Supporting Information for

Light absorption by brown carbon in the Southeastern United States is pH dependent

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Appendix 1. Details of the simplified forcing efficiency (SFE) calculations.

The SFE was calculated at each pH value and mixing state according to the formulation of Chen and Bond[1]:

$$SFE = \int_{300nm}^{800nm} \frac{dSFE}{d\lambda} = \int_{300nm}^{800nm} -\frac{1}{4}\frac{dS}{d\lambda}\tau_{atm}^{2}\left(1-F_c\right)\left[2\left(1-a_s\right)^{2}\bullet\beta\bullet MSC - 4a_s\bullet MAC\right] \quad \text{(S1)}$$

where a_s is the solar irradiance (taken from the ASTM G173-03 reference spectrum,[2] τ_{atm} is the atmospheric transmission (0.79 [3]), F_c is the cloud fraction (0.6 [3]), and a_s is the surface albedo (0.19 [3]). The backscatter fraction, β, is taken to be a constant value (0.17 [4]) at all wavelengths and for all particle diameters, and MSC and MAC are the mass scattering and mass absorption cross section of the particles, respectively. The MSC and MAC are calculated from Mie theory for coated spheres consisting of both black carbon and organic material. The value of k_{OA} was parameterized as a function of both wavelength and pH based on the results of this study (see Appendix 2).

Appendix 2. Details of the parameterization of k_{OA} as a function of λ and pH.

The imaginary part of the refractive index for the organic aerosol component, k_{OA}, was parameterized as a function of both λ and pH according to the findings of the present work.

The wavelength dependence of the value of k_{OA} was assumed to follow a power law function:

$$k_{OA}(\lambda, pH) = k_{550}(pH) \cdot \left(\frac{550}{pH} \right)^{w(pH)} \quad \text{(S2)}$$

with k_{550} the value of k_{OA} at λ = 550 nm and the exponent, w, describing the wavelength dependence. Both k_{550} and w are functions of pH:

$$k_{550}(pH) = k_{550}(pH = 2) \cdot \left[1 + 0.25 \cdot (pH - 2) \right] \quad \text{(S3)}$$

which is derived from the spectra shown in Figure 1 in the main text, and:

$$w(pH) = 6.16 - 0.17 \cdot pH \quad \text{(S4)}$$

which is derived from the observed trend of AAE vs. pH (Figure 4 in the main text) and the assumption that w = AAE - 1.[4]

Table S1. Summary of all samples collected and analyzed.

Date (2016)	Hours collected	Initial pH	AAE at pH7	Air mass source direction	Visibility (miles)
9/22-9/29	168	3.9	6.21	WNW	9
10/16-10/17	24	4	6.32	SE	9
9/29-9/30	24	4.9	6.42	NW	10
8/9-8/15	144	3.7	5.54	S	9.4
10/14-10/16	48	4.2	5.34	ENE	8.3
10/28-11/2	120	4.1	5.82	ENE	9
11/2-11/4	48	4.7	5.65	NW	7
4/27-4/30	72	4.2	5.51	WSW	9.5
10/17-10/18	24	4.1	6.02	SW	10
10/31-11/02	48		5.9	ENE	8
11/8-11/10	*47.5*	*4.9*	*N/A*	*N*	*8.6*
11/10-11/11	*24*	*4.3*	*N/A*	*NW*	*3.8*
11/11	*7*	*4.9*	*N/A*	*NW*	*3.8*
11/14-11/15	*25*		*N/A*	*WNW*	*2*
11/15-11/16	*24.5*	*4.1*	*N/A*	*NW*	*4*

Samples classified as “wildfire” samples from MODIS fire counts and HYSPLIT back trajectory calculations are indicated in italics. Air mass source direction was determined from HYSPLIT back trajectory calculations. Visibility was taken from https:/www.wunderground.com.

