Supporting Information for

Refractory Humic-like Substances: Tracking Environmental Impacts of Anthropogenic Groundwater Recharge

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Text S1. Sample Collection and Pretreatment

The study area is located in the Chaobai River Basin in Beijing, China, which belongs to the piedmont alluvial fan area. Most riverbed is dry except the reaches with reclaimed water recharged. The reaches with water are from S1 to DZ1 and from 15 to S5 in Figure 1A. The water from South-to-North Water Diversion Project is directly recharged at the sampling site S10. The stratigraphic structure is single, mainly gravel layer, and the surface lithologic particles are coarse with strong permeability, providing a recharge path. The reclaimed water from wastewater treatment plants have recharged this areas since 2008 and even deep groundwater (~ 130 m) was affected in 2010[1]. And all of the shallow groundwater was mixed by the reclaimed water with mixing proportion of 42% to 80% in dry season[2]. Since 2015, clean water from the South-to-North Water Diversion Project was intentionally recharged into the groundwater to control the pollution caused by reclaimed water. According to the location affected by different recharge sources and the anthropogenic recharge history, the study area was divided into reclaimed water recharge area (RWRA) and intentional South-to-North water recharge area (SNWRA). The water level of SNWRA area is the lowest, and its upstream and downstream are RWRA affected areas. The water source (S1, S7, and, S9 in Figure 1) of RWRA is the reclaimed water treated by sewage treatment plant since 2008, and the water source (S10 in Figure 1) of SNWRA area is clean water transferred through South-to-North Water Diversion Project since 2015. The annual average recharge contribution of reclaimed water and the water transferred through South-to-North Water Diversion Project is 1:2.

Fifty-seven groundwater and ten surface water samples were collected in Chaobai River Basin, Beijing, China from May 7th to May 13th, 2019 (Figure 1A). The surface water was collected by vertical water sampler, and the groundwater was collected by using GRUNDFOS submersible pump (SQ2-70, Denmark). They are divided into four groups: nine surface water samples contained the reclaimed samples from the wastewater water treatment plants in Shunyi (S9), Huairou (S7) , Miyun (S1) and thirty groundwater samples in RWRA, one surface water samples which is the discharge point of the water transferred through South-to-North Water Diversion Project and twenty-seven groundwater samples in SNWRA. The pH, water temperature, dissolved oxygen (DO), salinity, oxidation-reduction potential (Eh) and electronic conductivity (EC) of water samples were measured on site by a multi parameter analyzer (HI9828， HANNA, Italy). Physicochemical parameters of groundwater and surface water qualities in RWRA and SNWRA were tested in laboratory. On the same day, the water samples were filtered through 0.7 μm Micro-Quartz Fiber filter (Munktell, Sweden), which were pre-baked at 450 °C for 6 hours. Micro-Quartz filter were stored in a desiccator and the filtrate was stored at 4 ℃ until chemical extraction and spectral measurements, which were used for POM and DOM analysis in laboratory, respectively.

Text S2. Sample Analysis

Dissolved organic carbon (DOC) and absorption and fluorescent spectra of filtrate were measured for DOM samples[3]. The POM was extracted by alkaline solution: the Micro-Quartz filter was cut into pieces and extracted by 20 mL of 0.1 N NaOH at 4 °C for 24 h in the dark; after neutralization to a pH (> 6) with 1N HCl, which is close to that of the original sample, the extracted solution was subsequently filtered through a 0.22 μm polyethersulfone membrane. The POC and absorption and fluorescent spectra of the filtrate were measured for POM[4].

DOC and POC were determined by TOC analyzer (OI Aurora 1030w, U.S.A) with the detection limit of 0.01 mg/L. The anions (Cl^-, NO_3^-, NO_2^-, and SO_4^{2-}) and cations (Ca^{2+}, Mg^{2+}, and NH_4^+) in filtered water were determined by the Swiss Metrohm ECO IC ion chromatograph, and the chemical oxygen demand (COD_{Mn}), the total nitrogen (TN), and total phosphorus (TP) were measured by a spectrophotometer (Shimadzu UV-1800, Japan). COD_{Mn} was determined at the absorbance of 525 nm by digestion with potassium permanganate and sulfuric acid (GB11892-1989). Total nitrogen was determined at the absorbance of 220 nm and 275 nm by digestion with basic potassium persulfate (GB/T11894-1989). Total phosphorus was determined at the absorbance was 700 nm by digestion with potassium persulfate digestion and visualization with ascorbic acid solution and ammonium molybdate solution (GB/T11893-1989). The operation condition for fluorescence spectrometer (Fluoromax-4, HORIBA JboinYvon, France) was as follows: the light source was 150W xenon lamp. Excitation (Ex) wavelengths were from 250 to 400 nm at 4 nm intervals; emission (Em) wavelengths were from 300 to 500 nm at 2 nm intervals. The width of the slit was 3 nm and the integration time of the scanning signal was 0.1s. UV-vis absorbance was measured by the spectrophotometer (UV8100, LabTech Ltd., China) at 250 – 550 nm.

Text S3. Data Handling

The humification degree of organic matter was estimated by the humification index (HIX), which is the ratio of domain integral of the fluorescence intensities at Em of 434 – 480 nm to that at Em of 300 – 345 nm with an Ex of 254 nm[5]. The biological index (BIX), the ratio of fluorescence intensity at Ex/Em 310/380 nm to that at Ex/Em 310/430 nm, typically indicates microbial sources of the organic matter[6]. Alternatively, the fluorescence index (FI), the ratio of fluorescence intensity at Ex/Em 370/470 nm to that at Ex/Em 370/500 nm, has widely used to identify the source of NOM[7]. The concentration of OM with unsaturated structure (a_{254}) is generally evaluated by the absorption coefficient at 254 nm. The aromaticity index ($SUVA_{254}$) is the ratio of absorbance at 254 nm to TOC, reflecting the proportion of aromatic structure in NOM[8]. The spectral slope $S_{275\text{-}295}$ calculated by fitting an exponential model, which denotes the relative molecular weight[9]. The larger $S_{275\text{-}295}$ values indicates the smaller molecular weight.

