Supplementary Materials

Dissolved metal(loid) concentrations and their relations with chromophoric and fluorescent dissolved organic matter in an urban river in Shenzhen, South China

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Table 1. The maximum fluorescence intensity of the four fluorescent dissolved organic matter (FDOM) components (in Raman Unit) of different water types in Maozhou River. C1, terrestrially-derived humic-like component; C2, reprocessed terrestrially-derived humic-like component; C3, tyrosine-like component; and C4, tryptophan-like component.

Water type	Sites	C1	C2	C3	C4	Water type	Sites	C1	C2	C3	C4
Mainstream	M1	1.290	1.343	0.767	1.061	Tributary	T1-1	0.343	0.333	0.224	0.326
	M2	1.346	1.394	0.835	1.121		T1-2	0.430	0.466	0.363	0.610
	M3	1.280	1.332	0.798	1.137		T1-3	0.499	0.614	0.707	1.037
	M4	1.221	1.279	0.827	1.090		T2-1	0.358	0.404	0.586	0.757
	M5	1.087	1.130	0.788	1.125		T2-2	0.433	0.458	0.599	0.812
	M6	0.987	1.035	0.882	1.172		T3-1	0.594	0.517	0.622	0.537
	M7	0.969	1.015	0.881	1.189		T3-2	0.635	0.622	0.726	0.687
	M8	0.940	0.994	0.883	1.133		T4-1	0.721	0.805	0.401	1.949
	M9	0.983	0.969	1.662	1.578		T4-2	0.931	0.969	0.543	2.106
	M10	1.028	1.035	1.491	1.516		T4-3	1.017	1.013	0.687	2.086
	M11	0.967	0.980	1.353	1.388		T5-1	0.758	0.728	0.452	0.698
	M12	0.955	0.989	1.310	1.388		T5-2	1.236	1.042	0.613	0.615
	M13	0.915	0.962	1.285	1.429		T6	0.685	0.775	0.678	0.828
	M14	0.870	0.905	1.199	1.414		T7-1	1.061	0.868	1.809	2.396
	M15	1.476	1.302	2.562	3.261		T7-2	1.431	1.160	2.604	3.546
	M16	1.271	1.189	2.091	2.592		T7-3	1.614	1.292	3.066	4.077
	M17	1.497	1.354	2.708	3.391		T8	0.542	0.458	0.664	0.815
	M18	1.186	1.097	2.126	2.634		T9	2.211	1.673	4.307	5.687
	M19	1.212	1.143	2.067	2.511		T10	2.563	1.866	5.013	6.680

	M20	1.194	1.197	2.255	2.879
	M21	1.234	1.225	2.348	2.977
	M22	0.909	0.885	1.825	2.181
Pond	P1	0.972	0.829	0.855	0.853
	P2	1.041	1.222	1.029	1.394
	P3	1.772	1.647	0.723	0.578
	P4	1.983	1.800	0.855	0.912
	P5	0.551	0.463	0.367	0.292
	P6	2.405	2.099	3.398	2.309
	P7	1.063	0.981	0.734	0.741
	P8	0.831	0.524	0.871	0.578
	P9	0.669	0.562	0.524	0.444
	P10	2.108	1.941	3.259	1.743
	P11	0.833	0.769	0.553	0.752
Reservoir	R1	0.440	0.401	0.294	0.416
	R2	0.540	0.474	0.342	0.437
	R3	0.504	0.390	0.300	0.399
	R4	1.154	0.993	0.409	0.196
	R5	0.848	0.741	0.289	0.151
	R6	0.442	0.361	0.211	0.153
	T11	2.397	1.787	4.859	6.607
	T12	2.098	2.784	7.753	4.385
	T13	1.324	1.734	4.578	2.564
	T14-1	1.403	1.736	4.087	3.036
	T14-2	2.010	2.495	7.481	3.241
	T14-3	1.275	1.423	2.717	2.652
	T14-4	1.133	1.095	2.755	3.065
	T15	0.668	0.731	1.742	2.235
	T16	1.915	1.757	18.754	14.059
	T17	1.228	1.460	3.223	2.718
	T18-1	1.018	0.917	0.433	0.706
	T18-2	1.120	1.054	0.686	1.022
	T18-3	1.412	1.323	1.730	1.902
	T18-4	1.671	1.731	2.528	2.617
	T18-5	0.898	1.034	2.313	2.572
	T18-6	1.322	1.408	2.608	3.400
	T19-1	0.405	0.436	0.593	0.663
	T19-2	0.905	0.866	1.587	1.808
	T19-3	1.744	1.702	3.628	2.481
	T20-1	1.688	1.804	2.849	2.754
	T20-2	1.177	1.392	2.219	2.907
	T20-3	1.541	1.708	3.373	4.696
	T20-4	1.653	1.771	3.864	5.526
	T21	2.076	1.622	4.291	5.920

