Drivers of variability in disinfection by-product formation potential in a chain of thermally stratified drinking water reservoirs

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Text S1: Disinfection by-products (DBP) formation potential (FP) analytical procedure

Reagents

NDMA standard for GC-MS analysis (5000 µg/mL in methanol, Supelco) had a purity of > 99.9%. Deuterated d6-NDMA (> 98% Cambridge Isotope Laboratories, Inc) and d14-NDPA (*N*-nitrosodipropylamine, > 99% Restek) were used as surrogate and internal standard, respectively. NH_4Cl (> 99.5%, Sigma-Aldrich), NaOH (ACS, ISO, Scharlau) and NaClO (reagent grade, available chlorine ≥ 4%, Sigma-Aldrich) were used for the NDMA FP test. KH_2PO_4 (> 99%, Sigma-Aldrich) and Na_2HPO_4 (> 99%, Sigma-Aldrich) were used to prepare pH buffer solutions. Na_2SO_3 (> 98%, Sigma-Aldrich) was employed to quench residual disinfectant in the NDMA FP tests. THMs were purchased as a 1.0 mg/mL mix in methanol (TraceCERT® grade) from Sigma Aldrich. Deuterated 1,2-dibromopropane-d6 (99.6 atom % D) was purchased from CDN isotopes and used as internal standard during DBP FP analyses. Methyl tert-butyl ether (MtBE, Chromasolv™ Plus) and Na_2SO_4 (≥ 99.0 %, ACS grade) were obtained from Sigma Aldrich. The remaining volatile DBPs were purchased from Cluzeau lab as a mix of 5.0 mg/mL in acetone (> 95 % purity).

Commercial DPD test kits (LCK310, Hach Lange) were used for the analysis of free and total chlorine using a Hach DR2800 spectrophotometer. Ultrapure water and methanol (Optima® LC/MS grade) were purchased from Fisher Chemical. Nitrogen (99.995% purity) for extract drying was purchased from Abelló-Linde. Glass fibre filters (GF/F, 47 mm diameter, 0.7 µm mesh size) were obtained from Whatman. Activated charcoal cartridges (6 mL, 2 g) optimized for NDMA extraction were purchased from Resteck.

Analytical methods

All samples were filtered through 0.7 µm Glass fiber filters (GF/F, 47 mm diameter) prior to performing DBP FP tests. NDMA FP test followed standard procedure previously published by

Mitch and co-authors [1]. In summary, phosphate buffered (10 mM) water samples were chloraminated with a 140 ppm monochloramine solution and incubated at 25 °C for 7 days. A 7-10 day incubation period for NDMA analysis is standard practice because monochloramine reacts slowly with NDMA precursor compounds [2–4]. To prepare a monochloramine solution, free chlorine was added to an ammonium chloride solution at a 1.2:1 N:Cl molar ratio previously adjusted to pH 8. Afterwards, the samples were quenched with sodium sulfite and extracted. In extraction, 1-litre of each sample was spiked with 25 ng/L of d_6NDMA surrogate, passed through coconut charcoal and eluted with dichloromethane. The extracted volume was concentrated using a gentle stream of nitrogen gas until 1 ml was left, which was then spiked with a 25 µg/L of d_{14}NDPA internal standard. GC-MS/MS analysis of NDMA was performed by a Trace GC Ultra gas chromatograph equipped with a TriPlus™ autosampler coupled to a TSQ™ Quantum triple quadrupole mass spectrometer system (Thermo Fisher Scientific). Chromatographic separation was performed using a ZB 1701 column from Phenomenex (30 m x 0.25 mm x 0.25 µm). The injector temperature was 250 °C and was operated in splitless mode. The oven temperature program was as follows: 40 °C held for 1 min, ramp to 65 °C at 5 °C /min, ramp to 110 °C at 10 °C /min held for 1 min and finally ramp to 240 °C at 25 °C /min and held for 1 min. Mass spectrometric ionization was carried out in electron impact (EI) ionization mode (EI voltage of 70 eV and a source temperature of 250 °C as described in Farré and co-authors [5] . The method reporting limit was 1 ng/L, and the recoveries were above 70%.

On the other hand, volatile DBP FP analyses of trichloromethane, bromodichloromethane (BDCM), 1,1-dichloropropanone (DCP), dibromochloromethane (DBCM), 1,1,1-trichloropropanone, tribromomethane (TBM), trichloroacetonitrile (TCAN), trichloronitromethane (TCNM), dichloroacetonitrile and bromochloroacetonitrile (BCAN) were performed following a standard method as previously applied Liu and co-authors [6] . In summary, multiples of each sample were put in 250 ml headspace free glass bottles and chlorinated with 2, 5 and 10 ppm of sodium hypochlorite solution, capped and incubated in the dark at 25 °C for 24 hrs. The 24 hour incubation time is standard practice in the analysis of volatile DBPs because the reaction between hypochlorite and volatile DBPs is faster hence 24 hrs is deemed more realistic [7,8] . Afterwards, residual chlorine was measured with photometric cuvette test kits (LCK 310, Hach lange GmbH, Düsseldorf, Germany). For each sample, a glass bottle with residual chlorine in the range of 1-3 ppm was retained and quenched with ascorbic acid. Sample pH was adjusted to 3.5 with 0.2 N sulphuric acid in a 30 ml aliquot and extracted using 3 ml of MtBE containing 200 µg/L of d6-1,2-dibromopropane as internal standard. After the addition of ~10 g of high purity sodium sulphate, the samples were vortexed for 1 minute and left to settle for 5 min. Finally, ~1.5 mL of MtBE extract was transferred into 2 ml vials for injection into the GC/MS. The injector was operated in splitless mode. Chromatographic separation was performed using a ZB1701 column from Phenomenex (30 m x 0.25 mm x 0.25 µm). The oven temperature program was as follows: 40 °C for 25 min, ramp to 145 °C at 5 °C /min and held for 2 min and then ramp to 260 °C at 20 °C /min and held for 10 min as described elsewhere [9]. The limit of quantification for all volatile DBP FP was 0.1 µg/L, and the recoveries were above 90 %.

***Table S1**: DBP FP (L^{-1}) data for Ter*

Season	n	µgTCM	µgBDCM	µgTCAN	µgDCP	µgTCNM	µgDCAN	µgDBCM	µgTCP	µgTBM	µgBCAN	µgDBAN	µgNDMA
Winter	1	19.49	7.44	<LoQ	0.12	0.08	3.04	2.52	3.57	0.15	1.13	0.29	0.07
Summer	1	69.92	10.29	0.04	0.81	0.67	11.43	1.41	4.17	0.74	1.19	< LoQ	0.03

† LoQ = Limit of Quantification

***Table S2**: Specific DBP FP data for Ter*

Season	n	µgTCM/mgDOC	µgBDCM/mgDOC	µgTCAN/mgDOC	µgDCP/mgDOC	µgTCNM/mgDOC	µgDCAN/mgDOC	µgDBCM/mgDOC	µgTCP/mgDOC	µgTBM/mgDOC	µgBCAN/mgDOC	µgDBAN/mgDOC	µgNDMA/mgDOC
Winter	1	9.66	3.69	0.00	0.06	0.04	1.51	1.25	1.77	0.08	0.56	0.14	0.04
Summer	1	14.81	2.18	0.01	0.17	0.14	2.42	0.30	0.88	0.16	0.25	0.00	0.01

***Table S3**: Summaries of DBP FP (L^{-1}) data for Sau*

Season	n	Summary	µgTCM	µgBDCM	µgTCAN	µgDCP	µgTCNM	µgDCAN	µgDBCM	µgTCP	µgTBM	µgBCAN	µgDBAN	µgNDMA
Autumn	4	Min	57.66	8.37	< LoQ	< LoQ	1.46	7.59	0.37	2.07	< LoQ	0.77	< LoQ	0.01
		Max	70.45	10.07	< LoQ	< LoQ	1.68	11.89	0.55	2.41	< LoQ	1.31	< LoQ	0.03
		Mean	65.20	9.42	< LoQ	< LoQ	1.59	9.47	0.49	2.23	< LoQ	1.01	< LoQ	0.02
		Median	66.36	9.62	< LoQ	< LoQ	1.60	9.19	0.52	2.22	< LoQ	0.98	< LoQ	0.01
		Stdev	5.40	0.82	< LoQ	< LoQ	0.10	2.10	0.09	0.14	< LoQ	0.25	< LoQ	0.01
Winter	4	Min	31.20	5.92	< LoQ	0.20	0.16	2.44	1.29	3.75	0.06	0.42	0.06	0.02
		Max	44.87	10.04	< LoQ	0.38	0.41	4.09	1.89	7.13	0.09	0.92	0.14	0.03
		Mean	37.59	7.81	< LoQ	0.29	0.27	3.15	1.58	4.71	0.08	0.66	0.10	0.03
		Median	37.15	7.63	< LoQ	0.30	0.26	3.04	1.58	3.99	0.08	0.66	0.09	0.03
		Stdev	5.87	1.70	< LoQ	0.08	0.11	0.77	0.30	1.61	0.02	0.26	0.04	0.00
Summer	4	Min	48.98	10.13	0.00	0.37	0.60	5.91	1.54	3.02	0.74	0.73	0.00	0.01
		Max	50.85	12.94	0.13	0.49	1.10	8.48	2.20	4.07	0.79	1.45	0.04	0.03
		Mean	49.87	11.01	0.08	0.45	0.79	7.36	1.86	3.58	0.77	1.19	0.02	0.02
		Median	49.83	10.49	0.12	0.46	0.74	7.52	1.86	3.61	0.76	1.28	0.02	0.02
		Stdev	0.99	1.31	0.07	0.05	0.22	1.22	0.27	0.46	0.03	0.32	0.02	0.01

† LoQ = Limit of Quantification

Table S4: *Specific DBP FP for Sau*

Season	n	Summary	µgTCM/mgDOC	µgBDCM/mgDOC	µgTCAN/mgDOC	µgDCP/mgDOC	µgTCNM/mgDOC	µgDCAN/mgDOC	µgDBCM/mgDOC	µgTCP/mgDOC	µgTBM/mgDOC	µgBCAN/mgDOC	µgDBAN/mgDOC	µgNDMA/mgDOC
Autumn	4	Min	13.78	2.00	0.00	0.00	0.35	1.87	0.09	0.52	0.00	0.18	0.00	0.00
		Max	19.22	2.76	0.00	0.00	0.46	3.26	0.16	0.66	0.00	0.36	0.00	0.00
		Mean	17.10	2.48	0.00	0.00	0.42	2.73	0.13	0.58	0.00	0.29	0.00	0.00
		Median	18.29	2.67	0.00	0.00	0.46	3.08	0.15	0.57	0.00	0.32	0.00	0.00
		Stdev	2.91	0.41	0.00	0.00	0.06	0.75	0.04	0.07	0.00	0.09	0.00	0.00
Winter	4	Min	11.46	2.18	0.00	0.08	0.06	0.89	0.47	1.39	0.02	0.15	0.02	0.01
		Max	16.44	3.68	0.00	0.13	0.15	1.50	0.69	2.44	0.03	0.34	0.05	0.01
		Mean	13.59	2.83	0.00	0.11	0.10	1.14	0.57	1.69	0.03	0.24	0.04	0.01
		Median	13.22	2.72	0.00	0.11	0.09	1.09	0.57	1.46	0.03	0.24	0.03	0.01
		Stdev	2.08	0.64	0.00	0.03	0.04	0.30	0.12	0.50	0.01	0.10	0.01	0.00
Summer	4	Min	11.06	2.54	0.00	0.10	0.16	1.48	0.39	0.75	0.17	0.18	0.00	0.00
		Max	15.69	3.17	0.04	0.13	0.24	2.62	0.56	1.17	0.23	0.45	0.01	0.01
		Mean	12.96	2.83	0.02	0.11	0.20	1.94	0.48	0.93	0.20	0.31	0.00	0.01
		Median	12.55	2.81	0.02	0.12	0.21	1.82	0.49	0.91	0.20	0.31	0.00	0.01
		Stdev	1.96	0.26	0.02	0.01	0.04	0.55	0.07	0.21	0.02	0.11	0.01	0.00

***Table S5**: Summaries of DBP FP (L^{-1}) data for Susqueda*

Season	n	Summary	µgTCM	µgBDCM	µgTCAN	µgDCP	µgTCNM	µgDCAN	µgDBCM	µgTCP	µgTBM	µgBCAN	µgDBAN	µgNDMA
Autumn	4	Min	63.97	9.13	< LoQ	< LoQ	1.25	7.40	0.44	2.10	< LoQ	0.87	< LoQ	0.01
		Max	79.44	9.78	< LoQ	< LoQ	1.97	9.81	0.48	2.58	< LoQ	0.97	< LoQ	0.01
		Mean	71.17	9.49	< LoQ	< LoQ	1.52	8.77	0.46	2.41	< LoQ	0.92	< LoQ	0.01
		Median	70.63	9.51	< LoQ	< LoQ	1.44	8.93	0.46	2.47	< LoQ	0.92	< LoQ	0.01
		Stdev	6.47	0.27	< LoQ	< LoQ	0.33	1.09	0.02	0.22	< LoQ	0.04	< LoQ	0.00
Winter	4	Min	49.77	6.48	< LoQ	0.30	0.32	3.18	1.09	3.87	0.06	0.36	0.06	0.02
		Max	66.21	8.43	< LoQ	0.45	0.51	4.52	1.20	4.91	0.06	0.52	0.06	0.02
		Mean	57.57	7.41	< LoQ	0.38	0.42	3.85	1.15	4.34	0.06	0.43	0.06	0.02
		Median	57.16	7.36	< LoQ	0.38	0.43	3.84	1.16	4.29	0.06	0.43	0.06	0.02
		Stdev	8.82	1.06	< LoQ	0.06	0.09	0.64	0.05	0.43	< LoQ	0.07	< LoQ	0.00
Summer	4	Min	58.11	11.23	< LoQ	0.44	0.70	6.72	1.44	3.71	0.75	0.74	< LoQ	0.02
		Max	68.41	12.29	0.20	0.66	1.04	8.99	1.86	4.17	0.79	1.03	< LoQ	0.03
		Mean	63.74	11.64	0.06	0.57	0.85	7.41	1.66	3.95	0.77	0.88	< LoQ	0.02
		Median	64.23	11.51	0.03	0.59	0.82	6.97	1.68	3.96	0.77	0.87	< LoQ	0.02
		Stdev	4.27	0.46	0.09	0.09	0.16	1.06	0.17	0.23	0.02	0.12	< LoQ	0.01

† LoQ = Limit of Quantification

***Table S6**: Specific DBPs FP for Susqueda*

Season	n	Summary	µgTCM/mgDOC	µgBDCM/mgDOC	µgTCAN/mgDOC	µgDCP/mgDOC	µgTCNM/mgDOC	µgDCAN/mgDOC	µgDBCM/mgDOC	µgTCP/mgDOC	µgTBM/mgDOC	µgBCAN/mgDOC	µgDBAN/mgDOC	µgNDMA/mgDOC
Autumn	4	Min	20.14	2.83	0.00	0.00	0.37	2.33	0.13	0.63	0.00	0.26	0.00	0.00
		Max	23.11	2.88	0.00	0.00	0.59	2.93	0.15	0.76	0.00	0.28	0.00	0.00
		Mean	21.37	2.85	0.00	0.00	0.46	2.63	0.14	0.72	0.00	0.28	0.00	0.00
		Median	21.11	2.85	0.00	0.00	0.44	2.63	0.14	0.75	0.00	0.28	0.00	0.00
		Stdev	1.30	0.02	0.00	0.00	0.09	0.26	0.01	0.07	0.00	0.01	0.00	0.00
Winter	4	Min	15.22	1.98	0.00	0.09	0.10	0.98	0.34	1.19	0.02	0.11	0.02	0.01
		Max	19.44	2.48	0.00	0.13	0.15	1.33	0.35	1.44	0.02	0.15	0.02	0.01
		Mean	17.26	2.22	0.00	0.11	0.13	1.15	0.35	1.30	0.02	0.13	0.02	0.01
		Median	17.18	2.21	0.00	0.11	0.13	1.15	0.35	1.29	0.02	0.13	0.02	0.01
		Stdev	2.23	0.26	0.00	0.02	0.03	0.16	0.01	0.11	0.00	0.02	0.00	0.00
Summer	4	Min	13.04	2.33	0.00	0.09	0.16	1.38	0.33	0.75	0.15	0.15	0.00	0.00
		Max	20.55	4.05	0.06	0.20	0.26	2.53	0.61	1.46	0.28	0.31	0.00	0.01
		Mean	16.63	3.05	0.02	0.15	0.22	1.95	0.44	1.05	0.20	0.23	0.00	0.01
		Median	16.48	2.90	0.01	0.16	0.23	1.95	0.40	1.00	0.19	0.24	0.00	0.00
		Stdev	3.82	0.75	0.03	0.05	0.05	0.59	0.12	0.33	0.06	0.08	0.00	0.00

Table S7: *DBP FP (L^{-1}) data for Pasteral*

Season	n	µgTCM	µgBDCM	µgTCAN	µgDCP	µgTCNM	µgDCAN	µgDBCM	µgTCP	µgTBM	µgBCAN	µgDBAN	µgNDMA
Autumn	1	72.46	8.24	< LoQ	< LoQ	1.00	7.78	0.44	2.34	< LoQ	0.78	< LoQ	0.03
Winter	1	48.67	6.06	< LoQ	0.79	0.39	2.79	1.06	13.11	0.06	0.30	0.06	0.02
Summer	1	72.94	11.84	0.03	0.60	0.88	7.44	1.48	3.64	0.75	0.66	< LoQ	0.02

† LoQ = Limit of Quantification

Table S8: *Specific DBP FP for Pasteral*

Season	n	µgTCM/mgDOC	µgBDCM/mgDOC	µgTCAN/mgDOC	µgDCP/mgDOC	µgTCNM/mgDOC	µgDCAN/mgDOC	µgDBCM/mgDOC	µgTCP/mgDOC	µgTBM/mgDOC	µgBCAN/mgDOC	µgDBAN/mgDOC	µgNDMA/mgDOC
Autumn	1	21.37	2.43	0.00	0.00	0.30	2.30	0.13	0.69	0.00	0.23	0.00	0.01
Winter	1	13.20	1.64	0.00	0.21	0.11	0.76	0.29	3.55	0.02	0.08	0.02	0.01
Summer	1	13.61	2.21	0.01	0.11	0.17	1.39	0.28	0.68	0.14	0.12	0.00	0.00

Table S9: *Nutrients (L^{-1}) and DOM optical indices for Ter*

Season	n	mgN_NH4	mgC_DOC	mgN_TN	mgN_TKN	mgP_PO_4^{3-}	mgP_PT	mgN_NO_3^-	mgN_NO_2^-	Br^-	UVA_{254}	$SUVA_{254}$	FI	BIX	HIX
Winter	1	0.18	2.02	5.75	< LoQ	0.02	0.04	4.66	0.02	< LoQ	0.04	0.02	1.85	0.87	4.62
Summer	1	< LoQ	4.72	1.56	0.76	0.04	0.10	0.63	0.05	< LoQ	0.06	0.01	1.74	0.75	6.38

