Additional discussion on the decrease in isomeric percentage at high-flow condition

A significant decrease in isomer percentages at ESI- mode were observed. At base flow, isomer percentage was 11.3% under ESI-, and dropped to 7.72% at high flow. The change at ESI+ mode, on the other hand, is not significant. It is unclear what could drive this change at high flow at ESI- mode, but not at ESI+ mode. We speculate that this may be due to the preferential ionization of carboxyl-rich compounds at ESI-. Riverine DOM at high flow is dominated by terrestrial compounds that are enriched in carboxyl groups (as indicated by MS and MS/MS data;). The preference ionization of these compounds might have suppressed other molecules (Ohno et al., 2016), which could potentially lead to a decrease in the number of isomers detected.

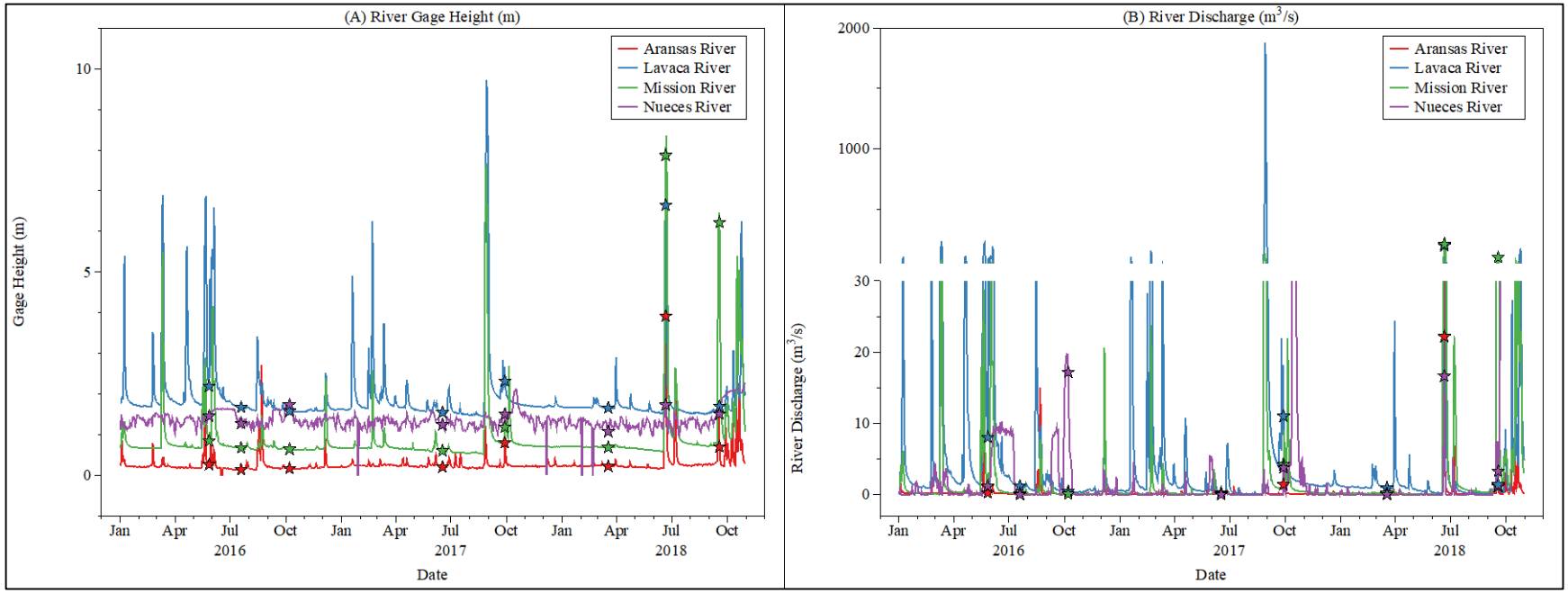

Figure S1. (A) Averaged daily value of gage height from USGS stations from 2016-03-01 to 2018-11-30. (B) Averaged river discharge from USGS stations from 2016-03-01 to 2018-11-30. Sampling dates are shown in black. On 2017-09-28, 2018-06-21, and 2018-09-19, samples were collected either during a high flow event or shortly after a high flow event. Samples collected on the other dates (2016-05-26, 2016-07-19, 2016-10-07, 2017-06-19, and 2018-03-21) represented the base flow condition.