Table 2. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in all samples. Values in bold indicate significant correlation at a level of $P < 0.05$, and values in red and blue indicate positive and negative correlations at a level of $P < 0.01$, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	-.022	.060	.184	**.539**	-.081	-.181						
UV_{254}	-.006	.063	**.221**	**.600**	-.042	-.144						
$Fmax_{C1}$	**.407**	**.257**	**.350**	**.494**	.020	.088						
$Fmax_{C2}$	**.410**	**.281**	**.450**	**.529**	.034	.078						
$Fmax_{C3}$	**.559**	**.537**	**.678**	**.486**	.206	**.311**						
$Fmax_{C4}$	**.623**	**.606**	**.702**	**.459**	**.287**	**.441**						
$SUVA_{254}$							**.375**	.210	.141	**.545**	**.375**	**.417**
$S_{275-295}$							**-.718**	**-.533**	**-.43**	**-.405**	**-.421**	**-.589**
HIX							-.212	**-.396**	**-.549**	.020	**-.211**	-.161
BIX							**.729**	**.676**	**.539**	**.266**	**.261**	**.536**
$Fmax/DOC_{C1}$							**.691**	**.449**	**.319**	**.552**	**.312**	**.592**
$Fmax/DOC_{C2}$							**.725**	**.521**	**.380**	**.580**	**.311**	**.601**
$Fmax/DOC_{C3}$							**.681**	**.670**	**.637**	**.319**	**.349**	**.538**
$Fmax/DOC_{C4}$							**.716**	**.659**	**.609**	**.496**	**.447**	**.666**

Table 3. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the mainstream and tributary samples. Values in bold indicate significant correlation at a level of P <0.05, and values in red and blue indicate positive and negative correlations at a level of P<0.01, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	.133	.229	**.349**	**.454**	-.143	-.198						
UV_{254}	.051	.156	**.334**	**.541**	-.094	-.189						
$Fmax_{C1}$	**.362**	.141	.230	**.352**	-.162	-.098						
$Fmax_{C2}$	**.325**	.136	**.368**	**.368**	-.223	-.177						
$Fmax_{C3}$	**.463**	**.388**	**.566**	**.463**	-.046	.036						
$Fmax_{C4}$	**.514**	**.420**	**.544**	**.496**	.029	.167						
$SUVA_{254}$							.206	.069	-.100	**.486**	**.377**	**.358**
$S_{275-295}$							**-.613**	**-.289**	.035	-.097	-.222	**-.345**
HIX							-.008	-.239	**-.350**	**.280**	.093	.119
BIX							**.690**	**.624**	**.350**	.095	.127	**.415**
$Fmax/DOC_{C1}$							**.573**	.212	-.030	**.332**	.154	**.377**
$Fmax/DOC_{C2}$							**.591**	**.258**	-.016	**.346**	.107	**.337**
$Fmax/DOC_{C3}$							**.579**	**.531**	**.322**	.044	.070	**.291**
$Fmax/DOC_{C4}$							**.590**	**.475**	**.279**	**.298**	.217	**.45**

