An international laboratory comparison of dissolved organic matter composition by high resolution mass spectrometry: Are we getting the same answer?

Supplementary Information

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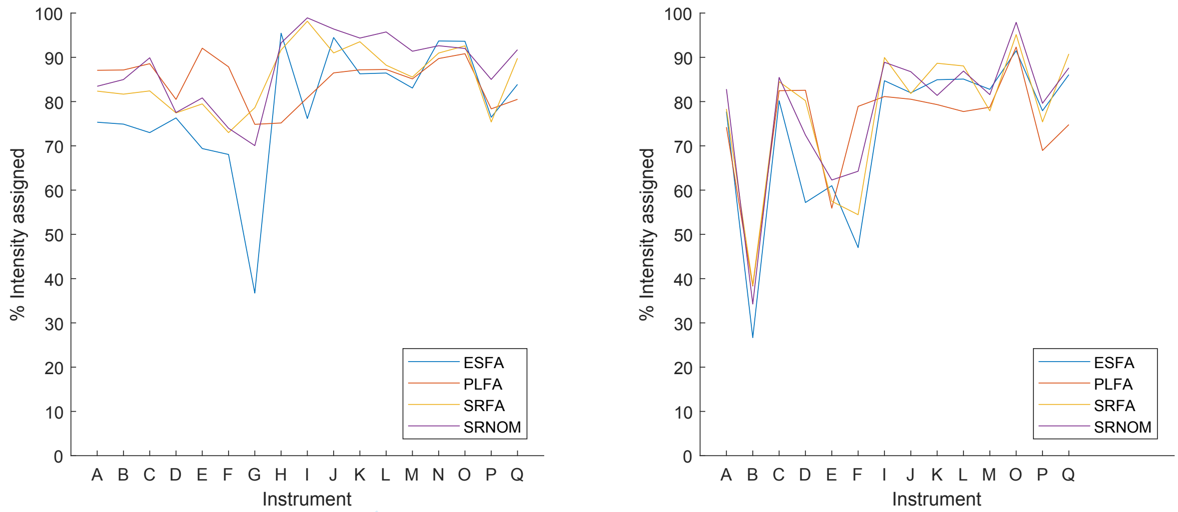

Figure SI1: % Assigned peaks for negative-ion mode (left) and positive-ion (right) modes across the 17 instruments (negative) and 14 instruments (positive). Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM). Instruments are identified by letters A-Q as in the main manuscript.

