Supporting Information

Impact of Different Environmental Drivers on Monomethylmercury Photodecomposition along the land-to-sea aquatic continuum

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Supplementary Discussion: **FDOM characteristics of the DOM extracts**

The degree of humification in the two humic acid extracts is close to 1, indicating humic substances constitute the majority of the fluorescence signal. In contrast, higher values for the fluorescence index, biological index, and freshness index in the Baltic extract compared to the two humic acid extracts confirm a higher contribution of microbial, freshly produced DOM in the Baltic Sea extract. This suggests that the BS-DOM contains higher concentrations of (I) aromatic substances, (II) labile organic compounds or higher microbial activity and (III) more complex molecules. Comparison of the peaks also revealed differences in between the two HA extracts. Peaks B, N and T are rather protein-like fluorescence, while peaks A,C,D and M are representative for humic-like DOM.[1,2] In comparison to SRHA and the Baltic extract, LHA had a stronger contribution of peaks representative for humic-like DOM (peak A,C,D and M, Table S2).

Supplementary Tables

Table S1: Measured $MM^{200}Hg$ and $^{200}Hg^{II}$ relative to the concentration of $MM^{200}Hg$ at T_0 and the sum of the two at each time point of the respective treatment.

Experiment	Time (min)	$MM^{200}Hg$	std dev	$^{200}Hg^{II}$	std dev	Sum (^{200}Hg)
Arctic (unaltered) (AOW)						
	0	1	0	0.01	0.01	1.01
	30	0.76	0.01	0.2	0.02	0.96
	90	0.45	0.02	0.28	0.01	0.73
	180	0.36	0.02	0.39	0.01	0.75
Arctic degassed (AOW)						
	0	1	0	0.02	0.01	1.02
	30	0.67	0.13	0.22	0.04	0.89
	90	0.35	0.16	0.38	0.03	0.73
	180	0.18	0.11	0.52	0.08	0.7
Värtan (unaltered) (BSW)						
	0	1	0.00	0.01	0.00	1.01
	30	0.79	0.04	0.08	0.01	0.87
	90	0.49	0.06	0.21	0.03	0.70
	180	0.35	0.03	0.31	0.04	0.66
	270	0.19	0.04	0.36	0.07	0.55
Värtan degassed (BSW)						
	0	1	0.00	0.01	0.00	1.01
	30	0.81	0.06	0.15	0.03	0.95
	90	0.49	0.07	0.38	0.07	0.87
	180	0.32	0.07	0.58	0.09	0.91
	270	0.16	0.06	0.67	0.07	0.83
NaCl 35 g L-1 unaltered						
	0	1	0	0.01	0.00	1.01
	30	0.97	0.02	0.17	0.03	1.14
	90	0.72	0.06	0.44	0.12	1.16
	150	0.45	0	0.60	0.22	1.05
	210	0.34	0.05	0.72	0.17	1.06
	270	0.24	0.05	0.78	0.21	1.02
NaCl 35 g L-1 degassed						
	0	1	0	0.03	0.01	1.01
	30	0.95	0.02	0.09	0.06	1.01
	90	0.83	0.17	0.22	0.12	0.95
	150	0.7	0.2	0.30	0.14	0.84
	210	0.58	0.19	0.39	0.15	0.73

	270	0.52	0.18	0.42	0.20	0.94
Laduviken unaltered (Pond)						
	0	1	0	0.01	0.00	1.01
	30	0.77	0.02	0.08	0.01	0.85
	90	0.54	0.02	0.21	0.01	0.75
	150	0.35	0	0.28	0.04	0.63
	210	0.23	0.01	0.36	0.05	0.59
	270	0.13	0.05	0.38	0.04	0.51
Laduviken degassed (Pond)						
	0	1	0	0.01	0.00	1.01
	30	0.77	0.04	0.07	0.00	0.84
	90	0.49	0.04	0.20	0.03	0.69
	150	0.31	0.06	0.26	0.03	0.57
	210	0.19	0.04	0.35	0.03	0.54
	270	0.12	0.05	0.37	0.02	0.49
salt gradient						
0 ‰	0	1		0.01		1.01
0 ‰	30	0.54		0.26		0.80
0 ‰	60	0.39		0.34		0.73
0 ‰	90	0.33		0.38		0.71
0 ‰	150	0.24		0.47		0.71
0 ‰	210	0.18		0.51		0.69
2 ‰	0	1		0.01		1.01
2 ‰	30	0.52		0.26		0.78
2 ‰	60	0.36		0.33		0.69
2 ‰	90	0.3		0.38		0.68
2 ‰	150	0.18		0.46		0.64
2 ‰	210	0.11		0.44		0.55
20 ‰	0	1		0.01		1.01
20 ‰	30	0.84		0.06		0.90
20 ‰	60	0.78		0.08		0.86
20 ‰	90	0.69		0.13		0.82
20 ‰	150	0.62		0.17		0.79
20 ‰	210	0.55		0.26		0.81
10 ‰	0	1		0.01		1.01
10 ‰	30	0.74		0.12		0.86
10 ‰	60	0.47		0.21		0.68
10 ‰	90	0.47		0.21		0.68
10 ‰	150	0.32		0.35		0.67
10 ‰	210	0.19		0.48		0.67
35 ‰	0	1		0.01		1.01
35 ‰	30	0.88		0.05		0.93
35 ‰	60	0.82		0.06		0.88
35 ‰	90	0.82		0.07		0.89
35 ‰	150	0.73		0.11		0.84

