Supporting Information

Where the river turns old: Urbanized deltas imprint a fossil signature on black carbon exported to the ocean

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Content: 22 pages, 6 texts, 7 tables, and 2 figures

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Supplementary Texts

Text S1. SPE-DOC extraction and carbon content measurements

DOC was isolated from water samples using solid phase extraction (SPE).[1] Briefly, prepacked SPE cartridges (Varian Bond Elut PPL cartridges, Agilent, the US) were conditioned with methanol and HCl (pH = 2). Filtered and acidified water samples were siphoned through the SPE cartridge with a cleaned PTFE (polytetrafluoroethylene) tube at a slow loading rate (<20 mL min^{-1}). This flow rate was monitored and maintained throughout the sample loading. After extraction, the cartridge sorbent was rinsed with two bed-volume of HCl (pH = 2) to remove salts, then the PPL cartridge was freeze-dried. Isolated DOC was eluted from the SPE cartridge with two bed-volume methanol. The methanol eluent was then condensed to ~5 mL via a rotary evaporator.

To determine the carbon content of SPE-DOC, an aliquot of the methanol eluent was transferred to a 20-mL glass bottle and dried under a stream of high-purity nitrogen gas at 40 ℃. The residue was redissolved in 10 mL ultrapure water (18.2 MΩ cm^{-1}, Sartorius), and the carbon content was quantified following the same method as DOC.

Text S2. Stable carbon ($\delta^{13}C$) and radiocarbon ($\delta^{14}C$) analysis of SPE-DOC and POC

The $\delta^{13}C$ of SPE-DOC and POC were determined by elemental analysis-isotope ratio mass spectrometry (EA-IRMS). The methanol eluent containing 20–40 μg C SPE-DOC was weighed into tin boats and evaporated to dryness in an oven at 60 ℃. Then the tin boats were folded and combusted using a Thermo Scientific Flash Elemental Analyser interfaced with a Thermo Scientific Delta V Plus IRMS. A two-point calibration was performed to calculate the $\delta^{13}C$ values using two international reference standards (USGS40, $\delta^{13}C$ = –26.39± 0.04‰; IAEA–CH–6, $\delta^{13}C$ = –10.45 ± 0.04‰)[2]. A working standard (Casein standard OAS, CatNo. B2155-Batch no. 2821, $\delta^{13}C$ = –26.98 ± 0.13‰, Elemental Microanalysis Ltd) was used for routine quality assurance. For POC analysis, the GF/F filters containing particulate material were treated with concentrated HCl (36%) vapor in a desiccator for at least 24 h to completely remove carbonates. After freeze-drying, organic matters were scraped off the filters, transferred into tin boats, and analyzed by EA-IRMS.

In similar procedures to $\delta^{13}C$ analysis, the SPE-DOC and POC samples were packed into the tin boats and combusted at 900 ℃ for 2.5 h to oxidize into CO_2, which was then reduced to graphite using hydrogen at 525 ℃ for 3 h over iron catalysts.[3] The graphite was pressed into aluminum targets for $\Delta^{14}C$ measurement with AMS at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences.[4]

Text S3. Parameter calculations for FT-ICR-MS

The modified aromatic index (AI_{mod}) is calculated using the equation:[5, 6]

$$AI_{mod} = (1 + c - 0.5o - s - 0.5h) / (c - 0.5o - s - n)$$

In order to consider the intensity of each formula and its contribution to the overall property, the intensity-weighted AI_{mod} ($AI_{mod\text{-}w}$) and elemental ratio ($H/C_{\text{-}w}$ and $O/C_{\text{-}w}$) were calculated based on the following equations. [7, 8]

$$AI_{mod\text{-}w} = \Sigma (In_i \times AI_{mod\ i}) / \Sigma In_i$$

$$H/C_{\text{-}w} = \Sigma (In_i \times H/C_i) / \Sigma In_i$$

$$O/C_{\text{-}w} = \Sigma (In_i \times O/C_i) / \Sigma In_i$$

Where $AI_{mod\ i}$, H/C_i, and O/C_i represent the AI_{mod}, H/C, and O/C of the individual molecular formula (i), respectively, In_i is the intensity for individual molecular formula (i), and i is the total number of identified molecular formulas in a given sample.

