Supporting information to

Chemical changes in fossil and biogenic heating oils on long-term storage

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Table S1: Distribution of the aromatic compounds in the two fossil heating oils A and B (as determined in a single determination by the Oel-Waerme-Institut, Germany).

	Monoaromatics	**Diaromatics**	**Triaromatics**	**Total**
		(% m/m)		
Heating oil A	23.9	6.2	0.8	30.9
Heating oil B	29.9	2.4	0.2	32.5

Table S2: FAME distribution in the FAMEs 1 and 2 in % on a mass basis, determined by GC-FID measurement with C15:0 as internal standard (n = 3).

	C16:0	**C18:0**	**C18:1**	**C18:2**	**C18:3**	**C20:0**
			(% m/m)			
FAME 1	4.6±0.10	1.9±0.08	61.3±0.7	20.3±0.4	9.0±0.18	0.6±0.05
FAME 2	6.4±0.12	2.3±0.07	52.1±0.5	28.3±0.4	8.2±0.14	0.5±0.04

Table S3: Concentration of free fatty acids in FAME mixture B6 after 0 and 6 months of storage as determined by ion chromatography; single determination.

	Concentration in mg/L and mM							
Storage time	**Lactic**	**Formic**	**Acetic**	**Propionic**	**Isobutyric**	**Butyric**	**Pentanoic**	**Hexanoic**
0 months								
(mg/L)	0.5	6.8	5.6	3.9	n.d.	n.d.	n.d.	n.d.
(mM)	0.01	0.15	0.09	0.05				
6 months								
(mg/L)	20.5	216.1	57.4	77.4	15.2	12.0	28.4	333.7
(mM)	0.23	4.78	0.96	1.05	0.17	0.14	0.28	2.88

n.d. = not detected

Table S4: (-)-ESI-MS measurement of fatty acids in the alkaline aqueous extract of FAME B6 after 12 months of storage.

m/z	Relative Intensity	Deviation (ppm)	DBE	Composition	Acid
59.01393	0.28	1.33	1	$C_2H_4O_2$	acetic
73.02953	0.35	0.36	1	$C_3H_6O_2$	propionic
89.02439	7.77	-0.27	1	$C_3H_6O_3$	lactic
87.04514	0.26	-0.14	1	$C_4H_8O_2$	butyric
99.04511	1.17	-0.40	2	$C_5H_8O_2$	pentenoic
101.06076	1.18	-0.45	1	$C_5H_{10}O_2$	pentanoic
111.04506	0.04	-0.87	3	$C_6H_8O_2$	hexadienoic
113.06070	0.82	-0.89	2	$C_6H_{10}O_2$	hexenoic
115.07628	35.69	-1.50	1	$C_6H_{12}O_2$	hexanoic
125.06064	0.74	-1.28	3	$C_7H_{10}O_2$	heptadienoic
127.07628	0.65	-1.33	2	$C_7H_{12}O_2$	heptenoic
129.09192	1.23	-1.39	1	$C_7H_{14}O_2$	heptanoic
139.07624	0.17	-1.54	3	$C_8H_{12}O_2$	octadienoic
141.09190	3.17	-1.47	2	$C_8H_{14}O_2$	octenoic
143.10752	2.53	-1.61	1	$C_8H_{16}O_2$	octanoic
153.09185	0.31	-1.67	3	$C_9H_{14}O_2$	nonadienoic
155.10747	2.31	-1.82	2	$C_9H_{16}O_2$	nonenoic
157.12310	6.12	-1.92	1	$C_9H_{18}O_2$	nonanoic
167.10745	0.46	-1.84	3	$C_{10}H_{16}O_2$	decadienoic
169.12308	0.43	-1.90	2	$C_{10}H_{18}O_2$	decenoic
201.11275	100.00	-2.39	2	$C_{10}H_{18}O_4$	azelaic acid monomethyl ester
171.13872	0.63	-1.97	1	$C_{10}H_{20}O_2$	decanoic
213.11278	2.31	-2.13	3	$C_{11}H_{18}O_4$	10-methoxy-10-oxodecenoic
183.13870	0.26	-1.95	2	$C_{11}H_{20}O_2$	undecenoic
215.12841	2.84	-2.20	2	$C_{11}H_{20}O_4$	10-methoxy-10-oxodecanoic
185.15436	0.02	-1.85	1	$C_{11}H_{22}O_2$	undecanoic
227.12836	7.34	-2.30	3	$C_{12}H_{20}O_4$	11-methoxy-11-oxoundecenoic
229.14403	0.65	-2.18	2	$C_{12}H_{22}O_4$	11-methoxy-11-oxoundecanoic
199.16998	0.17	-1.86	1	$C_{12}H_{24}O_2$	dodecanoic
241.14397	2.84	-2.33	3	$C_{13}H_{22}O_4$	12-methoxy-12-oxododecenoic
213.18555	0.10	-2.11	1	$C_{13}H_{26}O_2$	tridecanoic
253.14396	1.35	-2.26	4	$C_{14}H_{22}O_4$	13-methoxy-13-oxotridecadienoic
255.15962	0.16	-2.21	3	$C_{14}H_{24}O_4$	13-methoxy-13-oxotridecenoic
227.20116	0.42	-2.16	1	$C_{14}H_{28}O_2$	tetradecanoic
267.15957	0.15	-2.30	4	$C_{15}H_{24}O_4$	14-methoxy-14-oxotetradecadienoic
241.21677	0.28	-2.20	1	$C_{15}H_{30}O_2$	pentadecanoic
281.17520	0.14	-2.25	4	$C_{16}H_{24}O_4$	15-methoxy-15-oxopentadecadienoic
253.21673	0.45	-2.25	2	$C_{16}H_{30}O_2$	hexadecenoic
255.23236	0.99	-2.31	1	$C_{16}H_{32}O_2$	hexadecanoic
295.19082	0.17	-2.24	4	$C_{17}H_{28}O_4$	16-methoxy-16-oxohexadecadienoic
269.24801	0.14	-2.22	1	$C_{17}H_{34}O_2$	heptadecanoic
307.19079	1.08	-2.24	5	$C_{18}H_{28}O_4$	17-methoxy-17-oxoheptadecatrienoic
309.20644	0.64	-2.24	4	$C_{18}H_{30}O_4$	17-methoxy-17-oxoheptadecadienic

