Supporting Information – Analytical Chemistry

High-field FT-ICR-MS data evaluation of natural organic matter – are $CHON_5S_2$ molecular class formulas assigned to ^{13}C isotopic m/z and in reality CHO components?

Peter Herzsprung*[,1], Wolf v. Tümpling[1], Norbert Hertkorn[2], Mourad Harir[2], Kurt Friese[1], Philippe Schmitt-Kopplin[2]

*Corresponding author
peter.herzsprung@ufz.de; phone: +493918109330; fax: +493918109150

[1] *UFZ Helmholtz Centre for Environmental Research, Brückstrasse 3a, 39114 Magdeburg, Germany*
[2] *HelmholtzZentrum München, German Research Center for Environmental Health, Reasearch Unit AnalyticalBioGeoChemistry (BGC), Ingolstädter Landstraße 1, 85764 Neuherberg, Germany*

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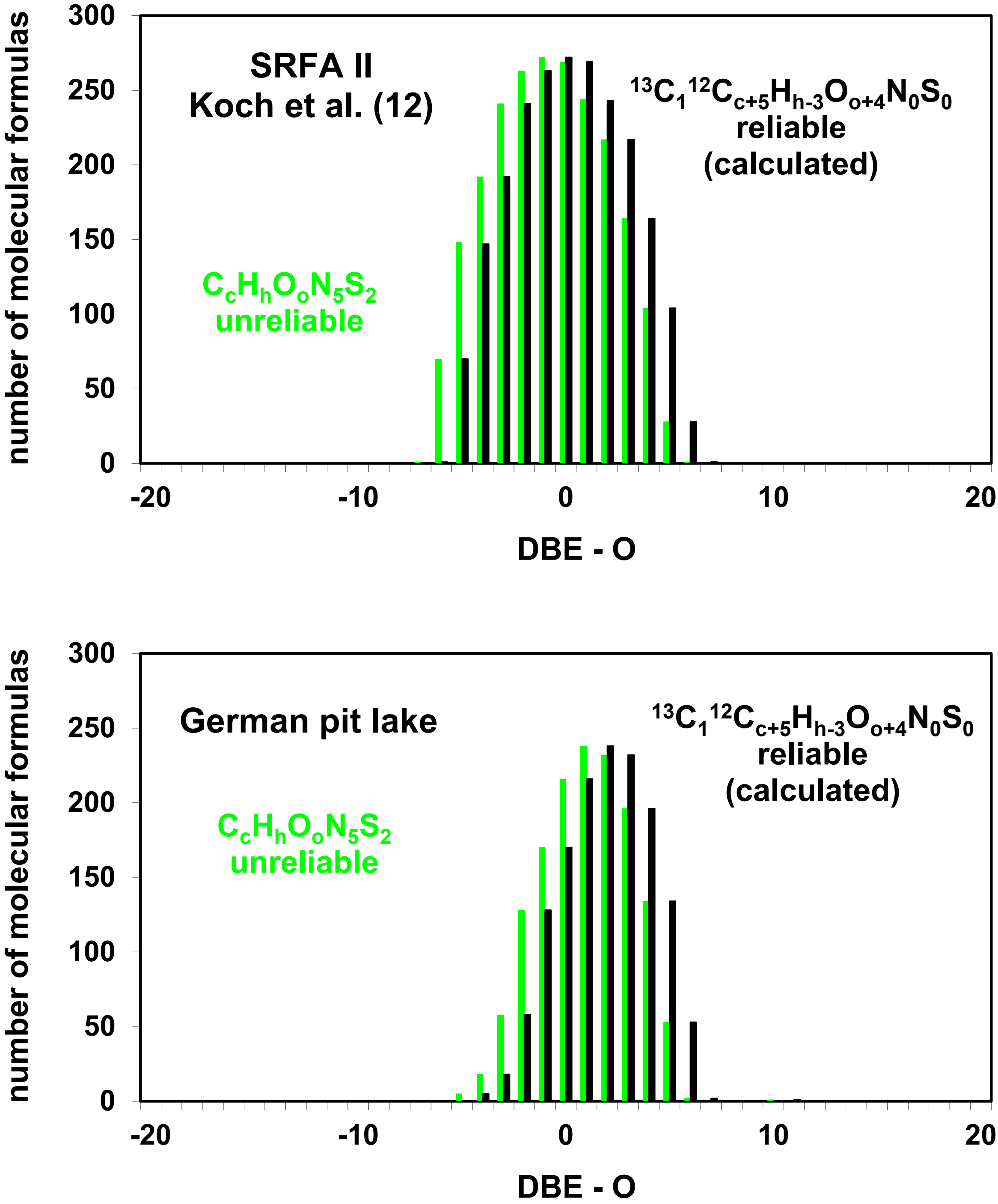