† LoQ = Limit of Quantification

Table S10: *Sau nutrients (L^{-1}) and DOM optical indices*

Season	n	Summary	mgN_NH4	mgC_DOC	mgN_TN	mgN_TKN	mgP_PO_4^{3-}	mgP_PT	mgN_NO_3^-	mgN_NO_2^-	Br^-	UVA_{254}	$SUVA_{254}$	FI	BIX	HIX
Autumn	4	Min	0.08	3.43	1.97	0.69	0.04	0.05	1.45	0.01	< LoQ	0.11	0.03	1.56	0.71	5.71
		Max	0.10	4.18	2.97	0.82	0.09	0.11	2.27	0.02	< LoQ	0.14	0.04	1.58	0.76	6.72
		Mean	0.09	3.76	2.48	0.76	0.07	0.08	1.88	0.01	< LoQ	0.13	0.04	1.57	0.73	6.15
		Median	0.09	3.65	2.49	0.76	0.06	0.08	1.90	0.01	< LoQ	0.13	0.04	1.57	0.73	6.09
		Stdev	0.02	0.39	0.48	0.09	0.02	0.03	0.40	0.01	< LoQ	0.01	0.01	0.01	0.02	0.45
Winter	4	Min	0.01	2.69	4.16	< LoQ	0.03	0.04	3.03	0.00	< LoQ	0.07	0.02	1.65	0.70	9.40
		Max	0.14	2.92	4.97	< LoQ	0.03	0.06	4.32	0.03	< LoQ	0.07	0.03	1.74	0.75	11.14
		Mean	0.06	2.77	4.54	< LoQ	0.03	0.05	3.77	0.02	< LoQ	0.07	0.03	1.69	0.72	10.40
		Median	0.05	2.73	4.52	< LoQ	0.03	0.05	3.86	0.02	< LoQ	0.07	0.03	1.69	0.72	10.53
		Stdev	0.06	0.11	0.41	< LoQ	0.00	0.01	0.58	0.01	< LoQ	0.00	0.00	0.04	0.02	0.82
Summer	4	Min	0.07	3.24	1.74	0.98	< LoQ	0.02	1.16	0.01	< LoQ	0.04	0.01	1.61	0.75	3.43
		Max	0.07	4.58	4.44	1.08	< LoQ	0.03	3.56	0.03	< LoQ	0.07	0.02	1.71	0.90	9.95
		Mean	0.07	3.91	2.73	1.03	< LoQ	0.02	2.01	0.03	< LoQ	0.05	0.01	1.67	0.83	6.81
		Median	0.07	3.91	2.37	1.03	<LoQ	0.02	1.66	0.03	< LoQ	0.05	0.01	1.68	0.83	6.93
		Stdev	N/A	0.55	1.21	0.05	< LoQ	0.01	1.09	0.01	< LoQ	0.01	0.00	0.05	0.08	3.27

† LoQ = Limit of Quantification

Table S11: *Susqueda nutrients (L^{-1}) and DOM optical indices*

Season	n	Summary	mgN_NH4	mgC_DOC	mgN_TN	mgN_TKN	mgP_PO_4^{3-}	mgP_PT	mgN_NO_3^-	mgN_NO_2^-	Br^-	UV_{254}	$SUVA_{254}$	FI	BIX	HIX
Autumn	4	Min	0.01	3.18	1.58	< LoQ	0.05	0.05	1.06	0.01	< LoQ	0.12	0.04	1.61	0.64	8.95
		Max	0.04	3.44	1.93	< LoQ	0.06	0.07	1.33	0.01	< LoQ	0.13	0.04	1.65	0.65	9.60
		Mean	0.02	3.33	1.74	< LoQ	0.06	0.06	1.17	0.01	< LoQ	0.12	0.04	1.63	0.65	9.27
		Median	0.02	3.35	1.73	< LoQ	0.06	0.06	1.15	0.01	< LoQ	0.12	0.04	1.63	0.65	9.26
		Stdev	0.02	0.11	0.17	< LoQ	0.01	0.01	0.13	0.00	< LoQ	0.01	0.00	0.02	0.01	0.30
Winter	4	Min	0.00	3.25	2.65	1.66	0.04	0.05	2.11	< LoQ	< LoQ	0.08	0.02	1.62	0.68	13.07
		Max	0.02	3.41	2.71	1.66	0.04	0.06	2.34	< LoQ	< LoQ	0.09	0.03	1.67	0.69	14.03
		Mean	0.01	3.33	2.69	1.66	0.04	0.05	2.24	< LoQ	< LoQ	0.09	0.03	1.65	0.69	13.73
		Median	0.00	3.33	2.70	1.66	0.04	0.05	2.25	< LoQ	< LoQ	0.09	0.03	1.66	0.69	13.90
		Stdev	0.01	0.08	0.02	N/A	0.00	0.00	0.10	< LoQ	< LoQ	0.01	0.00	0.02	0.01	0.44
Summer	4	Min	< LoQ	2.83	2.49	0.57	< LoQ	0.01	1.98	0.02	< LoQ	0.05	0.01	1.56	0.69	5.48
		Max	< LoQ	4.98	3.44	1.19	< LoQ	0.03	2.92	0.03	< LoQ	0.08	0.02	1.69	0.88	15.10
		Mean	< LoQ	4.00	2.95	0.89	< LoQ	0.02	2.33	0.03	< LoQ	0.07	0.02	1.65	0.79	9.44
		Median	< LoQ	4.10	2.94	0.91	< LoQ	0.02	2.20	0.02	< LoQ	0.07	0.02	1.68	0.78	8.59
		Stdev	< LoQ	0.99	0.44	0.25	< LoQ	0.01	0.42	0.00	< LoQ	0.01	0.00	0.07	0.08	4.28

† LoQ = Limit of Quantification

***Table S12**: Pasteral nutrients (L^{-1}) and DOM optical indices*

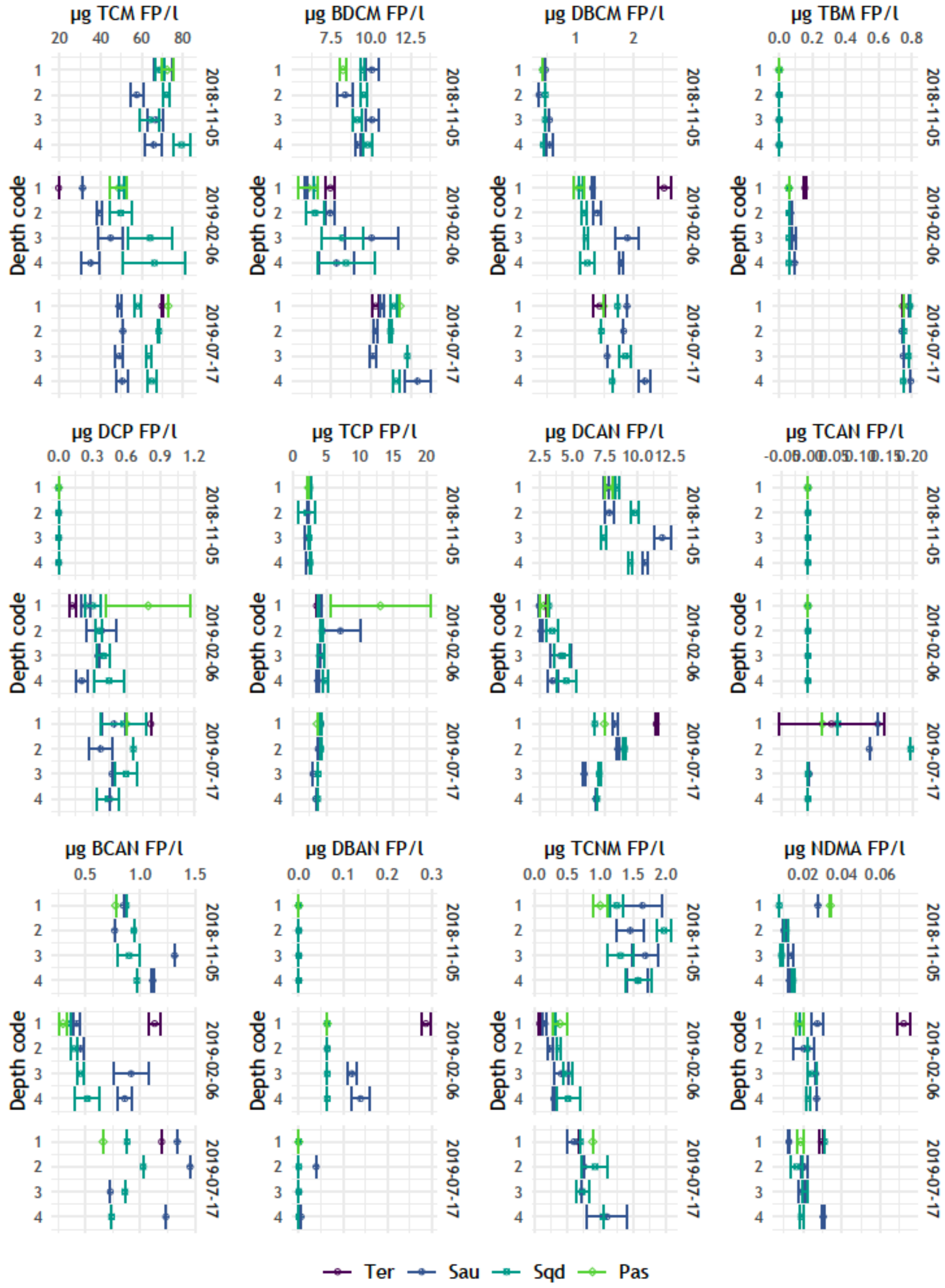
Season	n	mgN_NH4	mgC_TOC	mgN_TN	mgN_TKN	mgP_PO_4^{3-}	mgP_PT	mgN_NO_3^-	mgN_NO_2^-	Br^-	UVA_{254}	$SUVA_{254}$	FI	BIX	HIX
Autumn	1	0.01	3.39	1.58	1.75	0.05	0.05	1.00	< LoQ	< LoQ	0.13	0.04	1.62	0.68	8.60
Winter	1	0.01	3.69	2.66	< LoQ	0.04	0.05	2.24	< LoQ	< LoQ	0.10	0.03	1.66	0.73	8.80
Summer	1	< LoQ	5.36	3.17	< LoQ	< LoQ	0.01	2.54	0.02	< LoQ	0.08	0.02	1.70	0.72	12.48

† LoQ = Limit of Quantification

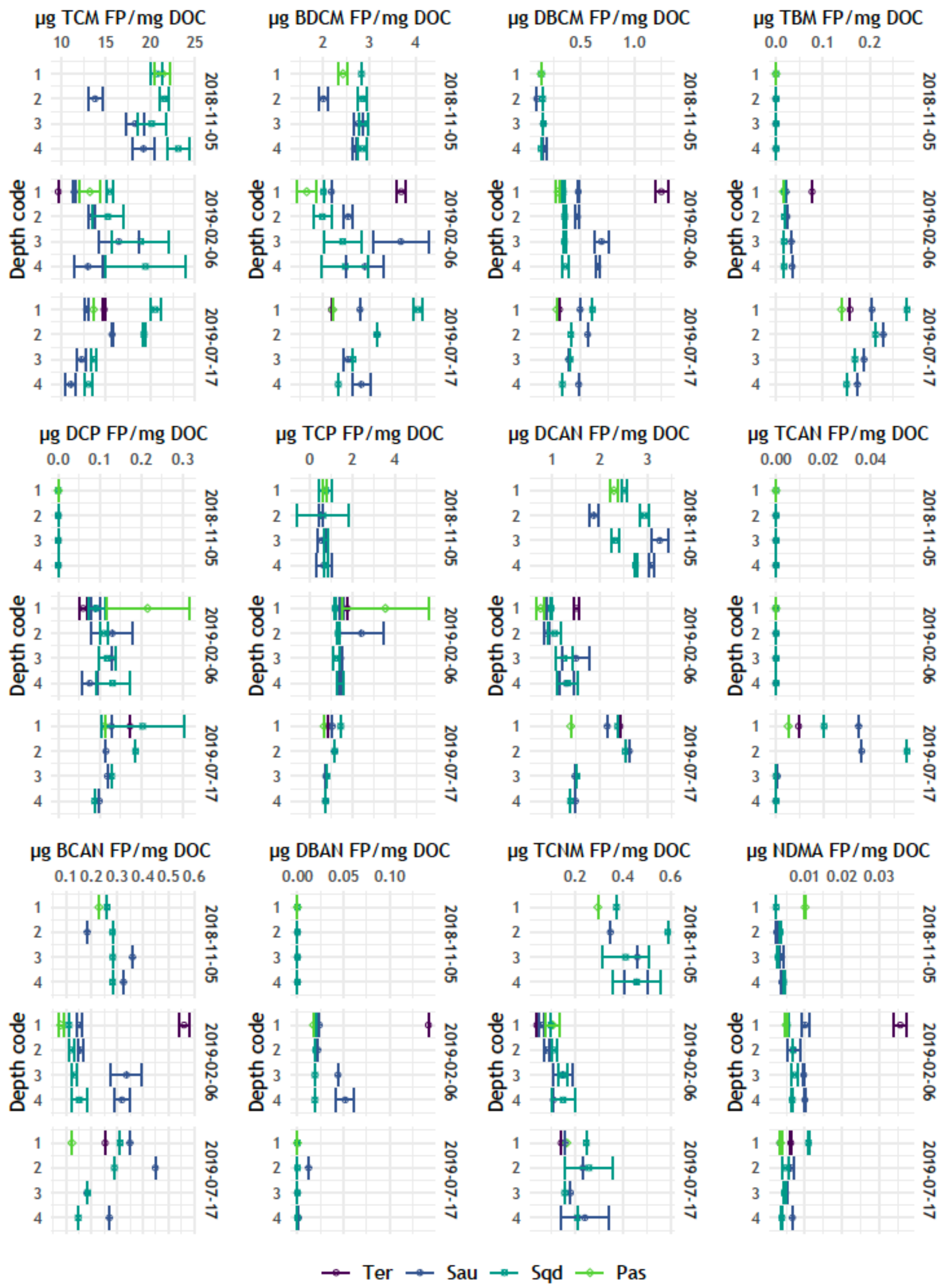
Table S13: Correlation matrix between measured nutrients and specific DBP

	SpTCM	SpBDCM	SpDCAN	SpTCP	SpNDMA	mgN_NH4	mgC_DOC	mgN_TN	mgN_TKN	mgP_PO$_4^{3-}$	mgP_PT	mgN_NO$_3^-$	mgN_NO$_2^-$	UVA$_{254}$	SUVA$_{254}$	FI	BIX	HIX
SpTCM	1																	
SpBDCM	0.25	1																
SpDCAN	0.57**	0.54**	1															
SpTCP	-0.27	0.08	-0.59***	1														
SpNDMA	-0.22	0.12	-0.43*	0.67****	1													
mgN_NH4	0.18	0.36	0.13	0.22	0.24	1												
mgC_DOC	-0.14	-0.44*	0.13	-0.59***	-0.55**	-0.65***	1											
mgN_TN	-0.59**	0.08	-0.48*	0.32	0.44*	0.25	-0.18	1										
mgN_TKN	0.06	0.05	0.24	-0.13	0.03	-0.37	0.2	-0.35	1									
mgP_PO$_4^{3-}$	0.58**	-0.19	0.28	-0.3	-0.28	0.48*	-0.17	-0.36	-0.31	1								
mgP_PT	0.48**	-0.09	0.27	-0.11	-0.14	0.54**	-0.24	-0.34	-0.21	0.87****	1							
mgN_NO$_3^-$	-0.57**	0.03	-0.58**	0.45*	0.45*	0.26	-0.24	0.96****	-0.35	-0.35	-0.31	1						
mgN_NO$_2^-$	-0.31	0.48*	0.3	-0.03	0.04	-0.16	0.21	0.18	0.35	-0.62***	-0.35	0.11	1					
UVA$_{254}$	0.56**	-0.34	0.18	-0.49**	-0.39*	0.25	0.12	-0.26	-0.32	0.86****	0.61***	-0.28	-0.64***	1				
SUVA$_{254}$	0.60***	-0.06	0.21	-0.22	-0.15	0.51**	-0.31	-0.21	-0.40*	0.89****	0.68****	-0.21	-0.69****	0.88****	1			
FI	-0.52**	0.04	-0.39*	0.3	0.37	-0.08	0.06	0.49**	-0.08	-0.51**	-0.31	0.50**	0.36	-0.52**	-0.53**	1		
BIX	-0.49**	0.28	0.11	0.23	0.23	-0.22	0.1	0.23	0.40*	-0.70****	-0.54**	0.2	0.62***	-0.77****	-0.71****	0.24	1	
HIX	-0.08	-0.46*	-0.66***	0.15	0.11	-0.12	0.03	0.35	-0.29	0	-0.09	0.39*	-0.34	0.2	0.05	0.29	-0.55**	1

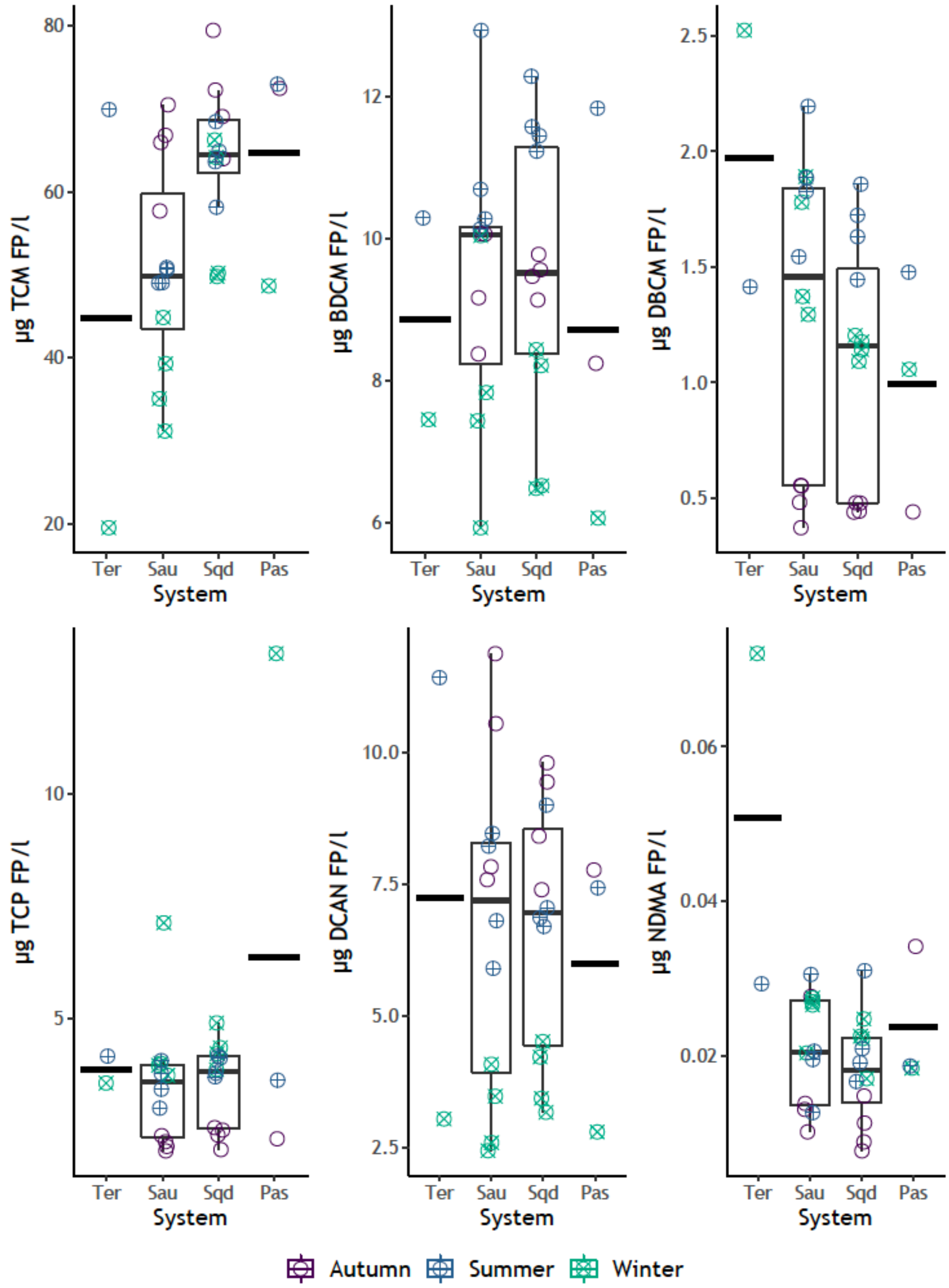
Note: **** = $p < 0.0001$, *** = $p < 0.001$, ** = $p < 0.01$, * = $p < 0.05$



