Supplementary Material for

Chemical identification and quantification of volatile organic compounds emitted by sewage sludge

K.M. Haider[1,2], F. Lafouge[2], Y. Carpentier[1], S. Houot[2], D. Petitprez[3], B. Loubet[2], C. Focsa[1], R. Ciuraru[2]

[1]Univ. Lille, CNRS, UMR 8523 - PhLAM - Physique des Lasers, Atomes et Molécules, Lille F-59000, France

[2]INRAE, UMR ECOSYS, INRAE, AgroParisTech, University of Paris-Saclay, 78850 Thiveral-Grignon, France

[3]Univ.Lille, CNRS, UMR 8522 – PC2A – PhysicoChimie des Processus de Combustion et de l'Atmosphère, Lille F-59000, France

1. Materials and methods

Table S1: Physicochemical properties of the bulk sewage sludge (SS) samples

Parameters	Unit	Bulk SS			
		UDSS	**DSS**	**SS 30%**	**SS 60%**
pH		8.4	8.5	6.1	7.3
Humidity	%	96.3	97.1	80.6	15.6
Dry matter	%	3.7	2.9	19.4	84.4
Organic matter	%	2.6	1.9	12.6	60.4
Mineral material	%	1.1	1	6.8	24
Organic nitrogen	g/kg	2.53	2.19	9.86	51.4
Total nitrogen (N)	g/kg	2.95	2.8	10.3	52.3
Organic carbon	%	1.3	1	6.3	30.2
Sulfur trioxide (SO_3)	g/kg	0.84	0.78	5.7	23
Density	kg/m3	1.03	0.97	0.99	0.41
Ammoniacal nitrogen (N-NH_4^+)	g/kg	0.424	0.612	0.437	0.952

Abbreviations: UDSS-Undigested sewage sludge; DSS-Digested sewage sludge; SS 30%-Sewage sludge with 30% dryness; SS 60%-Sewage sludge with 60% dryness.

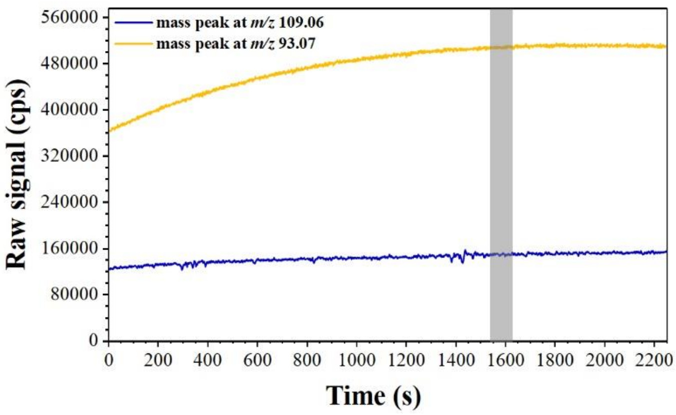


Figure S1: Example of a temporal variation of two protonated ions corresponding to *m/z* 93.07 and 109.06 assigned as $C_7H_8H^+$ (toluene) and $C_7H_8OH^+$ (cresol), respectively. The region marked in grey box corresponds to 120 mass spectra that chosen for further data analysis.

1.1. Mass calibrations of PTR-Qi-ToF spectra

For each spectrum, mass calibrations were performed using oxygen isotope of the ion source $H_3{}^{18}O^+$ (*m/z* 21.022) and protonated acetone, $C_3H_6O\text{-}H^+$ (*m/z* 59.0449) which are always present in the system. Another internal standard calibrant PerMaSCAL ($C_6H_4I_2$, 1,3-diiodobenzene, Permeation add-on for Mass Scale Calibration of PTR-MS, IONICON) was used for mass calibrations. This compound gives two peaks at *m/z* 330.848 ($C_6H_4I_2\text{-}H^+$) corresponding to the parent molecule and *m/z* 203.943 ($C_6H_4I\text{-}H^+$) corresponding to a fragment – I. Thus, four peaks at masses 21.022, 59.0449, 203.943 and 330.848 were chosen as calibration peaks for the calibration of the dataset.

1.2. Calculation of the concentration and emission flux

The mixing ratio of detected ions was calculated using the integrated peak area and applying the equation described in Cappellin et al., (2011) and Abis et al., (2018):

$$\text{Mixing ratio (ppb)} = 1.6575799.10^{-11} \text{ x } \frac{\text{Udrift [V]Tdrift}^2\text{[K]}}{\text{k pdrift}^2\text{[mbar]}} \cdot \frac{\text{Raw signal of R}^+}{\text{Raw signal of H3O}^+} \cdot \frac{\text{TR(H3O}^+\text{)}}{\text{TR(R}^+\text{)}} \qquad \textbf{(S.1)}$$

where U_{drift} is the voltage of the drift tube (V), T_{drift} is the temperature in the drift tube (K), p_{drift} is the pressure in the drift tube (mbar), k is the protonation rate constant (2 x 10^{-9} cm^3 s^{-1} assumed equal for all compounds) was used for the quantification of detected VOCs., TR_{H3O+} and TR_{R+} are the transmission factors for protonated mass of H_3O^+ and protonated mass of product ion, respectively. The raw signals of H_3O^+ and R^+ represent the integrated peak area of H_3O^+ and R^+ peaks, respectively.

To estimate the uncertainty in the mixing ratio calculation, calibrations were performed using a standard bottle (BTEX, Messer®) containing benzene, toluene, ethylbenzene and xylene with mixing ratios of 102 ppb, 97 ppb, 130 ppb and 336 ppb, respectively, as reference compounds diluted in a synthetic dry air. The correction factor was calculated as the slope of the regression between the theoretical mixing ratio of toluene and the measured mixing ratio by PTR-Qi-ToF-MS, assuming a zero intercept. The obtained correction factor for mixing ratio was 2.4 ± 0.02. This correction was applied to all masses in the peak list created for each SS sample.