Table 4. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the pond and reservoir samples. Values in bold indicate significant correlation at a level of $P < 0.05$, and values in red and blue indicate positive and negative correlations at a level of $P < 0.01$, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	.096	.147	**.583**	**.809**	**.580**	**.713**						
UV_{254}	.252	.130	**.699**	**.838**	.361	.459						
$Fmax_{C1}$	.331	.206	**.672**	**.858**	.385	.403						
$Fmax_{C2}$	.358	.240	**.669**	**.882**	.465	.429						
$Fmax_{C3}$	.230	.370	**.681**	**.733**	.479	**.608**						
$Fmax_{C4}$	.272	**.498**	**.544**	**.679**	**.623**	**.649**						
$SUVA_{254}$							**.701**	.363	**.571**	**.784**	-.022	-.103
$S_{275-295}$							**-.493**	-.358	-.338	-.453	-.240	.331
HIX							.301	.002	.260	.449	-.314	-.007
BIX							.140	.074	.029	-.110	-.297	.162
$Fmax/DOC_{C1}$							**.593**	.424	**.603**	**.718**	-.181	-.078
$Fmax/DOC_{C2}$							**.569**	.368	**.600**	**.801**	-.081	-.078
$Fmax/DOC_{C3}$							.439	**.654**	.387	.211	.203	-.042
$Fmax/DOC_{C4}$							.446	**.642**	.341	.238	**.532**	.328

Table 5. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the mainstream samples. Values in bold indicate significant correlation at a level of P <0.05, and values in red and blue indicate positive and negative correlations at a level of P<0.01, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	.151	.272	.276	**.572****	-.021	.113						
UV_{254}	-.241	-.127	.141	.398	-.353	-.315						
$Fmax_{C1}$	-.064	**-.438***	-.344	-.121	-.396	-.351						
$Fmax_{C2}$	-.208	**-.587****	-.344	-.146	**-.477***	**-.451***						
$Fmax_{C3}$	**.486***	**.682****	**.609****	**.727****	**.505***	**.531***						
$Fmax_{C4}$	**.475***	**.662****	**.586****	**.705****	**.474***	**.487***						
$SUVA_{254}$							-.280	**-.621****	-.205	-.432*	-.388	-.500*
$S_{275-295}$							**-.563****	.064	**.530***	**.523***	-.106	-.033
HIX							-.139	**-.731****	**-.506***	**-.575****	**-.470***	**-.574****
BIX							.268	**.773****	**.468***	**.613****	**.572****	**.682****
$Fmax/DOC_{C1}$							-.074	**-.693****	**-.583****	**-.793****	**-.534***	**-.539****
$Fmax/DOC_{C2}$							-.081	**-.665****	**-.511***	**-.694****	**-.435***	**-.511***
$Fmax/DOC_{C3}$							.422	**.650****	.333	.370	**.506***	**.599****
$Fmax/DOC_{C4}$							.216	**.567****	.412	**.486***	.390	**.484***

Table 6. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the tributary samples. Values in bold indicate significant correlation at a level of P <0.05, and values in red and blue indicate positive and negative correlations at a level of P<0.01, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	.189	.233	**.435**	**.458**	-.159	-.269						
UV_{254}	.241	.223	**.451**	**.547**	-.100	-.213						
$Fmax_{C1}$	**.499**	**.309**	**.381**	**.447**	-.098	.007						
$Fmax_{C2}$	**.436**	.291	**.508**	**.494**	-.130	-.085						
$Fmax_{C3}$	**.552**	**.354**	**.586**	**.414**	-.121	-.048						
$Fmax_{C4}$	**.681**	**.44+**	**.564**	**.393**	-.097	.135						
$SUVA_{254}$							**.407**	.230	.021	**.640**	**.528**	**.66**
$S_{275-295}$							**-.508**	-.281	-.088	-.257	**-.358**	**-.443**
HIX							-.053	-.131	-.317	.447	.279	**.339**
BIX							**.638**	**.575**	**.338**	.084	.072	**.319**
$Fmax/DOC_{C1}$							**.558**	.274	.030	**.563**	**.359**	**.619**
$Fmax/DOC_{C2}$							**.635**	**.397**	.084	**.580**	.273	**.565**
$Fmax/DOC_{C3}$							**.615**	**.479**	.260	-.020	-.063	.162
$Fmax/DOC_{C4}$							**.725**	**.474**	.259	**.336**	.203	**.495**

