Supporting Information for *n*-Alkane Profiles of Engine Lubricating Oil and Particulate Matter by Molecular Sieve Extraction

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Silica Gel Cleaning and Activation Procedure

Silica gel (Aldrich, 100-200 mesh, pore size 150Å, pore 1.2 $cm^3 g^{-1}$, and active surface 320 $m^2 g^{-1}$) was activated prior to use according to the procedure detailed in the SI. a batch of 200-300 g silica gel was placed in a 900 X 41-mm id. chromatography column with a coarse porosity fritted disk. The column was serially rinsed with 2 volumes of methanol followed by 2 volumes of dichloromethane. The silica gel was dried overnight at 110°C, then activated at 250°C for 24 hours and kept in an oven at that temperature until used.

ASE extraction parameters

The filters were extracted sequentially with dichloromethane followed by methanol. The operating conditions used in this work were as follows:

- Cell pressure and temperature: 2000 psi at 100°C
- Extraction time: 5-min heat up and 5-min static
- Nitrogen purge at 100 psi for 240 seconds

The dichloromethane soluble PM organics were subjected to solvent exchange to hexane by adding an excess of solvent and concentrating to ~1mL in an automated Zymark Turbovap II Concentration Workstation (Zymark) solvent evaporator.

Silica Gel Column Chromatography Separation

Sodium sulphate and distilled chromatographic grade solvents including acetone, hexane, dichloromethane (DCM) and methanol were used without further purification.

Silica gel (Aldrich;100-200 mesh, pore size 150Å, pore 1.2cm^3/g, and active surface 320 m^2/g), was washed and activated prior to use according to the following procedure. A batch of 200-300 g silica gel was placed in a 900 × 41-mm ID chromatography column with a coarse porosity fritted disk. The column was serially rinsed with 2 volumes of methanol followed by 2 volumes of DCM. The silica gel was dried overnight at 110°C, then activated at 250°C for 24 hours and kept in an oven at that temperature until used.

Approximately 5 g of 5% deactivated silica was prepared by adding 5 % water to activated silica (w/w) and shaking vigorously until no clumps were observed. Next, the deactivated silica was transferred to a 1.5 cm (id) × 25 cm chromatography column packed at the bottom with glass wool and topped with approximately 1 g of sodium sulphate. The height of the deactivated silica gel bed was approximately 4.5 cm. The column was pre-cleaned with 15 mL of hexane.

A vial was placed under the column and the sample loaded on column with approximately 2 mL of hexane rinses. The hexane rinse was also loaded onto the column and an additional 12 mL of hexane was added to collect all *n*-alkanes, alkylcyclohexanes and biomarkers in the first vial (Fraction F1). Prior to the column bed going dry the first vial was removed and replaced with a second one. The hexane:acetone (50:50 v/v) rinse was loaded on the column. The initial sample vial was rinsed with 1 mL hexane:acetone that was then transferred to the column. The column was immediately eluted with 15 mL of hexane/acetone. This fraction contained only the PAH suite of compounds (Fraction F2). Just as the column bed went dry, the second vial was removed and the methanol rinse loaded on the column along with a 1 mL methanol rinse of the starting sample vial.

The column was eluted with 13 mL and 15 mL aliquots of methanol collected in two separate vials (Fractions F3 and F4).

GC/MS parameters

GC/MS analyses were done with an Agilent 6890 GC equipped with an autosampler and a 5972A quadrupole mass selective detector operated in electron impact mode (electron energy 70 eV, ion source temperature 280°C). The chromatography was done with a DB-5, fused silica capillary column (0.25 μm film, 0.25 mm ID, 30 m) using the following conditions: column flow: 1.5 ml min^{-1}, inlet temperature: 275°C, temperature program: initial temperature: 50°C, final temperature: 280°C with a ramp of 8°C min^{-1} and the final temperature held for 15 minutes. The analyses were carried out either in selective ion mode for quantitative analysis (mz^{-1}: 85 for *n*-alkanes and 66 for deuterated *n*-alkanes with a dwell time of 50 msec per ion) or in scan mode (total ion count, mass range 40 to 550) for identification of compounds. *N*-alkane and other compounds were identified either by comparison with retention times of reference compounds and/or with the help of their MS fragmentation patterns using the National Institute of Standards and Technology NIST05 library database. MS data and chromatograms were recorded using Chemstation software.