Table S1 Concentrations and characteristics of DOM, POM, and DOM/POM ratio of surface water and groundwater in RWRA and SNWRA

	TOC (mg C/L)	a254 (m^{-1})	BIX	HIX	FI	$SUVA_{254}$	$S_{275-295}$	C1 (10^{-3} R.U.)	C2 (10^{-3} R.U.)	C3 (10^{-3} R.U.)	C4 (10^{-3} R.U.)
DOM											
RWRA Groundwater	1.31±0.67	6.34±3.41	0.88±0.15	3.41±1.97	1.40±0.09	2.25±1.28	14.35±7.36	53.0±7.46	26.0±11.8	22.0±12.4	20.4±3.38
	0.98 (0.65-2.89)	5.82 (2.26-14.09)	0.85 (0.57-1.34)	3.15 (1.15-11.94)	1.37 (1.22-1.60)	1.97 (0.90-8.09)	15.46 (2.56-33.20)	53.8 (35.7-66.3)	25.0 (5.38-63.6)	18.7 (3.73-58.6)	20.7 (11.7-28.5)
RWRA Surface water	5.92±1.42	26.01±7.34	0.94±0.06	2.97±1.24	1.37±0.09	1.96±0.48	15.74±3.80	58.5±8.70	26.4±15.4	28.6±9.60	27.0±2.03
	5.56 (3.51-7.89)	25.84 (14.30-37.26)	0.94 (0.86-1.02)	2.84 (1.60-4.97)	1.36 (1.24-1.48)	1.98 (0.81-2.49)	14.93 (11.12-24.33)	55.1 (48.5-71.5)	20.5 (5.00-45.3)	28.6 (16.3-44.9)	27.5 (24.3-31.3)
SNWRA Groundwater	0.73±0.22	2.94±1.28	0.92±0.08	3.23±1.60	1.47±0.08	1.72±0.50	13.20±7.05	38.7±8.22	22.1±10.0	14.1±3.44	16.9±2.31
	0.70 (0.49-1.18)	2.67 (1.13-6.26)	0.92 (0.77-1.14)	2.69 (1.41-7.07)	1.47 (1.37-1.66)	1.69 (1.01-3.73)	11.93 (4.11-40.88)	37.2 (28.5-56.9)	22.7 (6.50-44.0)	13.7 (7.60-22.1)	16.7 (12.7-20.7)
SNWRA Surface water	2.93	11.05	0.79	2.26	1.06	1.64	20.16	67.4	45	33.4	21.5
POM											
RWRA Groundwater	0.49±0.64	0.87±0.76	1.04±0.35	1.66±1.35	1.25±0.13	2.04±1.06	39.70±12.89	2.11±0.81	3.96±1.88	1.94±0.80	1.38±0.92
	0.17 (0.07-2.37)	0.57 (0.21-3.51)	0.97 (0.49-1.93)	1.43 (0.43-6.24)	1.22 (1.05-1.63)	1.94 (0.46-4.10)	38.08 (14.76-76.58)	1.84 (1.07-3.76)	3.35 (0.94-7.53)	1.73 (0.32-3.68)	1.10 (0.58-4.23)
RWRA Surface water	0.39±0.24	1.36±1.32	1.14±0.2	1.51±0.76	1.25±0.14	2.04±3.15	34.50±5.86	2.63±0.73	3.18±0.66	4.23±2.80	1.33±0.31
	0.36 (0.15-0.82)	1.18 (0.25-4.63)	1.14 (0.91-1.61)	1.45 (0.98-3.41)	1.32 (1.05-1.40)	1.10 (0.66-10.41)	37.76 (23.88-40.92)	2.92 (1.67-3.82)	3.06 (2.06-4.20)	2.91 (1.24-9.09)	1.28 (0.70-1.66)
SNWRA Groundwater	0.72±1.29	0.48±0.25	1.05±0.25	0.76±0.32	1.25±0.17	2.00±0.98	43.03±18.43	1.68±0.47	5.24±1.07	2.10±0.87	0.99±0.32
	0.11 (0.07-4.18)	0.47 (0.12-1.00)	1.05 (0.68-1.96)	0.65 (0.41-1.80)	1.25 (0.87-1.59)	2.00 (0.54-3.97)	40.05 (23.03-124.48)	1.52 (0.96-2.61)	5.33 (3.07-7.27)	1.98 (0.94-5.11)	0.97 (0.48-1.68)
SNWRA Surface water	0.04	0.27	0.99	0.43	1.31	0.83	29.69	1.47	7.73	2.89	0.63
DOM/POM											
RWRA Groundwater	7.0±5.0	9.6±6.2	0.9±0.3	3.0±2.0	1.1±0.1	1.6±1.3	0.4±0.3	27.8±8.4	7.8±4.6	12.9±9.0	18.6±7.5
	6.9 (0.3-21.5)	6.6 (3.8-31.2)	0.9 (0.4-1.6)	2.3 (0.6-9.0)	1.1 (1.0-1.3)	0.9 (0.3-5.1)	0.3 (0.1-1.6)	26.2 (16.8-47.1)	7.0 (1.9-22.2)	12.3 (2.5-52.8)	18.8 (5.1-32.2)
RWRA Surface water	20.3±12.1	39.7±42.5	0.8±0.1	2.3±1.3	1.1±0.1	1.9±1.1	0.5±0.1	23.8±7.2	9.0±6.3	9.0±4.6	22.0±8.9
	16.8 (7.4-40.9)	23.8 (7.8-136.7)	0.8 (0.6-1.0)	2.6 (0.0-4.6)	1.1 (0.9-1.3)	1.7 (0.2-3.6)	0.4 (0.3-0.7)	21.3 (17.2-37.6)	7.3 (1.3-21.7)	8.2 (3.2-15.8)	19.3 (16.4-44.8)
SNWRA Groundwater	5.3±4.0	8.0±5.3	0.9±0.2	4.6±2.6	1.2±0.2	1.1±0.7	0.3±0.2	24.5±7.1	4.4±2.1	7.8±4.1	19.2±7.3
	5.5 (1.1-14.7)	6.7 (1.8-24.1)	0.9 (0.5-1.6)	3.8 (1.3-11.5)	1.2 (1.0-1.8)	1.0 (0.4-3.2)	0.3 (0.1-1.0)	23.0 (11.1-27.9)	4.0 (1.1-8.7)	6.7 (3.6-20.4)	17.1 (9.1-36.1)
SNWRA Surface water	20.7	40.9	0.8	5.2	0.8	2.0	0.7	67.4	5.6	11.1	21.5

