Supporting Information for:

Complete and partial photo-oxidation of dissolved organic matter draining permafrost soils

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11 pages; 4 tables; 5 figures

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Table S1: Absolute and light normalized changes in chromophoric and fluorescent DOM (CDOM and FDOM, respectively) properties after exposure to sunlight.

DOM Source	Light vs. Dark Δ	[a]Decrease in *a*CDOM (m^{-1}) 280 - 600 nm	Decrease in *a*CDOM (m^{-1}) 305 nm	[b]Increase in SR	[c]Decrease in FI	[d]Qa (mol photons m^{-2})
Organic mat	Absolute Δ	2230 ± 138	26.8 ± 2.5	0.26 ± 0.01	0.23 ± 0.02	6.0 ± 0.2
	Q_a normalized Δ	372 ± 20	4.5 ± 0.4	0.04 < 0.01	0.04 < 0.01	
Permafrost	Absolute Δ	406 ± 126	4.1 ± 1.2	0.17 ± 0.01	0.19 ± 0.01	0.9 ± 0.1
	Q_a normalized Δ	411 ± 86	4.2 ± 0.8	0.18 ± 0.01	0.20 ± 0.02	

[a]Integrated loss in aCDOM from 280 - 600 nm; [b]SR = slope ratio;[2] [c]FI = fluorescence index;[3] [d]Total integrated light absorption by CDOM during photo-exposure from 280 - 600 nm.

Table S2: Percent of common peaks between dark-control and light-exposed treatments of organic mat and permafrost DOM as detected by FT-ICR MS.

Sample	Fraction[a]	Replicate	% Common[b]	Average	SD
Organic Mat	SPE	1	71%	70%	1%
		2	70%		
		3	69%		
Organic Mat	WW	1	79%	78%	1%
		2	77%		
		3	78%		
Permafrost	SPE	1	81%	77%	4%
		2	72%		
		3	78%		
Permafrost	WW	1	76%	77%	1%
		2	76%		
		3	78%		

[a]SPE = solid-phase extraction, WW = whole-water. [b]Percent common peaks between dark-control and light-exposed treatments of DOM.

Table S3: Spearman's rank correlation coefficients of peak intensities between light-exposed and dark-control, whole water and solid-phase extraction, organic mat and permafrost DOM. All correlations are significant at $\alpha = 0.05$.

			Organic Mat DOM											
			Whole water						Solid-Phase Extraction (SPE)					
			Light R1	Light R2	Light R3	Dark R1	Dark R2	Dark R3	Light R1	Light R2	Light R3	Dark R1	Dark R2	Dark R3
Organic Mat DOM	Whole water	Light R1	1.00	0.96	0.96	0.81	0.78	0.77	0.75	0.83	0.75	0.65	0.67	0.63
		Light R2	0.96	1.00	0.95	0.81	0.82	0.78	0.69	0.77	0.69	0.60	0.63	0.58
		Light R3	0.96	0.95	1.00	0.81	0.79	0.81	0.80	0.84	0.80	0.70	0.72	0.69
		Dark R1	0.81	0.81	0.81	1.00	0.96	0.96	0.68	0.70	0.68	0.77	0.81	0.77
		Dark R2	0.78	0.82	0.79	0.96	1.00	0.95	0.60	0.62	0.60	0.69	0.74	0.69
		Dark R3	0.77	0.78	0.81	0.96	0.95	1.00	0.70	0.69	0.70	0.79	0.83	0.80
	SPE	Light R1	0.75	0.69	0.80	0.68	0.60	0.70	1.00	0.96	0.99	0.92	0.90	0.91
		Light R2	0.83	0.77	0.84	0.70	0.62	0.69	0.96	1.00	0.96	0.85	0.86	0.84
		Light R3	0.75	0.69	0.80	0.68	0.60	0.70	0.99	0.96	1.00	0.91	0.91	0.91
		Dark R1	0.65	0.60	0.70	0.77	0.69	0.79	0.92	0.85	0.91	1.00	0.99	0.99
		Dark R2	0.67	0.63	0.72	0.81	0.74	0.83	0.90	0.86	0.91	0.99	1.00	0.99
		Dark R3	0.63	0.58	0.69	0.77	0.69	0.80	0.91	0.84	0.91	0.99	0.99	1.00

