We thank the referees 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 reviewers’ comments below and indicated where changes were made to the text (red).

Reply to RC C1113, Anonymous Referee #1

Pirjola et al. report their work aiming to model the behaviour of the aerosol particle number size distribution in engine exhaust emissions within the measurement set-up. The authors test several nucleation mechanisms and compare how well the output from the measurement set-up can be reproduced with the model when the different nucleation mechanisms and assumptions on condensing vapours are applied. Unfortunately, the manuscript suffers from unsatisfactory level of English language. Otherwise it is, however, interesting and the results are certainly valuable for the audience of ACP. If the authors manage to improve the English in the manuscript and respond to the few specific comments below, I will recommend publication in ACP.

Specific comments:
1) The authors state that the measurement set-up has been shown to represent the real world processes relatively well (page 4224). According to Fig. 3c the condensation sink in the end of the chamber, >2.5 s after the emission, is between 2 and 7 s\(^{-1}\). The typical atmospheric conditions very rarely reach 0.1 s\(^{-1}\). Are the values in range 2 to 7 s\(^{-1}\) realistic to roadside values or one to two orders of magnitude higher? If it is not realistic, how much would this affect the comparison between the model, measurements and the real-world conditions?

The comment is valuable. It is true that all the details in real-world exhaust dilution processes cannot be reproduced by laboratory systems. However, the sampling system used in the studies of Arnold et al. (2012) and Rönkkö et al. (2013) has been observed to reproduce relatively well the real-world formation and growth of diesel exhaust nucleation mode, particularly the geometric mean diameter of that mode. Related to that, we added one reference into the text where the topic is analyzed (Keskinen and Rönkkö, 2010). It is clear that the particle concentrations of the nucleation and pre-existing modes strongly depend on the distance from the source, i.e. on the dilution ratio DR within the exhaust. In the sampling system DR=12 at the end of the ageing chamber, however, the measurements were performed after the ejector diluter when the total DR=96. Between the ageing chamber and the ejector diluter no aerodynamic processes occur, only dilution. In this work both the modelled and measured results are given at the end of the ageing chamber (DR=12). In real-world conditions DR is easily even more than 1000 at the plume age of 2.7 s (Kittelson et al., 1998; Du and Yu, 2008). From this perspective, it is not a surprise that the condensation sink as well as the modal number concentrations are much higher than the atmospheric measurements.

We modified the text in section 2.1 (p. 6 lines 18-26): “The particle sampling and dilution system was a modified version of partial flow sampling system (Ntzhiachristos et al. 2004). The system consisted of a porous tube type primary diluter followed by an ageing chamber and an ejector type diluter (Fig. 1). Although it is clear that the system simplifies the real-world vehicle exhaust dilution process and thus does not completely reproduce all the details of the real-world process, it has been shown to reproduce the real-world exhaust nucleation particle formation and growth relatively well (Gieschaskiel et al., 2005; Rönkkö et al., 2006; Keskinen and Rönkkö, 2010). Therefore, the system has been used especially in laboratory studies focusing on vehicle exhaust nanoparticles (e.g. Vaaraslahti et al., 2005), Rönkkö et al., 2006), Arnold et al., 2012), Rönkkö et al., 2013).”

We added on p. 12 lines 21-26. “It should be noted that in this study the dilution ratio was only 12 whereas in atmospheric conditions it might be even more than 1000 at plume ages of 2.7 s (Kittelson et al., 1998, Du and Yu, 2008). Typically, the nucleation mode has been fully formed at the dilution ratio of approximately 100 (Keskinen and Rönkkö, 2010) or after less than 0.7 s residence time in the atmosphere (Rönkkö et al., 2007).”
The authors show that the HET nucleation mechanism can be adapted to all the measurement conditions with the same nucleation coefficients and COV concentrations, whereas the other mechanisms cannot. In the current version, this important finding is quite much buried under all the other results. I would suggest e.g. reforming Table 2 to a figure, where the required nucleation coefficient values and COV concentrations for the different nucleation mechanisms are presented as a function of GSA. This figure, and few more sentences on its significance would clarify the conclusions significantly.

We prepared the suggested figures, now Fig. 5. Due to additional information than shown by Fig. 5, old Table 2, now Table 3, was also kept in the manuscript.

Figure 5. Nucleation coefficients as a function of GSA and COVs concentrations when the nucleation mechanism was ACT (a), KIN and HET (b).