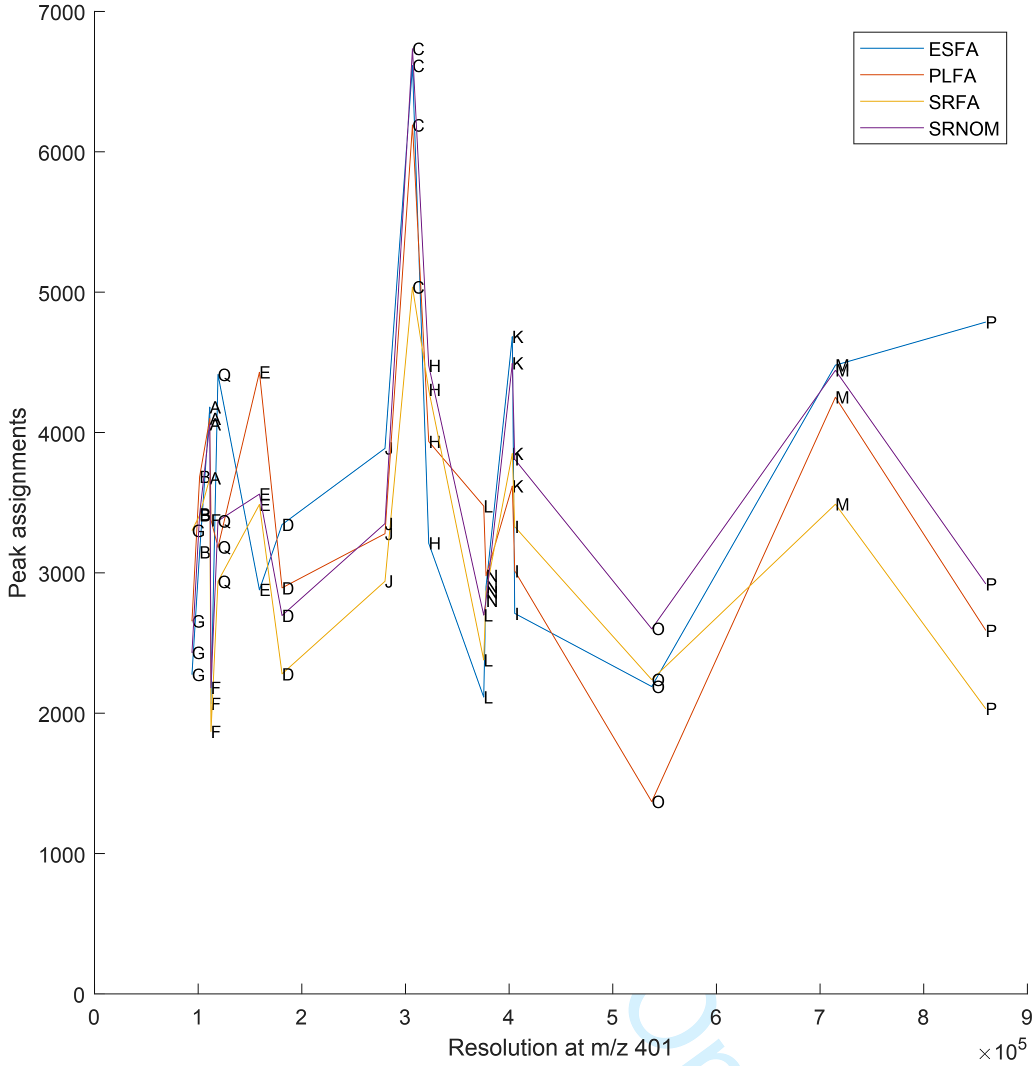

Figure SI2: Total number of assigned peaks in each instrument for the four samples as a function of resolution at *m/z* 401. Greater resolving power did not necessarily lead to a higher number of assigned peaks. Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM). Instruments are identified by letters A-Q as in the main manuscript.

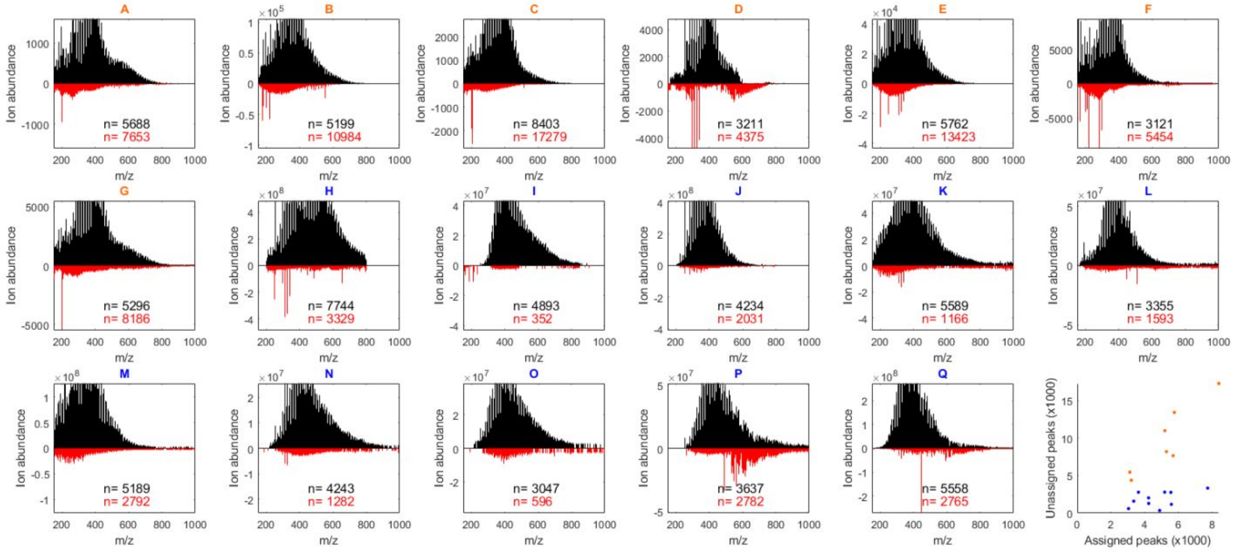

Figure SI3: Assigned peaks (black) vs unassigned peaks (red) in negative-ion mode for Suwannee River Fulvic Acid (SRFA) across all HRMS instruments. The axis is cropped at the 99th percentile to better show the main trends. The last panel is a scatter plot of unassigned versus assigned peak number for each instrument, demonstrating that Orbitraps (orange) have more unassigned peaks than FT-ICR MS (blue) instruments using our assignment constraints, and that the number of assigned and unassigned peaks scale together for each instrument type. Instruments are identified by letters A-Q as in the main manuscript.