Figure S-1 DBE – O values of the N_5S_2 components which are suspected to be unreliable and their potential correct counterpart components (^{13}CHO as calculated). Top: SRFA II sample; bottom: German pit lake sample

Can molecular classes be found as replacement for the $CHON_5S_2$ class?

To search for theoretical possible molecular classes as replacement for $CHON_5S_2$, a mass versus DBE - O diagram can be used as described by Herzsprung et al. (16). In Fig. S-2 such a diagram is configured for molecular classes with odd mass (like a $CHON_5S_2$ component) and $N \leq 7$ and $S \leq 3$. No other reasonable molecular class can be found in this coordinate system which might explain the large presence of $CHON_5S_2$ components in DOM. The neighbour classes $CHON_5S_1$, $CHON_5S_3$, $CHON_3S_2$, $CHON_3S_0$, $CHON_1S_3$, seem chemically not reasonable due to their considerable DBE - O differences (16) from the $CHON_5S_2$ molecular class. The other neighbour classes, $CHON_3S_1$, $CHON_7S_3$, $CHON_1S_1$, $CHON_7S_0$, and $CHON_5S_0$ have both more or less different Δm and DBE - O values compared to the $CHON_5S_2$ molecular class. Not to mention that most of these considered possible formula replacements would have similar non-oxygen hetero atom numbers which all seem unusual for DOM. As an example the allocation of a multiple formula assignment (septet) from the SRFA II (equivocal) data set is illustrated in a Δm versus DBE - O diagram (Fig. S-3). For better understanding, the seven formulas of this septet, their corresponding masses, DBE, and DBE - O values are listed in Table S-1.
The final answer is: No reasonable replacement for the $CHON_5S_2$ class can be identified from the pool of monoisotopic component classes.

