

## Reply to RC C1712, Anonymous Referee #2

We thank the referee for the valuable comments. The manuscript was revised according to the suggestions. Quality of the manuscript was improved, it is now much clearer, more logical, and more accurate. The English was checked. We have included responses to the reviewer's comments below and indicated where changes were made to the text (red).

**The scope and content of this manuscript is timely and important and I suggest that the manuscript can be published in ACP after my comments have been carefully addressed and the English has been improved. The main comment I have concerning the quite crude assumption of representing all condensable organic VOCs as one SVOC with thermodynamics properties of adipic acid. At least some sensitivity test needs to be performed where the condensable organic compounds are represented by ELVOCs instead.**

The sensitivity tests were performed and the results along with a figure (Fig. S6) were added in section 3.3.2 and Supplementary material. See also our reply to the comment on Page 16, L15-19 below.

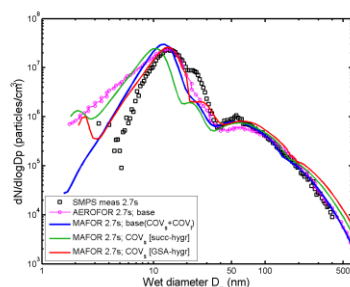


Figure S6. Number size distribution at the end of the simulation for the base case (HET nucleation) when the properties of the condensable organic vapours were changed as given in legend. COV<sub>s</sub> and COV<sub>l</sub> refer to semi-volatile and low-volatile vapours. Also shown is the measured size distribution as well as the predicted result from AEROFOR. See details in the text.

Page 3, L7-10 “The major source of diesel particulate mass is the soot mode. These particles, with sizes of 40–100 nm, are formed in the combustion process and are composed of non-volatile carbonaceous soot agglomerates, onto which semivolatile vapours can condense (e.g. Kittelson, 1998; Tobias et al., 2001).”

What do you mean with “size of 40-100 nm”? You need to specify this. Is it mobility diameter? If it is mobility diameter they seem to be quite small for a mass-mode. In figure 7 it seems as if most of soot mass is present above 100 nm in mobility diameter.

The sentence was changed to “The major source of diesel particulate mass is soot particles in the size range of 50 - 1000 nm by mass but in the size range of 40 - 100 nm by number (mobility diameter) (Kittelson, 1998).”

Page 3, L16-20: “The GSA has a very low saturation vapour pressure, and it has been shown to participate in condensation and nucleation processes during the dilution and cooling of the exhaust (Arnold et al., 2006, 2012; Rönkkö et al., 2013; Shi and Harrison, 1999; Tobias et al., 2001; Schneider et al., 2005; Khalek et al., 2003). These nucleation mode particles are volatile consisting of sulphate and hydrocarbons (Kittelson, 1998).”

These statements are somewhat contradictory. First you write that GSA has a very low saturation vapour pressure and that it is involved in the formation and growth of NUP but then you write that these particles are volatile. What do you mean with volatile and very low saturation vapour pressure? Is it the sulfuric acid particle volume fraction that is volatile or the hydrocarbon volume fraction and during which conditions are they volatile? Yes, I agree that GSA has a very low saturation vapour pressure in the presence of water in the particle phase. Maybe sulfuric acid evaporates from the NUP if you heat them in a TD? Is this what you mean when you write that the particles are volatile?

Yes, we mean that sulphuric acid and organic vapour evaporates from the NUP when heated in the TD indicating that both sulphuric acid and hydrocarbon volume fractions are volatile at 265 °C. The text was changed to “These nucleation mode particles (called hereafter volatile nucleation mode) consist of volatile material such as water, sulphate and hydrocarbons (Kittelson, 1998) which evaporates when heated at 265 °C. With some vehicle technologies and in some driving conditions, nanoparticles possessing a non-volatile core of around 10 nm or less in size have been observed (hereafter called core mode).”

