Supplemental Information for

Molecular Chemistry of Atmospheric Brown Carbon Inferred from a Nationwide Biomass Burning Event

Peng Lin,[1] Nir Bluvshtein,[2] Yinon Rudich,[2] Sergey A. Nizkorodov,[3] Julia Laskin,[4,†] Alexander Laskin[1,†,*]

[1] *Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA, 99354*

[2] *Department of Earth and Planetary Sciences, Weizmann Institute of Science, Rehovot 76100, Israel.*

[3] *Department of Chemistry, University of California, Irvine, CA, 92697*

[4] *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA, 99354*

[†]present address: *Department of Chemistry, Purdue University, West Lafayette, IN, 47907*

*email: alaskin@purdue.edu

Table S1. List of the $PM_{2.5}$ filter samples collected with a high volume air sampler. Four of them chosen for detailed chemical analysis and discussions in this study are indicated with bold characters.

Filter ID	Start time	End time	Volume sampled [m^3]	Remarks
f1	5/3/2015 12:00	5/4/2015 11:45	1335	Background ambient air before the biomass burning (BB) event
f2	**5/4/2015 12:00**	**5/5/2015 11:45**	**1608**	
f3	5/5/2015 12:00	5/6/2015 11:45	1609	
f4	5/6/2015 12:00	5/7/2015 1:00	896	BB start @ evening
f5	**5/7/2015 3:46**	**5/7/2015 6:46**	**203**	BB smoke dominant
f6	**5/7/2015 7:46**	**5/7/2015 11:45**	**273**	End of BB, morning mixing
f7	**5/7/2015 12:00**	**5/8/2015 11:45**	**1610**	Post BB

Table S2. List of identified BrC chromophores. Compounds corresponding to major light absorption peaks of HPLC-PDA chromatogram are indicated with bold characters.

retention time (RT) of major peak (min)	m/z	elemental composition	DBE	retention time (RT) of other isomers with smaller peaks (min)
8.60	137.02408	$C_7 H_6 O_3$	5	18.34, 21.74,
9.83	167.03479	$C_8 H_8 O_4$	5	14.15
10.30	151.03990	$C_8 H_8 O_3$	5	
10.50	142.01433	$C_5 H_5 N O_4$	4	
10.60	139.01466	$C_5 H_4 N_2 O_3$	5	
10.10	165.01886	$C_8 H_6 O_4$	6	10.63
10.96	170.00912	$C_6 H_5 N O_5$	5	
12.40	121.02925	$C_7 H_6 O_2$	5	10.10, 10.63
12.50	203.04596	$C_{10} H_8 N_2 O_3$	8	**11.54**, 16.42
13.00	177.05548	$C_{10} H_{10} O_3$	6	17.01, 17.95
13.07	209.04500	$C_{10} H_{10} O_5$	6	
13.10	163.03972	$C_9 H_8 O_3$	6	**8.45**
13.11	153.03029	$C_6 H_6 N_2 O_3$	5	
13.66	135.04501	$C_8 H_8 O_2$	5	**17.16**
14.65	210.04062	$C_9 H_9 N O_5$	6	19.62, 20.34, 22.65, **23.42, 24.18**
14.80	179.03484	$C_9 H_8 O_4$	6	
15.35	154.01413	$C_6 H_5 N O_4$	5	
16.08	184.02470	$C_7 H_7 N O_5$	5	
16.11	182.00928	$C_7 H_5 N O_5$	6	**21.10**
16.79	277.06647	$C_{21} H_{10} O$	17	
17.01	224.05618	$C_{10} H_{11} N O_5$	6	**18.85**
17.15	192.02982	$C_9 H_7 N O_4$	7	**23.78, 24.60**
18.26	168.02988	$C_7 H_7 N O_4$	5	**19.53**, **20.58**
19.08	138.01936	$C_6 H_5 N O_3$	5	
19.79	198.04044	$C_8 H_9 N O_5$	5	
21.34	178.01439	$C_8 H_5 N O_4$	7	**21.90**
21.64	182.04544	$C_8 H_9 N O_4$	5	**22.20**, **22.97**, **24.09**
21.97	152.03503	$C_7 H_7 N O_3$	5	**23.20**
22.21	220.02487	$C_{10} H_7 N O_5$	8	**16.79**, 21.08, 23.07
22.26	183.00444	$C_6 H_4 N_2 O_5$	6	
22.48	193.05040	$C_{10} H_{10} O_4$	6	
22.66	194.04546	$C_9 H_9 N O_4$	6	**20.88,** 21.77, 17.93
22.94	222.04053	$C_{10} H_9 N O_5$	7	
23.40	220.06111	$C_{11} H_{11} N O_4$	7	22.84, 24.13, 29.33, 30.16
24.33	269.04111	$C_{10} H_{10} N_2 O_7$	7	22.80, 23.59
24.60	196.06119	$C_9 H_{11} N O_4$	5	**25.13,** 25.80, 27.02
24.85	208.06120	$C_{10} H_{11} N O_4$	6	
25.20	166.05066	$C_8 H_9 N O_3$	5	**25.70, 26.46**
25.32	197.01993	$C_7 H_6 N_2 O_5$	6	
26.92	188.03497	$C_{10} H_7 N O_3$	8	
27.12	211.03564	$C_8 H_8 N_2 O_5$	6	28.00