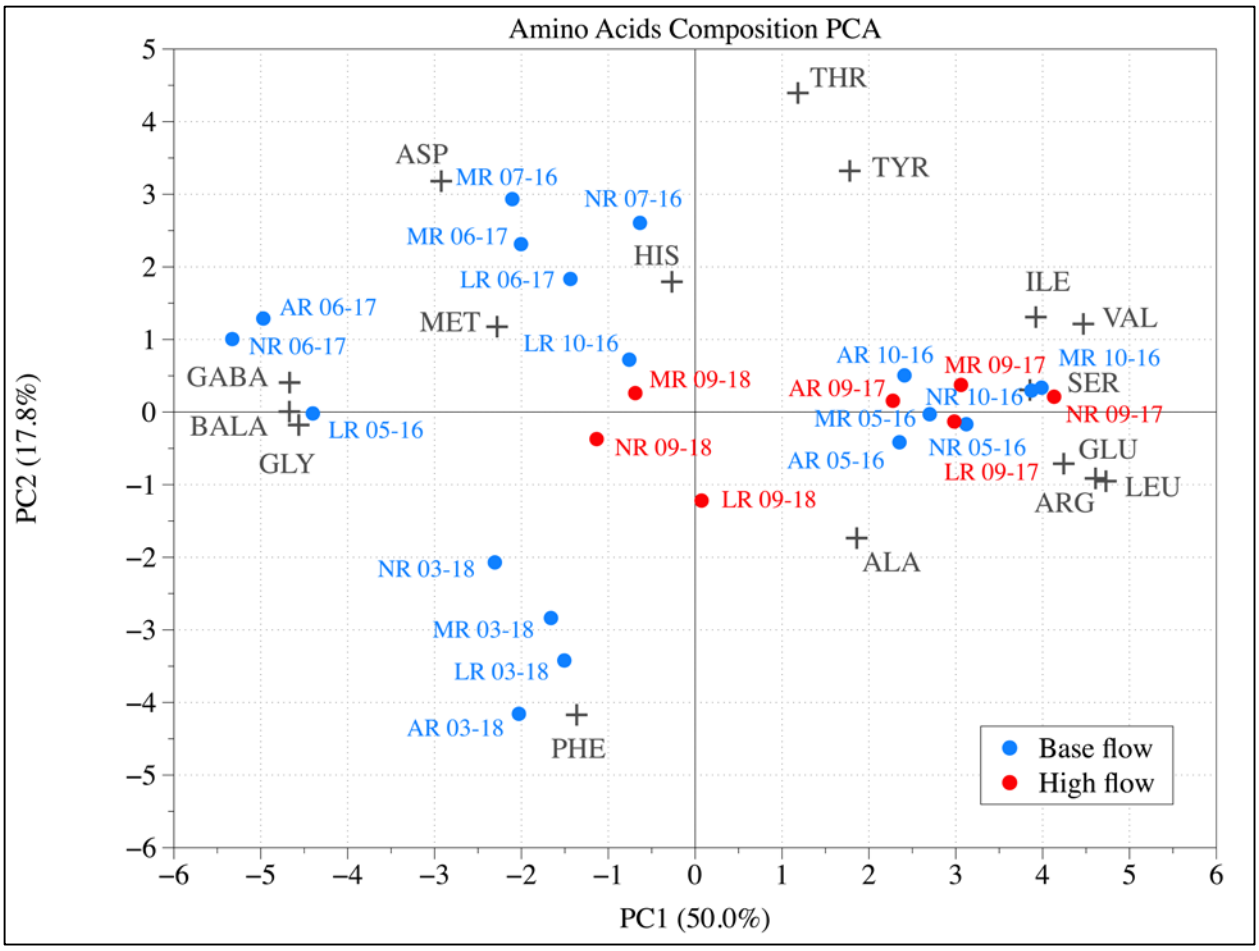

Figure S2. PCA based on amino acid composition (mol%). Samples from base flow are blue. Samples from high flow are red. AR: Aransas River; LR: Lavaca River; MR: Mission River; NR: Nueces River. 05-16: May-2016; 07-16: July-2016; 10-16: October-2016; 06-17: June-2017; 09-17: September-2017; 03-18: March-2018; 09-18: September-2018.