Table S5: Signals from (+)-ESI-MS spectrum of the sediment of the blend B3.

m/z	Relative Intensity	Theoretical Mass	Deviation (ppm)	Elemental Composition
474.35694	46.90	474.35779	-1.78	$C_{29}H_{48}O_4N$
488.37251	100.00	488.37344	-1.89	$C_{30}H_{50}O_4N$
502.35177	43.79	502.35270	-1.86	$C_{30}H_{48}O_5N$
502.38821	75.71	502.38909	-1.74	$C_{31}H_{52}O_4N$
504.36739	37.36	504.36835	-1.91	$C_{30}H_{50}O_5N$
504.40392	38.56	504.40474	-1.62	$C_{31}H_{54}O_4N$
514.38819	50.41	514.38909	-1.74	$C_{32}H_{52}O_4N$
516.36742	50.98	516.36835	-1.81	$C_{31}H_{50}O_5N$
516.40380	66.13	516.40474	-1.81	$C_{32}H_{54}O_4N$
518.38301	31.36	518.38400	-1.90	$C_{31}H_{52}O_5N$
528.36741	27.68	528.36835	-1.77	$C_{32}H_{50}O_5N$
528.40380	56.99	528.40474	-1.77	$C_{33}H_{54}O_4N$
530.38308	45.53	530.38400	-1.73	$C_{32}H_{52}O_5N$
530.41944	62.37	530.42039	-1.79	$C_{33}H_{56}O_4N$

Table S6: Nitrogen containing compounds in the sediment of the blend B3 after 19.5 months of storage as found by (+)-ESI-MS.

m/z	Theoretical mass	Deviation (ppm)	Elemental composition
190.15935	190.15957	1.69	$C_{13}H_{20}N$
202.15939	202.15957	1.81	$C_{14}H_{20}N$
204.17505	204.17522	1.84	$C_{14}H_{22}N$
216.17504	216.17522	1.69	$C_{15}H_{22}N$
218.19070	218.19087	1.69	$C_{15}H_{24}N$
230.19073	230.19087	1.76	$C_{16}H_{24}N$
232.20639	232.20652	1.79	$C_{16}H_{26}N$
242.19081	242.19087	1.98	$C_{17}H_{24}N$
244.20642	244.20652	1.82	$C_{17}H_{26}N$
246.22209	246.22217	1.87	$C_{17}H_{28}N$
256.20645	256.20652	1.84	$C_{18}H_{26}N$
258.22211	258.22217	1.88	$C_{18}H_{28}N$
284.23782	284.23782	1.91	$C_{20}H_{30}N$

