Supplement of Geosci. Model Dev., 15, 7731–7749, 2022
https://doi.org/10.5194/gmd-15-7731-2022-supplement

Geoscientific Model Development
Open Access
EGU

Supplement of

A lumped species approach for the simulation of secondary organic aerosol production from intermediate-volatility organic compounds (IVOCs): application to road transport in PMCAMx-iv (v1.0)

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A. Model requirements for the implementation of the new lumped species approach.

The new lumped species approach has been first implemented in PMCAMx, a regional/urban three-dimensional chemical transport model (CTM), for testing and evaluation. Different CTMs or global models can implement the proposed approach given that they fulfill certain requirements.

First, the model needs to be able to simulate the gas-phase chemistry of volatile organic compounds (VOCs) by using a lumped species gas-phase mechanism. For the simulations of the gas-phase chemistry, PMCAMx utilizes a modified version of the SAPRC gas-phase chemistry mechanism. The implementation of the new approach to models utilizing any version of SAPRC is straightforward. If the model utilizes a different gas-phase mechanism, then the new approach can be still implemented, but one would need to adjust the volatile products that are produced from the oxidation reactions of the new lumped IVOC species taking into account the simulated stable molecules and radicals simulated in the specific mechanism. The volatile products for the SAPRC application are given in reactions R3 and R4 of the main paper.

Second, for the implementation of the new approach, a model needs to simulate the formation of secondary organic aerosol (SOA) by using the volatility basis-set (VBS) approach. Specifically, the VBS framework is not needed for the simulation of the IVOC species, but rather for the simulation of the various SOA-iv products and their partitioning between the gas and particulate phases.

Finally, to calculate the new lumped IVOC species emissions, the temporally and spatially resolved source specific emissions of the total VOCs emitted over the domain are needed.

Table S1: Major components of each lumped VOC in the SAPRC mechanism.

Species	Components	Type of Source
ALK1	Ethane (100%)	Anthropogenic
ALK2	Propane (59%) Acetylene (41%)	Anthropogenic
ALK3	n-Butane (68%) Isobutane (30%) 2,2-Dimethyl Butane (2%)	Anthropogenic
ALK4	Iso-Pentane (45%) n-Pentane (18%) 2-Methyl Pentane (11%) 3-Methyl Pentane (8%) 2,4-Dimethyl Pentane (5%) Methylcyclopentane (5%) n-Hexane (4%) 2,3-Dimethyl Butane (3%) Cyclopentane (2%)	Anthropogenic
ALK5	2,4-Dimethyl Hexane (11%) n-Decane (10%) 3-Methyl Hexane (10%) n-Heptane (7%) 2,3-Dimethyl Pentane (6%) 2-Methyl Heptane (6%) 4-Methyl Heptane (6%) 2,4-Dimethyl Heptane (5%) Methylcyclohexane (4%) 2,6-Dimethyl Octane (4%) n-Nonane (4%) n-Octane (4%) Cyclohexane (4%) 2-Methyl Hexane (3%) 4-Methyl Octane (2%) 2-Methyl Octane (2%) 4-Methyl Nonane (2%) 2-Methyl Nonane (2%) n-Dodecane (2%) Ethylcyclohexane (1%) n-Undecane (1%) 3,6-Dimethyl Decane (1%)	Anthropogenic
OLE1	Propene (29%) 1-Butene (12%) 1-Hexene (24%) 1-Pentene (12%) 1-Heptene (11%) 1-Nonene (5%) 3-Methyl-1-Butene (3%) 1-Octene (2%) 1-Undecene (2%) 1-Decene (0.9%)	Anthropogenic
OLE2	cis-2-Pentene (14%)	Anthropogenic