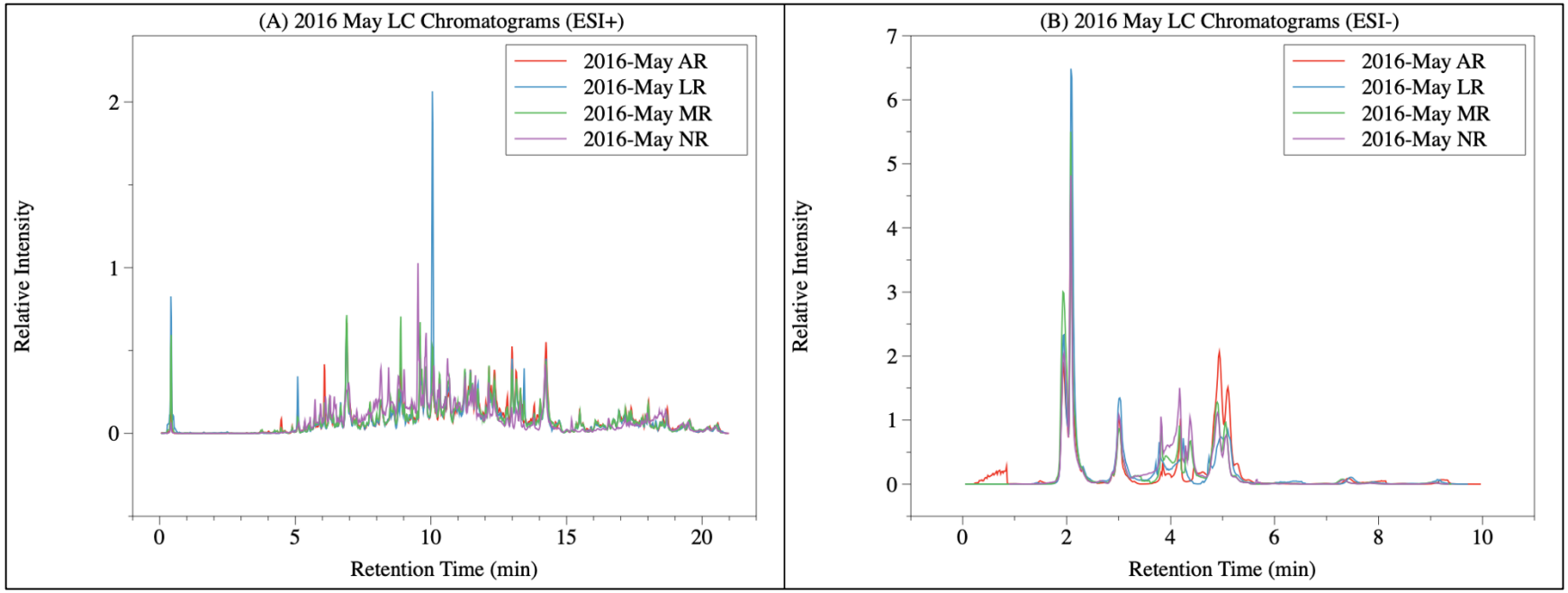

Figure S3. Chromatograms of DOM samples from different rivers at the same sampling time under ESI+ (A) and ESI- (B) modes. Note that positions of peaks across different rivers were very similar.

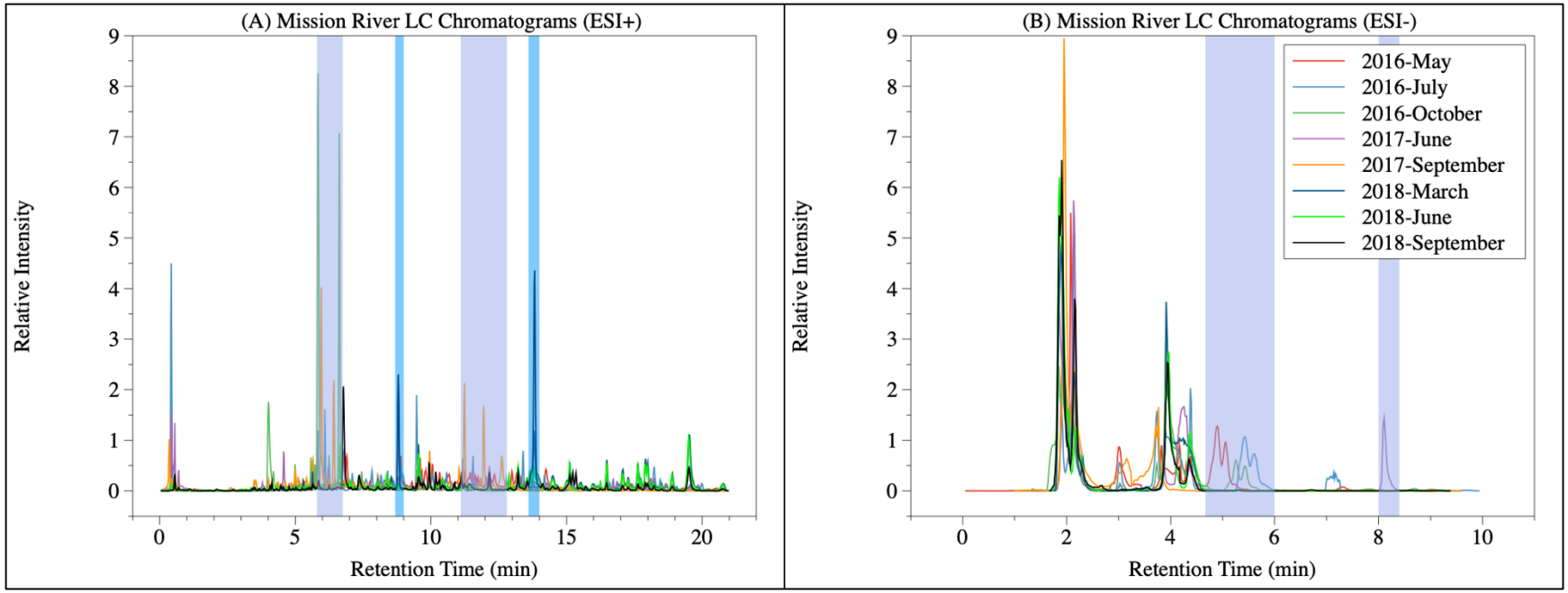

Figure S4. Chromatograms of DOM samples from same rivers at different sampling time under ESI+ (A) and ESI- (B) modes. Purple shades indicate peaks only present at base-flow. Blue shades indicate peaks only present at high-flow.

