Supporting Information

How Representative Are Dissolved Organic Matter (DOM) Extracts?

A Comprehensive Study of Sorbent Selectivity for DOM Isolation

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Table S1. Properties of SPE sorbents

sorbent	category	functional group	Size (mg)	carbon loading (%)	mean pore size (Å)	particle size (µm) and shape	end-capped
2OH	polar	diol/silica based	100	6.8	60	40, irregular	no
C1	very weakly non-polar	methyl/silica based	100	4.1	60	40, irregular	yes
C2	weakly non-polar	ethyl/silica based	100	5.6	60	40& 120, irregular	yes
C8	moderately non-polar	octyl/silica based	100	12.2	60	40& 120, irregular	yes
C18	strongly non-polar	trifunctional octadecyl/silica based	100	17.4	60	40 & 120, irregular	yes
C18OH	moderately non-polar, significant polar interactions	octadecyl/silica based	100	14.9	150	40 & 120, irregular	no
CBA	mid-polar, weak cation exchange	carboxylic acid/silica based	100	7.4	60	40, irregular	yes
CH	moderately non-polar	cyclohexyl/silica based	100	9.6	60	40 & 120, irregular	yes
CN-E	medium polar, weak non-polar	cyanopropyl/silica based	100	8.1	60	40-120, irregular	yes
CN-U	medium polar, weak non-polar	cyanopropyl/silica based	100	7.8	60	40-120, irregular	no
DPA-6S	reversed phase (polar)	polyamide/polymer	100	n.a.		50-160	-
ENV	non-polar	styrene divinybenzene/polymer	100	n.a.	450	125, spherical	-
HLB	non-polar	divinylbenzene/polymer, N-vinylpyrrolidone	60	n.a.	80	30	-
MAX	mixed mode, strong anion exchange	divinylbenzene, CH_2NR_3, poly(divinylbenzene-co-N-vinylpyrrolidone)	60	n.a.	80	30	-
MCX	mixed mode, strong cation exchange	divinylbenzene, sulfonic acid group, poly(divinylbenzene-co-N-vinylpyrrolidone)	60	n.a.	80	30	-
NH2	polar, weak anion exchange	aminopropyl/silica based	100	6.7	60	40, irregular	no
PH	moderately non-polar	phenyl/silica based	100	10.7	60	40-120, irregular	yes
PPL	non-polar	functionalized styrene divinybenzene	100	n.a.	150	125, spherical	yes
SAX	strong anion exchange	trimethylaminopropyl/silica based	100	7.5	60	40, irregular	no
SCX	strong cation exchange	benzenesulfonic acid/silica based	100	10.9	60	40-120, irregular	no
SI	strongly polar	native silica/silica based	100	n.a.	60	40, irregular	no
Strata™-X-C	mixed mode, strong cation exchange	sulfonic acid/polymer	100	n.a.	n.a.	33	-
WAX	mixed mode, weak anion exchange	divinylbenzene	60	n.a.	80	30	-
WCX	mixed mode, weak cation exchange	divinylbenzene,	60	n.a.	80	30	-

Table S2. Counts of mass peaks as computed from FT-ICR MS data of SR DOM extracts for singly charged ions.

SPE cartridges	CHO	CHOS	CHNO	CHNOS	Σ (*)	H_a [%]	C_a [%]	O_a [%]	N_a [%]	S_a [%]	H/C ratio	O/C ratio	average intensity	DBE_a	$(DBE/C)_a$	$(m/z)_a$
2OH	191	41	19	8	258	7.68	65.35	22.25	0.80	3.92	1.41	0.26	4471606	6.3	0.30	355.0
C1	920	46	79	13	1058	6.31	61.14	31.60	0.19	0.76	1.24	0.39	6244875	8.2	0.40	394.3
C2	887	56	95	11	1049	6.29	61.17	31.57	0.17	0.79	1.23	0.39	7082693	8.2	0.40	394.0
C8	1209	97	277	12	1595	5.76	59.02	34.53	0.21	0.48	1.17	0.44	8568421	8.5	0.44	393.0
C18	1368	142	373	11	1894	5.50	58.15	35.65	0.23	0.46	1.14	0.46	9701574	8.8	0.46	395.7
C18OH	1349	115	364	9	1837	5.49	57.88	35.92	0.25	0.45	1.14	0.47	9273357	8.6	0.46	390.0
CBA	1031	70	116	7	1224	6.20	60.84	32.11	0.16	0.70	1.22	0.40	6773088	8.3	0.41	395.4
CH	1191	84	244	9	1528	5.76	59.01	34.49	0.20	0.54	1.17	0.44	8455181	8.6	0.44	394.6
CN-E	660	36	25	11	732	6.63	63.08	28.74	0.23	1.31	1.26	0.34	4238305	8.1	0.39	388.9
CN-U	524	30	26	16	596	7.07	62.69	27.25	0.49	2.50	1.35	0.33	3664798	6.8	0.34	368.4
DPA-6S	1073	105	129	4	1311	5.74	58.32	34.82	0.56	0.55	1.18	0.45	7984887	8.8	0.46	391.7
ENV	1227	125	260	8	1620	5.50	58.21	35.62	0.21	0.46	1.13	0.46	8584892	9.3	0.49	388.8
HLB	1336	154	350	12	1852	5.42	57.57	36.32	0.22	0.47	1.13	0.47	9787625	8.7	0.46	388.1
MAX	1242	114	341	9	1706	5.55	57.62	36.12	0.23	0.48	1.16	0.47	10413927	8.4	0.45	387.6
MCX	1151	89	233	10	1483	5.88	59.26	34.04	0.20	0.62	1.19	0.43	8623018	8.3	0.43	388.5
NH2	31	32	13	5	81	8.43	67.28	19.20	1.19	3.90	1.50	0.21	2802192	5.3	0.26	341.3
PH	1135	89	235	8	1467	6.12	60.21	32.67	0.20	0.80	1.22	0.41	8323500	8.2	0.41	393.2
PPL	1335	179	366	9	1898	5.47	57.75	36.02	0.25	0.51	1.14	0.47	9201721	8.7	0.46	392.6
SAX	403	40	32	18	493	7.06	62.47	27.05	0.63	2.79	1.36	0.32	3715928	6.6	0.34	363.2
SCX	187	34	8	10	239	7.31	63.44	22.90	1.09	5.26	1.38	0.27	9151084	6.2	0.34	340.5
SI	367	43	24	9	443	7.25	62.91	26.40	0.53	2.90	1.38	0.31	3571828	6.5	0.33	364.9
Strata XC	1140	76	214	12	1442	5.97	59.82	33.41	0.23	0.57	1.20	0.42	7614210	8.2	0.43	384.6
WAX	1275	129	331	10	1745	5.40	57.18	36.74	0.23	0.45	1.13	0.48	9678118	8.6	0.46	390.2
WCX	1171	80	244	6	1501	5.89	59.15	34.17	0.22	0.57	1.20	0.43	8337589	8.2	0.43	387.4