Table S1: Coding Scheme for Lubricating Oils

Lubricating oil code	Vendor #	Lubricating oil Type
L1	1	SAE-10W30 LDV
L2	2	SAE-10W30 LDV
L3	3	SAE-10W30 LDV
L4	4	SAE-10W30 LDV
L5	5	SAE-10W30 LDV
L6	6	SAE-10W30 LDV
L7	7	SAE-10W30 LDV
L8	8	SAE-10W30 LDV
H1	1	SAE15W40 HDV
H3	3	SAE15W40 HDV
H7	7	SAE15W40 HDV
H9	9	SAE15W40 HDV

TABLE S2: Surrogates Spiked on PM Filters

Surrogate	Volume of spike (ul)	Conc
Deuterated alkane dC_{24}[1]	25	50 ug ml^{-1}
BB-hopane[2]	25	10 ug ml^{-1}
PAH mixture [2] Acenaphthene-d10 Anthracene-d10 Pyrene-d10 Benz(a)anthracene-d12 Benzo(a)pyrene-d12 Dibenz(ah)anthracene-d14 Benzo(ghi)perylene-d12	100	10 ug ml^{-1}
Nitro PAH[2] d9-2-Nitrofluorene d9-9-Nitroanthracene d9-3-Nitrofluoranthene d9-1-Nitropyrene d11-6-Nitrochrysene d11-6-Nitrobenzo(a)pyrene d8-1,3-Dinitropyrene d8-1,6-Dinitropyrene d8-1,8-Dinitropyrene	100	10 ug ml^{-1}
d-C8 free fatty acid[2] d-C18, free fatty acid[2]	100	32.06 ng ul^{-1} 31.94 ng ul^{-1}
2-fluoro-9-fluorenone[2] and 2-chloro-anthroquinone[2]	400	10.02 ng ul^{-1} 11.32 ng ul^{-1}

NOTE: 1: dC24 used as surrogate for *n*-alkanes correction losses due to ASE extraction.
2: surrogates from another study not discussed in this paper

Table S3: ASE Operating Parameters Used to Extract the *n*-Alkanes from the Molecular Sieve

Trial	Pres. (PSI)	Temp (°C)	Static time (min)	Cycles	Solvents
1	2000	100	5	1	Pentane & hexane
2	2000	100	5	3	Hexane
3	2000	150	30	5	Hexane
4	2000	200	30	5	Hexane

TABLE S4: Recovery of *n*-Alkanes in Lubricating Oil With and Without Sonication (non optimized method)

Tests	With sonication		Without sonication	
Conc. μg ml^{-1}	5		5	
Trials	N=6		N=4	
Carbon #	Avg. Rec. %	Std dev %	Avg. Rec. %	Std dev %
dC_{12}	53	13	25	24
dC_{16}	51	9	18	55
dC_{20}	56	5	22	30
dC_{24}	62	6	25	51
dC_{30}	67	11	29	54
dC_{36}	63	20	28	72
Ave.	59	12	24	48

Table S5: Recovery of Deuterated and Regular *n*-Alkanes from Stock Solutions Set A (results from optimized method without lubricating oil matrix oil)

Conc (μg ml^{-1})	2.5		5		10	
Trials	N=3		N=3		N=2	
Carbon #	Recovery %	Adjusted Recovery%	Recovery %	Adjusted Recovery%	Recovery %	Adjusted Recovery%
C10	29	74	73	96	45	80
dC12	40	87	76	99	55	96
C12	45	96	77	100	56	96
C14	49	96	75	96	58	97
dC16	62	110	79	100	63	103
C16	59	105	77	98	62	100
C18	66	109	78	97	64	101
dC20	74	114	83	101	67	104
C20	70	108	81	99	66	102
C22	71	103	82	100	66	101
dC24	67	93	83	100	66	100
C24	64	88	82	99	66	99
C26	65	86	82	98	65	96
C28	76	97	84	98	65	94
dC30	74	92	84	98	66	96
C30	76	95	81	93	63	92
dC32	81	98	92	70	67	96
C32	78	94	80	92	62	89
C34	74	88	79	89	64	91
dC36	91	106	87	97	73	104
C36	73	85	77	86	64	91
C38	71	82	79	87	65	92
Average	66	96	80	96	63	96