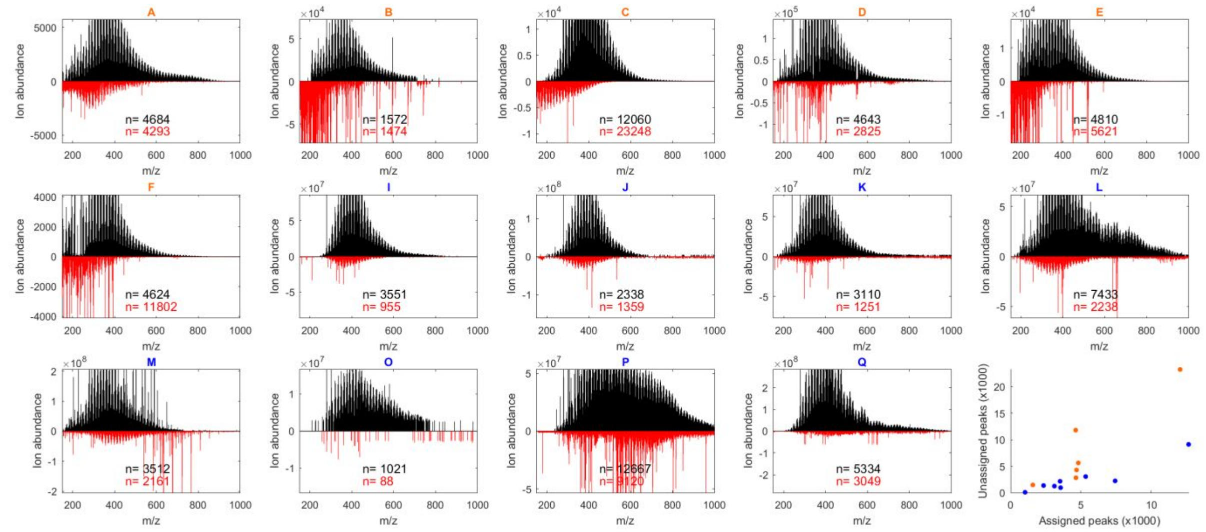

Figure SI4: Assigned peaks (black) vs unassigned peaks (red) in positive-ion mode for Suwannee River Fulvic Acid (SRFA) across all HRMS instruments. The axis is cropped at the

99^{th} percentile to better show the main trends. The last panel is a scatter plot of unassigned versus assigned peak number for each instrument, demonstrating that Orbitraps (orange) have more unassigned peaks than FT-ICR MS (blue) instruments using our assignment constraints, and that the number of assigned and unassigned peaks scale together for each instrument type. Instruments are identified by letters A-Q as in the main manuscript.