(*) total number of assigned mass peaks

Table S3. Counts of mass peaks as computed from FT-ICR MS data of NS DOM extracts for singly charged ions.

SPE cartridges	CHO	CHOS	CHNO	CHNOS	Σ (*)	H_a [%]	C_a [%]	O_a [%]	N_a [%]	S_a [%]	H/C ratio	O/C ratio	average intensity	DBE_a	$(DBE/C)_a$	$(m/z)_a$
2OH	132	72	64	18	286	8.57	64.94	20.28	1.56	4.65	1.58	0.23	5246668	4.5	0.22	341.1
C1	718	92	123	27	960	7.40	64.12	26.17	0.80	1.50	1.38	0.31	4774477	6.7	0.32	369.2
C2	900	127	303	19	1349	6.63	61.32	30.84	0.47	0.73	1.30	0.38	6077560	7.6	0.37	389.9
C8	1254	399	949	42	2644	6.14	58.98	33.03	0.95	0.91	1.25	0.42	8571800	7.8	0.41	386.7
C18	1274	458	1036	47	2815	6.01	58.47	33.58	1.00	0.93	1.23	0.43	9139953	7.8	0.42	386.8
C18OH	1309	435	993	38	2284	6.12	58.85	33.11	0.99	0.94	1.25	0.42	8528194	7.7	0.41	383.3
CBA	714	101	104	21	940	7.13	62.54	28.29	0.51	1.53	1.37	0.34	4755935	6.9	0.33	382.2
CH	1178	350	830	37	2395	6.16	59.31	32.95	0.80	0.78	1.25	0.42	8322768	7.9	0.41	391.4
CN-E	291	67	77	27	462	8.29	62.88	22.89	1.48	4.46	1.58	0.27	4442221	4.5	0.22	345.7
CN-U	280	87	68	21	456	8.35	62.11	23.47	1.10	4.97	1.61	0.28	4543800	4.0	0.20	342.3
DPA-6S	370	67	94	21	552	7.37	62.63	25.29	2.30	2.40	1.41	0.30	3656535	6.2	0.32	364.3
ENV	1169	390	929	35	2523	5.85	58.04	34.15	1.12	0.84	1.21	0.44	7642038	8.0	0.43	384.5
HLB	1231	461	1068	47	2807	5.74	57.50	34.53	1.26	0.97	1.20	0.45	8740834	8.0	0.44	382.6
MAX	1205	244	930	36	2415	5.91	58.66	33.91	0.91	0.61	1.21	0.43	8973866	8.1	0.43	384.9
MCX	1204	316	825	31	2376	6.05	58.93	33.31	0.87	0.84	1.23	0.42	8243136	7.8	0.42	381.0
NH2	35	40	23	14	112	7.51	62.42	21.36	2.16	6.55	1.44	0.26	3987440	5.9	0.30	358.0
PH	880	146	393	38	1457	6.49	61.34	30.58	0.75	0.84	1.27	0.37	5832630	7.8	0.39	386.8
PPL	1228	468	1121	69	2886	5.65	57.01	34.98	1.45	0.92	1.19	0.46	8391180	8.1	0.44	382.6
SAX	192	57	62	21	332	8.24	65.03	21.74	1.45	3.54	1.52	0.25	4110567	5.2	0.25	349.6
SCX	486	142	88	27	743	10.42	72.61	14.29	0.49	2.19	1.72	0.15	18280711	3.1	0.16	308.1
SI	45	28	36	23	132	7.48	60.18	23.29	2.57	6.48	1.49	0.29	3523599	5.7	0.28	360.9
Strata XC	1200	239	696	26	2161	6.30	60.31	31.77	0.84	0.79	1.25	0.40	7380022	7.6	0.40	373.4
WAX	889	127	523	26	1565	6.02	59.06	33.25	0.88	0.79	1.22	0.42	6139175	7.9	0.42	379.4
WCX	1201	331	824	30	2386	6.05	59.17	33.10	0.85	0.82	1.23	0.42	8356873	7.9	0.42	381.9