**Page 5, L10-13: “The main objective of this paper is to quantify the relevant nucleation mechanism and the concentration of a semi-volatile condensable organic vapour (COV) to explain the diesel particle evolution in an ageing chamber under laboratory conditions which mimic well the atmospheric dilution conditions.”**

**In reality I expect that there are thousands of different low and semi-volatile condensable organic vapours that contributes to the particle evolution but you write “ a semivolatile condensable vapour”. What do you mean with a “semi-volatile condensable vapour”? If the aim is to develop a 1-product SVOC model parameterization that can represent the formation and growth of NUP this should be written clearly. As the main objective is formulated now it is not clear to me if you mean an actual measurable SVOC compound or a model compound which is used to represent VOCs in the exhausts.**

We do not apply a “1-product SVOC” approach since the models do not include an oxidation step to form COV<sub>s</sub>. We clarified the sentence: “Based on the model simulations, the main objective of this study is to quantify the relevant nucleation mechanism and the concentrations of semi-volatile (COV<sub>s</sub>) and/or low-volatile (COV<sub>l</sub>) condensable organic vapours needed to explain the diesel particle evolution in an ageing chamber...”

We added on p. 8, lines 18-28 : “The condensable organic vapours that contribute to particle evolution are not yet identified. However, Arnold et al. (2012), Kawamura and Kaplan (1987) and Zervas et al (2001) have observed, based on their measurements, condensable dicarboxylic acids in vehicles’ exhaust. On the other hand, the TDMA volatility measurements by Sakurai et al. (2003) indicate that the organic component of diesel nanoparticles was comprised of compounds with carbon numbers in the C<sub>24</sub>–C<sub>32</sub> range, which were derived almost entirely from unburned oil. Although there might be thousands of different low and semi-volatile condensable organic vapours we have used in AEROFOR a semi-volatile organic compound called COV<sub>s</sub> with the properties of adipic acid to represent all condensable organic vapours. Moreover, a low-volatile organic compound with volatility corresponding to that of n-alkane C<sub>34</sub>H<sub>70</sub> (constituent of the engine oil) called COV<sub>l</sub> was used in MAFOR.”

The references were added as well.

**Page 8, L15-17: “Condensable organic vapours (COV) are not yet identified, however, the CIMS results indicated that a good candidate might be adipic acid although its concentration could not be accurately measured.”**

**Change to e.g.: “The condensable organic vapours (VOC) in the diesel exhausts were not identified, however, : : ..**

**What do you mean by “indicated that a good candidate might be adipic acid although its concentration could not be accurately measured.”? Could you explain why the adipic acid could not be measured accurately and why you then still believe that the adipic acid is a good candidate? Maybe you could provide a figure with an example of the measured adipic acid concentration in the supplementary material.**

As explained in Arnold et al (2012), the acidic trace gases were measured in a way analogous to GSA by the CIMS. However, only a lower limit concentration was obtained for all other acidic gases than GSA.

We added on p. 7 the lines 19-22: “The uncertainty of the measured GSA present in the flow tube reactor was ±30% whereas only a lower limit concentration was obtained for all other acidic gases, several of which could be identified as dicarboxylic acids, including malonic, succinic, glutaric and adipic acids.”

**Page 8, L17-20: “We have used adipic acid as a representative of all COVs. Besides condensation, adipic acid was also assumed to participate in heteromolecular nucleation.**

The thermodynamical properties of adipic acid were adopted from the literature (Bilde et al., 2003)."

So is it correct that you used values of surface tension, mass accommodation coefficient and the vapour pressure of adipic acid from Bilde et al., 2003? Since I expect that these values are crucial for the model results I suggest that you also provide them in the text. I also wonder which surface tension you used for sulfuric acid and if you used the Kelvin effect down to 1.5 nm in diameter or some other theory e.g. Nano-Köhler theory.

The Kelvin effect was taken into account in the condensation processes of organic vapour and sulfuric acid. We used the temperature-dependent expression for the surface tension of (pure) adipic acid by Riipinen et al. (2007), based on the method of Macleod-Sugden.  $\sigma = 0.058592 - 0.083 \times 10^{-3} T(K)$  in N/m. The adipic acid molar weight of  $146 \text{ g mol}^{-1}$  and the liquid phase density of  $1085 \text{ kg m}^{-3}$  were used. The mass accommodation coefficient was assumed to be unity, which might overestimate the condensation flux of the organic vapour. The vapour pressure of adipic acid was calculated according to Bilde et al. (2003), and for example at 300 K it was  $2.46 \times 10^{-5} \text{ Pa}$  ( $=5.95 \times 10^9 \text{ cm}^{-3}$ ).

