New Insights into the Seasonal Variation of DOM Quality of a Humic-Rich Drinking-Water Reservoir—Coupling 2D-Fluorescence and FTICR MS Measurements

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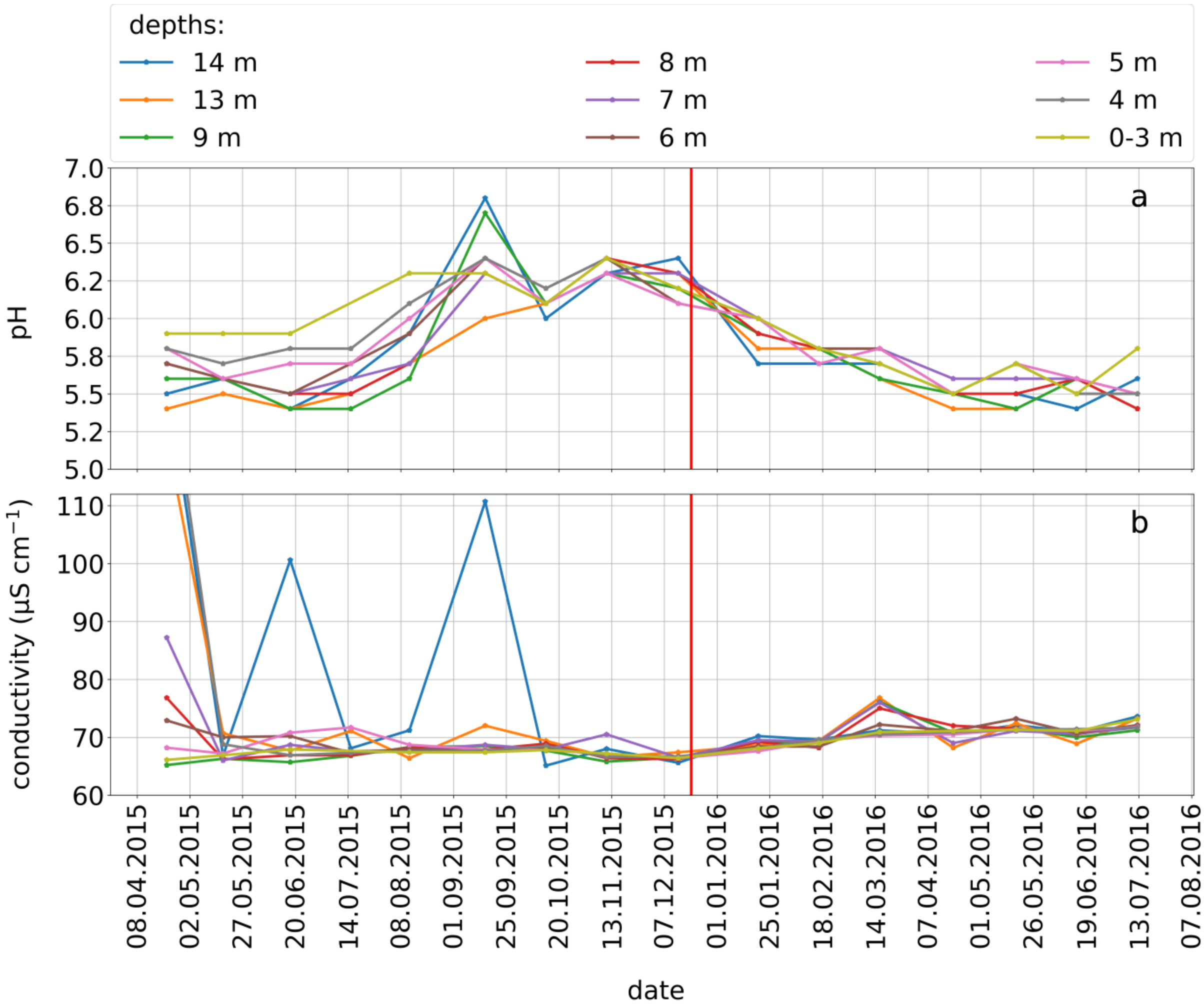

Figure S1: pH values (a) and conductivity in µS cm^{-1} (b) at all depth of the Muldenberg reservoir from April 2015 to August 2016. The first values of the conductivity in April 2015 was 132 µS cm^{-1} for 14 m, 122 µS cm^{-1} for 13 m and 136.4 µS cm^{-1} for 4 m.

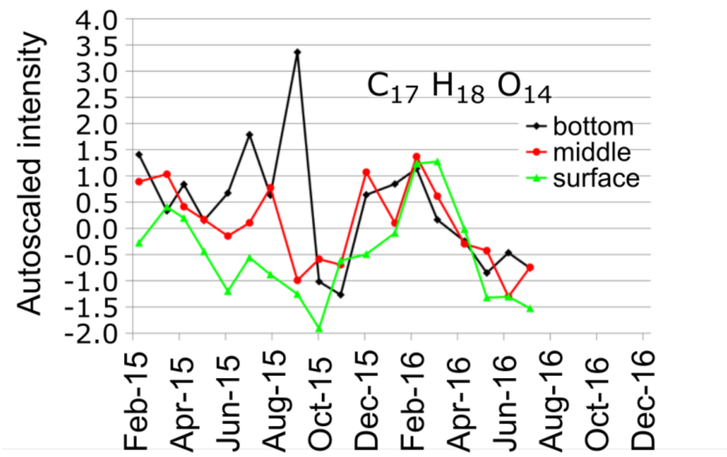

Figure S2: Autoscaled intensity of the MF $C_{17} H_{18} O_{14}$ at all three depths (bottom: 14 m, middle: 9m and surface: 0 m) from February 2015 to December 2016.