	trans-2-Pentene (14%) trans-2-Butene (14%) Isobutene (11%) cis-2-Butene (9%) 2-Methyl-1-Butene (8%) 1,3-Butadiene (6%) 2-Methyl-2-Butene (5%) Cis-2-Hexene (5%) Trans-2-Hexene (5%) Trans-3-Heptene (4%) Trans-4-Nonene (2%) Trans-4-Octene (2%) Trans-5-Undecene (2%) Trans-2-Heptene (2%) Cyclohexene (2%) Trans-4-Decene (0.7%) 3,4-Diethyl-2-Hexene (0.2%)	
ARO1	Toluene (70%) n-Propyl Benzene (10%) Ethyl Benzene (10%) Benzene (7%) s-Butyl Benzene (2%) Isopropyl Benzene (1%)	Anthropogenic
ARO2	m-Xylene (22%) p-Xylene (22%) o-Xylene (20%) 1,3,5-Trimethyl Benzene (14%) 1,2,3-Trimethyl Benzene (14%) 1,2,4-Trimethyl Benzene (9%)	Anthropogenic
TERP	α-Pinene (38%) β-Pinene (27%) 3-Carene (17%) Sabinene (10%) d-Limonene (9%)	Biogenic
ISOP	Isoprene (100%)	Biogenic
SESQ	Sesquiterpenes	Biogenic

Table S2: On-road emission factors and molar fractions of the individual compounds lumped in the new lumped IVOC species.

Lumped Species	Nº Carbons	Compound	EFs for diesel vehicles (mg / kg_{fuel})	EFs for gasoline vehicles (mg / kg_{fuel})	Molar fraction
ALK6	12	Dodecane	9.8	0.6	0.02
	13	Tridecane	10.3	0.4	0.02
	14	Tetradecane	6.0	0.2	0.01
	14	2,6,10-Trimethylundecane	6.1	0.2	0.01
	12	Hexylcyclohexane	1.5	0.0	<0.01
		Unspeciated b-alkanes B12	34.0	8.9	0.10
		Unspeciated b-alkanes B13	28.5	3.9	0.07
		Unspeciated b-alkanes B14	18.2	2.1	0.04
		Unspeciated cyclic alkanes B12	124.2	0	0.22
		Unspeciated cyclic alkanes B13	168.2	0	0.30
		Unspeciated cyclic alkanes B14	119.3	0	0.21
ALK7	15	Pentadecane	5.5	0.1	0.02
	16	Hexadecane	4.3	0.1	0.01
	17	Heptadecane	3.4	<0.01	0.01
	15	2,6,10-Trimethyldodecane	3.0	0.1	0.01
	16	2,6,10-Trimethyltridecane	1.9	<0.01	0.01
	13	Heptylcyclohexane	1.3	<0.01	<0.01
	14	Octylcyclohexane	0.7	<0.01	<0.01
	15	Nonylcyclohexane	0.7	<0.01	<0.01
		Unspeciated b-alkanes B15	16.3	1.1	0.05
		Unspeciated b-alkanes B16	15.9	0.8	0.05
		Unspeciated b-alkanes B17	9.0	0.6	0.03
		Unspeciated cyclic alkanes B15	107.4	0	0.31
		Unspeciated cyclic alkanes B16	93.8	0	0.27
		Unspeciated cyclic alkanes B17	72.7	2.1	0.22
ALK8	18	Octadecane	3.4	0.1	0.02
	19	Nonadecane	2.0	<0.01	0.01
	20	Eicosane	1.3	<0.01	0.01
	18	2,6,10-Trimethylpentadecane	2.3	<0.01	0.01
	19	Pristane	3.1	<0.01	0.01
	20	Phytane	2.1	<0.01	0.01
	16	Decylcyclohexane	0.4	<0.01	<0.01
	17	Undecylcyclohexane	0.3	<0.01	<0.01
	18	Dodecylcyclohexane	0.3	<0.01	<0.01
		Unspeciated b-alkanes B18	11.7	0.5	0.06
		Unspeciated b-alkanes B19	8.3	0.4	0.04
		Unspeciated b-alkanes B20	5.6	0.4	0.03
		Unspeciated cyclic alkanes B18	73.9	2.1	0.37
		Unspeciated cyclic alkanes B19	50.7	1.6	0.25
		Unspeciated cyclic alkanes B20	33.0	1.5	0.17