(*) total number of assigned mass peaks

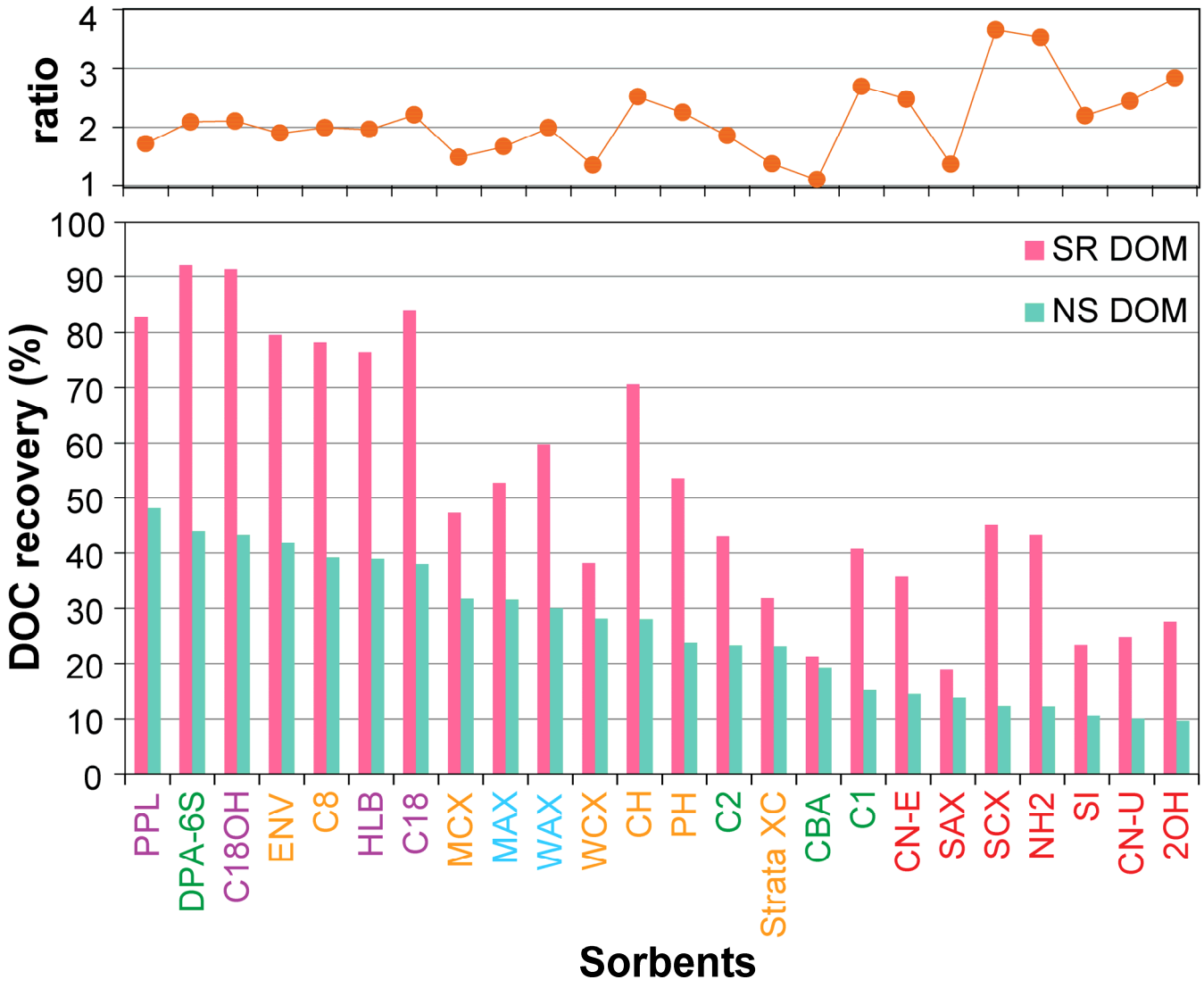

Figure S1. DOC recoveries of DOM extracts obtained with 24 commercially available sorbents. The ratio was calculated with DOC recovery of SR DOM / DOC recovery of NS DOM. Purple: non-polar; blue: mixed mode with anion exchange; orange: moderately non-polar and mixed mode with cation exchange; green: weekly non-polar and mid-polar; red: polar and strong ion exchange.

Table S4. ^{1}H NMR (800 MHz, CD_3OD, 283K) section integrals of SR DOM and NS DOM.

δ(^{1}H) [ppm]	**key substructures**	**SR DOM**	**NS DOM**
10.0 - 7.0 ppm	$C_{ar}\underline{H}$	5.1	3.2
7.0 - 5.1 ppm	$=C\underline{H}$, $O_2C\underline{H}$	5.6	3.0
4.9 - 3.1 ppm	$OC\underline{H}$	25.8	27.2
3.1 - 1.9 ppm	$OCC\underline{H}$	33.3	28.8
1.9 - 0.5 ppm	$CCC\underline{H}$	30.2	37.8