The mass concentration of each assigned VOC was calculated based on its mixing ratio, taking into account the molecular weight of the compound. The emission flux of each VOC was calculated using the following equation:

$$F_{VOC} = Q/A \text{ x } C_{VOC} \qquad \textbf{(S.2)}$$

where F (µg m^{-2} min^{-1}) is the flux of the assigned VOC, Q (m^3 min^{-1}) is the air flow rate through the chamber, and A (m^2) is the surface area of the sample. C_{VOC} (µg m^{-3}) is the averaged mass concentration of a VOC obtained from the three replicates performed for each sample.

1.3. Statistical analysis

1.3.1. Principal component analysis (PCA)

PCA was performed on a matrix containing the integrated peak areas (variables) against the mass spectra (observations). PCA reveals the interrelationships between the cases and the variables (Li et al., 2014). A special preparation procedure was applied on mass spectrometric data prior applying PCA (Tanaka, 1988): calibration of mass scale, baseline removal, construction of a peak list, peak area integration and normalization. All mass spectra were normalized relative to the total ion count (TIC). The S/N > 3 peak list included major-abundance isotopic species (excluded all the mass peaks corresponding to minor-abundance isotopes "e.g. ^{13}C isotopic peaks").

1.3.2. Volcano plot

When comparing only two samples, known to be different, it is useful to determine what chemical compounds contribute the difference between two samples. In statistics, a volcano plot is applied to quickly seek out changes in large data sets composed of replicate data. It plots fold-change versus significance on the x and y-axes, respectively. A volcano plot combines a measure of statistical significance from a statistical test (e.g. a p value from an ANOVA model) with the magnitude changes, enabling quick visual determination of these data-points that represent large magnitude changes that are also statistically significant. To improve the readability of the plot when the variance in the data set is rather high, the fold-change (FC) can be replaced by its logarithm (log_2 (FC)) (Baldi & Long, 2001; W. Li, 2012). A volcano plot consists of the three main region illustrated in Figure S2. The two regions (ii and iii) are used for making meaningful conclusions about the mass spectrometric data since they contain statistically significant information.

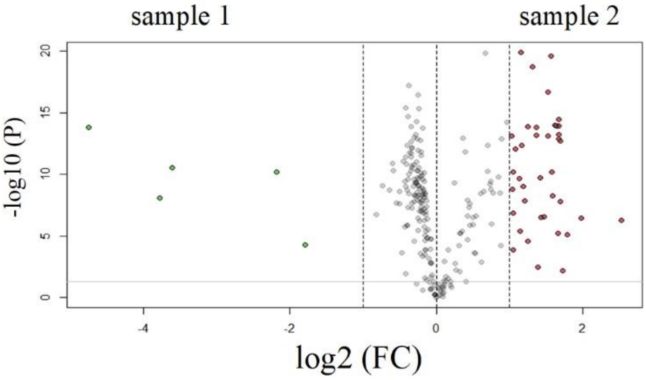


Figure S2: Example of a volcano plot illustrating the three main regions: (i) points with either a small fold change or statistical significance – grey markers, (ii) with high contribution to the sample 1 with a high statistical significance – (iii) green markers, and points with high contribution to the sample 2 with a high statistical significance – red markers.

2. Results

2.1. PTR-Qi-ToF mass spectra

An example of a PTR-Qi-ToF average mass spectrum for each sample is given in (Figure S3). The vast majority of the detected peaks were assigned to a suitable molecular formula and only a few were unassigned (Table 2).

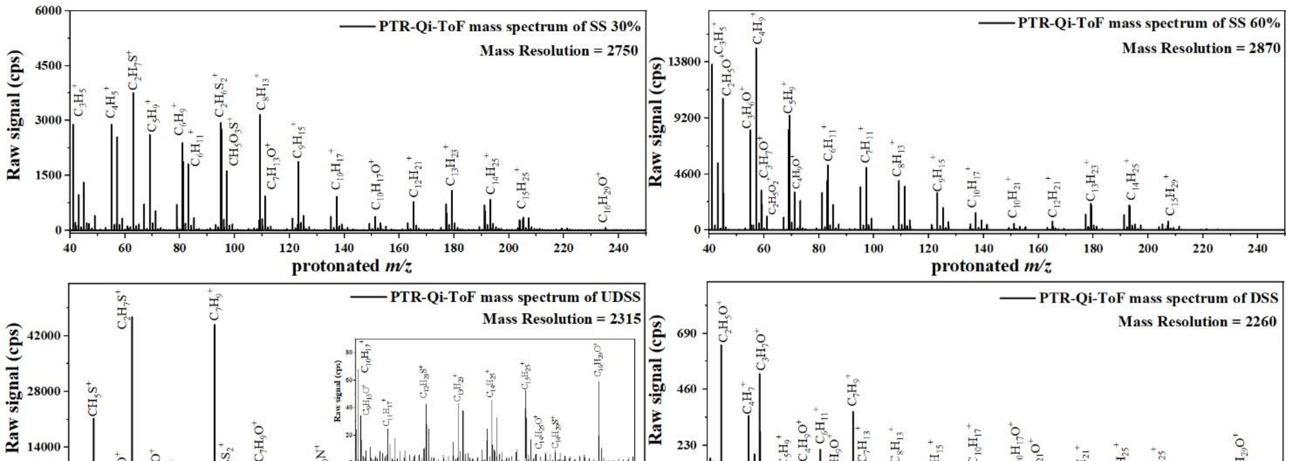


Figure S3: PTR-Qi-ToF average mass spectrum for each sample and the chemical assignments of some protonated mass peaks. All the assigned molecular formulas are protonated $VOCH^+$. Abbreviations: UDSS-Undigested sewage sludge; DSS-Digested sewage sludge; SS 30%-Sewage sludge with 30% dryness; SS 60%-Sewage sludge with 60% dryness.

Table S2: List of compounds emitted exclusively from one sample by decreasing order of the mass concentration. The chemical group of each compound, the average mass concentration and emission flux are shown. The number of tracers in each SS is shown in parenthesis.