Table S6: Recovery of *n*-Alkanes in the Presence of Different Solvents

Solvent	Cyclohexane		Hexane	
Conc (μg ml^{-1})	5		5	
Trials	4		4	
Carbon #	Recovery %	Standard deviation %	Recovery%	Standard deviation %
dC12	50	6	35	3
dC16	45	9	49	4
dC20	49	10	58	4
dC24	53	12	68	4
dC30	60	11	80	6
dC36	52	11	58	8

Table S7. CPI of LDV and HDV Lubricating Oils Before and After Sieve Treatment

Code	Type	CPI before treatment	Deviation % from unity	CPI after treatment	Deviation % from unity
L1	LDV	1.02	2	1.00	0.3
H1	HDV	0.95	5	1.01	1
L2	LDV	1.15	15	0.96	4
L3	LDV	1.02	2	0.94	6
H3	HDV	0.97	3	1.06	6
L4	LDV	0.90	9	0.94	6
L5	LDV	0.92	8	0.94	6
L6	LDV	0.88	12	1.01	2
L7	LDV	0.93	7	1.01	2
H7	HDV	0.99	1	0.90	10
L8	LDV	0.95	5	0.95	5
H9	HDV	1.28	28	0.93	7
Range (min – max)		**0.88-1.28**		**0.90-1.06**	
Std Dev %		**11**		**5**	

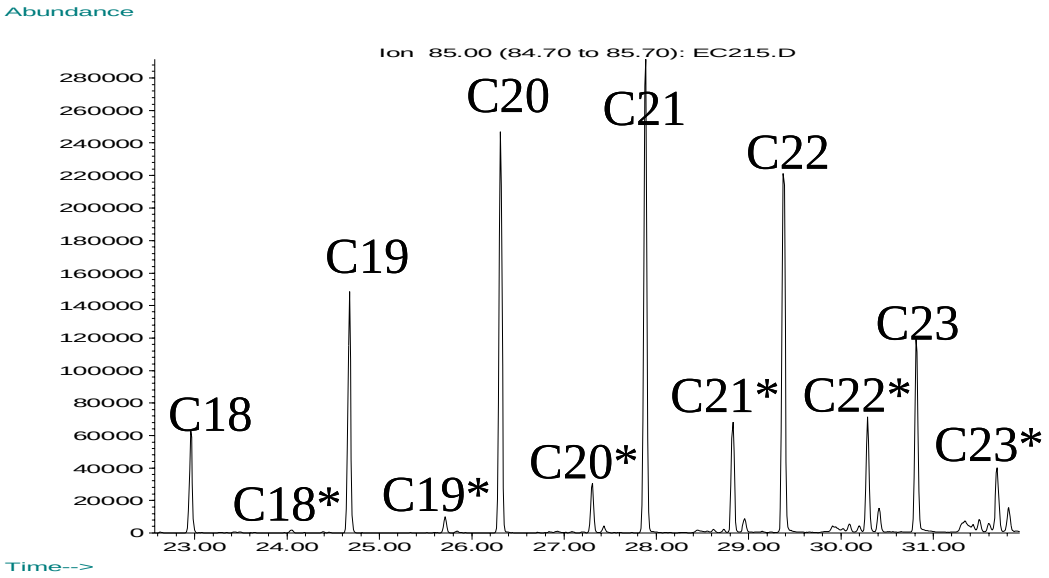

Figure S1: Section of the chromatogram (m/z 85) of the HDV Lube H1 processed by the molecular sieve procedure showing a series of n-alkanes (C18 to C23) interspersed with a series of 2-methyl branched alkanes (C18* to C20*) identified with the NIST05 library database.

