

Supplement

S1 Influence of sample dilution

To test the possible influence of different dilutions on the pH-related changes in fluorescence (Patel-Sorrentino et al., 2002; Baker et al., 2007), dilution series, in the range used in the freezing experiment depending on sample type, with samples (n = 14) from the same plots and same sample types but with different sampling dates where measured for pH, absorption and fluorescence according to the protocol in sec. 2.3. We had 31 dilutions in total for all samples. The dilutions depending on sample types and are in the range used in the freezing experiment. We calculated the differences between the dilutions per sample for pH and DOM composition variables (PARAFAC components %C1-%C4, SUVA₂₅₄ and HIX) and calculated means, standard deviations and mean absolute deviations (MAD). These were compared to the values of measurement accuracy, determined by analyzing 11 samples in 3 replications (Table S1). For the PARAFAC components %C1, %C2 and %C3 and SUVA₂₅₄ the MAD caused by dilution were less or equal than the precision, so that we assume that there is no influence of dilution on the three humic-like components and the specific UV absorbance at 254 nm. For %C4 and HIX the effect of dilution can exceed the precision of fluorescence measurements. Differences found for different treatments could be related to differences in sample dilution for these two variables

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Table S1: Mean absolute deviation for DOM composition variables calculated for measurement accuracy and dilution experiment

mean absolute deviation (MAD)	%C1	%C2	%C3	%C4	HIX	SUVA	FI	ab
accuracy	0.59	0.73	1.10	0.45	0.008	0.21	0.026	0.012
dilution	0.28	0.58	0.87	0.96	0.010	0.22	0.045	0.014

S2 Data availability

All graphics and statistical analyses in the manuscript were based on the data provided in the following tables. Table S1 contains the DOC concentrations measured in fresh samples (fresh) and after freezing and storage at -18°C (-18°C) as well as after fast-freezing with liquid nitrogen and storage at -18°C (N₂). Table S2 also contains the changes between both freezing treatments and the fresh samples given as concentration and percent. Similar Tables are given for SUVA₂₅₄ (Table S3) and HIX (Table S4). The relative percentage distribution of the four PARAFAC components and the change between the fresh and both frozen treatments are given in Table S5 (%C1 and %C2) and Table S6 (%C3 and %C4).

Table S2: DOC concentrations of fresh samples, after freezing (-18°C) and after fast-freezing with liquid nitrogen (N₂) and related changes (absolute and %).

Sample Type	Plot	DOC (mg L ⁻¹)				DOC (mg L ⁻¹)			
		Fresh	-18°C	Change (mg L ⁻¹)	Change (%)	Fresh	N ₂	Change (mg L ⁻¹)	Change (%)
TF	G5	5.35	4.64	-0.71	-13.29	5.35	4.71	-0.64	-11.91
	W1	15.44	15.25	-0.19	-1.26	15.44	15.92	0.48	3.11
	W2	17.54	15.79	-1.75	-9.98	17.54	15.02	-2.52	-14.38
	W3	13.27	12.76	-0.51	-3.82	13.27	12.69	-0.58	-4.33
	W5	7.26	5.42	-1.84	-25.40	7.26	5.51	-1.75	-24.14
SF	W9	7.92	6.97	-0.95	-11.99	7.92	7.10	-0.81	-10.25
	W1	29.74	33.04	3.30	11.10	29.74	36.24	6.50	21.87
	W2	74.51	69.23	-5.29	-7.10	74.51	67.23	-7.28	-9.78
	W3	138.47	135.93	-2.54	-1.84	138.47	134.51	-3.96	-2.86
	W5	24.39	23.89	-0.50	-2.06	24.39	23.86	-0.53	-2.16
LL	W9	12.45	11.32	-1.12	-9.03	12.45	12.22	-0.22	-1.81
	W1	43.90	48.75	4.86	11.06	43.90	51.88	7.98	18.19
	W2	74.60	68.60	-5.99	-8.03	74.60	66.46	-8.14	-10.91
	W3	68.15	64.52	-3.63	-5.32	68.15	67.15	-1.00	-1.47
	W5	32.18	30.13	-2.05	-6.37	32.18	30.39	-1.80	-5.58
Top	W9	22.53	22.82	0.29	1.30	22.53	23.69	1.17	5.18
	G3	39.46	34.91	-4.56	-11.54	39.46	40.39	0.92	2.34
	G39	30.65	26.67	-3.98	-12.98	30.65	26.67	-3.98	-12.98
	G5	31.30	31.26	-0.04	-0.13	31.30	31.50	0.19	0.62
	W3	12.95	12.80	-0.15	-1.15	12.95	12.40	-0.55	-4.22
Sub	W5	124.24	122.56	-1.68	-1.35	124.24	124.47	0.23	0.18
	W9	29.67	27.93	-1.74	-5.86	29.67	30.53	0.86	2.89
	G3	36.71	30.99	-5.71	-15.57	36.71	34.86	-1.85	-5.03
	W1	11.21	9.81	-1.41	-12.55	11.21	10.12	-1.10	-9.77
	W2	21.94	21.51	-0.44	-1.98	21.94	23.12	1.17	5.35
	W3	47.01	44.85	-2.16	-4.60	47.01	46.83	-0.18	-0.39
	W9	8.53	6.91	-1.62	-19.00	8.53	7.75	-0.79	-9.23