Compound chemical group	Raw formula	Molecular weight (exact mass)	Average Mass concentration (μg m^{-3})	SD Mass concentration (μg m^{-3})	Average Emission Flux (μg min^{-1} m^{-2})	SD Emission Flux (μg min^{-1} m^{-2})
Undigested Sewage Sludge - UDSS - (93 compounds)						
O-compounds	C7H8O	108.0575	329.5124	156.3284	8.7527	4.1525
O-compounds	C6H6O	94.0419	14.2524	1.9243	0.3786	0.0511
Others	C18H29NO	275.2249	9.6890	1.0437	0.2574	0.0277
O-compounds	C18H26O	258.1984	9.4634	1.0536	0.2514	0.0280
O-compounds	C16H24O2	248.1776	9.0063	0.4973	0.2392	0.0132
N-compounds	C16H26N2	246.2096	8.9427	0.7607	0.2375	0.0202
O-compounds	C16H28O2	252.2089	8.9067	0.4962	0.2366	0.0132
O-compounds	C16H30O2	254.2246	8.8718	0.6850	0.2357	0.0182
Others	C14H30N2O	242.2358	8.8585	0.5614	0.2353	0.0149
Others	C13H28N2O2	244.2151	8.7460	0.6740	0.2323	0.0179
O-compounds	C16H30O	238.2297	8.6761	0.6533	0.2305	0.0174
Others	C14H28N2O	240.2202	8.5238	0.6582	0.2264	0.0175
S-compounds	C14H26S	226.1756	8.2512	0.7925	0.2192	0.0211
N-compounds	C14H24N2	220.1939	8.2510	0.6676	0.2192	0.0177
O-compounds	C15H28O	224.2140	8.1919	0.6393	0.2176	0.0170
O-compounds	C15H26O	222.1984	7.9393	0.7015	0.2109	0.0186
O-compounds	C14H24O	208.1827	7.7742	0.7272	0.2065	0.0193
O-compounds	C14H26O	210.1984	7.7459	0.6398	0.2058	0.0170
Others	C12H23NS	213.1551	7.6587	0.5724	0.2034	0.0152
N-compounds	C15H27N	221.2143	7.6379	0.5555	0.2029	0.0148
Others	C13H25NO	211.1936	7.3502	0.3997	0.1952	0.0106
Others	C11H22N2O	198.1732	7.2297	0.5786	0.1920	0.0154
O-compounds	C13H22O	194.1671	7.2236	0.5900	0.1919	0.0157
O-compounds	C12H20O2	196.1463	6.9480	0.5568	0.1846	0.0148
N-compounds	C11H20N2	180.1626	6.3521	0.4906	0.1687	0.0130
N-compounds	C12H23N	181.1831	6.0746	0.4222	0.1614	0.0112
N-compounds	C9H8N	130.0657	6.0703	1.3912	0.1612	0.0370
Others	C8H7NS2	181.0020	6.0070	0.5055	0.1596	0.0134
Others	C9H9NO3	179.0584	5.8689	0.4410	0.1559	0.0117
Others	C9H9NO	147.0684	5.8610	0.9407	0.1557	0.0250
Others	C10H11NS	177.0612	5.7435	0.4155	0.1526	0.0110
Others	C10H7NS	173.0299	5.5660	0.3678	0.1478	0.0098
S-compounds	C10H12S	164.0660	5.5569	0.5071	0.1476	0.0135
O-compounds	C11H18O	166.1358	5.5535	0.3953	0.1475	0.0105
O-compounds	C11H20O	168.1514	5.5499	0.3065	0.1474	0.0081
O-compounds	C10H16O2	168.1150	5.5331	0.3182	0.1470	0.0085
O-compounds	C10H10O2	162.0681	5.4366	0.4239	0.1444	0.0113
O-compounds	C9H18O2	158.1307	5.2508	0.3953	0.1395	0.0105
Others	C6H7NS	125.0299	5.1639	0.8256	0.1372	0.0219
N-compounds	C10H6N2	154.0531	5.0592	0.4028	0.1344	0.0107
O-compounds	C8H4O3	148.0160	5.0185	0.6090	0.1333	0.0162
O-compounds	C5H10O4	134.0579	5.0145	0.0630	0.1332	0.0017
O-compounds	C8H8O	120.0575	4.9611	0.1980	0.1318	0.0053
Others	C7H8N2O2	152.0586	4.9592	0.4345	0.1317	0.0115