ALK9	21	Heneicosane	0.7	<0.01	0.02
	22	Docosane	0.5	0.1	0.01
	19	Tridecylcyclohexane	0.2	<0.01	<0.01
	20	Tetradecylcyclohexane	0.1	<0.01	0.01
	21	Pentadecylcyclohexane	0.0	<0.01	<0.01
	22	Hexadecylcyclohexane	0.0	<0.01	<0.01
	23	Heptadecylcyclohexane	0.0	<0.01	<0.01
		Unspeciated b-alkanes B21	3.4	0.3	0.08
		Unspeciated b-alkanes B22	2.6	0.4	0.07
		Unspeciated cyclic alkanes B21	19.2	1.2	0.44
		Unspeciated cyclic alkanes B22	14.9	1.2	0.36
ARO3	11	Pentylbenzene	0.5	0.2	0.25
	12	Hexylbenzene	0.4	0.1	0.15
	13	Heptylbenzene	0.5	<0.01	0.13
	14	Octylbenzene	0.2	<0.01	0.06
	15	Nonylbenzene	0.1	<0.01	0.03
	16	Decylbenzene	0.1	<0.01	0.20
	17	Undecylbenzene	0.1	<0.01	0.16
	18	Dodecylbenzene	<0.01	<0.01	0.01
	19	Tridecylbenzene	<0.01	<0.01	0.01
	20	Tetradecylbenzene	<0.01	<0.01	<0.01
	22	Pentadecylbenzene	<0.01	<0.01	<0.01
PAH1	10	Naphthalene	4.0	8.5	0.10
	11	2-methylnaphthalene	5.0	3.2	0.05
	11	1-methylnaphthalene	2.8	1.6	0.03
	12	C2-naphthalene	7.7	1.8	0.05
	13	Fluorene	0.2	0.1	<0.01
	14	Phenanthrene	0.4	0.3	<0.01
	15	C1-Phenanthrene	0.3	0.1	<0.01
	16	Fluoranthene	<0.01	0.1	<0.01
	16	Pyrene	0.1	0.1	<0.01
		Unspeciated aromatic compounds B12	0	44.7	0.46
		Unspeciated aromatic compounds B13	0	20.0	0.21
		Unspeciated aromatic compounds B14	0	8.4	0.09
PAH2	12	Acenaphthylene	0.2	0.4	0.05
	12	Acenaphthene	0.1	0.1	0.04
	13	C3-naphthalene	4.7	0.6	0.08
	13	C4-naphthalene	0.5	0.1	0.03
	14	C1-Fluorene	0.4	0.1	0.03
	14	Anthracene	<0.01	0.1	0.01
	16	C2-Phenanthrene/anthracene	0.2	0.1	0.01
	17	C1-Fluoranthene/pyrene	<0.01	0.1	0.01

		Unspeciated aromatic compounds B15	0	4.3	0.42
		Unspeciated aromatic compounds B16	0	3.4	0.33

Table S3: Reactions and reaction rate constants for the seven lumped IVOC species. (Definition of the products is given in the main document.)

Reactants	**Products**	k_{OH} (ppm^{-1} min^{-1})
ALK6 + OH	0.653 RO2R + 0.347 RO2N + 0.948 R2O2 + 0.026 HCHO + 0.099 CCHO + 0.204 RCHO + 0.072 ACET + 0.089 MEK + 0.417 PROD + $\sum_{i}^{n=5} a_i OCG_i$	1.4×10^4
ALK7 + OH	0.653 RO2R + 0.347 RO2N + 0.948 R2O2 + 0.026 HCHO + 0.099 CCHO + 0.204 RCHO + 0.072 ACET + 0.089 MEK + 0.417 PROD + $\sum_{i}^{n=5} a_i OCG_i$	1.4×10^4
ALK8 + OH	0.653 RO2R + 0.347 RO2N + 0.948 R2O2 + 0.026 HCHO + 0.099 CCHO + 0.204 RCHO + 0.072 ACET + 0.089 MEK + 0.417 PROD + $\sum_{i}^{n=5} a_i OCG_i$	1.4×10^4
ALK9 + OH	0.653 RO2R + 0.347 RO2N + 0.948 R2O2 + 0.026 HCHO + 0.099 CCHO + 0.204 RCHO + 0.072 ACET + 0.089 MEK + 0.417 PROD + $\sum_{i}^{n=5} a_i OCG_i$	1.4×10^4
ARO3 + OH	0.187 HO2 + 0.804 RO2R + 0.009 RO2N + 0.097 GLY + 0.287 MGLY + 0.087 BACL + 0.187 CRES + 0.05 BALD + 0.561 DCB1+ 0.099 DCB2 + 0.093 DCB3 + $\sum_{i}^{n=5} a_i OCG_i$	3.9×10^4
PAH1 + OH	0.187 HO2 + 0.804 RO2R + 0.009 RO2N + 0.097 GLY + 0.287 MGLY + 0.087 BACL + 0.187 CRES + 0.05 BALD + 0.561 DCB1+ 0.099 DCB2 + 0.093 DCB3 + $\sum_{i}^{n=5} a_i OCG_i$	3.9×10^4
PAH2 + OH	0.187 HO2 + 0.804 RO2R + 0.009 RO2N + 0.097 GLY + 0.287 MGLY + 0.087 BACL + 0.187 CRES + 0.05 BALD + 0.561 DCB1+ 0.099 DCB2 + 0.093 DCB3 + $\sum_{i}^{n=5} a_i OCG_i$	3.9×10^4

