

Supplementary information to

Formation of organic aerosol in the Paris region during the MEGAPOLI summer campaign: evaluation of the Volatility-Basis-Set approach within the CHIMERE model

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Table S1. Parameters used to simulate the partitioning of POA emissions into different volatility bins; the mass weight of each lumped species is 250 g mol^{-1} . The enthalpies are derived from measurements and theoretical estimation for specific low-volatile species in POA emissions by Dohanue et al., (2006).

	Lumped species								
C* ($\mu\text{g m}^{-3}$) at 298K	10^{-2}	10^{-1}	10^0	10^1	10^2	10^3	10^4	10^5	10^6
ΔH_v (kJ mol^{-1})	112	106	100	94	88	82	76	70	64
Emission factors	0.03	0.06	0.09	0.14	0.18	0.3	0.4	0.5	0.8

Table S2. Lumped anthropogenic and biogenic VOCs and their major components for the 4 bins VBS approach for SOA formation.

Anthropogenic origin		Biogenic origin	
Lumped species	Major components	Lumped species	Major components
ALK4	n-pentane, n-hexane, Branched Cyclopentane, Trimethyl Butane, Trimethyl Isopropyl alcohol, n-Propyl Alcohol	Terp	α -pinene and sabinene; β -pinene and δ^3 -carene; limonene; ocimene and myrcene
ALK5	C7-C22 n-Alkanes, C6-C16 Cycloalkanes, branched/Unspeciated C8-C18 Alkanes		
OLE1	Propene, C4-C15 terminal Alkanes		
OLE2	Isobutene, C4-C15 Internal Alkenes, C6-C15 Cyclic or di-olefins, Styrenes	ISO	Isoprene
ARO1	Toluene, benzene, Ethyl benzene, C9-C13 Monosubstituted Benzenes		
ARO2	Xylenes, Ethyl Toluenes, Dimethyl and Trimethyl Benzenes, Ethylbenzenes, naphthalene, C8-C13 Di-, Tri-, Tetra-, Penta-, Hexa-substituted Benzenes, Unspeciated C10-C12 Aromatics		

Table S3. Normalized SOA yields α_i in the 4 bins VBS approach with saturation concentrations from 1 to $10^3 \mu\text{g m}^{-3}$; ΔH : enthalpy of products; Molar mass (MW) of products; the density of OA is assumed as 1.5 g cm^{-3} (Murphy and Pandis, 2009).

VOC precursors	Mass yields of each bin				ΔH (kJ mol^{-1})	MW (g mol^{-1})	
	C^* ($\mu\text{g m}^{-3}$)	1	10	100			1000
ALK4		0.0	0.075	0.0	0.0	30	120
ALK5		0.0	0.300	0.0	0.0	30	150
OLE1		0.0045	0.009	0.060	0.225	30	120
OLE2		0.0225	0.435	0.129	0.375	30	120
ARO1		0.075	0.225	0.375	0.525	30	150
ARO2		0.075	0.300	0.375	0.525	30	150
TERP		0.1073	0.0918	0.3587	0.6075	30	180
ISOP		0.009	0.03	0.015	0.000	30	180

Table S4. Statistics for comparisons between MM5 results and meteorological measurements at SIRTA, based on 30 days of comparisons with hourly data (corresponding to the frequency of the model output). R is the correlation coefficient; RMSE is root mean square error.

Statistics at SIRTA	Wind speed (m s^{-1})	Temperature (K)	PBL height (m)
Bias (relative)	+1.07 (+42%)	-0.86	-268 (-28%)
RMSE (relative RMSE)	1.64 (+64%)	1.93	764 (+79%)
R	0.73	0.92	0.37

Table S5. Statistics for comparison of modelled and measured NO_x , BC, O_3 , inorganic aerosol, and organic aerosol from three configurations (CSS, VBS-T1 and VBS-T2) by using the LA emission inventory at GOLF, LHVP and SIRTA, based on 30 days of comparisons with hourly data (corresponding to the frequency of the model output). R is the correlation coefficient; RMSE is root mean square error.