N-compounds	C8H8N	118.0657	4.8017	0.4625	0.1275	0.0123
Others	C9H17NO	155.1310	4.7491	0.3257	0.1261	0.0087
O-compounds	C10H10O	146.0732	4.6886	0.3065	0.1245	0.0081
Others	C6H7NOS	145.0561	4.6535	0.3808	0.1236	0.0101
Others	C8H9NO2	151.0633	4.6327	0.3136	0.1231	0.0083
O-compounds	C7H10O2	126.0681	4.5852	0.3858	0.1218	0.0102
N-compounds	C9H8N2	144.0687	4.5306	0.1960	0.1203	0.0052
Others	C7H12NO2	142.0868	4.4689	0.3000	0.1187	0.0080
Others	C5H6N2OS	142.0201	4.2701	0.3048	0.1134	0.0081
Others	C6H6N2O2	138.0429	4.2015	0.2341	0.1116	0.0062
Others	C4H4N4O2	140.0343	4.1937	0.2180	0.1114	0.0058
Others	C6H9NO3	143.0582	4.1858	0.2599	0.1112	0.0069
Others	C8H15NO	141.1154	4.1552	0.2105	0.1104	0.0056
Others	C6H7NOS	141.0248	4.1211	0.2599	0.1095	0.0069
Others	C7H7NO2	137.0477	4.0761	0.3618	0.1083	0.0096
Others	C6H5NO3	139.0269	4.0524	0.2494	0.1076	0.0066
O-compounds	C7H8O2	124.0524	3.8623	0.1160	0.1026	0.0031
N-compounds	C8H11N	121.0891	3.5678	0.2210	0.0948	0.0059
Others	C7H17NO	121.0528	3.5335	0.1216	0.0939	0.0032
O-compounds	C5H4O3	112.0160	3.2469	0.3691	0.0862	0.0098
N-compounds	C8H9N	119.0735	3.1879	0.1807	0.0847	0.0048
Others	C6H9NO	111.0684	2.9168	0.0936	0.0775	0.0025
Others	C5H7NS	113.0299	2.8207	0.1446	0.0749	0.0038
HC	C6H4	76.0313	2.4571	0.0673	0.0653	0.0018
Others	C4H9NO2	103.0633	2.4203	0.1542	0.0643	0.0041
O-compounds	C4H4O2	84.0211	2.4189	0.4817	0.0643	0.0128
O-compounds	C8H10O	122.0732	2.0415	0.2727	0.0542	0.0072
Others	C4H5NO	83.0371	1.6825	0.0125	0.0447	0.0003
O-compounds	C13H24O	196.1827	1.5058	0.0216	0.0400	0.0006
O-compounds	C12H22O	182.1671	1.3840	0.1154	0.0368	0.0031
Others	C9H17NO2	171.1259	1.1966	0.0823	0.0318	0.0022
S-compounds	C11H18S	182.1129	1.1942	0.0924	0.0317	0.0025
Others	C10H21NO	171.1623	1.1150	0.0253	0.0296	0.0007
Others	C5H6N2S	126.0252	1.0387	0.1026	0.0276	0.0027
O-compounds	C5H4O	80.0262	0.9459	0.0347	0.0251	0.0009
O-compounds	C5H8O3	116.0473	0.9078	0.1828	0.0241	0.0049
Others	C6H8OS	128.0296	0.8577	0.0297	0.0228	0.0008
Others	C6H9NO2	127.0633	0.7793	0.0006	0.0207	0.0000
N-compounds	C6H9N3	123.0796	0.7755	0.0427	0.0206	0.0011
Others	C7H13NO	127.0997	0.7555	0.0062	0.0201	0.0002
O-compounds	C4H2O	66.0106	0.7078	0.3147	0.0188	0.0084
O-compounds	C5H6O	82.0419	0.5826	0.0176	0.0155	0.0005
N-compounds	C2H3N	41.0265	0.5815	0.0410	0.0154	0.0011
O-compounds	C3H4O2	72.0211	0.5736	0.1916	0.0152	0.0051
Others	C5H9NO	99.0684	0.4889	0.0563	0.0130	0.0015
N-compounds	C5H11N	85.0891	0.3579	0.0343	0.0095	0.0009
N-compounds	C3H3N3	81.0327	0.3294	0.0236	0.0087	0.0006
N-compounds	C4H5N	67.0422	0.3110	0.0111	0.0083	0.0003

N-compounds	C2H5N	43.0422	0.1113	0.0020	0.0030	0.0001
Digested Sewage Sludge -DSS- (30 compounds)						
O-compounds	C9H8O2	148.0524	11.1557	3.3478	0.4781	0.1435
O-compounds	C18H36O	268.2662	10.4345	2.1795	0.4472	0.0934
Others	C15H24N2O	248.1889	10.4332	2.2273	0.4471	0.0955
Others	C16H27NO2	265.2042	10.3934	2.2719	0.4454	0.0974
Others	C15H28N2O	252.2202	10.2176	2.2399	0.4379	0.0960
Others	C16H31NO	253.2406	10.1397	2.2151	0.4346	0.0949
Others	C15H29NO	239.2249	10.0437	2.4039	0.4304	0.1030
N-compounds	C15H30N2	238.2409	10.0038	2.2207	0.4287	0.0952
O-compounds	C16H14O2	238.0994	9.9745	2.3161	0.4275	0.0993
Others	C15H27NO	237.2093	9.8540	2.2722	0.4223	0.0974
O-compounds	C15H10O2	222.0681	9.8389	2.8520	0.4217	0.1222
O-compounds	C14H10O4	242.0579	9.8213	2.1096	0.4209	0.0904
Others	C16H27NO	249.2093	9.7025	1.9897	0.4158	0.0853
Others	C15H13NO2	239.0946	9.3225	2.0409	0.3995	0.0875
O-compounds	C14H8O3	224.0473	9.2842	2.2158	0.3979	0.0950
Others	C14H9NO2	223.0633	8.8400	2.0041	0.3789	0.0859
Others	C7H12NO2	142.0868	7.4815	1.9171	0.3206	0.0822
Others	C10H15NO	165.1154	7.4498	2.4321	0.3193	0.1042
Others	C11H21NO	183.1623	7.2440	1.7655	0.3105	0.0757
Others	C9H11NO	149.0841	6.1301	1.4575	0.2627	0.0625
Others	C2H5NO	59.0371	5.3023	2.6116	0.2272	0.1119
Others	C7H5NS	135.0143	5.2667	0.9002	0.2257	0.0386
Others	C6H11N2O2	143.0821	5.2593	1.2009	0.2254	0.0515
Others	C5H7NOS	129.0248	4.2484	0.8961	0.1821	0.0384
S-compounds	C4H6S2	117.9911	3.9787	0.9086	0.1705	0.0389
S-compounds	C6H13S	117.0738	3.7501	0.9517	0.1607	0.0408
Others	C6H7NO	109.0528	1.1713	0.3845	0.0502	0.0165
O-compounds	C6H6O2	110.0368	1.1269	0.3907	0.0483	0.0167
Others	CH3NO2	61.0164	0.3703	0.1400	0.0159	0.0060
N-compounds	C2H8N2	60.0687	0.3678	0.1259	0.0158	0.0054
Sewage Sludge with 30% dryness -SS 30%- (22 compounds)						
HC	C15H18	198.1409	7.1278	0.6240	0.3055	0.0267
O-compounds	C14H28O2	228.2089	9.6047	0.8187	0.4116	0.0351
O-compounds	C19H32O	276.2453	8.6472	0.6758	0.3706	0.0290
O-compounds	C16H32O2	256.2402	8.2001	0.6803	0.3514	0.0292
N-compounds	C16H31N	237.2456	7.6062	0.6319	0.3260	0.0271
HC	C15H16	196.1252	6.5635	0.5314	0.2813	0.0228
S-compounds	C8H14S	142.0816	7.5354	1.2741	0.3229	0.0546
Others	C9H16N2O2	184.1212	6.5201	0.5980	0.2794	0.0256
Others	C11H21NO2	199.1572	6.2504	0.4427	0.2679	0.0190
N-compounds	C13H15N	185.1204	5.5948	0.5311	0.2398	0.0228
O-compounds	C9H10O3	166.0630	5.2307	0.2918	0.2242	0.0125
Others	C8H17NO2	159.1259	4.7161	0.3723	0.2021	0.0160
N-compounds	C10H5N3	167.0483	4.6538	0.1827	0.1994	0.0078
Others	C7H11NS	141.0612	3.9683	0.3419	0.1701	0.0147
Others	C7H15NO2	145.1103	3.9571	0.2346	0.1696	0.0101

