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Impact of biogenic secondary organic aerosol (SOA) loading on the molecular composition of wintertime $PM_{2.5}$ in urban Tianjin: an insight from Fourier transform ion cyclotron resonance mass spectrometry

Shujun Zhong et al.

Correspondence to: Pingqing Fu (fupingqing@tju.edu.cn)

Table S1. The elemental composition criteria of molecular formula classification (Merder et al., 2020;Šantl-Temkiv et al., 2013;Coward et al., 2019).

Classification	Classification	AI_{mod}	H/C	O/C
Polycyclic aromatic hydrocarbons	O-rich	>0.66	-	>0.5
(PAHs-like)	O-poor	>0.66		≤0.50
Polyphenols and PAHs with alphatic chains	O-rich	0.50-0.66	-	>0.50
(Polyphenols-like)	O-poor	0.50-0.66	-	≤0.50
Highly unsaturated and phenolics formulae	O-rich	<0.50	<1.5	>0.50
(Phenols-like)	O-poor	<0.50	<1.5	≤0.50
Unsaturated aliphatic compounds	O-rich	<0.50	1.5-2.0	>0.50
(Aliphatics-like)	O-poor	<0.50	1.5-2.0	≤0.50
Carbohydrates, saturated fatty and sulfonic acids, carbohydrates		<0.50	2.0-2.5	-
(Carbohydrates-like)				

Table S2. The number of formulas in each subgroup, the molecular weight, average values of elemental ratios, double bond equivalents (DBE), and aromaticity index (AI_{mod}).

Sample ID	Elemental composition	Number	MW_w	O/C_w	H/C_w	OM/OC_w	DBE_w	$AImod_{,w}$
High SOA-loading - D	CHO	1154	323	0.38	1.19	1.60	7.86	0.35
	CHON	1254	346	0.44	1.05	1.76	9.44	0.41
	CHOS	1635	360	0.43	1.80	1.90	2.56	0.02
	CHONS	1869	386	0.63	1.72	2.27	3.67	0.02
	Total	5912	332	0.47	1.69	1.95	3.64	0.07
High SOA-loading - N	CHO	1820	322	0.35	1.29	1.58	7.05	0.29
	CHON	2513	326	0.44	1.12	1.79	8.33	0.37
	CHOS	1194	333	0.49	1.78	2.00	2.54	0.02
	CHONS	1432	352	0.72	1.75	2.44	3.15	0.01
	Total	6959	334	0.51	1.56	1.98	4.58	0.13
Moderate SOA-loading - D	CHO	596	326	0.40	0.99	1.62	9.53	0.45
	CHON	272	356	0.44	0.92	1.73	10.74	0.48
	CHOS	1663	357	0.44	1.81	1.91	2.49	0.02
	CHONS	1527	387	0.61	1.67	2.23	3.98	0.03
	Total	4995	361	0.46	1.75	1.95	3.08	0.05
Moderate SOA-loading - N	CHO	1588	317	0.35	1.22	1.57	7.62	0.34
	CHON	1692	326	0.42	1.10	1.74	8.66	0.38
	CHOS	1038	337	0.48	1.79	1.98	2.49	0.02
	CHONS	1091	360	0.66	1.71	2.32	3.52	0.02
	Total	5409	334	0.47	1.54	1.90	4.76	0.15
Low SOA-loading - D	CHO	1967	313	0.28	1.31	1.48	7.13	0.31
	CHON	2438	322	0.34	1.16	1.65	8.54	0.38
	CHOS	853	332	0.40	1.79	1.87	2.67	0.04
	CHONS	575	356	0.57	1.69	2.19	3.61	0.03
	Total	5833	322	0.33	1.39	1.64	6.39	0.26
Low SOA-loading - N	CHO	1789	299	0.31	1.22	1.51	7.45	0.36
	CHON	2300	277	0.43	1.05	1.79	7.78	0.44
	CHOS	1124	321	0.44	1.69	1.93	3.32	0.08
	CHONS	1045	338	0.63	1.61	2.29	4.08	0.05
	Total	6258	304	0.42	1.34	1.79	6.09	0.27

Table S3. The number of formulae in different molecular classifications.