	GOLF			LHVP			SIRTA		
	Bias (relative)	RMSE (relative)	R	Bias (relative)	RMSE (relative)	R	Bias (relative)	RMSE (relative)	R
NO_x (ppb)	+6.1 (+58%)	11.6 (111%)	0.56	+2.7 (+16%)	14.8 (86%)	0.56	+1.7 (+23%)	5.6 (77%)	0.65
O_3 (ppb)	+0.3 (+1.0%)	9.6 (32%)	0.80	-1.2 (-4.1%)	9.6 (33%)	0.79	2.6 (8.7%)	10.0 (34%)	0.74
BC ($\mu\text{g m}^{-3}$)	+2.07 (+180%)	3.00 (261%)	0.51	+2.08 (+167%)	2.95 (235%)	0.52	-0.24 (-38%)	0.66 (104%)	0.36
SO_4^{2-} ($\mu\text{g m}^{-3}$)	+0.97 (+84%)	1.40 (122%)	0.74	+0.83 (+65%)	1.36 (108%)	0.70	+0.60 (+50%)	1.0 (84%)	0.73
NO_3^- ($\mu\text{g m}^{-3}$)	+0.44 (+137%)	1.11 (347%)	0.78	+0.23 (+59%)	0.82 (203%)	0.85	+0.36 (+138%)	0.88 (342%)	0.85
NH_4^+ ($\mu\text{g m}^{-3}$)	+0.40 (+73%)	0.62 (112%)	0.81	+0.45 (+97%)	0.62 (136%)	0.82	+0.42 (108%)	0.55 (142%)	0.84
OA- CCS	+1.17 (+33%)	4.02 (114%)	0.22	+1.53 (+46%)	3.58 (108%)	0.43	-1.11 (-49%)	1.96 (86%)	0.66
OA- VBS-T1	-1.99 (-56%)	3.13 (88%)	0.58	-1.76 (-53%)	2.71 (82%)	0.59	-1.46 (-64%)	2.13 (94%)	0.78
OA- VBS-T2	-0.47 (-13%)	2.04 (63%)	0.79	-0.27 (-8.2%)	2.14 (65%)	0.76	-0.42 (-18%)	1.46 (64%)	0.84

Table S6. Statistics for comparison of modelled and measured NO_x, BC, O₃, inorganic aerosol, and organic aerosol from the configuration VBS-MPOLI by using the TNO-MEGAPOLI emission inventory at GOLF, LHVP and SIRTA. R is the correlation coefficient; RMSE is root mean square error.

VBS-MPOLI	GOLF			LHVP			SIRTA		
	Bias (relative)	RMSE (relative)	R	Bias (relative)	RMSE (relative)	R	Bias (relative)	RMSE (relative)	R
NO _x (ppb)	+10.0 (+95%)	15.6 (148%)	0.57	+7.2 (+42%)	17.8 (104%)	0.51	+1.6 (+22%)	6.1 (84%)	0.64
O ₃ (ppb)	-1.97 (-6.7%)	10.0 (34%)	0.78	-3.7 (-13%)	10.8 (38%)	0.76	+2.65 (8.9%)	10.3 (35%)	0.72
BC (µg m ⁻³)	+0.33 (+29%)	0.97 (84%)	0.55	+0.52 (+41%)	1.29 (103%)	0.50	-0.05 (-7.3%)	0.53 (84%)	0.51
SO ₄ ²⁻ (µg m ⁻³)	+0.87 (+76%)	1.31 (114%)	0.73	+0.75 (+59%)	1.28 (102%)	0.69	+0.55 (+46%)	0.96 (81%)	0.71
NO ₃ ⁻ (µg m ⁻³)	+0.01 (+2.1%)	0.48 (148%)	0.90	-0.11 (-27%)	0.48 (118%)	0.91	+0.04 (+17%)	0.36 (140%)	0.89
NH ₄ ⁺ (µg m ⁻³)	+0.24 (+43%)	0.45 (80%)	0.82	+0.32 (+69%)	0.49 (107%)	0.81	+0.32 (+81%)	0.43 (111%)	0.82
OA (µg m ⁻³)	-1.15 (-32%)	2.16 (61%)	0.80	-0.95 (-29%)	2.10 (64%)	0.77	-0.39 (+17%)	1.36 (60%)	0.84

Table S7. Statistic for comparison of modelled POA and SOA with measured HOA and OOA derived from the 3 factor PMF analysis from the four configurations (CSS, VBS-T1, VBS-T2 and VBS-MPOLI) at LHVP. R is the correlation coefficient; RMSE is root mean square error.