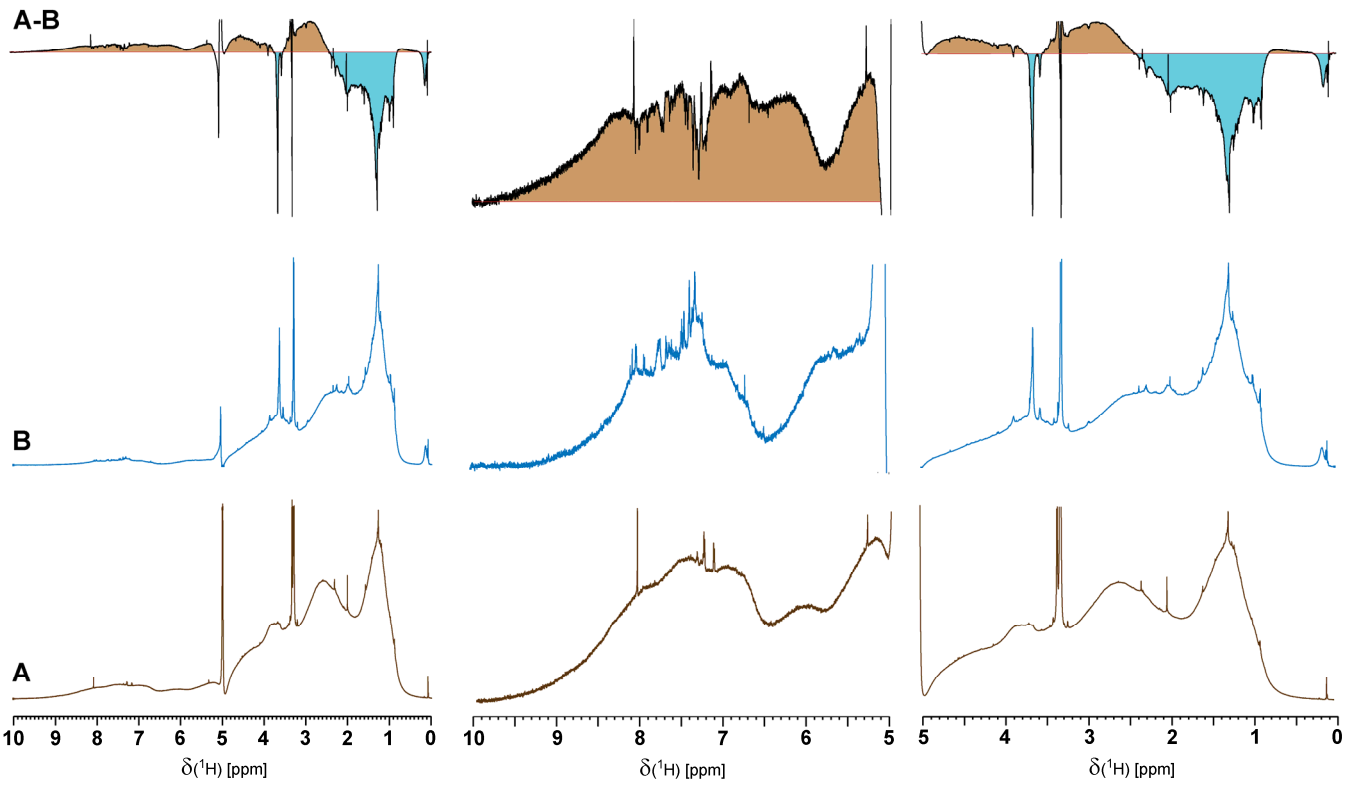

Figure S2. ^{1}H NMR spectra (800 MHz, CD_3OD, 283K) of (panel A) Suwannee River DOM (SR DOM) and (panel B) North Sea DOM (NS DOM), together with (panel A-B) manual difference NMR spectrum [up (brown color): SR DOM > NS DOM; down (blue color) NS DOM > SR DOM].

As shown by NMR section integrals (Table S4) and difference NMR spectra, NS DOM showed higher aliphaticity than SR DOM whereas unsaturated chemical environments (C_{sp2}**H**) were comparatively less abundant in NS DOM. This referred to all chemical environments in the chemical shift range δ_H ~ 10 – 5 ppm, i.e. aromatic and olefin protons as well as O_2C**H** units. Non-functionalized (δ_H < 1.9 ppm) as well as aliphatic carboxylic acids (δ_H ~ 2.1-2.4 ppm) were comparatively more common in NS DOM, whereas typical CRAM (δ_H > 2.4 ppm) were more prevalent in SR DOM, indicating more abundant aromatic carboxylic acids. The rather sharp NMR resonance at δ_H ~ 3.7 ppm in NS DOM may have resulted from scavenging of reactive CHOS compounds by methanol, forming aliphatic methyl esters.