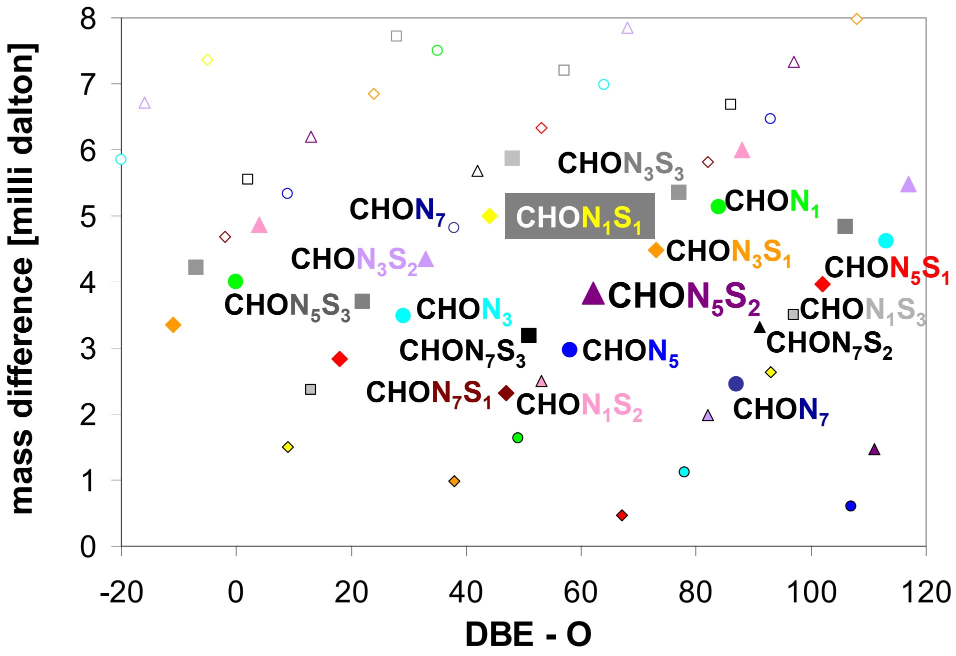

Figure S-2 Δm versus DBE - O diagram for components with odd mass (even mass for M – H molecular ions). Chemical constraints: $N \leq 7$; $S \leq 3$

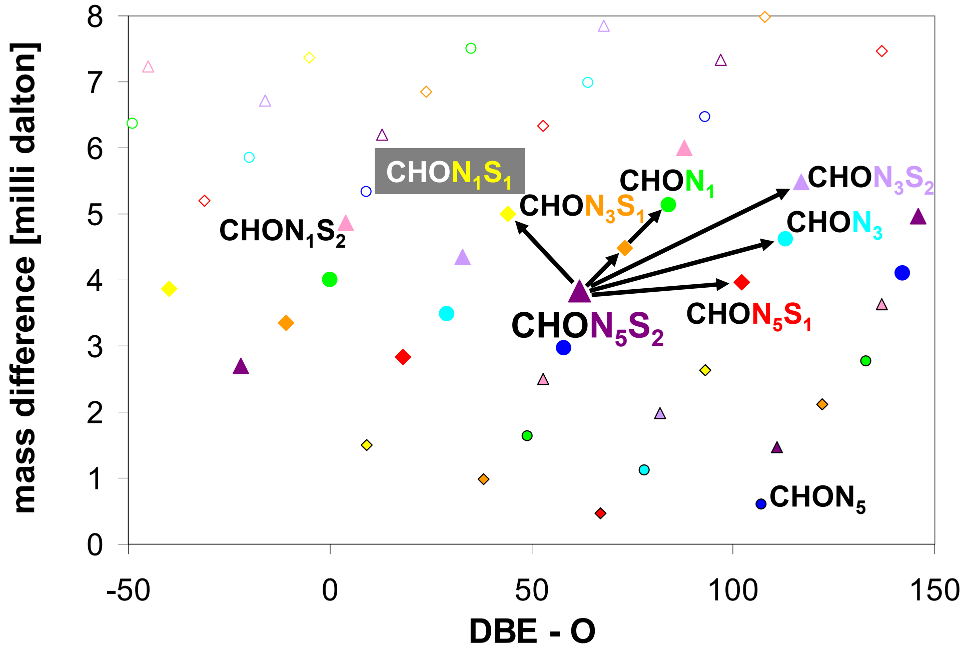

Figure S-3 Allocation of equivocal components derived from a septet (connection by arrows) as found in the data set from Koch et al. (4) in a Δm versus. DBE - O diagram

Table S-1 Formulas, corresponding masses, DBE, DBE – O, Δm, and Δ(DBE – O) values specific to each formula pair