			Permafrost DOM											
			Whole water						Solid-Phase Extraction (SPE)					
			Light R1	Light R2	Light R3	Dark R1	Dark R2	Dark R3	Light R1	Light R2	Light R3	Dark R1	Dark R2	Dark R3
Permafrost DOM	Whole water	Light R1	1.00	0.92	0.93	0.92	0.85	0.88	0.79	0.75	0.75	0.74	0.66	0.69
		Light R2	0.92	1.00	0.95	0.90	0.89	0.92	0.81	0.80	0.81	0.77	0.74	0.76
		Light R3	0.93	0.95	1.00	0.88	0.86	0.90	0.79	0.80	0.81	0.74	0.70	0.74
		Dark R1	0.92	0.90	0.88	1.00	0.93	0.94	0.77	0.69	0.69	0.79	0.71	0.72
		Dark R2	0.85	0.89	0.86	0.93	1.00	0.96	0.78	0.74	0.73	0.81	0.79	0.80
		Dark R3	0.88	0.92	0.90	0.94	0.96	1.00	0.79	0.77	0.77	0.81	0.80	0.81
	SPE	Light R1	0.79	0.81	0.79	0.77	0.78	0.79	1.00	0.94	0.93	0.95	0.91	0.91
		Light R2	0.75	0.80	0.80	0.69	0.74	0.77	0.94	1.00	0.98	0.88	0.90	0.92
		Light R3	0.75	0.81	0.81	0.69	0.73	0.77	0.93	0.98	1.00	0.86	0.88	0.91
		Dark R1	0.74	0.77	0.74	0.79	0.81	0.81	0.95	0.88	0.86	1.00	0.95	0.95
		Dark R2	0.66	0.74	0.70	0.71	0.79	0.80	0.91	0.90	0.88	0.95	1.00	0.98
		Dark R3	0.69	0.76	0.74	0.72	0.80	0.81	0.91	0.92	0.91	0.95	0.98	1.00

Table S4: Bulk chemical characteristics of dark-control and light-exposed organic mat and permafrost DOM chemical composition as detected by ESI (-) Orbitrap-MS.

DOM Source	Treatment	Replicate	N	MW	O:C	H:C	DBE
Organic Mat	Dark-control	#1	312	177	0.41	1.10	5.2
Organic Mat	Dark-control	#2	315	179	0.41	1.09	5.3
Organic Mat	Dark-control	#3	311	176	0.40	1.08	5.3
Organic Mat	Light-exposed	#1	357	179	0.40	1.07	5.4
Organic Mat	Light-exposed	#2	363	180	0.41	1.08	5.3
Organic Mat	Light-exposed	#3	340	179	0.41	1.06	5.4
Light - Dark Average			41	2	<0.01	-0.02	0.1
Light -Dark SD			10	<1	<0.01	0.01	0.1
DOM Source	**Treatment**	**Replicate**	**N**	**[a]MW**	**O:C**	**H:C**	**[b]DBE**
Permafrost	Dark-control	#1	302	184	0.37	1.21	4.9
Permafrost	Dark-control	#2	280	186	0.37	1.16	5.2
Permafrost	Dark-control	#3	242	185	0.37	1.14	5.2
Permafrost	Light-exposed	#1	307	182	0.39	1.18	5.0
Permafrost	Light-exposed	#2	300	184	0.40	1.17	5.0
Permafrost	Light-exposed	#3	315	183	0.39	1.20	4.9
Light - Dark Average			33	-2	0.02	0.01	-0.2
Light -Dark SD			36	<1	<0.01	<0.01	0.2

[a]MW = molecular weight; [b]DBE = double bond equivalents. All values are number-weighted.