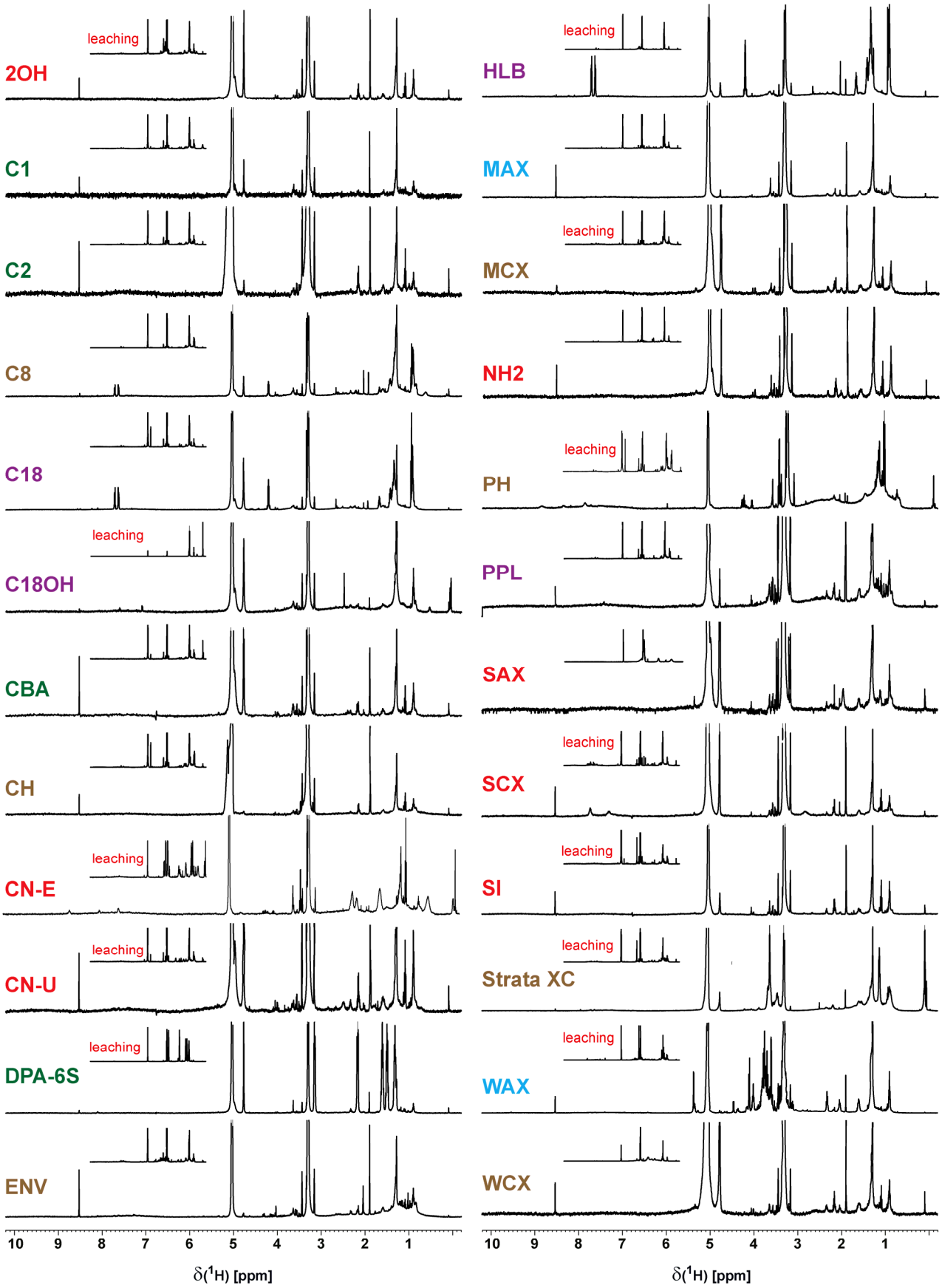

Figure S3. ^{1}H NMR spectra (500 MHz, CD_3OD) of SR SPE-DOM extracts obtained with different cartridges. The spectra of blanks were shown on the left of each extract.

