# **Supporting Information for:**

## "Simulation of particle diversity and mixing state over Greater Paris: A model-measurement intercomparison"

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Mass	Particle	Mass fraction of each groups					
ratio $\%$	class	EC	$SO_4$	$NO_3$	OA	NH <sub>4</sub>	
< 0.01	ОТ	0.09	0.09	< 0.01	0.08	0.74	
60.09	OA	< 0.01	0.03	0.04	0.90	0.03	
< 0.01	$NO_3$	0.03	0.02	0.68	0.08	0.19	
19.79	$OA-NO_3$	0.02	0.05	0.19	0.65	0.09	
0.01	$SO_4$	0.07	0.31	< 0.01	0.08	0.54	
1.27	$OA-SO_4$	0.02	0.13	0.03	0.74	0.09	
< 0.01	$SO_4$ - $NO_3$	0.03	0.27	0.39	0.07	0.24	
0.78	$OA-SO_4-NO_3$	0.03	0.12	0.20	0.53	0.12	
0.71	EC+	0.89	0.01	0.01	0.09	< 0.01	
13.13	EC-OA	0.33	0.03	0.02	0.60	0.02	
0.08	$EC-NO_3$	0.61	0.01	0.29	0.06	0.03	
1.01	$EC-OA-NO_3$	0.32	0.03	0.18	0.43	0.04	
< 0.01	$EC-SO_4$	0.46	0.34	0.01	0.05	0.14	
0.19	$EC-OA-SO_4$	0.14	0.15	0.03	0.54	0.14	
< 0.01	$EC-SO_4-NO_3$	0.21	0.23	0.25	0.09	0.22	
0.02	$EC-OA-SO_4-NO_3$	0.19	0.15	0.18	0.31	0.17	
2.90	EC	0.93	$<\!0.01$	< 0.01	0.06	< 0.01	

Table S1: Average mass fractions of each chemical component at the LHVP site and mass fractions of each particle class within  $PM_1$  concentration.

Table S2: Average mass fractions of each chemical component at the LHVP site and mass fractions of each particle class within  $PM_1$  concentration.

Particle	Mass	Mean	Mass fraction of each group					
class	ratio	mass	EC	$SO_4$	$NO_3$	OA	$\mathrm{NH}_4$	
	%	$\mu { m g}~{ m m}^{-3}$						
OA	60.09	7.21	< 0.01	0.03	0.04	0.90	0.03	
$OA-NO_3$	19.79	2.37	0.02	0.05	0.19	0.65	0.09	
$OA-SO_4$	1.29	0.15	0.02	0.13	0.03	0.73	0.09	
$OA-SO_4-NO_3$	0.78	0.09	0.03	0.12	0.20	0.53	0.12	
$\mathrm{EC}$	3.61	0.43	0.92	0.01	< 0.01	0.06	< 0.01	
EC-OA	13.13	1.57	0.33	0.03	0.02	0.60	0.02	
$EC-OA-NO_3$	1.09	0.13	0.35	0.02	0.19	0.40	0.04	
$EC-OA-SO_4$	0.21	0.03	0.15	0.16	0.04	0.51	0.14	

#### S1 Classification of particle composition

In the EM simulation, 17 particle classes are discretised based on the combination of the mass-fraction sections of the different chemical components (or group of chemical components). The average mass fraction of each chemical component at the site of LHVP for these 17 particle classes are presented in Table S1, as well as the mass fraction of each particle class within the  $PM_1$  concentration.

To facilitate the comparisons to measurements, the particle classes that have low mass concentrations compared to the total particle mass (lower than 0.1 %), are merged together or regrouped with particle classes of larger mass fractions. Table S2 shows the mass ratio of each of the 8 classes to the total particle mass after merging, as well as the mass fraction of each chemical group within each particle class. The merging does not affect the classes OA and EC-OA, while the classes EC and EC+ are merged into EC; NO<sub>3</sub> and OA-NO<sub>3</sub> are merged into OA-NO<sub>3</sub>; SO<sub>4</sub> and OA-SO<sub>4</sub> are merged into OA-SO<sub>4</sub>; EC-OA and EC-NO<sub>3</sub> are merged into EC-OA-NO<sub>3</sub>; SO<sub>4</sub>-NO<sub>3</sub> and OA-SO<sub>4</sub>-NO<sub>3</sub> are merged into OA-SO<sub>4</sub>, EC-OA-SO<sub>4</sub>, EC-

Class	Class	Mass	Mean	Mass fraction of each group				
SCRAM	ATOFMS	ratio	mass	EC	$SO_4$	$NO_3$	OA	$NH_4$
		%	$\mu { m g~m^{-3}}$					
OA-NO <sub>3</sub>	K-OA	8.80	1.50	0.14	0.09	0.21	0.52	0.07
	$ ext{K-OA-NO}_x$	28.73	4.91	0.06	0.07	0.52	0.27	0.07
	$OA-NO_x$	13.99	2.39	0.07	0.09	0.27	0.40	0.17
$OA-SO_4$	$OA-SO_x$	8.92	1.52	0.08	0.31	0.10	0.40	0.11
$OA-SO_4-NO_3$	$ ext{K-OA-SO}_x$	19.68	3.36	0.05	0.23	0.22	0.36	0.13
	OA-TMA	3.10	0.53	0.04	0.12	0.17	0.45	0.21
EC-OA	EC-OA	8.27	1.41	0.62	0.06	0.02	0.30	0.01
	K-EC	2.00	0.34	0.57	0.04	0.08	0.24	0.06
EC-OA-NO <sub>3</sub>	$EC-OA-NO_x$	3.83	0.65	0.32	0.06	0.23	0.33	0.06
$EC-OA-SO_4$	$\text{EC-OA-SO}_x$	2.70	0.46	0.21	0.33	0.05	0.21	0.04