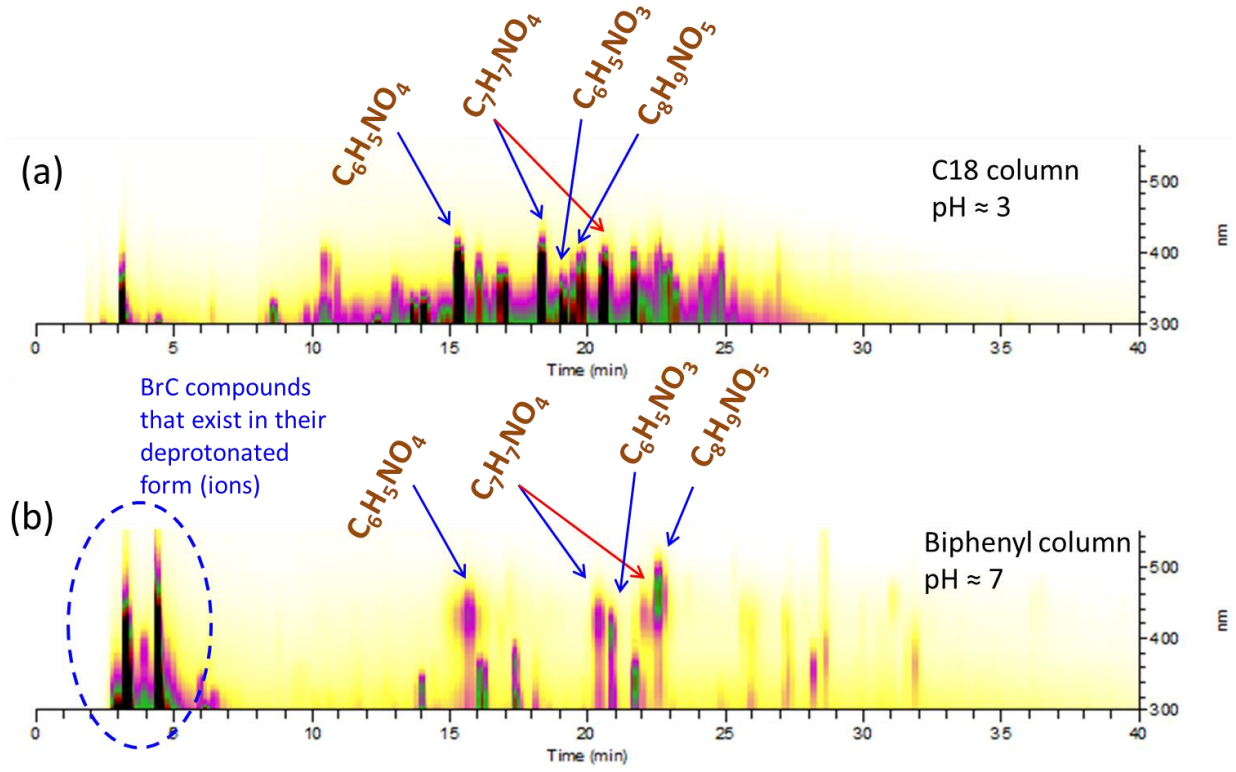

Figure S1. (a) HPLC-PDA chromatogram obtained with a C18 column at pH≈3. Under this condition, we have good retention of BrC and better separation. This is a good dataset to evaluate the contribution of identified BrC chromophores to the overall WSOC absorption. However, the absorption maximum observed under this condition were at 300-400nm, which differs from the UV-Vis spectra measured from the bulk WSOC solution. (b) HPLC-PDA chromatogram obtained with a biphenyl column at pH≈7. Under this condition, many BrC chromophores are in their deprotonated form (ions) so that they eluted from the column close to the dead time (in the blue cycle). Some chromophores can be retained by the column via π-π interaction (RT = 10-40 min).

