

MOLECULAR COMPOSITION OF DISSOLVED ORGANIC MATTER IN THE CHANGJIANG (YANGTZE RIVER) – IMPRINTS OF ANTHROPOGENIC IMPACT

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Supporting Online Material

Figure S1 Variation of (O/C)_{wa} (a) and (H/C)_{wa} (b) vs filtration volume and of (O/C)_{wa} (c) and (H/C)_{wa} (d) vs DOC loadings between two years.

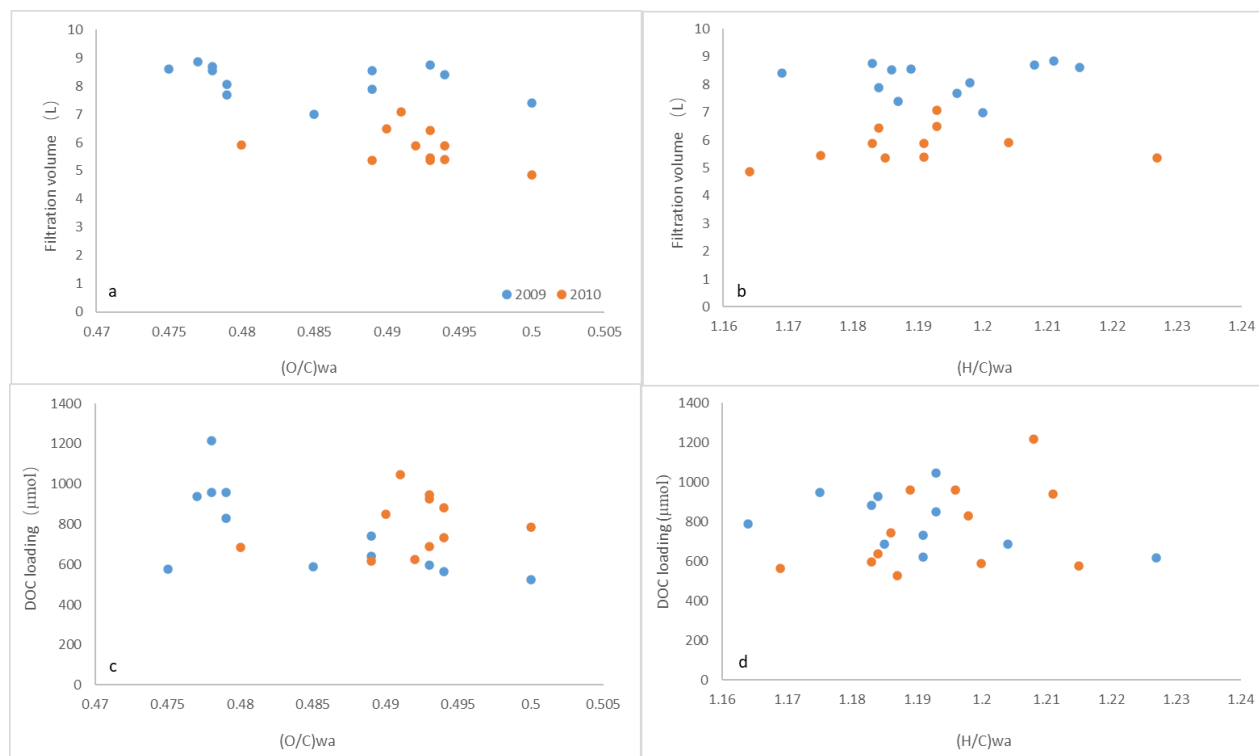


Table S1 T test of 2009 and 2010 major parameters of bulk, CDOM parameters and DOM elemental compositions.

Number of samples	Significance level	$p < 0.001$	$0.001 \leq p < 0.05$	$0.05 \leq p < 0.1$
n=25	2009 vs 2010	DOC, S/V, C1, C3/C5, Swa, (S/C)wa, CHOSx	(Ad/Al)v, POC, a254, C2, C4, C5, DON, n(nf), Cwa, (O/C)wa, CHONx	Hwa
n=14	2009 main stream vs tributaries		S/V, (Ad/Al)v, $\delta^{13}\text{C}$, DON	TSM, $S_{275-295}$
n=11	2010 main stream vs tributaries		TSM, S/V, n(mf), (N/C)wa	CHONx
n=16	Main stream of 2009 vs main stream of 2010	DOC, C1, C2, C3/C5, Swa, (S/C)wa, CHOSx, CHONx	lig8, a254, DON	n(mf), (O/C)wa
n=9	Tributaries of 2009 vs tributaries of 2010	S/V	(Ad/Al)v, V, POC, C2/C4, DON	
n=8	2009 Upper vs middle & lower reaches (only main stream)	Hwa	DOC, TSM, POC%, C1, C2, C4, C5, Owa, (O/C)wa, (H/C)wa	Λ_8 , POC, a254, C3, S, V, C

Table S2 General parameters and biomarker proxies of organic matter collected from the Changjiang, detailed information about parameters please refer to text of methods.