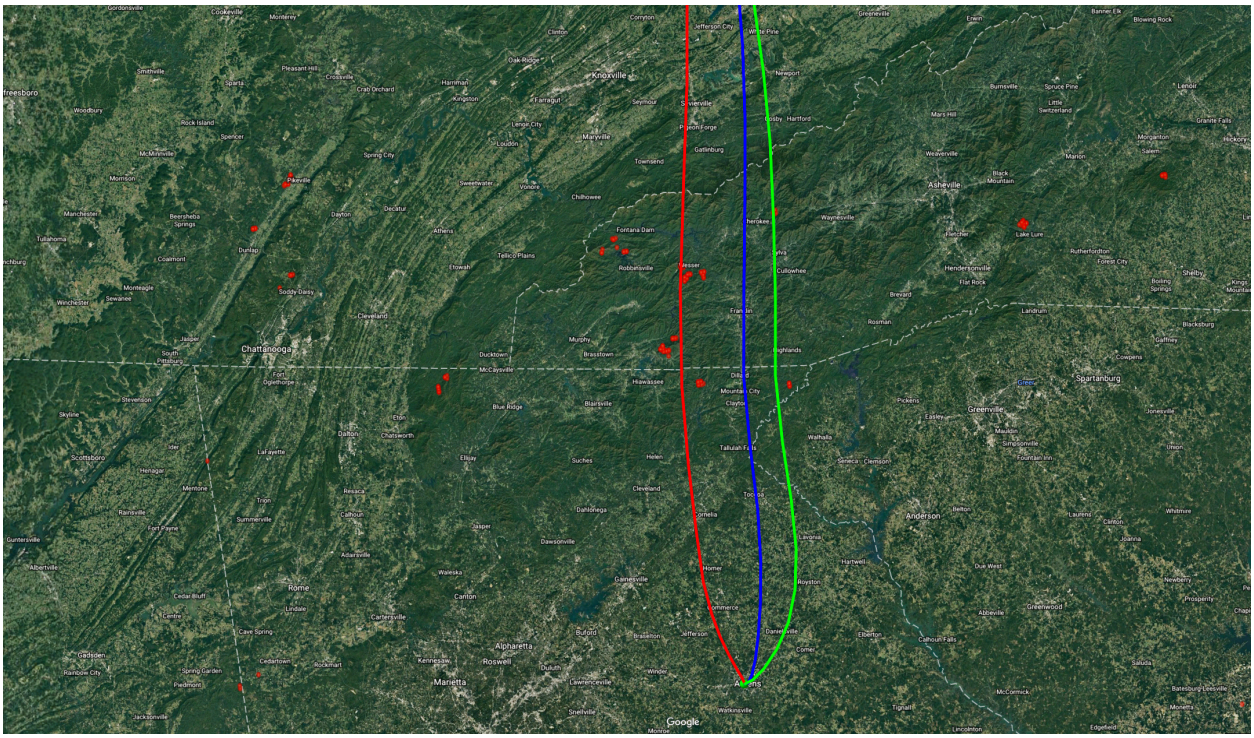

Figure S1. Map of overlaid MODIS fire counts (red dots) and calculated HYSPLIT back trajectories (50 m, red line; 250 m, blue line; 500 m, green line) for air mass sampled at Athens, GA on November 10, 2016. The other designated wildfire samples also show sampled air masses traveled through regions impacted by wildfires. (Map data: Google, IBCAO Data SIO, NOAA, U.S. Navy, NGA, GEBCO Landsat/Copernicus).