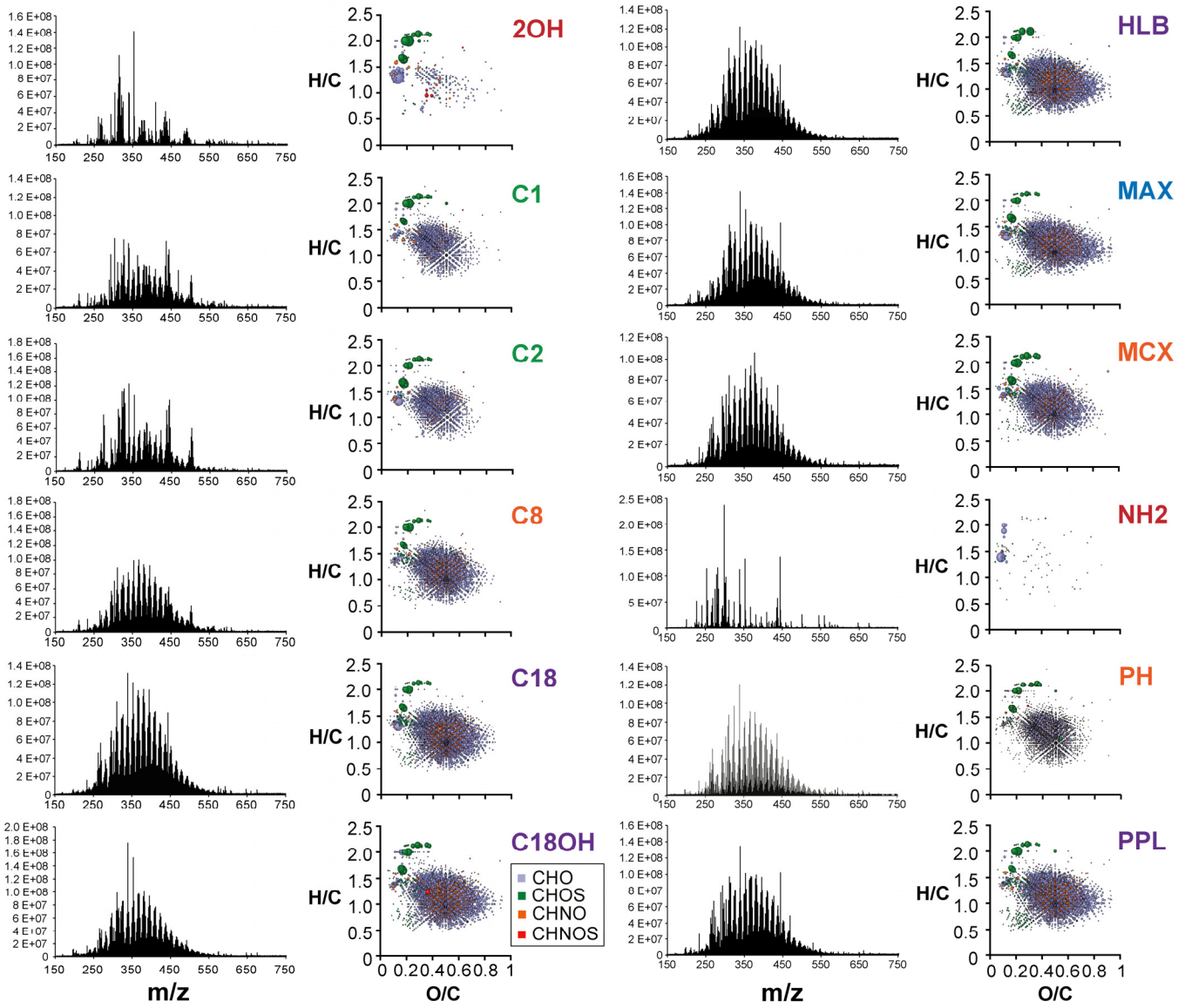

Figure S4. Negative ESI FTICR mass spectra (left) and (right) van Krevelen diagrams of SR SPE-DOM extracts obtained with different cartridges. Purple: non-polar; blue: mixed mode with anion exchange; orange: moderately non-polar and mixed mode with cation exchange; green: weekly non-polar and mid-polar; red: polar and strong ion exchange.

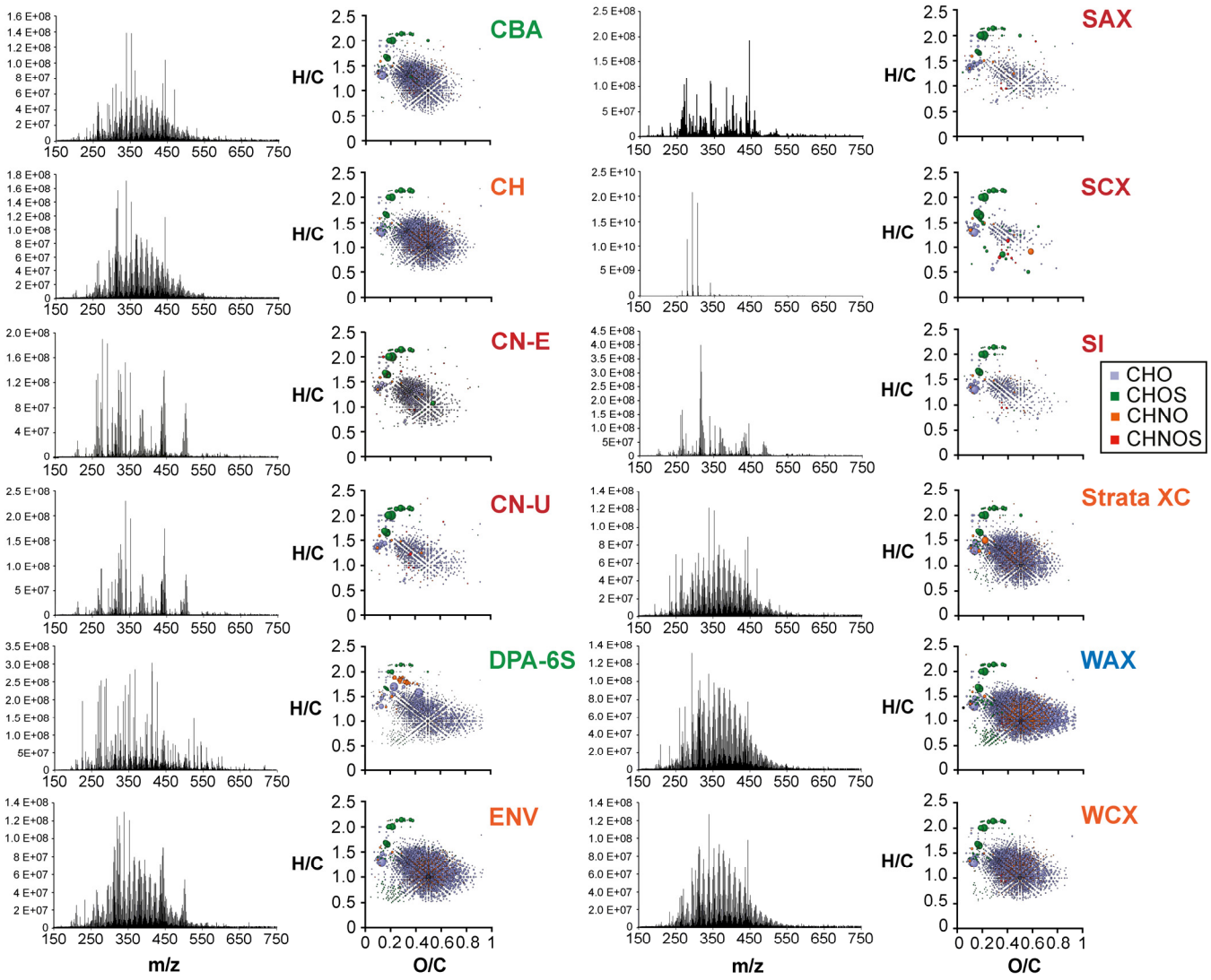

Figure S5. Negative ESI FTICR mass spectra (left) and (right) van Krevelen diagrams of SR SPE-DOM extracts obtained with different cartridges. Purple: non-polar; blue: mixed mode with anion exchange; orange: moderately non-polar and mixed mode with cation exchange; green: weekly non-polar and mid-polar; red: polar and strong ion exchange.