Sample ID	Classification	Total	CHO	CHON	CHOS	CHONS
High SOA-loading - D	PAHs-like, O-rich	23	7	16	0	0
	PAHs-like, O-poor	153	75	78	0	0
	Polyphenols-like, O-rich	66	17	41	2	6
	Polyphenols-like, O-poor	381	154	201	11	15
	Phenols-like, O-rich	1025	148	168	275	434
	Phenols-like, O-poor	1770	442	599	348	381
	Aliphatics-like, O-rich	691	30	43	201	417
	Aliphatics-like, O-poor	1417	270	108	555	484
	Carbohydrates-like	386	11	0	243	132
High SOA-loading - N	PAHs-like, O-rich	33	5	28	0	0
	PAHs-like, O-poor	255	102	153	0	0
	Polyphenols-like, O-rich	73	18	54	0	1
	Polyphenols-like, O-poor	548	213	322	6	7
	Phenols-like, O-rich	1133	208	389	222	314
	Phenols-like, O-poor	2197	657	1049	194	297
	Aliphatics-like, O-rich	737	63	118	201	355
	Aliphatics-like, O-poor	1594	491	400	367	336
	Carbohydrates-like	389	63	0	204	122
Moderate SOA-loading - D	PAHs-like, O-rich	10	7	3	0	0
	PAHs-like, O-poor	84	59	25	0	0
	Polyphenols-like, O-rich	56	23	16	9	8
	Polyphenols-like, O-poor	248	148	68	20	12
	Phenols-like, O-rich	822	68	32	309	413
	Phenols-like, O-poor	1024	198	128	398	300
	Aliphatics-like, O-rich	541	10	0	188	343
	Aliphatics-like, O-poor	947	83	0	522	342
	Carbohydrates-like	326	0	0	217	109
Moderate SOA-loading - N	PAHs-like, O-rich	19	4	15	0	0
	PAHs-like, O-poor	232	110	122	0	0
	Polyphenols-like, O-rich	57	21	35	0	1
	Polyphenols-like, O-poor	484	225	254	2	3
	Phenols-like, O-rich	777	152	238	184	203
	Phenols-like, O-poor	1823	626	765	182	250
	Aliphatics-like, O-rich	527	47	59	171	250
	Aliphatics-like, O-poor	1180	358	204	323	295
	Carbohydrates-like	310	45	0	176	89
Low SOA-loading - D	PAHs-like, O-rich	19	4	15	0	0
	PAHs-like, O-poor	336	157	179	0	0
	Polyphenols-like, O-rich	44	17	26	1	0
	Polyphenols-like, O-poor	759	332	413	13	1
	Phenols-like, O-rich	428	95	160	90	83
	Phenols-like, O-poor	2207	761	1109	201	136
	Aliphatics-like, O-rich	326	43	45	102	136
	Aliphatics-like, O-poor	1455	491	491	295	178
	Carbohydrates-like	259	67	0	151	41
Low SOA-loading - N	PAHs-like, O-rich	40	6	34	0	0
	PAHs-like, O-poor	329	136	188	4	1
	Polyphenols-like, O-rich	72	18	41	9	4
	Polyphenols-like, O-poor	729	279	370	42	38
	Phenols-like, O-rich	775	135	255	176	209
	Phenols-like, O-poor	2347	708	1001	311	327
	Aliphatics-like, O-rich	424	45	66	133	180
	Aliphatics-like, O-poor	1254	409	345	287	213
	Carbohydrates-like	288	53	0	162	73