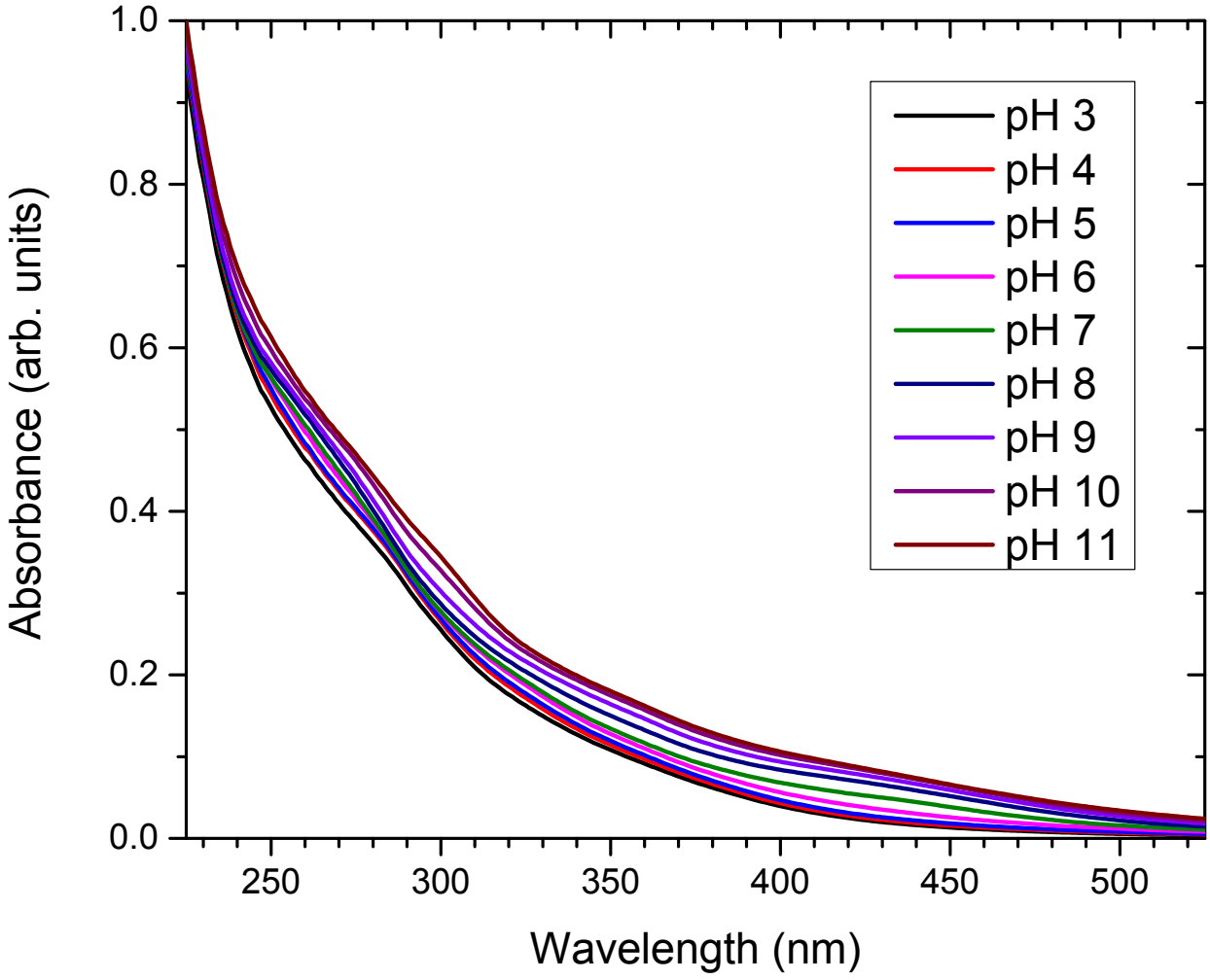

Figure S2. Averaged absorbance spectra of ambient Athens, GA samples affected by wildfires (November, 2016). The spectra are not fit by a power law function as well as the baseline ambient spectra are.