Text S4. Concentration measurements of DBC and PBC

Both DBC and PBC were determined using the BPCA method following our previous studies.[9-11] Briefly, SPE-DOC extracts (~500 mL water sample equivalents) were transferred into a 10 mL ampoule and dried at 40 ℃ under high-purity nitrogen blowing. Concentrated nitric acid (2 mL, 65%, p.a., Sigma Aldrich) was added to each ampule, then the ampules were flame-sealed and heated to 180 ℃ for 8 h. After oxidation, the solutions were dried under high-purity nitrogen at 50 °C. The BPCA-containing residue was re-dissolved in ultrapure water and filtered with a syringe filter (13 mm × 0.22 μm, PTFE, ANPEL Laboratory Technologies) for further analysis.

For PBC analysis, the GF/F filters containing particulate material were treated with concentrated HCl (36%) vapor in a desiccator for at least 24 h to completely remove carbonates. After freeze-drying, organic matters were scraped off the filters and transferred into a 10 mL ampoule. Concentrated nitric acid (2 mL) was added to each ampule. The ampoules were flame-sealed and heated to 180 ℃ for 8 h. After oxidation, the sample solutions were dried under a stream of high-purity nitrogen gas at 50 °C. The dried samples were re-dissolved in ultrapure water and passed through a glass column packed with cation exchange resin (Dowex 50 WX8 400, Sigma Aldrich) to remove extensive metal ions.[12-14] The eluate was freeze-dried and re-dissolved in ultrapure water, followed by filtration with a syringe filter (13 mm × 0.22 μm, PTFE, ANPEL Laboratory Technologies) for further analysis.

BPCAs were separated on an Agilent InfinityLab Poroshell 120 SB-C18 (4.6 × 100 mm, 2.7 μm, the US) column and quantified by a high-performance liquid

chromatography system equipped with a photodiode array detector (HPLC-PAD, Shimadzu, Japan). Mobile phase A was an aqueous solution prepared by mixing 20 mL of phosphoric acid (85%; Sigma-Aldrich) in 980 mL ultrapure water. HPLC-grade acetonitrile (Sigma-Aldrich) was used as mobile phase B. The mixing gradients of mobile phases A and B are shown in Table S2. The flow rate and column oven temperature were 0.4 mL min/L and 30 ℃, respectively. Peak identifications of BPCAs in samples were based on the retention times and absorbance spectra (190–400 nm). The intensities of BPCA peaks at a wavelength of 240 nm were used for quantification.

Seven BPCAs were quantified, including 1,2,3,4,5,6-benzenehexacarboxylic acid (B6CA), 1,2,3,4,5-benzenepentacarboxylic acid (B5CA), 1,2,4,5-benzenetetracarboxylic acid, 1,2,3,5-benzenetetracarboxylic acid, 1,2,3,4-benzenetetracarboxylic acid (B4CAs), 1,2,3-benzenetricarboxylic acid, and 1,2,4-benzenetricarboxylic acid (B3CAs). A conversion factor of 5.7 from BPCAs-C to PBC was used to calculate PBC concentrations based on our previous study.[9, 15, 16] DBC concentrations were calculated using the established relationship between DBC and BPCAs shown below.[17]

$$[PBC] = 5.7 \times ([B6CA] + [B5CA] + [B4CAs] + [B3CAs])$$

$$[DBC] = 33.4 \times ([B6CA] + [B5CA] + 0.5 \times [B4CAs] + 0.5 \times [B3CAs])$$

The units of PBC(DBC) and BPCA are μM-C and μM, respectively. It is worth noting that there are no two commercially available standards for 1,2,3,5-B4CA and 1,2,3,4-B4CA, these two B4CAs were quantified using the calibration curve of their isomer (i.e., 1,2,4,5-B4CA).