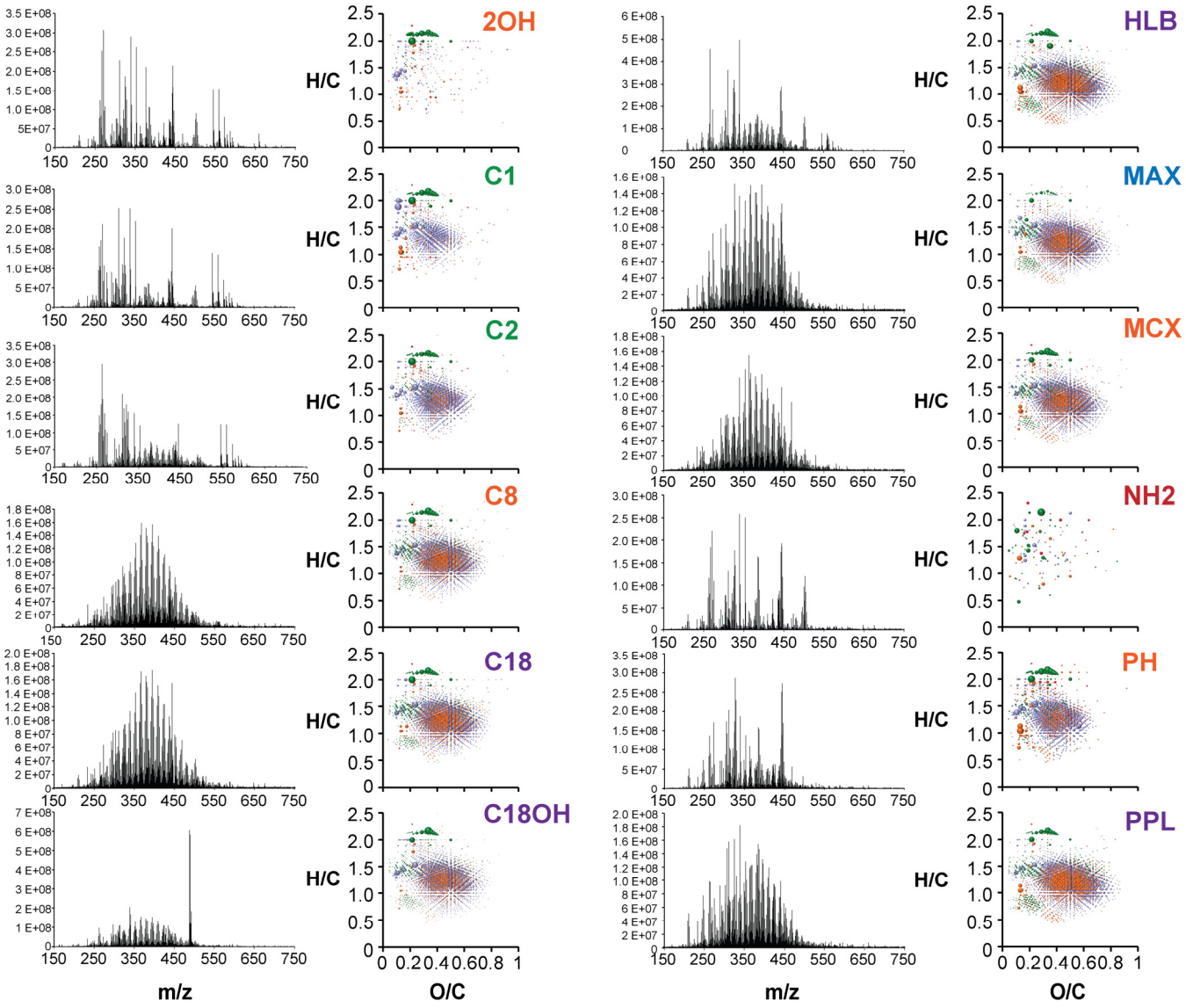

Figure S6. Negative ESI FTICR mass spectra (left) and (right) van Krevelen diagrams of NS SPE-DOM extracts obtained with different cartridges. Purple: non-polar; blue: mixed mode with anion exchange; orange: moderately non-polar and mixed mode with cation exchange; green: weekly non-polar and mid-polar; red: polar and strong ion exchange.

