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Measurement report: Brown carbon aerosol in polluted urban air of the North China Plain – day–night differences in the chromophores and optical properties

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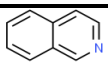
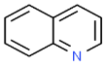
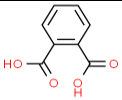
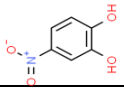
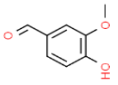
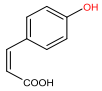
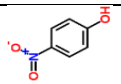
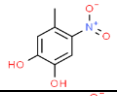
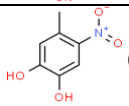
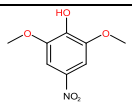
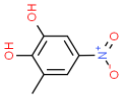
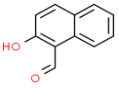
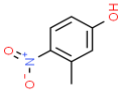
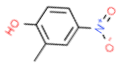
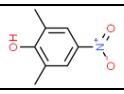
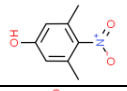
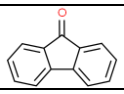
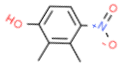
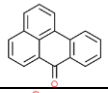
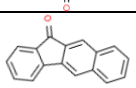
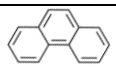
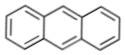
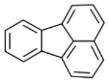
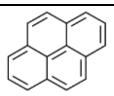
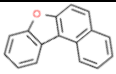
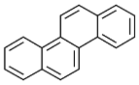
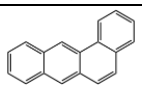
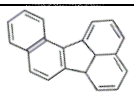
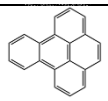
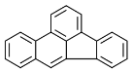
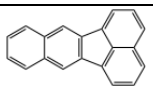
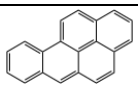
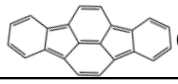
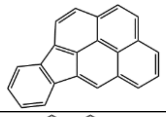
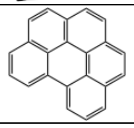
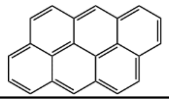
Table S1. Retention Times (RTs), Abbreviation, Elemental Formulas, and Assigned Structures of Identified BrC Chromophores. (*) represent tentative structure components.

Peak #	RT (min)	m/z &ion. Mech.	Formula	Name (Abbreviation)	Unambiguous/Tentative stucture (*)	Quantificatied with
1#	1.69	130.0652 $[M + H]^+$	C_9H_7N	Isoquinoline (ISO)	 (*)	surrogates (QUI)
2#	2.03	130.0652 $[M + H]^+$	C_9H_7N	Quinoline (QUI)		standards
3#	6.06	165.0192 $[M - H]^-$	$C_8H_6O_4$	Phthalic acid (PA)		standards
4#	7.21	154.0144 $[M - H]^-$	$C_6H_5NO_4$	4-nitrocatechol (4NC)		standards
5#	7.87	153.0544 $[M + H]^+$	$C_8H_8O_3$	vanillin (VAN)		standards
6#	9.15	163.0401 $[M - H]^-$	$C_9H_8O_3$	p-cis-coumaric acid (PCCA)	 (*)	surrogates (PA)
7#	11.48	138.0195 $[M - H]^-$	$C_6H_5NO_3$	4-nitrophenol (4NP)		standards
8#	13.53	168.0301 $[M - H]^-$	$C_7H_7NO_4$	4-methyl-5-nitrocatechol (4M5NC)		standards
9#	13.82	168.0302 $[M - H]^-$	$C_7H_7NO_4$	3-methyl-6-nitrocatechol (3M6NC)	 (*)	surrogates (4M5NC)
10#	16.06	198.0406 $[M - H]^-$	$C_8H_9NO_5$	4-nitrosyringol (4NS)	 (*)	surrogates (3M5NC)
11#	18.23	168.0301 $[M - H]^-$	$C_7H_7NO_4$	3-methyl-5-nitrocatechol (3M5NC)		standards
12#	18.72	171.0451 $[M - H]^-$	$C_{11}H_8O_2$	1-Formyl-2-naphthol (1F2N)	 (*)	surrogates (5-hydroxy-1,4-naphthoquinone)
13#	19.43	152.0352 $[M - H]^-$	$C_7H_7NO_3$	3-methyl-4-nitrophenol (3M4NP)		standards
14#	20.06	183.0440 $[M + H]^+$	$C_{12}H_6O_2$	1,2-acenaphthylenedione (1,2ACE)	 (*)	surrogates (1,8NA)