Text S5. Preparative high-performance liquid chromatography (prep-HPLC)

In a procedure similar to the concentration measurement, DBC and PBC samples were oxidized with concentrated nitric acid. After drying the oxidized solutions, the samples were re-dissolved in ultrapure water and passed through a cation exchange column (Dowex 50 WX8 400). The eluate was freeze-dried and re-dissolved in 0.38% TFA (mobile phase A of prep-HPLC), followed by filtration with a syringe filter (13 mm × 0.22 μm, PTFE). BPCAs were separated with an Agilent Poroshell 120 SB-C18 (4.6 × 150 mm, 2.7 μm, the US) column and collected by a preparative liquid chromatography using an HPLC system equipped with a photodiode array detector (prep-HPLC-PAD, LC-20AT/SPD-M20A, Shimadzu). Mobile phase A was prepared by mixing 3.8 mL trifluoroacetic acid (TFA) in 1 L ultrapure water (pH~1.3), acetonitrile was used as mobile phase B. The mixing gradients of mobile phases A and B are shown in Table S3. It took a total run time of 62.10 min. Flow rate and column oven temperature were 0.4 mL min^{-1} and 30 ℃. Individual BPCA was collected in a separate glass tube via a fraction collector (FRC-10A, Shimadzu). The collected fractions were put into 25-mL glass flasks and concentrated to ~1 mL using a rotary evaporator. They were then transferred to 1.5 mL glass vials and dried under high-purity nitrogen (99.999%) gas at 70 ℃ for 1 h. B4CA isomers were pooled together for subsequent isotopic analysis. B3CAs were not collected due to their low abundance.

Text S6. Stable carbon isotope analysis ($\delta^{13}C$) of DBC and PBC

The $\delta^{13}C$ measurements of BPCAs were performed on an UltiMate 3000 HPLC system connected to a Delta V Plus IRMS via an Isolink interface (HPLC-IRMS, Thermo Scientific). Before $\delta^{13}C$ analysis, the isolated BPCA was redissolved in 0.5 mL of ultrapure water and sonicated for 5 min to ensure complete dissolution. The HPLC-IRMS setup was as follows: Ultrapure water was used as the mobile phase at a flow rate of 200 μL/min. Online oxidation quantitatively converted individual BPCA to CO_2 in the Isolink oxidation chamber (98 ℃) by adding H_3PO_4 and oxidant ($Na_2S_2O_8$). The flow rates of acid and oxidant were optimized to yield an O_2 signal (m/z = 32) of 8–12 V to ensure full oxidation capacity. The derived CO_2 was then extracted from the mobile phase and dried prior to detection by IRMS.

The HPLC-IRMS system did not require an LC column because of the preliminary isolation of individual BPCA, which took only 6.5 min for each measurement run. A two-point calibration was performed to calculate the BPCA-$\delta^{13}C$ values with two international reference standards (USGS40, $\delta^{13}C$ =-26.39 ± 0.04‰; IAEA-CH-6, $\delta^{13}C$ =-10.45 ± 0.04‰). BPCA standards were analyzed daily before sample analysis to assess the stability of HPLC-IRMS.

Supplementary Tables

Table S1. Concentrations of DOC and POC, and $\delta^{13}C$-$\Delta^{14}C$ of SPE-DOC and POC along the urbanization gradient of the Liuxi River.