Table 7. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the pond samples. Values in bold indicate significant correlation at a level of P <0.05, and values in red and blue indicate positive and negative correlations at a level of P<0.01, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	.136	.064	.282	.473	.527	.560						
UV_{254}	.573	.282	**.709**	**.782**	.545	.410						
$Fmax_{C1}$	.591	.455	**.627**	**.855**	.573	.424						
$Fmax_{C2}$	**.627**	.464	**.664**	**.882**	**.655**	.346						
$Fmax_{C3}$	.455	.427	.536	.445	.491	.360						
$Fmax_{C4}$	.518	**.609**	.409	.545	**.664**	.460						
$SUVA_{254}$							**.736**	.155	**.736**	**.800**	.336	-.009
$S_{275-295}$							-.355	-.345	-.236	-.364	-.227	.409
HIX							.064	-.336	.127	.273	-.264	.273
BIX							.064	.173	-.127	-.109	-.400	.009
$Fmax/DOC_{C1}$							.573	.100	**.636**	**.664**	.091	-.036
$Fmax/DOC_{C2}$							**.673**	.145	.573	**.809**	.436	-.064
$Fmax/DOC_{C3}$							.345	.473	.273	.200	.209	-.291
$Fmax/DOC_{C4}$							.418	.464	.218	.536	.545	.155

Table 8. *P* values of correlation analysis between dissolved metal(loid) concentrations and DOM parameters in the reservoir samples. Values in bold indicate significant correlation at a level of P <0.05, and values in red and blue indicate positive and negative correlations at a level of P<0.01, respectively.

	Zn	Cu	Cr	As	Pb	Cd	Zn/DOC	Cu/DOC	Cr/DOC	As/DOC	Pb/DOC	Cd/DOC
DOC	-0.036	0.286	**.821***	0.750	-0.450	-0.222						
UV_{254}	-0.321	-0.071	0.714	0.643	-0.685	-0.259						
$Fmax_{C1}$	-0.107	0.071	0.750	0.714	-0.541	-0.408						
$Fmax_{C2}$	-0.107	0.071	0.643	**.857***	-0.577	-0.111						
$Fmax_{C3}$	0.036	0.714	0.643	0.429	-0.306	-0.371						
$Fmax_{C4}$	0.071	**.893****	0.393	-0.143	0.072	0.037						
$SUVA_{254}$							0.214	-0.143	-0.107	**.857***	0.286	-0.071
$S_{275-295}$							-0.500	-0.071	0.071	-0.464	-0.571	0.071
HIX							-0.071	-0.286	0.143	**.786***	-0.107	-0.286
BIX							-0.214	-0.429	0.071	-0.679	-0.321	0.143
$Fmax/DOC_{C1}$							-0.107	-0.179	0.214	0.714	-0.143	-0.214
$Fmax/DOC_{C2}$							-0.214	-0.286	0.214	0.750	-0.250	0.000
$Fmax/DOC_{C3}$							0.036	0.321	-0.071	**-.857***	0.000	0.107
$Fmax/DOC_{C4}$							0.571	**.857***	0.143	-0.464	0.643	0.429

Table 9. Dissolved organic carbon (DOC) concentrations and optical properties of dissolved organic matter for the mainstream, tributary, reservoir and pond water. The average values are showed followed by the ranges in parentheses.