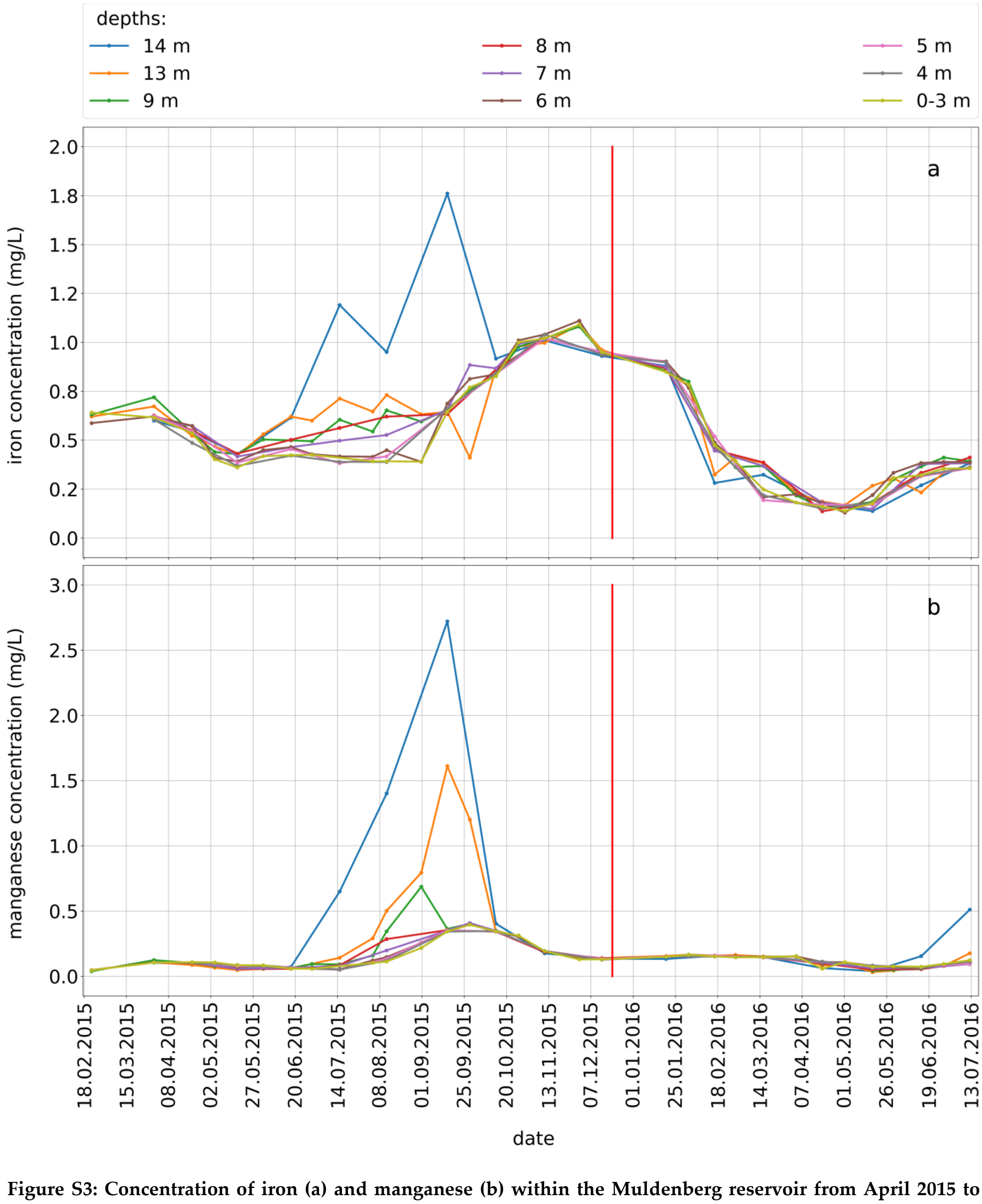

Figure S3: Concentration of iron (a) and manganese (b) within the Muldenberg reservoir from April 2015 to August2016.