Sample ID	Dissolved Phase						Particulate Phase					
From upstream to downstream	DOC (μM-C)		$\delta^{13}C_{SPE\text{-}DOC}$ (‰)		$\Delta^{14}C_{SPE\text{-}DOC}$ (‰)		POC (μM-C)		$\delta^{13}C_{POC}$ (‰)		$\Delta^{14}C_{POC}$ (‰)	
	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season	Wet season	Dry season
1	50.60	44.17	-28.60	-29.05	-62.82	-90.98	77.33	16.62	-27.79	-28.59	-77.40	-236.25
2	52.77	45.56	-28.41	-28.87	-78.43	-114.76	40.44	12.34	-29.16	-27.04	-84.54	-218.85
3	64.97	51.38	-28.42	-28.77	-73.66	-94.72	441.39	36.80	-27.38	-27.07	-54.23	-144.09
4	76.42	56.67	-28.36	-28.27	-80.00	-124.34	166.63	62.17	-29.15	-27.06	-53.91	-198.39
5	88.06	65.56	-28.14	-28.07	-110.14	-122.83	137.56	175.85	-32.16	-26.89	-64.50	-164.83
6	111.11	68.61	-27.48	-28.06	-139.10	-159.49	192.88	28.54	-24.94	-27.84	-67.49	-200.85
7	123.06	88.33	-27.63	-27.85	-167.00	-186.42	272.58	35.55	-30.74	-28.12	-86.74	-246.64
8	154.17	122.50	-27.20	-27.38	-177.78	-205.77	255.69	138.65	-29.86	-27.55	-156.89	-274.13
Average	90.14 ± 36.66	67.85 ± 26.37	-28.03 ± 0.52	-28.29 ± 0.57	-111.12 ± 44.92	-137.41 ± 42.15	198.06 ± 126.59	63.32 ± 60.71	-28.90 ± 2.21	-27.52 ± 0.61	-80.71 ± 33.22	-210.51 ± 42.80

188 **Table S2. BPCAs Concentrations of DBC along the urbanization gradient of the Liuxi River.**

Sample ID From upper reaches to lower reaches	Wet season					Dry season				
	B3CAs (μg/L)	**B4CAs (μg/L)**	**B5CAs (μg/L)**	**B6CAs (μg/L)**	**DBC (μmol/L)**	**B3CAs (μg/L)**	**B4CAs (μg/L)**	**B5CAs (μg/L)**	**B6CAs (μg/L)**	**DBC (μmol/L)**
1	0.37	3.34	2.83	0.92	1.45	0.34	2.59	2.26	0.79	1.17
2	0.43	3.68	3.03	0.97	1.57	0.45	3.15	2.74	0.92	1.42
3	0.52	4.72	4.34	1.25	2.13	0.38	3.17	3.83	0.99	1.70
4	0.66	6.04	4.85	1.38	2.49	0.59	4.71	4.41	1.37	2.18
5	0.99	9.21	7.19	2.00	3.72	0.66	5.07	5.43	1.70	2.58
6	1.13	9.92	7.95	2.08	4.05	0.62	4.92	4.00	1.29	2.09
7	1.49	13.18	9.33	2.58	5.02	0.74	5.74	4.59	1.55	2.43
8	2.09	17.57	12.22	3.63	6.70	1.11	10.00	7.65	2.20	4.01
Average	0.96 ± 0.60	8.46 ± 5.03	6.47 ± 3.30	1.85 ± 0.93	3.39 ± 1.84	0.61 ± 0.25	4.92 ± 2.33	4.36 ± 1.67	1.35 ± 0.46	2.20 ± 0.88

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Table S3. BPCAs Concentrations of PBC along the urbanization gradient of the Liuxi River.

Sample ID From upper reaches to lower reaches	Wet season					Dry season				
	B3CAs (μg/L)	B4CAs (μg/L)	B5CAs (μg/L)	B6CAs (μg/L)	PBC (μmol/L)	B3CAs (μg/L)	B4CAs (μg/L)	B5CAs (μg/L)	B6CAs (μg/L)	PBC (μmol/L)
1	0.57	6.19	7.41	8.47	10.75	0.07	0.73	0.78	0.92	1.18
2	0.19	1.65	2.11	2.26	2.94	0.05	0.48	0.56	0.81	0.90
3	2.70	24.00	26.85	25.87	37.72	0.15	1.94	2.83	2.08	3.32
4	0.80	3.55	3.39	3.09	5.15	0.19	2.80	3.60	3.37	4.73
5	0.76	1.89	1.67	1.54	2.78	0.78	10.98	11.79	13.27	17.49
6	0.74	1.29	0.94	0.97	1.87	0.10	1.20	1.50	1.53	2.05
7	1.11	1.71	1.21	1.27	2.51	0.13	1.60	1.80	2.03	2.64
8	1.63	10.66	8.58	9.84	14.58	0.79	11.94	10.32	16.05	18.58
Average	1.06 ± 0.78	6.37 ± 7.81	6.52 ± 8.71	6.66 ± 8.47	9.79 ± 12.17	0.28 ± 0.31	3.96 ± 4.69	4.15 ± 4.40	5.01 ± 6.06	6.36 ± 7.31