Notes: The concentrations and characteristics are statistically presented as mean ± standard deviation, median, and ranges in brackets.

Table S2 Physicochemical parameters of groundwater and surface water qualities in RWRA and SNWRA

	RWRA		SNWRA	
	Groundwater	Surface water	Groundwater	Surface water
Ca^{2+} (mg/L)	49.75 (4.29 - 101)	28.90 (13.80 - 52.20)	66.9 (14.30 - 98.30)	n. a.
Mg^{2+} (mg/L)	22.80 (11.20 - 35.60)	18.30 (16.60 - 21.80)	26.8 (9.70 - 37.70)	n. a.
NH_4^+ (mg/L)	0.21 (0.01 - 5.72)	0.19 (0.06 - 0.71)	0.01 (0.01 - 0.10)	0.13
Cl^- (mg/L)	71.65 (3.70 - 120)	122 (89.8 - 162)	35.10 (12.30 - 88.70)	5.90
NO_3^- (mg/L)	0.06 (0.002 - 18.80)	4.44 (0.34 - 16.20)	1.70 (0.002 - 5.47)	0.23
NO_2^- (mg/L)	0.01 (0 - 0.28)	0.20 (0.01 - 0.92)	0.001 (0 - 0.20)	0.03
SO_4^{2-} (mg/L)	33.1 (0.18 - 109)	75.9 (66.20 - 119)	46.70 (14.60 - 99.30)	27.40
pH (mg/L)	8.04 (7.32 - 8.76)	8.49 (8.26 - 8.86)	7.92 (7.33 - 8.28)	8.47
DO (mg/L)	2.54 (0.36 - 4.49)	10.26 (7.40 - 11.13)	3.33 (1.24 - 7.09)	8.80
TP (mg/L)	0.03 (0.01 - 0.11)	0.03 (0.01 - 0.66)	0.04 (0.02 - 0.06)	0.03
TN (mg/L)	2.31 (0.20 - 20.40)	6.91 (2.47 - 17.10)	2.22 (0.06 - 6.03)	0.72
COD (mg/L)	1.79 (0.25 - 5.16)	5.74 (4.50 - 9.70)	0.9 (0.25 - 2.07)	1.75
Hardness (mg/L)	200.5 (65.40 - 395)	178 (106 - 349)	294 (83 - 376)	129

Note: The concentrations are statistically presented as median and ranges in brackets

Table S3 Coble fluorescence component average values (FRI method) of groundwater samples from RWRA and SNWRA

	sample	T	A	M	C
DOM	RWRA	7.74	20.53	2.19	7.74
	SNWRA	5.71	15.58	1.71	5.77
POM	RWRA	0.61	0.94	0.14	0.31
	SNWRA	0.62	0.80	0.11	0.22

Notes: The FRI is calculated by a self-developed EFC software, following the methods proposed by Chen et al. (2003)[10].

Table S4 Comparison of excitation/emission peak maxima and the median of $\%F_{max}$ in POM and DOM fluorescence combined with DOM−POM PARAFAC model components

Components	Ex (nm)	Em (nm)	DOM (%)	POM (%)	Assignment corresponding to previous studies
C1	<240	460	42.4	18.2	Terrestrial or ubiquitous diagenetic mixture of fulvic-like and humic-like components[11]; allochthonous[12]; resembles a mixture of Coble A and C peaks[13]
C2	278	308	20.3	46.6	UVB protein-like[14], tyrosine-like component, associated with microbial activity[15] and often appears in the fluorescence signals of domestic sewage
C3	280	350	16.6	20.2	Coble T[16], tryptophan-like which could originate from both autochthonous production (algal bloom) and sewage[17]
C4	320	395	18.1	11.8	soluble microbial product-like, similar to Coble M[18]; dominating the fluorescence of wastewater DOM[14]; low molecular weight[19]

Table S5 Spearman correlation analysis of fluorescence components, spectral indexes and water quality parameters