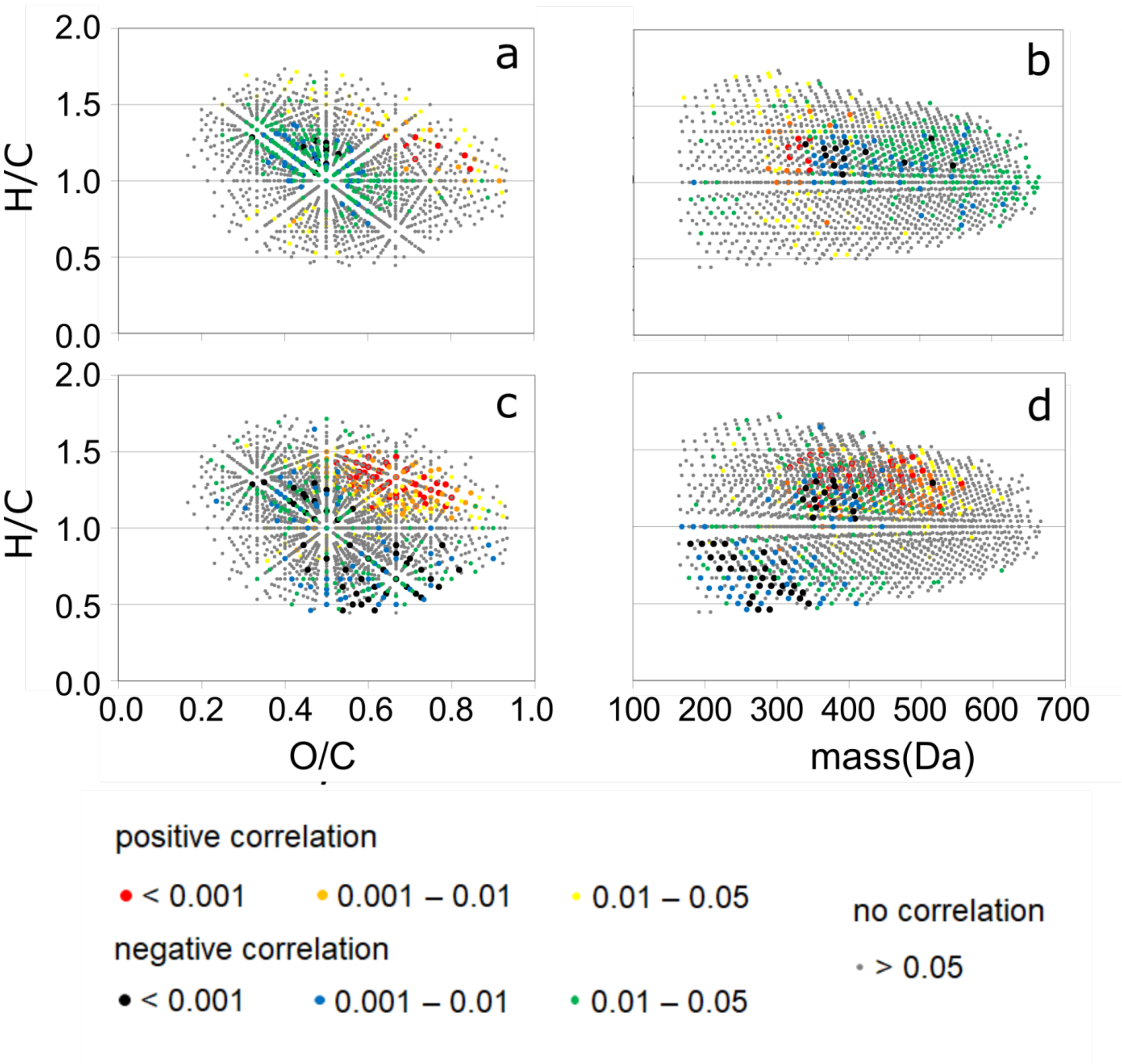

Figure S4: Spearman rank correlations between relative intensities of molecular formulas (MF) and Mn (a, b) and Fe (c and d) of all CHO-MF found in all 55 samples. The legend shows positive and negative correlations and MF with no correlations ($p > 0.05$) and different p-values ($p < 0.001$; $0.001 < p < 0.01$ and $0.01 < p < 0.05$).

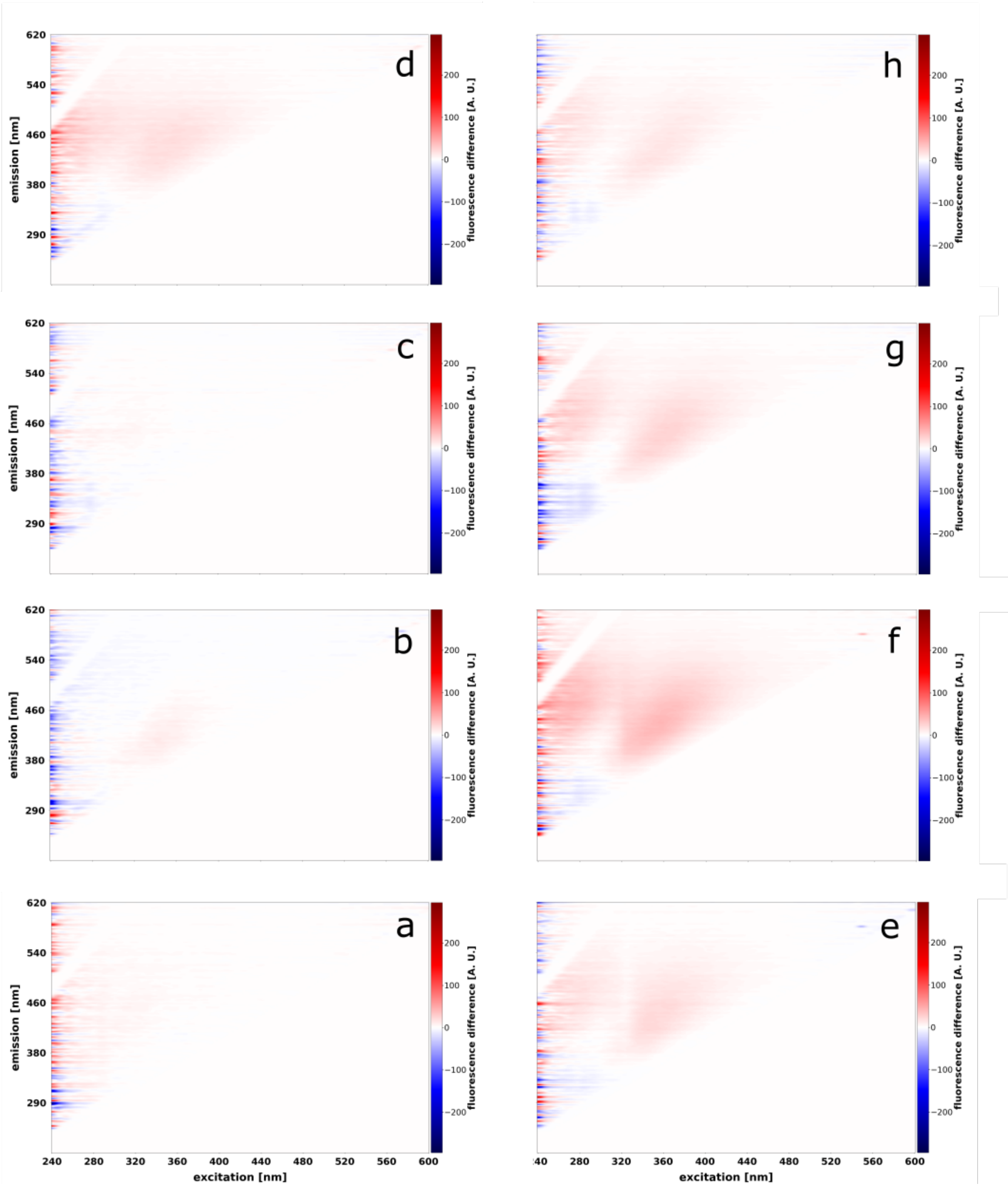

Figure S5: Fluorescence difference spectra at the different depths of the reservoir in June 2015. Figure 9 a shows the difference of 14 and 13 m, b: 13 and 9 m, c: 9 and 8 m, d: 8 and 7 m, e: 7 and 6 m, f: 6 and 5 m, g: 5 and 4 m and h 4 m and the surface water. On the x-axis the excitation wavelength from 240 to 600 nm and on the y-axis the emission wavelength from 290 to 620 nm are shown. The red color reflects the positive and the blue color reflects the negative fluorescence difference in A.U.