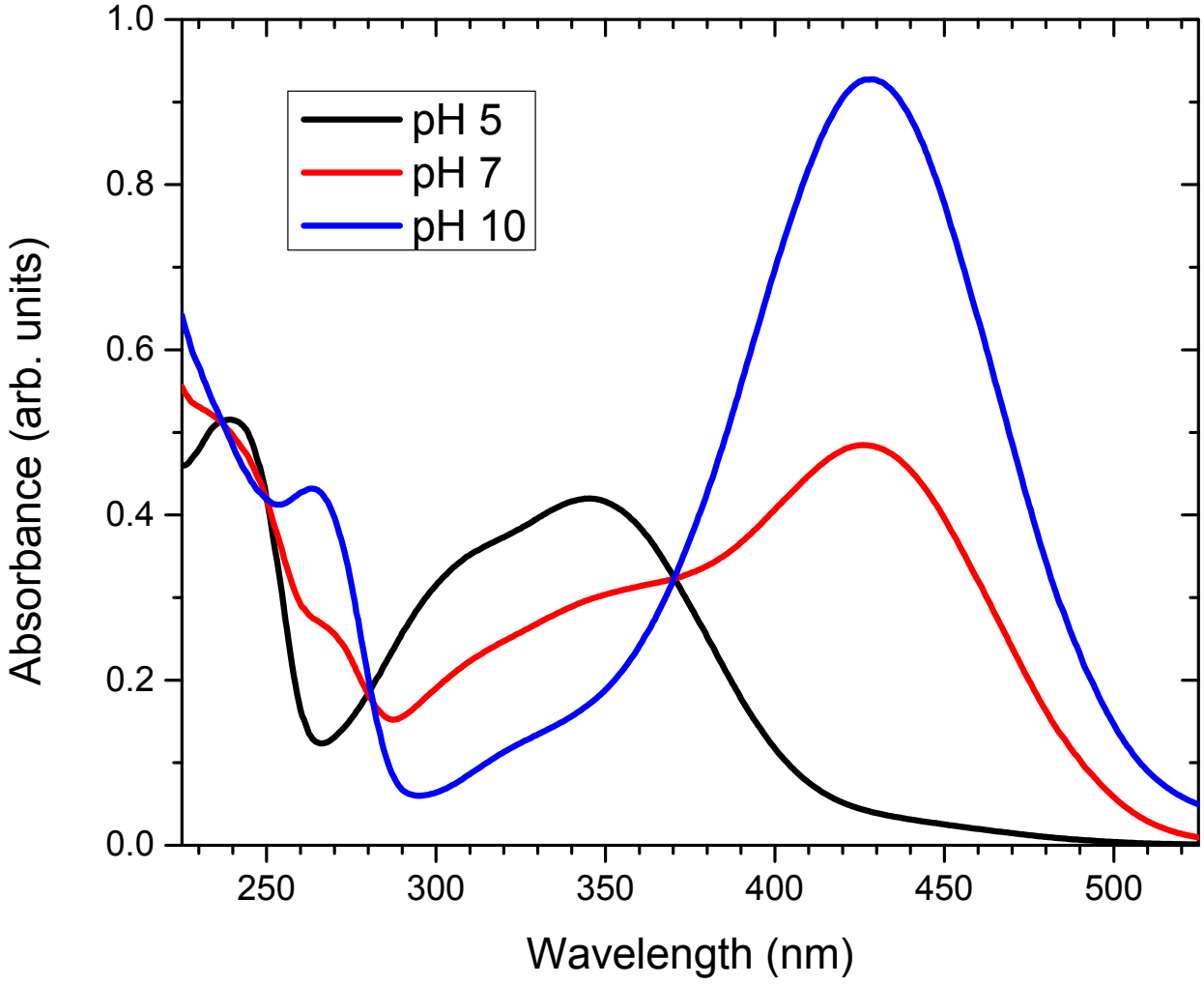

Figure S3. Absorbance spectra of a 50 mg/L aqueous 4-nitrocatechol solution at pH = 5, pH = 7, and pH = 10. The peak at 430 nm present at pH =7 and pH = 10 corresponds to the deprotonated phenolate form.