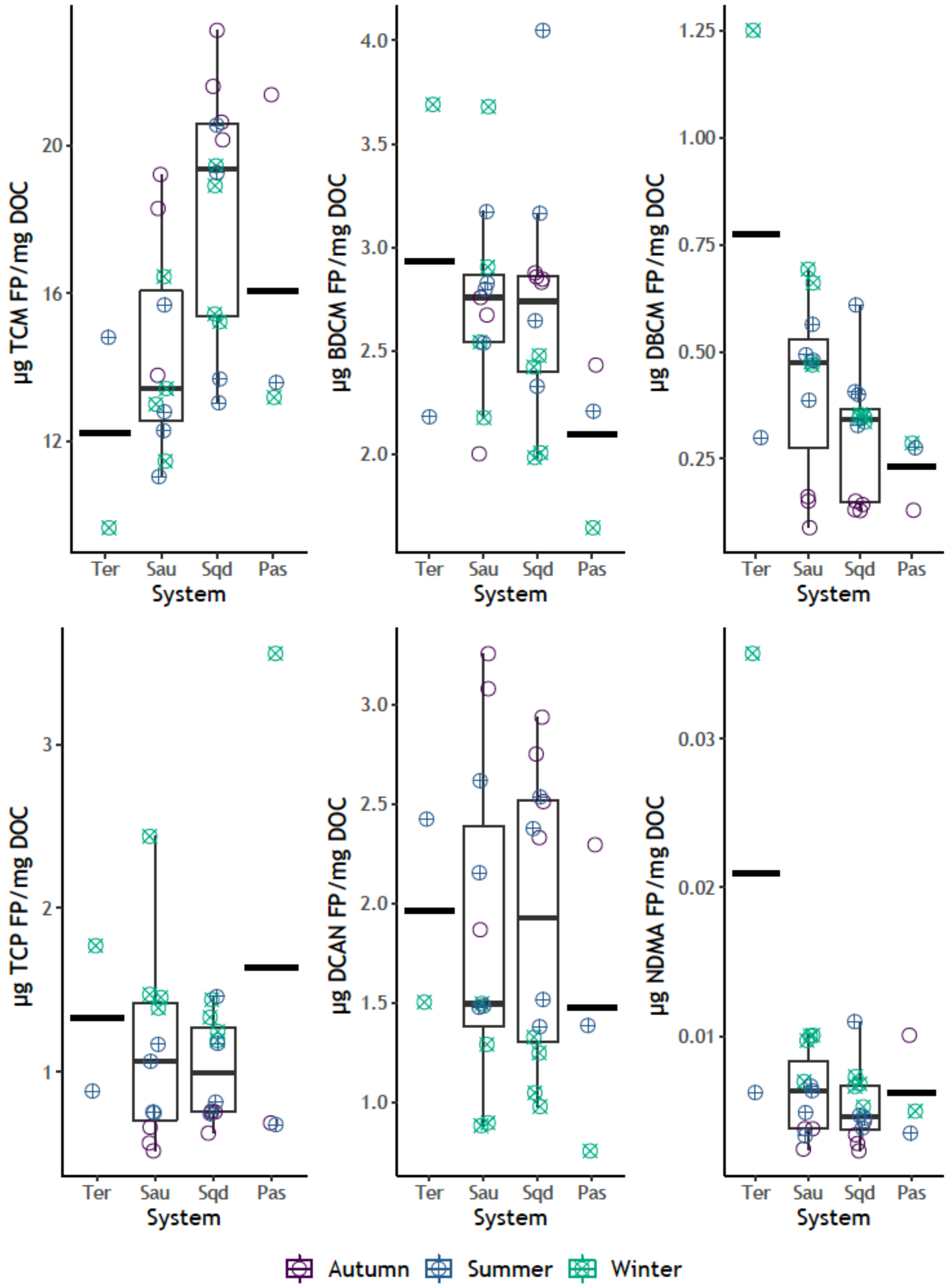
***Supplementary Figure S1**: Spatio-temporal variability of all DBP FP. The violet color represent samples from Ter River, the blue color represents samples from Sau Reservoir, the deep green color represents samples from Susqueda Reservoir whereas the bright green color represent samples from Pasteral Reservoir. Depth codes represent surface (1), thermocline (2), upper hypolimnion (3) and bottom hypolimnion (4).*



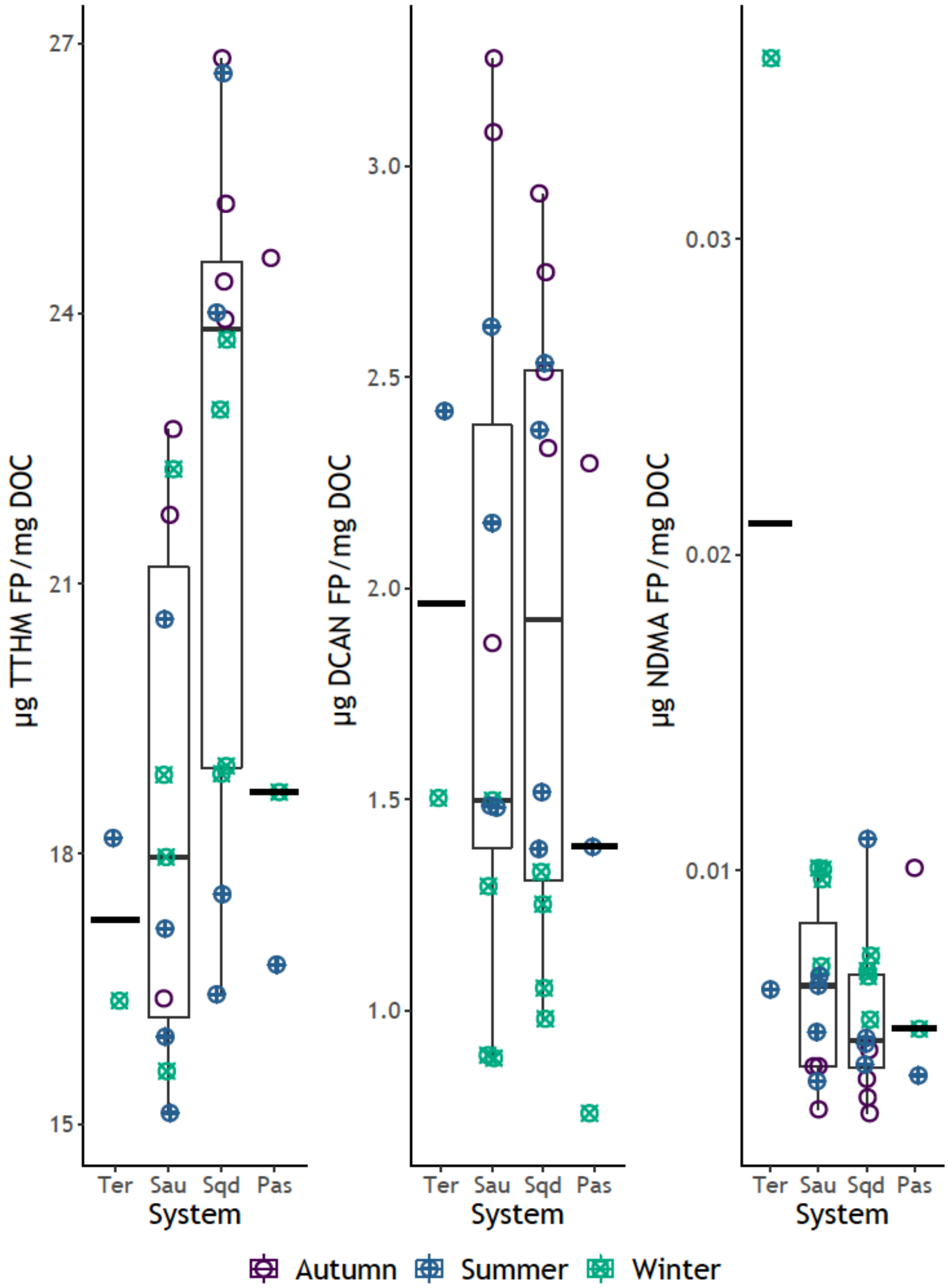
Supplementary Figure S2*: Spatio-temporal variability of all yields of DBP. The violet color represent samples from Ter River, the blue color represents samples from Sau Reservoir, the deep green color represents samples from Susqueda Reservoir whereas the bright green color circles represent samples from Pasteral Reservoir. Depth codes represent surface (1), thermocline (2), upper hypolimnion (3) and bottom hypolimnion (4).*



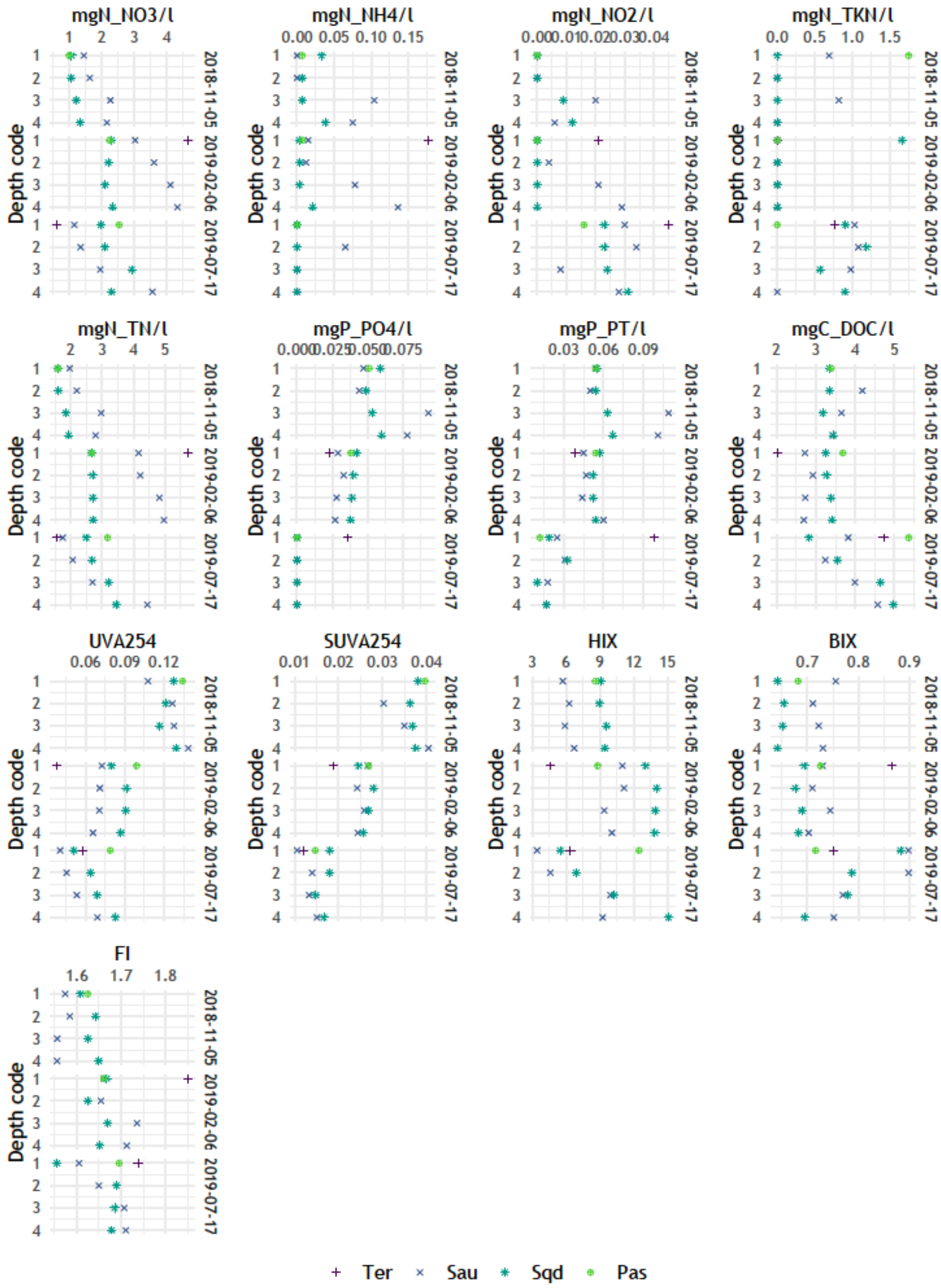
Supplementary Figure S3: *Spatial variability of all significantly formed µg/L DBP. The green crossed circles represent winter values, the blue crossed circles represent summer values whereas the violet circles represent autumn values. The circles represent the actual formation potential data. The thick horizontal bar on each of the four systems represents the median value for all data of that particular system.*



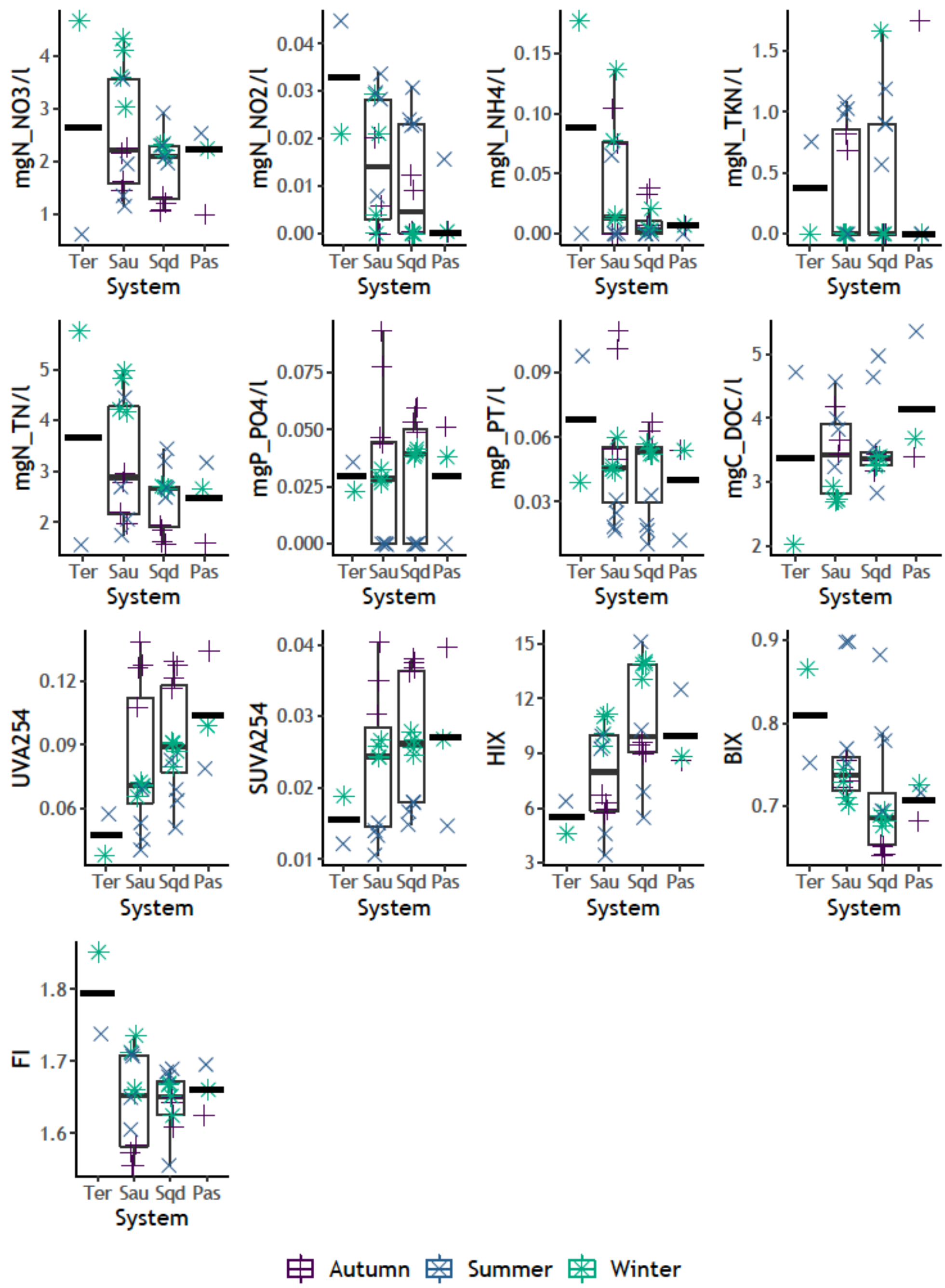
Supplementary Figure S4: *Spatial variability of yields for all significantly formed DBP. The green crossed circles represent winter values, the blue crossed circles represent summer values whereas the violet circles represent autumn values. The thick horizontal bar on each of the four systems represents the median value for all data of that particular system.*