35 ‰	210	0.76	0.13	0.89
SRHA gradient				
0 mg C L^{-1}	0	1	0.01	1.01
0 mg C L^{-1}	30	0.87	0.13	1.00
0 mg C L^{-1}	60	0.7	0.23	0.93
0 mg C L^{-1}	90	0.63	0.30	0.93
0 mg C L^{-1}	150	0.52	0.42	0.94
0 mg C L^{-1}	210	0.41	0.47	0.88
0.027 mg C L^{-1}	0	1	0.01	1.01
0.027 mg C L^{-1}	30	0.82	0.12	0.94
0.027 mg C L^{-1}	60	0.74	0.21	0.95
0.027 mg C L^{-1}	90	0.59	0.28	0.87
0.027 mg C L^{-1}	150	0.45	0.41	0.86
0.027 mg C L^{-1}	210	0.34	0.48	0.82
0.27 mg C L^{-1}	0	1	0.01	1.01
0.27 mg C L^{-1}	30	0.88	0.07	0.95
0.27 mg C L^{-1}	60	0.72	0.11	0.83
0.27 mg C L^{-1}	90	0.63	0.16	0.79
0.27 mg C L^{-1}	150	0.41	0.23	0.64
0.27 mg C L^{-1}	210	0.29	0.29	0.58
2.6 mg C L^{-1}	0	1	0.01	1.01
2.6 mg C L^{-1}	30	0.71	0.05	0.76
2.6 mg C L^{-1}	60	0.66	0.10	0.76
2.6 mg C L^{-1}	90	0.49	0.11	0.60
2.6 mg C L^{-1}	150	0.39	0.22	0.61
2.6 mg C L^{-1}	210	0.28	0.29	0.57
26 mg C L^{-1}	0	1	0.00	1.00
26 mg C L^{-1}	30	0.85	0.03	0.88
26 mg C L^{-1}	60	0.52	0.02	0.54
26 mg C L^{-1}	90	0.69	0.03	0.72
26 mg C L^{-1}	150	0.51	0.06	0.57
26 mg C L^{-1}	210	0.47	0.08	0.55
salt & SRHA				
35 ‰, 0.27 mg C L^{-1}	0	1	0.01	1.01
35 ‰, 0.27 mg C L^{-1}	30	0.84	0.10	0.94
35 ‰, 0.27 mg C L^{-1}	90	0.62	0.22	0.84
35 ‰, 0.27 mg C L^{-1}	150	0.49	0.30	0.79
35 ‰, 0.27 mg C L^{-1}	270	0.34	0.40	0.74
35 ‰, 26 mg C L^{-1}	0	1	0.00	1.00
35 ‰, 26 mg C L^{-1}	30	0.89	-0.01	0.88
35 ‰, 26 mg C L^{-1}	90	0.97	0.02	0.99
35 ‰, 26 mg C L^{-1}	150	0.84	0.05	0.89

35 ‰, 26 mg C L^{-1}	270	0.82		0.11		0.93
20 ‰, 2.6 mg C L^{-1}	0	1		0.01		1.01
20 ‰, 2.6 mg C L^{-1}	30	0.99		0.06		1.05
20 ‰, 2.6 mg C L^{-1}	90	0.63		0.15		0.78
20 ‰, 2.6 mg C L^{-1}	150	0.46		0.21		0.67
20 ‰, 2.6 mg C L^{-1}	270	0.25		0.32		0.57
2 ‰, 26 mg C L^{-1}	0	1		-0.01		0.99
2 ‰, 26 mg C L^{-1}	30	1.00		0.00		1.00
2 ‰, 26 mg C L^{-1}	90	1.00		0.03		1.03
2 ‰, 26 mg C L^{-1}	150	0.89		0.10		0.98
2 ‰, 0.27 mg C L^{-1}	0	1		0.01		1.01
2 ‰, 0.27 mg C L^{-1}	30	0.77		0.06		0.83
2 ‰, 0.27 mg C L^{-1}	90	0.6		0.14		0.74
2 ‰, 0.27 mg C L^{-1}	150	0.39		0.15		0.54
2 ‰, 0.27 mg C L^{-1}	270	0.18		0.24		0.42
SRHA/LHA						
SRHA	0	1	0	0.01	0.00	1.01
SRHA	30	0.85	0.06	0.05	0.00	0.90
SRHA	90	0.62	0.04	0.17	0.02	0.79
SRHA	150	0.39	0.06	0.23	0.04	0.62
SRHA	210	0.26	0.04			
SRHA	270	0.17	0.01	0.34	0.02	0.51
LHA	0	1	0	0.01	0.00	1.01
LHA	30	0.86	0.05	0.05	0.02	0.91
LHA	90	0.61	0.05	0.12	0.08	0.73
LHA	150	0.41	0.01	0.22	0.04	0.63
LHA	210	0.3	0.02			
LHA	270	0.22	0.04	0.46	0.16	0.68
mix	0	1	0	0.01		1.01
mix	30	0.91	0	0.05		0.96
mix	90	0.58	0	0.11		0.69
mix	150	0.43	0	0.17		0.60
mix	210	0.34	0			
mix	270	0.25	0	0.30		0.55
SRHA/BS-DOM						
SRHA	0	1	0	0.01	0.01	1.01
SRHA	30	0.89	0.09	0.09	0	0.98
SRHA	90	0.48	0.1	0.23	0.02	0.71
SRHA	150	0.32	0.05	0.32	0.02	0.64
SRHA	210	0.16	0	0.48	0.01	0.64
SRHA	270	0.02	0.01	0.5	0.05	0.52
BS-DOM	0	1	0	0.01	0	1.01
BS-DOM	30	0.68	0.12	0.13	0.01	0.81
BS-DOM	90	0.3	0.07	0.23	0.02	0.53
BS-DOM	150	0.13	0.02	0.26	0.02	0.39

BS-DOM	210	0.01	0.01	0.31	0.01	0.32
BS-DOM	270	0		0.33		0.33
mix	0	1		0.02		1.02
mix	30	0.7		0.08		0.78
mix	90	0.56		0.21		0.77
mix	150	0.3		0.29		0.59
mix	210	0.25		0.36		0.61
mix	270	0		0.39		0.39

Table S2: Loss of light across the 6 cm reaction vessel (%).