Table S3: Absolute SUVA₂₅₄ values of fresh samples, after freezing (-18°C) and after fast-freezing with liquid nitrogen (N₂) and related changes (absolute and %).

Sample Type	Plot	SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)				SUVA ₂₅₄ (L mg ⁻¹ m ⁻¹)			
		Fresh	-18°C	Change (L mg ⁻¹ m ⁻¹)	Change (%)	Fresh	N ₂	Change (L mg ⁻¹ m ⁻¹)	Change (%)
TF	G5	1.88	2.94	56.79	1.07	1.88	2.54	0.66	35.34
	W1	2.42	2.69	11.12	0.27	2.42	2.46	0.04	1.66
	W2	2.13	2.72	27.65	0.59	2.13	2.70	0.57	26.65
	W3	2.34	2.38	1.66	0.04	2.34	2.48	0.14	6.15
	W5	2.05	2.84	38.65	0.79	2.05	2.62	0.58	28.15
	W9	2.37	3.32	39.76	0.94	2.37	2.77	0.39	16.58
SF	W1	3.06	3.25	6.29	0.19	3.06	2.86	-0.20	-6.59
	W2	2.64	2.87	8.79	0.23	2.64	2.92	0.28	10.52
	W3	2.76	2.92	5.87	0.16	2.76	3.39	0.63	22.83
	W5	2.77	3.21	15.74	0.44	2.77	2.90	0.12	4.38
	W9	2.40	2.95	22.95	0.55	2.40	2.46	0.06	2.45
LL	W1	4.49	4.21	-6.35	-0.29	4.49	4.03	-0.46	-10.17
	W2	3.77	3.72	-1.28	-0.05	3.77	4.69	0.93	24.65
	W3	3.11	4.05	30.05	0.94	3.11	4.43	1.32	42.45
	W5	3.70	4.03	9.02	0.33	3.70	4.13	0.43	11.69
	W9	3.92	4.38	11.72	0.46	3.92	4.09	0.17	4.26
Top	G3	2.26	2.85	26.42	0.60	2.26	2.57	0.32	14.09
	G39	2.54	2.75	8.02	0.20	2.54	3.01	0.47	18.46
	G5	2.93	2.79	-4.65	-0.14	2.93	2.87	-0.06	-2.20
	W3	1.13	2.76	145.01	1.64	1.13	2.92	1.79	158.79
	W5	4.28	4.52	5.44	0.23	4.28	4.38	0.10	2.29
	W9	3.47	4.18	20.45	0.71	3.47	4.27	0.80	23.09
Sub	G3	3.68	3.74	1.66	0.06	3.68	3.65	-0.03	-0.86
	W1	1.62	1.98	22.81	0.37	1.62	2.47	0.85	52.84
	W2	1.58	1.79	13.32	0.21	1.58	1.78	0.20	12.93
	W3	3.05	3.02	-1.08	-0.03	3.05	3.16	0.11	3.75
	W9	2.03	2.87	41.71	0.85	2.03	4.06	2.03	100.09