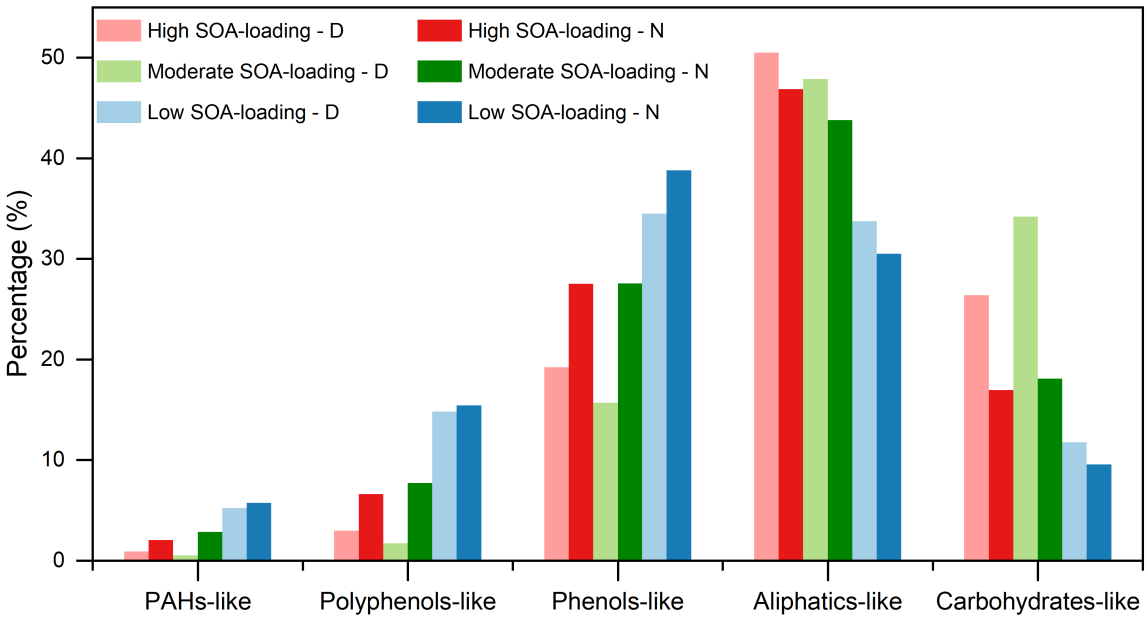

Figure S1. Intensity-weighted contributions of five compound classifications to each $PM_{2.5}$ sample. (1) PAHs-like: polycyclic aromatic hydrocarbons, (2) Polyphenols-like: polyphenols and PAHs with aliphatic chains, (3) Phenols-like: highly unsaturated and phenolic compounds, (4) Aliphatics-like: unsaturated aliphatic compounds, (5) Carbohydrates-like: carbohydrate, saturated fatty and sulfonic acids.

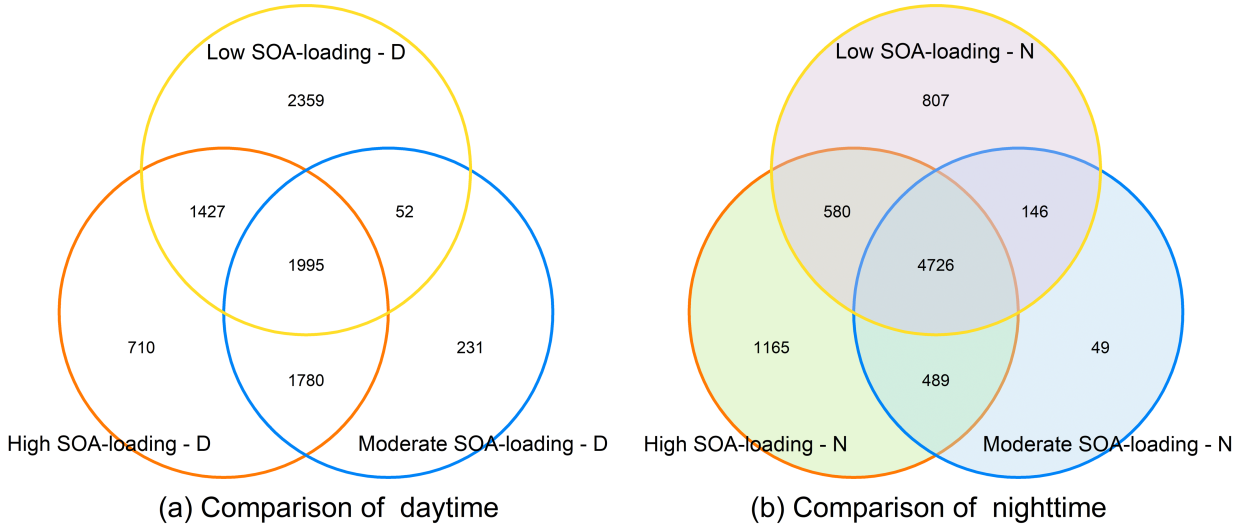

Figure S2. Venn diagrams showing the distributions of all molecular formulae in all samples. The number in overlap areas are counts of molecular formulae that appear in both, and all three of those samples. The number in areas with no overlap is unique to the individual sample.