Table S4. Dual-carbon isotopic compositions (Δ14C-δ13C) and 14C ages of DBC and PBC at the forest and urban sites.

Compounds		DBC						PBC					
		Wet Season		Dry Season		Mix Season		Wet Season		Dry Season		Mix Season	
		Forest site	Urban site	Forest site	Urban site	Forest site	Urban site	Forest site	Urban site	Forest site	Urban site	Forest site	Urban site
$\delta^{13}C$ (‰)	B6CA	-29.26 ± 0.39	-27.56 ± 0.40	-29.41 ± 0.39	-27.31 ± 0.40	-29.47 ± 0.42	-27.96 ± 0.39	-25.73 ± 0.39	-21.02 ± 0.39	-29.12 ± 0.45	-24.70 ± 0.39	-24.95 ± 0.39	-22.67 ± 0.41
	B5CA	-29.33 ± 0.22	-27.72 ± 0.24	-27.11 ± 0.23	-27.43 ± 0.27	-28.52 ± 0.23	-27.72 ± 0.22	-25.80 ± 0.22	-21.93 ± 0.23	-26.14 ± 0.23	-22.36 ± 0.23	-24.84 ± 0.22	-23.20 ± 0.22
	B4CAs	-28.51 ± 0.18	-27.50 ± 0.21	-28.91 ± 0.18	-27.47 ± 0.23	-29.07 ± 0.18	-27.73 ± 0.18	-27.70 ± 0.19	-23.46 ± 0.18	-30.45 ± 0.18	-25.12 ± 0.19	-26.05 ± 0.18	-25.70 ± 0.18
	$\delta^{13}C_{BC}$ [a]	**-28.92 ± 0.49**	**-27.60 ± 0.52**	**-28.26 ± 0.49**	**-27.44 ± 0.53**	**-28.90 ± 0.51**	**-27.75 ± 0.49**	**-26.36 ± 0.49**	**-22.16 ± 0.49**	**-28.59 ± 0.54**	**-24.23 ± 0.49**	**-25.24 ± 0.49**	**-24.04 ± 0.50**
$\Delta^{14}C$ (‰)	B6CA	-2.0 ± 14.8	-182.9 ± 6.9	-12.3 ± 21.2	-220.7 ± 8.2	-5.1 ±15.2	-152.7 ± 8.4	-172.8 ± 17.6	-362.5 ± 13.2	-345.6 ± 52.8	-599.3 ± 11.8	-98.6 ± 17.3	-354.9 ± 35.9
	B5CA	-36.0 ± 12.1	-134.5 ± 3.6	-4.9 ± 16.7	-163.0 ± 4.1	-2.6 ± 11.2	-121.8 ± 3.4	-44.8 ± 29.1	-187.1 ± 34.7	n.d.	-294.3 ± 96.3	3.5 ± 51.5	-190.7 ± 143.4
	B4CAs	-65.7 ± 12.0	-282.8 ± 2.7	-71.7 ± 14.5	-312.2 ± 2.8	-38.9 ± 11.0	-239.9 ± 3.1	-177.8 ± 55.1	-320.5 ± 36.1	-145.5 ± 126.8	-392.3 ± 63.2	-66.1 ± 48.4	-329.8 ± 119.6
	$\Delta^{14}C_{BC}$ [a]	**-46.7 ± 7.8**	**-210.9 ± 2.1**	**-39.3 ± 10.1**	**-245.8 ± 2.3**	**-20.2 ± 7.2**	**-182.7 ± 2.2**	**-134.5 ± 20.4**	**-290.4 ± 17.5**	**-245.5 ± 68.7**	**-418.3 ± 39.9**	**-54.5 ± 23.5**	**-292.1 ± 67.0**
	^{14}C ages	**386 ± 71**	**1934 ± 22**	**328 ± 87**	**2300 ± 25**	**166 ± 65**	**1641 ± 24**	**1177 ± 197**	**2796 ± 196**	**2334 ± 683**	**5211 ± 543**	**467 ± 198**	**2811 ± 745**