	UVB	UVA
SRHA (0.027 mg C L^{-1})	0.64	0.32
SRHA (0.27 mg C L^{-1})	6.23	3.18
SRHA (2.6 mg C L^{-1})	47.69	27.06
SRHA (26.6 mg C L^{-1})	100.00	97.48
BSW	39.22	18.86
Arctic	4.06	1.09
Pond	48.45	20.07
LHA (2.6 mg C L^{-1})	65.16	43.74
BS-DOM (2.6 mg C L^{-1})	9.54	2.94

Table S3. Modelled Hg speciation in the brackish and saline waters (assuming a MMHg concentration of 2 ng L^{-1} in all systems)

Media	$[Cl^-]$ (M)	[DOC] (mg L^{-1})	[DOC-SH] (nM)	MeHg-Cl (%)	MeHg-DOC (%)
NaCl solution	0.6	0.2	9.4	< 0.13	> 99.8
NaCl solution with SRHA	0.6	0.27 (SRHA) 0.2 (NaCl)	22	<0.05	>99.95
Arctic Ocean Water	0.53	2.3	110	<0.01	>99.99
Arctic Ocean Water[1)]	0.53	2.3	0.2	0.3 - 5	95 – 99.7
Baltic Sea Water	0.04	8.1	380	<0.0002	>99.99

1) For the Arctic ocean water, the speciation was also modelled assuming a DOC-SH concentration of 0.2 nM (based on reported concentrations from Northwest Atlantic Ocean)[3].

Table S4: Fluorescence peaks and indices values of the DOM extracts based on the DREEM toolbox in Matlab.[4]

	FluI	FrI	BIX	HIX	A	B	C	D	M	N	T
SRHA	1.08	0.34	0.35	0.96	0.17	0.01	0.10	0.06	0.07	0.02	0.01
LHA	1.05	0.37	0.39	0.98	0.32	0.02	0.16	0.12	0.14	0.03	0.02
Baltic	1.59	0.83	0.85	0.81	0.17	0.05	0.10	0.03	0.11	0.08	0.06

	Humic-like	Tyrosine-like	Fulvic acid-like	Fulvic acid-like	Aquatic / microbial humic-like	Protein-like	Tryptophan-like

Supplementary Figures

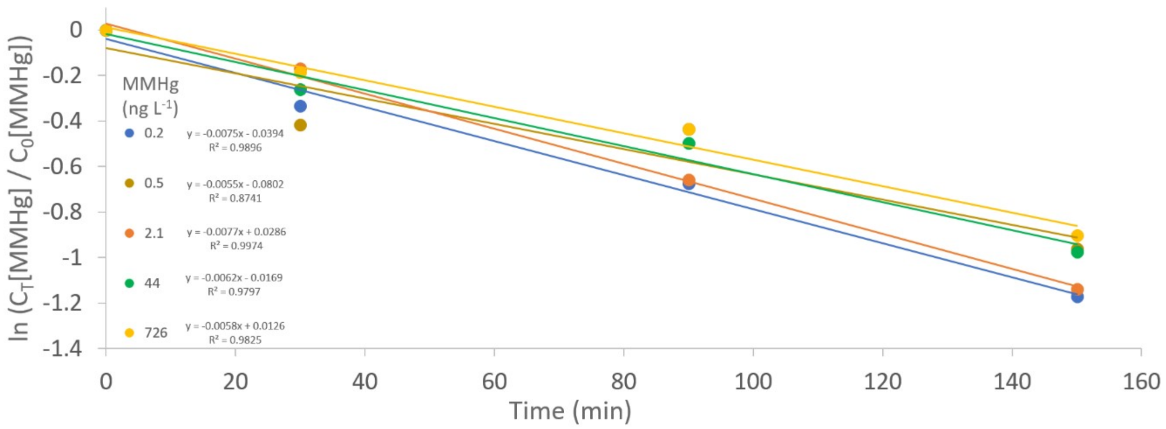

Figure S1: Photodegradation rates of MMHg comparing different starting concentrations (represented by the different colors ranging from 0.1 to 690 ng L^{-1}) over time. All waters were prepared to contain 2.7 mg C L^{-1} DOC (using SRHA) at pH 7 and no salt.

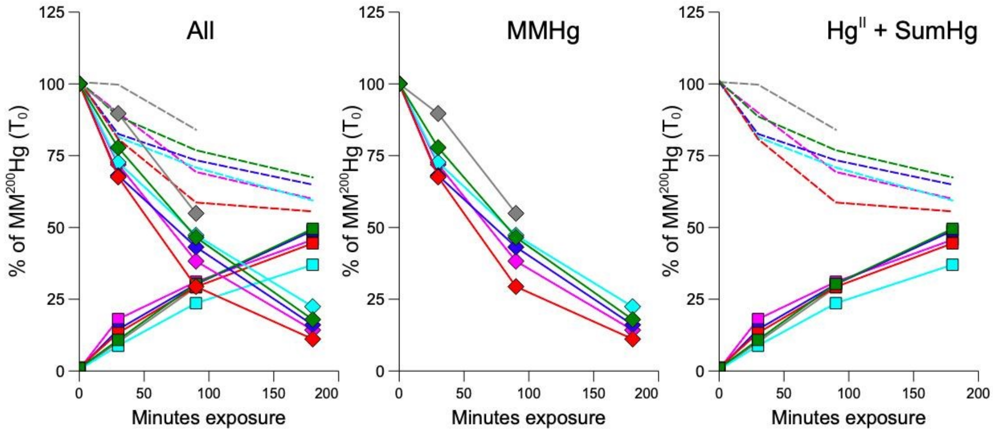

Figure S2: Intercomparability experiment testing MMHg photodegradation rate constants ($k_{d\ MMHg}$) in the different reactor flasks with identical treatment.