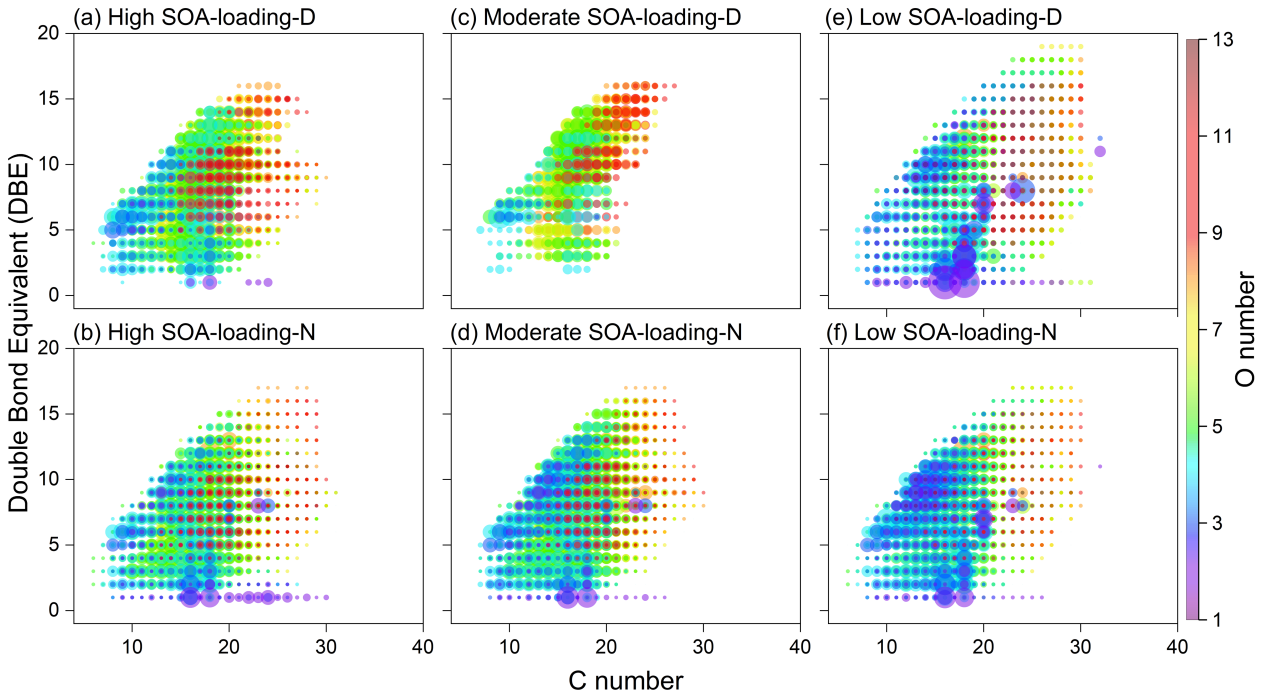

Figure S3. Double bond equivalent (DBE) vs. C number for all the CHO compounds. The color bar and marker size denote the number of O atoms and the relative peak intensities of molecular formulae on a logarithmic scale.