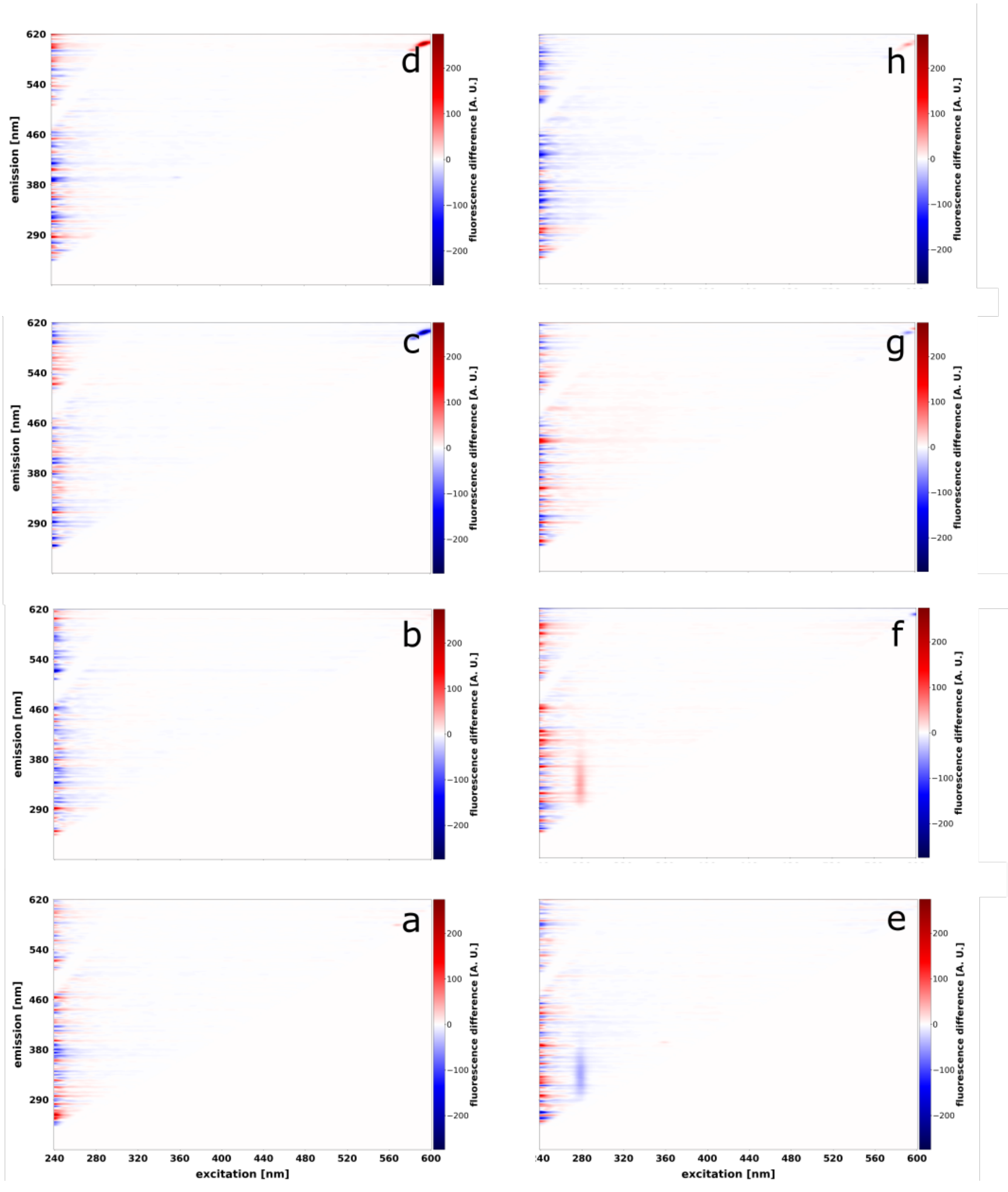

Figure S6: Fluorescence difference spectra at the different depths of the reservoir in December 2015. Figure a show the difference of 14 and 13 m, b: 13 and 9 m, c: 9 and 8 m, d: 8 and 7 m, e: 7 and 6 m, f: 6 and 5 m, g: 5 and 4 m and h 4 m and the surface water. On the x-axis the excitation wavelength from 240 to 600 nm and on the y-axis the emission wavelength from 290 to 620 nm are shown. The red color reflects the positive and the blue color reflects the negative fluorescence difference in A.U.