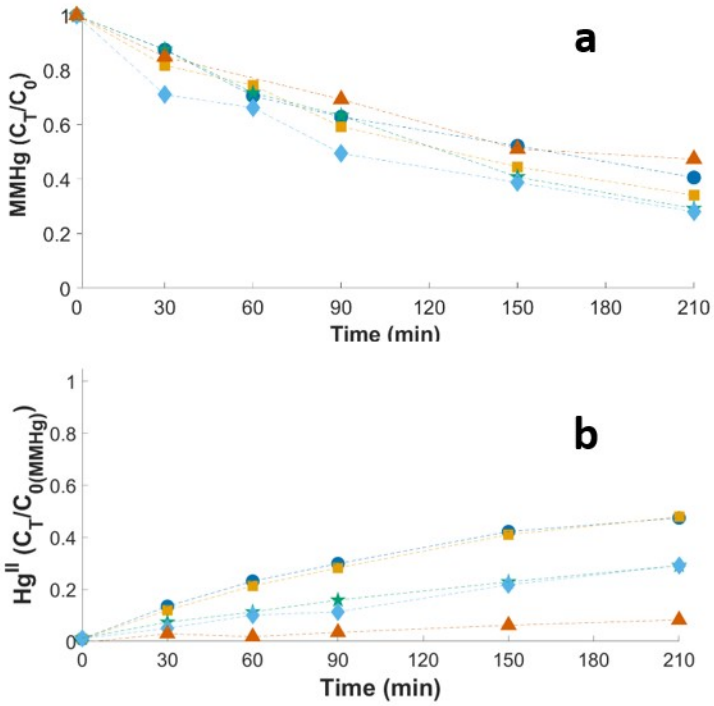

Figure S3: (a) Photodegradation of the added MMHg tracer and (b) production of Hg^{II} from the tracer over time in solutions containing SRHA along a gradient from 0 to 26 mg C L^{-1}. Blue circles represent 0 mg C L^{-1}. Yellow squares represent 0.027 mg C L^{-1}. Turquoise rhombs represent 0.27 mg C L^{-1}. Green stars represent 2.6 mg C L^{-1}. Orange triangles represent 26 mg C L^{-1}.

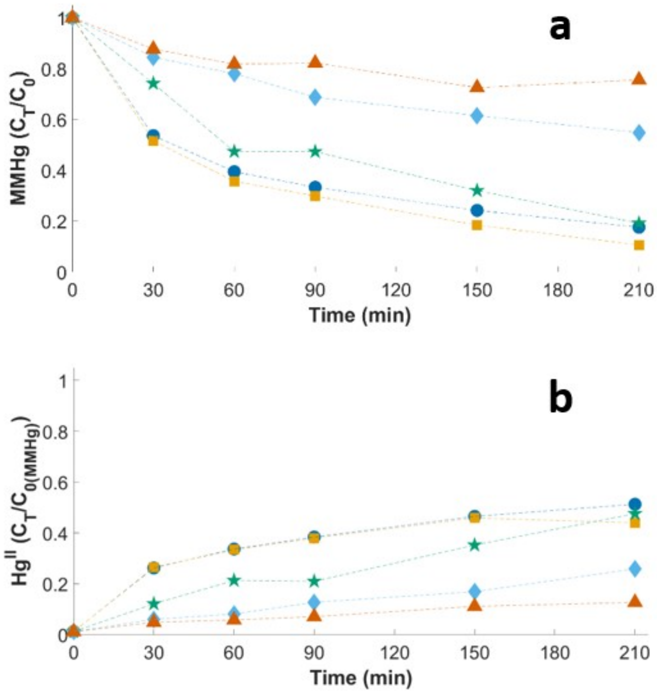

Figure S4: (a) Photodegradation of the added MMHg tracer and (b) formation of Hg^{II} from the MMHg tracer over time in solutions containing NaCl along a gradient from 0 to 35 g L^{-1}. Blue circles represent 0 g L^{-1}. Yellow squares represent 2 g L^{-1}. Green stars represent 10 g L^{-1}. Turquoise rhombs represent 20 g L^{-1}. Orange triangles represent 35 g L^{-1}.