The sulfuric acid vapour pressure was calculated according to eq. (8) in Vehkamäki et al., 2003, and surface tension as explained in Vehkamäki et al., 2003. These equations are valid at least up to 360-400 K.

These have now been explained in section 2.2, p. 8 and in the new table, Table 2.

Table 2. Physical properties of the condensable vapours.  $\text{COV}_s$  was used in AEROFOR whereas  $\text{COV}_s$  and  $\text{COV}_l$  were used in MAFOR.

	$p^0(298 \text{ K})$ (Pa)	molar weight (g/mol)	surface tension (298 K) (N/m)	hygroscopic	nucleation
$\text{COV}_s$	$1.63 \times 10^{-5a}$	146	$0.34^b$	yes	yes
$\text{COV}_l$	$5.0 \times 10^{-11c}$	478	$-^d$	no	no

<sup>a</sup> Bilde et al., 2003

<sup>b</sup> Riipinen et al., 2007

<sup>c</sup> Lemmon and Goodwill, 2000

<sup>d</sup> Kelvin effect not considered:  $\text{Ke}=1$  (due to low vapor pressure)

Page 8, L27-28: "To minimise the effect of numerical diffusion, typical for sectional models, 100 size sections turned out to be sufficient." Which sectional approach was used to represent the growth of the particles? Full-moving, full-stationary, moving-center : : : ?

We used the fixed sectional approach. This is now mentioned in the text (p. 9, lines 9-10).

Page 8, L21-23: "In this study, 120 size bins were used to represent the aerosol size distribution ranging from 1.5nm to 10  $\mu\text{m}$  diameter. Effective density of  $1200 \text{ kg m}^{-3}$  (Virtanen et al., 2002) was used for soot particles"

Did you use 120 size bins in the MAFOR and 100 size bins in AEROFOR?

The number of sections is optional, but in this work 120 size bins were used in the MAFOR and 100 size bins in AEROFOR. The results from AEROFOR did not practically change even though 300 size bins were used.

On page 22, L3-6 you write "The aerosol dynamics models used in this work are process models that describe the main aerosol processes in details. They use sectional representations for particle size distributions with 100 size sections to prevent numerical diffusion and are free from assumptions of lognormal particle modes that are used in modal models."

The word "at least" was added: "They use sectional representations for particle size distributions with at least 100 size sections to prevent numerical diffusion"

It seem to be quite crude to use a fixed effective density of the soot particles. See e.g. Fig. 5 from Park et al., Environ. Sci. Technol. 2003, 37, 577-583. But maybe the model results are not very sensitive to the particle density?

The referee is right; the model results were not sensitive to the soot particle density, probably because at the time of the ageing chamber, soot has become a minor component of the aerosol,

as can be seen in the published mass distribution plots (Fig. 7). We repeated the simulations by using a density of 1500 kg/m<sup>3</sup> and of 1000 kg/m<sup>3</sup> (Park et al. (2003) for 50 nm particles). A sentence “The tests with 1000 and 1500 kg m<sup>-3</sup> showed that the results were not sensitive to the applied density value.” was added on p. 10 lines 12-13:

**On page 7, L26 you write that you take into account wall losses according to Voutsis et al., (2005). Do you then mean both wall losses of particles and gases? Voutsis et al., (2005) refer to Williams and Loyalka (1991) for their wall loss calculations. I suggest you refer to this article too. According to Williams and Loyalka (1991) the deposition velocity depend on Reynolds number. What Reynolds number did you use for the wall loss calculations? Are the model results sensitive to the wall losses?**

Wall losses according to eq. (15) in Voutsis et al (2005) were taken into account only for GSA. This formula takes into account the Sherwood number for the condition in the chamber as well as condensation flux of sulphuric acid onto the walls. Reynolds number varied in the range of 1325-1375 in the ageing chamber demonstrating laminar flow. The temperature dependent wall losses decreased the momentary GSA concentration by 1% - 0.5%, and altogether in the ageing chamber around 2%. Subsequently, with this model wall losses had only very small effect on the results.