DBE	DBE - O	formula/mass	N_3S_2	N_1S_0	N_1S_1	N_3S_0	N_3S_1	N_5S_1	N_5S_2
54	+54	$C_{64}H_{25}O_{0}N_{3}S_{2}$ 899.148989 Da	XXX XXX	+33	+73	+4	+44	+15	+55
37	+21	$C_{50}H_{29}O_{16}N_{1}S_{0}$ 899.148639	+0.350	XXX XXX	+40	-29	+11	-18	+22
10	-19	$C_{29}H_{41}O_{29}N_{1}S_{1}$ 899.148505	+0.484	+0.134	XXX XXX	-69	-29	-58	-18
55	+50	$C_{63}H_{21}O_{5}N_{3}S_{0}$ 899.148122	+0.867	+0.517	+0.383	XXX XXX	+40	+11	+51
28	+10	$C_{42}H_{33}O_{18}N_{3}S_{1}$ 899.147988	+1.001	+0.651	+0.517	+0.134	XXX XXX	-29	+11
46	+39	$C_{55}H_{25}O_{7}N_{5}S_{1}$ 899.147471	+1.518	+1.168	+1.034	+0.651	+0.517	XXX XXX	+40
19	-1	**$C_{34}H_{37}O_{20}N_{5}S_{2}$ 899.147337**	+1.652	+1.302	+1.168	+0.785	+0.651	+0.134	XXX XXX
24	0	**$^{13}C_{1}{}^{12}C_{39}H_{34}O_{24}$ 899.147364**	Isotope solution of the assignment problem						**+0.027**

Δ(DBE – O) values

Δm values

Table S-2 List of Δm, Δ(DBE – O) and their corresponding fragments

Δm (mDa)	Δ(DBE – O)	numbers of elemental and DBE differences
+0.027	**+1**	**$^{13}C_{+1}{}^{12}C_{+5}H_{-3}O_{+4}N_{-5}S_{-2}$ / DBE_{+5}**
+0.134	+40	$C_{+21}H_{-12}O_{-13}S_{-1}$ / DBE_{+27}
+0.167	-62	$C_{-27}H_{+12}O_{+27}N_{-4}S_{-2}$ / DBE_{-35}
+0.182	+6	$C_{+8}H_{+4}O_{-3}N_{-6}S_{+1}$ / DBE_{+3}
+0.201	-75	$C_{-42}H_{+16}O_{+27}N_{+4}$ / DBE_{-48}
+0.216	-7	$C_{-7}H_{+8}O_{-3}N_{+2}S_{+3}$ / DBE_{-10}
+0.301	-22	$C_{-6}O_{+14}N_{-4}S_{-3}$ / DBE_{-8}
+0.316	+46	$C_{+29}H_{-8}O_{-16}N_{-6}$ / DBE_{+30}
+0.335	-35	$C_{-21}H_{+4}O_{+14}N_{+4}S_{-1}$ / DBE_{-21}
+0.350	+33	$C_{+14}H_{-4}O_{-16}N_{+2}S_{+2}$ / DBE_{+17}
+0.383	-69	$C_{-34}H_{+20}O_{+24}N_{-2}S_{+1}$ / DBE_{-45}
+0.417	-82	$C_{-49}H_{+24}O_{+24}N_{+6}S_{+3}$ / DBE_{-58}
+0.469	+5	$H_{-8}O_{+1}N_{+4}S_{-2}$ / DBE_{+6}