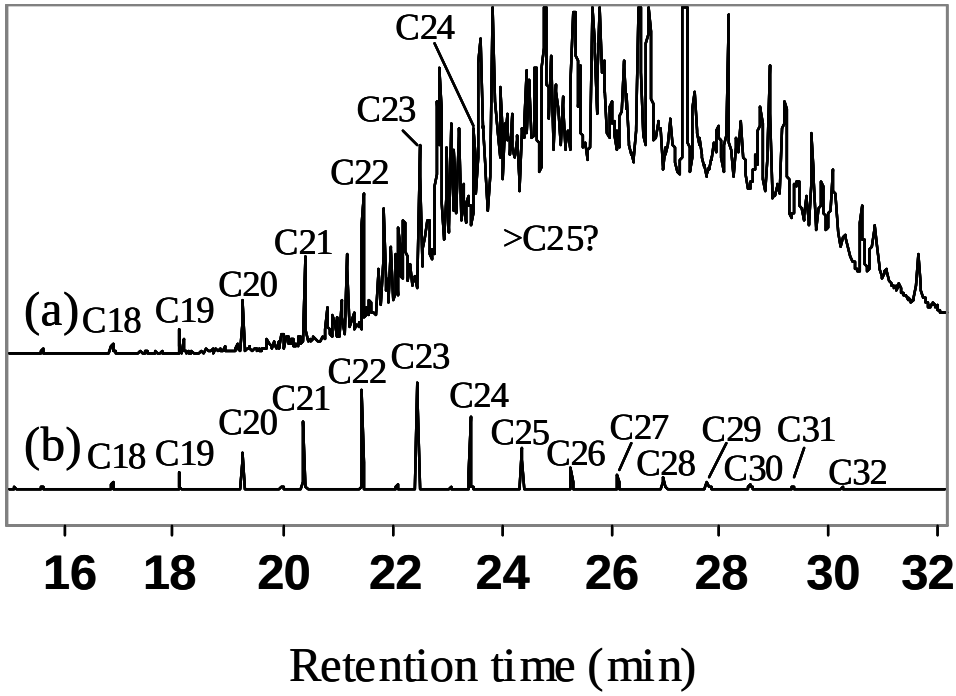

Figure S2. Chromatograms (mz^{-1} 85) of lubricating oil L1 (a) before and (b) after molecular sieve treatment.

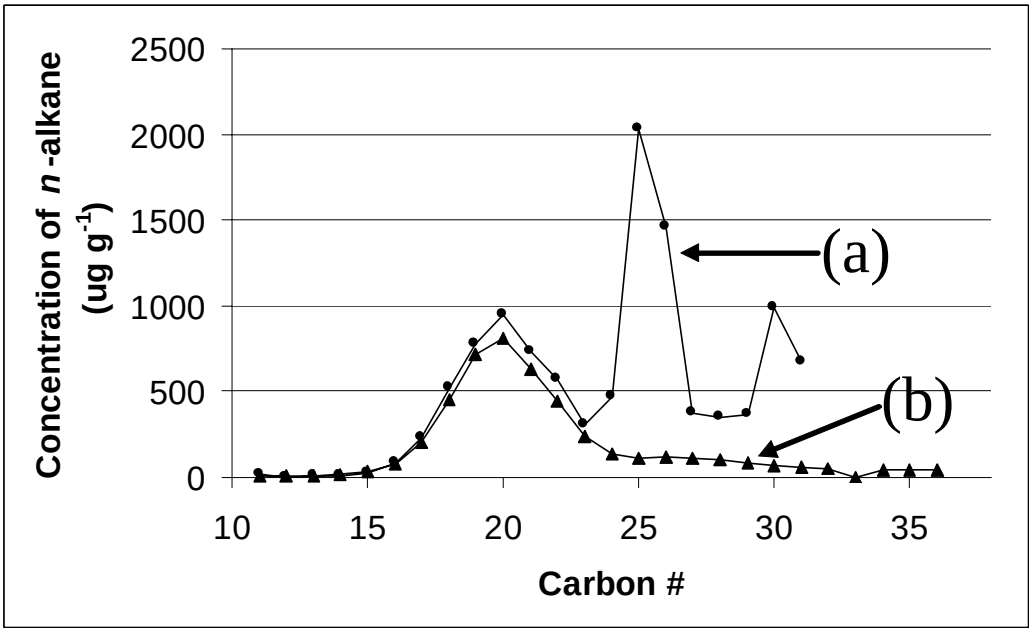

Figure S3. Concentration of *n*-alkanes as a function of carbon number in lubricating oil L3 (a) before and (b) after sieve treatment.