Spearman	$C1_d$	$C2_d$	$C3_d$	$C4_d$	$C1_p$	$C2_p$	$C3_p$	$C4_p$	$SUVA_{254d}$	$S_{275-295d}$	FI_d	HIX_d	BIX_d	$a254_d$	DOC	$SUVA_{254p}$	$S_{275-295p}$	FI_p	HIX_p	BIX_p	$a254_p$	POC	DO	TP	TN	NH_4^+	NO_3^-	NO_2^-	Cl^-	SO_4^{2-}	pH	COD_{Mn}
$C1_d$	1																															
$C2_d$	-.185	1																														
$C3_d$	.165	.571**	1																													
$C4_d$	.661**	-.152	.492**	1																												
$C1_p$	.560**	-.200	.095	.370**	1																											
$C2_p$	-.478**	.185	-.206	-.439**	-.634**	1																										
$C3_p$	.024	.279*	.339**	.264*	-.121	.202	1																									
$C4_p$	.137	.175	.439**	.291*	.288*	-.426**	.183	1																								
$SUVA_{254d}$	.417**	-.155	-.090	.282*	.139	-.078	-.115	.048	1																							
$S_{275-295d}$	.237	.135	.464**	.358**	.276*	-.301*	.054	.176	-.420**	1																						
FI_d	-.585**	-.068	-.306*	-.371**	-.407**	.431**	-.085	-.202	-.040	-.310*	1																					
HIX_d	.435**	-.911**	-.567**	.202	.234	-.173	-.288*	-.203	.330**	-.217	-.058	1																				
BIX_d	-.518**	.306*	.474**	.073	-.365**	.115	.313*	.297*	-.299*	.162	.271*	-.529**	1																			
$a254_d$	.817**	-.184	.232	.794**	.482**	-.452**	.065	.198	.590**	.114	-.429**	.338**	-.278*	1																		
DOC	.775**	-.253*	.273*	.830**	.464**	-.480**	.086	.145	.239	.277*	-.427**	.359**	-.236	.873**	1																	
$SUVA_{254p}$	-.047	-.163	-.201	-.224	.309*	-.157	-.355**	-.134	-.026	-.047	-.147	.124	-.259	-.074	-.086	1																
$S_{275-295p}$	-.146	-.116	-.169	-.278*	-.040	-.132	-.078	.139	-.091	-.093	-.069	.043	-.060	-.178	-.173	.204	1															
FI_p	-.107	.018	.005	.069	-.490**	.360**	.343**	.006	-.055	-.131	.303*	-.005	.219	-.058	-.017	-.378**	.066	1														
HIX_p	.552**	-.221	.167	.420**	.821**	-.897**	-.290*	.460**	.116	.309*	-.448**	.251*	-.286*	.473**	.480**	.196	.131	-.388**	1													
BIX_p	-.152	.290*	.386**	.170	-.430**	.132	.657**	.343**	-.120	.055	.124	-.323**	.487**	-.099	-.063	-.551**	.054	.450**	-.280*	1												
$a254_p$	.480**	-.125	.171	.378**	.794**	-.627**	-.041	.366**	.043	.262*	-.454**	.148	-.265*	.466**	.472**	.390**	.136	-.359**	.744**	-.319**	1											
POC	.217	.098	.267*	.359**	.235	-.222	.445**	.438**	.083	.155	-.259*	-.067	.146	.223	.180	-.416**	.043	.123	.262*	.417**	.292*	1										
DO	.045	.130	.209	.098	.217	-.111	.074	.033	-.150	.186	-.089	-.170	.160	.179	.231	-.032	-.150	-.101	.049	-.064	.147	-.032	1									
TP	.174	.007	-.030	.090	.127	-.007	.138	-.015	.072	-.056	-.048	.014	-.108	.257*	.303*	-.203	-.085	-.017	-.020	.087	.000	-.134	.480**	1								
TN	-.137	-.168	-.339**	-.067	-.236	.331**	-.134	-.306*	.239	-.396**	.341**	.228	-.079	-.061	-.102	-.032	-.151	.167	-.278*	-.135	-.293*	-.109	-.303*	-.229	1							
NH_4^+	.555**	.054	.429**	.635**	.327**	-.295*	.140	.130	.383**	.129	-.391**	.073	-.154	.537**	.496**	-.123	-.280*	-.113	.298*	-.081	.279*	.261*	-.084	-.014	.126	1						
NO_3^-	-.028	-.183	-.208	.123	-.157	.346**	.104	-.225	.307*	-.433**	.419**	.199	.089	.195	.176	-.298*	-.292*	.170	-.349**	.076	-.222	-.090	.200	.395**	.460**	-.052	1					
NO_2^-	.687**	-.145	.272*	.681**	.460**	-.385**	.090	.065	.397**	.107	-.454**	.261*	-.209	.712**	.652**	.017	-.138	-.097	.401**	-.217	.451**	.258*	.079	.093	.058	.789**	.101	1				
Cl^-	.536**	-.160	.250*	.755**	.276*	-.406**	.148	.278*	.405**	.047	-.116	.215	-.004	.794**	.754**	-.135	-.195	.124	.364**	.118	.368**	.173	.122	.121	.000	.382**	.287*	.529**	1			
SO_4^{2-}	.108	-.119	-.146	.194	-.143	.263*	.120	-.202	.328**	-.330**	.292*	.194	.019	.300*	.265*	-.157	-.142	.293*	-.257*	.174	-.153	-.031	.048	.164	.374**	-.042	.718**	.125	.481**	1		
pH	.280*	.224	.508**	.372**	.334**	-.531**	.173	.425**	.016	.399**	-.447**	-.272*	.182	.318**	.265*	-.104	-.006	-.133	.425**	.176	.266*	.276*	.399**	.210	-.576**	.284*	-.367**	.271*	.136	-.410**	1	
COD_{Mn}	.712**	-.195	.261*	.832**	.416**	-.470**	.151	.254*	.434**	.180	-.347**	.285*	-.154	.926**	.867**	-.118	-.197	.009	.447**	.016	.476**	.243*	.113	.170	-.026	.527**	.204	.681**	.890**	.335**	.265*	1

*. At the 0.05 level (two-tailed), there was a significant correlation.