Table S7: Nitrogen containing compounds in the sediment of the blend B3 after 19.5 months of storage as found by (-)-ESI-MS.

m/z	Theoretical mass	Deviation (ppm)	Elemental composition	Putative product
190.05098	190.05042	0.06	$C_{10}H_8O_3N$	oxidized, alkylated indole
192.06668	192.06607	0.32	$C_{10}H_{10}O_3N$	oxidized, alkylated indole
206.08237	206.08172	0.49	$C_{11}H_{12}O_3N$	oxidized, alkylated indole
216.06672	216.06607	0.46	$C_{12}H_{10}O_3N$	oxidized, alkylated indole
220.09795	220.09737	0.16	$C_{12}H_{14}O_3N$	oxidized, alkylated indole
228.17585	229.18305	0.33	$C_{16}H_{22}N$	alkylated indole

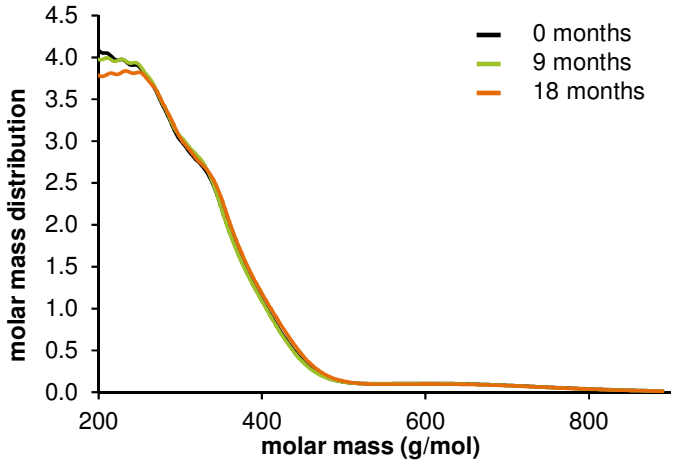

Figure S1: Size exclusion chromatogram showing the molar mass distribution of the fossil heating oil B1 before and after storage for up to 18 months. Conditions as detailed in the experimental section.

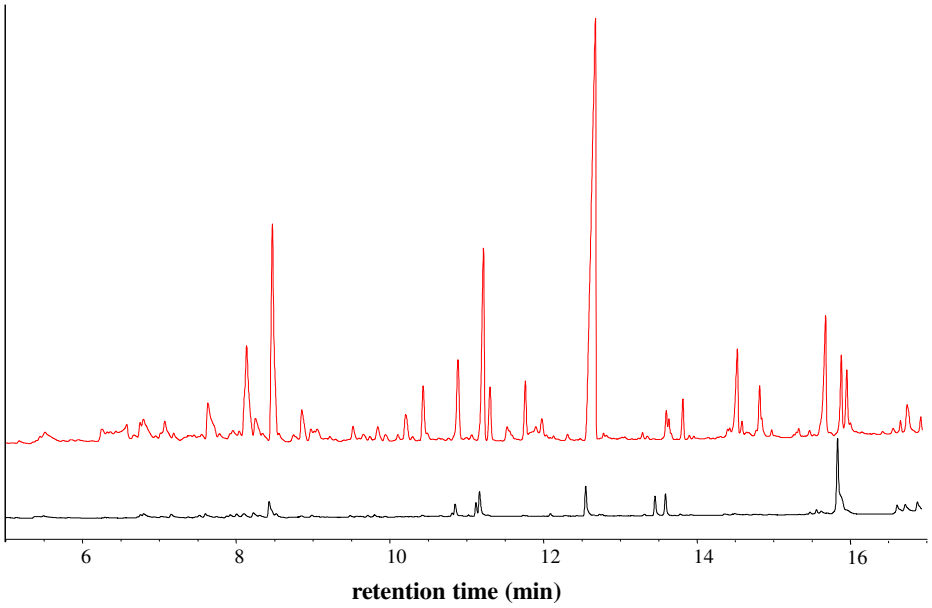

Figure S2: Gas chromatogram with flame ionization detection of the FAME mixture B5 after 0 months (bottom, black) and 12 months (top, red) of storage. Only the portion of the chromatogram that elutes before the C18 FAMEs is shown here.