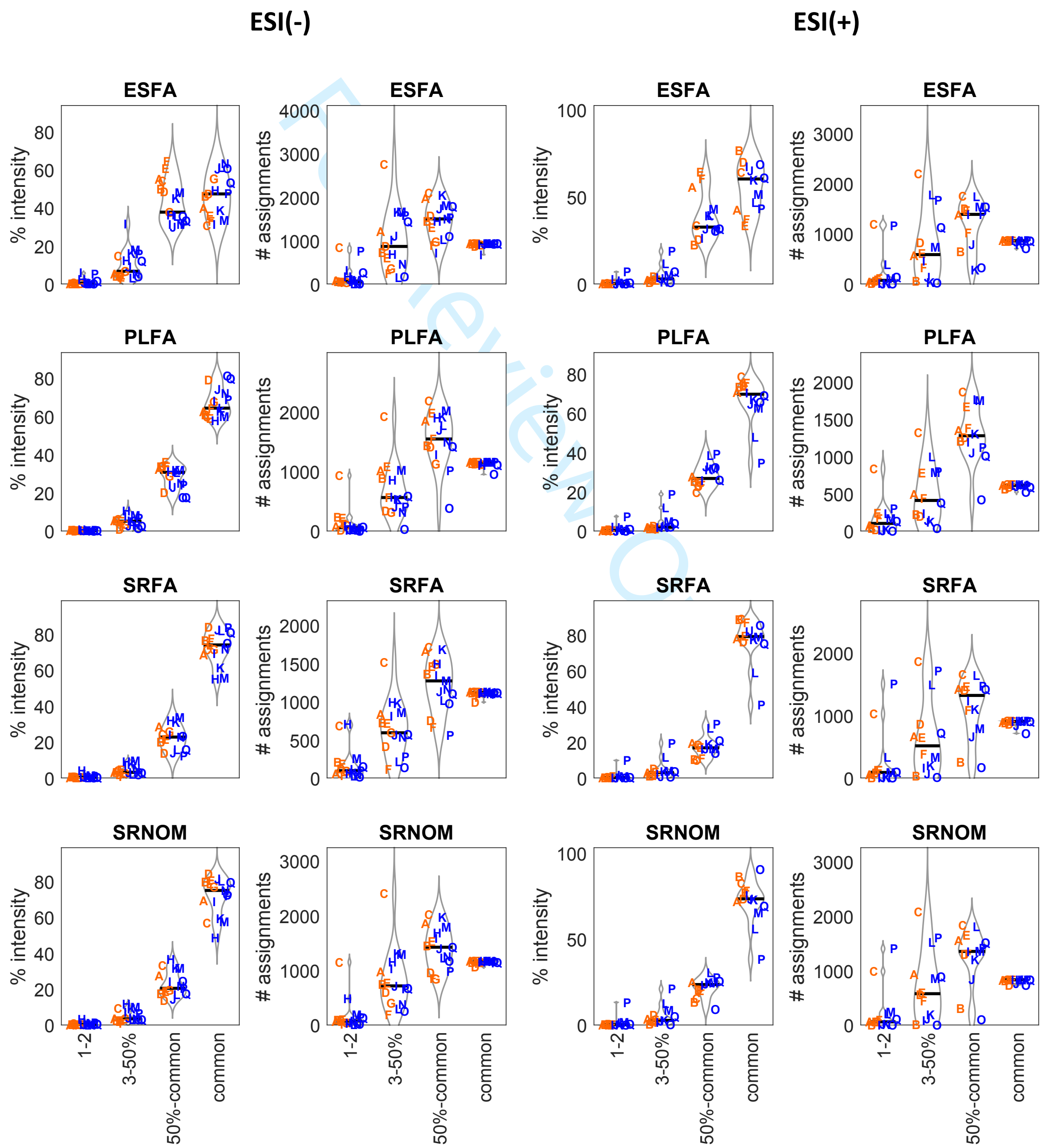

Figure SI5: Violin plots showing the % intensity and number of peaks assigned in different ion categories for negative-ion (left) and positive-ion (right) modes for the four samples. ‘Common’ ions made up the majority (>50%) of intensity in all cases except ESFA. Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM).