Table S4: The surrogate compounds assigned to the compounds with insufficient experimental yield data.

Compound	**Surrogate compound**
Compounds lumped in ALK6	
2,6,10-Trimethylundecane	n-undecane
Hexylcyclohexane	n-dodecane
Unspeciated b-alkanes B12	n-decane
Unspeciated b-alkanes B13	n-undecane
Unspeciated b-alkanes B14	n-dodecane
Unspeciated cyclic alkanes B12	n-dodecane
Unspeciated cyclic alkanes B13	n-tridecane
Unspeciated cyclic alkanes B14	n-tetradecane
Compounds lumped in ALK7	
2,6,10-Trimethyldodecane	n-dodecane
2,6,10-Trimethyltridecane	n-tridecane
Heptylcyclohexane	n-tridecane
Octylcyclohexane	n-tetradecane
Nonylcyclohexane	n-pentadecane
Unspeciated b-alkanes B15	n-tridecane
Unspeciated b-alkanes B16	n-tetradecane
Unspeciated b-alkanes B17	n-pentadecane
Unspeciated cyclic alkanes B15	n-pentadecane
Unspeciated cyclic alkanes B16	n-hexadecane
Unspeciated cyclic alkanes B17	n-heptadecane
Compounds lumped in ALK8	
Octadecane	n-heptadecane
Nonadecane	n-heptadecane
Eicosane	n-heptadecane
2,6,10-Trimethylpentadecane	n-pentadecane
Pristane	n-pentadecane
Phytane	n-hexadecane
Decylcyclohexane	n-hexadecane
Undecylcyclohexane	n-heptadecane
Dodecylcyclohexane	n-heptadecane
Unspeciated b-alkanes B18	n-heptadecane
Unspeciated b-alkanes B19	n-heptadecane
Unspeciated b-alkanes B20	n-heptadecane
Unspeciated cyclic alkanes B18	n-heptadecane
Unspeciated cyclic alkanes B19	n-heptadecane
Unspeciated cyclic alkanes B20	n-heptadecane
Compounds lumped in ALK9	
Heneicosane	n-heptadecane
Docosane	n-heptadecane
Tridecylcyclohexane	n-heptadecane
Tetradecylcyclohexane	n-heptadecane
Pentadecylcyclohexane	n-heptadecane
Hexadecylcyclohexane	n-heptadecane
Heptadecylcyclohexane	n-heptadecane
Unspeciated b-alkanes B21	n-heptadecane
Unspeciated b-alkanes B22	n-heptadecane
Unspeciated cyclic alkanes B21	n-heptadecane
Unspeciated cyclic alkanes B22	n-heptadecane

Compounds lumped in PAH1	
C2-naphthalene	2-methylnaphthalene
Fluorene	2-methylnaphthalene
Phenanthrene	2-methylnaphthalene
C1-Phenanthrene	2-methylnaphthalene
Fluoranthene	2-methylnaphthalene
Pyrene	2-methylnaphthalene
Unspeciated aromatic compounds B12	2-methylnaphthalene
Unspeciated aromatic compounds B13	2-methylnaphthalene
Unspeciated aromatic compounds B14	2-methylnaphthalene
Compounds lumped in PAH2	
Acenaphthylene	2-methylnaphthalene
Acenaphthene	2-methylnaphthalene
C3-naphthalene	2-methylnaphthalene
C4-naphthalene	2-methylnaphthalene
C1-Fluorene	2-methylnaphthalene
Anthracene	2-methylnaphthalene
C2-Phenanthrene/anthracene	2-methylnaphthalene
C1-Fluoranthene/pyrene	2-methylnaphthalene
Unspeciated aromatic compounds B15	2-methylnaphthalene
Unspeciated aromatic compounds B16	2-methylnaphthalene

Table S5: Estimated mass-based yields of the individual compounds.