+0.484	+73	$C_{+35}H_{-16}O_{-29}N_{+2}S_{+1}$ / DBE_{+44}
+0.517	-29	$C_{-13}H_{+8}O_{+11}N_{-2}$ / DBE_{-18}
+0.532	+39	$C_{+22}O_{-19}N_{-4}S_{+3}$ / DBE_{+20}
+0.551	-42	$C_{-28}H_{+12}O_{+11}N_{+6}S_{+2}$ / DBE_{-31}
+0.603	+45	$C_{+21}H_{-20}O_{-12}N_{+4}S_{-3}$ / DBE_{+33}
+0.651	+11	$C_{+8}H_{-4}O_{-2}N_{-2}S_{-1}$ / DBE_{+9}
+0.685	-2	$C_{-7}O_{-2}N_{+6}S_{+1}$ / DBE_{-4}
+0.785	+51	$C_{+29}H_{-16}O_{-15}N_{-2}S_{-2}$ / DBE_{+36}
+0.818	-51	$C_{-19}H_{+8}O_{+25}N_{-6}S_{-3}$ / DBE_{-26}
+0.819	+38	$C_{+14}H_{-12}O_{-15}N_{+6}$ / DBE_{+23}
+0.852	-64	$C_{-34}H_{+12}O_{+25}N_{+2}S_{-1}$ / DBE_{-39}
+0.867	+4	$C_{+1}H_{+4}O_{-5}S_{+2}$ / DBE_{-1}
+0.986	-24	$C_{-13}O_{+12}N_{+2}S_{-2}$ / DBE_{-12}
+1.001	+44	$C_{+22}H_{-8}O_{-18}S_{+1}$ / DBE_{+26}
+1.034	-58	$C_{-26}H_{+16}O_{+22}N_{-4}$ / DBE_{-36}
+1.120	+16	$C_{+8}H_{-12}O_{-1}N_{+2}S_{-3}$ / DBE_{+15}
+1.135	+84	$C_{+43}H_{-20}O_{-31}$ / DBE_{+53}
+1.168	-18	$C_{-5}H_{+4}O_{+9}N_{-4}S_{-1}$ / DBE_{-9}
+1.202	-31	$C_{-20}H_{+8}O_{+9}N_{+4}S_{+1}$ / DBE_{-22}
+1.302	+22	$C_{+16}H_{-8}O_{-4}N_{-4}S_{-2}$ / DBE_{+18}
+1.336	+9	$C_{+1}H_{-4}O_{-4}N_{+4}$ / DBE_{+5}
+1.470	+49	$C_{+22}H_{-16}O_{-17}N_{+4}S_{-1}$ / DBE_{+32}
+1.518	+15	$C_{+9}O_{-7}N_{-2}S_{+1}$ / DBE_{+8}
+1.552	+2	$C_{-6}H_{+4}O_{-7}N_{+6}S_{+3}$ / DBE_{-5}
+1.652	+55	$C_{+30}H_{-12}O_{-20}N_{-2}$ / DBE_{+35}
+1.686	+42	$C_{+15}H_{-8}O_{-20}N_{+6}S_{+2}$ / DBE_{+22}
+1.719	-60	$C_{-33}H_{+16}O_{+20}N_{+2}S_{+1}$ / DBE_{-40}
+1.853	-20	$C_{-12}H_{+4}O_{+7}N_{+2}$ / DBE_{-13}
+1.953	+33	$C_{+24}H_{-12}O_{-6}N_{-6}S_{-3}$ / DBE_{+27}
+2.504	-9	$C_{-4}H_{0}O_{+5}N_{0}S_{-1}$ / DBE_{-4}
+3.371	-5	$C_{-3}H_{+4}O_{0}N_{0}S_{+1}$ / DBE_{-5}