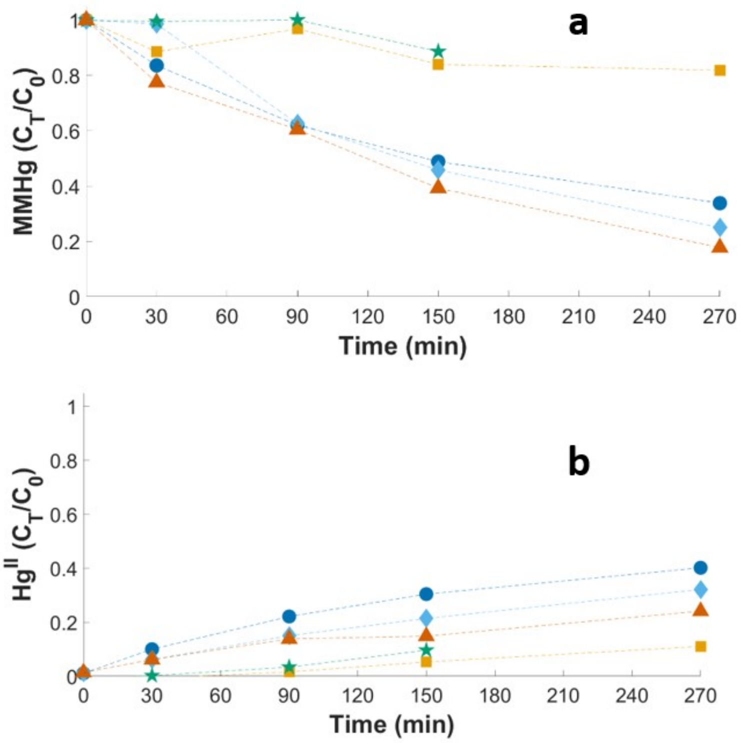

Figure S5: (a) Photodegradation of the added MMHg tracer and (b) production of Hg^{II} from the tracer over time in solutions containing (different combinations of SRHA and NaCl concentrations. Blue circles represent 35 g L^{-1} NaCl and 0.27 mg C L^{-1}. Yellow squares represent 35 g L^{-1} NaCl and 26 mg C L^{-1}. Turquoise rhombs represent 20 g L^{-1} NaCl and 2.6 mg C L^{-1}. Green stars represent 2 g L^{-1} NaCl and 26 mg C L^{-1}. Orange triangles represent 2 g L^{-1} NaCl and 0.27 mg C L^{-1}.

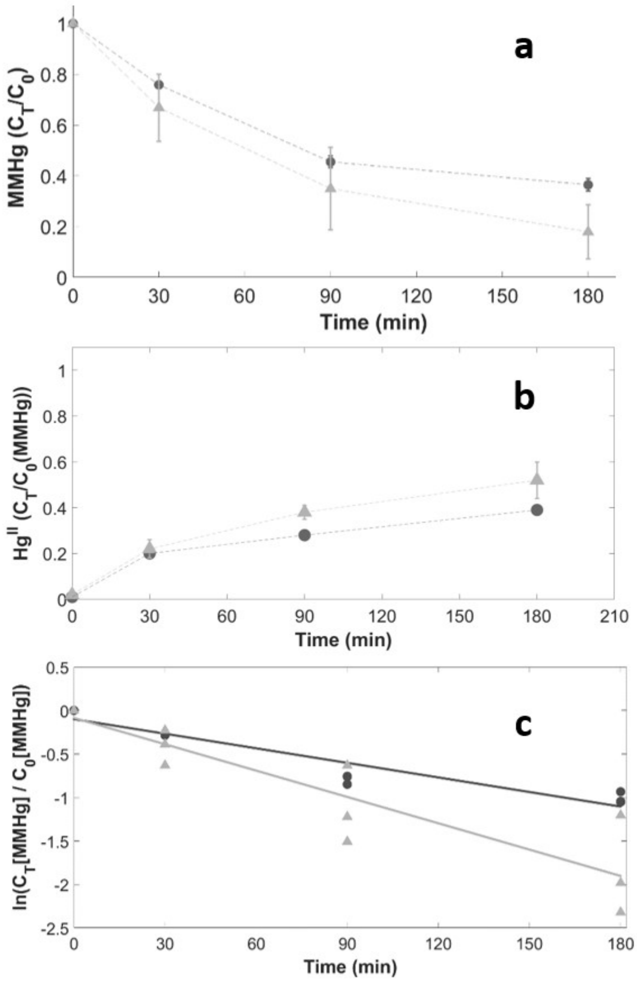

Figure S6: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates in **Arctic Ocean water**. Dark grey dots represent unaltered water, and light grey triangles represent waters purged with N_2 gas. Both degradation and formation are expressed relative to the MMHg tracer concentration at T_0.