Table S4: Absolute HIX values of fresh samples, after freezing (-18°C) and after fast-freezing with liquid nitrogen (N₂) and related changes (absolute and %).

Sample Type	Plot	HIX				HIX			
		Fresh	-18°C	Change	Change (%)	Fresh	N ₂	Change	Change (%)
TF	G5	0.852	0.750	-0.102	-11.96	0.852	0.792	-0.060	-7.06
	W1	0.834	0.777	-0.057	-6.87	0.834	0.812	-0.022	-2.61
	W2	0.806	0.803	-0.004	-0.44	0.806	0.807	0.001	0.14
	W3	0.816	0.838	0.022	2.68	0.816	0.782	-0.034	-4.13
	W5	0.866	0.836	-0.030	-3.41	0.866	0.841	-0.025	-2.91
	W9	0.880	0.752	-0.128	-14.55	0.880	0.848	-0.032	-3.62
SF	W1	0.873	0.844	-0.029	-3.36	0.873	0.847	-0.026	-2.96
	W2	0.819	0.833	0.013	1.62	0.819	0.834	-0.015	-1.84
	W3	0.806	0.839	0.034	4.21	0.806	0.832	0.027	3.30
	W5	0.883	0.914	0.032	3.59	0.883	0.897	0.014	1.63
	W9	0.931	0.861	-0.070	-7.55	0.931	0.896	-0.036	-3.82
LL	W1	0.942	0.895	-0.046	-4.92	0.942	0.919	-0.022	-2.38
	W2	0.850	0.920	0.070	8.28	0.850	0.900	0.050	5.89
	W3	0.926	0.903	-0.023	-2.52	0.926	0.910	-0.016	-1.72
	W5	0.915	0.914	-0.001	-0.13	0.915	0.933	0.018	1.97
	W9	0.963	0.900	-0.064	-6.63	0.963	0.944	-0.020	-2.04
Top	G3	0.969	0.943	-0.026	-2.69	0.969	0.953	-0.017	-1.72
	G39	0.931	0.929	-0.002	-0.22	0.931	0.939	0.008	0.88
	G5	0.970	0.961	-0.009	-0.90	0.970	0.958	-0.012	-1.25
	W3	0.931	0.916	-0.015	-1.63	0.931	0.898	-0.033	-3.58
	W5	0.941	0.939	-0.002	-0.27	0.941	0.952	0.011	1.17
	W9	0.962	0.942	-0.020	-2.07	0.962	0.935	-0.027	-2.82
Sub	G3	0.975	0.955	-0.020	-2.03	0.975	0.959	-0.016	-1.65
	W1	0.905	0.881	-0.024	-2.67	0.905	0.864	-0.041	-4.55
	W2	0.905	0.896	-0.009	-0.97	0.905	0.856	-0.049	-5.40
	W3	0.928	0.920	-0.008	-0.85	0.928	0.913	-0.015	-1.64
	W9	0.947	0.917	-0.031	-3.24	0.947	0.872	-0.076	-7.98

Table S5: Relative percentage distribution of PARAFAC components C1 and C2 of fresh samples, after freezing (-18°C) and after fast-freezing with liquid nitrogen (N₂) and related changes.