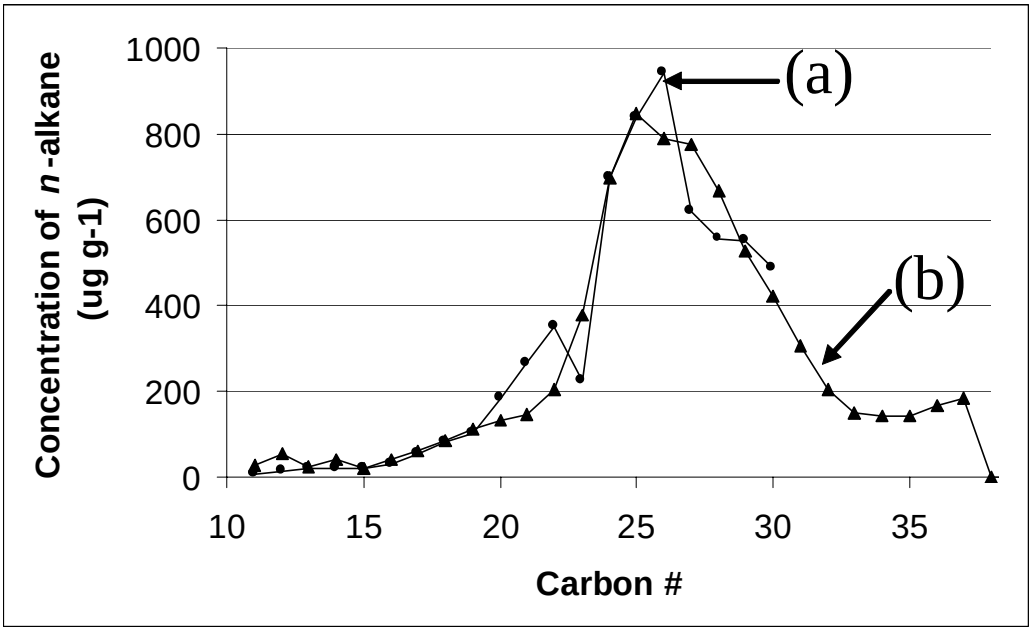

Figure S4. Concentration of *n*-alkanes as a function of carbon number in lubricating oil L6 (a) before and (b) after sieve treatment.

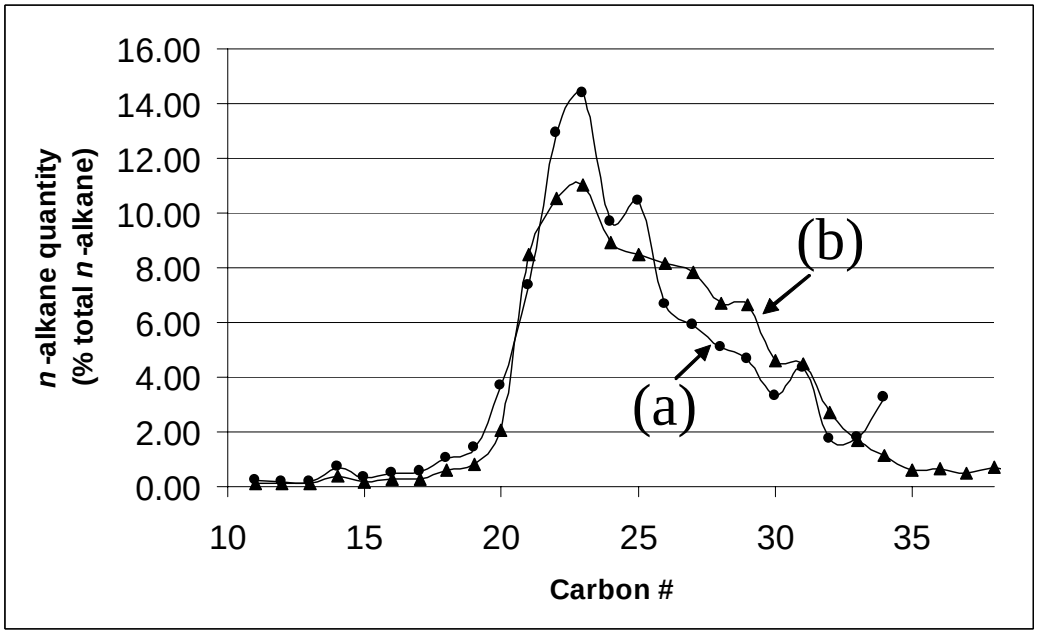

Figure S5: Average *n*-alkane profiles of the 3 hour PM sample: (a) before and (b) after sieve treatment.