Peak #	RT (min)	m/z &ion. Mech.	Formula	Name (Abbreviation)	Unambiguous/Tentative stucture (*)	Quantificatied with
15#	20.53	199.0389 $[M + H]^+$	$C_{12}H_6O_3$	1,8-naphthalic anhydride (1,8NA)		standards
16#	21.95	152.0352 $[M - H]^-$	$C_7H_7NO_3$	2-methyl-4-nitrophenol (2M4NP)		standards
17#	26.08	166.0509 $[M - H]^-$	$C_8H_9NO_3$	2,6-Dimethyl-4-nitrophenol (2,6D4NP)		standards
18#	26.39	166.0509 $[M - H]^-$	$C_8H_9NO_3$	3,5-Dimethyl-4-nitrophenol (3,5D4NP)	 (*)	surrogates (2,6D4NP)
19#	27.12	181.0648 $[M + H]^+$	$C_{13}H_8O$	9-fluorenone (9FLU)		standards
20#	28.21	166.0509 $[M - H]^-$	$C_8H_9NO_3$	2,3-Dimethyl-4-nitrophenol (2,3D4NP)	 (*)	surrogates (2,6D4NP)
21#	36.93	231.0806 $[M + H]^+$	$C_{17}H_{10}O$	Benzanthrone (BEN)		standards
22#	38.41	231.0801 $[M + H]^+$	$C_{17}H_{10}O$	Benzo[b]fluoren-11-one (BbF11O)		standards
23#	39.27	/	$C_{14}H_{10}$	Phenanthrene (PHE)		standards
24#	39.88	/	$C_{14}H_{10}$	Anthracene (ANT)		standards
25#	41.23	/	$C_{16}H_{10}$	Fluoranthene (FLU)		standards
26#	41.7	/	$C_{16}H_{10}$	Pyrene (PYR)		standards
27#	42.48	/	$C_{16}H_{10}O$	Benzo[b]naphtho[1,2-d]furan (BbN[1,2d]F)		standards
28#	43.46	/	$C_{18}H_{12}$	Chrysene (CHR)		standards
29#	43.63	/	$C_{18}H_{12}$	Benz(a)anthracene (BaA)		standards
30#	44.94	/	$C_{20}H_{12}$	Benzo(j)fluoranthen (BjF)		standards
31#	45.23	/	$C_{20}H_{12}$	Benzo(e)pyrene (BeP)		standards
32#	45.29	/	$C_{20}H_{12}$	Benzo(b)fluoranthene (BbF)		standards
33#	45.46	/	$C_{20}H_{12}$	Benzo(k)fluoranthene (BkF)		standards
34#	45.79	/	$C_{20}H_{12}$	Benzo(a)pyrene (BaP)		standards
35#	46.73	/	$C_{22}H_{12}$	Indeno[1,2,3-cd]fluoranthene (I[1,2,3cd]F)	 (*)	surrogates (I[1,2,3cd]P)

Peak #	RT (min)	m/z &ion. Mech.	Formula	Name (Abbreviation)	Unambiguous/Tentative stucture (*)	Quantificatied with
36#	47.43	/	$C_{22}H_{12}$	Indeno(1,2,3-cd)pyrene (I[1,2,3cd]P)		standards
37#	47.53	/	$C_{22}H_{12}$	Benzo(g,h,i)perylene (B(g,h,i)P)		standards
38#	48.25	/	$C_{22}H_{12}$	Anthanthrene (ANTHA)	 (*)	surrogates (I[1,2,3cd]P)

Note: In this study, for chromophores with standards (28 chromophores), unambiguous structures were identified with the standards; for chromophores without standards (10 chromophores), it was assigned by comparing with the reference UV-Vis spectrum.

Table S2. Average (± standard deviation) values Abs_{365nm}, $MAE_{365nm,}$ and AAE of WS-BrC and WIS-BrC, as well as concentrations of WSOC and WISOC, measured organic species in the PM 2.5 aerosols from the urban. [a] represents the determination of the HULIS extraction solution. Here $\mathbf{Abs_{365,\ MS\text{-}BrC}}$ is the light absorption coefficient of methanol-soluble BrC at 365 nm.