Others	C6H11NO2	129.0790	3.3394	0.2085	0.1431	0.0089
S-compounds	C5H10S	102.0532	2.3256	0.2096	0.0997	0.0090
Others	C4H5NS	99.0143	2.3091	0.0746	0.0990	0.0032
Others	C3H9NO	75.0684	1.1014	0.1162	0.0472	0.0050
S-compounds	C6H10S	114.0503	0.8350	0.0973	0.0358	0.0042
S-compounds	C3H8S	76.0347	0.5752	0.1872	0.0247	0.0080
Others	CH3NOS	76.9935	0.3989	0.0242	0.0171	0.0010
Sewage Sludge with 60% dryness -SS 60%- (32 compounds)						
O-compounds	C5H4O2	96.0211	50.7594	7.4601	2.1754	0.3197
HC	C13H26	182.2035	17.7148	1.9185	0.7592	0.0822
HC	C17H30	234.2348	11.6862	0.4866	0.5008	0.0209
O-compounds	C6H4O	92.0262	10.9541	4.3608	0.4695	0.1869
Others	C6H6N4O2	166.0491	9.5214	2.9690	0.4081	0.1272
S-compounds	C20H10S	282.0503	8.9154	0.2659	0.3821	0.0114
O-compounds	C17H12O4	280.0736	8.7653	0.4052	0.3757	0.0174
HC	C19H30	258.2348	8.3856	0.1166	0.3594	0.0050
S-compounds	C6H12S2	148.0380	8.1898	1.3361	0.3510	0.0573
HC	C17H32	236.2504	8.0373	0.3360	0.3445	0.0144
HC	C18H28	244.2191	8.0161	0.1578	0.3435	0.0068
HC	C18H34	250.2661	7.8992	0.2946	0.3385	0.0126
HC	C17H24	228.1878	7.6570	0.2543	0.3282	0.0109
Others	C13H8N2S	224.0408	7.6355	0.5262	0.3272	0.0226
O-compounds	C8H14O2	142.0994	6.4508	0.9586	0.2765	0.0411
O-compounds	C8H8O4	168.0423	5.5705	0.5783	0.2387	0.0248
O-compounds	C12H8O2	184.0524	5.3181	0.1739	0.2279	0.0075
Others	C5H5N5O2	167.0443	5.2422	0.5725	0.2247	0.0245
Others	C9H17NS	171.1082	4.8869	0.2218	0.2094	0.0095
S-compounds	C8H10S2	170.0224	4.8113	0.1624	0.2062	0.0070
Others	C8H13NO2	155.0946	4.4407	0.1731	0.1903	0.0074
Others	C8H17NS	159.1082	4.2402	0.1259	0.1817	0.0054
Others	C8H15NS	157.0925	4.2177	0.0805	0.1808	0.0034
Others	C7H13NO2	143.0946	3.8149	0.1896	0.1635	0.0081
Others	C2H5N5O3	147.0392	3.7329	0.0942	0.1600	0.0040
O-compounds	C7H14O2	130.0994	3.1945	0.1116	0.1369	0.0048
Others	C5H7NO2	113.0477	2.8839	0.1572	0.1236	0.0067
Others	C5H13NS	119.0769	2.7601	0.0563	0.1183	0.0024
Others	C5H9NO2	115.0633	2.5057	0.1401	0.1074	0.0060
Others	CH4N2S	76.0095	1.6736	0.6130	0.0717	0.0263
Others	C2H3NO3	89.0113	1.4430	0.0574	0.0618	0.0025
Others	C2H7N3O	89.0589	1.3970	0.0607	0.0599	0.0026

SD: standard deviation of calculation. Abbreviations: HC (hydrocarbons), O-compounds (Oxygenated compounds), N-compounds (Nitrogenated compounds), S-compounds (Sulphuric compounds), Others (compounds that include more than one heteroatom in the molecular formula).

2.2. Double bond equivalent method

Figure S4 shows the sub-classification of hydrocarbons with corresponding DBE value. Calculated DBE values of all the HC detected in SS 60% are listed in Table S3.

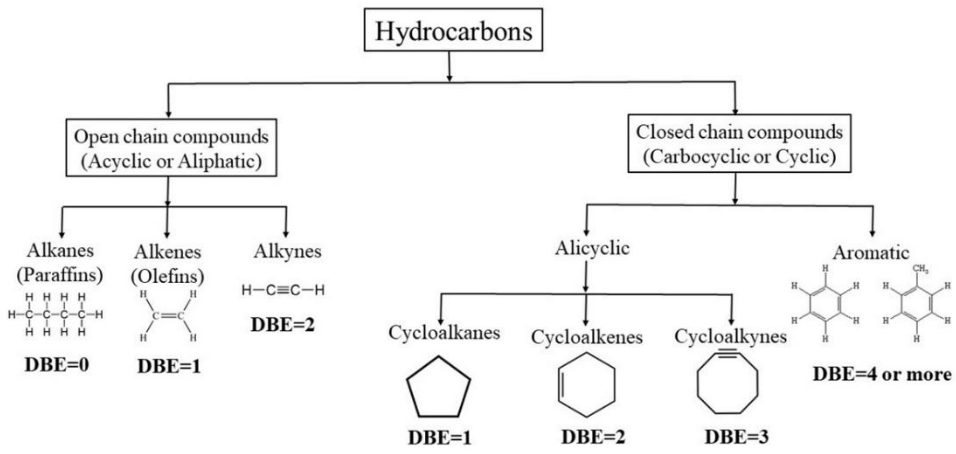


Figure S4: Sub-classification of hydrocarbons. Example of each subclass are shown with the value of corresponding double bond equivalent (DBE).