PMF 3 factor at LHVP	POA (µg m ⁻³)			SOA (µg m ⁻³)		
	Bias (relative)	RMSE (relative)	R	Bias (relative)	RMSE (relative)	R
CCS	+3.42 (+555%)	4.36 (708%)	0.53	-0.73 (-48%)	1.40 (92%)	0.66
VBS-T1	+0.01 (+1.8%)	0.61 (99%)	0.45	-0.61 (-40%)	1.18 (78%)	0.76
VBS-T2	+0.10 (+17%)	0.61 (100%)	0.49	+0.79 (+52%)	2.04 (134%)	0.87
VBS-MPOLI	-0.51 (-75%)	0.67 (99%)	0.55	+0.61 (+37%)	1.80 (108%)	0.91

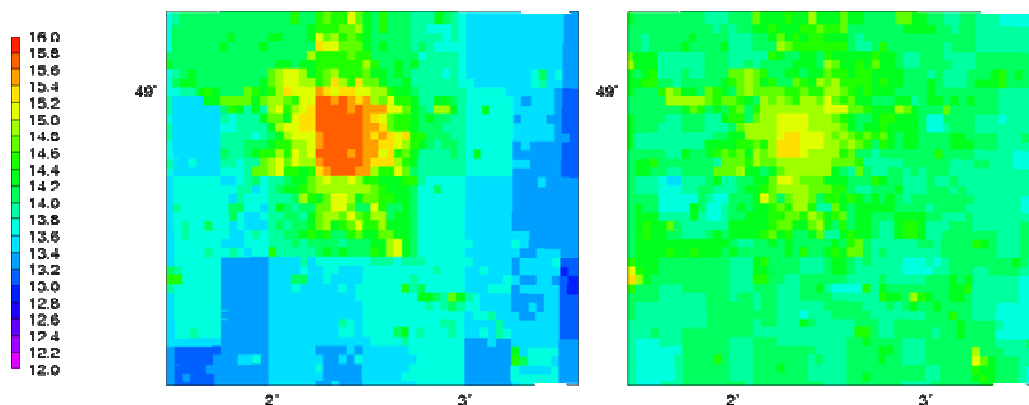


Fig. S1. $\log_{10}(\text{OM})$ emissions (unit: molecule cm^{-2} of a typical weekday in July) centred for the Paris region from LA inventory (left) and the MEGAPOLI database (right), for fine PM ($\text{PM}_{2.5}$)

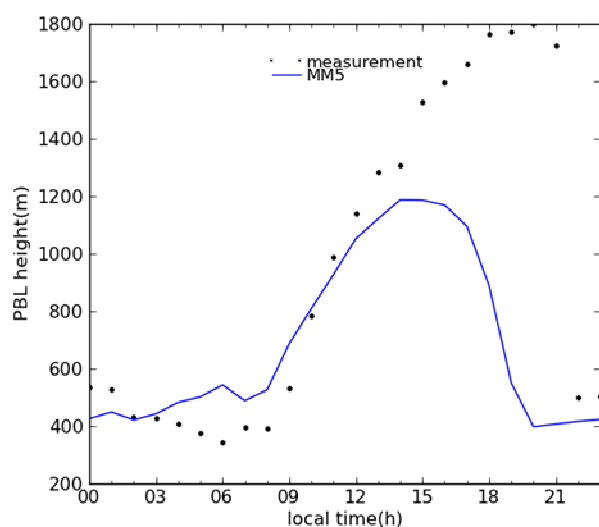


Fig. S2 Comparison of simulated (blue line) and observed (black dots) July 2009 average daily variation of the PBL height at SIRT A