Sample Type	Plot	%C1			%C1			%C2			%C2		
		Fresh	-18°C	Change	Fresh	N ₂	Change	Fresh	-18°C	Change	Fresh	N ₂	Change
TF	G5	28.9	26.3	-2.7	28.9	24.9	-4.0	35.8	29.0	-6.8	35.8	32.7	-3.2
	W1	34.1	30.3	-3.8	34.1	28.9	-5.2	23.5	19.7	-3.8	23.5	18.8	-4.7
	W2	28.4	26.1	-2.3	28.4	27.3	-1.0	35.1	33.1	-2.0	35.1	34.0	-1.1
	W3	32.7	31.6	-1.1	32.7	31.2	-1.4	22.8	22.9	0.1	22.8	21.1	-1.6
	W5	31.3	29.1	-2.2	31.3	29.4	-1.9	34.0	30.7	-3.4	34.0	33.6	-0.4
SF	W9	36.4	31.9	-4.6	36.4	31.3	-5.1	27.9	21.6	-6.3	27.9	22.8	-5.1
	W1	36.6	31.5	-5.1	36.6	31.8	-4.7	23.5	19.2	-4.3	23.5	19.6	-3.9
	W2	32.2	29.7	-2.5	32.2	30.5	-1.7	21.6	19.4	-2.2	21.6	19.3	-2.3
	W3	32.5	31.4	-1.1	32.5	31.4	-1.2	19.0	19.1	0.2	19.0	19.0	0.1
	W5	36.3	34.8	-1.5	36.3	34.2	-2.1	25.9	23.6	-2.3	25.9	25.4	-0.5
LL	W9	34.5	30.7	-3.9	34.5	30.8	-3.7	24.6	19.2	-5.3	24.6	20.4	-4.2
	W1	44.1	39.0	-5.2	44.1	38.6	-5.5	23.7	18.2	-5.5	23.7	17.4	-6.2
	W2	41.4	41.1	-0.3	41.4	40.8	-0.6	17.9	18.8	1.0	17.9	18.2	0.3
	W3	44.3	41.3	-3.0	44.3	42.3	-1.9	15.9	16.1	0.2	15.9	17.0	1.0
	W5	45.8	42.5	-3.3	45.8	42.3	-3.5	23.2	21.5	-1.8	23.2	20.5	-2.7
Top	W9	44.1	38.7	-5.4	44.1	38.5	-5.5	25.1	19.7	-5.4	25.1	19.7	-5.4
	G3	27.8	25.0	-2.8	27.8	25.7	-2.1	25.5	21.9	-3.7	25.5	22.5	-3.1
	G39	33.0	31.1	-1.9	33.0	31.6	-1.4	27.8	19.7	-8.1	27.8	19.7	-8.1
	G5	30.3	28.4	-2.0	30.3	27.3	-3.0	24.0	22.5	-1.5	24.0	20.7	-3.3
	W3	27.5	25.8	-1.7	27.5	25.6	-1.9	28.7	25.3	-3.4	28.7	24.9	-3.7
Sub	W5	47.4	45.6	-1.8	47.4	44.4	-3.1	20.6	19.0	-1.6	20.6	18.3	-2.3
	W9	41.6	36.5	-5.2	41.6	35.7	-5.9	27.2	21.7	-5.6	27.2	20.9	-6.3
	G3	34.0	30.2	-3.7	34.0	30.4	-3.6	20.6	18.7	-2.0	20.6	17.9	-2.7
	W1	20.6	17.2	-3.4	20.6	18.2	-2.4	34.1	29.1	-5.0	34.1	28.8	-5.3
	W2	22.1	20.7	-1.5	22.1	20.5	-1.6	31.7	30.1	-1.6	31.7	28.4	-3.3
	W3	32.0	29.5	-2.5	32.0	30.4	-1.5	26.2	23.2	-3.0	26.2	23.8	-2.4
	W9	24.7	22.1	-2.7	24.7	23.6	-1.2	32.2	28.0	-4.2	32.2	26.0	-6.2

Table S6: Relative percentage distribution of PARAFAC components C3 and C4 of fresh samples, after freezing (-18°C) and after fast-freezing with liquid nitrogen (N₂) and related changes.