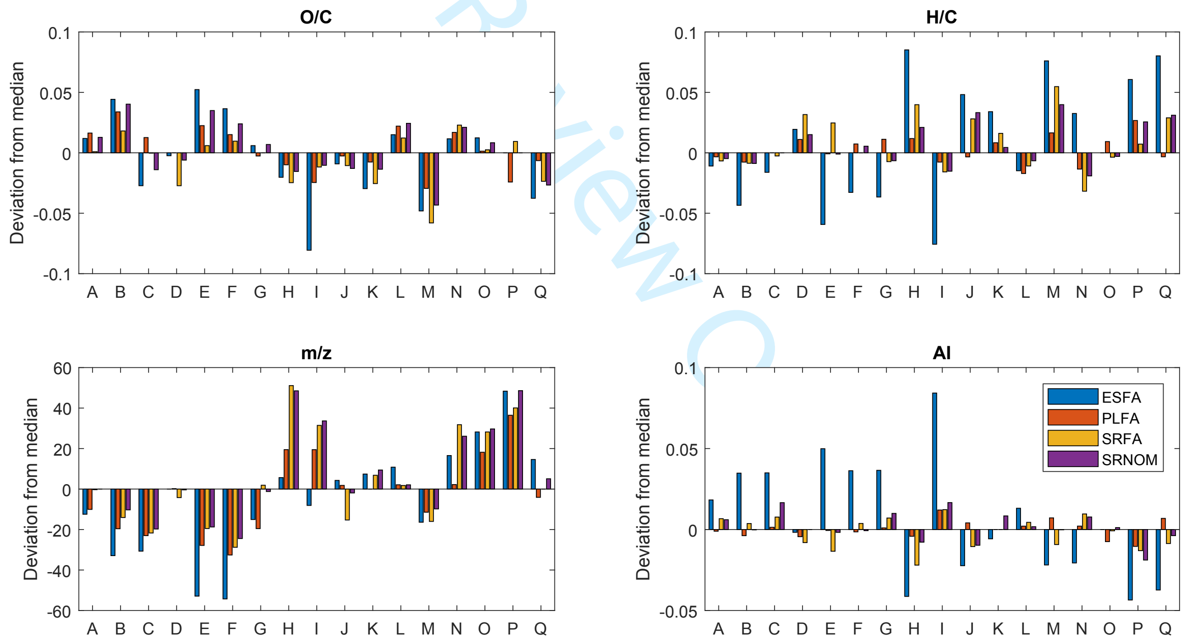

Figure SI6: Following the median deviation graph (Figure 5), this bar chart shows the deviation from the median for each calculated metric across the four samples for each instrument in negative-ion mode. The bars should be a similar height (e.g., instrument L for O/C) if the deviation is reproducible across the four samples. Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM). Instruments are identified by letters A-Q as in the main manuscript.

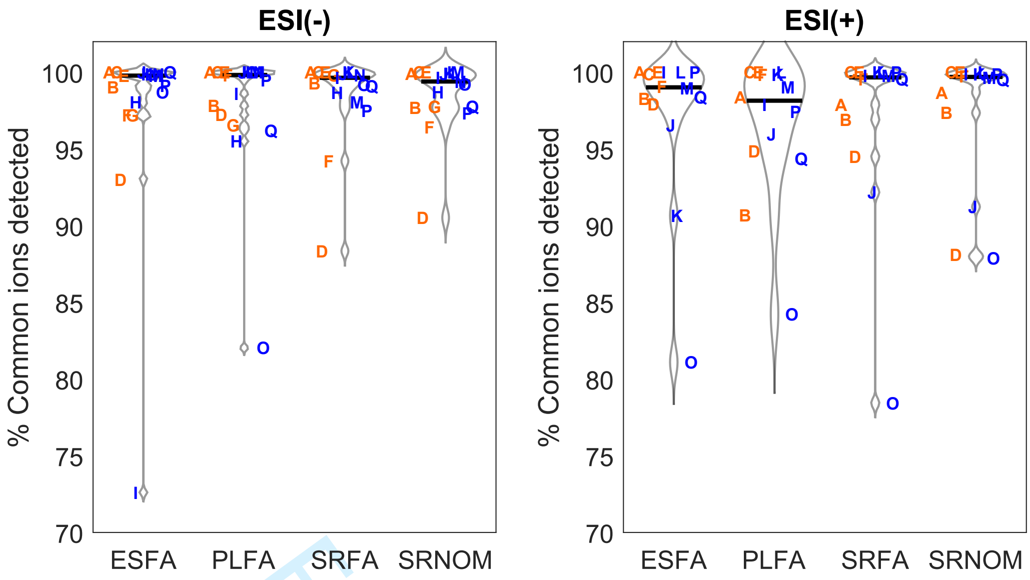

Figure SI7: % Common ions detected by each instrument for the four samples in negative-ion and positive-ion ESI modes. Because common ions are defined as those detected in at least n-1 instruments, it is possible for an instrument to not detect 100%. Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM). Instruments are identified by letters A-Q as in the main manuscript.