**. At the 0.01 level (two-tailed), there was a significant correlation.

Table S6 Total variance of interpretation of six factors in principal component analysis

Factors	Initial eigenvalue		
	Total	% of variance	Cumulative variance (%)
1	6.69	29.07	29.07
2	4.08	17.75	46.81
3	2.46	10.71	57.53
4	1.88	8.18	65.71
5	1.63	7.10	72.81
6	1.15	5.01	77.82

Table S7 Component matrix of six factors in terms of PARAFAC components, traditional spectral indicators and water quality indicators based on DOM and POM

	Factors					
	1	2	3	4	5	6
$C1_d$	0.674	-0.400	0.035	0.272	0.011	-0.449
$C2_d$	0.059	0.655	-0.442	0.125	-0.323	-0.079
$C3_d$	0.513	0.602	-0.333	0.276	-0.147	-0.095
$C4_d$	0.836	0.005	0.283	0.267	0.035	0.044
$C1_p$	0.622	-0.550	-0.297	-0.012	-0.081	0.130
$C2_p$	-0.605	0.416	0.431	-0.045	-0.317	-0.235
$C3_p$	0.529	0.494	0.312	-0.152	-0.114	-0.152
$C4_p$	0.270	0.275	-0.307	0.239	0.739	0.025
FI_d	-0.490	0.103	0.428	0.008	0.214	0.583
HIX_d	-0.008	-0.693	0.274	-0.008	0.214	-0.206
BIX_d	0.063	0.676	-0.112	0.034	-0.064	0.426
FI_p	-0.142	0.343	0.513	0.285	0.310	-0.312
HIX_p	0.485	-0.578	-0.456	0.209	0.108	0.111
BIX_p	0.102	0.740	0.033	0.173	0.518	-0.179
DO	0.679	0.181	0.202	-0.510	-0.150	0.009
TN	-0.157	-0.057	0.497	0.638	-0.231	0.142
TP	0.714	0.172	0.297	-0.417	-0.081	-0.117
$a254_d$	0.875	-0.041	0.306	-0.107	-0.086	0.116
$a254_p$	-0.304	-0.461	0.049	0.081	-0.103	-0.095
pH	0.669	0.284	-0.343	-0.223	0.086	0.005
Cl^-	0.716	-0.088	0.385	0.281	0.125	0.210
COD_{Mn}	0.894	-0.085	0.308	0.054	-0.065	0.180
NH_4^+	0.196	0.112	-0.183	0.644	-0.489	0.003

Table S8 Concentrations and characteristics of DOM and POM in groundwater at different depths in RWRA and SNWRA

	DOM						POM					
	C1d(R.U.)10^{-3}	C2d(R.U.) 10^{-3}	C3d(R.U.) 10^{-3}	C4d(R.U.) 10^{-3}	DOC(mg C/L)	a254d(m-1)	C1p(R.U.) 10^{-3}	C2p(R.U.) 10^{-3}	C3p(R.U.) 10^{-3}	C4p(R.U.) 10^{-3}	POC(mg C/L)	a254p(m-1)
RWRA												
0m	58.5±8.70	26.4±15.4	28.6±9.60	27.0±2.03	5.92±1.42	26.01±7.34	2.63±0.73	3.18±0.66	4.23±2.80	1.33±0.31	0.39±0.24	1.36±1.32
	55.1 (48.5-71.5)	20.5 (5.00-45.3)	28.6 (16.3-44.9)	27.5 (24.3-31.3)	5.56 (3.51-7.89)	25.84 (14.30-37.26)	2.92 (1.67-3.82)	3.06 (2.06-4.20)	2.91 (1.24-9.09)	1.28 (0.70-1.66)	0.36 (0.15-0.82)	1.18 (0.25-4.63)
30m	59.6±5.77	20.7±4.62	21.1±6.35	23.1±1.09	2.36±0.47	10.73±3.07	3.10±0.65	1.99±0.87	1.69±1.00	1.38±0.60	0.34±0.12	1.84±1.09
	60.8 (51.2-66.3)	19.7 (15.9-27.1)	17.9 (15.7-30.8)	22.9 (22.1-25.1)	2.46 (1.53-2.89)	11.00 (5.94-14.09)	3.19 (2.05-3.76)	2.11 (0.94-3.01)	1.57 (0.32-3.26)	1.25 (0.83-2.47)	0.40(0.16-0.48)	1.47 (0.87-3.51)
50m	57.4±4.15	22.5±9.26	20.7±12.6	20.1±3.20	1.44±0.44	7.55±2.56	2.33±0.70	3.10±1.27	1.54±0.60	2.00±1.38	0.61±0.76	0.97±0.54
	58.0 (51.4-65.2)	20.2 (10.5-36.6)	17.0 (9.81-43.3)	20.9 (13.0-23.3)	1.57 (0.65-2.00)	7.47 (3.50-12.18)	2.24 (1.33-3.47)	2.77 (1.52-5.60)	1.33 (0.85-2.49)	1.42 (0.85-4.23)	0.18(0.07-2.01)	0.72 (0.56-1.99)
80m	48.3±6.09	29.8±13.8	23.0±14.4	19.6±3.64	0.84±0.14	4.09±1.565	1.63±0.49	5.12±1.57	2.23±0.74	1.07±0.56	0.47±0.72	0.46±0.15
	46.2 (35.7-57.4)	27.0 (5.38-63.6)	19.2 (3.73-58.6)	20.3 (11.7-28.5)	0.85 (0.67-1.16)	3.48 (2.26-8.89)	1.55 (1.07-2.82)	5.52 (2.79-7.53)	2.20 (1.33-3.68)	0.97 (0.58-2.97)	0.13(0.08-2.37)	0.47 (0.21-0.82)
SNWRA												
0m	67.4	45	33.4	21.5	2.93	11.05	1.47	7.73	2.89	0.63	0.14	0.27
30m	45.9±4.97	12.4±6.65	11.5±3.22	18.7±2.41	0.99±0.27	3.98±1.35	1.78±0.32	5.31±1.14	1.81±0.43	0.77±0.15	1.10±0.02	0.68±0.26
	47.5 (37.3-50.0)	9.64 (7.66-24.1)	10.43 (7.60-15.3)	19.8 (14.6-20.7)	1.09 (0.51-1.18)	4.31 (1.75-5.40)	1.81 (1.44-2.21)	5.56 (3.91-6.50)	1.98 (1.17-2.3)	0.75 (0.55-0.97)	0.10 (0.07-0.13)	0.66 (0.39-0.95)
50m	46.7±7.06	17.6±6.62	13.0±2.53	17.4±2.92	0.79±0.16	3.22±0.70	2.00±0.50	4.82±1.53	2.13±0.83	0.96±0.25	1.17±1.72	0.61±0.26
	47.9 (39.8-56.9)	16.9 (12.0-28.5)	12.7 (10.2-17.1)	17.8 (12.7-20.6)	0.85 (0.52-0.91)	3.32 (2.07-3.96)	1.91 (1.32-2.53)	5.66 (3.07-6.39)	2.01 (0.98-3.11)	0.99 (0.64-1.27)	0.11 (0.10-4.05)	0.59 (0.27-1.00)
80m	33.3±4.53	27.4±8.10	15.5±3.18	16.0±1.58	0.61±0.11	2.43±1.20	0.95±0.54	1.97±2.09	15.9±9.70	56.3±43.9	0.70±1.34	0.40±0.21
	32.7 (28.5-44.4)	25.7 (17.0-44.0)	14.7 (11.3-22.1)	16.1 (13.3-19.1)	0.56 (0.49-0.80)	2.23 (1.13-6.26)	0.74 (0.50-2.61)	0.65 (0.53-5.63)	20.0 (1.37-28.0)	60.8 (0.75-130.8)	0.13 (0.07-4.18)	0.41 (0.12-0.72)