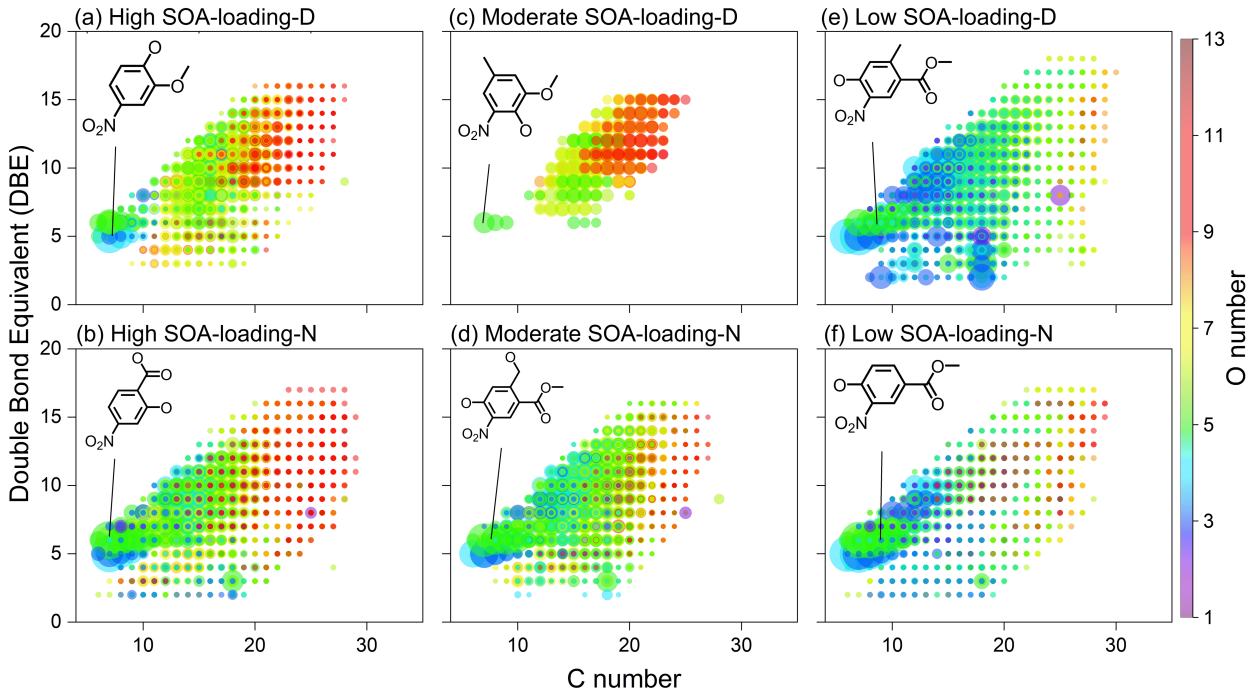

Figure S4. Double bond equivalent (DBE) vs. C number for all the CHON compounds. The color bar and marker size denote the number of O atoms and the relative peak intensities of molecular formulae on a logarithmic scale. The formulae with highest intensity were $C_7H_7O_4N$, $C_7H_5O_5N$, $C_8H_9O_3N$, $C_8H_7O_5N$, $C_9H_9O_5N$, $C_9H_7O_6N$, respectively. Note that the proposed structures were representative, not determined.