Detection of low molecular weight compounds: The production of low molecular weight compounds (100 - 250 *m/z*) after sunlight exposure was determined by comparing Orbitrap mass spectra (Exactive, Thermo Scientific) of light-exposed and dark-control organic mat and permafrost DOM. DOM spectra were collected in negative mode. For each spectrum, 200 scans were averaged using Xcalibur software. Formulas were assigned following the criteria described in the main text for FT-ICR mass spectra, however, only formulas that agreed within an error of $\leq \pm 5$ ppm to the calculated exact mass of the formula were considered.

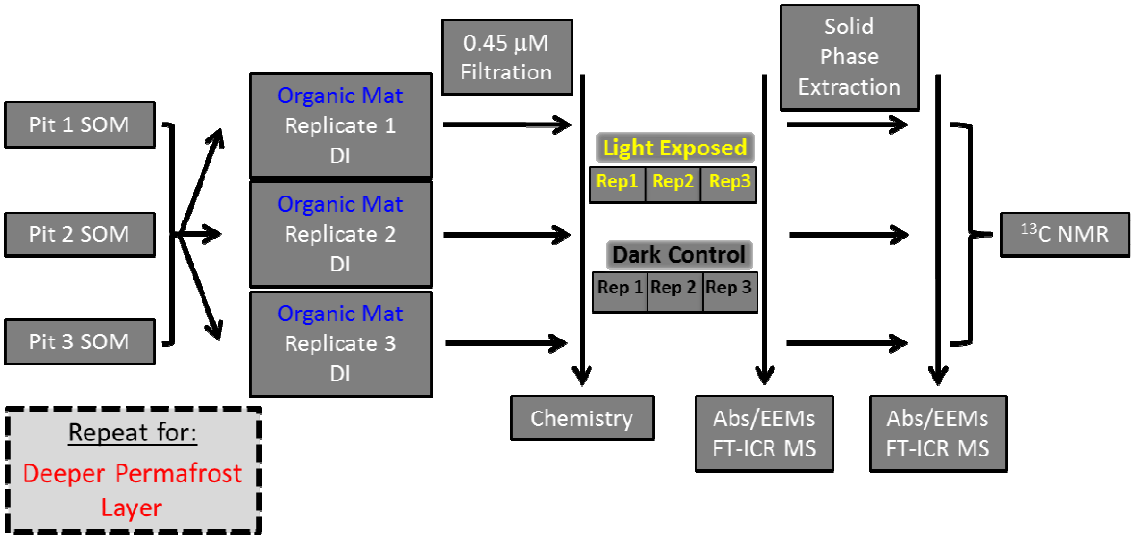

Figure S1: Experimental design for photochemical degradation of DOM leached from the shallower organic mat and deeper permafrost layers of arctic soils.