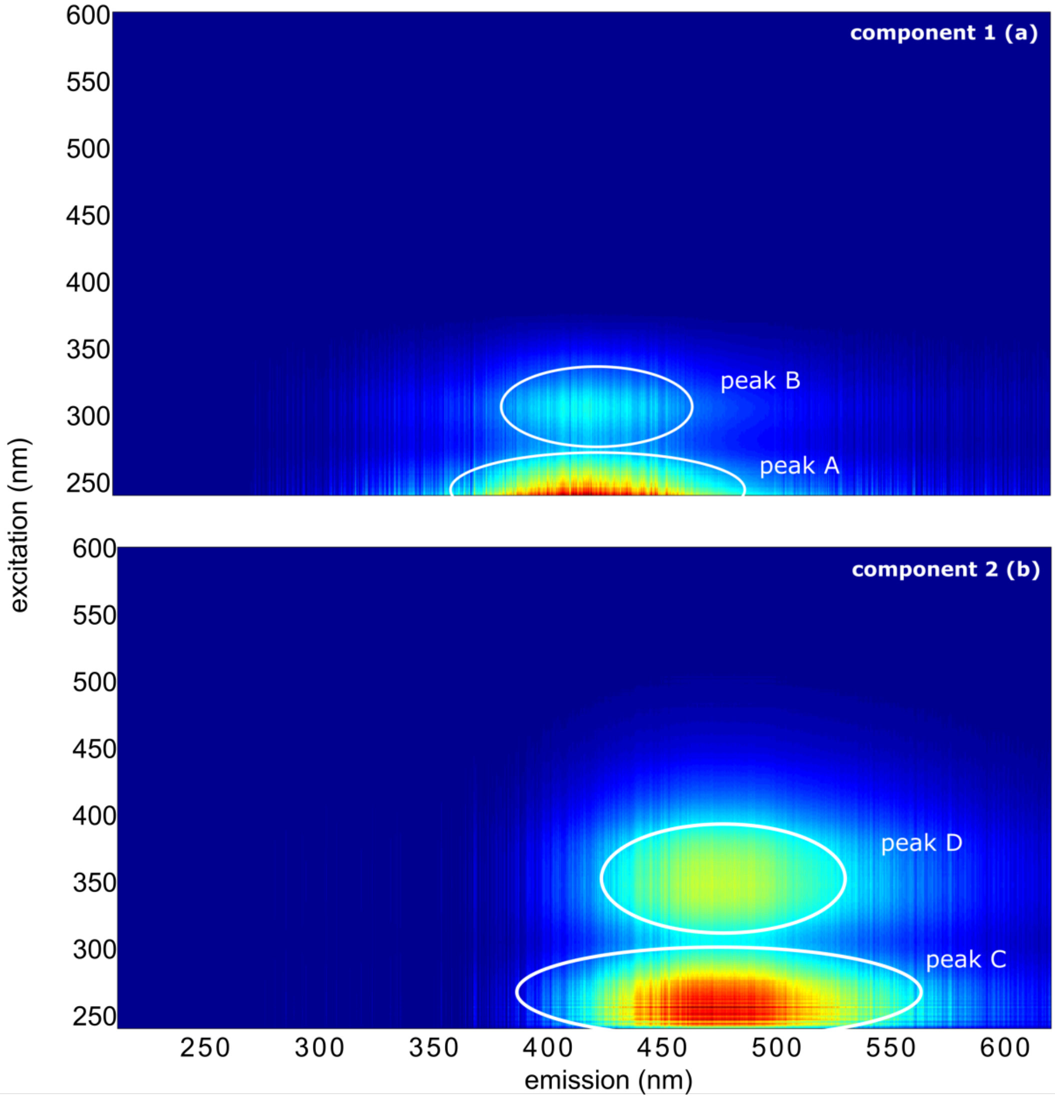

Figure S7: PARAFAC-components of the experiment. Both components are humic-like. The first component (a) has its emission maximum at 410 nm and two excitation maxima at 250 nm (peak A) and 310 nm (peak B). The second component (b) has its emission maximum at 480 nm and two excitation maxima at 260 nm (peak C) and 360 nm (peak D).

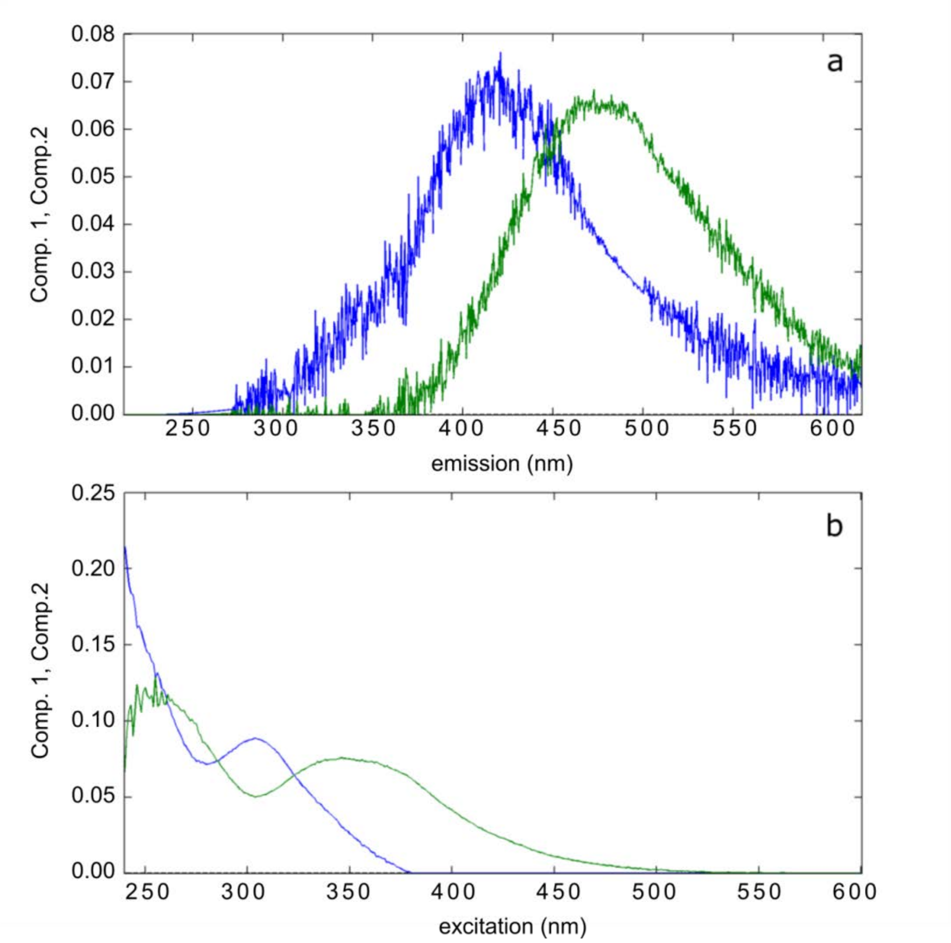

Figure S8: Emission and excitation loadings of the first component (blue) and the second component (green).