Speciated n-alkanes under high NO_x conditions	**Aerosol mass-based yields**				
	0.1 μg m^{-3}	1 μg m^{-3}	10 μg m^{-3}	100 μg m^{-3}	10^3 μg m^{-3}
n-decane ($C_{10}H_{22}$)	0	0	0.112	0.184	0
n-undecane ($C_{11}H_{24}$)	0.011	0.004	0	0	0.325
n-dodecane ($C_{12}H_{26}$)	0.014	0.022	0.043	0.153	0.183
n-tridecane ($C_{13}H_{28}$)	0.055	0.051	0.022	0	0.424
n-tetradecane ($C_{14}H_{30}$)	0.069	0.056	0	0	0.434
n-pentadecane ($C_{15}H_{32}$)	0	0.111	0.523	0	0
n-hexadecane ($C_{16}H_{34}$)	0	0.233	0.233	0.235	0
n-heptadecane ($C_{17}H_{36}$)	0.077	0.024	0.629	0.151	0
Speciated PAH species	**Aerosol mass-based yields**				
	0.1 μg m^{-3}	1 μg m^{-3}	10 μg m^{-3}	100 μg m^{-3}	10^3 μg m^{-3}
High NO_x conditions					
naphthalene ($C_{10}H_8$)	0	0.02	0.35	0	0
1-methylnaphthalene ($C_{11}H_{10}$)	0	0	0.41	0.08	0.16
2-mehtylnaphthtalene ($C_{11}H_{10}$)	0	0.06	0.31	0.26	0.62
Low NO_x conditions					
naphthalene ($C_{10}H_8$)	0	0.01	0.44	0	0
1-methylnaphthalene ($C_{11}H_{10}$)	0	0	0.63	0	0.07
2-mehtylnaphthtalene ($C_{11}H_{10}$)	0	0	0.46	0	0.05

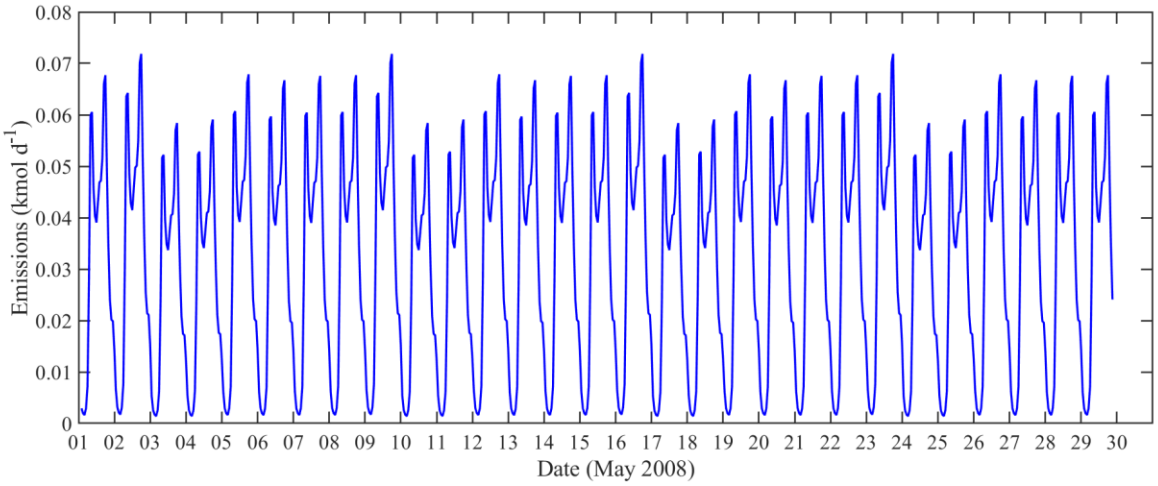

Figure S1: Temporal distribution of the estimated n-dodecane emissions from diesel and gasoline vehicle emissions over Paris for May 2008.