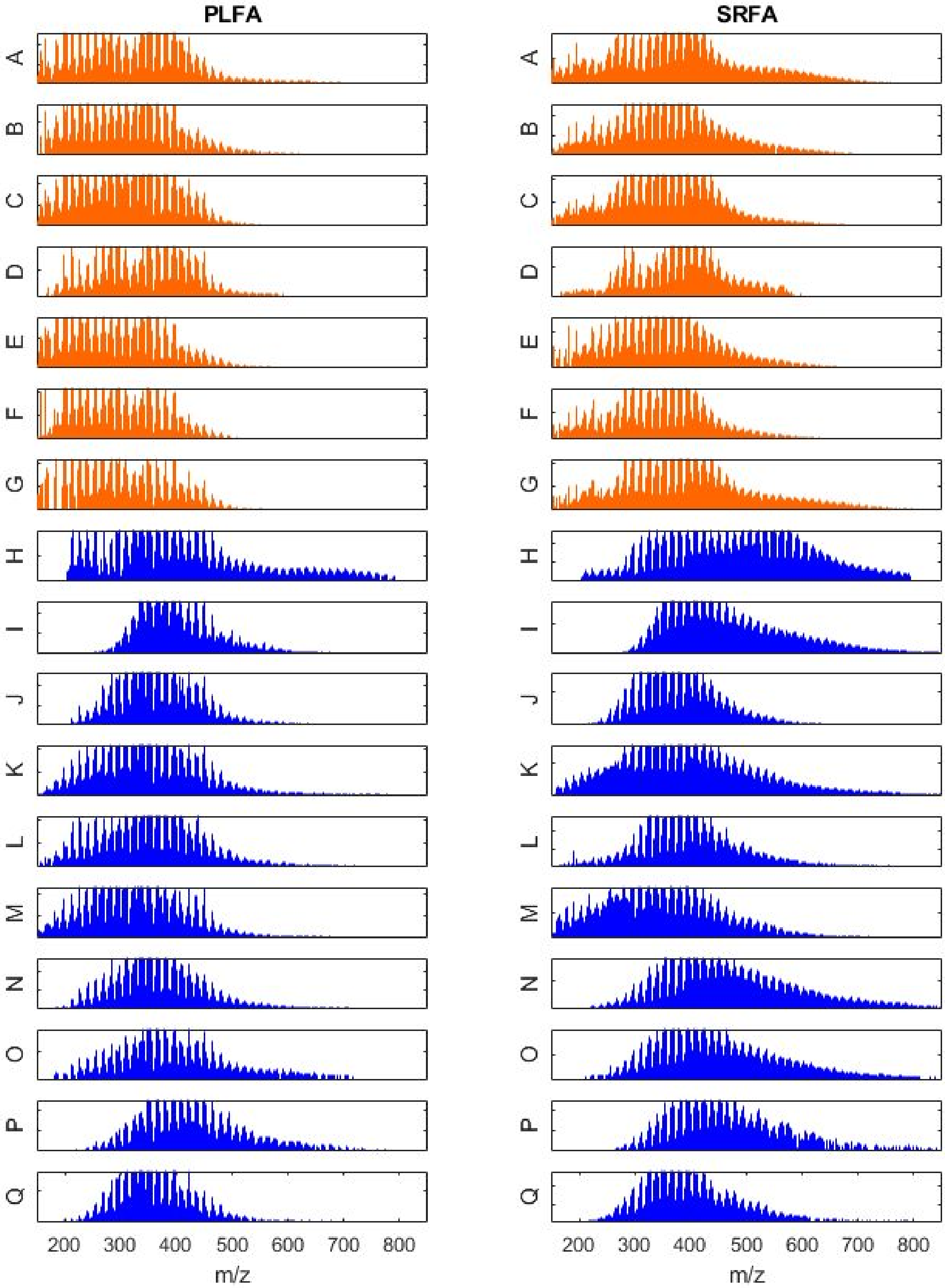

Figure SI8: Mass spectral peaks corresponding to assigned molecular formulas in negative-ion mode for Pony Lake and Suwannee River Fulvic Acids (PLFA and SRFA) across 17 laboratories. The scale on the y axis is normalized intensity, and this is cropped to exclude the most abundant 1% of peaks, so that the bulk distribution can be inspected. Orbitraps are orange and FT-ICRs are blue. Instruments are identified by letters A-Q as in the main manuscript.