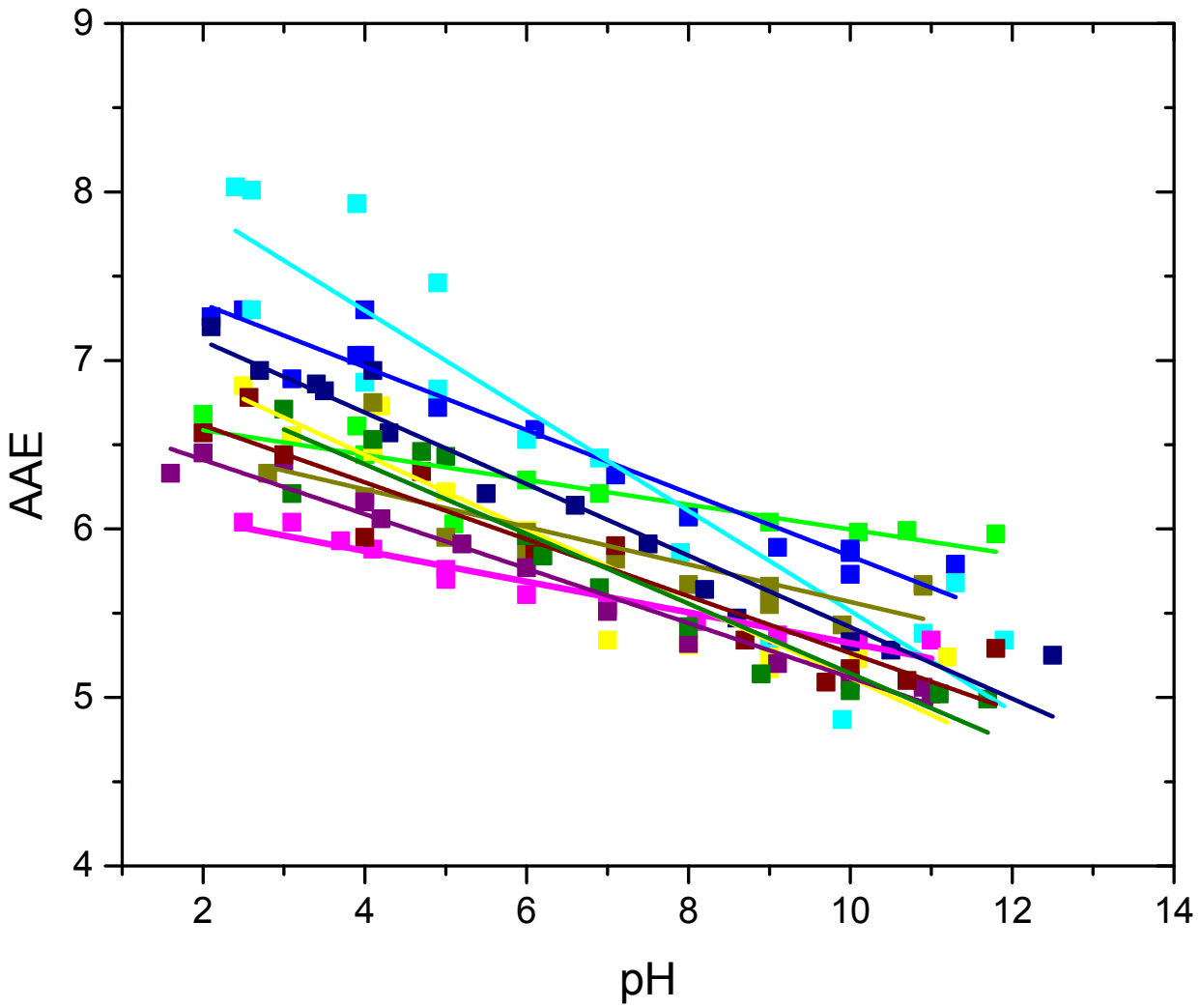

Figure S4. Absorption Ångström exponent (AAE) as a function of pH for individual baseline ambient Athens, GA filter samples. All samples show a similar trend of decreasing AAE with increasing pH.

References

(1) Chen, Y.; Bond, T. C. Light Absorption by Organic Carbon From Wood Combustion. Atmos. Chem. Phys. 2010, 10, 1773–1787.

(2) ASTM G173-03(2012), Standard Tables for Reference Solar Spectral Irradiances: Direct Normal and Hemispherical on 37° Tilted Surface; ASTM International: West Conshohocken, PA, 2012.

(3) Chylek, P.; Wong, J. Effect of Absorbing Aerosols on Global Radiation Budget. Geophys. Res. Lett. 1995, 22, 929–931.

(4) Saleh, R.; Robinson, E. S.; Tkacik, D. S.; Ahern, A. T.; Liu, S.; Aiken, A. C.; Sullivan, R. C.; Presto, A. A.; Dubey, M. K.; Yokelson, R. J.; et al. Brownness of Organics in Aerosols From Biomass Burning Linked to Their Black Carbon Content. Nature Geosci. 2014, 7, 647–650.