Electronic Supplementary Material (ESI) for Environmental Science: Processes & Impacts.

Supporting information for:

Insights into the complete and partial photooxidation of black carbon in surface waters

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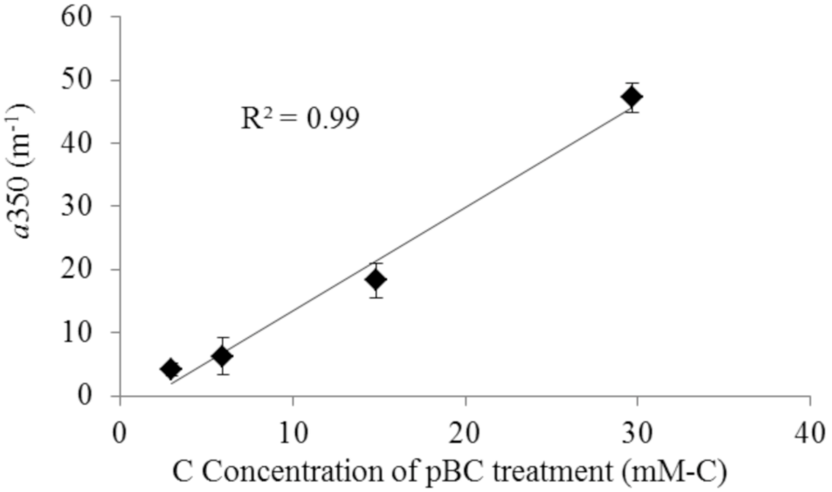

Figure S1. Absorption coefficients at 350 nm (*a*350; m^{-1}, Napierian) of the particulate BC (pBC) treatment derived from a dilution series ranging in C concentration from 3 to 30 mM-C. The linear increase in absorption with increasing C concentration suggested similar contributions from scattering at all C concentrations, and multiple scattering effects were likely minimized at high concentrations. Error bars show ± standard error from the mean ($n = 2$).

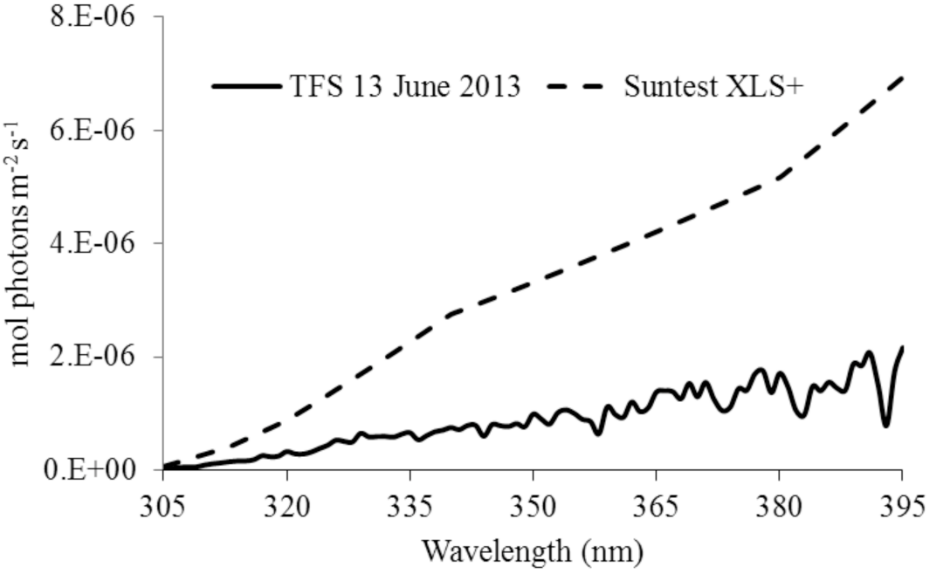

Figure S2. Comparison of the sunlight spectrum collected at Toolik Lake Field Station on 13 June 2013 to the simulated sunlight spectrum emitted from a Suntest XLS+ (Atlas Materials Testing, Inc.). Integration of both spectra from 305 to 395 nm revealed that the simulated sunlight spectrum was approximately three times more intense than the natural sunlight spectrum. UVA and UVB measurements were collected every 5 minutes throughout the 17 hour experiment, averaged, and then normalized to a modeled sunlight spectrum using the National Center for Atmospheric Radiation (NCAR) tropospheric ultraviolet and visible (TUV) radiation model. Irradiance measurements (W m^{-2} nm^{-1}) of the simulated sunlight spectrum were collected at six discrete wavelengths (Biospherical Instruments, Inc.; 305, 313, 320, 340, 380, 395 nm), interpolated to 1-nm increments, and converted to a photon flux density spectrum (mol photons m^{-2} s^{-1}).