Table S3: DBE value of each assigned HC detected in this work in the decreasing order of the DBE value.

HC	Exact mass	DBE value	Detected in?
C3H6	42.0470	1	All samples
C4H8	56.0626	1	All samples
C5H10	70.0783	1	All samples
C6H12	84.0939	1	All samples
C7H14	98.1096	1	All samples
C8H16	112.1252	1	All samples
C9H18	126.1409	1	SS60% , SS30% , DSS
C10H20	140.1565	1	SS60% , SS30%
C11H22	154.1722	1	SS60% , SS30%
C12H24	168.1878	1	SS60% , SS30% , DSS
C13H26	182.2035	1	SS60%
C14H28	196.1252	1	SS60% , SS30% , DSS
C15H30	210.2348	1	SS60% , SS30% , DSS
C16H32	224.2504	1	SS60% , SS30% , DSS
C17H34	238.2661	1	SS60% , SS30%
C18H36	252.2817	1	SS60% , SS30%
C3H4	40.0313	2	All samples
C4H6	54.0470	2	All samples
C5H8	68.0626	2	All samples
C6H10	82.0783	2	All samples
C7H12	96.0939	2	All samples
C8H14	110.1096	2	All samples
C9H16	124.1252	2	All samples
C10H18	138.1409	2	All samples
C11H20	152.1565	2	SS60% , SS30%
C12H22	166.1722	2	SS60% , SS30% , DSS
C13H24	180.1878	2	SS60% , SS30% , DSS
C14H26	194.2035	2	SS60% , SS30% , DSS
C15H28	208.2191	2	SS60% , SS30% , DSS

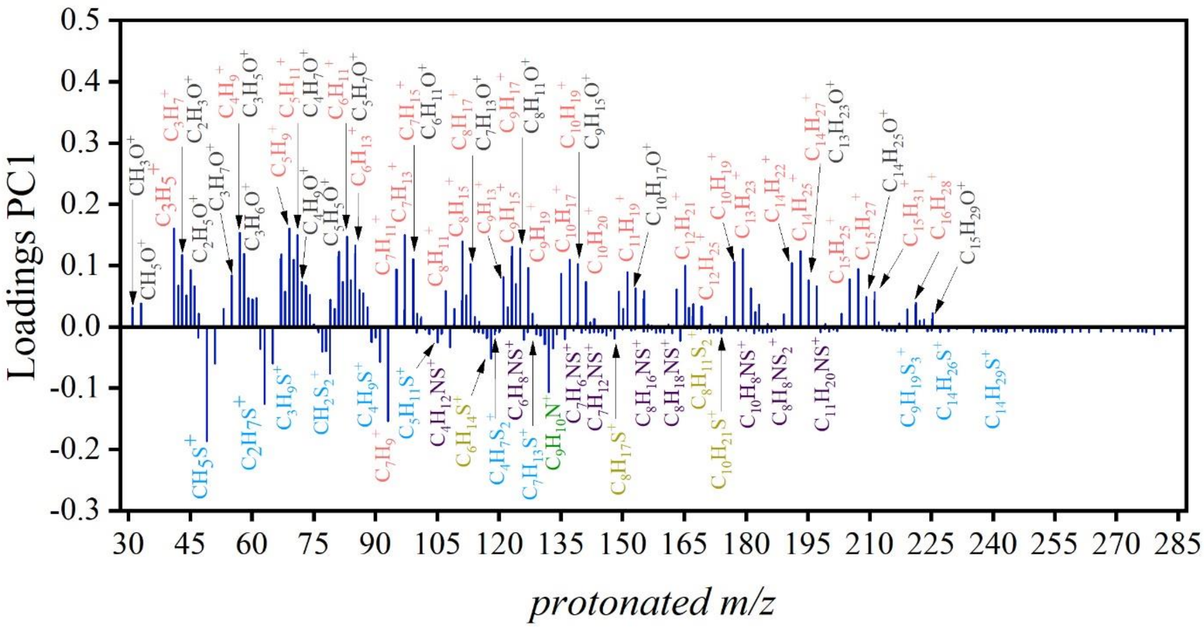
C16H30	222.2348	2	SS60% , SS30% , DSS
C17H32	236.2504	2	SS60%
C18H34	250.2661	2	SS60%
C4H4	52.0313	3	All samples
C5H6	66.0470	3	All samples
C6H8	80.0621	3	All samples
C7H10	94.0783	3	All samples
C8H12	108.0939	3	SS60% , SS30% , DSS
C9H14	122.1096	3	All samples
C10H16	136.1252	3	All samples
C11H18	150.1409	3	All samples
C12H20	164.1565	3	All samples
C13H22	178.1722	3	All samples
C14H24	192.1878	3	All samples
C15H26	206.2035	3	All samples
C16H28	220.2191	3	SS60% , SS30% , DSS
C17H30	234.2348	3	SS60%
C18H32	248.2504	3	SS60% , SS30%
C19H34	262.2661	3	SS60% , SS30%
C4H2	50.0157	4	SS60%, DSS
C5H4	64.0313	4	SS60%, DSS
C6H6	78.0470	4	All samples
C7H8	92.0626	4	All samples
C8H10	106.0783	4	All samples
C9H12	120.0939	4	All samples
C10H14	134.1096	4	All samples
C11H16	148.1252	4	All samples
C12H18	162.1409	4	All samples
C13H20	176.1565	4	All samples
C14H22	190.1722	4	All samples
C15H24	204.1878	4	All samples
C16H26	218.2035	4	All samples
C17H28	232.2191	4	All samples
C18H30	246.2348	4	SS60% , SS30% , DSS
C19H32	260.2504	4	SS60% , SS30% ,UDSS
C20H34	274.2661	4	All samples
C6H4	76.0313	5	UDSS
C5H2	78.0106	5	SS30%, UDSS
C7H6	90.0470	5	All samples
C8H8	104.0626	5	SS60% , SS30% , DSS
C9H10	118.0783	5	SS60% , SS30% , DSS
C10H12	132.0939	5	SS60% , SS30% , DSS
C11H14	146.1096	5	All samples
C12H16	160.1252	5	All samples
C13H18	174.1409	5	All samples
C14H20	188.1565	5	All samples
C15H22	202.1722	5	All samples
C16H24	216.1878	5	All samples