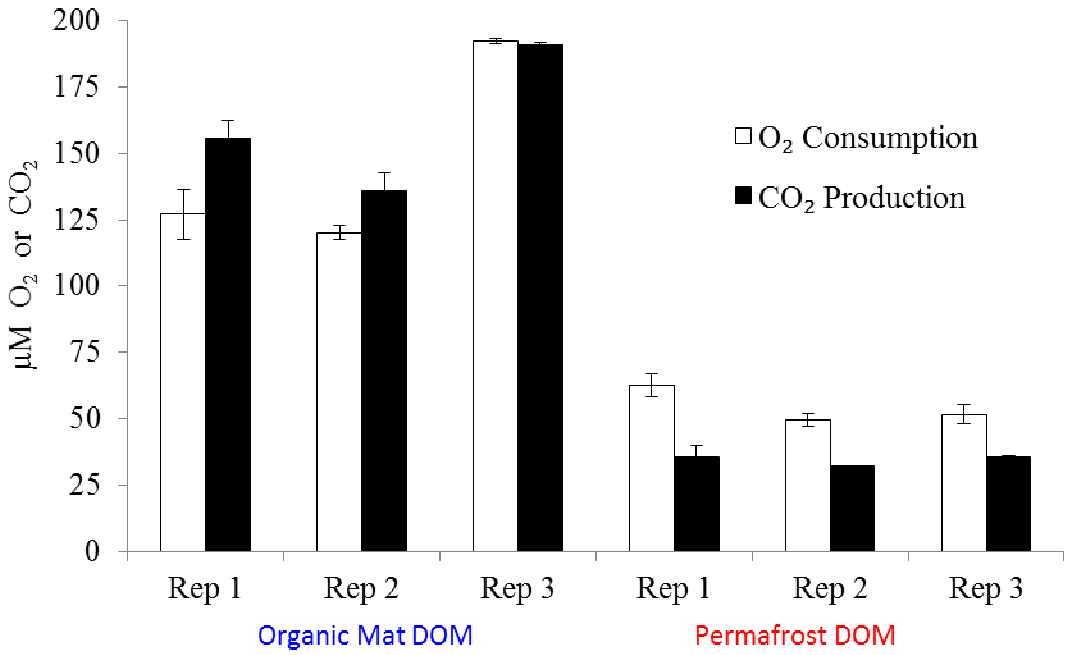

Figure S2: Photochemical oxidation (clear bars) and mineralization (filled bars) of organic mat and permafrost DOM. Error bars show standard error of analytical duplicates. Organic mat and permafrost DOM were pre-equilibrated with air in the dark at room temperature, transferred to DI rinsed, pre-combusted, air-tight borosilicate vials (Labco Limited), and exposed to natural sunlight at Toolik Lake Field Station. Organic mat DOM was exposed to 6.7 kW m^{-2} (UVA + UVB) over 25 hours, while permafrost DOM was exposed to 5.8 kW m^{-2} over 16 hours alongside dark-controls wrapped in aluminum foil. Average air temperature, measured every 5 minutes throughout the irradiation period, was 8.2 ± 4.0°C for organic mat DOM and 13.0 ± 1.5°C for permafrost DOM. Following the experiment, the light-exposed and dark-control treatments were equilibrated at room temperature in the dark, and then analyzed for their dissolved oxygen concentration using a membrane inlet mass spectrometer (Bay Instruments LLC), and dissolved inorganic carbon (DIC) concentration using a DIC analyzer (Apollo SciTech).