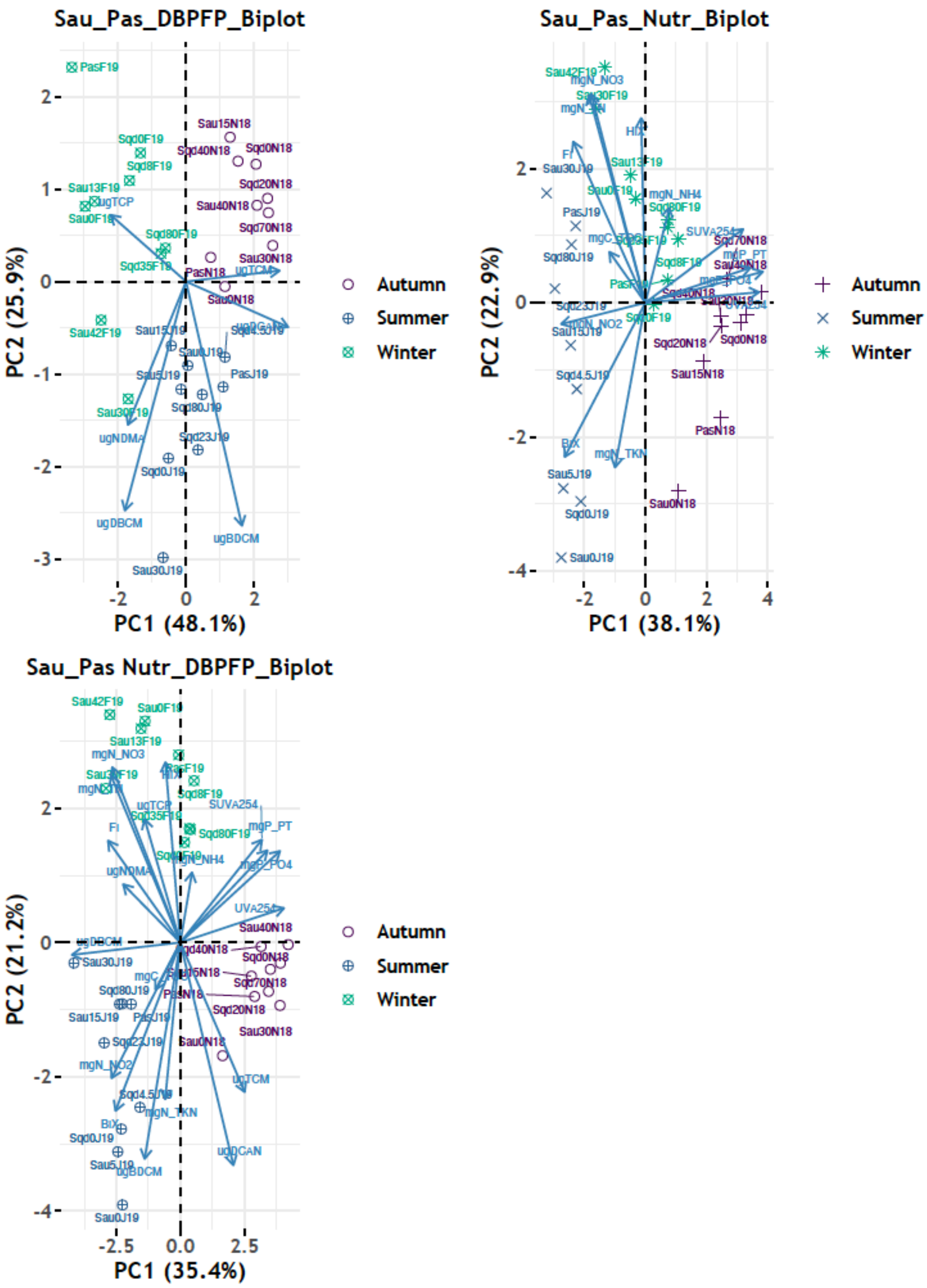
Supplementary Figure S5: *Box and jitter plots for specific DBP FP of TTHMs, DCAN and NDMA, grouped by system and season. The green crossed circles represent formation potential values in winter, the blue crossed circles represent formation potential values in summer and the violet circles represent formation potential values in autumn. The circles represent the actual formation potential data. The thick horizontal bar on each of the four systems represents the median value for all data of that particular system.*



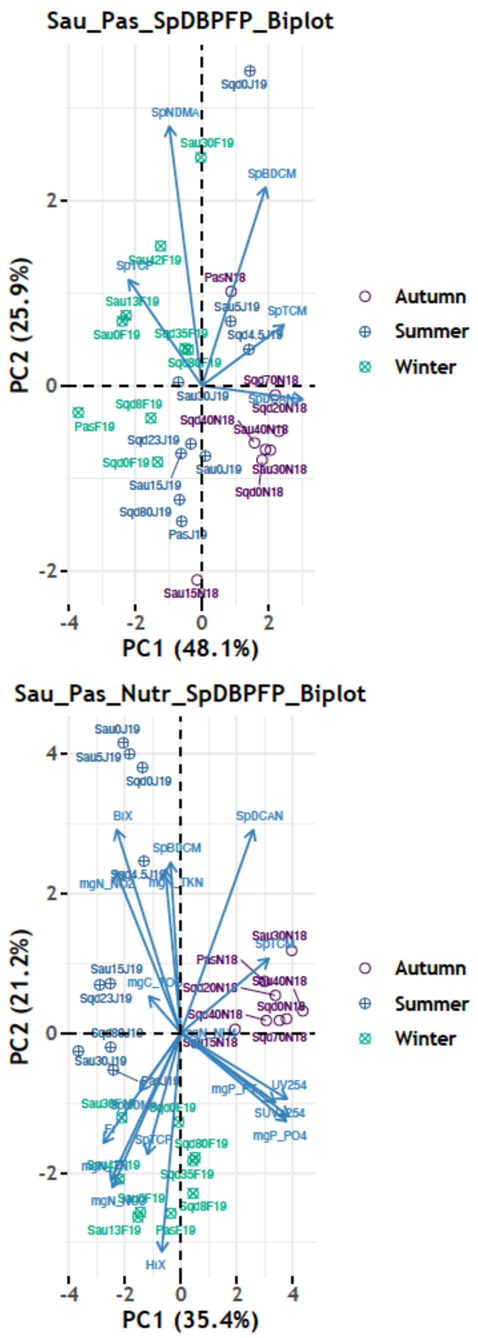
Supplementary Figure S6: *Nutrients and DOM optical indices variability across depths. The brown crosses represent samples from Ter River, the blue crosses represent samples from Sau Reservoir, the deep green stars represent samples from Susqueda Reservoir whereas the bright green crossed circles represent samples from Pasteral Reservoir. Depth codes represent surface (1), thermocline (2), upper hypolimnion (3) and bottom (4).*



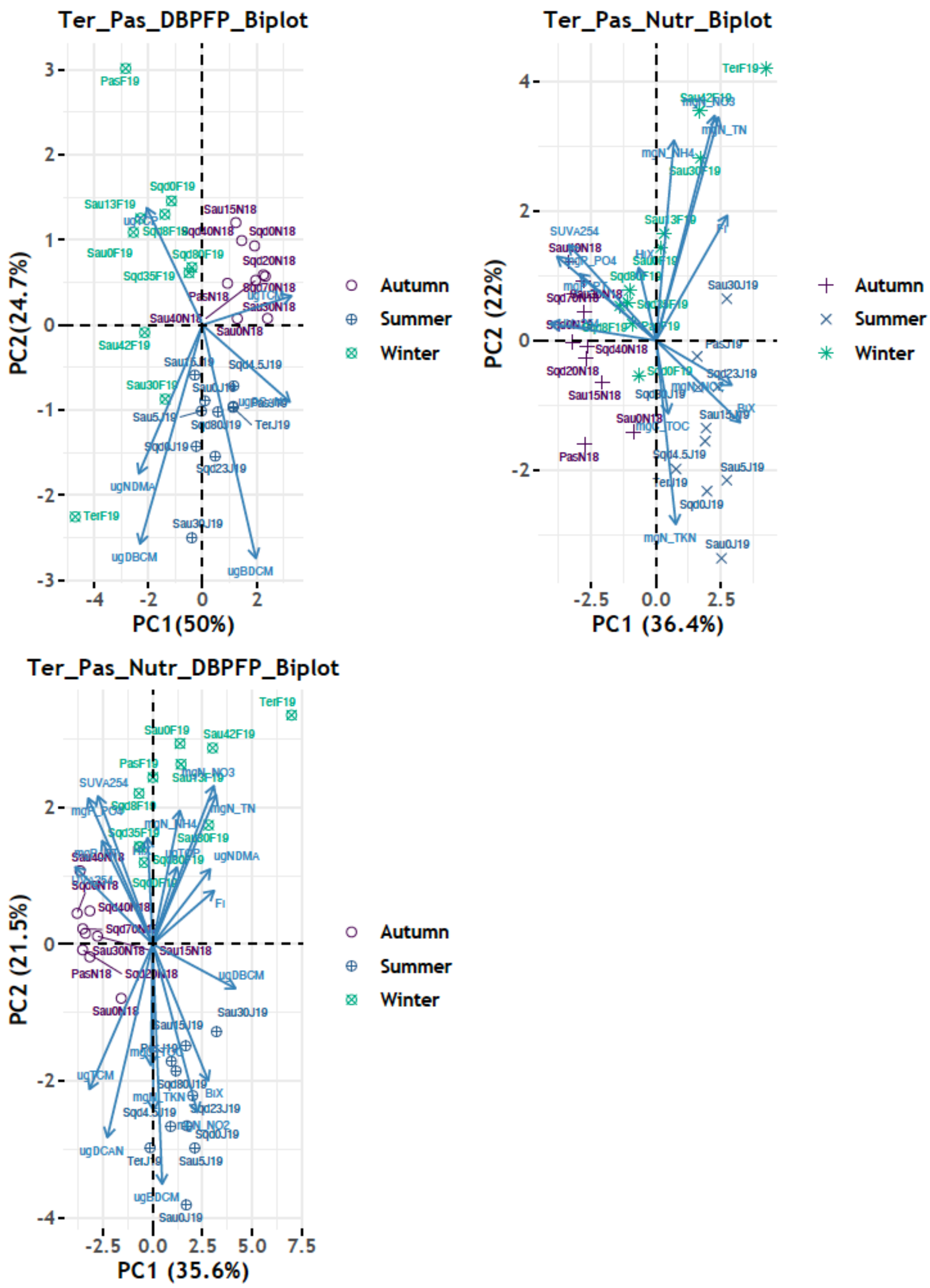
***Supplementary Figure S7**: Spatial-temporal distribution of nutrients and DOM optical indices across the Ter-Sau-Susqueda-Pasteral system. The green stars represent winter values, the blue crosses represent summer values whereas the violet crosses represent autumn values. The thick horizontal bar on each of the four systems represents the median value for all data of that particular system.*



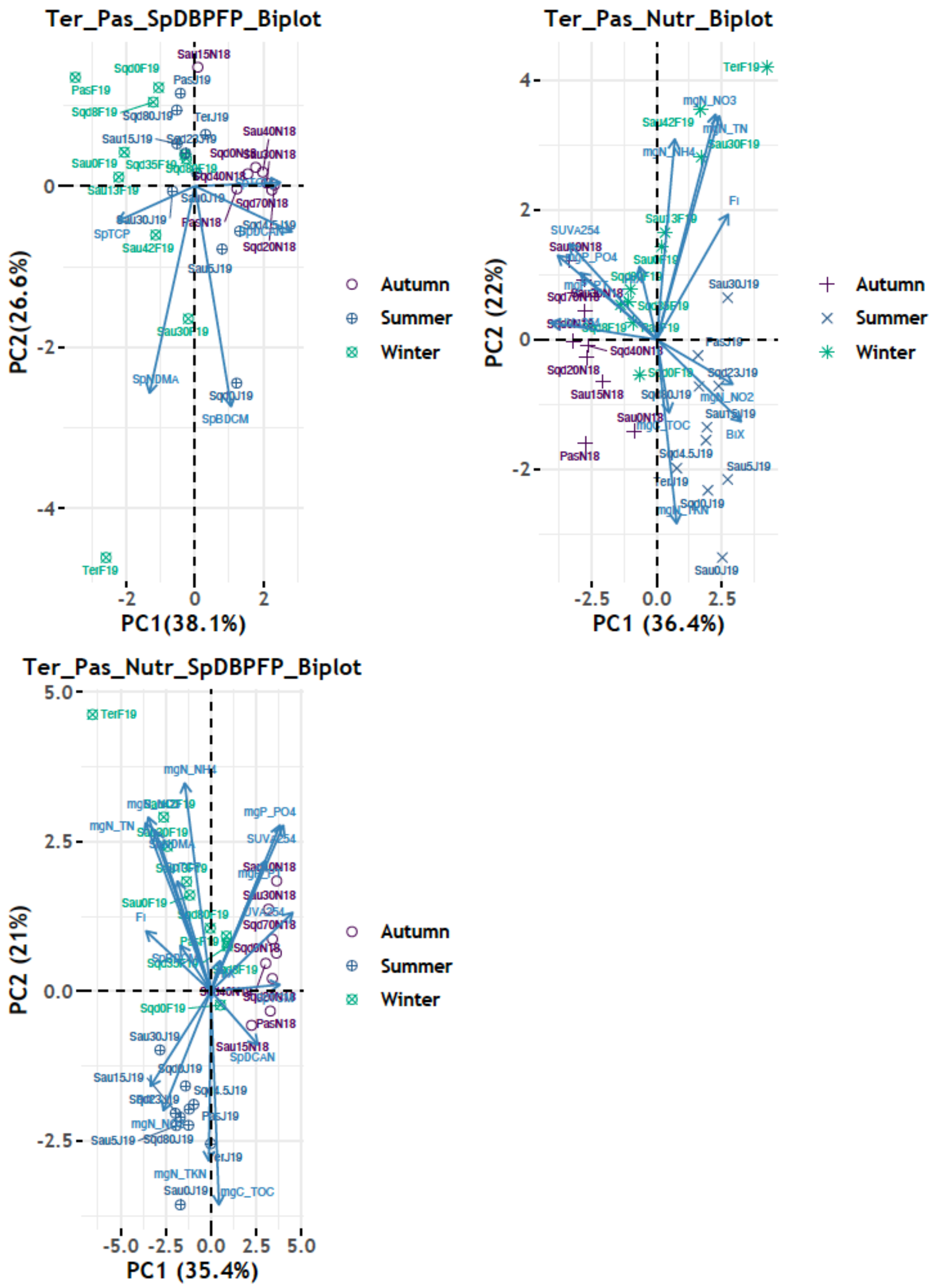
***Supplementary Figure S8**: PCA biplots for DBP FP, nutrients, and DBP FP +nutrients, excluding a Ter River sample, illustrating clustering by season. Violet circles represent samples collected in autumn, green crossed circles represent samples collected in winter, whereas blue crossed circles represent samples collected in summer. The blue labeled arrows represent the projection of the measured nutrients, DOM optical indices and DBP FPs on the two-dimensional plots. Samples were coded as: the first 3 letters are an abbreviation of the location (Ter = Ter, Sau = Sau, Sqd = Susqueda, Pas = Pasteral), followed by depth(m) from which the sample was collected (e.g. 0 = surface, 40m…80m) and, finally, an abbreviation of sampling month and year (e.g. N18 = November 2018, F19 = February 2019, J19 = July 2019).*



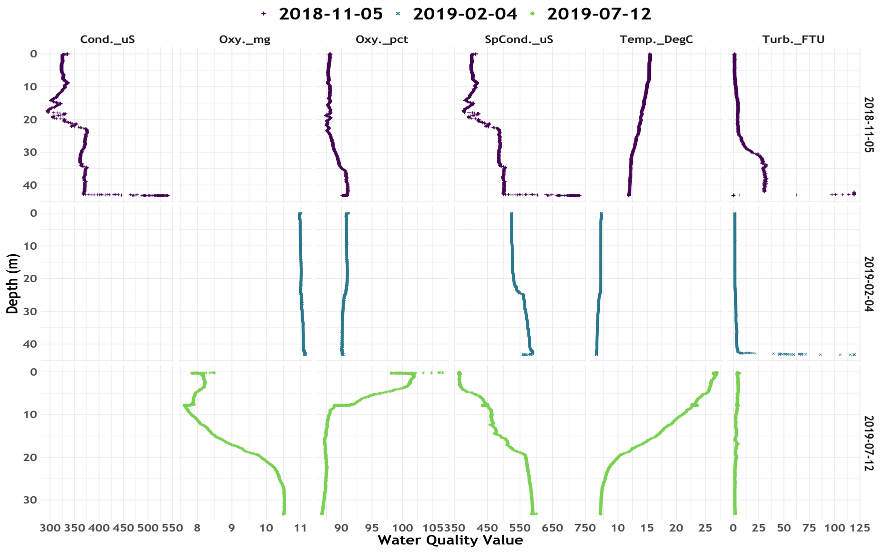
***Supplementary Figure S9**: PCA biplots for specific DBP FP, nutrients and specific DBP FP + nutrients, excluding a Ter River sample, illustrating clustering by season. Violet circles represent samples collected in autumn, green crossed circles represent samples collected in winter, whereas blue crossed circles represent samples collected in summer. The blue labeled arrows represent the projection of the measured nutrients, DOM optical indices and DBP FPs on the two-dimensional plots. Samples were coded as: the first 3 letters are an abbreviation of the location (Ter = Ter, Sau = Sau, Sqd = Susqueda, Pas = Pasteral), followed by depth(m) from which the sample was collected (e.g. 0 = surface, 40m…80m) and, finally, an abbreviation of sampling month and year (e.g. N18 = November 2018, F19 = February 2019, J19 = July 2019).*



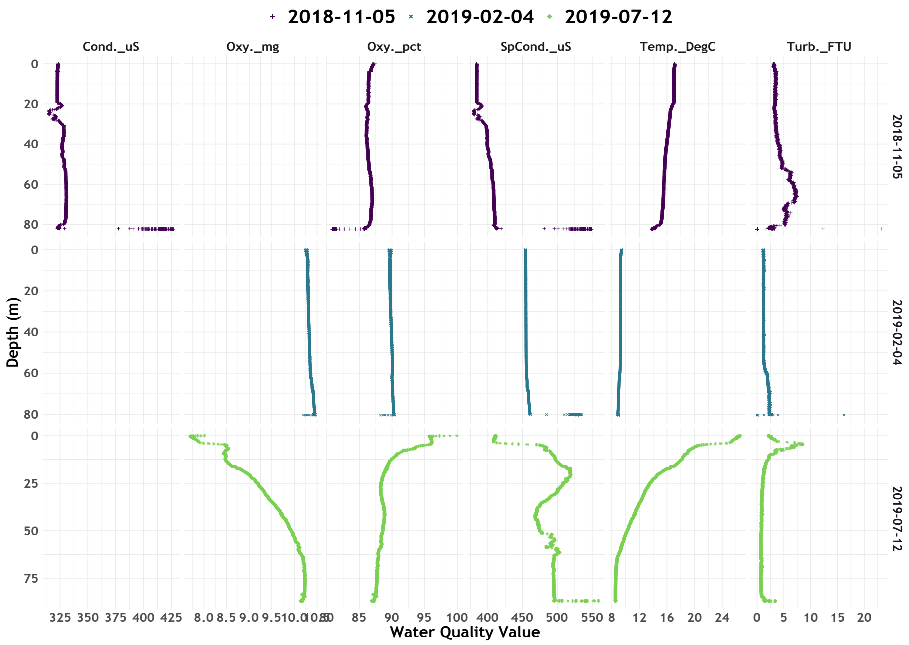
***Supplementary Figure S10**: PCA biplots for DBPs FP, nutrients and DBP FP + nutrients, including a Ter River sample, illustrating clustering by season. Violet circles and crosses represent samples collected in autumn, green crossed circles and stars represent samples collected in winter, whereas blue crossed circles and crosses represent samples collected in summer. The blue labeled arrows represent the projection of the measured nutrients, DOM optical indices and DBP FPs on the two-dimensional plots. Samples were coded as: the first 3 letters are an abbreviation of the location (Ter = Ter, Sau = Sau, Sqd = Susqueda, Pas = Pasteral), followed by depth(m) from which the sample was collected (e.g. 0 = surface, 40m…80m) and, finally, an abbreviation of sampling month and year (e.g. N18 = November 2018, F19 = February 2019, J19 = July 2019).*