C17H26	230.2035	5	All samples
C18H28	244.2191	5	SS60% , SS30% , DSS
C19H30	258.2348	5	SS60%
C20H32	272.2504	5	All samples
C21H34	286.2661	5	SS60% , SS30% ,UDSS
C10H10	130.0783	6	SS30%, DSS
C12H14	158.1096	6	SS60% , SS30% , DSS
C14H18	186.1409	6	All samples
C15H20	200.1565	6	All samples
C16H22	214.1722	6	All samples
C17H24	228.1878	6	SS60%
C18H26	242.2035	6	SS60% , SS30%
C12H12	156.0939	7	SS60% , SS30% , DSS
C13H14	170.1096	7	All samples
C14H16	184.1252	7	DSS, UDSS
C15H18	198.1409	7	SS30%
C16H20	212.1565	7	SS30%, UDSS
C15H16	196.1252	8	SS30%

Abbreviations: UDSS-Undigested sewage sludge; DSS-Digested sewage sludge; SS 30%-Sewage sludge with 30% dryness; and SS 60%-Sewage sludge with 60% dryness.

2.3. PCA results

The loading plots of each PC is shown in Figure S5 .The positive values of PC1 are mainly explained by the dominance of O-compounds and HC while its negative values are dominated by S-compounds and thiazole compounds. The positive PC2 is associated with O- and N&O-containing compounds while receiving little contribution from N-compounds. The negative PC2 receives high contribution from HC, O-compounds and S-compounds. The main contributions to positive PC3 come from HC and S-compounds while the negative values of PC3 are attributed by O-compounds.



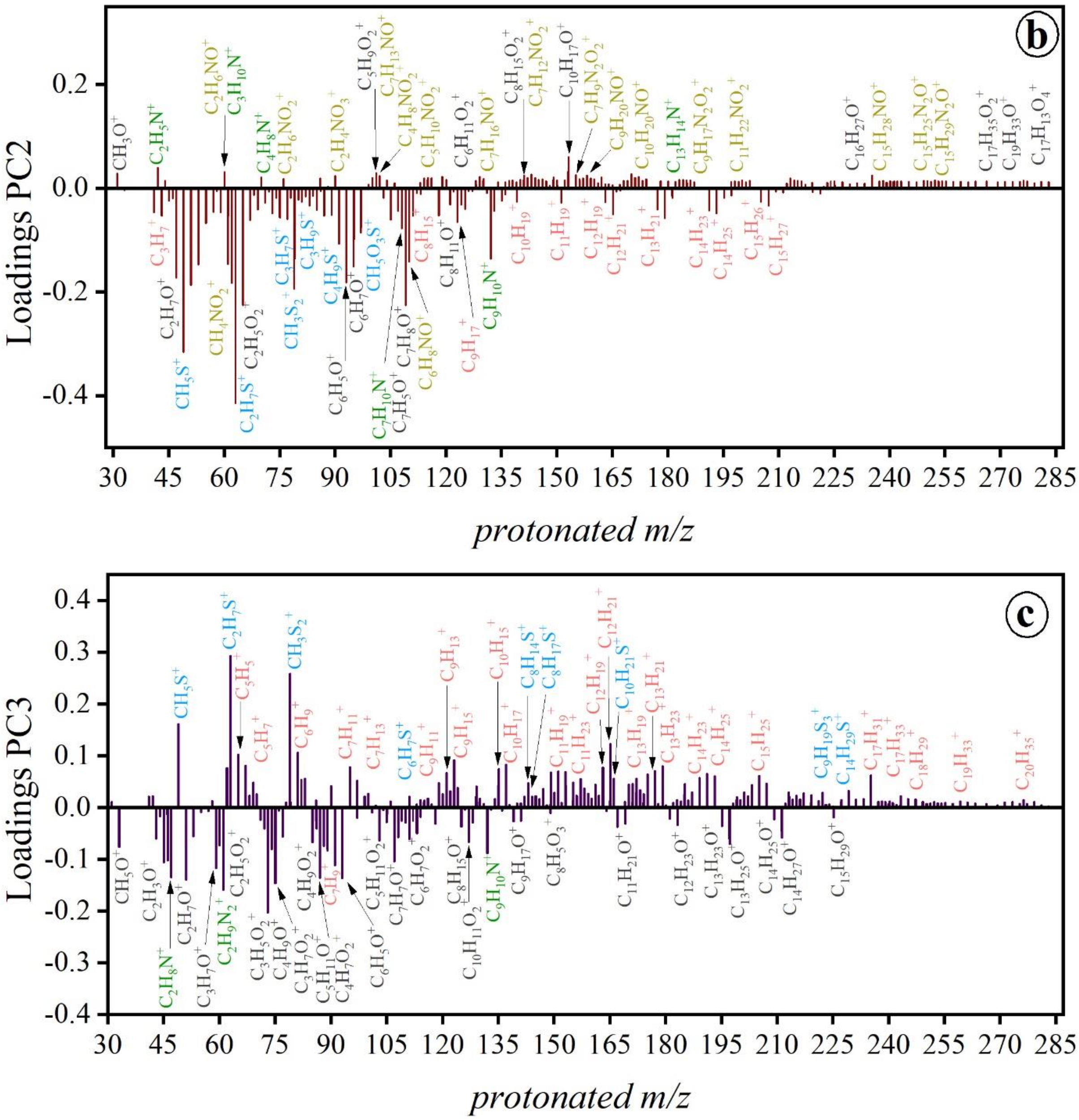


Figure S5: Loading plots for the first three principal components obtained from the mass spectra of sewage sludge samples. Chemical compounds contribute to positive and negative value of each PC is shown. All the assigned molecular formulas are protonated $VOCH^+$. Hydrocarbons (light red), oxygenated compounds (dark grey), nitrogenated compounds (green), sulfur-containing compounds (blue), nitrogen and oxygen bearing species (yellow) and other species containing more than one heteroatom in the molecular formula (in violet) are displayed.