Water type	DOC ($mg \cdot L^{-1}$)	UV_{254} (m^{-1})	Fmax-C1 (R.U.)	Fmax-C2 (R.U.)	Fmax-C3 (R.U.)	Fmax-C4 (R.U.)	$SUVA_{254}$ ($L \cdot mg^{-1} m^{-1}$)	$S_{275-295}$ (μm^{-1})	Humification index (HIX)	Biological index (BIX)
Mainstream	4.01 (3.22-5.76)	0.074 (0.061-0.093)	1.13 (0.87-1.50)	1.13 (0.88-1.39)	1.5 (0.77-2.71)	1.82 (1.07-3.39)	1.87 (1.55-2.18)	12.18 (9.92-15.95)	2.74 (2.13-3.89)	1.03 (0.98-1.07)
Tributary	6.87 (1.54-29.00)	0.116 (0.030-0.329)	1.21 (0.34-2.56)	1.20 (0.33-2.78)	2.68 (0.22-18.76)	2.78 (0.33-14.06)	2.00 (1.05-3.43)	15.41 (10.56-20.72)	2.39 (1.23-4.19)	0.98 (0.85-1.11)
Reservoir	3.21 (2.08-4.60)	0.073 (0.051-0.129)	0.65 (0.44-1.15)	0.56 (0.36-0.99)	0.31 (0.21-0.41)	0.29 (0.15-0.44)	2.00 (1.77-2.20)	19.00 (18.43-20.41)	3.98 (3.28-4.89)	0.90 (0.89-0.92)
Pond	11.97 (6.99-29.58)	0.149 (0.095-0.234)	1.29 (0.55-2.40)	1.16 (0.46-2.10)	1.20 (0.37-3.40)	0.96 (0.29-2.31)	1.39 (0.78-2.00)	20.79 (15.66-24.81)	3.16 (2.27-4.30)	0.91 (0.82-1.00)

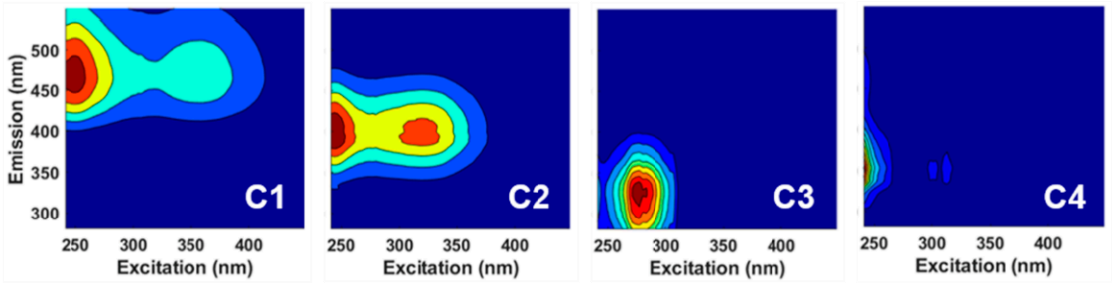

Figure 1. Four fluorescent dissolved organic matter (FDOM) components resolved by parallel factor analysis. C1, terrestrially-derived humic-like component; C2, reprocessed terrestrially-derived humic-like component; C3, tyrosine-like component; and C4, tryptophan-like component.