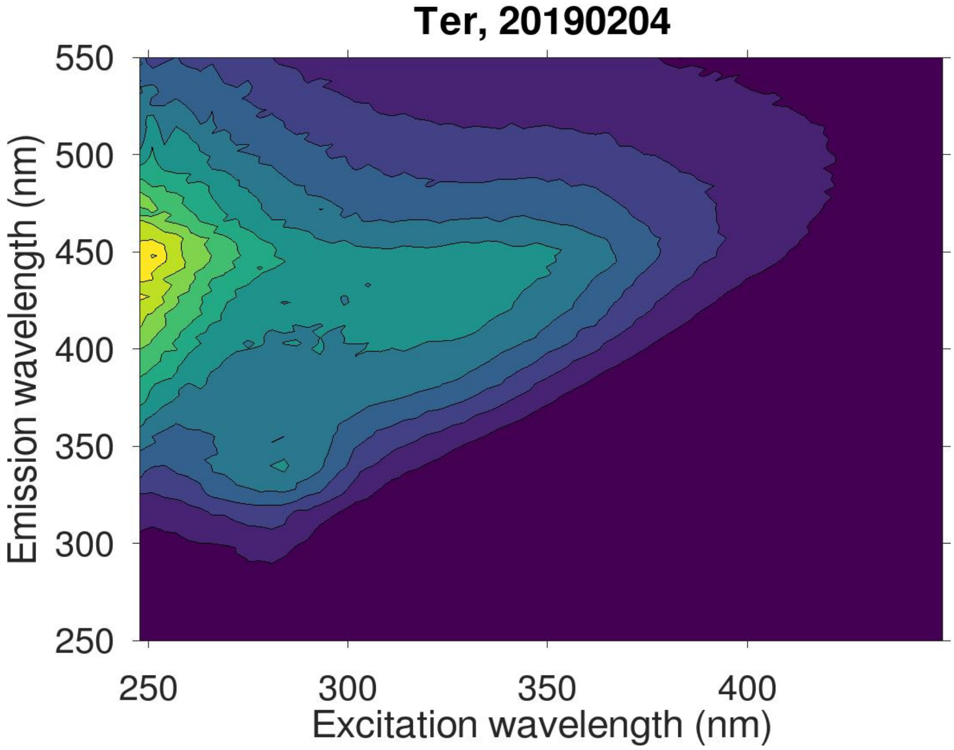
Supplementary Figure S11*: PCA biplots for specific DBP FP, nutrients and specific DBP FP + nutrients, including a Ter River sample, illustrating clustering by season. Violet circles and crosses represent samples collected in autumn, green crossed circles and stars represent samples collected in winter, whereas blue crossed circles and crosses represent samples collected in summer. The blue labeled arrows represent the projection of the measured nutrients, DOM optical indices and DBP FPs on the two-dimensional plots. Samples were coded as: the first 3 letters are an abbreviation of the location (Ter = Ter, Sau = Sau, Sqd = Susqueda, Pas = Pasteral), followed by depth(m) from which the sample was collected (e.g. 0 = surface, 40m…80m) and, finally, an abbreviation of sampling month and year (e.g. N18 = November 2018, F19 = February 2019, J19 = July 2019).*



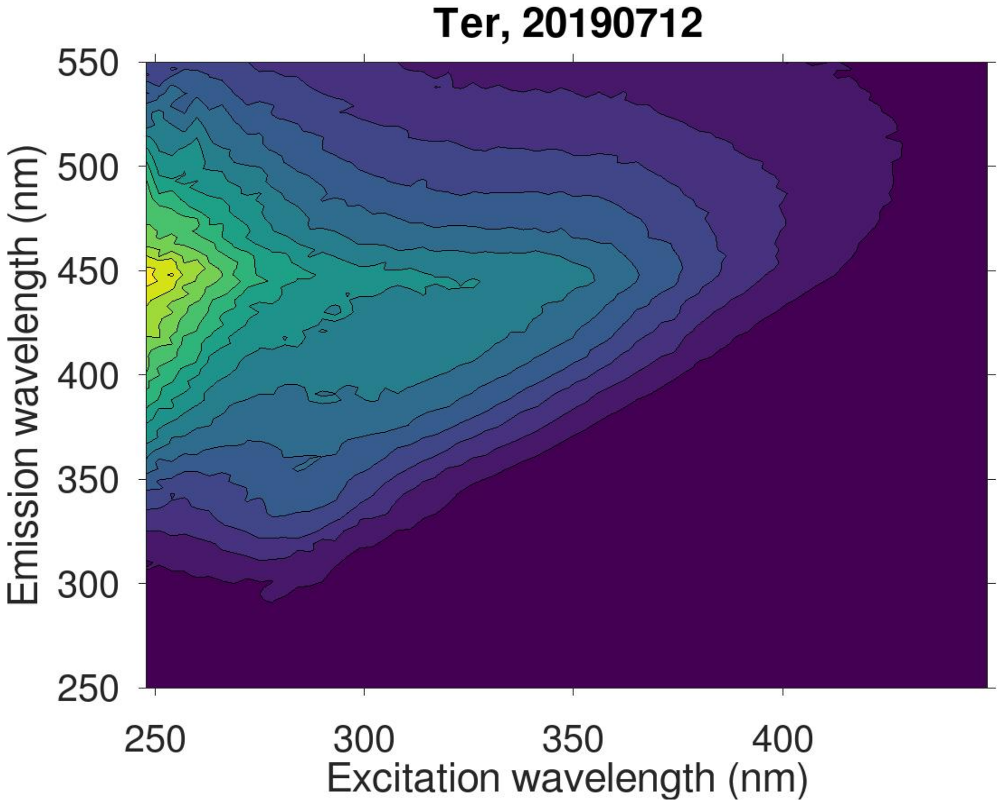
Supplementary Figure S12: Point plots for Sau CTD profile data for all the sampling events. Cond.uS = Conductivity (µS/cm); Oxy._mg = Oxygen (mg/l); Oxy._pct = Oxygen (%); SpCond._uS = Specific Conductance (µS/cm); Temp._DegC = Temperature (°C) and Turb._FTU = Turbidity (FTU).



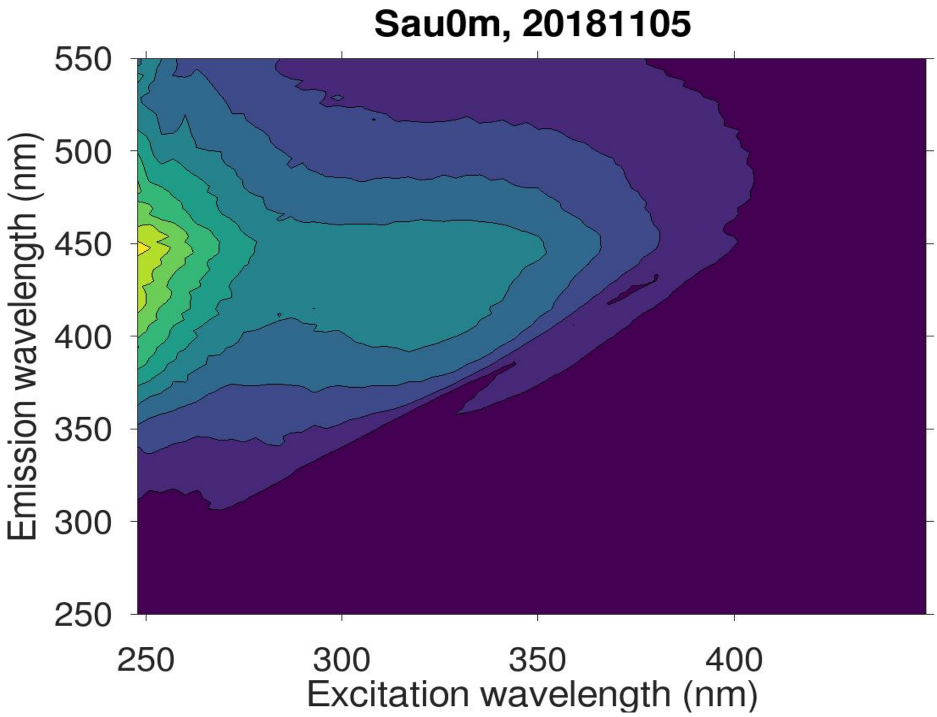
Supplementary Figure S13: Point plots for Susqueda CTD profile data for all sampling events. Cond.uS = Conductivity (µS/cm); Oxy._mg = Oxygen (mg/l); Oxy._pct = Oxygen (%); SpCond._uS = Specific Conductance (µS/cm); Temp._DegC = Temperature (°C) and Turb._FTU = Turbidity (FTU).



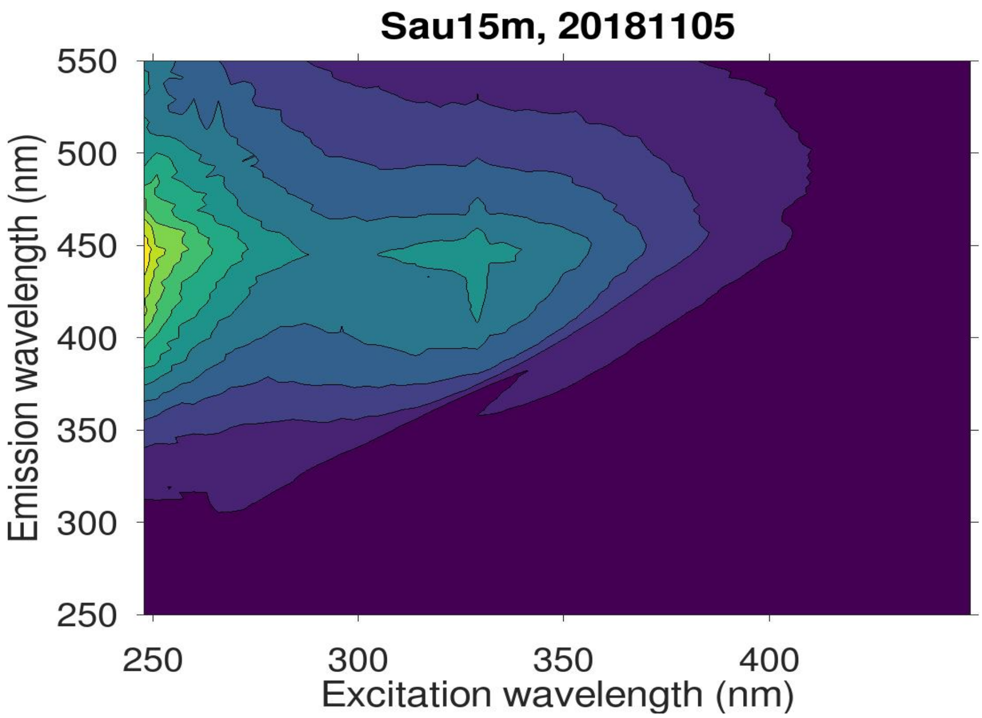
Supplementary Figure S14: Excitation-Emission matrix (EEM) for a sample collected from Ter River on 2019-02-04.



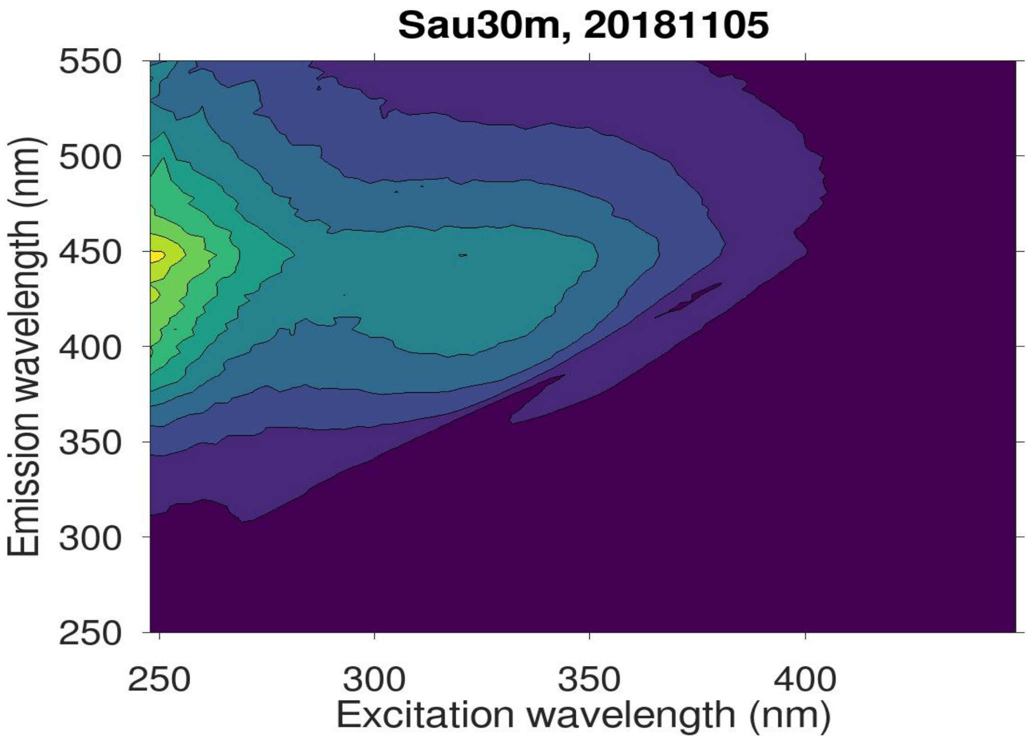
Supplementary Figure S15: Excitation-Emission matrix (EEM) for a sample collected from Ter River on 2019-07-12.



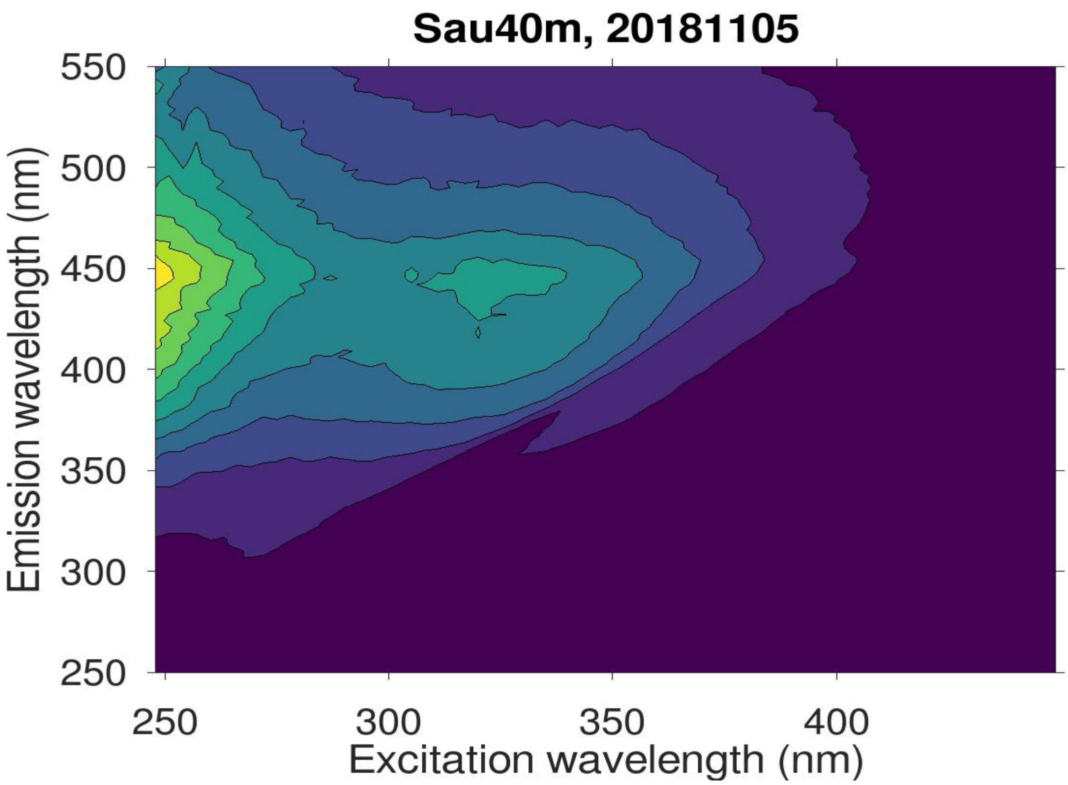
Supplementary Figure S16: Excitation-Emission matrix (EEM) for a sample collected from the surface of Sau Reservoir on 2018-11-05.



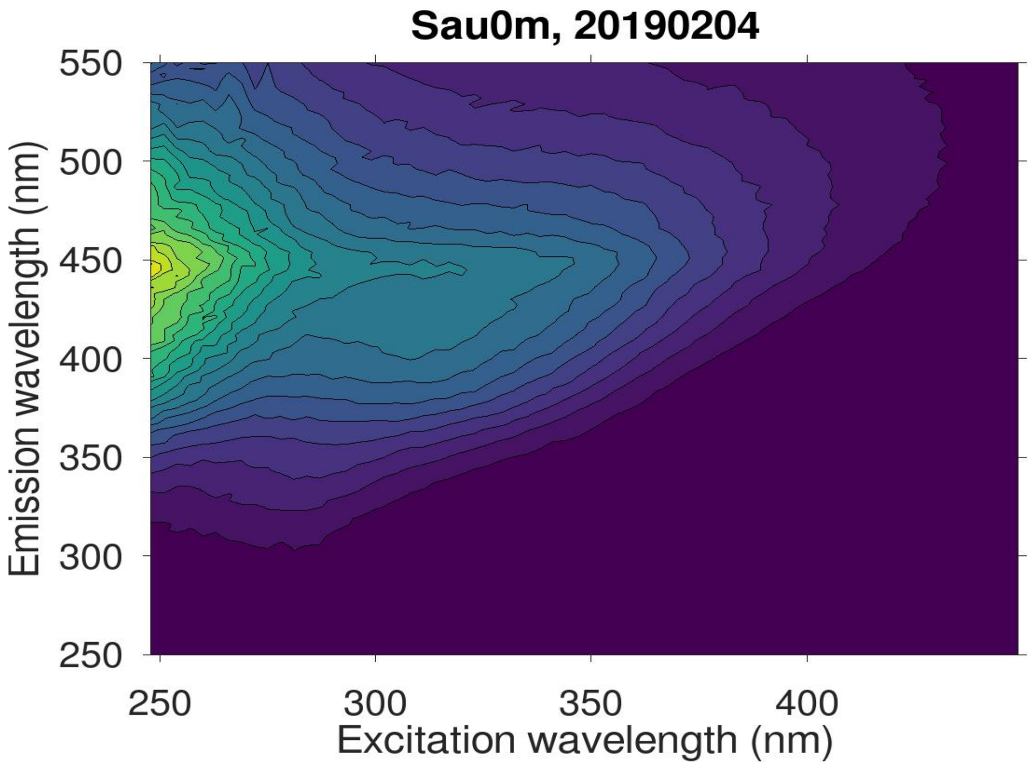
Supplementary Figure S17: Excitation-Emission matrix (EEM) for a sample collected at a depth of 15 m from the surface of Sau Reservoir on 2018-11-05.