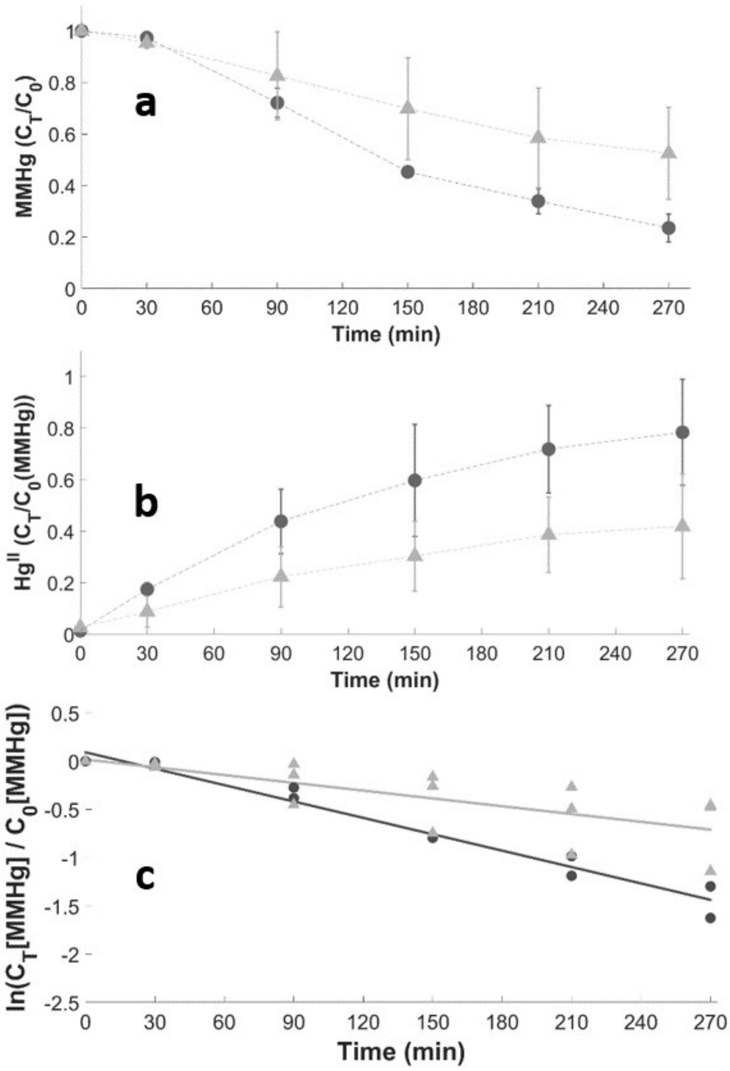

Figure S7: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates in **35 g L^{-1} NaCl solution**. Dark grey dots represent unaltered water, light grey triangles represent waters purged with N_2 gas. Both degradation and formation are expressed relative to the MMHg tracer concentration at T_0.

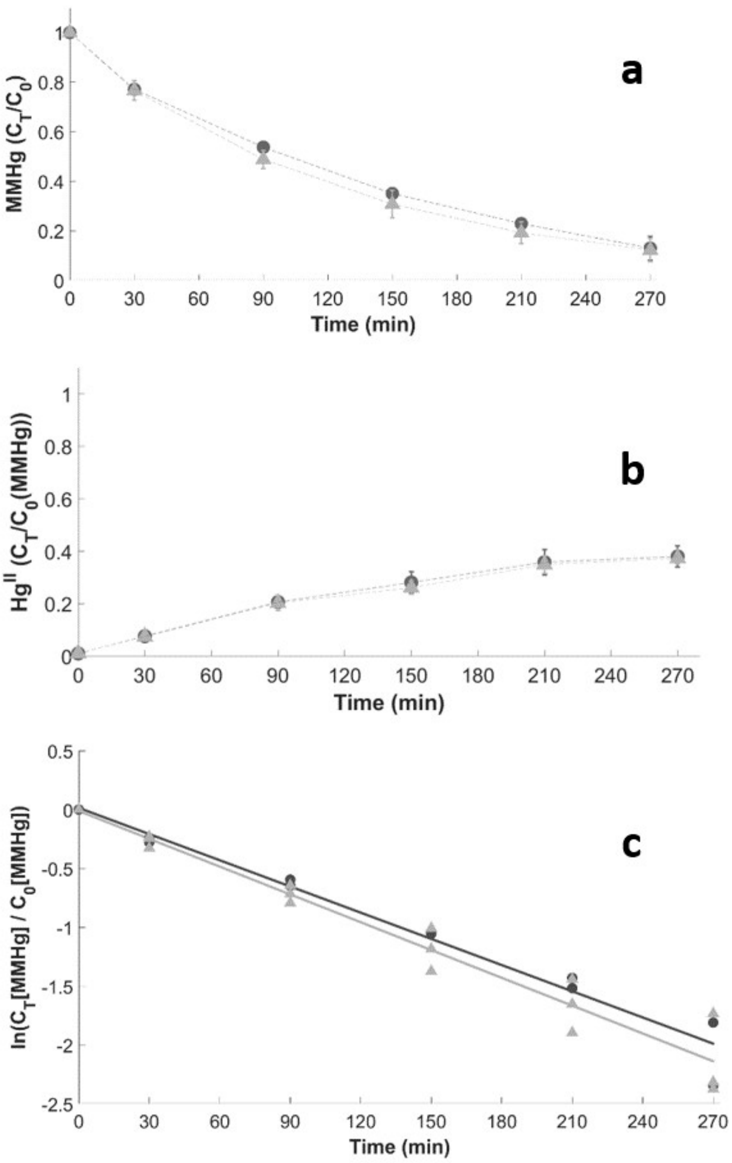

Figure S8: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates in **Laduviken pond water**. Dark grey dots represent unaltered water, light grey triangles represent waters purged with N_2 gas. Both degradation and formation are expressed relative to the MMHg tracer concentration at T_0.