Components	This study		Li et al. (2020)		Huang et al. (2020)		Li et al. (2021)	
	Day	Night	Day	Night	Xi'an	Beijing	Day	Night
WSOC (μg m^{-3})	17.29±14.49	12.90±13.36	22.1±8.0	21.7±10.4	12.4 ± 6.50[a]	6.4 ± 3.80 [a]	/	/
WISOC (μg m^{-3})	29.78±22.39	31.07±12.47	21.9±10.1	26.2±17.3	20.80±7.90	16.30±8.90	/	/
$\mathbf{Abs_{365,\ WS\text{-}BrC}}$ **(Mm^{-1})**	46.04±38.91	35.68±35.50	19.2±6.8	19.9±9.5	31.50±16.40 [a]	15.00±9.50 [a]	/	/
$\mathbf{Abs_{365,\ MS\text{-}BrC}}$ **(Mm^{-1})**	79.86±66.50	82.69±55.84	/	/	/	/	50.0±5.00	75.0±7.50
$\mathbf{Abs_{365,\ WIS\text{-}BrC}}$ **(Mm^{-1})**	27.90±24.80	40.88±23.42	17.2±8.2	26.7±15.8	33.90±16.40	26.10±18.40		
$\mathbf{MAE_{365,\ WS\text{-}BrC}}$ **($m^2g\ C^{-1}$)**	2.58±0.14	2.88±0.24	0.92±0.21	0.94±0.28	1.80 ± 0.30 [a]	1.80 ± 0.40 [a]	/	/
$\mathbf{MAE_{365,\ WIS\text{-}BrC}}$ **($m^2g\ C^{-1}$)**	1.02±0.49	1.43±0.83	0.85±0.34	1.05±0.28	1.50±0.50	1.50±0.40	1.73±0.64	2.13±0.65
$\mathbf{AAE_{WS\text{-}BrC}}$	5.10±0.28	5.51±0.40	5.14±0.2	5.07±0.72	8.20 ± 1.00	9.40 ± 2.60	/	/
$\mathbf{AAE_{WIS\text{-}BrC}}$	6.36±0.45	6.97±0.80	5.94±0.12	6.15±0.24	5.4 ± 0.20	5.7 ± 0.20	5.16 ±1.15	4.07 ±0.87

Table S3. The concentrations of day and night mass of the 38 identified BrC chromophores.

Name	Mass concentration (ng m^{-3})	
	Day	Night
Isoquinoline	2.7 ± 1.0	2.0 ± 1.3
Quinoline	6.7 ± 7.7	5.3 ± 4.5
1-Formyl-2-naphthol	6.8 ± 5.6	1.8 ± 1.2
1,2-acenaphthylenedione	12.6 ± 10.8	7.6 ± 5.9
1,8-naphthalic anhydride	8.2 ± 7.6	1.8 ± 1.2
9-fluorenone	0.6 ± 0.4	0.7 ± 0.4
4-nitrocatechol	20.7 ± 18.9	11.2 ± 7.7
4-methyl-5-nitrocatechol	6.6 ± 6.1	5.8 ± 3.3
3-methyl-6-nitrocatechol	1.3 ± 0.6	1.0 ± 0.4
3-methyl-5-nitrocatechol	10.9 ± 11.0	2.8 ± 3.2
4-nitrophenol	20.2 ± 14.7	41.9 ± 29.4
3-methyl-4-nitrophenol	2.2 ± 1.5	5.6 ± 3.3
2-methyl-4-nitrophenol	2.0 ± 1.5	8.1 ± 4.6
2,6-Dimethyl-4-nitrophenol	0.6 ± 0.4	2.4 ± 1.4
3,5-Dimethyl-4-nitrophenol	0.4 ± 0.2	2.5 ± 1.3
2,3-Dimethyl-4-nitrophenol	0.6 ± 0.5	1.2 ± 0.6
Phthalic acid	25.1 ± 12.9	12.1 ± 6.3
vanillin	4.1 ± 1.6	3.8 ± 2.8
p-cis-coumaric acid	2.9 ± 1.5	4.6 ± 2.6
4-nitrosyringol	5.8 ± 4.8	6.3 ± 3.2
Benzanthrone	0.5 ± 0.4	0.5 ± 0.3
Benzo[b]fluoren-11-one	0.2 ± 0.2	0.2 ± 0.1
Benzo[b]naphtho[1,2-d]furan	0.1 ± 0.1	0.2 ± 0.1
Phenanthrene	1.3 ± 1.2	1.1 ± 0.8
Anthracene	0.5 ± 0.4	0.5 ± 0.4
Fluoranthene	4.4 ± 4.0	7.9 ± 7.8
Pyrene	3.4 ± 3.1	4.8 ± 3.4
Chrysene	3.8 ± 4.2	8.0 ± 5.5
Benzo(a)anthracene	1.7 ± 1.4	3.5 ± 2.0
Benzo(j)fluoranthene	0.2 ± 0.2	0.3 ± 0.1
Benzo(e)pyrene	3.2 ± 3.0	5.2 ± 3.6
Benzo(b)fluoranthene	2.3 ± 2.1	2.6 ± 1.6
Benzo(k)fluoranthene	2.5 ± 2.5	3.7 ± 2.5
Benzo(a)pyrene	1.4 ± 1.3	1.7 ± 1.3
Indeno[1,2,3-cd]fluoranthene	0.7 ± 0.6	0.9 ± 0.6
Indeno(1,2,3-cd)pyrene	1.3 ± 1.2	1.3 ± 0.5
Benzo(g,h,i)perylene	0.7 ± 0.6	0.9 ± 0.7
Anthanthrene	0.3 ± 0.3	0.4 ± 0.3