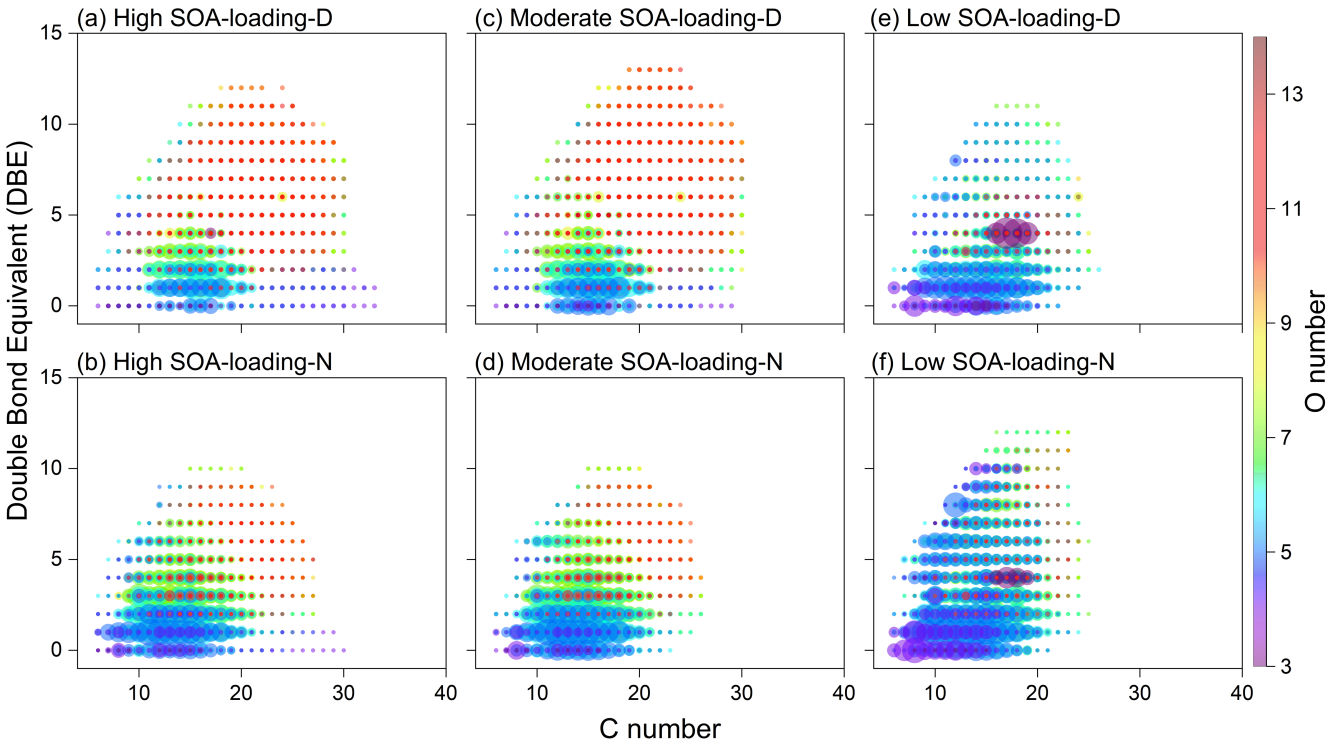

Figure S5. Double bond equivalent (DBE) vs. C number for all the CHOS compounds. The color bar and marker size denote the number of O atoms and the relative peak intensities of molecular formulae on a logarithmic scale.

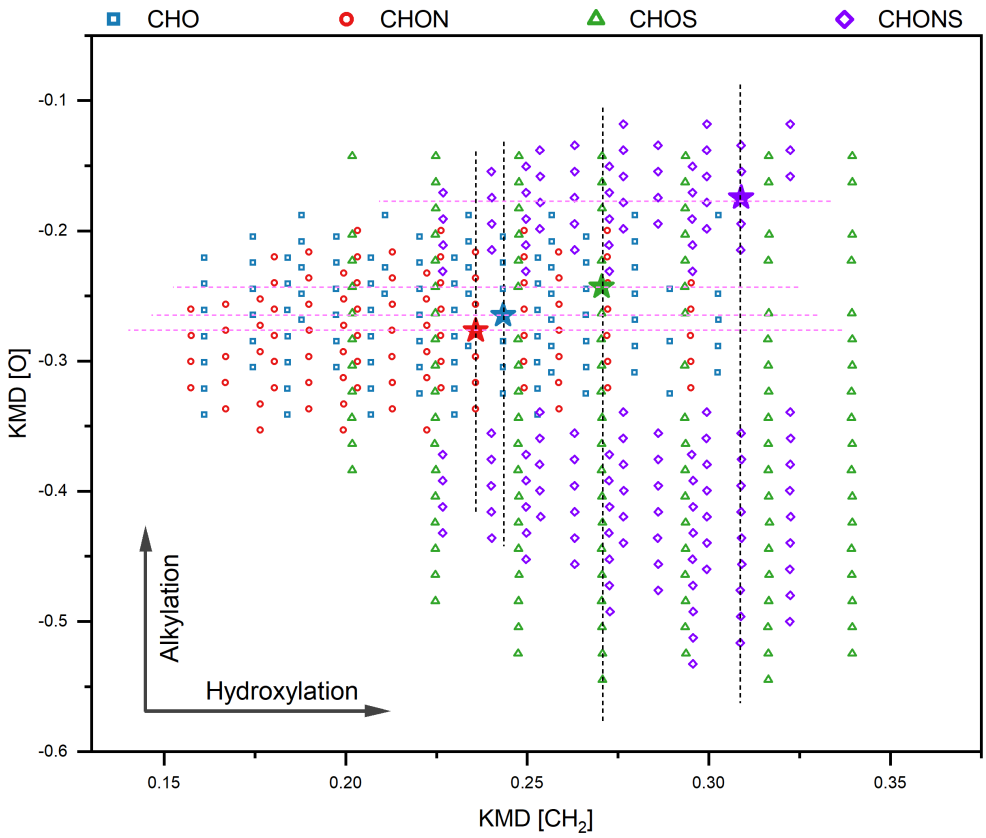

Figure S6. Two-dimensional Kendrick mass defect (KMD) matrix plot for CHO, CHON, CHOS and CHONS compounds of High SOA-loading-D sample. The KMD [O] denotes the Kendrick mass defect of hydroxyl functional group (-OH). The KMD [CH_2] denotes the Kendrick mass defect of methylene group (CH_2). The magnified star symbols represent $C_{16}H_{24}O_8$, $C_{15}H_{25}NO_8$, $C_{15}H_{24}O_7S$ and $C_{10}H_{17}NO_9S$ with relative high abundance, respectively.

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