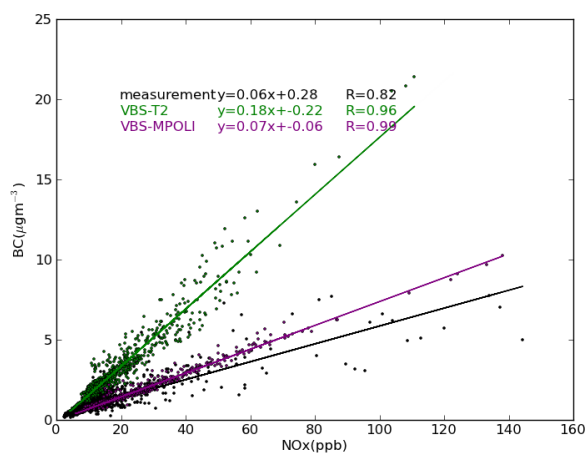


Fig. S3 BC vs. NO_x at LHVP from measurements (black), from VBS-T2 for the LA-EMEP inventory (green) and from VBS-MPOLI for the MEGAPOLI inventory (purple).

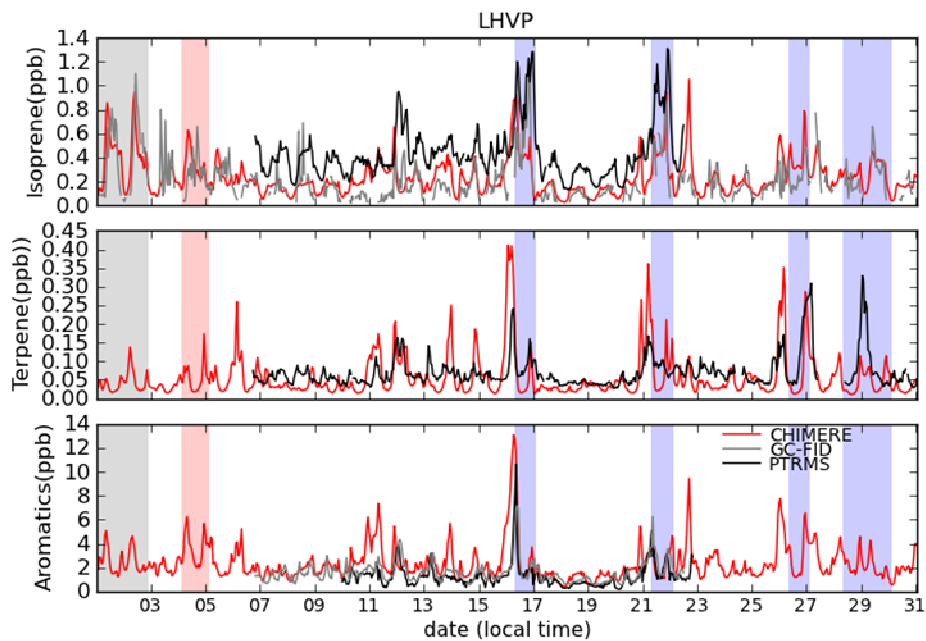


Fig. S4. Comparisons of simulated and observed isoprene, terpenes and aromatics (sum of benzene, toluene, xylene ethyltoluene and 1,2,4-TMB from GC-FID; sum of m/z 79, 93, 107 and 121 from PTRMS which are corresponding to the sum of benzene, toluene, aromatic C8 and C9) at LHVP.