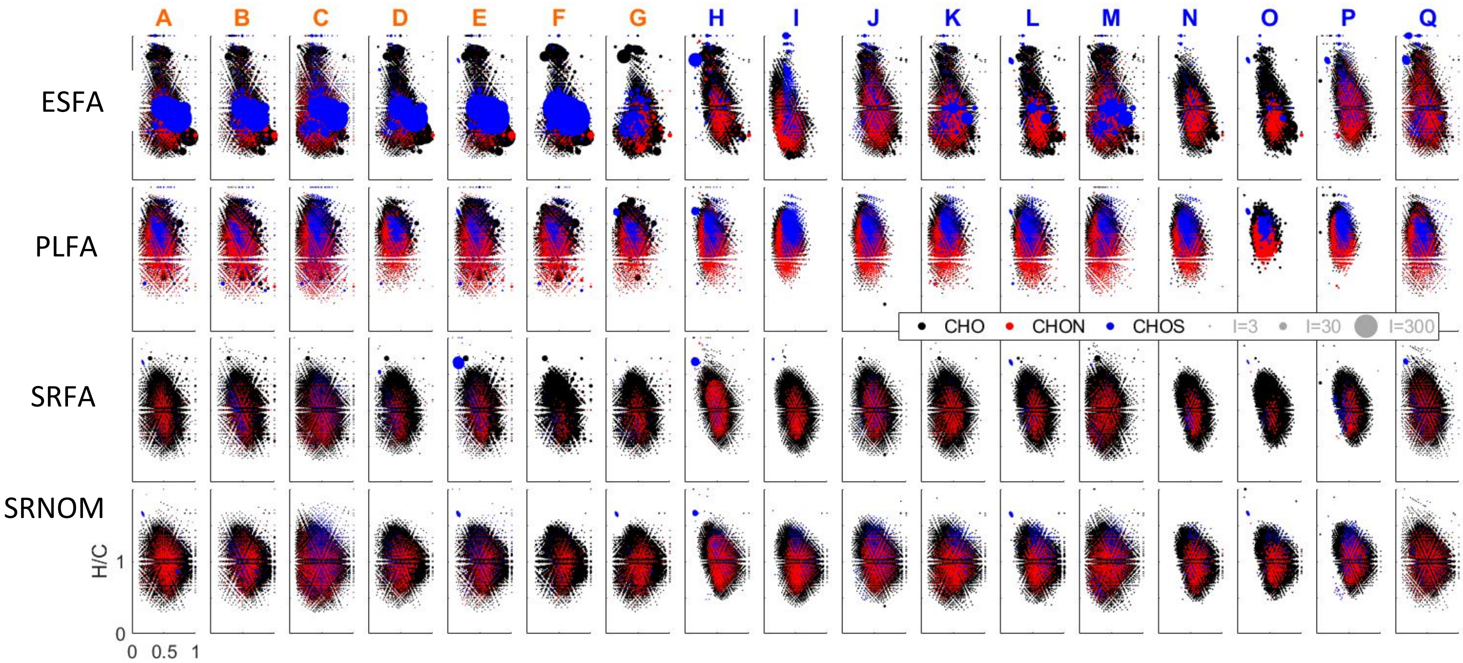

Figure SI9: van Krevelen diagrams (H/C on y-axis, scaled from 0-2 *vs.* O/C on x-axis, scaled from 0-1) for negative-ion mode assignments across 17 instruments analyzing the four samples. Samples included Elliot Soil, Pony Lake, and Suwannee River Fulvic Acids (ESFA, PLFA, and SRFA) and Suwannee River Natural Organic Matter (SRNOM). Formulas containing nitrogen are shown in red and formulas containing sulfur are shown in blue. Relative peak abundance is shown as point size, these sum to 10,000. Orbitraps have orange laboratory labels and FT-ICRs have blue laboratory labels. Instruments are identified by letters A-Q as in the main manuscript.