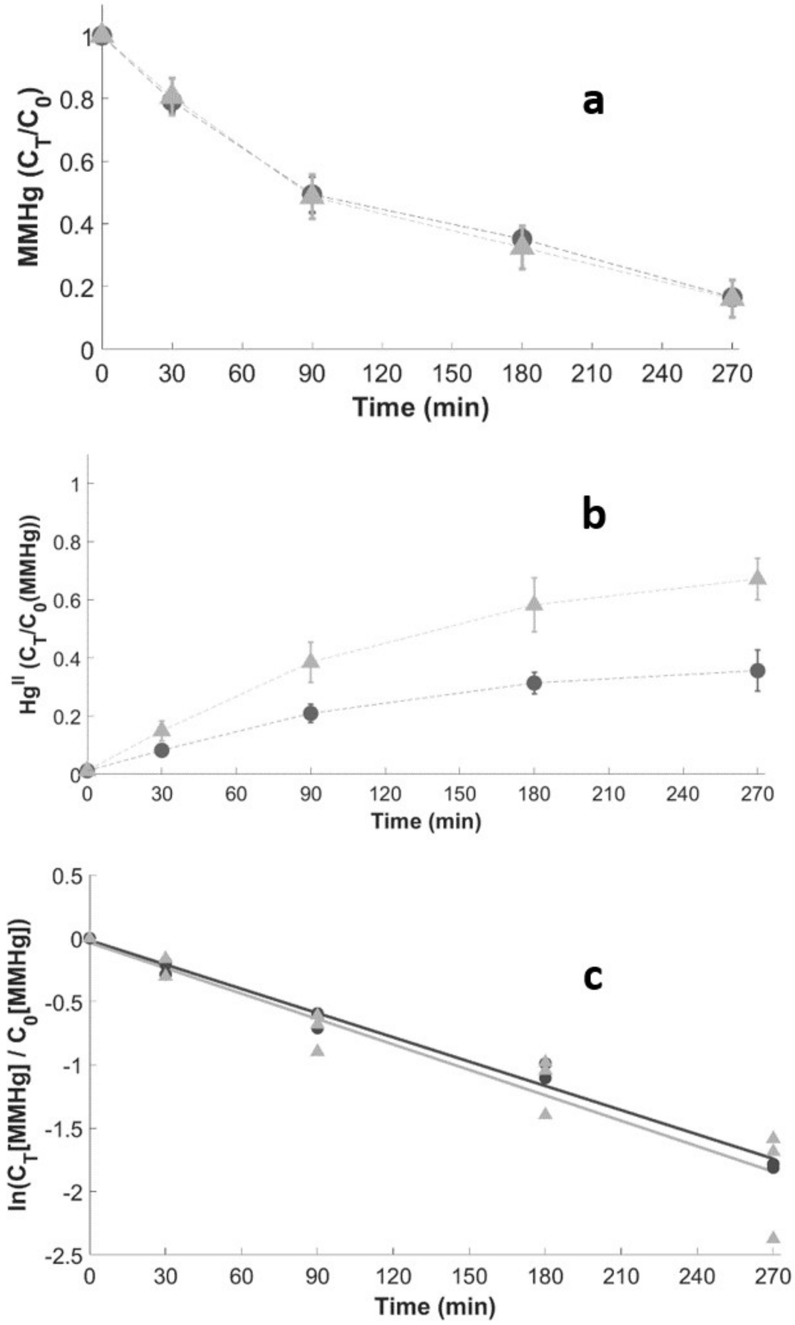

Figure S9: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates in **Värtan brackish water**. Dark grey dots represent unaltered water, light grey triangles represent waters purged with N_2 gas. Both degradation and formation are expressed relative to the MMHg tracer concentration at T_0.

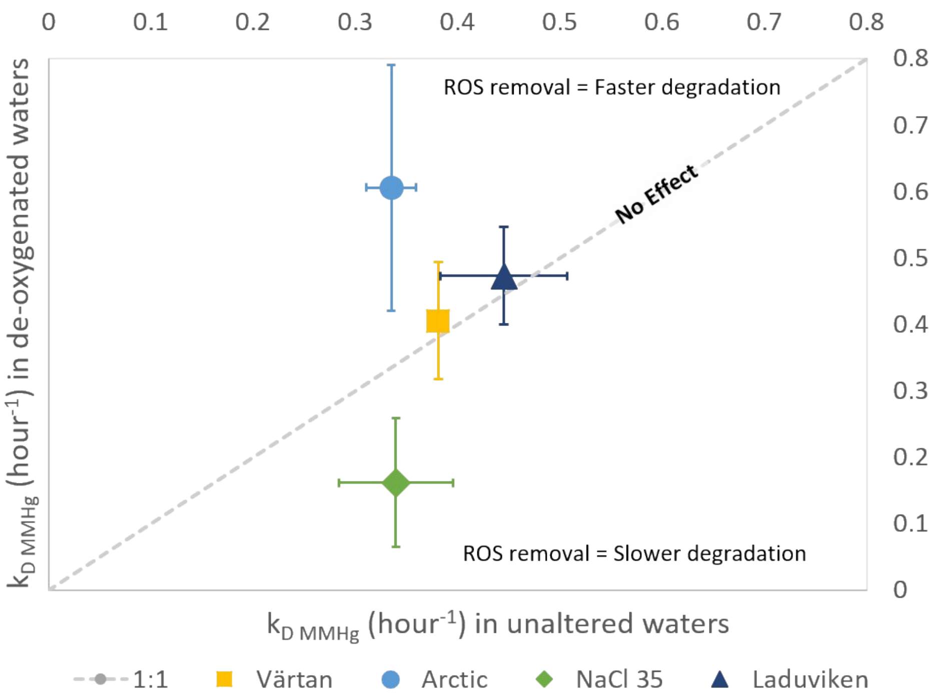

Figure S10: Relationship between in $k_{D\ MMHg}$ in unaltered (non-degassed) waters and waters purged with N_2 to remove O_2 and limit ROS formation. The dotted grey line represents the 1:1 line where no difference in $k_{D\ MMHg}$ between degassed and non-degassed waters was observed.