**Page 11, L3-6: “The history of the after-treatment system (ATS) had a large effect on the concentrations, especially, during the first 100% engine load the increasing trend in the GSA concentration indicates strong storage effect of sulphuric acid.”, and on Page 14, L21-23 you write “The obtained coefficients A and K vary strongly as a function of the initial GSA concentration. This indicates that nucleation is affected by some other factors than the sulphuric acid concentration.”**

**When I read this I also wonder if SA on the walls of the ageing chamber can influence the nucleation rate. If SA is re-evaporating from the walls it may be important when the raw exhaust GSA concentration was low. Could this improve the agreement between the model and measured particle number concentrations for the simulations where only SA is involved in the nucleation process?**

The referee is right, for example, the release effect of GSA from the walls of the after-treatment systems might have a strong effect on the nucleation rate. The measurements (Fig.2) indicate that at 13:00 - 13:30 the particle number concentration (red crosses). In fact, the nucleation mode concentration (not shown in this figure) is almost one order of magnitude higher than at the stabilized phase at 14:00-14.15 although the measured GSA concentration (black dots) is one to two orders of magnitude lower. However, the model predicted that storage (and consequent release) of GSA onto the ageing chamber walls was marginal.

In any case, modelling of the release effect is out of the scope of this paper, and therefore we have only used the stabilized values obtained during the latter 100% engine load.

**Page 14, L4-6: What do you mean with this sentence? “It is not expected that the activation coefficient A was not constant but varied in the range of  $2.5 \times 10^{-5}$  –  $2 \times 10^{-1}$  s<sup>-1</sup> as the initial GSA concentration varied from  $2.8 \times 10^9$  to  $2 \times 10^{12}$  cm<sup>-3</sup> (Table 2).”**

**Do you mean that if SA activation nucleation was the actual nucleation mechanism A should be constant?**

Based on the measurements (Fig. 2) it can be seen that at the steady state driving cycle, e.g. at 100% engine load, the exhaust GSA concentrations increased even more than 2 orders of magnitude although all other measured raw exhaust parameters (e.g. T, [H<sub>2</sub>O], RH, core and soot mode particles) were constant. The lowest GSA values indicate that either a small fraction of fuel sulfur was converted to GSA or that the majority of fuel sulfur was stored in the after-treatment systems and exhaust lines. In any case, it is reasonable to expect that the nucleation coefficients A and K should have constant values when simulating different GSA cases with the same steady engine load.

However, the model simulations showed that to match the modelled and measured size distributions the activation coefficient A (and kinetic coefficient K) had different values from case to case (Table 2 and Fig. 5) unlike in the HET nucleation when the coefficients K1 and K2 had constant values independently of the GSA concentration during the steady engine load.



**Page 15, Eq. 4: Did you use the model results from the kinetic nucleation simulations to parameterize the heteromolecular nucleation mechanism coefficients? If this is the case. Please explain this in the text.**

The sentence on p. 15 was slightly modified to “The nucleation coefficients  $K_1$  and  $K_2$  of the HET mechanism were parameterized by using the results from the KIN mechanism, i.e. statistically by making a least square fit for the equation  $K[\text{GSA}]^2 = K_1[\text{GSA}]^2 + K_2[\text{GSA}][\text{COV}_s]$  (4), where we assumed that the nucleation rates by the kinetic theory (left-hand side) and by the heteromolecular nucleation theory (right-hand side) were equal. This procedure resulted in constant values of  $3.8 \times 10^{-17}$  and  $5.6 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}$  for  $K_1$  and  $K_2$ , respectively, independently of the initial GSA concentration, whereas the ACT and KIN mechanisms could not (Fig. 5).

**Page 16, L10-12: “Hygroscopic properties of COV in MAFOR are that of sodium succinate(Peng and Chan, 2001) with a growth factor of 1.85 at RH > 48 %” Do you mean that it start to take up water at RH>48% and has a growth factor of 1.85 at 90 % RH?**

The statement was changed by: “Hygroscopic properties of  $\text{COV}_s$  in MAFOR are that of sodium succinate (Peng and Chan, 2001), i.e.  $\text{COV}_s$  starts to take up water at  $\text{RH}>48\%$ , and has a growth factor of 1.85 from 10% to 90% RH.” now in section 2.2 p. 9 lines 25-27