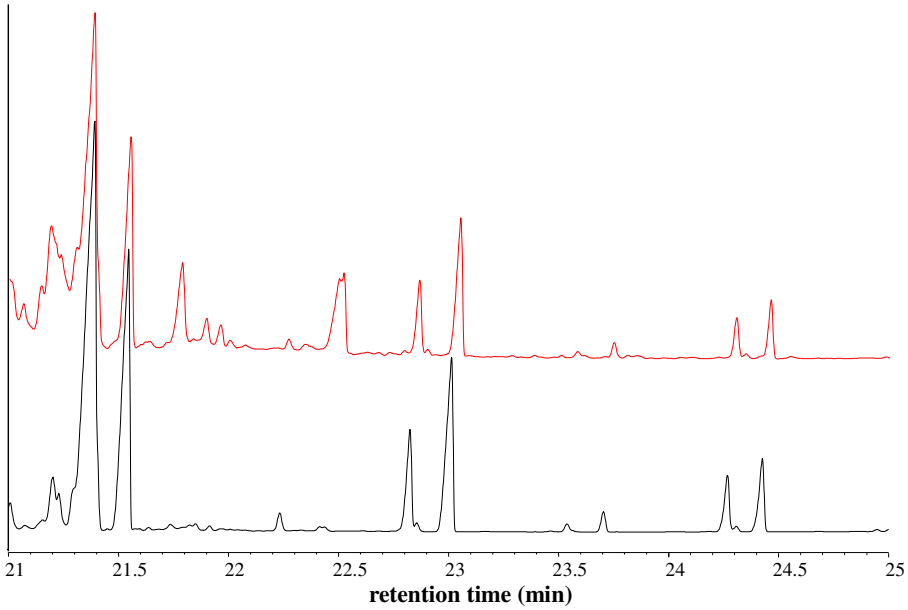

Figure S3: Gas chromatogram with flame ionization detection of the FAME mixture B5 after 0 months (bottom, black) and 12 months (top, red) of storage. Only the portion of the chromatogram that elutes after the C18 FAMEs is shown here.

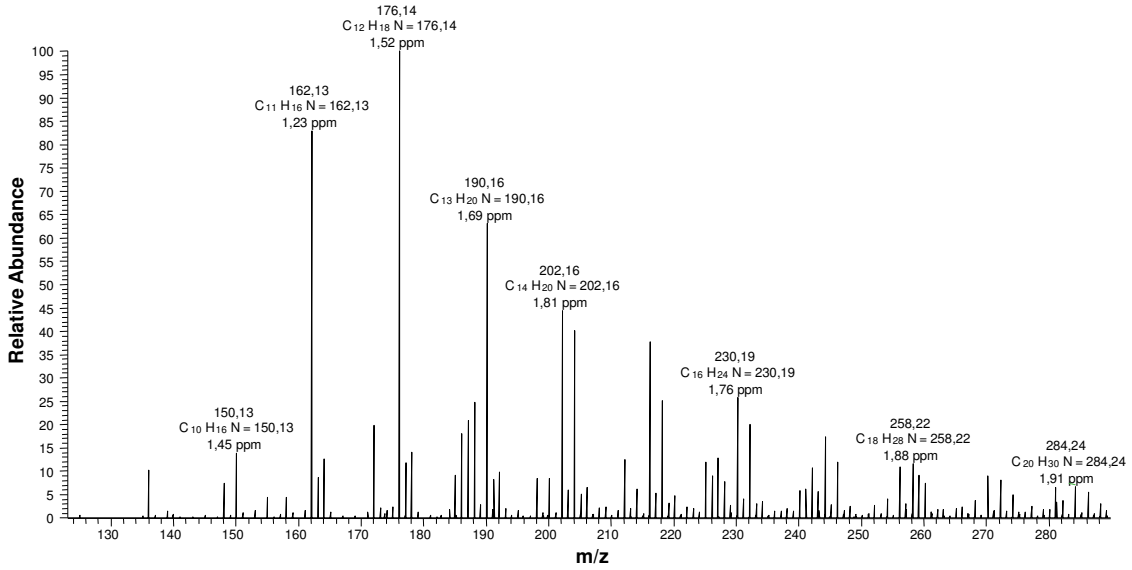

Figure S4: (+)-ESI-MS of the sediment of blend B3 after 19.5 months of storage.