[a] $\delta^{13}C_{BC}$ and $\Delta^{14}C_{BC}$ were calculated based on mass balance using the abundances and $\delta^{13}C$ and $\Delta^{14}C$ values of individual BPCAs.

n.d.: No $\Delta^{14}C$ data was reported for dry-season PBC because the B5CA yield was insufficient for reliable $\Delta^{14}C$ measurement.

Table S5. Information on eight sampling sites during the first sampling campaign.

Sample ID From upstream to downstream	**Longitude (°E)**	**Latitude (°N)**
1	113.72	23.72
2	113.66	23.66
3	113.60	23.55
4	113.52	23.49
5	113.44	23.42
6	113.35	23.41
7	113.30	23.34
8	113.20	23.25

Table S6. Binary gradient of HPLC method for BPCA quantification. (Mobile phase A: 2% H_3PO_4 in ultrapure water; Mobile phase B: 100% acetonitrile. Flow rate = 0.4 mL/min)

Time (min)	Mobile phase B (vol %)
0	0.5
5	0.5
25.9	30
26	95
28	95
28.1	0.5
30	0.5
50.5	0.5

Table S7. Binary gradient of preparative high-performance liquid chromatography (prep-HPLC). (Mobile phase A: 0.38% TFA in ultrapure water; Mobile phase B: 100% acetonitrile. Flow rate = 0.4 mL/min)

Time (min)	Mobile phase B (vol %)
0	0.5
5	0.5
18	20
37.9	30
38	95
40	95
40.1	0.5
62.01	0.5