Parameters	Year	Sampling site	DOC ($\mu\text{mol L}^{-1}$)	DON ($\mu\text{mol L}^{-1}$)	TSM (mg L^{-1})	Λ_8 ($\text{mg}(100\text{mgOC})^{-1}$)	lig 8 ($\mu\text{g L}^{-1}$)	S/V	C/V	(Ad/Al)v	S ($\text{mg}(100\text{mgOC})^{-1}$)	V ($\text{mg}(100\text{mgOC})^{-1}$)	C ($\text{mg}(100\text{mgOC})^{-1}$)	POC% (%)	POC (mg L^{-1})	Isotope (‰)	δ_{254} (m^{-1})	$S_{275-295}$ (μm^{-1})	Fl	SUVA254 ($\text{L mg}^{-1} \text{m}^{-1}$)	C1 (%)	C2 (%)	C3 (%)	C4 (%)	C5 (%)
JIM10	2010	Jiujiang	144	6.6	157	0.78	13.4	0.79	0.27	0.92	0.30	0.38	0.10	1.05	1.65	-25.6	10.6	16.7	1.70	0.07	0.20	0.18	0.06	0.32	0.09
YCM10	2010	Yichang	162	3.2	332	0.99	19.2	0.80	0.25	1.06	0.39	0.48	0.12	1.09	3.61	-24.6	12.7	14.4	1.79	0.08	0.24	0.21	0.06	0.29	0.08
CLJM10	2010	Yueyang	150	1.7	200	0.86	10.8	0.83	0.14	0.71	0.36	0.44	0.06	0.69	1.38	-24.4	13.0	14.4	1.63	0.09	0.24	0.24	0.08	0.39	0.09
JDSM10	2010	Jiuduansha	115	/	95	0.50	6.9	0.72	0.24	0.87	0.18	0.26	0.06	0.37	0.35	-23.5	/	/	/	/	/	/	/	/	/
XLJM10	2010	Xuliujing	131	4.9	85	0.69	10.9	0.72	0.04	0.85	0.28	0.39	0.01	0.62	0.53	-25.6	/	/	/	/	/	/	/	/	/
WHM10	2010	Hankou	106	/	160	1.27	13.5	0.89	0.34	0.81	0.42	0.48	0.16	1.20	1.92	-25.2	10.9	16.4	1.65	0.10	0.20	0.18	0.06	0.30	0.08
SXM10	2010	Sanxia	174	/	307	0.91	19.1	0.76	0.26	1.20	0.34	0.45	0.12	1.28	3.93	-24.8	14.2	14.8	1.67	0.08	0.25	0.22	0.07	0.20	0.08
BCM10	2010	Beicao	128	/	223	0.57	8.7	0.80	0.28	0.76	0.22	0.27	0.08	0.65	1.45	-24.8	/	/	/	/	/	/	/	/	/
Average			139	4.1	195	0.82	12.8	0.79	0.23	0.90	0.31	0.39	0.09	0.87	1.85	-24.8	12.3	15.3	1.69	0.08	0.22	0.21	0.07	0.30	0.08
STDEV			23	2.1	90	0.25	4.5	0.06	0.09	0.16	0.08	0.09	0.05	0.33	1.30	0.7	1.5	1.1	0.06	0.01	0.02	0.02	0.01	0.07	0.01
HJT10	2010	Hanjiang	136	3.1	123	0.85	13.8	0.88	0.22	0.94	0.35	0.40	0.09	1.28	1.58	-24.5	11.2	16.7	1.71	0.08	0.21	0.17	0.05	0.23	0.08
DTHT10	2010	Dongting Lake	148	3.3	14.8	0.97	17.3	0.95	0.34	1.05	0.40	0.42	0.16	8.94	1.33	-29.2	13.0	14.4	1.64	0.09	0.24	0.24	0.08	0.39	0.09
PYHT10	2010	Poyang Lake	116	/	28.6	0.51	7.1	0.85	0.07	0.63	0.23	0.26	0.02	3.20	0.92	-30.4	7.3	16.6	1.71	0.06	0.14	0.10	0.05	0.15	0.07
Average			133	3.2	55.5	0.78	12.7	0.89	0.21	0.87	0.33	0.36	0.09	4.47	1.27	-28.0	10.5	15.9	1.69	0.08	0.19	0.17	0.06	0.26	0.08
STDEV			16	0.1	58.9	0.24	5.2	0.05	0.13	0.22	0.09	0.09	0.07	3.99	0.33	3.1	2.9	1.3	0.04	0.01	0.05	0.07	0.02	0.12	0.01