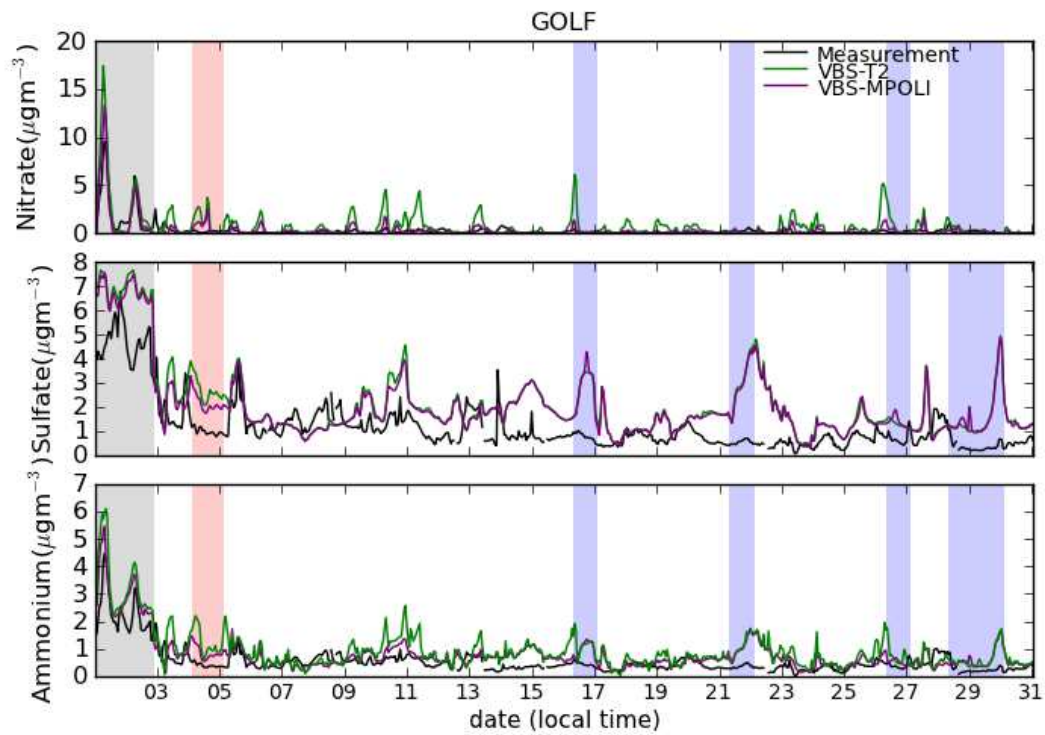


Fig. S5 Comparison of simulated and observed inorganic aerosol species at GOLF

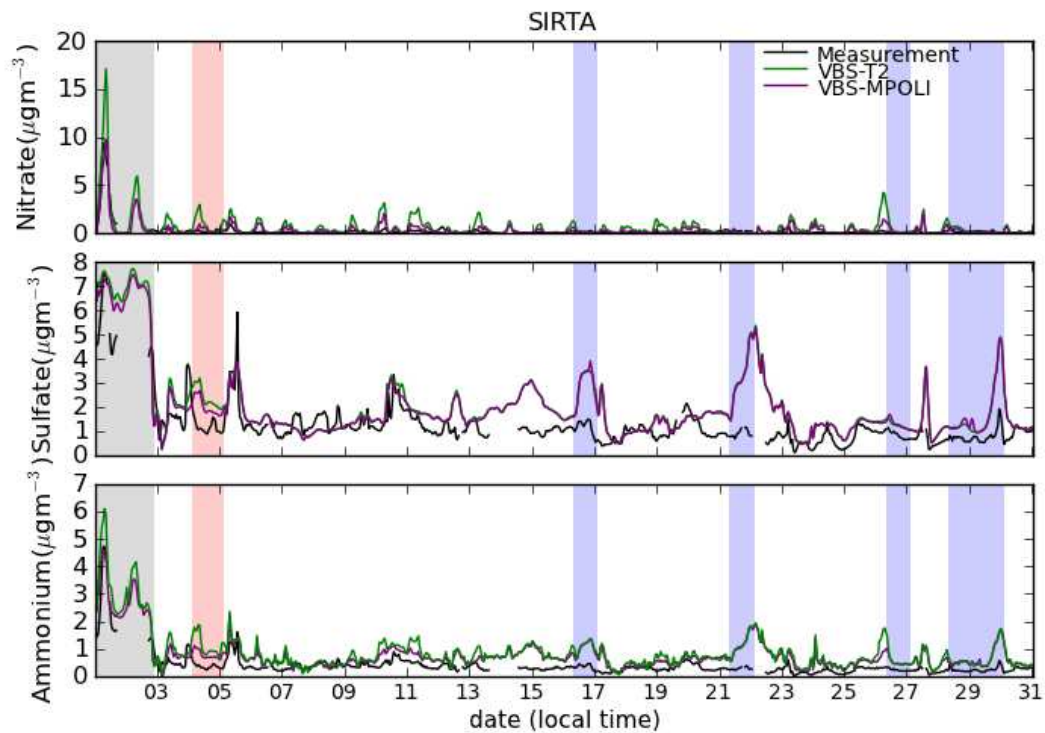


Fig. S6 Comparison of simulated and observed inorganic aerosol species at SIRTA.