Table S4. The identified 38 BrC chromophores are divided into ten subgroups.

Categories	Subgroups	Name
I	quinolines	Isoquinoline Quinoline
II	2–3-ring OPAHs	1-Formyl-2-naphthol 1,2-acenaphthylenedione 1,8-naphthalic anhydride 9-fluorenone
III	nitrocatechols	4-nitrocatechol 4-methyl-5-nitrocatechol 3-methyl-6-nitrocatechol 3-methyl-5-nitrocatechol
IV	nitrophenols	4-nitrophenol 3-methyl-4-nitrophenol 2-methyl-4-nitrophenol 2,6-Dimethyl-4-nitrophenol 3,5-Dimethyl-4-nitrophenol 2,3-Dimethyl-4-nitrophenol
V	aromatic alcohols and acids	Phthalic acid vanillin p-cis-coumaric acid 4-nitrosyringol
VI	4-ring OPAHs	Benzanthrone Benzo[b]fluoren-11-one Benzo[b]naphtho[1,2-d]furan
VII	3-ring PAHs	Phenanthrene Anthracene
VIII	4-ring PAHs	Fluoranthene Pyrene Chrysene Benzo(a)anthracene
IX	5-ring PAHs	Benzo(j)fluoranthene Benzo(e)pyrene Benzo(b)fluoranthene Benzo(k)fluoranthene Benzo(a)pyrene
X	6-ring PAHs	Indeno[1,2,3-cd]fluoranthene Indeno(1,2,3-cd)pyrene Benzo(g,h,i)perylene Anthanthrene

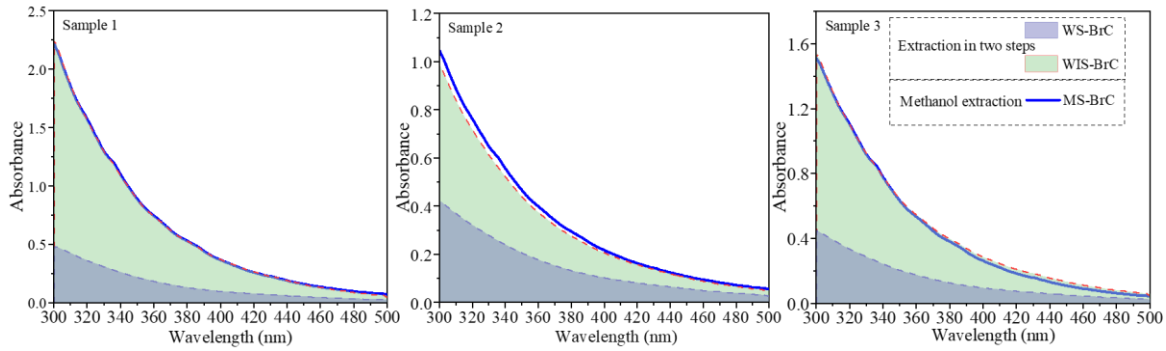


Figure S1. Comparison of the UV-Vis spectra of BrC extracts between sequential extraction with water and methanol and direct extraction with methanol.