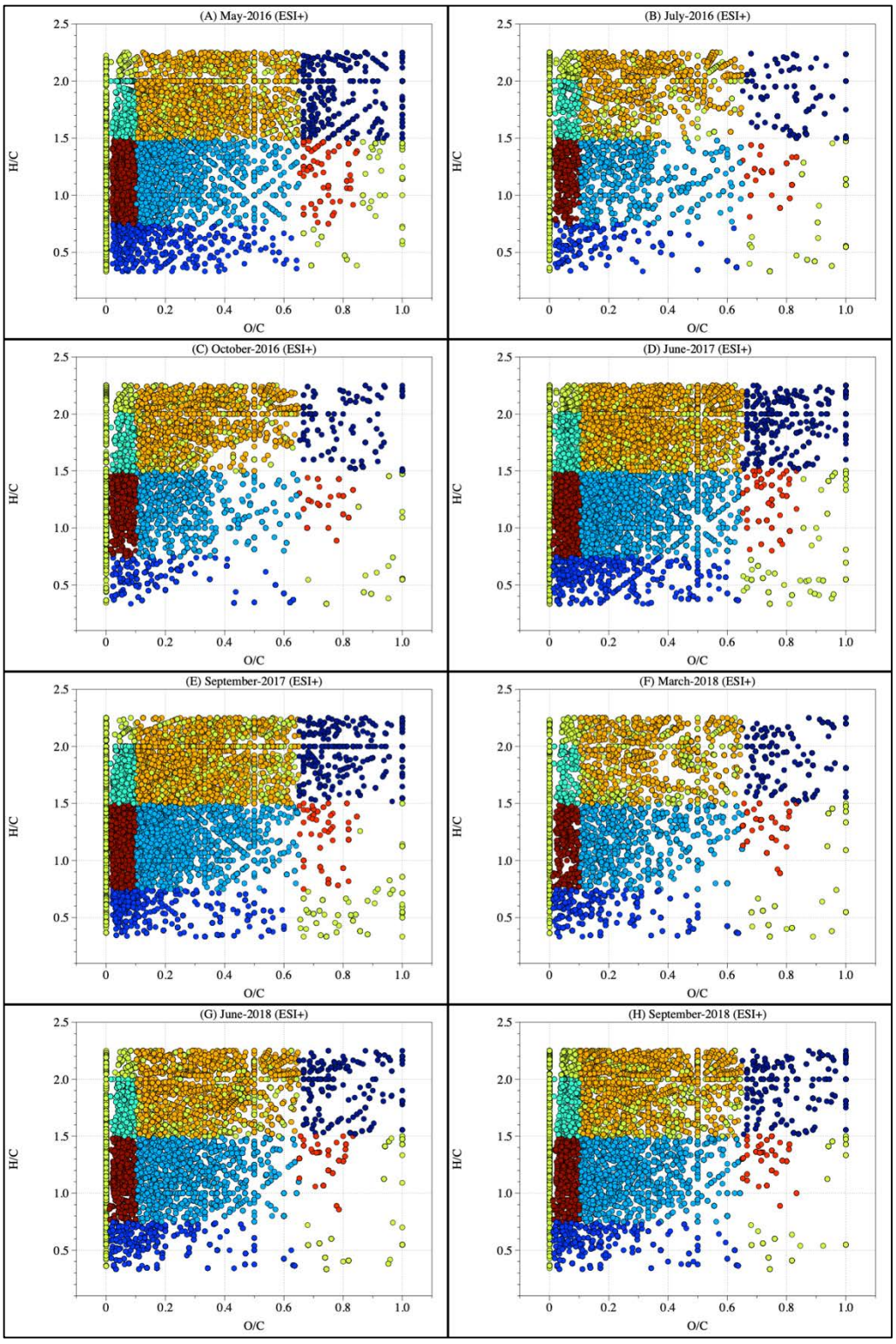

Figure S5. van Krevelen diagrams of riverine DOM from all four rivers at a particular sampling time under ESI+ mode. Color codes: Carbohydrate, Condensed Aromatic Structure, Lignin, Lipid, Protein, Tannin, Unsaturated Hydrocarbon, Others.