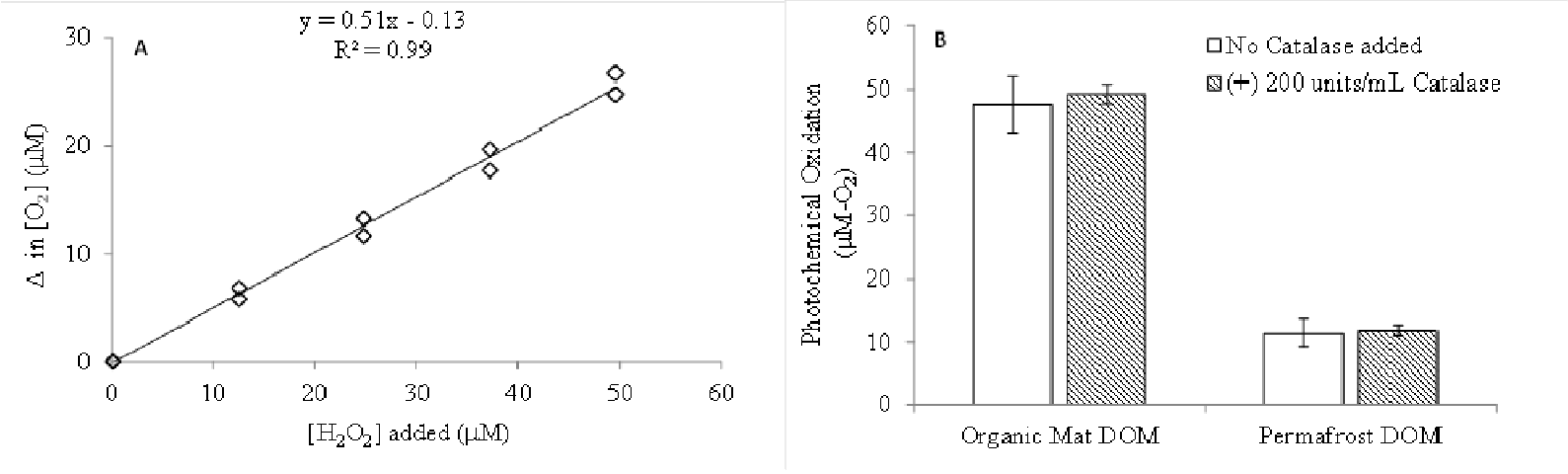

Figure S3: A: Increase in dissolved O_2 concentration after addition of catalase solution to vials spiked with known amounts of H_2O_2. **B:** Contribution of H_2O_2 to the photochemical O_2 consumption. The contribution of H_2O_2 production to photochemical O_2 consumption was quantified as the difference in dissolved O_2 concentration upon addition of catalase (200 units mL^{-1}; Sigma Aldrich)[4] to photo-exposed samples. The capacity for catalase to disproportionate H_2O_2 was measured as a quality control check by adding catalase (200 units mL^{-1}) to vials spiked with known quantities of H_2O_2 and measuring changes in dissolved O_2 after reaction (Fig. SI-2A). As expected, H_2O_2 disproportionation produced 0.5 mol O_2 per mol H_2O_2 consumed (Fig. SI-2A). Immediately following light-exposure of organic mat and permafrost DOM, catalase (200 units/mL) was added to the photo-exposed sample vials and compared to the vials containing the same photo-exposed sample with no catalase added. Addition of catalase did not result in detectable increases in dissolved O_2 concentrations (Fig. SI-2B), suggesting that H_2O_2 produced photochemically by DOM during the experiment was less than the limit of detection of this method (~ 1 μm H_2O_2).

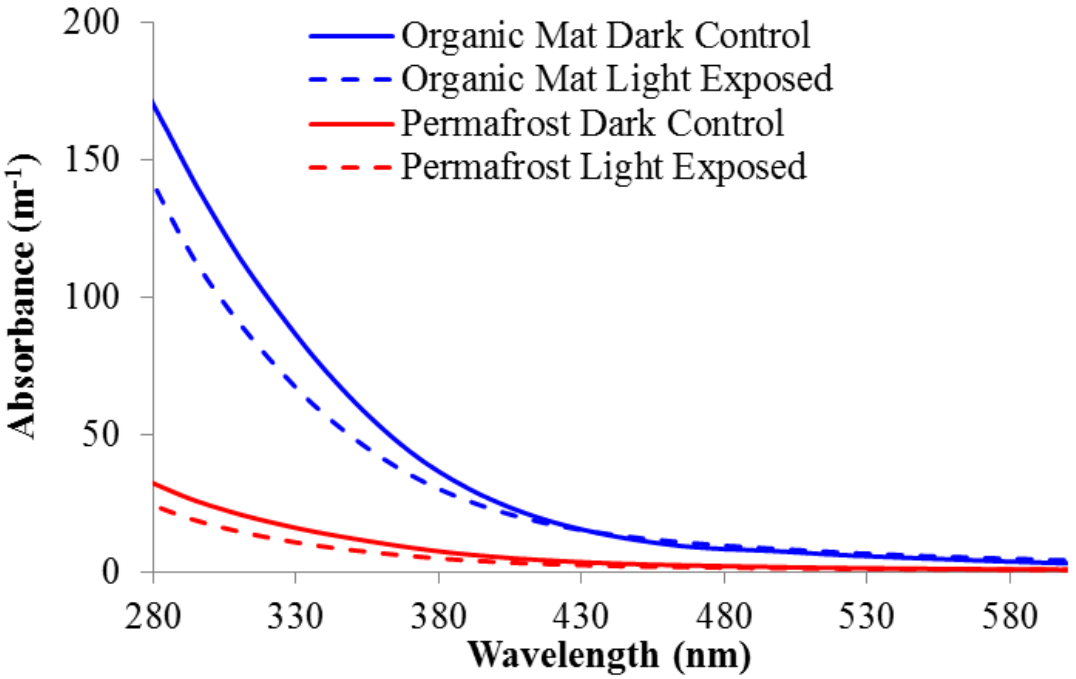

Figure S4: Absorbance spectra of dark-control and light-exposed treatments of organic mat and permafrost DOM.