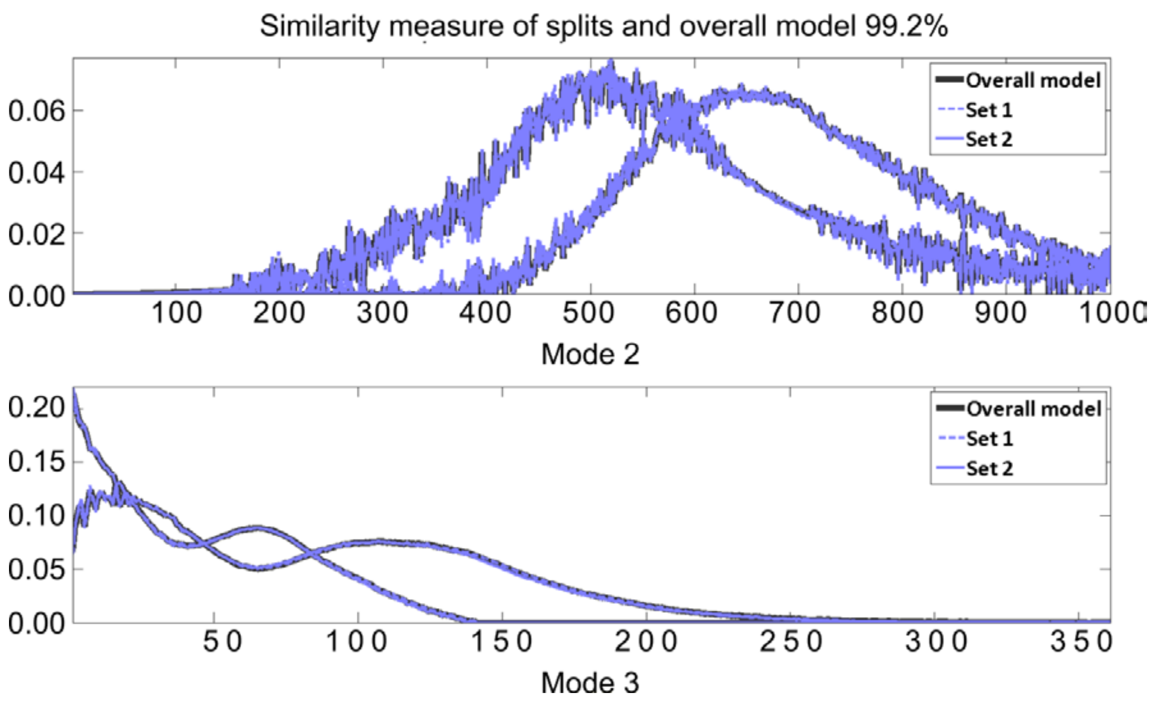

Figure S9: Results of the split half validation of Mode 2 and Mode 3 of the PARAFAC model. The accordance of the halves is 99.2% and the model is valid.

Relative intensities over the sample period and the intensity over global radiation of different photo reactive components

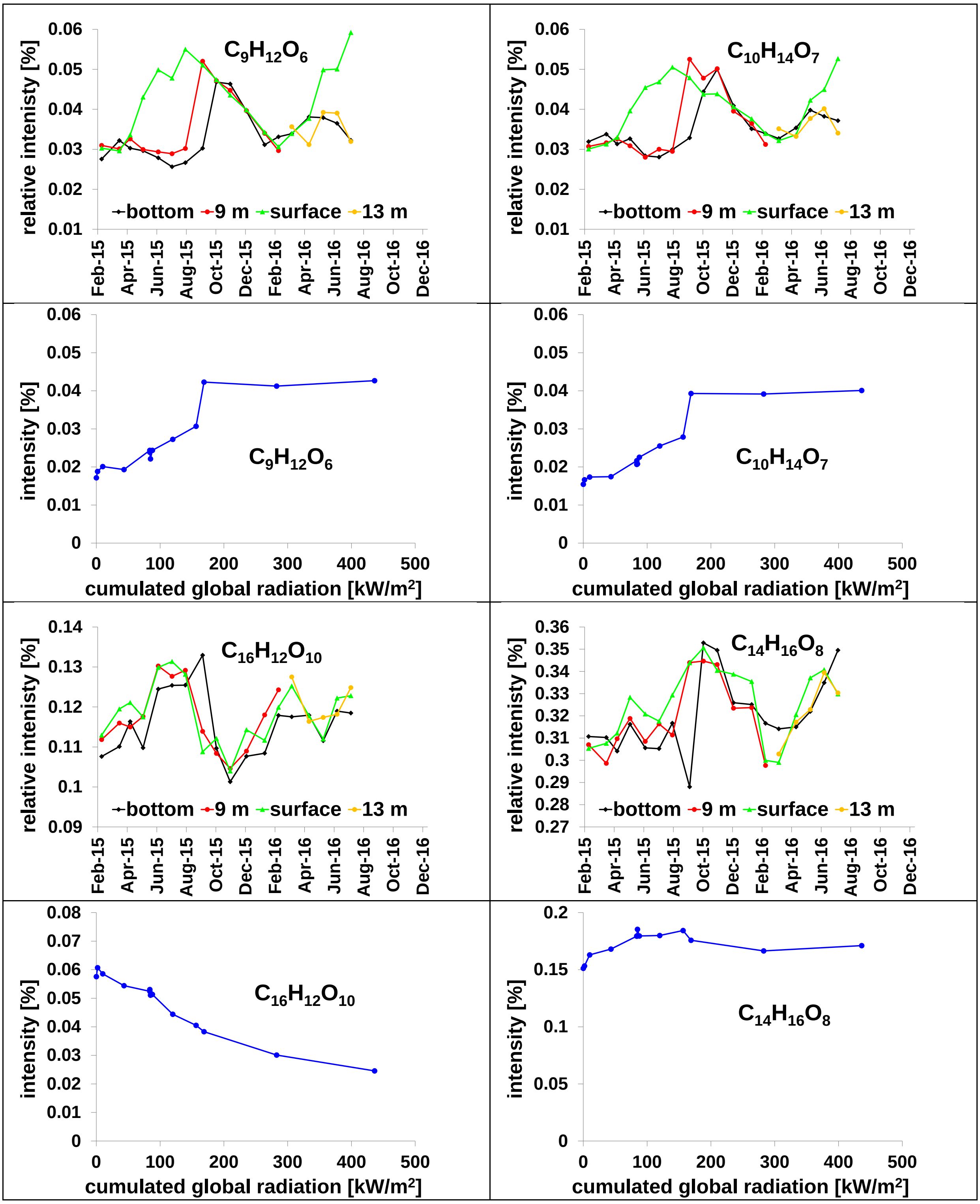

Figure S10: Relative intensities (RI) of the reduced substances with the molecular formulas (MF) in the three different depths of the Muldenberg reservoir. The black line stand for the water on the bottom (14 m), the red and orange line stand for the water in the middle (9 – 13 m) and the green line stand for the surface water. The figures with the blue line show the intensity of these elemental formulas over the cumulated global radiation radiation in a photodegradation experiment.