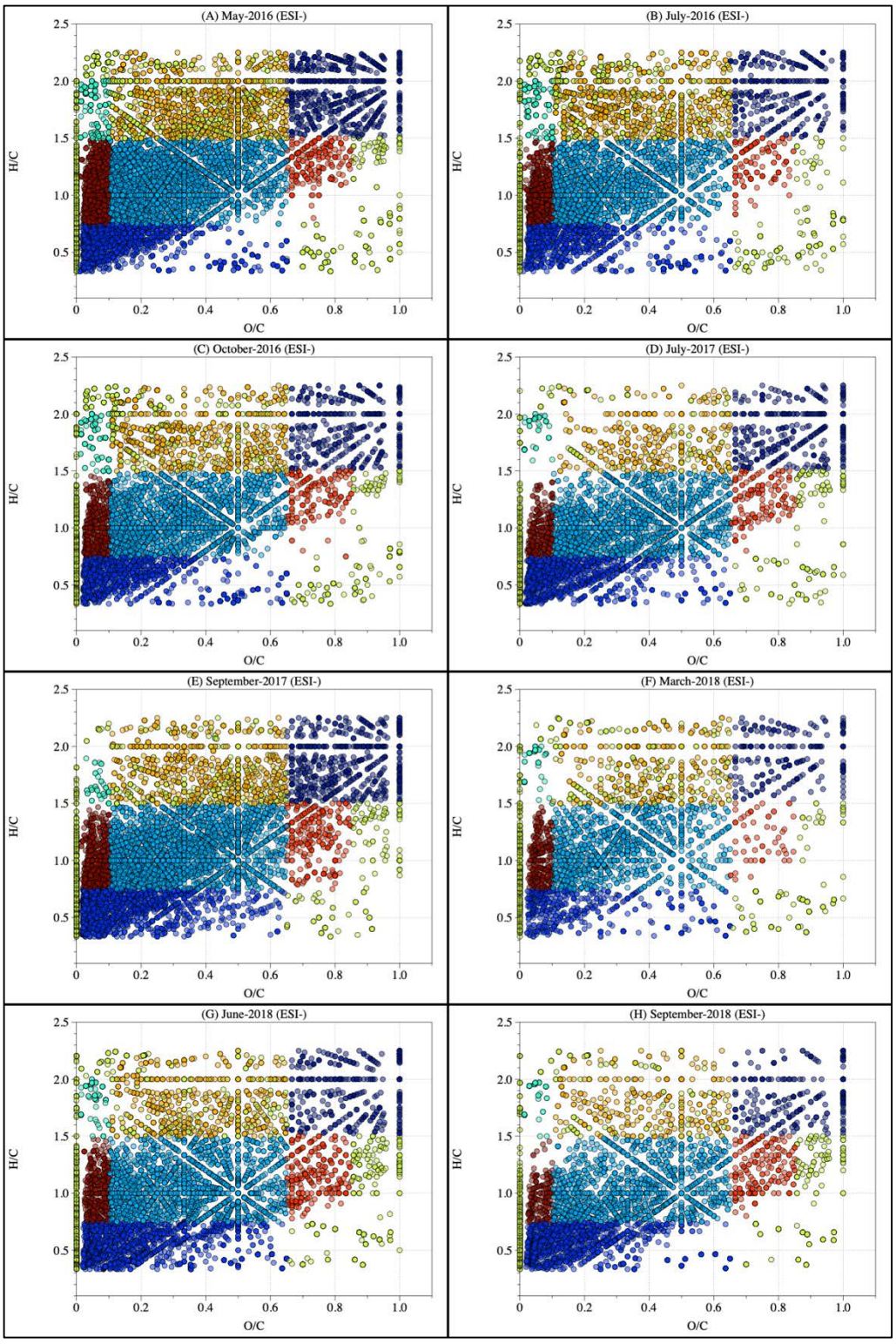

Figure S6. van Krevelen diagrams of riverine DOM from all four rivers at a particular sampling time under ESI- mode. Color codes: Carbohydrate, Condensed Aromatic Structure, Lignin, Lipid, Protein, Tannin, Unsaturated Hydrocarbon, Others.