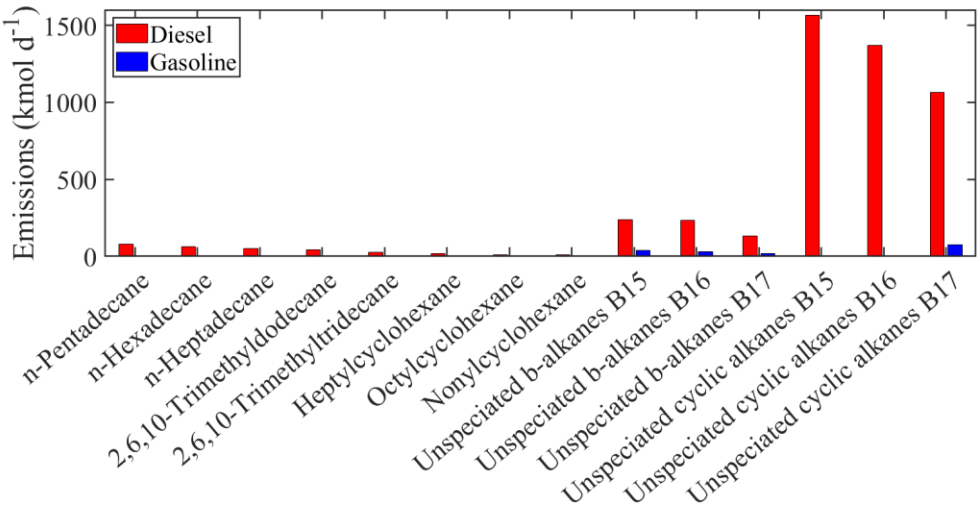

Figure S2: Estimated total gasoline and diesel emissions of the individual compounds lumped in ALK7 for Europe.

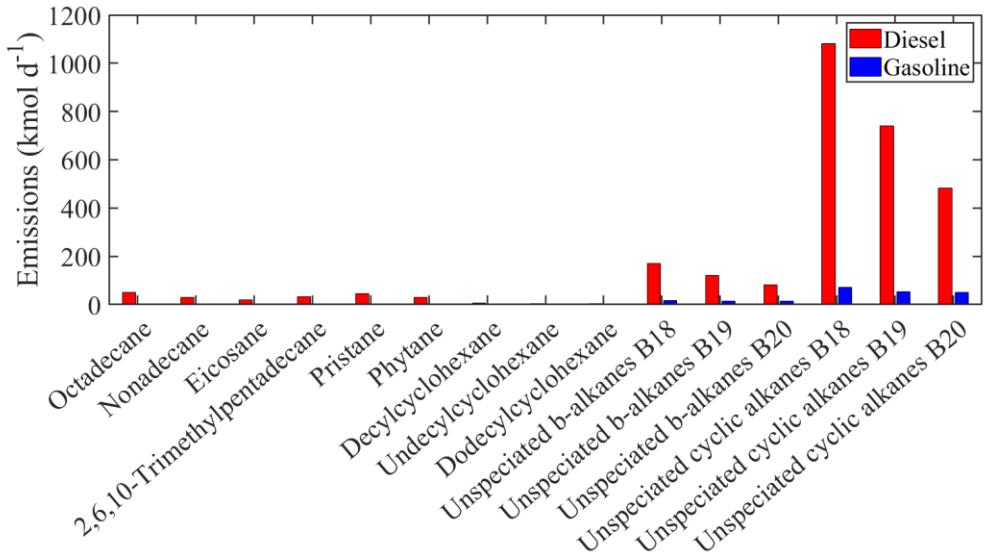

Figure S3: Estimated total gasoline and diesel emissions of the individual compounds lumped in ALK8 for Europe.