SGM09	2009	Shigu	71	4.6	318	0.82	7.0	0.64	0.34	1.39	0.26	0.41	0.14	0.35	1.11	-23.5	/	/	/	/	/	/	/	/	/
WZM09	2009	Wanzhou	81	14.2	29	0.97	9.4	0.76	0.21	0.83	0.38	0.49	0.10	0.59	0.17	-24.6	8.1	16.3	1.56	0.10	0.14	0.12	0.07	0.18	0.07
YCM09	2009	Yichang	112	12.0	23	0.83	11.2	0.65	0.27	0.99	0.28	0.43	0.12	1.04	0.24	-24.6	10.2	14.6	1.68	0.09	0.17	0.15	0.08	0.19	0.07
HHM09	2009	Xiantao	125	11.0	49	0.56	8.4	0.76	0.28	0.99	0.21	0.28	0.08	0.92	0.45	-24.0	9.7	17.9	1.48	0.08	0.16	0.14	0.10	0.25	0.08
XLJM09	2009	Xuliujing	106	9.6	27	0.48	6.1	0.84	0.27	0.76	0.19	0.23	0.06	1.33	0.36	-25.5	8.5	18.9	1.49	0.08	0.15	0.13	0.13	0.22	0.09
YBM09	2009	Yibin	68	5.1	331	1.43	11.6	0.75	0.23	1.18	0.54	0.73	0.16	0.51	1.69	-24.2	5.3	17.1	1.78	0.08	0.11	0.09	0.06	0.11	0.05
JJM09	2009	Jiangjin	87	7.3	444	0.78	8.2	0.77	0.29	0.83	0.29	0.38	0.11	0.40	1.77	-24.3	5.5	15.9	1.76	0.06	0.10	0.08	0.07	0.11	0.05
AQM09	2009	Anqing	103	12.6	57	0.65	8.0	0.80	0.26	0.75	0.25	0.31	0.08	0.82	0.47	-25.1	8.9	19.8	1.33	0.09	0.15	0.16	0.09	0.35	0.10
Average			94	9.5	160	0.82	8.7	0.75	0.27	0.97	0.30	0.41	0.11	0.75	0.78	-24.5	8.0	17.2	1.58	0.08	0.14	0.12	0.09	0.20	0.07
STDEV			20	3.5	174	0.30	1.9	0.07	0.04	0.23	0.11	0.16	0.03	0.34	0.65	0.6	1.9	1.8	0.16	0.01	0.03	0.03	0.02	0.08	0.02
GJT09	2009	Ganjiang	84	6.0	10	1.10	11.0	0.59	0.14	1.94	0.37	0.64	0.09	10.71	1.07	-26.2	4.2	14.8	1.78	0.05	0.10	0.08	0.06	0.10	0.05
XJT09	2009	Xiangjiang	108	6.5	3	0.98	12.7	0.63	0.16	1.51	0.34	0.55	0.09	9.48	0.28	-28.5	/	/	/	/	/	/	/	/	/
WJT09	2009	Wujiang	67	4.1	8.4	0.99	7.9	0.63	0.15	1.44	0.35	0.56	0.08	3.20	0.27	-25.9	11.3	15.7	1.28	0.17	0.19	0.16	0.09	0.20	0.07
JLJT09	2009	Jialingjiang	140	6.2	31	1.17	19.7	0.68	0.26	1.18	0.41	0.60	0.16	0.88	0.27	-25.2	/	/	/	/	/	/	/	/	/
YLJT09	2009	Yalongjiang	67	5.6	13.9	0.77	6.2	0.66	0.26	1.22	0.27	0.40	0.10	1.34	0.19	-24.5	11.3	15.7	1.69	0.17	0.21	0.17	0.05	0.24	0.08
HJT09	2009	Hanjiang	140	5.4	84.8	0.81	13.7	0.75	0.26	1.02	0.30	0.41	0.11	0.89	0.75	-25.8	8.9	15.1	1.77	0.06	0.10	0.08	0.07	0.10	0.04
Average			101	5.6	25.2	0.97	11.8	0.66	0.20	1.39	0.34	0.53	0.11	4.42	0.47	-26.0	8.9	15.3	1.63	0.11	0.15	0.12	0.07	0.16	0.06
STDEV			34	0.8	30.7	0.16	4.8	0.06	0.06	0.32	0.05	0.10	0.03	4.50	0.36	1.3	3.4	0.4	0.24	0.06	0.06	0.05	0.02	0.07	0.02