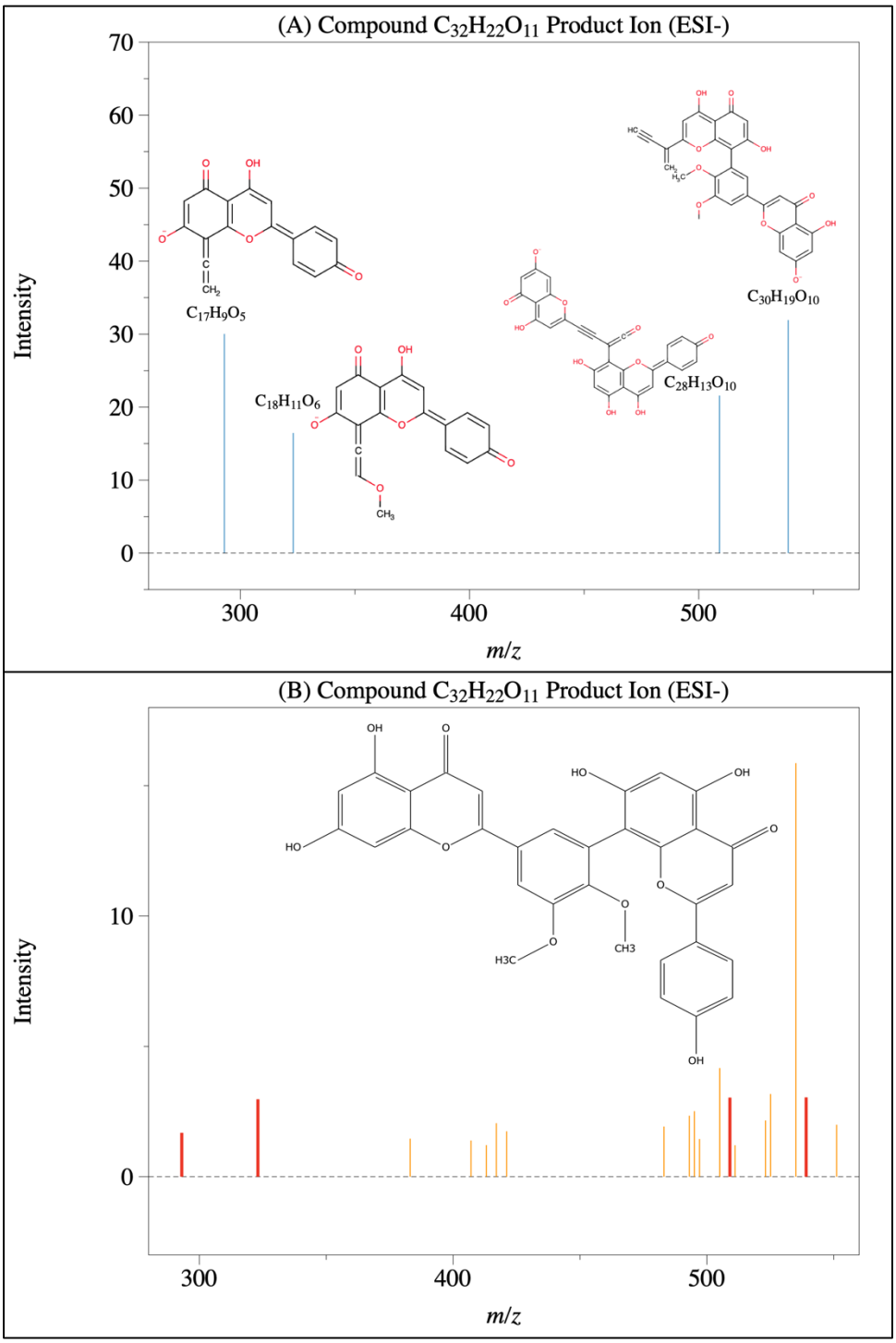

Figure S7. Examples of MS/MS identification based on product ions. (A) Product ions spectra of compound $C_{32}H_{22}O_{11}$. Structures of each product ions were confirmed with database (METILIN). (B) Structure of compound $C_{32}H_{22}O_{11}$ and its predicted product ions spectra (Human Metabolome Database http://www.hmdb.ca/). Matches between detected and predicted spectra were in bold red.

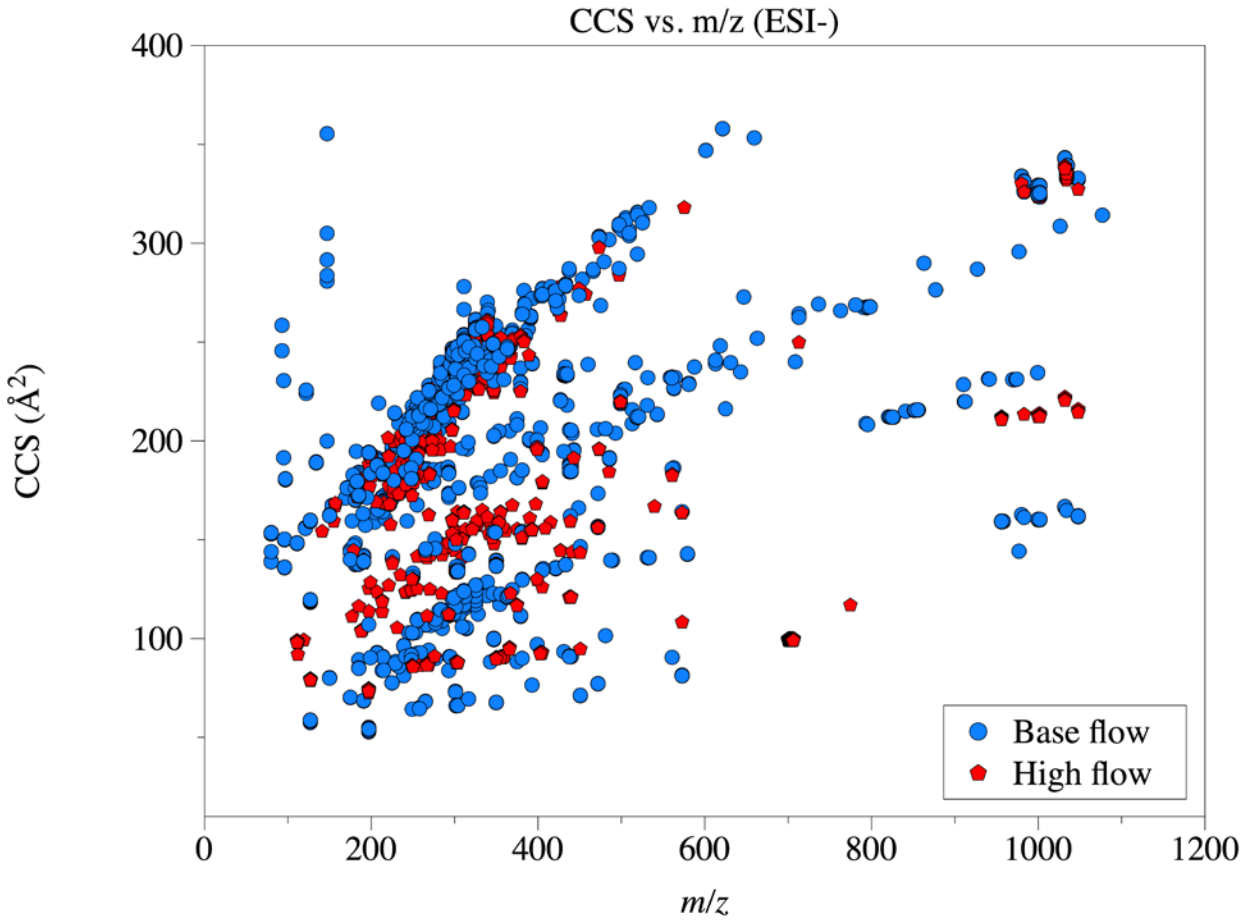

Figure S8. CCS vs. *m/z* under ESI- mode. Base-flow samples cannot be separated from those at high flow.