2.4. Volcano plot results

Table S4: Chemical assignements of protonated mass peaks that show high statistical significance and FC > 1 or < -1.

Chemical compound	Fold change
DSS [(a)]	
C10H16O	1.4457
C10H16	1.3609
C4H7N	1.3560
C2H3N	1.2293
C6H8	1.0597

C3H5O	1.0575
C7H14	1.0191
C6H10O	1.0040
UDSS [(a)]	
C2H6S	-6.4355
CH4S	-5.8979
C7H8	-4.1604
C5H4	-3.5247
C4H2	-3.4212
C2H6S2	-3.2911
C7H8O	-3.1651
C9H9N	-3.0337
CH2S2	-3.0001
CH3NO2	-2.7435
C8H12	-2.6523
CH2O2	-2.6255
C7H6	-2.2149
C6H7NO	-2.0443
C2H4O2	-1.9543
C4H4	-1.9382
C5H2	-1.7687
C6H6O	-1.5409
C5H5N3	-1.4651
C7H9N	-1.3535
C3H8O2	-1.2849
C6H13S	-1.2684
C8H7N	-1.2597
C6H4	-1.2357
CH4O3S	-1.1671
C7H4O	-1.1090
C4H8O2	-1.0551
C4H8S	-1.0464
C2H6O	-1.0399
C3H6O2	-1.0217
SS 30% [(b)]	
C2H6S	-5.256
CH2S2	-3.084
C2H6S2	-2.936
CH4S	-2.684
C8H12	-2.552
C9H14	-2.535
C7H10	-2.499
C5H4	-2.490
C13H22	-2.414
C12H20	-2.346
C5H6	-2.315
C5H8	-2.313
C7H12	-2.267
C3H4	-2.192
C6H10	-2.159
CH3NO2	-2.156
C14H24	-2.137
C6H8	-2.078
C8H14	-2.074
C5H2	-2.002

C13H20	-1.948
C14H22	-1.916
C4H8	-1.897
C3H4O	-1.890
C9H16	-1.678
C5H10	-1.627
C11H18	-1.626
C15H26	-1.603
C10H14	-1.601
C9H12	-1.573
C4H4	-1.540
C4H6O	-1.515
C6H12	-1.481
C4H6	-1.480
C10H16	-1.453
C15H24	-1.443
CH2O2	-1.424
C12H18	-1.420
C3H6	-1.360
C6H7NO	-1.350
C5H8O	-1.319
C10H18	-1.155
C7H14	-1.129
C6H6	-1.104
C2H4O2	-1.060
CH4O3S	-1.041
SS 60% [c]	
C2H8N2	-5.256
C6H6	-3.084
C5H4O2	-2.936
C2H6O	-2.684
C7H9N	-2.552
C9H10	-2.535
C7H12	-2.499
CH3NO2	-2.490
C5H5N5O2	-2.414
C10H20O	-2.346
C2H6S	-2.315
C5H4	-2.313
C7H14	-2.267
C3H4	-2.192
C6H12	-2.159
C2H4O2	-2.156
C13H20	-2.137
C5H8O	-2.078
C6H6O2	-2.074
C5H5N	-2.002
C12H22	-1.948
C13H18	-1.916
C3H4O	-1.897
C4H6	-1.890
C7H5NO	-1.678
C4H7N	-1.627
C2H5N5O3	-1.626
C14H22	-1.603

C7H14O2	-1.601
C4H6S2	-1.573
C4H2	-1.540
C5H8	-1.515
C4H6O2	-1.481
C4H4	-1.480
C8H7NO	-1.453
C14H20	-1.443
C2H7N	-1.424
C8H13NO2	-1.420
C2H2O	-1.360
C8H12	-1.350
C4H7NO	-1.319
C10H14	-1.155
C5H8O2	-1.129
C6H8	-1.104
C2H5NO	-1.060
C6H10O	-1.041
SS 30% [d]	
C2H6S	-4.753
CH4S	-3.778
CH2S2	-3.609
C2H6S2	-2.183
C5H4	-1.794
SS 60% [d]	
C4H8O	2.526
C2H4O	1.976
C5H10O	1.788
C2H6O	1.725
C2H2O	1.696
C2H7N	1.694
C5H10	1.679
C4H6O	1.675
C3H6	1.673
C6H12	1.670
C4H6O2	1.659
C5H8O	1.645
C9H18	1.619
C7H6O	1.592
C2H4O2	1.579
C8H16	1.572
C8H14O	1.528
C4H8	1.526
C3H6O2	1.473
C3H6S	1.436
C14H28	1.419
C3H6O	1.390
C7H12O	1.372
C3H4	1.364
C9H16	1.315
C3H7NO	1.256
C10H18	1.255
C8H10	1.213
C15H30	1.186
C2H5N3	1.163

C_8H_{14}	1.159
CH_4O	1.143
$C_{14}H_{26}$	1.140
C_5H_8	1.088
C_7H_{14}	1.056
C_3H_9N	1.051
C_4H_9NO	1.048
C_3H_5O	1.043
$C_{10}H_{20}$	1.034

Abbreviations: UDSS-Undigested sewage sludge; DSS-Digested sewage sludge; SS 30%-Sewage sludge with 30% dryness; and SS 60%-Sewage sludge with 60% dryness.

[a]: chemical compounds observed in volcano plot in Figure 9, a.

[b]: chemical compounds observed in volcano plot in Figure 9, b.

[c]: chemical compounds observed in volcano plot in Figure 9, c.

[d]: chemical compounds observed in volcano plot in Figure 9, d.

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