Supplementary Figures

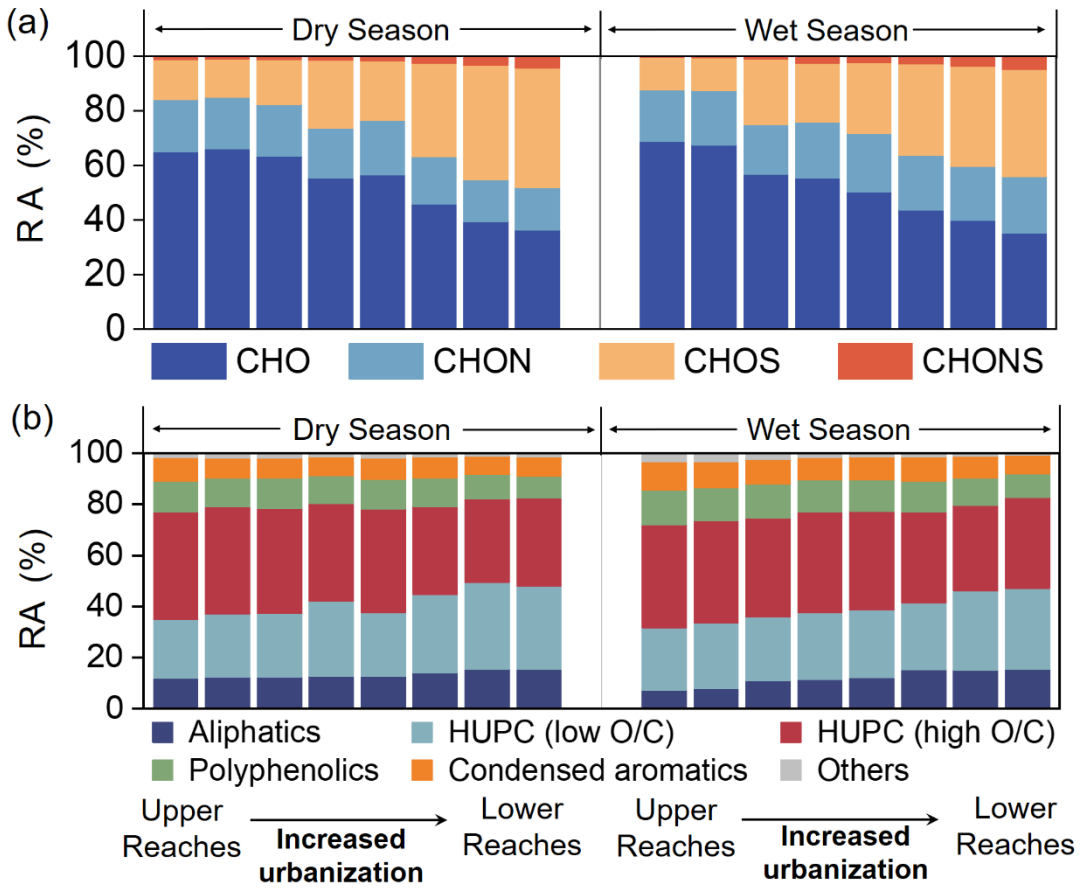
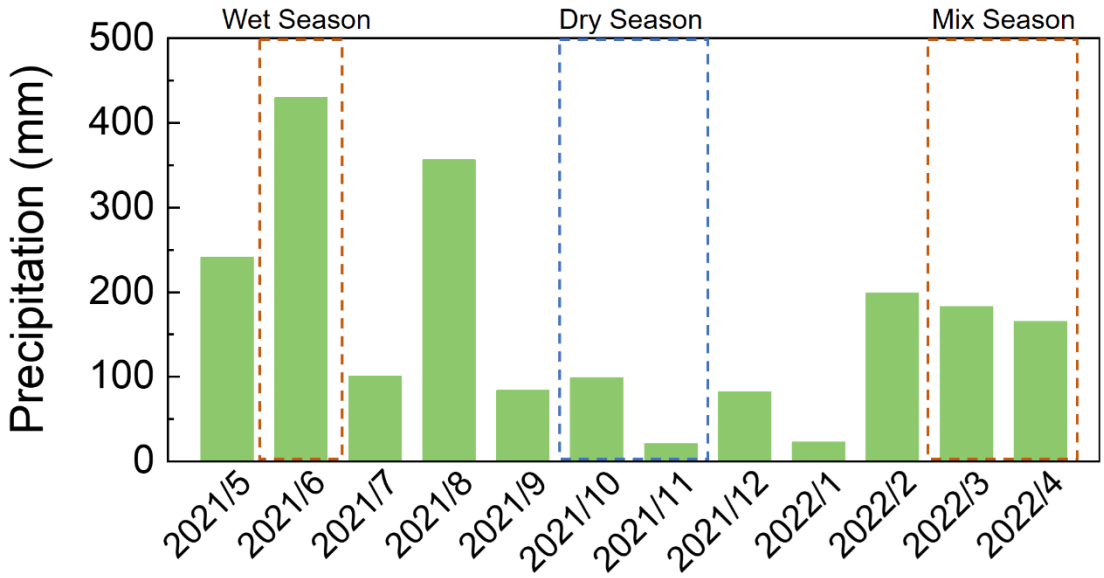


Figure S1. DOM molecular compositions along the urbanization gradient of the Liuxi River. (a) The relative abundance (RA) of CHO-, CHON-, CHOS- and CHONS-containing formulae. (b) The relative abundance (RA) of four groups of compounds, including aliphatic compounds, highly unsaturated and phenolic compounds (HUPs) (low oxygen), HUPs (high oxygen), polyphenolic compounds, and condensed aromatic compounds.



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215 **Figure S2.** Monthly precipitation during the second sampling campaign (May 2021 to

216 April 2022) of Guangzhou (Baiyun International Station, 23.39°N, 113.30°E). The data

217 were obtained from https://www.ncei.noaa.gov/maps/daily/.

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