Table S1. *In situ* hydrological data

Time	Sites	Temperature (°C)	Salinity (‰)	DO (%)	DO (mg/L)	Discharge (m^3/s) *
27-May-2016	AR	29.69	0.16	91.2	6.92	0.21
27-May-2016	LR	27.20	0.18	91.8	7.24	8.01
27-May-2016	MR	28.08	0.15	72.4	5.56	1.09
27-May-2016	NR	30.41	1.63	99.0	7.37	1.16
19-Jul-2016	AR	33.72	0.83	92.2	6.95	0.10
19-Jul-2016	LR	31.05	0.30	85.8	6.30	1.19
19-Jul-2016	MR	30.03	0.88	74.1	5.51	0.12
19-Jul-2016	NR	33.94	0.53	123	8.87	0.00
07-Oct-2016	AR	28.60	0.62	71.8	5.49	0.11
07-Oct-2016	LR	28.67	0.91	87.8	6.80	0.46
07-Oct-2016	MR	26.21	0.81	58.9	4.54	0.06
07-Oct-2016	NR	27.80	0.36	79.3	6.22	17.2
19-June-2017	AR	24.05	0.33	53.1	3.75	0.04
19-June-2017	LR	30.24	1.12	65.4	4.88	0.25
19-June-2017	MR	29.95	0.61	26.6	2.00	0.03
19-June-2017	NR	33.03	0.84	61.8	4.42	0.00
28-Sep-2017	AR	29.63	0.34	56.6	4.30	1.39
28-Sep-2017	LR	27.78	0.20	78.8	6.17	11.0
28-Sep-2017	MR	27.08	0.79	56.5	4.41	4.19
28-Sep-2017	NR	29.00	8.35	10.0	0.74	3.77
21-Mar-2018	AR	23.70	1.02	144	12.1	0.11
21-Mar-2018	LR	20.50	9.63	87.5	7.35	0.93
21-Mar-2018	MR	22.20	1.12	102	8.78	0.14
21-Mar-2018	NR	23.45	10.5	94.7	7.57	0.00
21-Jun-2018	AR	25.52	0.07	41.1	3.37	22.2
21-Jun-2018	LR	25.44	1.05	46.0	3.75	196
21-Jun-2018	MR	25.48	0.05	35.8	2.92	209
21-Jun-2018	NR	27.82	0.44	68.0	5.35	16.6
19-Sep-2018	AR	28.08	0.09	68.1	5.32	1.12
19-Sep-2018	LR	28.48	1.92	108.1	8.30	1.36
19-Sep-2018	MR	27.93	0.07	46.4	3.63	98.0
19-Sep-2018	NR	28.07	0.28	52.2	4.07	3.26

*Discharge data based on USGS stations

Table S2. DOC, TDAA concentration and TDAA-C yield

Flow Condition	Sampling Time	DOC (μmol C L^{-1})					TDAA (μmol L^{-1})					TDAA-C/DOC (%)				
		AR	LR	MR	NR	Average	AR	LR	MR	NR	Average	AR	LR	MR	NR	Average
Base-flow	27-05-2016	625	911	919	560	754	15.9	4.41	20.9	22.6	16.0	10.5	1.67	9.49	17.0	9.65
	19-07-2016	N.D.	N.D.	431	605	518	N.D.	N.D.	4.30	11.01	7.65	N.D.	N.D.	3.67	6.87	5.27
	07-10-2016	605	561	506	621	573	25.5	4.14	19.3	14.1	15.8	18.5	2.93	16.8	9.88	12.0
	19-06-2017	962	629	1089	677	839	5.76	4.85	10.29	4.12	6.26	2.16	2.87	3.46	2.08	2.64
	21-03-2018	422	396	316	673	457	2.93	2.89	2.23	3.91	2.99	3.18	3.68	3.59	2.61	3.27
High-flow	28-09-2017	943	561	328	672	626	18.1	18.4	12.2	37.0	21.4	7.82	13.9	15.9	24.6	15.5
	21-06-2018	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	19-09-2018	N.D.	429	1008	600	679	N.D.	1.00	9.14	4.19	4.78	N.D.	0.90	3.36	2.58	2.28

*No DOC or TDAA data was acquired for 21-Jun-2018 samples due to sample loss.