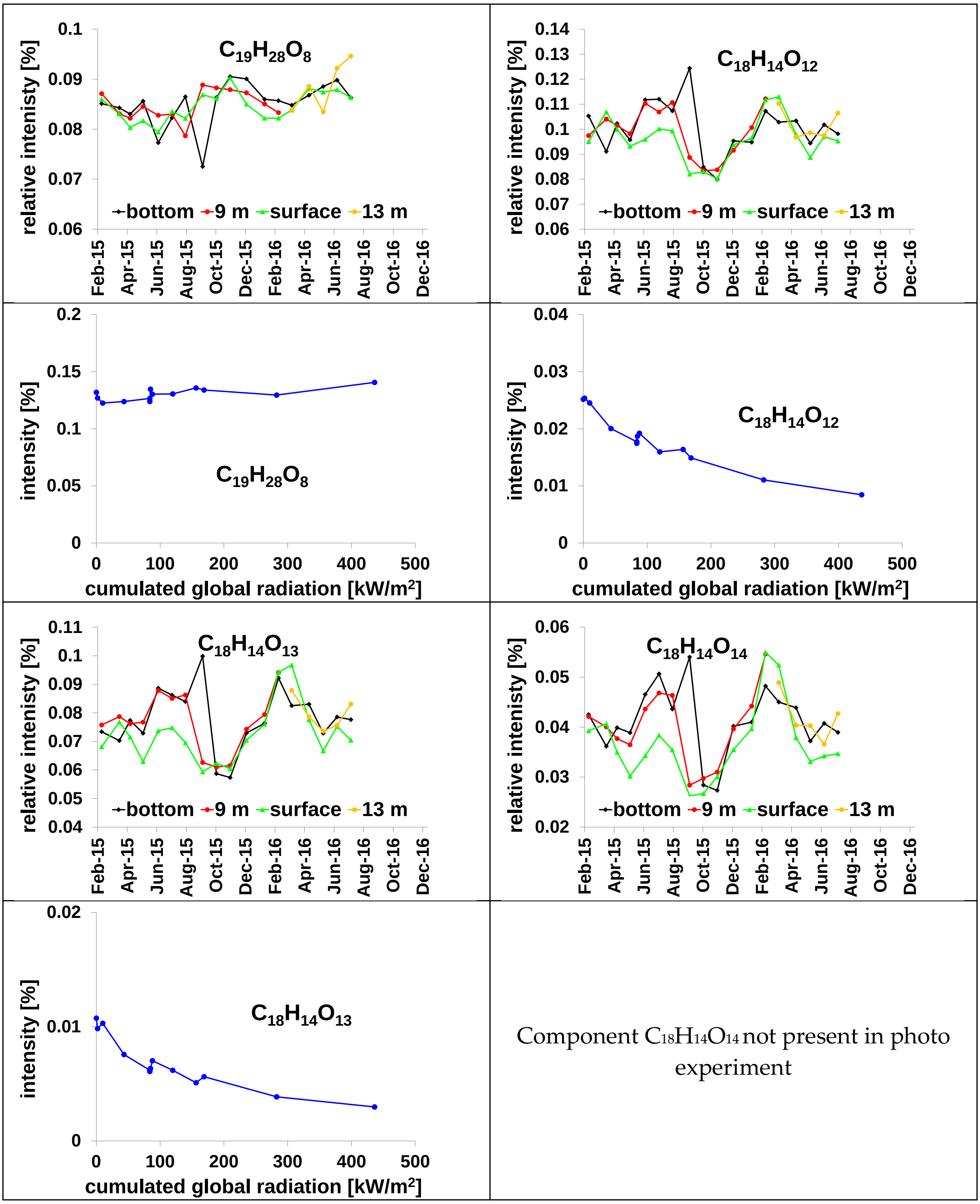

Figure S11: Relative intensities of the reduced substances with the molecular formulas (MF) in the three different depths of the Muldenberg reservoir. The black line stand for the water on the bottom (14 m), the red and orange line stand for the water in the middle (9 – 13 m) and the green line stand for the surface water. The figures with the blue line show the intensity of these elemental formulas over the cumulated global radiation radiation in a photodegradation experiment. The last MF $C_{18}H_{14}O_{14}$ was not present in the photo experiment.

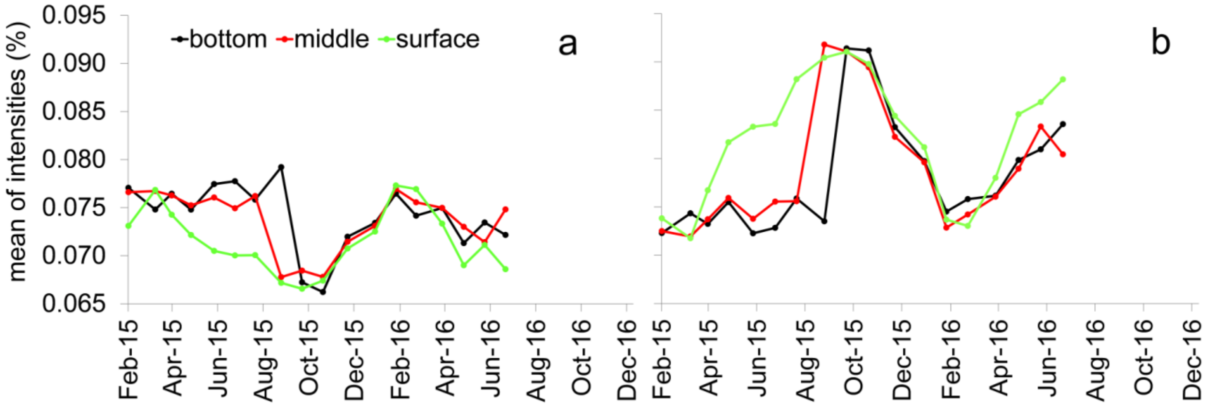

Figure S12: Distribution of the product group and degraded group with highly negative correlation between MF and PARAFAC component 1 (a) and 2 (b).

Table S1: Chemical data and calculated values at all depths over the whole sampling period. The cells with (-) shows missing values. This parameter wasn´t measured at this time.