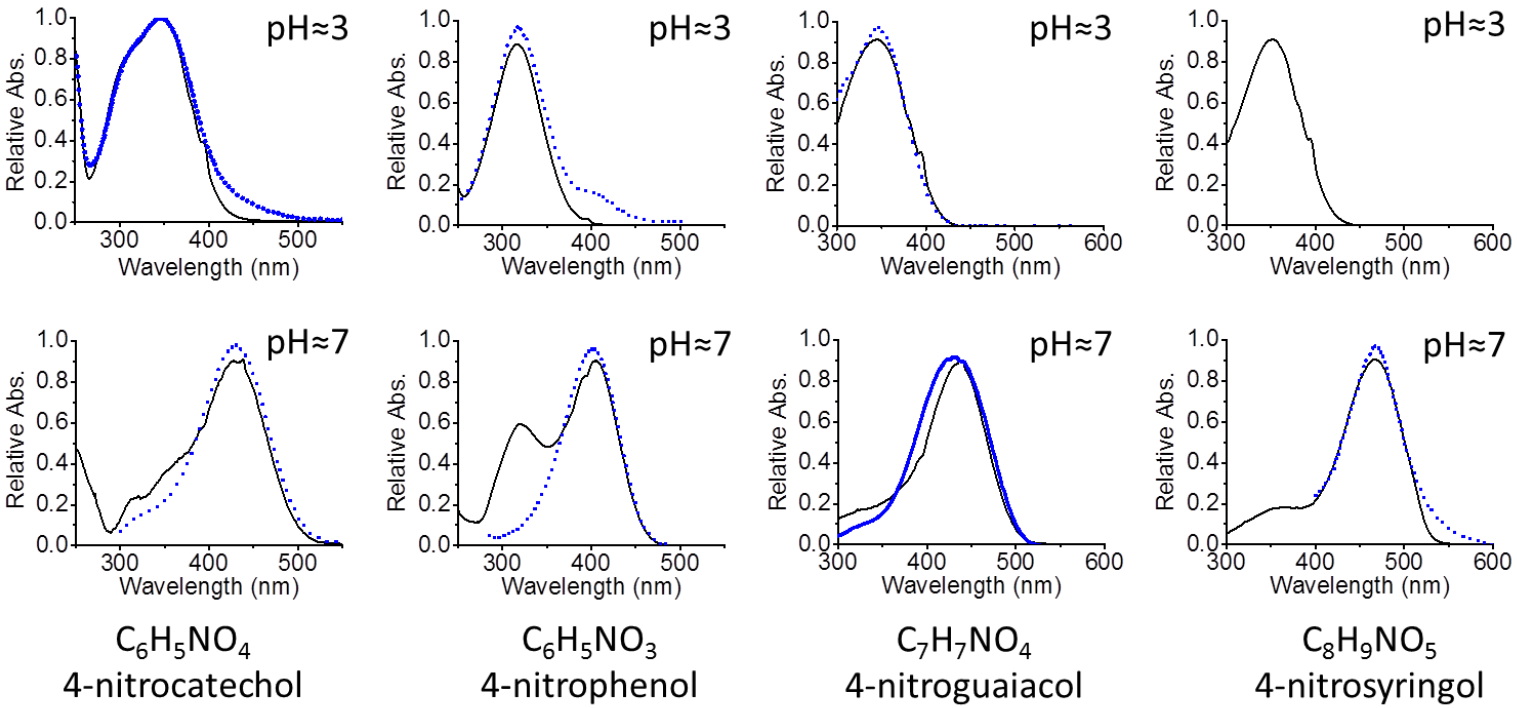

Figure S2. UV-Vis spectra of several BrC chromophores measured with HPLC-PDA analysis at different pH conditions (black solid line). The blue-dot line shows the UV-Vis spectra of known NACs digitized from the literatures: 4-nitrocatechol,[1] 4-nitrophenol,[2] 4-nitroguaiacol,[3] and 4-nitrosyringol.[4] The UV-Vis spectrum of 4-nitroguaiacol at pH≈7 (blue solid line) was direct measurement from a standard.

References:

1. Cornard, J. P.; Rasmiwetti; Merlin, J. C., Molecular structure and spectroscopic properties of 4-nitrocatechol at different pH: UV-visible, Raman, DFT and TD-DFT calculations. *Chem Phys* **2005,** *309*, (2-3), 239-249.
2. Biggs, A. I., A Spectrophotometric Determination of the Dissociation Constants of Para-Nitrophenol and Papaverine. *T Faraday Soc* **1954,** *50*, (8), 800-802.
3. Kitanovski, Z.; Cusak, A.; Grgic, I.; Claeys, M., Chemical characterization of the main products formed through aqueous-phase photonitration of guaiacol. *Atmos Meas Tech* **2014,** *7*, (8), 2457-2470.
4. Tang H.; Thompson, J. E., Light-Absorbing Products Form during the Aqueous Phase Reaction of Phenolic Compounds in the Presence of Nitrate and Nitrite with UV Illumination. *Open Journal of Air Pollution* **2012,** *1*, (2), 13-21.