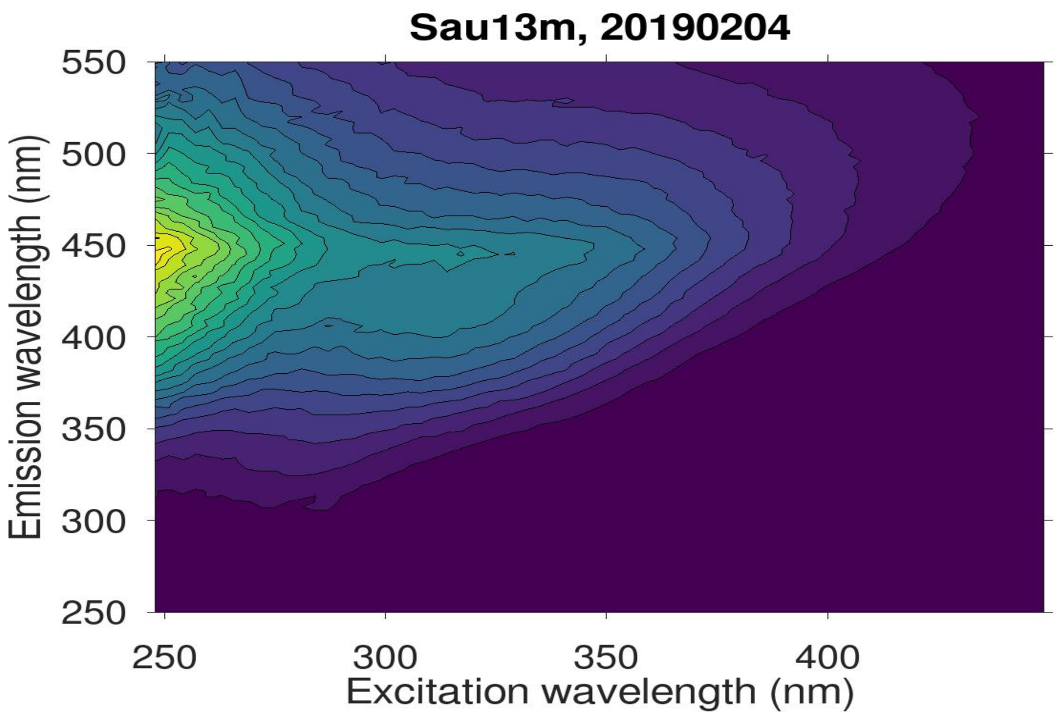
Supplementary Figure S18: Excitation-Emission matrix (EEM) for a sample collected at a depth of 30 m from the surface of Sau Reservoir on 2018-11-05.



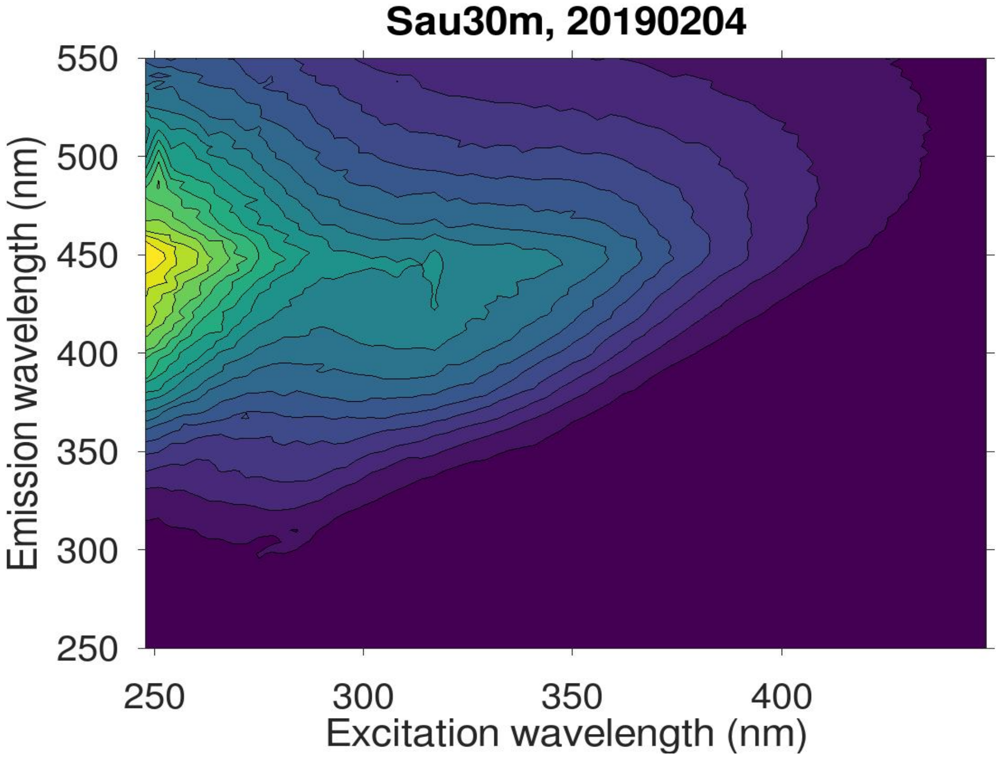
Supplementary Figure S19: Excitation-Emission matrix (EEM) for a sample collected at a depth of 40 m from the surface of Sau Reservoir on 2018-11-05.



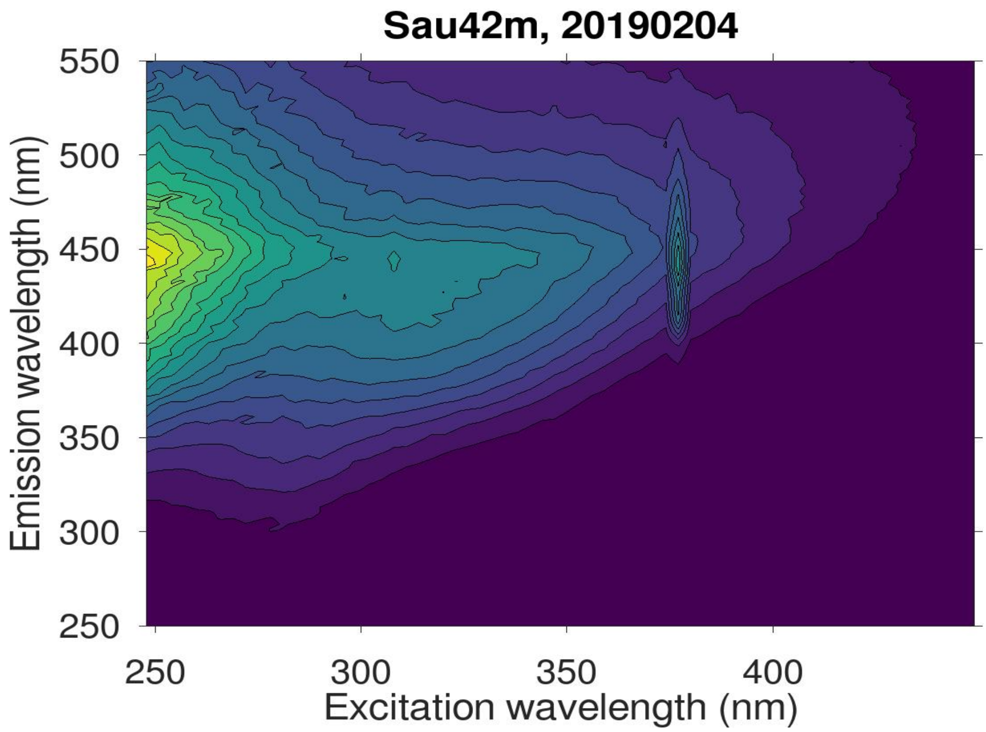
Supplementary Figure S20: Excitation-Emission matrix (EEM) for a sample collected from the surface of Sau Reservoir on 2019-02-04.



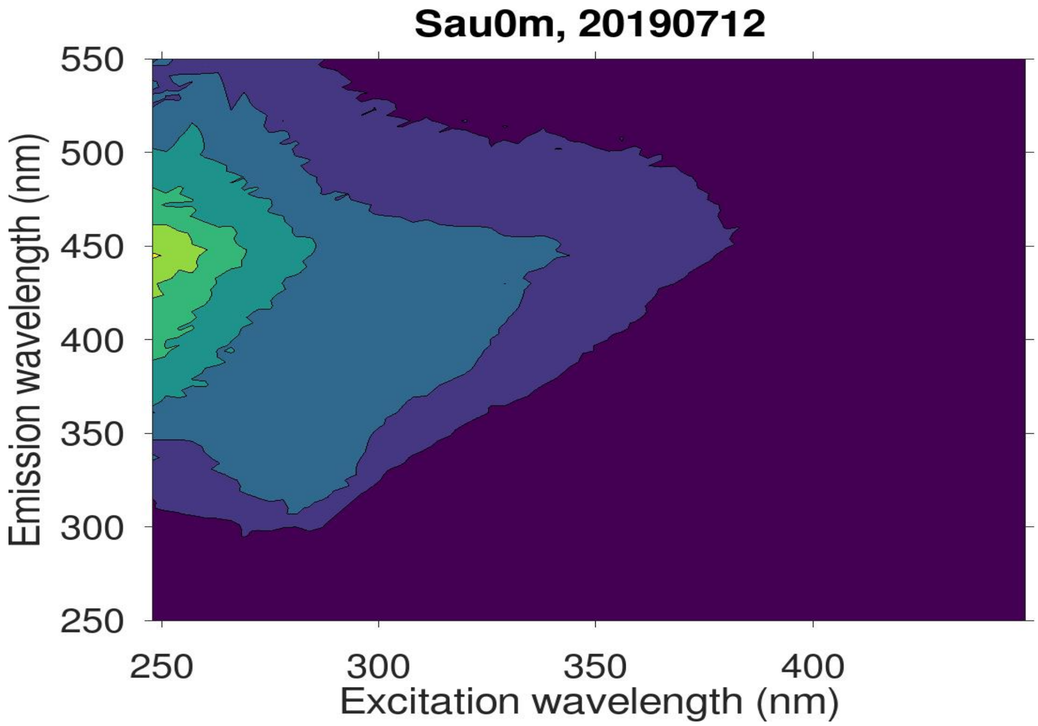
Supplementary Figure S21: Excitation-Emission matrix (EEM) for a sample collected at a depth of 13 m from the surface of Sau Reservoir on 2019-02-04.



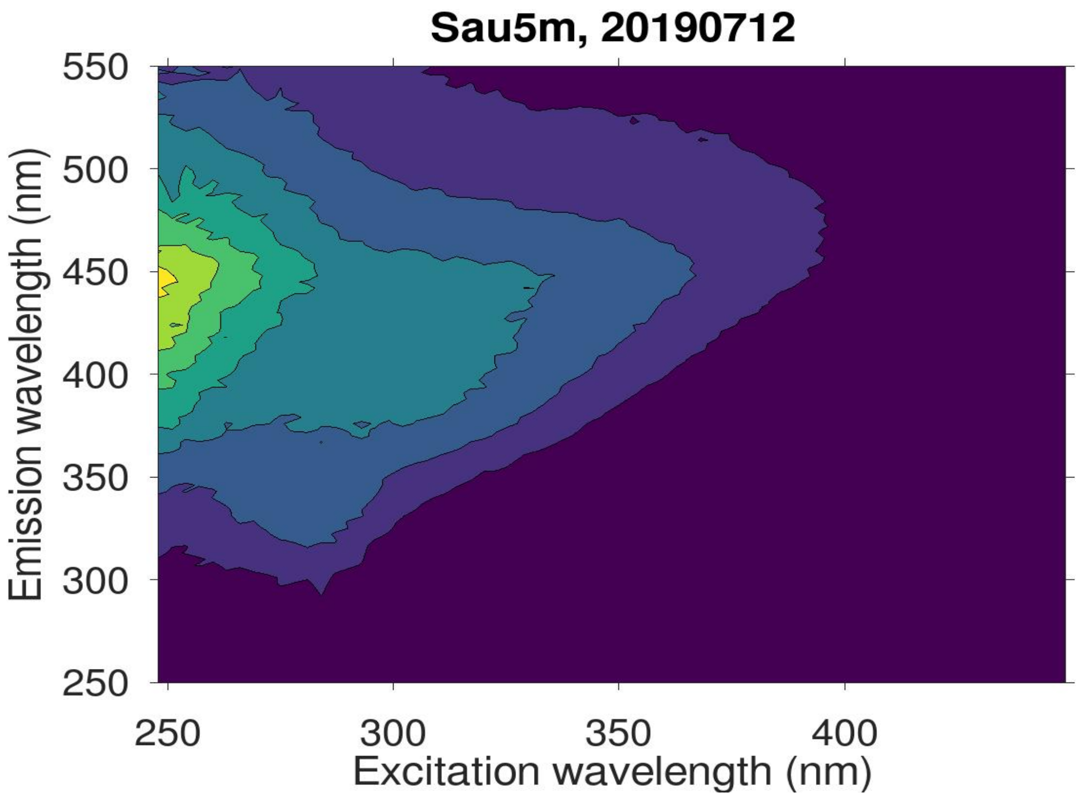
Supplementary Figure S22: Excitation-Emission matrix (EEM) for a sample collected at a depth of 30 m from the surface of Sau Reservoir on 2019-02-04.



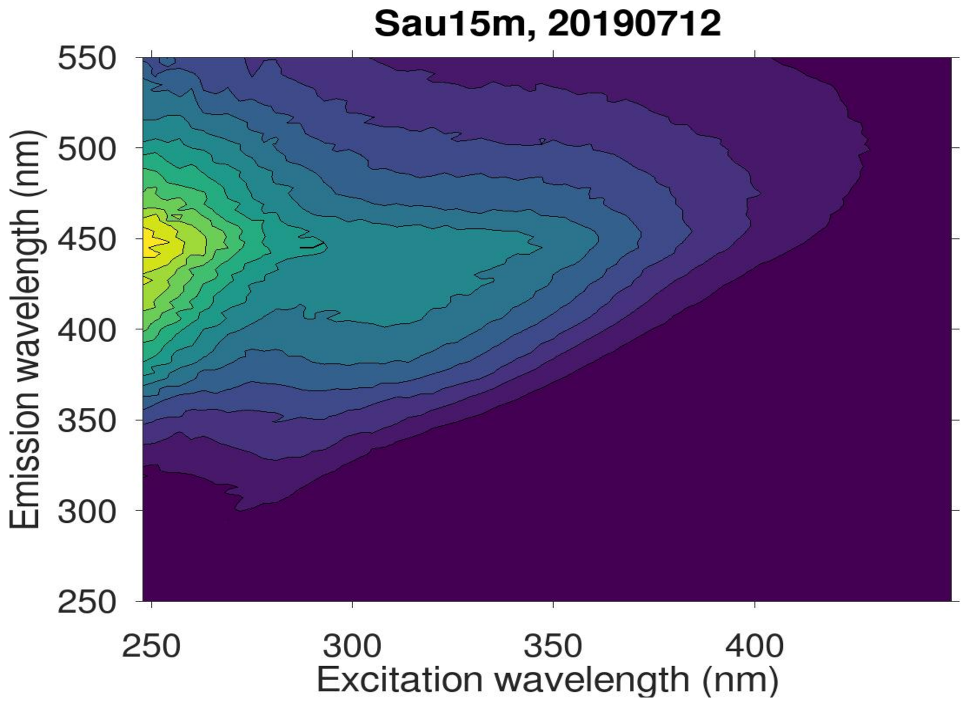
Supplementary Figure S23: Excitation-Emission matrix (EEM) for a sample collected at a depth of 42 m from the surface of Sau Reservoir on 2019-02-04.



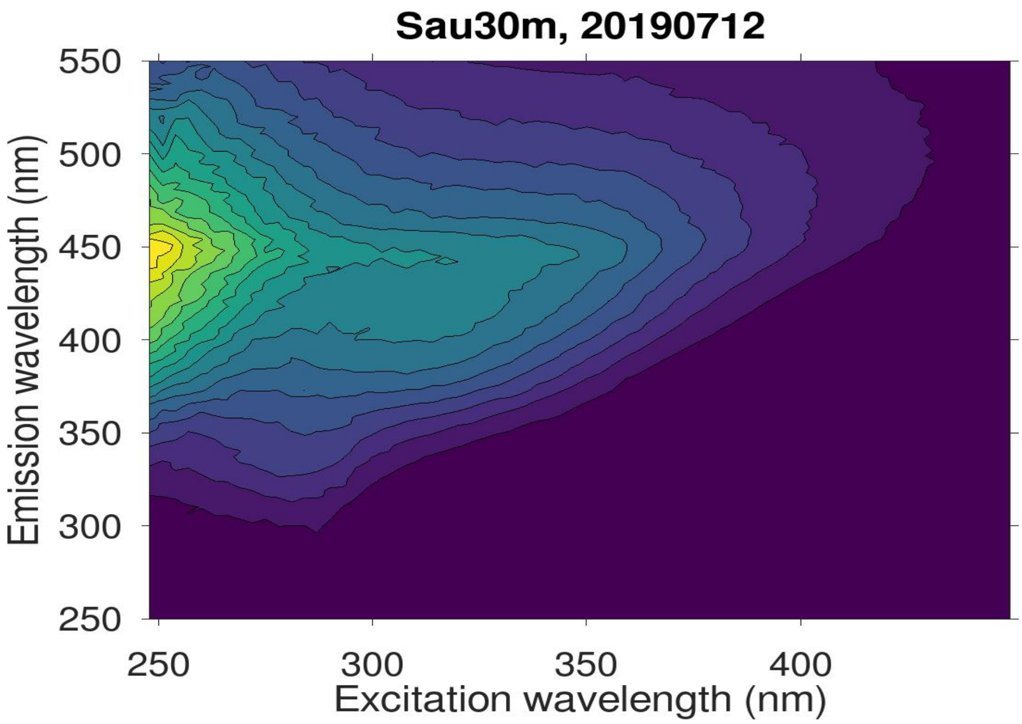
Supplementary Figure S24: Excitation-Emission matrix (EEM) for a sample collected from the surface of Sau Reservoir on 2019-07-12.