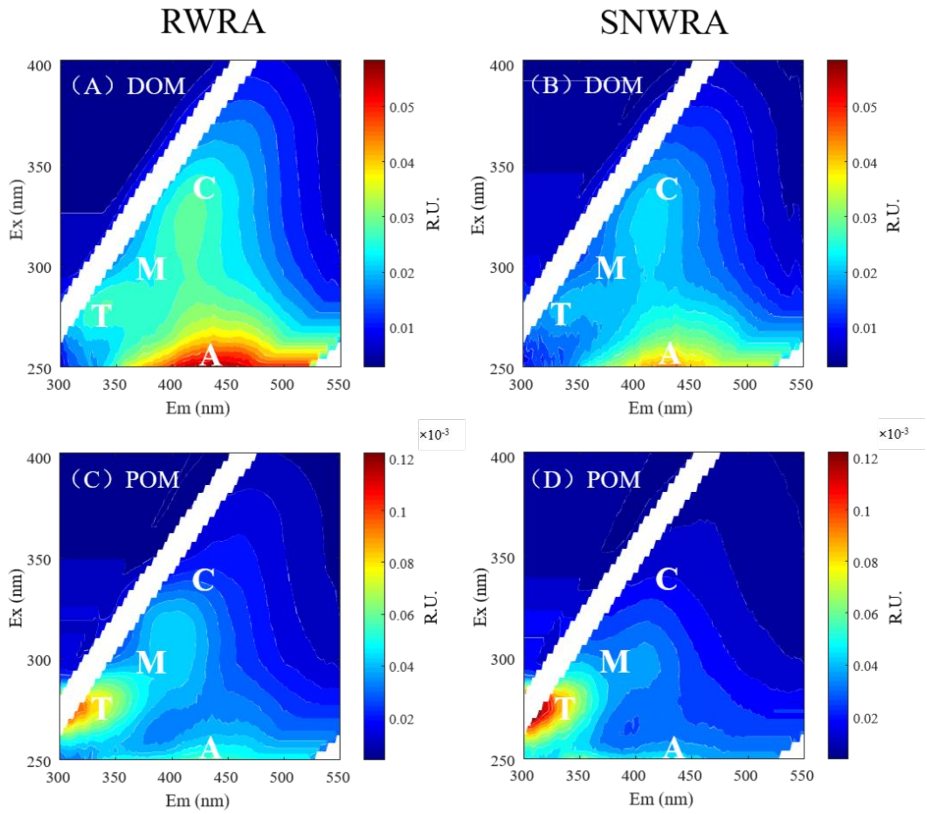


Figure S1 Comparison of DOM (top) and POM (bottom) EEM fluorescence (R.U.) of groundwater in the RWRA and SNWRA. The EEMs were the average spectra of samples in corresponding areas. According to Coble's fluorescence peak position (FRI method), the fluorescence peaks in water environment can be divided into four categories: peak T, Ex/Em = 275/340 nm, tryptophan-like fluorescence peak; peak A, Ex/EM = 260/400-460 nm, humic-like and fulvic acid-like fluorescence peak; peak M, Ex/Em= 290-310/370-410 nm, microbial humic-like fluorescence peak; peak C, Ex/Em = 320-360/420-460 nm, humic-like and fulvic acid-like fluorescence peak[20, 21]. The average EEM characteristics of DOM for groundwater samples in RWRA and SNWRA showed that the intensity of each Coble peak as indicated by fluorescence regional integration (FRI) in RWRA was higher than that in SNWRA[20], indicating the higher abundance of FOM in DOM samples. Furthermore, the clear FRI comparison of peak A between RWRA and SNWRA showed that RWRA contained a larger amount of humified organic matter (Table S3). Similar to EEMs in the surface water[4], RWRA had a feature that the peak A region was extended into a plateau situated between the peaks M and C. The average fluorescence intensity of POM (~ 10^{-3} R.U.) was much lower than that of DOM (~ 10^{-2} R.U.). In addition, the EEM features of POM were significantly different from those of DOM. The Peak T signal in the EEM of POM in groundwater from both two recharge areas was much stronger than those of other peaks, indicating the dominant role of bioactive tryptophan-like substances in the POM. These results were consistent with the previous studies observing Peak T in POM of surface water samples from urbanized rivers and estuaries[4, 22]