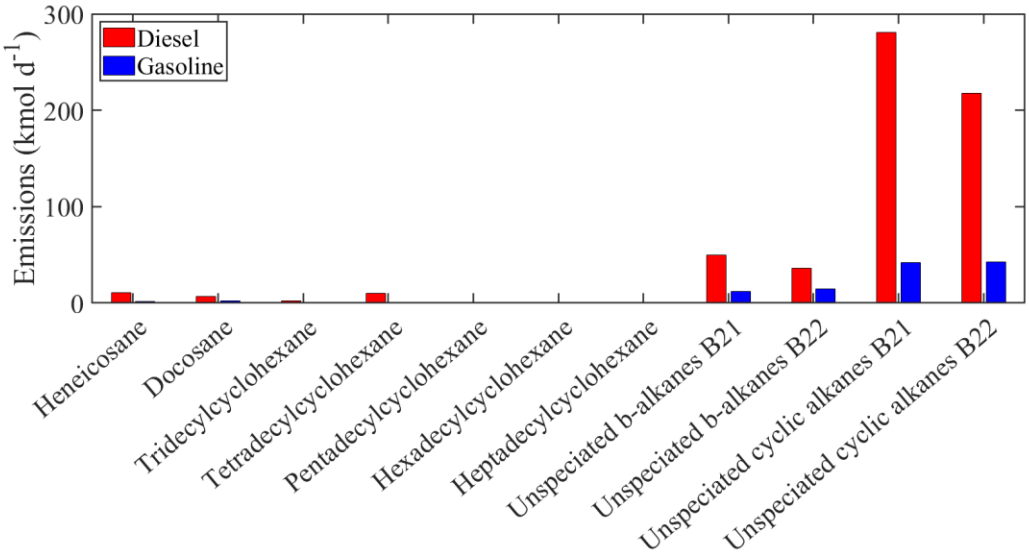

Figure S4: Estimated total gasoline and diesel emissions of the individual compounds lumped in ALK9 for Europe.

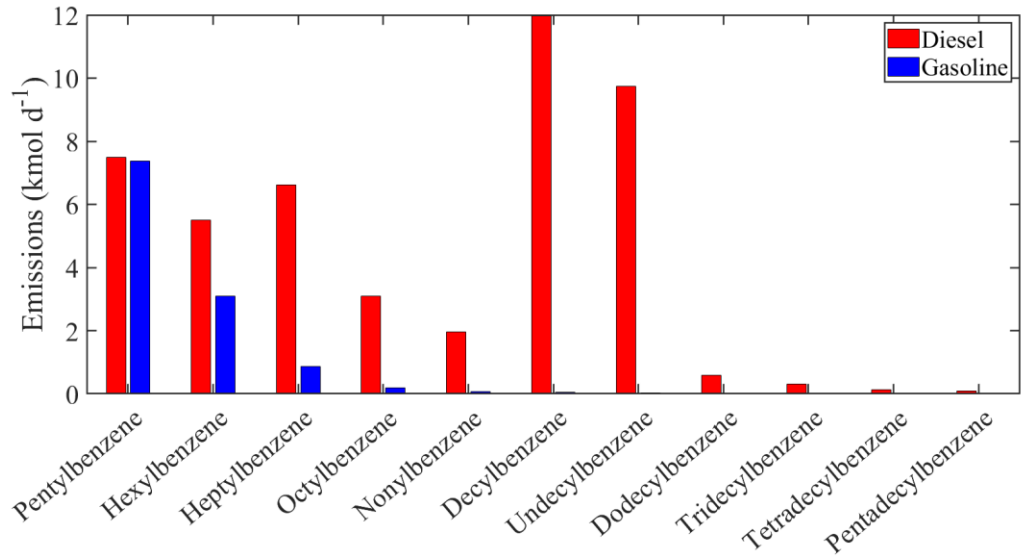

Figure S5: Estimated total gasoline and diesel emissions of the individual compounds lumped in ARO3 for Europe.