dephts	date	DOC (mgC L-1)	pH	temp. (°C)	DO (mgL-1)	conductivity (µS cm-1)	SUVA (L mgC-1m-1)	Mn (mgL-1)	Fe (mgL-1)	HIX	BIX	FI
13 m	23.02.2015	7.71	-	-	-	-	4.93	0.05	0.62	-	-	-
9 m	23.02.2015	7.44	-	-	-	-	5.12	0.04	0.63	-	-	-
0 – 3m	23.02.2015	8.08	-	-	-	-	4.84	0.05	0.59	-	-	-
14 m	31.03.2015	7.95	-	-	-	-	4.93	0.05	0.64	-	-	-
9 m	31.03.2015	8.01	-	-	-	-	4,80	0.10	0.60	-	-	-
0 – 3m	31.03.2015	7.71	-	-	-	-	4,80	0.12	0.72	-	-	-
14 m	22.04.2015	7.33	5.50	7.50	9.20	132.20	4.72	0.09	0.54	0.92	0.56	1.30
9 m	22.04.2015	7.24	5.60	6.90	9.90	65.20	4.77	0.10	0.54	0.91	0.59	1.30
0 – 3 m	22.04.2015	7.02	5.90	8.00	9.90	66.10	4.59	0.11	0.54	0.91	0.57	1.26
14 m	18.05.2015	7.24	5.60	8.30	8.40	66.80	4.45	0.05	0.43	0.92	0.59	1.30
9 m	18.05.2015	6.95	5.60	7.70	8.70	66.30	4.60	0.07	0.43	0.93	0.59	1.32
0 – 3 m	18.05.2015	6.47	5.90	11.90	9.20	66.90	4.64	0.08	0.36	0.91	0.58	1.24
14 m	18.06.2015	6.84	5.40	9.90	5.80	100.60	4.61	0.07	0.62	0.92	0.59	1.33
9 m	18.06.2015	6.93	5.40	8.20	6.30	65.70	4.56	0.06	0.50	0.92	0.56	1.30
0 – 3 m	18.06.2015	6.59	5.90	14.00	8.30	67.90	4.23	0.06	0.42	0.89	0.56	1.25
14 m	16.07.2015	7.93	5.60	10.80	2.50	68.10	4.53	0.65	1.19	0.93	0.61	1.31
9 m	16.07.2015	6.69	5.40	10.10	4.10	66.80	4.44	0.09	0.60	0.92	0.61	1.36
0 – 3 m	16.07.2015	6.53	-	-	-	-	-	0.05	0.39	0.90	0.58	1.23
14 m	12.08.2015	6.29	5.90	11.80	2.00	71.20	3.90	1.40	0.95	0.90	0.55	1.31
9 m	12.08.2015	6.39	5.60	12.20	3.70	68.30	4.40	0.34	0.65	0.91	0.61	1.32
0 – 3 m	12.08.2015	6.51	6.30	17.20	8.20	67.40	3.75	0.11	0.39	0.86	0.56	1.21
14 m	19.09.2015	10.50	6.80	11.80	1.30	110.70	5.77	2.72	1.76	0.82	0.58	1.33
9 m	19.09.2015	5.92	6.70	14.50	7.80	68.50	4.48	0.36	0.66	0.89	0.60	1.23
0 – 3 m	19.09.2015	5.97	6.30	14.90	8.10	67.40	4.39	0.34	0.64	0.88	0.60	1.21
14 m	14.10.2015	5.82	6.00	13.20	8.13	65.10	5.00	0.40	0.92	0.90	0.57	1.28
9 m	14.10.2015	5.81	6.10	11.20	8.20	67.70	4.96	0.35	0.83	0.89	0.58	1.24

0 – 3 m	14.10.2015	6.12	6.10	11.20	8.80	67.80	4.69	0.34	0.83	0.89	0.60	1.28
14 m	11.11.2015	5.51	6.30	9.90	9.40	68.00	5.34	0.18	1.01	0.89	0.59	1.28
9 m	11.11.2015	5.85	6.40	9.90	9.70	66.60	5.46	0.19	1.00	0.92	0.59	1.27
0 – 3 m	11.11.2015	5.59	6.40	9.60	9.70	67.20	5.24	0.19	1.02	0.89	0.61	1.22
14 m	14.12.2015	6.82	6.40	5.80	10.40	65.60	4.81	0.13	0.93	0.91	0.59	1.21
9 m	14.12.2015	7.27	6.20	4.60	10.70	66.50	4.48	0.13	0.95	0.90	0.62	1.21
0 – 3 m	14.12.2015	6.40	6.20	3.90	11.10	66.40	5.08	0.13	0.95	0.90	0.62	1.28
14 m	20.01.2016	6.56	5.70	2.20	10.30	70.20	4.86	0.13	0.88	0.90	0.60	1.30
9 m	20.01.2016	6.54	5.90	2.20	11.20	69.30	4.83	0.15	0.85	0.91	0.61	1.27
0 – 3 m	20.01.2016	6.76	6.00	2.00	11.30	68.10	4.63	0.15	0.85	0.91	0.59	1.32
14 m	17.02.2016	7.57	5.70	2.60	10.90	69.60	4.65	0.16	0.28	0.92	0.61	1.31
9 m	17.02.2016	7.41	5.80	2.50	11.20	69.20	4.75	0.15	0.47	0.93	0.59	1.28
0 – 3 m	17.02.2016	7.56	5.80	2.20	11.40	69.00	4.67	0.15	0.47	0.92	0.60	1.34
14 m	16.03.2016	7.24	5.70	4.10	10.50	71.20	4.52	0.15	0.32	0.92	0.62	1.30
13 m	16.03.2016	7.16	5.60	4.30	10.60	76.80	4.57	0.15	0.38	0.90	0.58	1.36
0 – 3 m	16.03.2016	7.07	5.70	3.90	11.10	70.90	4.67	0.15	0.25	0.93	0.63	1.31
14 m	19.04.2016	6.38	5.50	7.10	9.50	70.60	4.61	0.06	0.17	0.91	0.63	1.28
13 m	19.04.2016	6.59	5.40	7.50	9.70	68.20	4.48	0.08	0.19	0.93	0.59	1.28
0 – 3 m	19.04.2016	6.21	5.50	7.80	9.60	71.10	4.52	0.06	0.16	0.91	0.62	1.26
14 m	18.05.2016	6.40	5.50	9.50	6.90	72.10	4.09	0.04	0.14	0.92	0.63	1.29
13 m	18.05.2016	6.24	5.40	9.00	8.50	72.40	4.20	0.03	0.27	0.90	0.62	1.32
0 – 3 m	18.05.2016	6.12	5.70	11.30	9.20	71.30	4.20	0.07	0.18	0.92	0.61	1.30
14 m	15.06.2016	6.61	5.40	10.50	5.90	70.90	3.98	0.15	0.27	0.90	0.61	1.33
13 m	15.06.2016	6.13	5.60	11.10	7.50	68.90	4.26	0.07	0.23	0.92	0.62	1.31
0 – 3 m	15.06.2016	5.87	5.50	12.50	8.40	71.10	4.22	0.07	0.32	0.90	0.62	1.32
14 m	13.07.2016	7.07	5.60	11.00	2.80	73.60	4.02	0.51	0.38	0.91	0.62	1.28
13 m	13.07.2016	5.71	5.40	11.30	4.90	73.20	4.64	0.18	0.36	0.93	0.62	1.29
0 – 3 m	13.07.2016	6.50	5.80	15.10	7.20	73.10	4.18	0.12	0.36	0.89	0.60	1.25