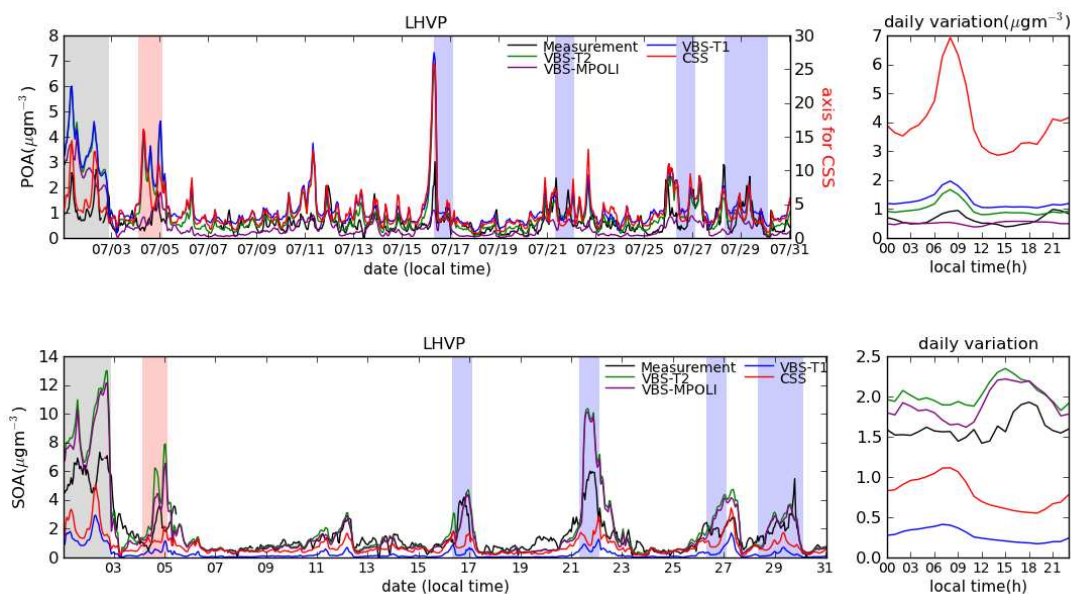


Fig. S7 Comparison of simulated and observed primary and secondary organic aerosol when simulated OPOA is considered as part of HOA, on the left side time series, on the right side daily average for July 2009. The color code in the diurnal variations (right side) is the same as in the time series (left side).

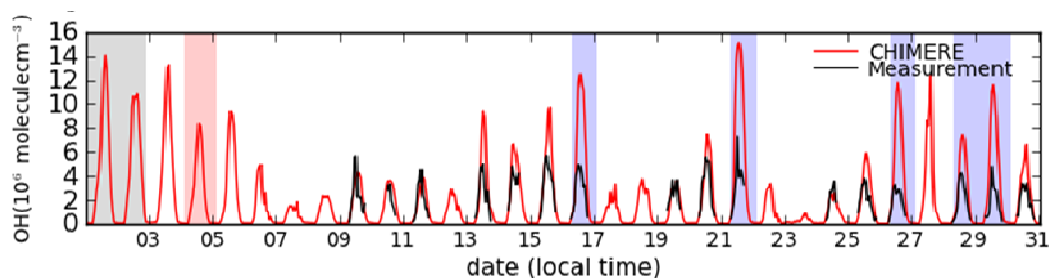


Fig S8. Comparison of simulated and observed OH at SIRTAs.

Predicted OH concentrations are correlated ($R=0.62$) with the measurement at SIRTAs, the driving force for correlation being the strong diurnal cycle with a noon maximum due to enhanced UV radiation. Daily maxima are mostly overestimated with a factor up to three. This overestimation could be due to a variety of reasons: OH and HO_x radical sources (O_3 , H_2O , HONO formed by heterogeneous reactions, photolysable VOC, photolysis frequencies) and sinks of HO_x radicals (NO_2 , ...) and in NO and VOC levels responsible for radical inter-conversion reactions.