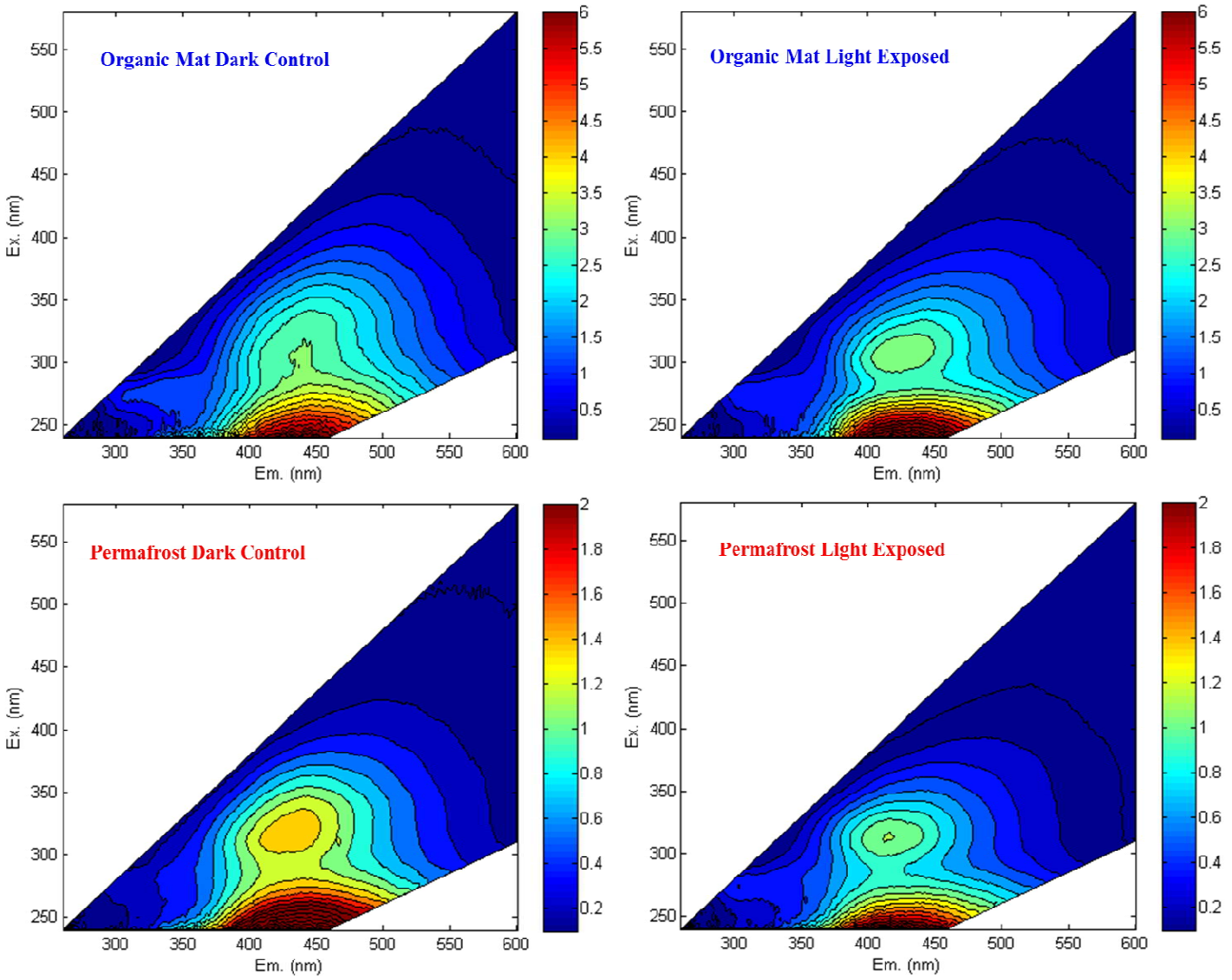

Figure S5: Fluorescence spectra of dark-control and light-exposed treatments of organic mat and permafrost DOM.

References:

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