Table S3: Mass fractions of each chemical group determined for each ATOFMS class<sup>1</sup>, and their corresponding SCRAM classes

To obtain comparable particle classes in the simulations and observations, merging of some of the observed particle classes is also done. Table S3 shows the association between ATOFMS particle classes from the measurements and the merged particle classes from the simulations, as well as the mass fractions of each chemical component within each particle type from the measurements. In the study of<sup>1</sup>, potassium (K) is used to identify the biomass burning origin of the particles. Since K is not included in the current version of SCRAM and its mass fraction is very small, the particle class K-OA-NO<sub>x</sub> from the measurements is merged with the OA-NO<sub>x</sub> class, and it is compared to the OA-NO<sub>3</sub> class of the simulation. The classes from the measurements are assigned to the classes of the simulation depending on the mass fraction of the chemical components of the class. For example, the class OA-TMA from the measurements, which links organics to trimethylamine (TMA), is merged in the OA-SO<sub>4</sub>-NO<sub>3</sub> class of the simulation, because it contains OA (45%) but also 12% of SO<sub>4</sub> and 17% of NO<sub>3</sub>.

#### S2 Redistribution method

In SCRAM, the condensation/evaporation of organics is done with the bulk equilibrium assumption. First, at each time step, the total condensed/evaporated mass is estimated, regardless of the particle sizes. Then the OA mass that condensed or evaporated during the time step is distributed onto each bin j using a weighting factor  $W_j^j$  defined by the following equation:

$$W_{i}^{j} = \frac{N_{j} d_{p}^{j} f(K_{n}, \alpha_{i})}{\sum_{k=1}^{N_{s}} N_{k} d_{p}^{k} f(K_{n}, \alpha_{i})}$$
(1)

where  $N_j$  is the number concentration of bin j,  $d_p^k$  is the particle wet diameter of bin j, and  $f(K_n, \alpha_i)$ describes the non-continuous effects<sup>2</sup> based on Knudsen number  $K_n = \frac{2\lambda}{d_p^j}$  (with  $\lambda$  representing the air mean free path), and  $\alpha_i$  is the accommodation coefficient (0.5).  $d_p^j f(K_n, \alpha_i)$  represents the condensation/evaporation kernel of a particle in bin j. Thus, the numerator in equation (1) represents the condensation/evaporation kernel of all particles within bin j, while the denominator represents the total condensation/evaporation kernel of particles from all bins. Generally, larger particles have higher  $d_p^j f(K_n, \alpha_i)$  values but they also have lower number concentrations. It has been found from the simulation that bins with smaller diameters dominate the weighting factors due to their high number concentrations, and as a result, the newly formed OA tends to condense preferentially into the smallest bins. However, in agreement with the measurements of Healy *et al.*<sup>1</sup>, condensation on small particles should be limited by the Kelvin effect. In SCRAM, the condensation/evaporation of inorganic species is computed dynamically, taking into account the Kelvin effect explicitly, thus condensation onto relatively larger particles is favoured, as shown in Figure S1. To estimate the influence of the weighting factors used for redistribution on the size distribution, an attempt has been made to take into account the Kelvin effect during the redistribution process after the bulk-equilibrium condensation/evaporation, with an updated



Figure S1: Comparison of the mass-size distributions (up, stacked) and size-resolved average mass fractions (down, stacked) for each chemical species between the redistribution with the original weighting factors (left column) and the redistribution with the updated weighting factors (right column) for the first 24 hours of simulation.

weighting factor:

$$W_i^j = \frac{N_j \ d_p^j f(K_n, \alpha_i) (1/(K_e(d_p) - 1))}{\sum_{k=1}^{N_s} N_k \ d_p^k f(K_n, \alpha_i) (1/(K_e(d_p) - 1))}$$
(2)

where  $K_e(d_p)$  represents the Kelvin effect for a particle of diameter  $d_p$ ,  $(K_e(d_p))$  is close to 1 for large particles and, for small particles, it becomes larger as the particle diameters become smaller). In section 4.3 of the paper, comparison to the measurements of Healy et al.<sup>1</sup> show that in the model, the OA mass is under-estimated at high diameters and over-estimated at low diameters. A test simulation of externally mixed particles was conducted with the updated weighting factors for the redistribution of OA. Figure S1 compares the mass-size distributions and size-resolved average mass fraction for each chemical species between the redistribution with the original weighting factors (left column) and the redistribution with the updated weighting factors (right column) for the first 24 hours of simulation. It is clear that more OA mass has been distributed into higher size bins with the updated weighting factors, as expected. The resulting size-resolved average mass fraction distribution is more consistent with the observations of Healy et al.<sup>1</sup>. This suggests that the redistribution weighting factors defined in equation (2) are better suited for redistribution than the previously used factors, which did not take into account the Kelvin effect. On the other hand, most of the OA mass is still concentrated on the first size bin due to the cascade effect of using the old weighting factors in the Europe and France simulations, which generate boundary conditions for the Greater Paris simulation, with high concentrations of OA in the first size bin. A more consistent size-mass distribution with the measurements is expected if the boundary conditions are regenerated with the updated weighting factors for OA.

### References

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