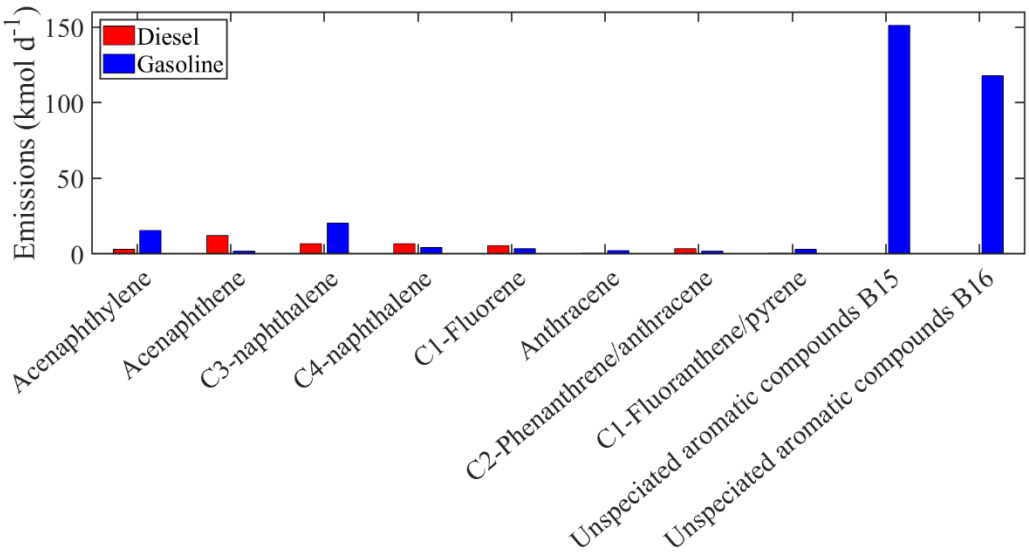

Figure S6: Estimated total gasoline and diesel emissions of the individual compounds lumped in PAH2 for Europe

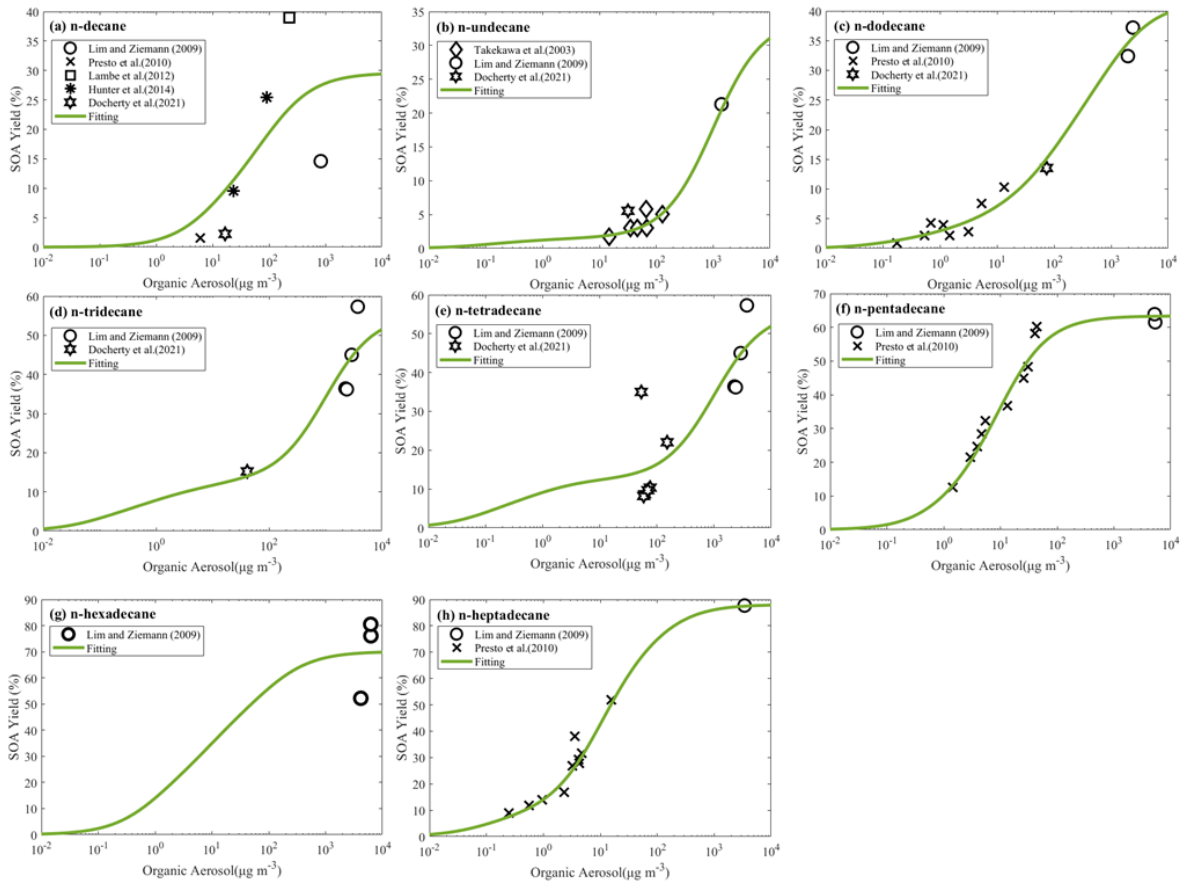

Figure S7: Estimated SOA yields of linear alkanes with 10 to 17 carbons.