Table S3 The data used in PCA analysis of land use etc. (a) and path analysis model (b).

(a)

Sub-watershed	Agricultural area (km ²)	Forest area (km ²)	Wetlands area (km ²)	Industrial sewage (10 ⁴ ton)
Ganjiang	12145	46524	1194	71742
Xiangjiang	32142	62117	2094	112966
Wujiang	26816	54849		20087
Jianglingjiang	72858	93450		40142
Hanjiang	53619	89916		87741
Poyang Lake			6831	
Dongting Lake			6964	

(b)

[illegible]

UME report for Wu et al.

Results for the final dataset

Date of report: Wed Aug 08:37:09 2022 UTC

Total processing time in UltraMassExplorer: 17.7 sec

Final number of analyses in dataset:	25
Total number of peaks having formula assignments:	47334
Total number of formulas:	47334
Total number of unique formulas:	3167
Average number of formulas per sample:	1893
Total number of multiple assignments:	0

Overview original peak list

Total number of peaks:	212589
Mass range:	200.1737 - 649.3596 m/z
Peaks having formula assignments (incl. isotopes):	95.1 %
Magnitude explained by assignments:	98.8 %

Settings for molecular formula calculation

Maximum mass error: 0.5 ppm

Mode: negative ionization

Specification of the molecular formula library

Version: 2

Versionated key: 20000000000001 - 2000007170597

Type: lib_02

Number of formulas: 7170597

Neutral mass range: 14.02 - 702 Da

Range of isotopes considered:

¹²C : 1 - 58

¹³C : 0 - 1

¹H : 1 - 100

¹⁴N : 0 - 6

¹⁵N : 0 - 1

¹⁶O : 0 - 26

³¹P : 0 - 3

32S : 0 - 3

34S : 0 - 1

UltraMassExplorer filter settings

Mass accuracy: +/- 0.5 ppm

File IDs:

ESI_neg_Blank_001, ESI_neg_Blank_002, ESI_neg_Blank_003, ESI_neg_Blank_Solv 001,
GJT09, HHM09, HJT09, HJT10, JDSM10, JIM10, JJM09, LJJT09, PYHT10, SGM09, SXM10,
WHM10, WJT09, WZM09, XJT09, XLJM09, XLJM10, YBM09, YCM09, YCM10, YLJT09,
AQM09, BCM10, CLJM10, DTHT10

Selected category for known formulas: all

Blanks removed:

ESI_neg_Blank_001, ESI_neg_Blank_002, ESI_neg_Blank_003, ESI_neg_Blank_Solv 001

Surfactant formulas: removed

Peaks without ¹³C-isotopologue: removed

Peaks without ³⁴S-isotopologue: not removed

Peaks without ¹⁵N-isotopologue: not removed

Normalization by: base peak

N range: 0 to 3 atoms

S range: 0 to 2 atoms

P range: 0 to 0 atoms

O/C range: 0 to 1.3

H/C range: 0 to 3.5

Formulas have to occur in at least: 1 sample(s)

DBE max: 46

DBE-O range: -21 to 10

m/z min: 199

m/z max: 650

Range of elements and ratios in final dataset

Range of considered isotopes:

^{12}C : 13 - 35

^1H : 12 - 50

^{14}N : 0 - 3

^{16}O : 2 - 19

^{31}P : 0 - 0

^{32}S : 0 - 2

DBE: 0 - 21

DBE-O: -17 - 9

O/C-ratio: 0.13 - 0.94

H/C-ratio: 0.57 - 2.21