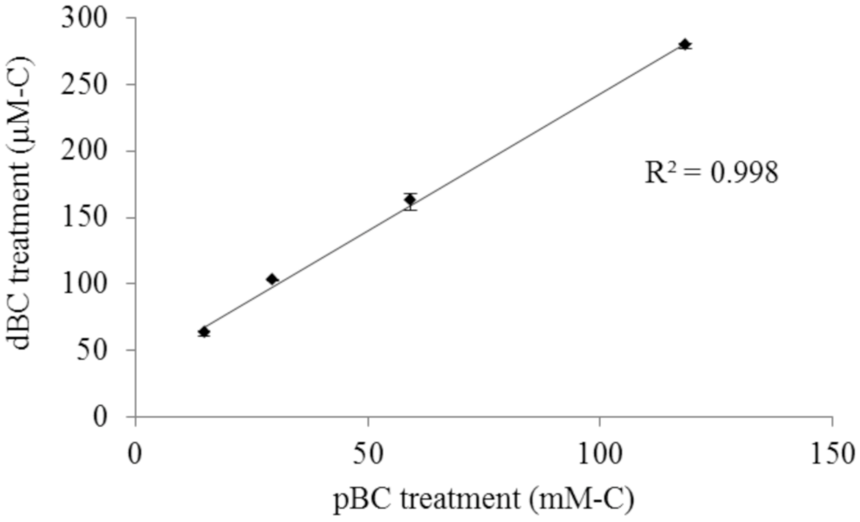

Figure S3. Particulate BC (pBC) treatments ranging in C concentration from 15 to 118 mM-C resulted in dissolved BC (dBC) treatments ranging in C concentration from 63 to 279 μM-C after GF/F filtration. Because > 99% of the C in the unfiltered treatment was retained by a GF/F filter, independent of the initial C concentration, the unfiltered treatment was operationally defined as particulate BC (pBC). Similarly, the filtered BC treatment was operationally defined as dissolved BC (dBC). Error bars show ± standard deviation of the mean (*n* = 3).

Table S1: Mass balance calculations for the complete and partial photooxidation of dBC.

	Measured	Calculated	Measured	Calculated: dBC Remaining after Complete Photooxidation		Calculated: Complete Photooxidation as % of Initial dBC		Measured	Calculated: Partial Photooxidation	Measured	Calculated	Calculated: Partial Photooxidation as % of initial dBC	
Sample	Min dBC	Max dBC[1]	Complete Photooxidation	Min	Max	Min[2]	Max[2]	Photooxidation	O_2 incorporated into dBC[3]	Min Initial O/C[4]	Partially Photooxidized-C[5]	Min[6]	Max[6]
	(μM-C)		(μM-CO_2)	(μM-C)		(%)		(μM-O_2)		Max	(μM-C)	(%)	
dBC Rep 1	61	73	8	69	53	10	13	45	38	1.1	68	89	112
dBC Rep 2	63	75	7	70	54	9	11	36	29	1.1	52	68	85
dBC Rep 3	64	77	6	71	55	8	10	45	39	1.1	72	93	117
										Min	(μM-C)	(%)	
										0.82	91	119	150
										0.82	70	91	115
										0.82	96	125	157

Shaded values are the results shown in Figure 3.

[1] Assuming the calculated dBC concentration may be up to 20% higher than the measured concentration. Aromatic compounds have been shown to be on average 20% less efficiently oxidized to CO_2 by high-temperature catalytic combustion compared to aliphatic compounds used as standards for quantifying C.[40]

[2] Min = ([CO_2]/ [max dBC]) * 100; Max = ([CO_2] / [min dBC]) * 100

[3] Assuming that 1 mol of O_2 was consumed for 1 mol of CO_2 produced.[50]

[4] Max stoichiometry is highest detected O/C in FT-ICR MS spectrum of dBC dark control; Min stoichiometry is lowest O/C ratio detected in the dBC dark control that did not produce more oxidized C than was available for oxidation (e.g. initial dBC concentration minus CO_2 produced).

[5] Partially photooxidized-C calculated as (2*[O_2 incorporated into dBC]) / (O/C stoichiometry)

[6] Min = ([partially photooxidized-C] / [max dBC]) * 100; Max = ([partially photooxidized-C] / [min dBC]) * 100

Table S2. Optical characterization of the dark control and light exposed dBC treatments. This table shows that both absorbance and fluorescence intensity of the dBC treatment decreased after exposure to sunlight. The observed increase in slope ratio (S_R) indicated that the average molecular weight of the compounds in the dBC treatment decreased upon exposure to sunlight.

dBC Treatment	*a*305 (m^{-1})	S_R	Peak 1 (RU)	Peak 2 (RU)
Dark Control	1.81 ± 0.04	1.60 ± 0.10	0.38 ± 0.01	0.22 ± 0.01
Light Exposed	1.37 ± 0.03	1.88 ± 0.05	0.07 ± 0.01	0.03 ± 0.01

*a*305 = absorption coefficient at 305 nm (Napierian), S_R = spectral slope ratio, Peak 1 = excitation/emission wavelength maxima at 245/415 nm/nm in Raman units (RU), Peak 2 = excitation/emission wavelength maxima at 305/415 nm/nm in RU. Values show ± standard deviation from the mean ($n = 3$).