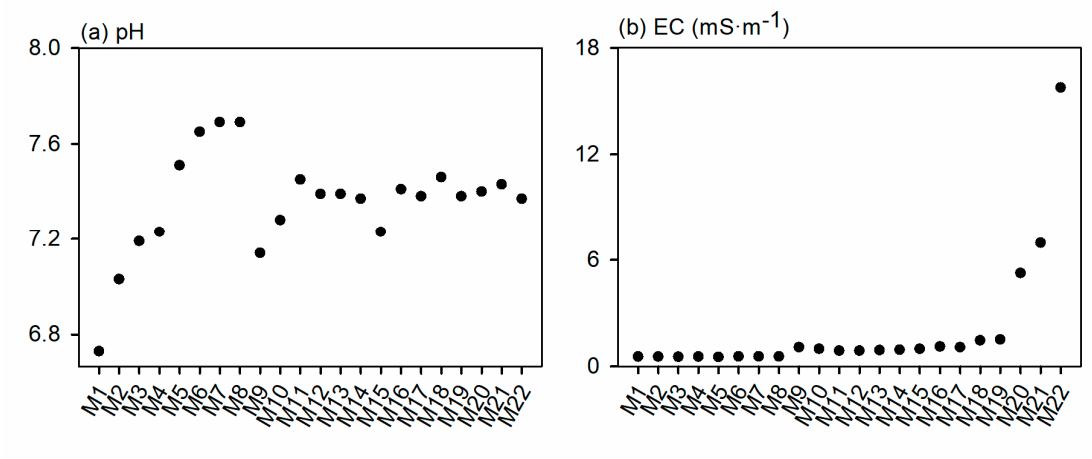

Figure 2. The pH and electrical conductivity (EC) values of mainstream samples in Maozhou River.