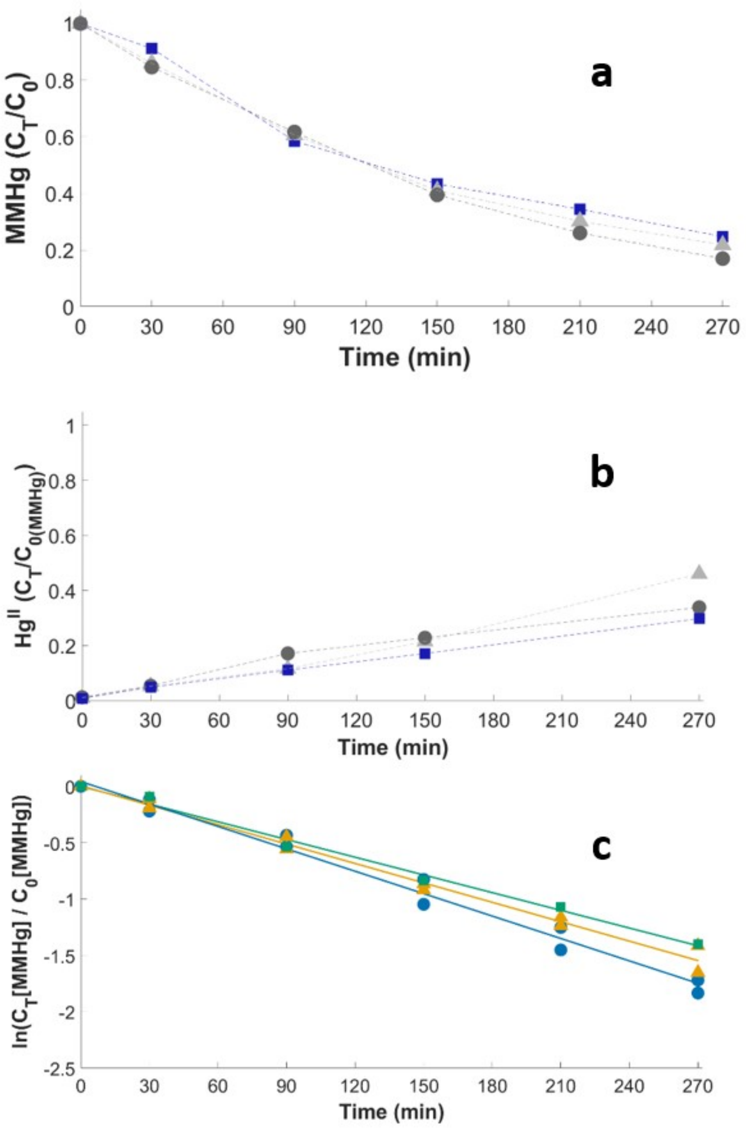

Figure S11: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates testing the DOM type. Dots represent **SRHA** (2.6 mg CL^{-1}), triangles represent **LHA** (2.6 mg CL^{-1}), squares represent **mixed endmembers** (2.6 mg CL^{-1}).

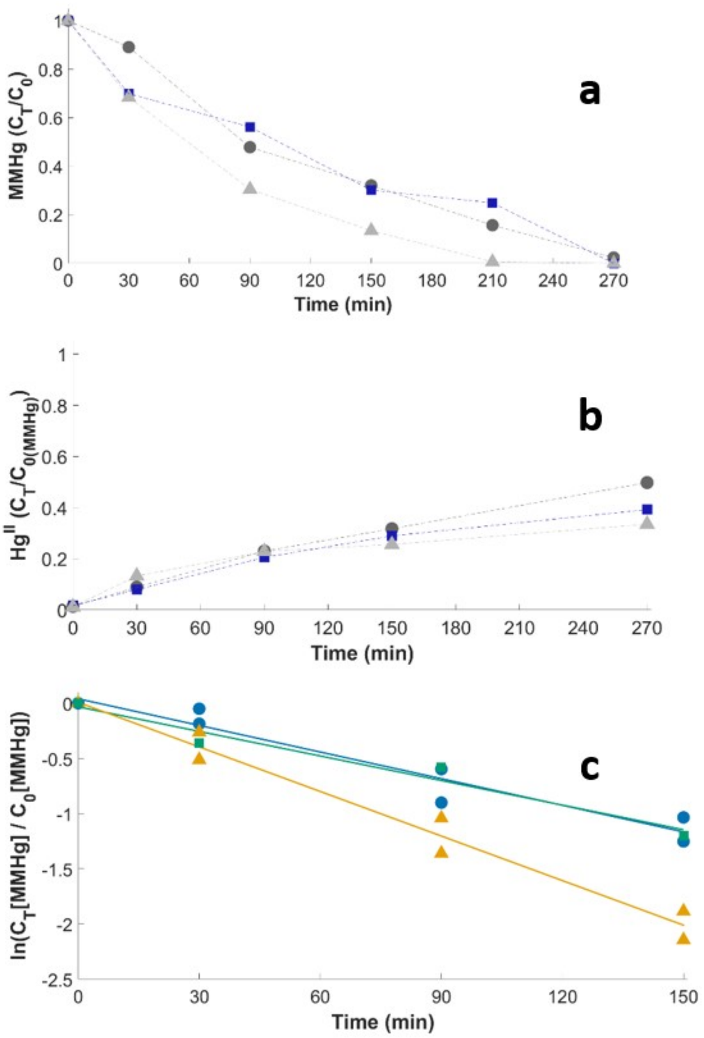

Figure S12: Experimental results of (a) MMHg degradation, (b) Hg^{II} formation over time, and (c) degradation rates testing the DOM type. Dots represent **SRHA** (2.6 mg CL^{-1}), triangles represent **BS-DOM** (2.6 mg CL^{-1}), squares represent **mixed endmembers** (2.6 mg CL^{-1}). Note that the rate plot ends at 150 minutes as no MMHg tracer was left in the solution containing Baltic DOM.

References

1 P. G. Coble, Marine optical biogeochemistry: The chemistry of ocean color, *Chem. Rev.*, 2007, **107**, 402–418.

2 C. H. Lochmüller and S. S. Saavedra, Conformational Changes in a Soil Fulvic Acid Measured by Time-Dependent Fluorescence Depolarization, *Anal. Chem.*, 1986, **58**, 1978–1981.

3 T. Kading, Distribution of Thiols in the Northwest Atlantic Ocean. Joint Program in Oceanography/Applied Ocean Science and Engineering (Massachusetts Institute of Technology; and the Woods Hole Oceanographic Institution), Master Thesis, http://hdl.handle.net/1721.1/79298, 2013.

4 K. R. Murphy, C. A. Stedmon, D. Graeber and R. Bro, Fluorescence spectroscopy and multi-way techniques. PARAFAC, *Anal. Methods*, 2013, **5**, 6557–6566.