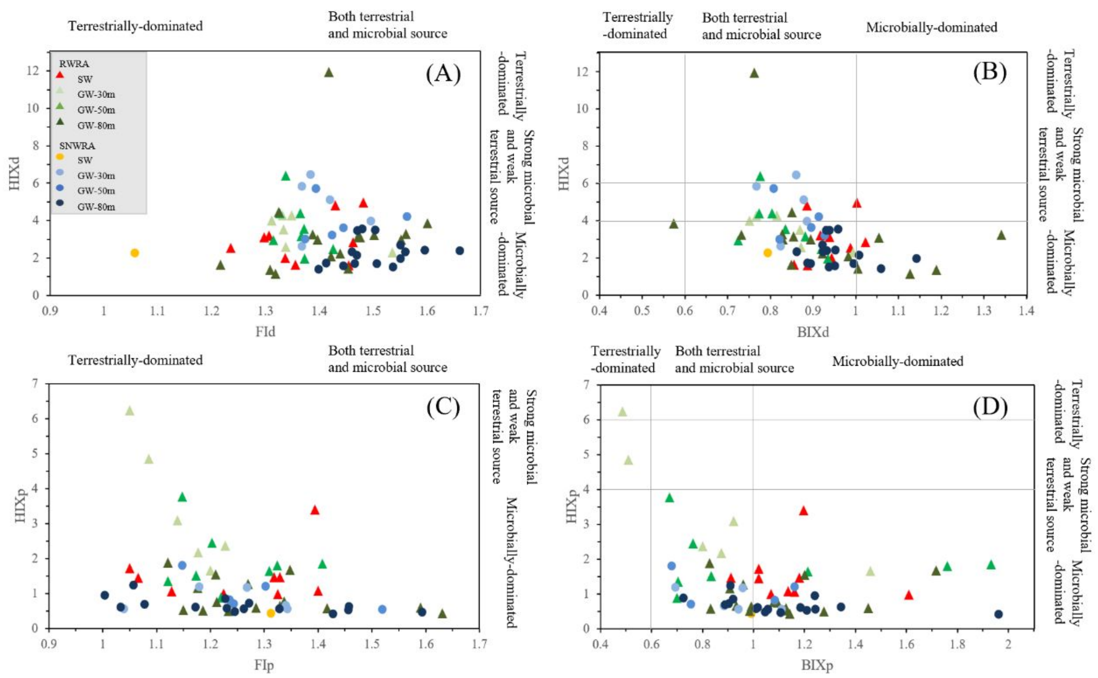


Figure S2 FI-HIX (A and C) and BIX-HIX (B and D) distributions of DOM (A and B) and POM (C and D) in RWRA (triangle) and SNWRA (circle)

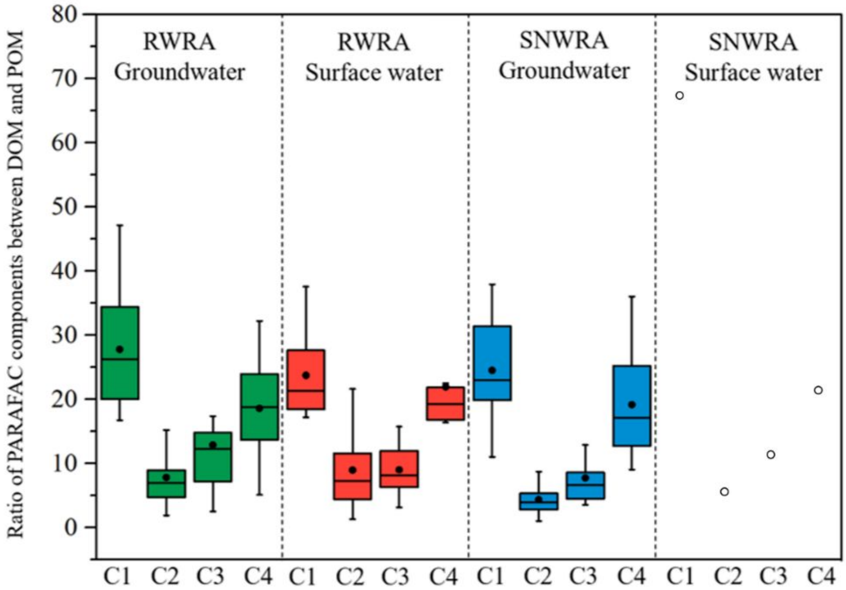


Figure S3 Box-whisker plots of $F_{max\text{-}DOM}$/ $F_{max\text{-}POM}$ (the ratio of DOM F_{max} (R.U.) to POM F_{max} (R.U.)) between each PARAFAC component of groundwater and surface water in RWRA (left) and SNWRA (right)