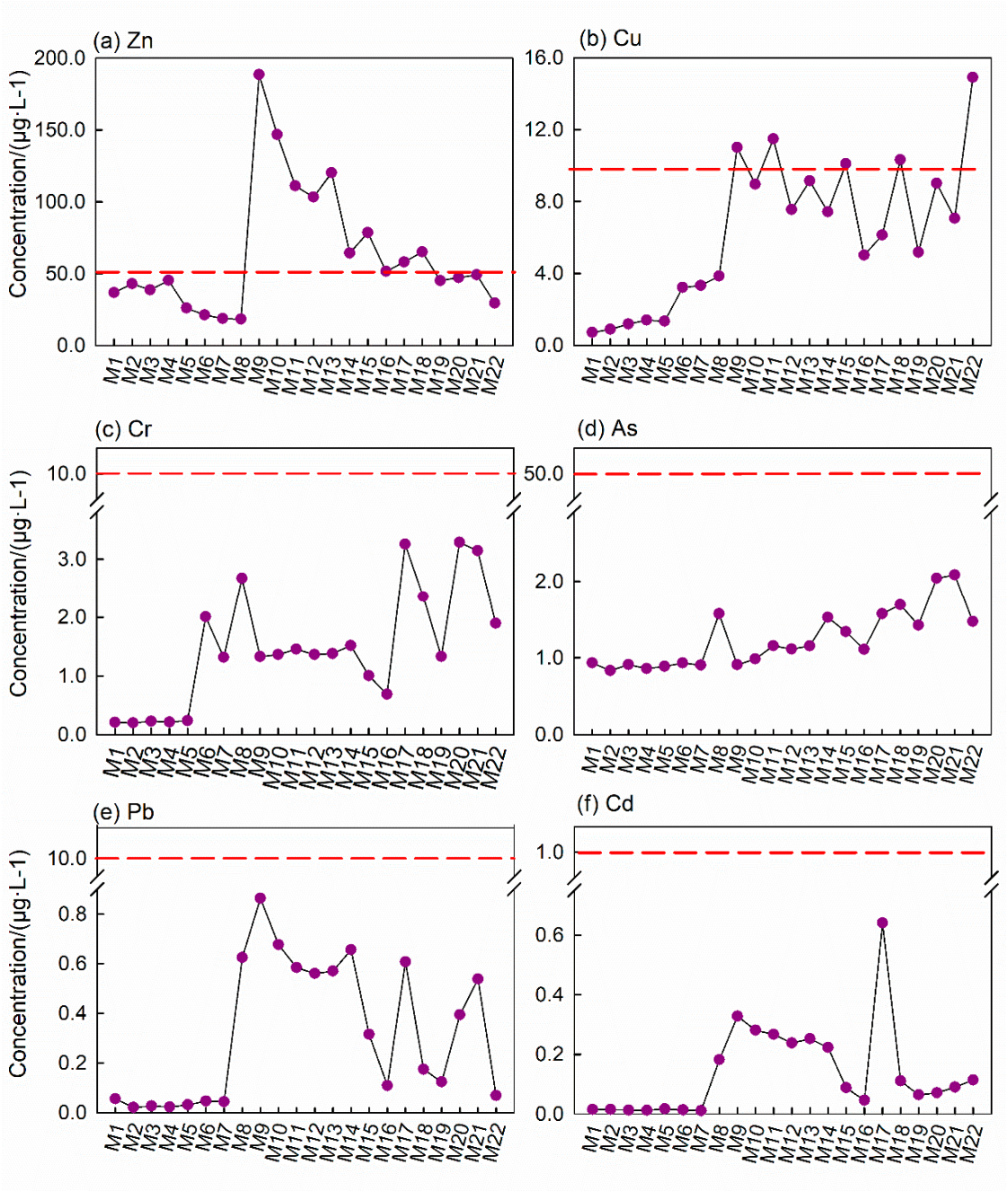

Figure 3. Dissolved metal(loid) concentrations mainstream samples in Maozhou River; red line indicate the Class I thresholds of the National Environmental Standard for Surface Water Quality of China (GB 3838-2002).

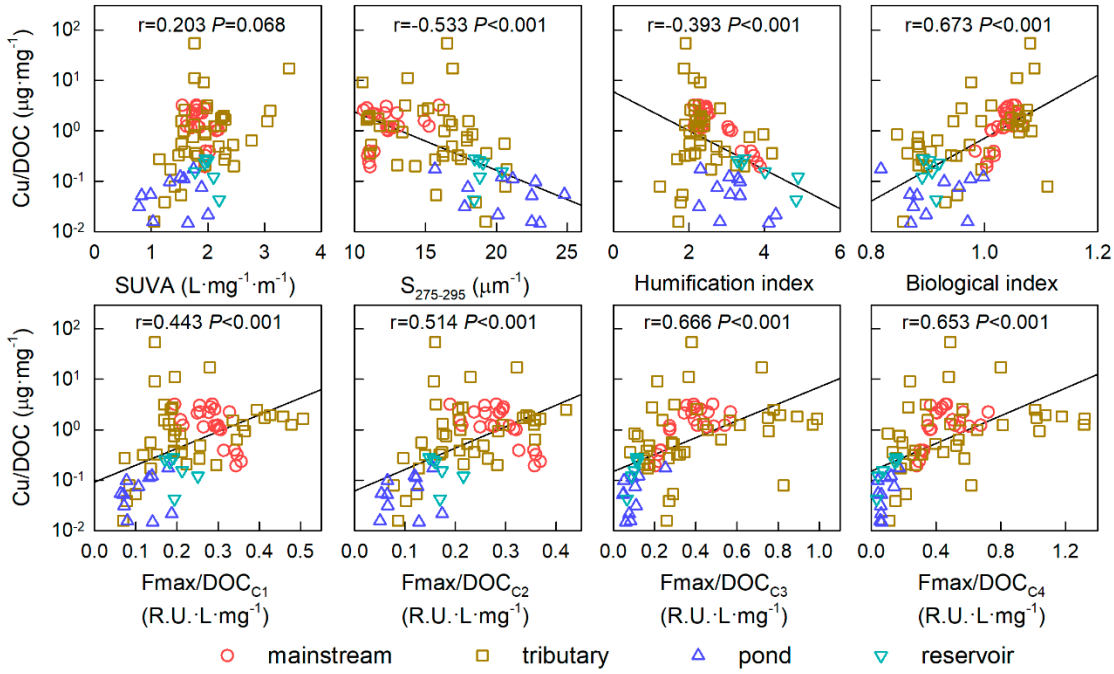

Figure 4. Correlations between Cu to DOC concentration ratio (Cu/DOC) and the dissolved organic matter characteristics. $SUVA_{254}$, specific ultraviolet absorbance at 254 nm; $S_{275\text{-}295}$, the absorbance slope between 275 nm and 295 nm; HIX, humification index; BIX biological index; $Fmax/DOC_{Ci}$, Fmax to DOC ratio of fluorescent component *i*.