Sample Type	Plot	%C3			%C3			%C4			%C4		
		Fresh	-18°C	Change	Fresh	N ₂	Change	Fresh	-18°C	Change	Fresh	N ₂	Change
TF	G5	17.6	26.0	8.4	17.6	25.1	7.5	17.6	18.7	1.1	17.6	17.3	-0.4
	W1	25.4	32.1	6.7	25.4	35.8	10.4	17.0	17.8	0.9	17.0	16.5	-0.5
	W2	21.6	25.8	4.2	21.6	24.9	3.3	15.0	15.1	0.1	15.0	13.7	-1.2
	W3	25.9	27.9	2.0	25.9	29.9	4.0	18.7	17.7	-1.0	18.7	17.7	-0.9
	W5	20.8	26.5	5.7	20.8	23.8	3.0	13.9	13.8	-0.1	13.9	13.2	-0.7
SF	W9	23.0	29.2	6.2	23.0	31.5	8.5	12.7	17.3	4.6	12.7	14.3	1.6
	W1	25.7	35.1	9.5	25.7	34.7	9.0	14.3	14.2	-0.1	14.3	13.9	-0.4
	W2	29.6	36.5	6.9	29.6	35.3	5.7	16.6	14.4	-2.2	16.6	14.9	-1.8
	W3	32.7	35.7	3.0	32.7	35.4	2.8	15.8	13.8	-2.1	15.8	14.2	-1.7
	W5	26.8	34.5	7.8	26.8	32.2	5.4	11.0	7.1	-3.9	11.0	8.2	-2.8
LL	W9	31.8	39.1	7.3	31.8	40.2	8.5	9.1	11.1	1.9	9.1	8.5	-0.6
	W1	25.2	34.2	9.0	25.2	37.1	11.8	7.0	8.6	1.6	7.0	6.9	-0.1
	W2	29.2	32.6	3.4	29.2	33.1	3.9	11.5	7.5	-4.1	11.5	7.9	-3.6
	W3	32.2	35.0	2.8	32.2	32.9	0.7	7.6	7.6	0.0	7.6	7.7	0.2
	W5	23.5	28.8	5.3	23.5	31.1	7.7	7.5	7.2	-0.3	7.5	6.0	-1.5
Top	W9	25.7	34.8	9.1	25.7	36.5	10.8	5.1	6.8	1.7	5.1	5.3	0.2
	G3	42.4	48.7	6.3	42.4	48.1	5.7	4.3	4.4	0.1	4.3	3.8	-0.5
	G39	33.0	42.9	9.8	33.0	42.9	9.9	6.1	6.4	0.2	6.1	5.8	-0.3
	G5	41.3	45.0	3.7	41.3	48.2	6.9	4.4	4.2	-0.3	4.4	3.8	-0.6
	W3	38.0	42.7	4.7	38.0	42.4	4.4	5.8	6.3	0.4	5.8	7.1	1.2
Sub	W5	27.7	31.7	4.0	27.7	34.5	6.8	4.3	3.8	-0.5	4.3	2.8	-1.4
	W9	28.3	38.5	10.1	28.3	39.6	11.2	2.8	3.4	0.6	2.8	3.8	1.0
	G3	41.6	47.4	5.8	41.6	48.3	6.7	3.8	3.7	-0.1	3.8	3.4	-0.4
	W1	36.1	44.3	8.2	36.1	43.0	6.9	9.2	9.4	0.2	9.2	10.1	0.9
	W2	36.7	40.2	3.5	36.7	40.4	3.7	9.5	9.0	-0.4	9.5	10.8	1.3
	W3	35.8	41.5	5.7	35.8	39.6	3.8	6.0	5.8	-0.3	6.0	6.2	0.1
	W9	37.1	43.4	6.4	37.1	41.7	4.6	6.0	6.5	0.5	6.0	8.8	2.8

References

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