component 1)	0.015	-0.074	0.875	0.006
C2 (PARAFAC component 2)	0.164	-0.451	0.002	0.230
C3 (PARAFAC component 3)	-0.064	-0.251	0.213	0.067
C4 (PARAFAC component 4)	-0.095	0.349	0.041	0.131

S _R (spectral ratio)	-0.385	0.399	0.001	0.307
Succinic acid	0.267	-0.074	0.159	0.077
Fumaric acid	0.428	-0.075	0.008	0.189
Glyoxylic acid	0.259	-0.392	0.004	0.221
Pyruvic acid	0.283	-0.213	0.049	0.125
Glycolic acid	0.401	-0.146	0.009	0.182
Malonic acid	0.393	-0.175	0.009	0.185
Malic acid	0.417	-0.068	0.008	0.179
Acetic Acid	0.268	0.049	0.175	0.074

S6. Detailed methods

S6.1 Biofilm chl-*a* detailed method

Biofilm chl-*a* content ($\mu\text{g}/\text{cm}^2$) was measured by visible spectroscopy. Samples were prepared by mixing 1 mL of homogenised
145 biofilm sample with 9 mL of 100% analytical grade ethanol (Uvasol, Merck). The mixture was heated for five minutes at 75°C
and refrigerated overnight at 4°C, protected from light. After incubation, samples were centrifuged at 3,000 rpm for 10 minutes
(Beckman-Coulter Allegra X-15R Centrifuge rotor type SX4750, Beckman Coulter, Inc. USA) and the supernatant was
analysed by visible spectrometry at 665 nm and 750 nm, using 90% ethanol (Uvasol, Merck) as a reference (Shimadzu UV-
2700, Shimadzu Corporation, Kyoto, Japan). Biofilm chl-*a* content ($\mu\text{g}/\text{cm}^2$) was calculated from rock surface areas as per
150 standard procedures (Rice et al., 2012).

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