Evaluation procedure: Search for pairs of CHO and their potential corresponding “$CHON_5S_2$” isotopic peaks

The FT-ICR-MS data can be arranged as described in the table below. All CHO components are extracted using autofilter. In an additional column (IUPAC Mass ^{13}C) the masses of the corresponding ^{13}C-isotopes are calculated.

Sample Nr	IUPAC Mass	Intensity	C	H	O	N	S	IUPAC Mass ^{13}C		Additional information
21	288.048135	28824364	11	12	9	0	0	289.051489		
21	288.063390	229245760	15	12	6	0	0	289.066744		
21	290.042655	273747100	14	10	7	0	0	291.046009		
22	288.120905	28368697	13	20	7	0	0	289.124259		
22	290.006270	43563025	13	6	8	0	0	291.009624		
22	290.042655	221018170	14	10	7	0	0	291.046009		

As second step all $CHON_5S_2$ components are extracted and the masses are simply copied to the additional column.

Sample Nr	IUPAC Mass	Intensity	C	H	O	N	S	IUPAC Mass (copy)		Additional information
21	289.066717	36575224	9	15	2	5	2	289.066717		
21	291.045982	41394551	8	13	3	5	2	291.045982		
22	291.009597	4649184	7	9	4	5	2	291.009597		
22	291.045982	28974350	8	13	3	5	2	291.045982		

To search for the pairs these two data sheets are merged and sorted to increasing mass (additional IUPAC Mass ^{13}C column). The potential $\delta^{13}C$‰ values can be calculated (using the mass intensities as explained in the letter) for pairs of CHO and $CHON_5S_2$ components if there were any.

Sample Nr	IUPAC Mass	Intensity	C	H	O	N	S	IUPAC Mass ^{13}C	$\delta^{13}C$‰ value	Additional information
21	288.048135	28824364	11	12	9	0	0	289.051489		
21	289.066717	36575224	9	15	2	5	2	289.066717		
21	288.063390	229245760	15	12	6	0	0	289.066744	-53.5	
21	291.045982	41394551	8	13	3	5	2	291.045982		
21	290.042655	273747100	14	10	7	0	0	291.046009	-38.8	
22	288.120905	28368697	13	20	7	0	0	289.124259		
22	291.009597	4649184	7	9	4	5	2	291.009597		
22	290.006270	43563025	13	6	8	0	0	291.009624	-269	
22	291.045982	28974350	8	13	3	5	2	291.045982		
22	290.042655	221018170	14	10	7	0	0	291.046009	-167	

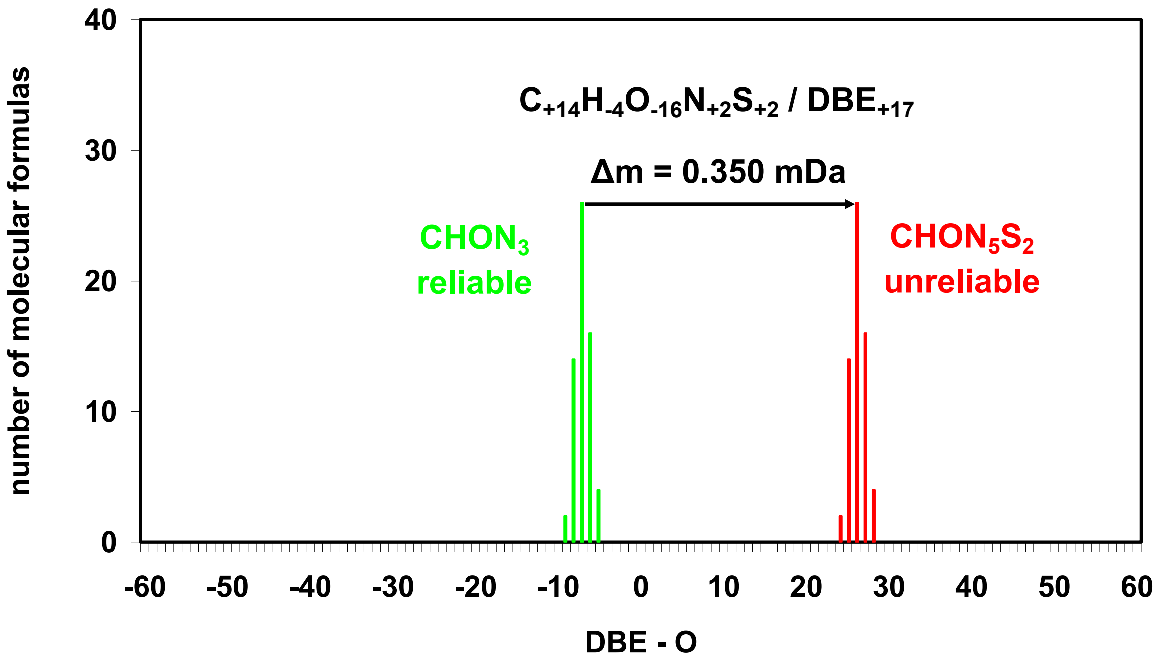

Figure S-4 Illustration of the doublet $CHON_3$ / $CHON_5S_2$ in a frequency versus DBE – O diagram, sample from a German pit lake