Table SI1: Elliot Soil Fulvic Acid assigned peak types by instrument *no CHOS in positive mode

ESFA	ESI(-)				ESI(+)			
	CHO	CHON	CHON2	CHOS	CHO	CHON	CHON2	CHOS*
A	2776	914	327	164	2574	209	62	0
B	2033	594	279	243	1473	68	21	0
C	3540	1483	773	819	4386	1251	362	0
D	2378	593	121	252	2766	402	65	0
E	1764	571	222	322	2518	386	115	0
F	1442	365	104	158	1977	265	71	0
G	1596	374	160	145				
H	2587	447	80	97				
I	1688	489	217	317	2199	402	129	0
J	2259	846	411	371	1562	159	50	0
K	3180	971	300	232	1069	16	12	0
L	1617	378	62	58	3922	745	107	0
M	2766	923	465	326	2458	569	213	0
N	2140	528	107	126				
O	1842	294	23	31	1047	1	0	0
P	3008	1075	271	433	3886	1053	146	0
Q	2817	1109	224	263	3053	546	51	0
Common	811	112	1	7	861	2	5	0
Detected≥3	3714	1386	629	580	3983	924	218	0

Table SI2: Pony Lake Fulvic Acid assigned peak types by instrument *no CHOS in positive mode

PLFA	ESI(-)				ESI(+)			
	CHO	CHON	CHON2	CHOS	CHO	CHON	CHON2	CHOS*
A	1719	1177	680	524	1619	706	204	0
B	1667	1034	595	389	1223	600	204	0
C	2546	1651	950	1044	2781	1376	479	0
D	1195	854	511	333	1358	539	163	0
E	1815	1232	767	615	1970	991	343	0
F	1320	995	596	466	1588	800	221	0
G	1022	795	497	341				
H	1646	1120	593	577				
I	1256	800	444	514	1108	627	314	0
J	1348	900	571	460	978	511	303	0
K	1529	1012	576	501	1243	562	253	0
L	1438	952	548	538	2245	1086	284	0
M	1762	1173	711	605	1876	1024	420	0
N	1308	840	387	444				
O	801	343	127	99	840	137	5	0
P	1159	725	355	351	1924	748	148	0
Q	1438	927	412	406	1435	550	118	0

Common	555	359	176	68	493	128	1	0
Detected≥3	2259	1484	858	845	2438	1255	427	0

Table SI3: Suwannee River Fulvic Acid assigned peak types by instrument *no CHOS in positive mode

SRFA	ESI(-)				ESI(+)			
	CHO	CHON	CHON2	CHOS	CHO	CHON	CHON2	CHOS*
A	3141	447	48	39	2909	107	6	0
B	2696	373	166	177	1162	8	2	0
C	3490	997	117	432	4339	930	184	0
D	1822	186	161	111	2952	256	1	0
E	2602	523	140	222	2813	298	34	0
F	1705	105	22	38	2241	224	31	0
G	2913	243	96	49				
H	3234	916	39	115				
I	2911	397	9	12	2151	154	0	0
J	2193	461	117	169	1479	91	6	0
K	3346	465	22	17	2075	128	2	0
L	2054	255	20	50	4027	337	2	0
M	2796	548	84	61	1940	179	5	0
N	2529	282	5	48				
O	2152	71	2	14	892	0	0	0
P	1659	256	11	105	4621	957	15	0
Q	2301	499	7	132	2897	235	10	0
Common	1099	26	0	0	909	0	0	0
Detected≥3	3771	837	163	279	4273	505	5	0

Table SI4: Suwannee River Natural Organic Matter assigned peak types by instrument *no CHOS in positive mode

SRNOM	ESI(-)				ESI(+)			
	CHO	CHON	CHON2	CHOS	CHO	CHON	CHON2	CHOS*
A	3028	800	157	73	3072	256	34	0
B	2465	544	222	186	1111	20	2	0
C	3756	1480	593	905	4341	1096	290	0
D	1872	437	239	148	2416	221	10	0
E	2364	643	228	326	2693	356	78	0
F	1754	304	77	47	2352	283	44	0
G	1827	413	154	36				
H	3128	1034	118	197				
I	2834	694	131	150	2017	223	21	0
J	2120	681	231	319	1518	180	34	0
K	3264	818	184	227	1979	233	21	0
L	1924	452	121	202	3803	522	40	0
M	3012	868	281	282	2560	532	191	0

N	2244	442	34	83				
O	2193	316	22	70	835	0	0	0
P	2040	533	86	262	4263	945	47	0
Q	2534	675	39	122	2918	396	21	0
Common	1034	135	2	0	831	2	0	0
Detected≥3	3726	1232	383	569	4219	700	125	0