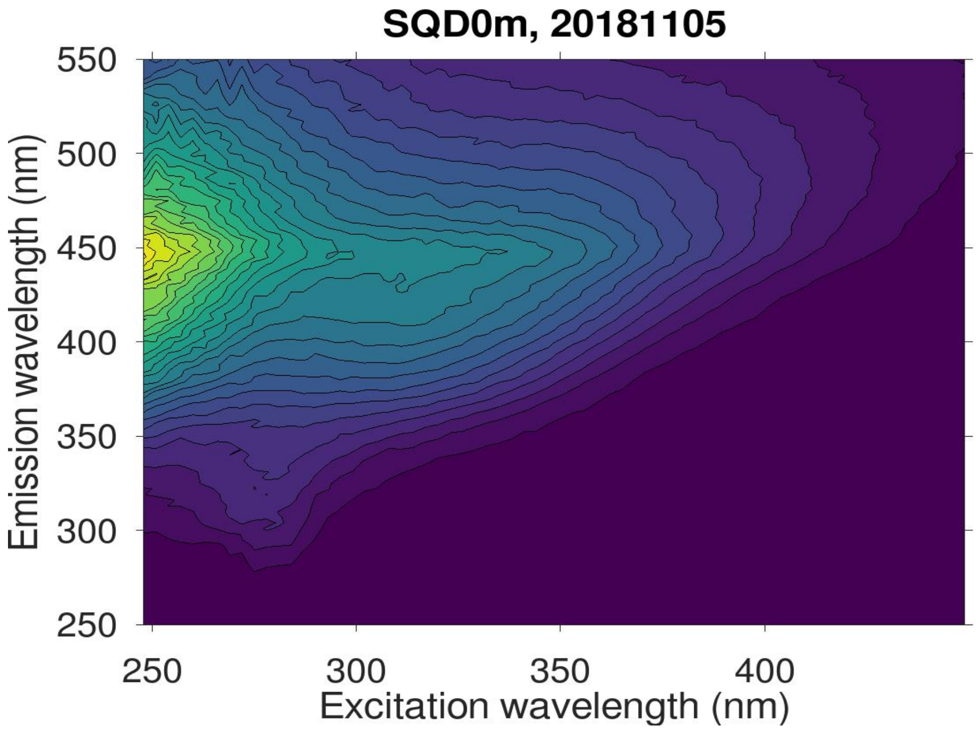
Supplementary Figure S25: Excitation-Emission matrix (EEM) for a sample collected at a depth of 5 m from the surface of Sau Reservoir on 2019-07-12.



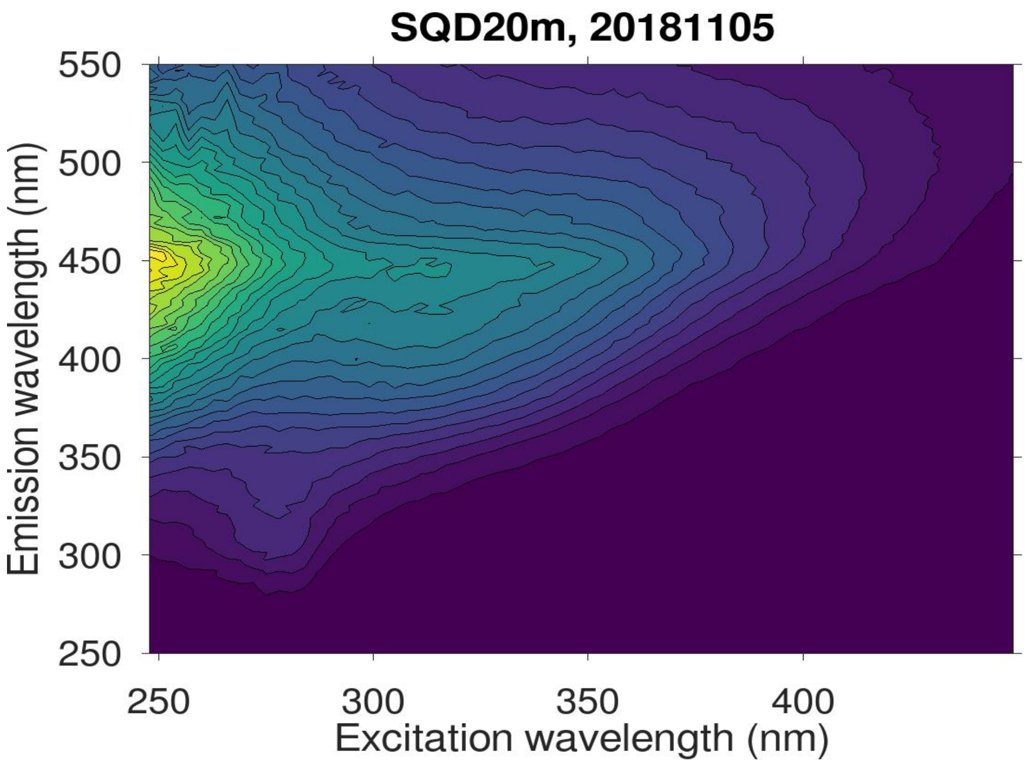
Supplementary Figure S26: Excitation-Emission matrix (EEM) for a sample collected at a depth of 15 m from the surface of Sau Reservoir on 2019-07-12.



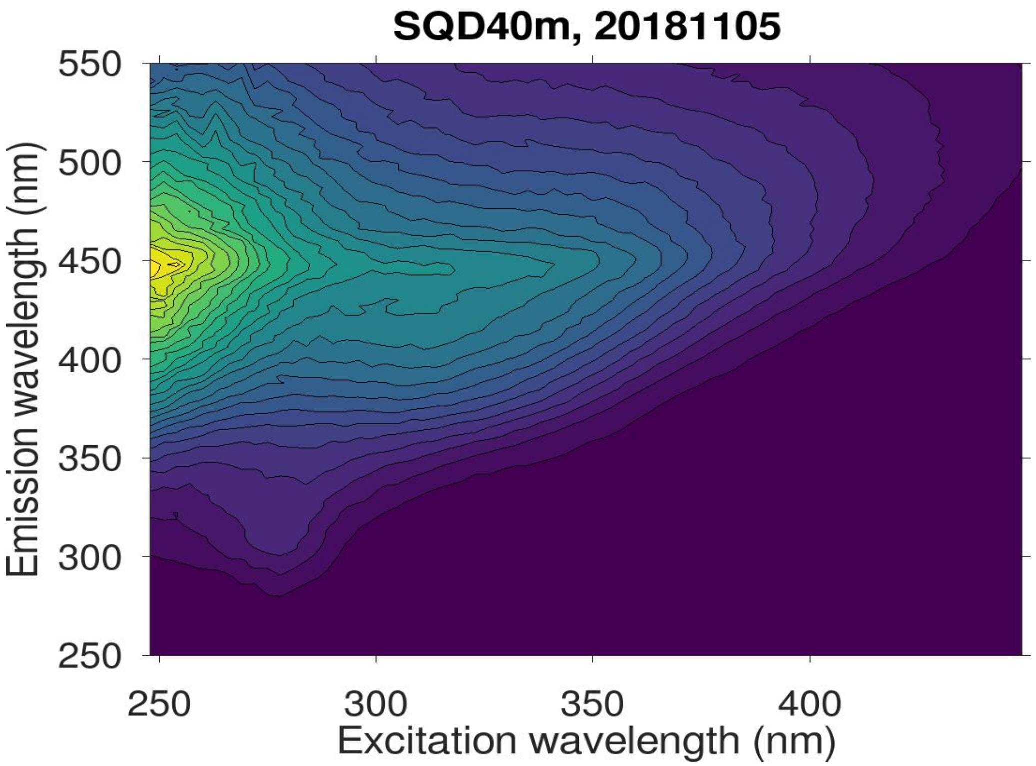
Supplementary Figure S27: Excitation-Emission matrix (EEM) for a sample collected at a depth of 15 m from the surface of Sau Reservoir on 2019-07-12.



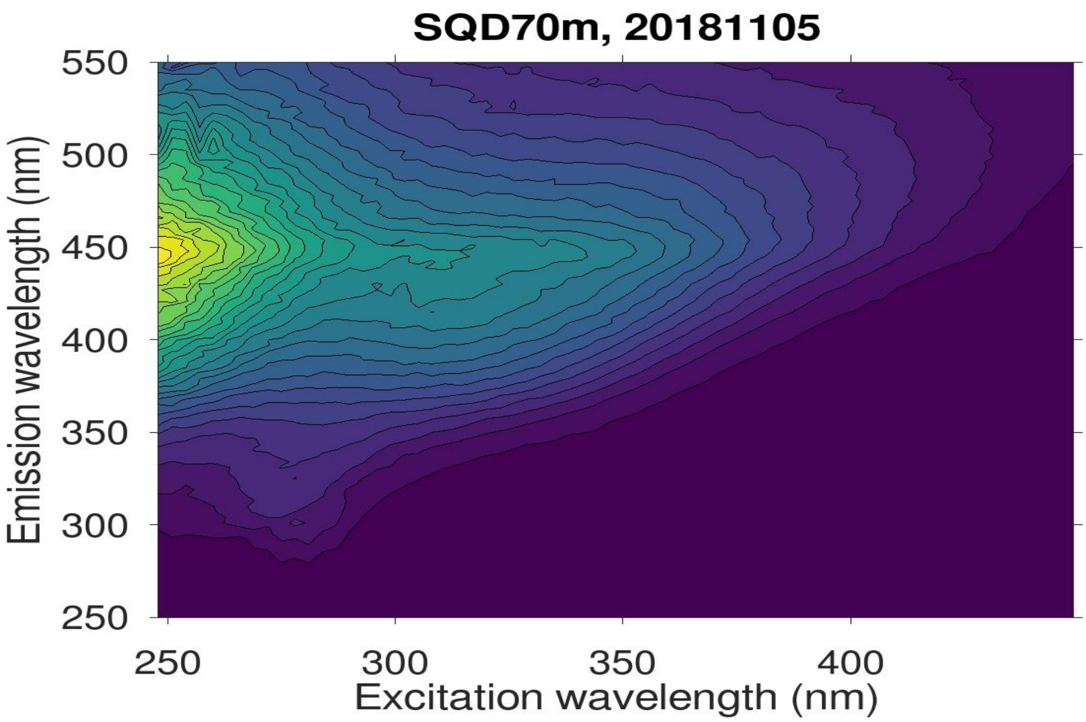
Supplementary Figure S28: Excitation-Emission matrix (EEM) for a sample collected from the surface of Susqueda Reservoir on 2018-11-05.



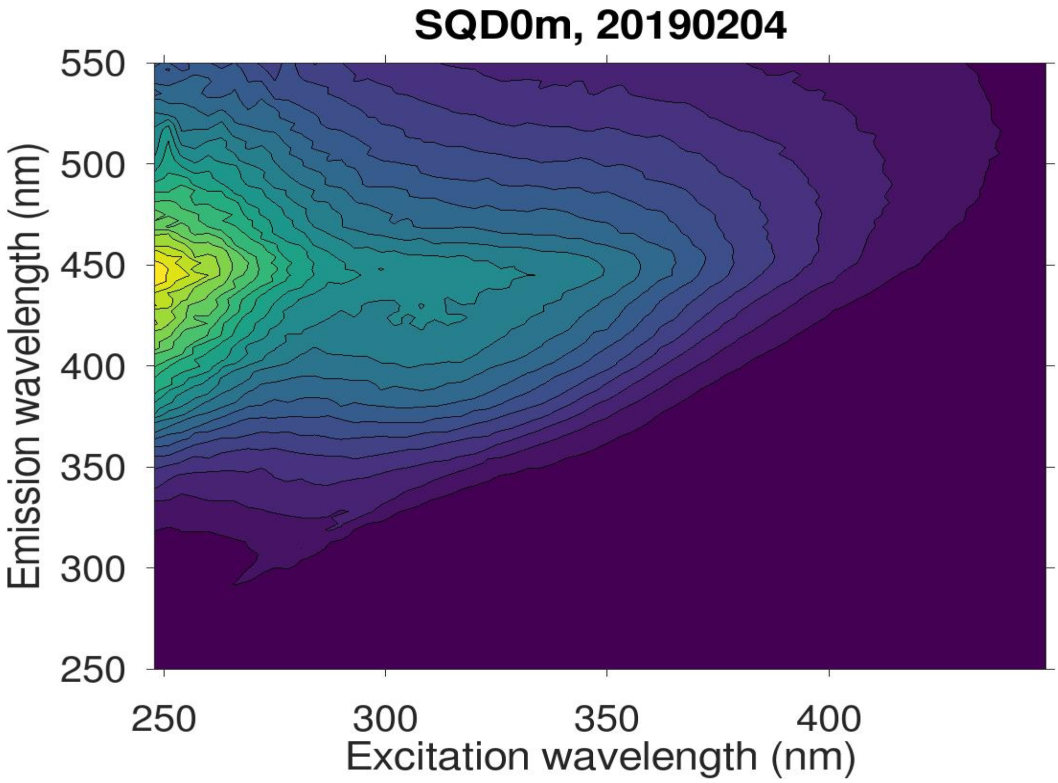
Supplementary Figure S29: Excitation-Emission matrix (EEM) for a sample collected at a depth of 20 m from the surface of Susqueda Reservoir on 2018-11-05.



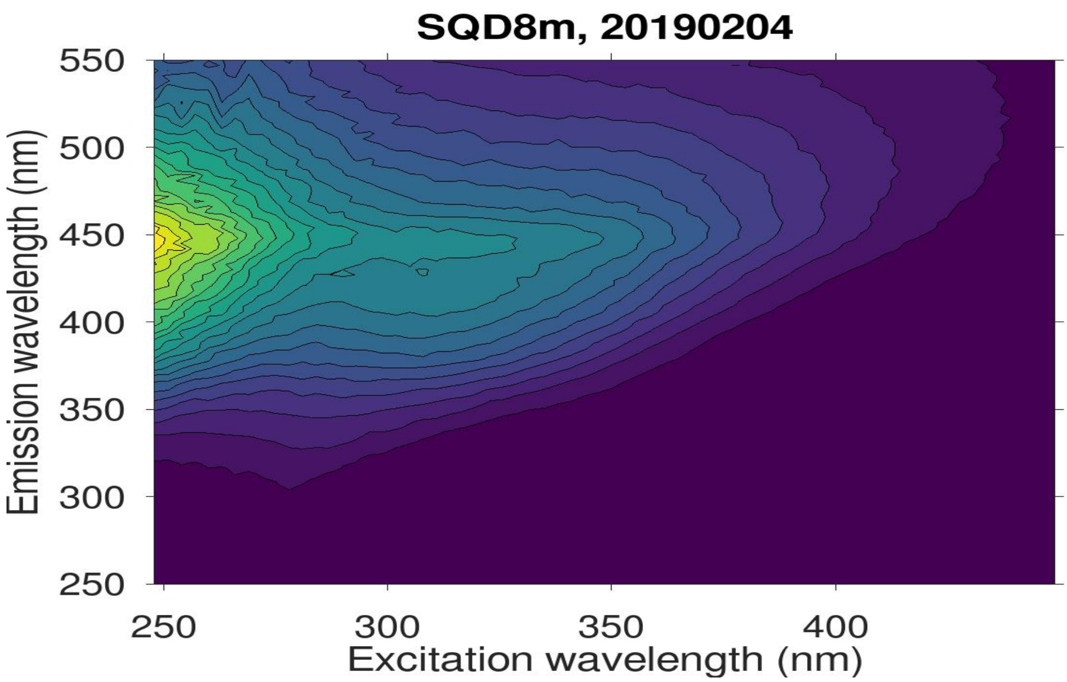
Supplementary Figure S30: Excitation-Emission matrix (EEM) for a sample collected at a depth of 40 m from the surface of Susqueda Reservoir on 2018-11-05.



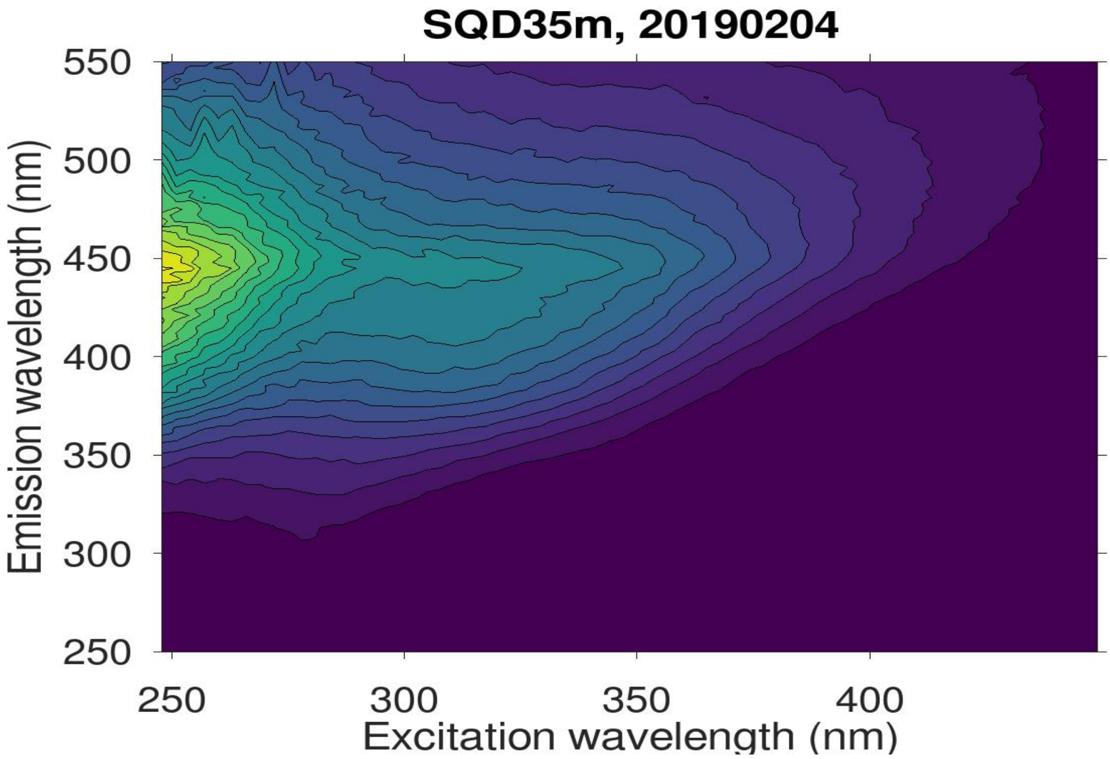
Supplementary Figure S31: Excitation-Emission matrix (EEM) for a sample collected at a depth of 70 m from the surface of Susqueda Reservoir on 2018-11-05.



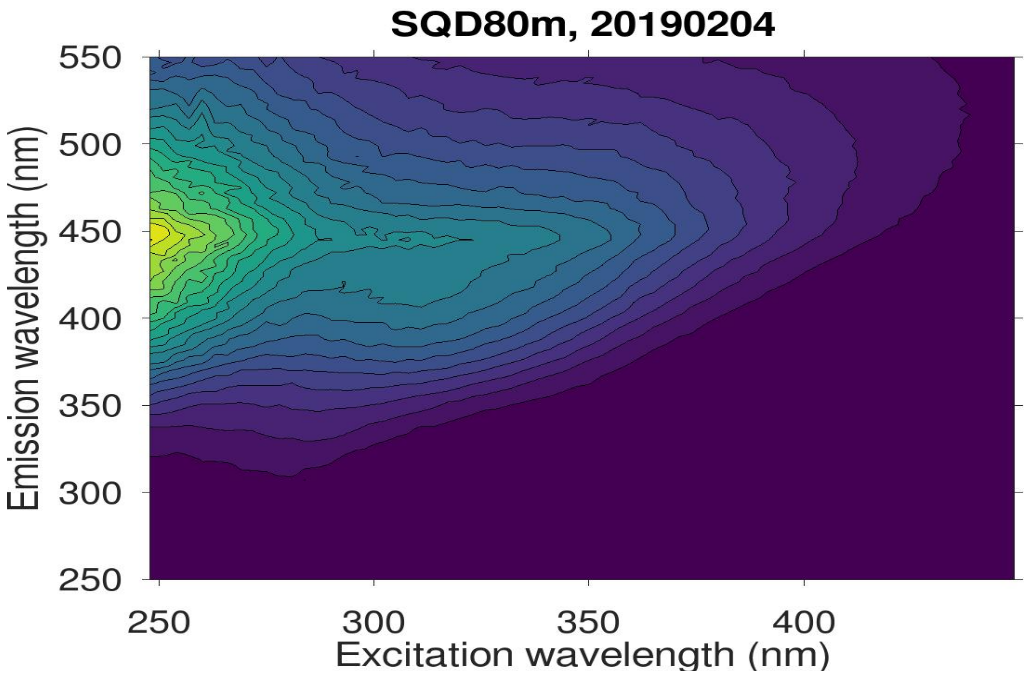
Supplementary Figure S32: Excitation-Emission matrix (EEM) for a sample collected from the surface of Susqueda Reservoir on 2019-02-04.