Table S3. Molecular composition of riverine DOM

Flow condition	Sampling Time	Sites	ESI+			ESI-		
			H/C	O/C	N/C	H/C	O/C	N/C
Base flow	27-05-2016	AR	1.48	0.26	0.09	1.26	0.28	0.07
		LR	1.47	0.25	0.09	1.20	0.30	0.07
		MR	1.47	0.26	0.09	1.24	0.29	0.07
		NR	1.44	0.26	0.09	1.26	0.28	0.07
		Average	1.46	0.26	0.09	1.24	0.29	0.07
	19-07-2016	AR	1.55	0.21	0.06	1.28	0.27	0.07
		LR	1.55	0.22	0.06	1.20	0.30	0.07
		MR	1.54	0.22	0.06	1.31	0.27	0.06
		NR	1.54	0.23	0.06	1.25	0.30	0.08
		Average	1.55	0.22	0.06	1.26	0.29	0.07
	07-10-2016	AR	1.59	0.21	0.07	1.21	0.31	0.07
		LR	1.60	0.21	0.07	1.10	0.33	0.07
		MR	1.61	0.21	0.07	1.17	0.30	0.07
		NR	1.60	0.21	0.07	1.25	0.29	0.07
		Average	1.60	0.21	0.07	1.18	0.31	0.07
	19-06-2017	AR	1.44	0.26	0.07	1.01	0.33	0.08
		LR	1.55	0.24	0.07	1.12	0.33	0.08
		MR	1.48	0.26	0.08	1.00	0.33	0.08
		NR	1.55	0.24	0.07	1.16	0.34	0.09
		Average	1.50	0.25	0.07	1.07	0.33	0.08
	21-03-2018	AR	1.47	0.26	0.06	1.19	0.31	0.09
		LR	1.45	0.27	0.06	1.19	0.32	0.08
		MR	1.48	0.27	0.06	1.17	0.32	0.08
		NR	1.47	0.26	0.06	1.22	0.31	0.09
		Average	1.47	0.27	0.06	1.19	0.32	0.08

Continued

Flow condition	Sampling time	Sites	ESI+			ESI-		
			H/C	O/C	N/C	H/C	O/C	N/C
High flow	28-09-2017	AR	1.53	0.21	0.09	1.09	0.31	0.08
		LR	1.52	0.21	0.10	1.06	0.31	0.08
		MR	1.50	0.21	0.10	1.16	0.32	0.08
		NR	1.48	0.22	0.10	1.19	0.32	0.09
		Average	1.51	0.21	0.10	1.12	0.32	0.08
	21-06-2018	AR	1.57	0.26	0.06	1.05	0.33	0.08
		LR	1.44	0.26	0.06	1.07	0.35	0.08
		MR	1.44	0.25	0.06	1.07	0.33	0.08
		NR	1.49	0.26	0.06	1.10	0.32	0.08
		Average	1.48	0.26	0.06	1.07	0.33	0.08
	19-09-2018	LR	1.56	0.26	0.06	1.04	0.32	0.08
		MR	1.55	0.24	0.06	1.06	0.34	0.09
		NR	1.52	0.26	0.07	0.99	0.35	0.08
		Average	1.55	0.25	0.06	1.03	0.34	0.08

Table S4. Compound categories (%) at base-flow and high-flow (ESI+)

Flow condition	Sampling Time	Lipids	Unsaturated Hydrocarbons	Condensed Aromatic Structures	Proteins	Lignin	Tannins	Carbohydrates	Others
Base flow	27-05-2016	5.19	12.8	6.30	34.8	16.8	1.26	4.85	18.1
	19-07-2016	9.28	13.6	4.91	28.4	18.3	0.78	2.46	22.3
	07-10-2016	6.87	12.5	3.49	36.4	14.8	0.71	2.09	23.2
	19-06-2017	5.21	9.87	5.51	30.2	24.3	0.75	2.91	21.3
	21-03-2018	4.99	10.5	7.98	24.1	25.1	1.26	4.63	21.4
	Average	6.31	11.9	5.64	30.8	19.8	0.95	3.39	21.3
High flow	28-09-2017	8.94	13.2	4.69	28.5	16.8	0.73	2.80	24.3
	21-06-2018	5.88	10.3	5.92	28.6	27.0	0.90	3.47	17.9
	19-09-2018	5.43	9.6	5.33	28.7	23.8	0.91	3.37	22.8
	Average	6.75	11.1	5.31	28.6	22.6	0.85	3.21	21.7

Table S5. Compound aromatic classes (%) at base-flow and high-flow (ESI+)

Flow condition	Sampling Time	Aromatic	Condensed Aromatic	Non-Aromatic
Base flow	27-05-2016	13.27	6.86	79.9
	19-07-2016	8.28	5.16	86.6
	07-10-2016	7.63	3.64	88.7
	19-06-2017	9.04	5.66	85.3
	21-03-2018	9.40	7.45	83.1
	Average	9.52	5.75	84.7
High flow	28-09-2017	7.88	4.99	87.1
	21-06-2018	9.13	5.36	85.5
	19-09-2018	8.38	5.24	86.4
	Average	8.46	5.20	86.3

Table S6. Examples of compounds with higher CCS values than TAA salts (ESI+)

m/z	Formula	H/C	O/C	Category	Aromatic
223.0638	$C_8H_{14}O_5S$	1.75	0.63	Others	Non-aromatic
179.0912	$C_7H_{14}O_5$	2.00	0.71	Carbohydrates	Non-aromatic