**Page 16, L15-19: “An additional non-hygroscopic condensing organic vapour ELVOC with saturation vapour pressure of C34H17 ( $p_0$  (298 K) =  $5.0 \times 10^{-11} \text{ Pa}$ , Lemmon and Goodwin, 2000) was added in the MAFOR simulations to compensate for the initially lower hygroscopic growth and to promote NUP growth to measured size. This should be explained in the method Section 2.2 and not in the results part. I don’t really understand why ELVOCs was need in MAFOR but not in AEROFOR. In reality I would expect that ELVOCs are important at least for the initial growth of the clusters and should be considered in both models. I suggest that you perform some sensitivity test where you instead of using adipic acid use and ELVOC compound to simulate the growth of the particles.**

This is now explained in section 2.2 (p. 9, lines 21-31) “Further aerosol processes are condensation of  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ ,  $\text{COV}_s$  and an extremely low-volatile non-hygroscopic vapor  $\text{COV}_l$  (Table 2), as well as Brownian coagulation, and mixing with the particle-free dry diluted air.  $\text{COV}_s$  has the properties of adipic acid (same as in AEROFOR) but different water uptake since the hygroscopic properties of  $\text{COV}_s$  in MAFOR were that of sodium succinate (Peng and Chan, 2001), i.e.  $\text{COV}_s$  starts to take up water at  $\text{RH}>48\%$ , and has a growth factor of 1.85 from 10% to 90% RH. The saturation vapour pressure for  $\text{COV}_l$  was adopted from Lemmon and Goodwill (2000). Due to its extremely low vapour pressure,  $\text{COV}_l$  assists in the initial growth of nucleated particles of 1-2 nm diameter in size for which the Kelvin barrier is huge. The Kelvin effect drops sharply as the particle size increases due to its exponential dependence on diameter, enabling condensation of more volatile compounds, such as  $\text{COV}_s$ . Since n-alkanes do not form hydrogen bonds with sulfuric acid, it is further assumed that  $\text{COV}_l$  is not a nucleating compound.”

Two sensitivity tests were performed with MAFOR to illustrate the effect of using condensable organic vapors with different volatility and hygroscopic properties. A figure (Fig. S6) with the results of the sensitivity tests was added to the Supplementary Materials.

The following text was added to section 3.3.2 p. 19, lines 5-15: “With MAFOR we tested how much the volatility properties of the condensing organic vapours affect the size distribution (Fig S6). In the first test,  $\text{COV}_l$  was not included (green line in Fig. S6). This resulted in a smaller GMD of 10.7 nm (measured: 13.1 nm) for the volatile mode in the distribution after 2.7 s. In the second test,  $\text{COV}_l$  was not included as well, and in addition  $\text{COV}_s$  was used with the hygroscopic properties of sulfuric acid (red line in Fig. S6). The resulting GMD of the volatile mode was in agreement with AEROFOR and the measured diameter. In both tests, the growth of large particles (>200 nm diameter) was overestimated due to the enhanced water uptake of the soot mode. The second test used the same parameterization of  $\text{COV}_s$  as in AEROFOR and the resulting final size distributions were similar. The remaining differences for the number concentration of small particles below 9 nm diameter were probably due to higher coagulation rates in MAFOR.”

**Minor corrections:**

**Abstract L19-21:** “On the other hand, NUP formation was ceased if the GSA concentration was less than  $10^{10} \text{ cm}^{-3}$  which suggests, based on the measurements, the usage of biofuel to prevent volatile particles in diesel exhaust.”

I would reformulate this sentence slightly to: “On the other hand, NUP formation ceased if the GSA concentration was less than  $10^{10} \text{ cm}^{-3}$ , which suggests, based on the measurements, that the usage of biofuel prevents volatile particles in diesel exhaust.”

We changed the text to: “On the other hand, the model predicted that the NUP formation ceased if the GSA concentration in the raw exhaust was less than  $10^{10} \text{ cm}^{-3}$ , which was the case when biofuel was used.”

**Abstract L2:** I would replace “during” with “when”.

Done.

**Page 4, L5-6:** “Because vehicle exhaust includes similar species than the atmosphere, NUP formation might occur in the same way.”

Replace “than” with “as in”

Done.

**Figure 2** need to be saved with higher resolution and all data points should be explained

The resolution is now 300 x 300 ppi instead of 96 x 96 ppi, and all data points are explained in figure caption.