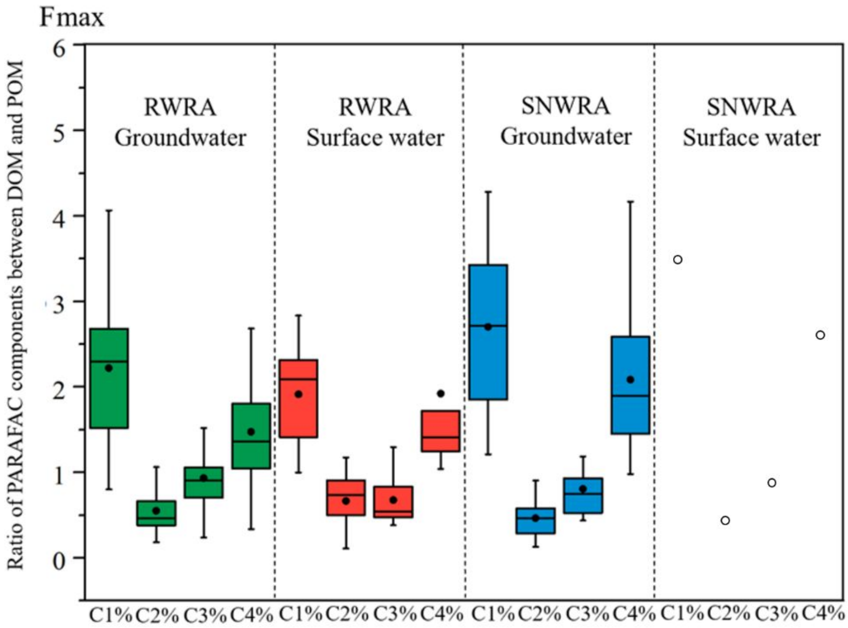
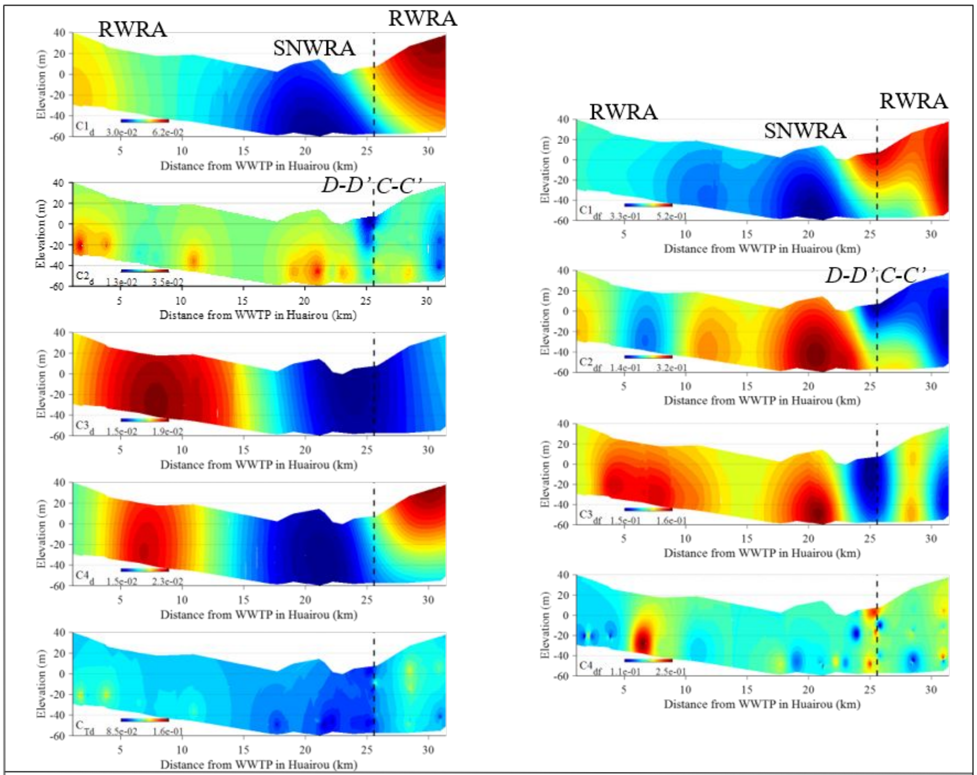


Figure S4 Box-whisker plots of % $F_{max\text{-}DOM}$/ % $F_{max\text{-}POM}$ (the ratio of DOM % F_{max} to POM % F_{max}) between PARAFAC components of groundwater and surface water from RWRA (left) and SNWRA (right).

（A）



（B）

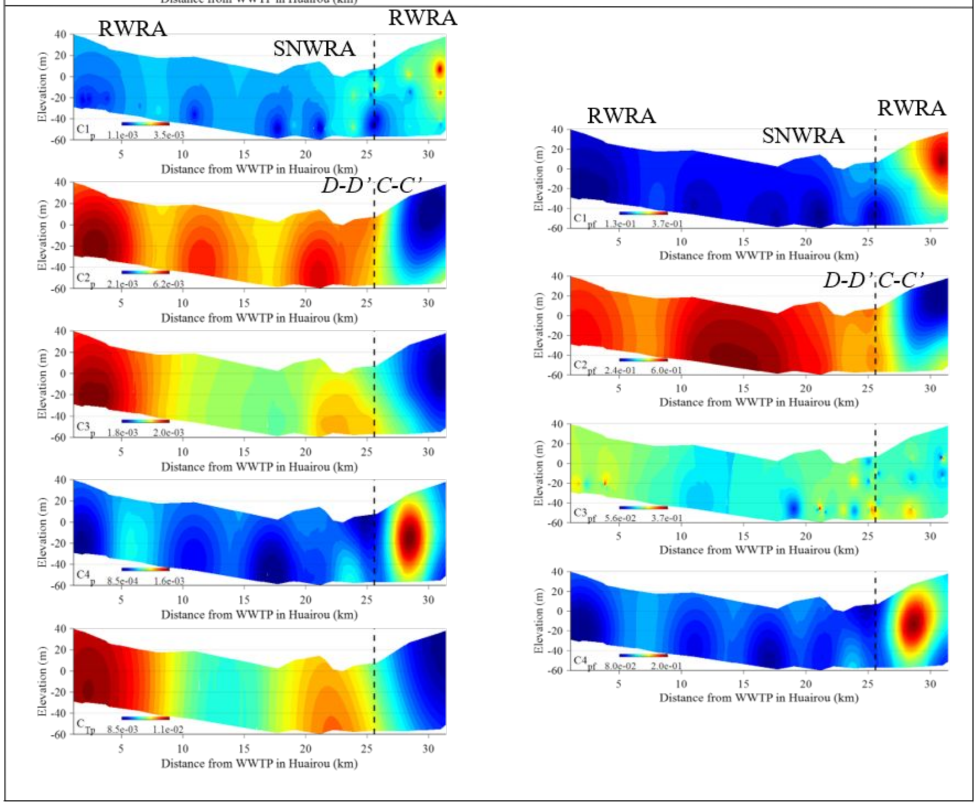


Figure S5 Concentrations (left) and proportions (right) of PARAFAC components in DOM (A) and POM (B) along the D-D’ and C-C’ profiles plotted by Kriging interpolation method. The upper boundary of the map is water level line. The bottom boundary is 10 m below the deepest sampling point The colorbar from blue to red denotes fluorescent intensities (R. U.) from the smallest to the largest.

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