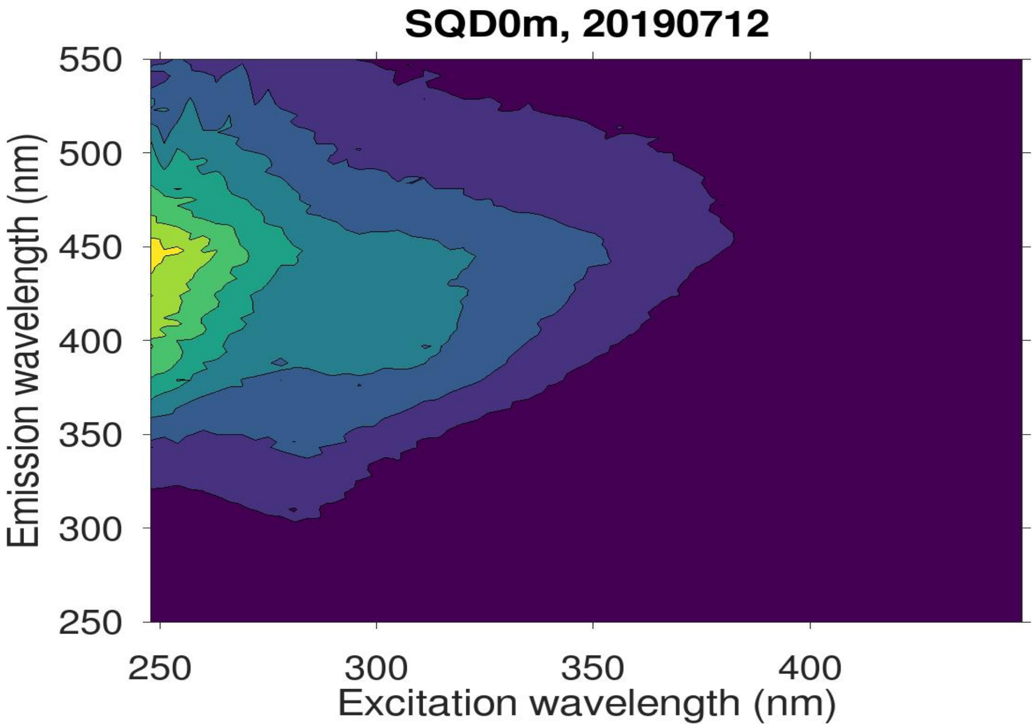
Supplementary Figure S33: Excitation-Emission matrix (EEM) for a sample collected at a depth of 8 m from the surface of Susqueda Reservoir on 2019-02-04.



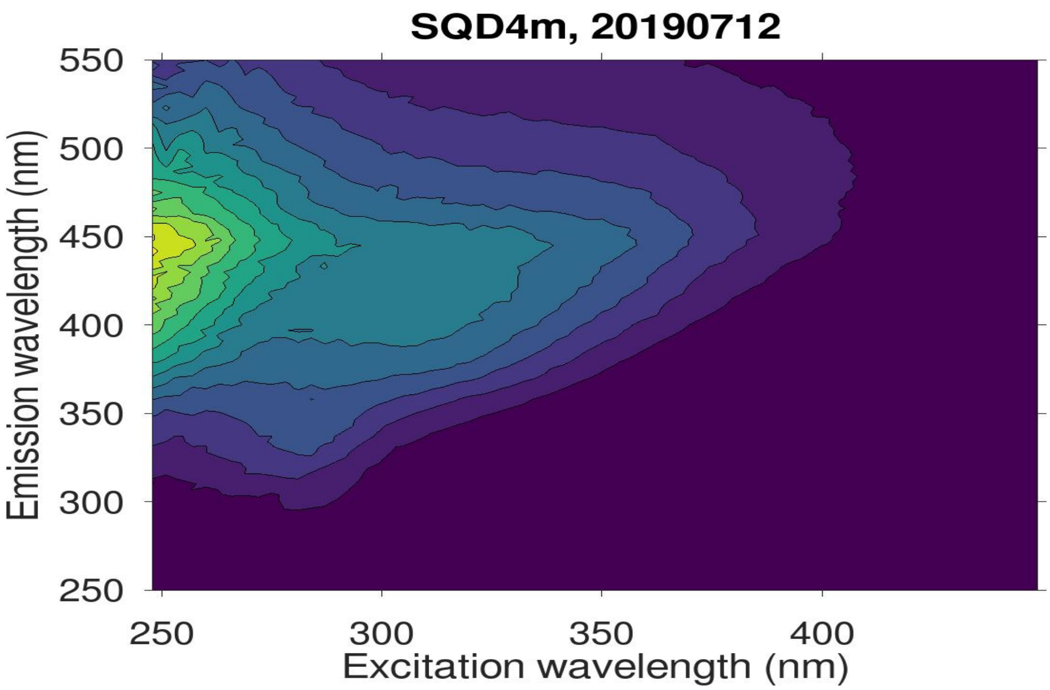
Supplementary Figure S34: Excitation-Emission matrix (EEM) for a sample collected at a depth of 35 m from the surface of Susqueda Reservoir on 2019-02-04.



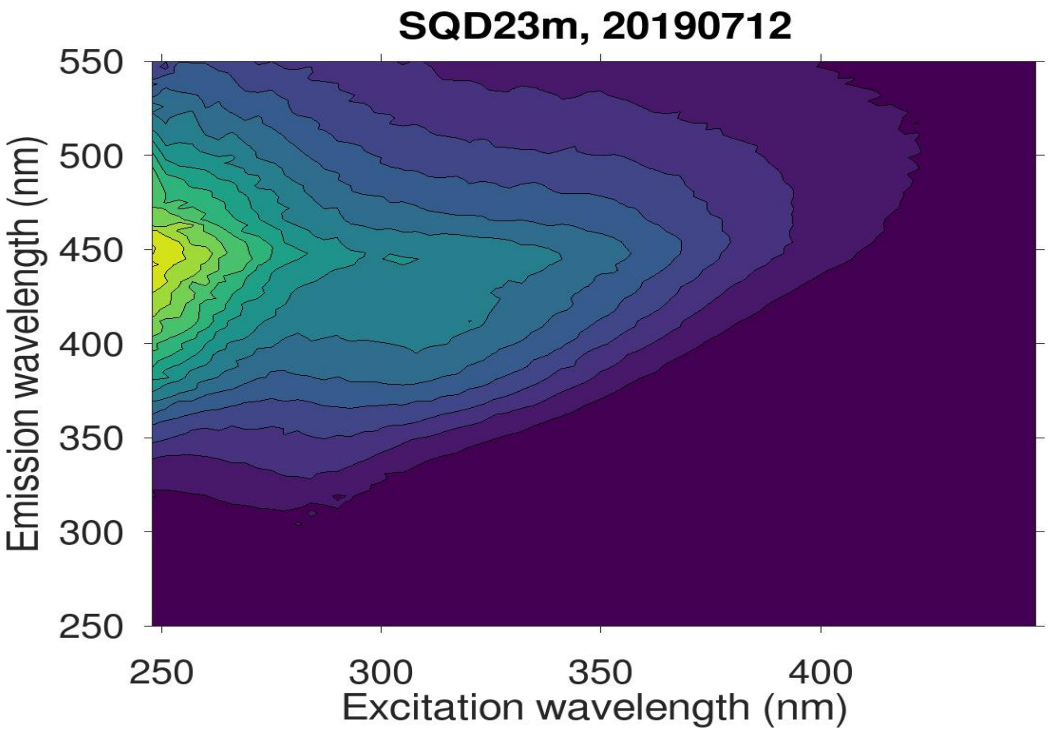
Supplementary Figure S35: Excitation-Emission matrix (EEM) for a sample collected at a depth of 80 m from the surface of Susqueda Reservoir on 2019-02-04.



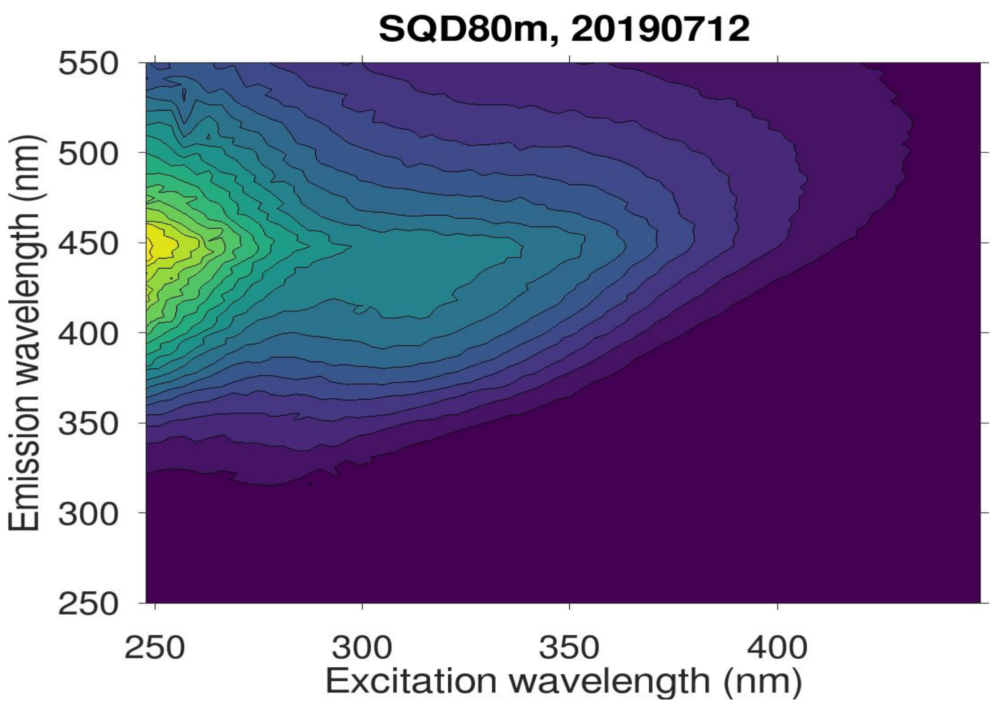
Supplementary Figure S36: Excitation-Emission matrix (EEM) for a sample collected from the surface of Susqueda Reservoir on 2019-07-12.



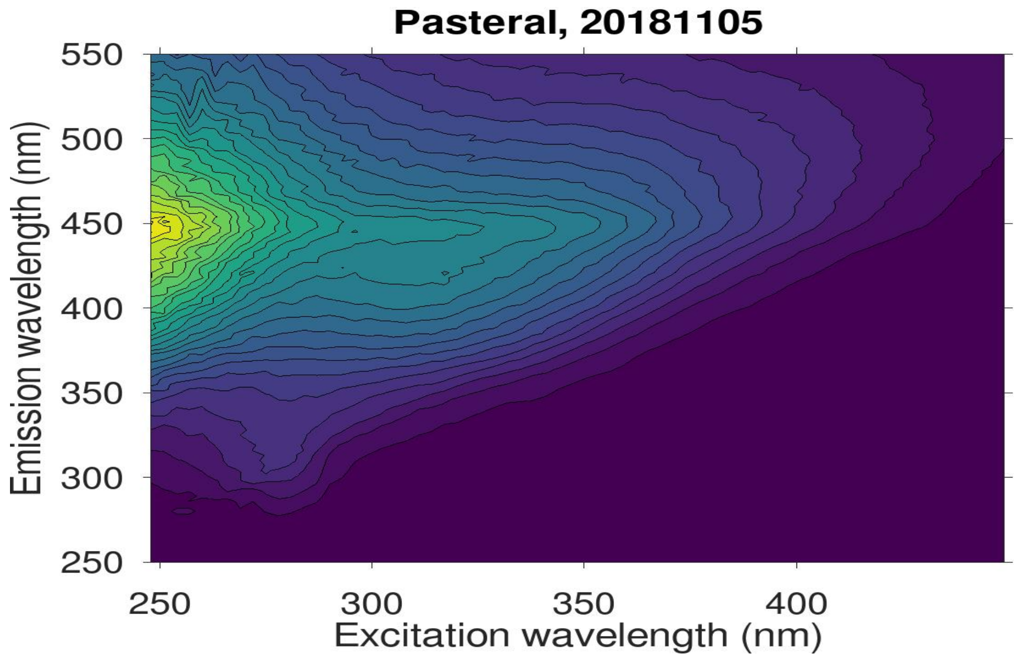
Supplementary Figure S37: Excitation-Emission matrix (EEM) for a sample collected at a depth of 4 m from the surface of Susqueda Reservoir on 2019-07-12.



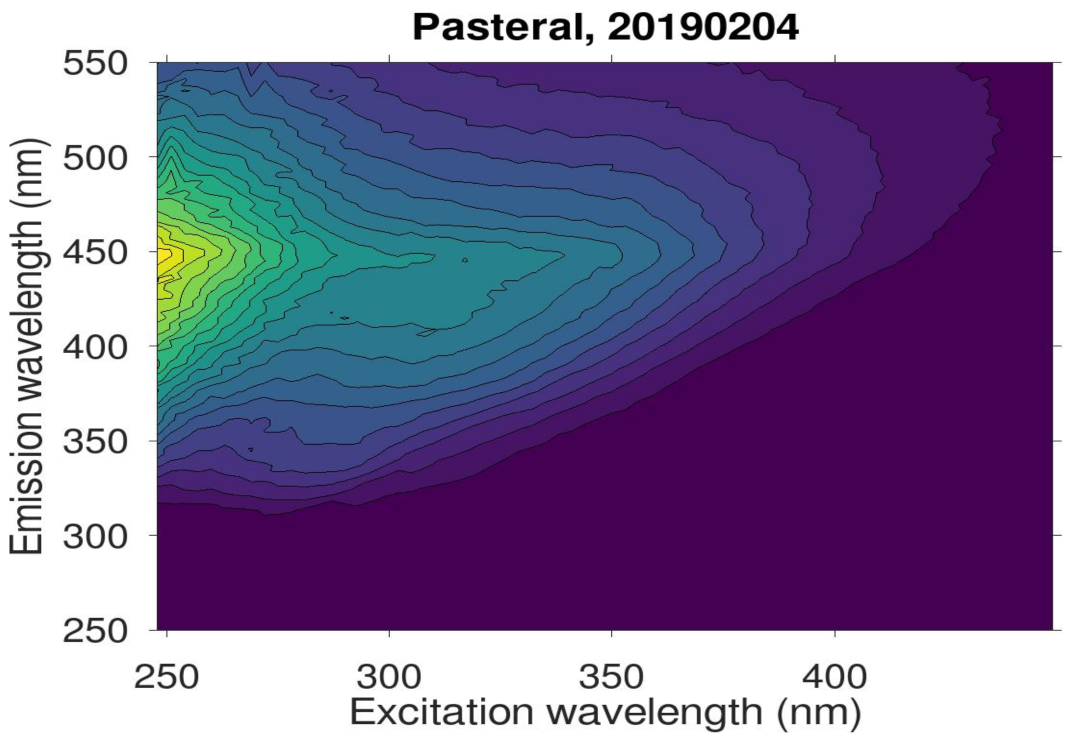
Supplementary Figure S38: Excitation-Emission matrix (EEM) for a sample collected at a depth of 23 m from the surface of Susqueda Reservoir on 2019-07-12.



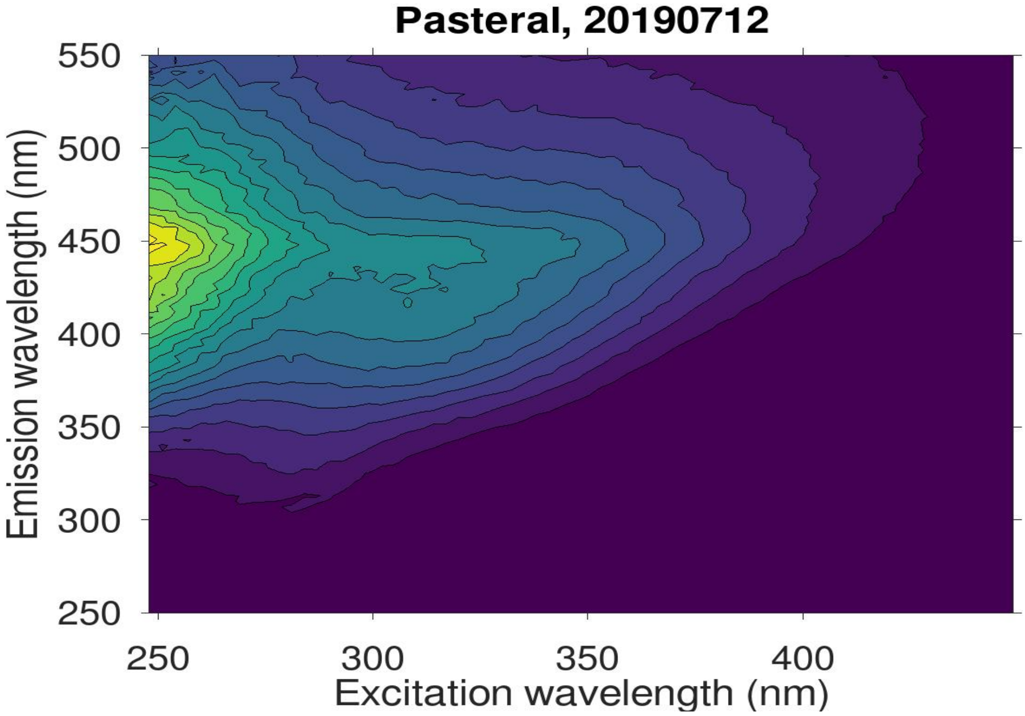
Supplementary Figure S39: Excitation-Emission matrix (EEM) for a sample collected at a depth of 80 m from the surface of Susqueda Reservoir on 2019-07-12.



Supplementary Figure S40: Excitation-Emission matrix (EEM) for a sample collected from the surface of Pasteral Reservoir on 2018-11-05.



Supplementary Figure S41: Excitation-Emission matrix (EEM) for a sample collected from the surface of Pasteral Reservoir on 2019-02-04.



Supplementary Figure S42: Excitation-Emission matrix (EEM) for a sample collected from the surface of Pasteral Reservoir on 2019-07-12.

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