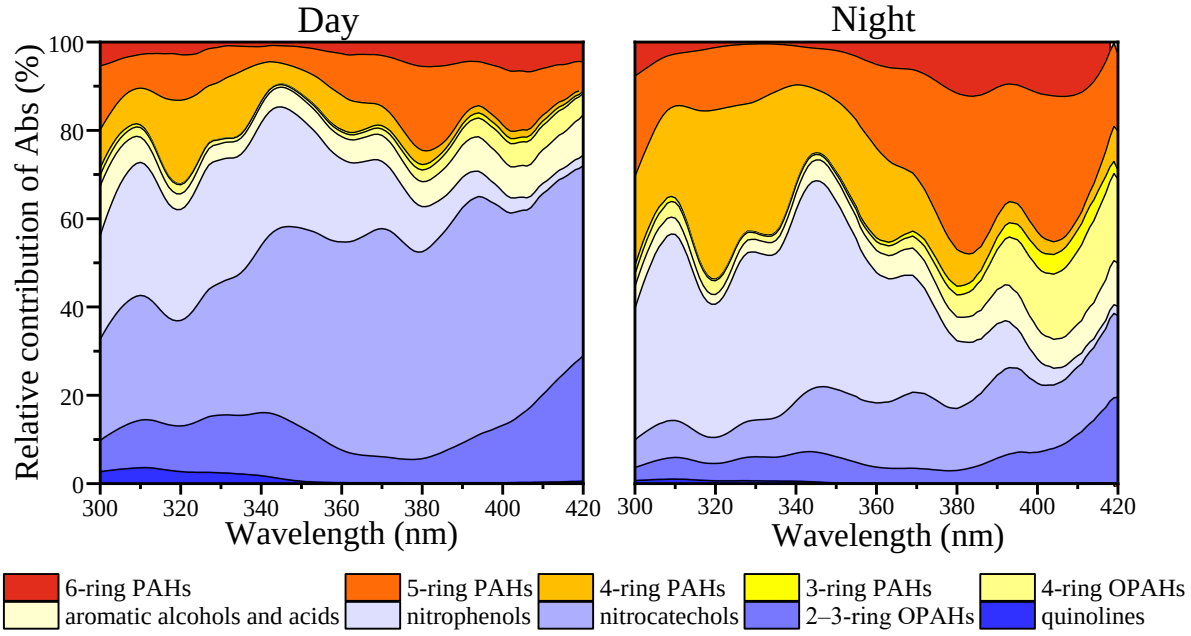


Figure S2. Relative contributions of light absorption of ten BrC subgroups during the day and night.

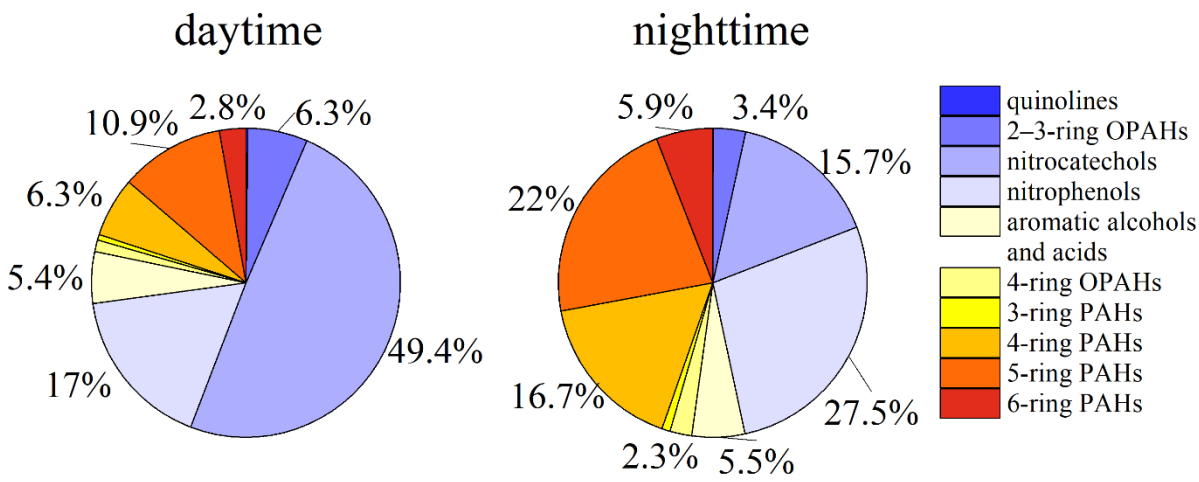


Figure S3. Light-absorbing contributions of ten BrC subgroups at 365nm in the daytime and nighttime.

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