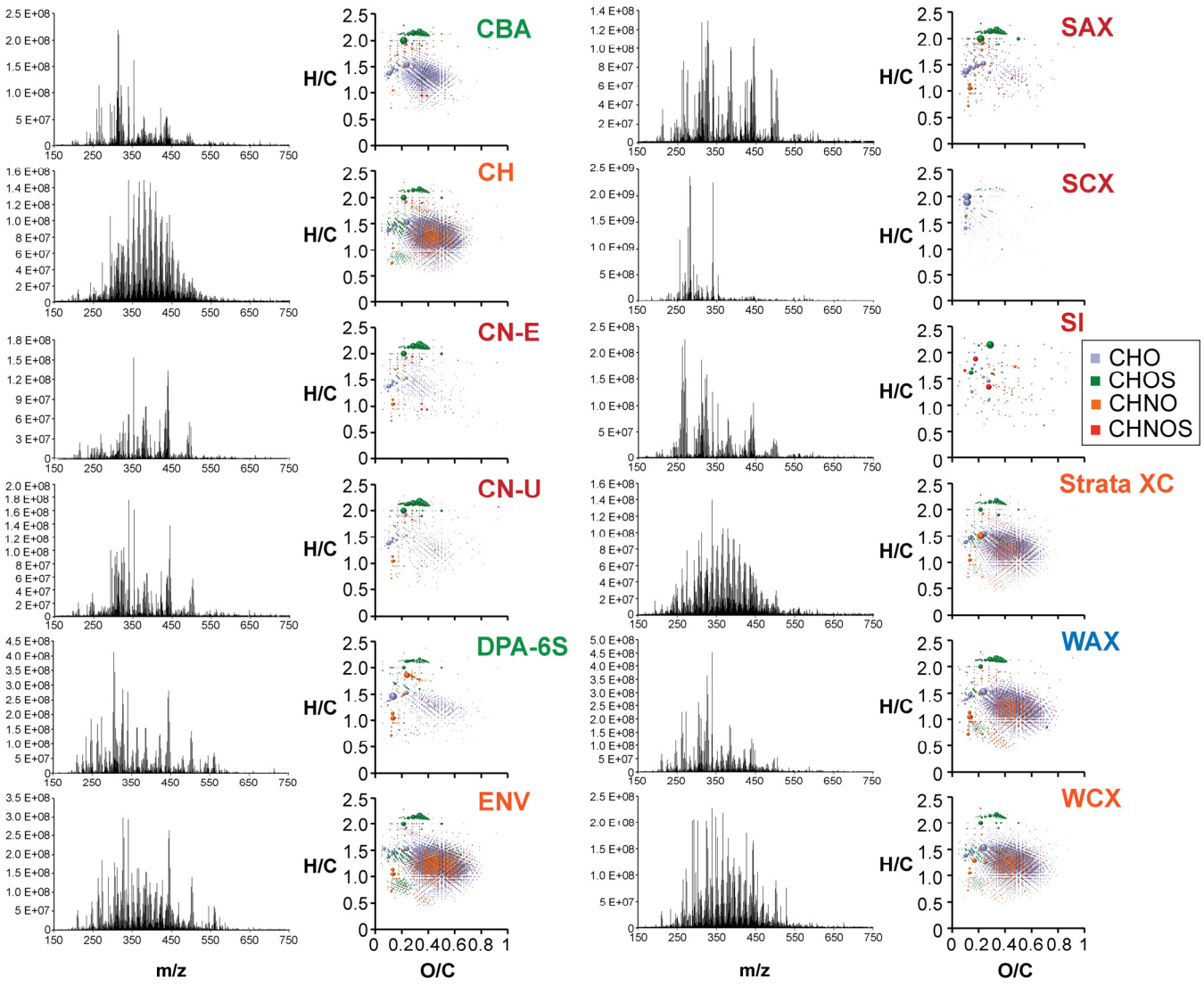

Figure S7. Negative ESI FTICR mass spectra (left) and (right) van Krevelen diagrams of NS SPE-DOM extracts obtained with different cartridges. Purple: non-polar; blue: mixed mode with anion exchange; orange: moderately non-polar and mixed mode with cation exchange; green: weekly non-polar and mid-polar; red: polar and strong ion exchange.

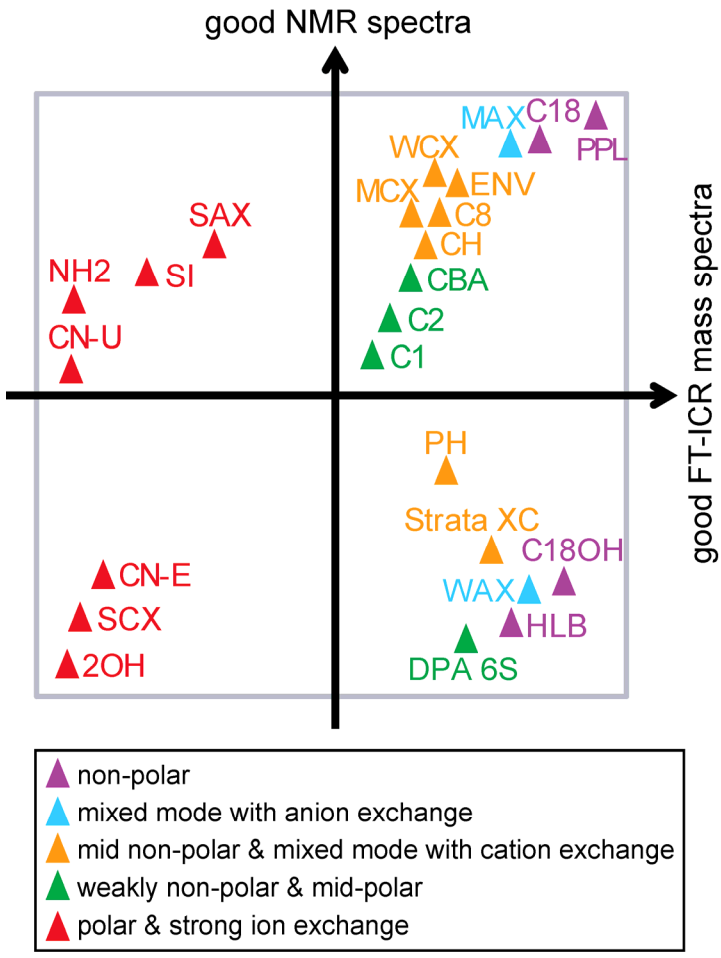

Figure S8. Quality assessment of solid-phase extraction (SPE) as deduced from FT-ICR mass spectra (horizontal axis: count of assigned molecular formulas and absence of obvious leachate molecules) and NMR spectra (vertical axis: proportions of leachate molecules). The first quadrant presents SPE sorbents with both satisfactory FT-ICR mass spectra and NMR spectra; the second quadrant presents the sorbents with few signals in FT-ICR mass spectra and virtual absence of leaching behavior in NMR spectra; the third quadrant presents sorbents with FT-ICR mass spectra and NMR spectra dominated by leachate molecules; the fourth quadrant presents the sorbents with inconspicuous FT-ICR mass spectra but leaching behavior in NMR spectra.