A few sentences were added in section 3.1.2, p. 15 lines 8-14: “As with the ACT mechanism, the nucleation coefficient K varied strongly as a function of the initial GSA concentration (Table 3 and Fig. 5b) with the KIN mechanism. However, during the steady state driving cycle (100% engine load), the measured raw exhaust parameters such as temperature, H2O concentration, RH, core and soot mode particle concentrations, were constant, only GSA varied, probably due to the storage effect in the ATS as mentioned in section 2.3. Therefore, it was expected that the nucleation coefficients A and K should have constant values when simulating the different cases within the same engine load.”

and in section 3.1.3: “This procedure resulted in constant values of 3.8x10^{17} and 5.6x10^{17} cm^3 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). “

To avoid too much lengthening the paper old Fig. 9 was moved to Supplementary Material, now Fig. S5.

3) Biofuel/diesel is mentioned only in the last sentences of the abstract and of the concluding remarks. There should be some analysis and/or sentences with references also in the text to back up the conclusions. Currently, it seems like the related part of the manuscript would have been excluded from the submitted version.

We added in the experimental section 2.1 a mention of biofuel measurements. “The FSC was 36 ppm, additionally the FSC of 6 ppm and biofuel (FSC < 1 ppm) were used in some experiments. “

In section 3.4. (p 21, lines 2-5) it is now stated: “In both cases, the NUP concentrations decreased with lower GSA concentrations, and ceased when the GSA concentration was around 10^{10} cm^{-3}. This value corresponds to the usage of biofuel with FSC < 1 ppm as seen from Fig. 3 in Arnold et al. (2012).”

The sentence in Abstract was clarified: “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} cm^{-3}, which was the case when biofuel was used.”

Technical comments: Many of these are related to the language, but as I am not native English speaker, not all the suggestions are necessarily correct. The authors should review the whole manuscript in terms of the English language.

The English language was improved.
- P. 4220 line 2 “during exhaust cools and dilutes” does not sound good, perhaps “while the exhaust cools and dilutes”/“during cooling and dilution of the exhaust”
  
  We replaced “during” with “when” as also suggested by Referee #2.

- P. 4220 line 8: “running with low fuels sulphur content (FSC) FUEL”
  
  Done.

- P. 4220 lines 23-24: give reference
  
  Pey et al. (2009) was added.

- P. 4220 line 24: ”due to the tightened” would be better a bit later, after ”...have been reduced”
  
  Done.

- P. 4221 line 11: pPDF should probably be pDPF
  
  Corrected.

- P. 4222 line 4: also sulphuric acid - organic vapour nucleation should be mentioned, e.g. Riccobono et al., 2014
  
  This is now mentioned on p. 4 lines 9-10, the reference was also added.

- P. 4222 lines 12-17. The sentences should be recoupled: “Recently: : : into two groups. Some of them are process models: : : in this paper, whereas some are computational: : :”
  
  The sentence was changed according to the suggestion.

- P. 4222 lines 21-25: You have not used the word “barrierless” so far, please clarify and give reference. More importantly, in their conclusions Vouitsis et al. state that “it is shown that a nucleation rate without an energy barrier should be considered for qualitative stable predictions”, and in their Results-section that with high FSC fuel barrierless nucleation scheme overestimates the nucleation mode concentrations (and saturation ratio scheme works adequately) whereas with low FSC fuel barrierless nucleation is more appropriate. In this manuscript the authors have mixed these to the opposite.

  We changed the text to: “The simulation results reported by Vouitsis et al. (2005) showed that the barrierless nucleation scheme, where clusters are always stable against evaporation (Clement and Ford, 1999), could predict the NUP concentration rather well for low sulphur fuel (FSC=10 ppm), whereas the nucleation rate proportional to the square of sulphuric acid saturation vapour pressure was more appropriate for high sulphur fuel (FSC=250 ppm).” Clement and Ford (1999) was added in References.

- P. 4226 lines 15-16: which CIMS measurements are referred to here?
  
  We referred to the measurements by Arnold et al. (2012). This is now explicitly mentioned in the text.

- P. 4226 lines 18-20: is it so that the adipic acid in the model condenses on all particle sizes and nucleates? What does it then mean that the thermodynamic properties are taken from the literature?

  The vapour pressure of adipic acid was calculated according to Bilde et al. (2003), and for example at 300 K it was 2.46x10⁻⁵ Pa (=5.95x10⁹ cm⁻³). Kelvin effect was taken into account in calculating the condensation flux of adipic acid. For the surface tension we used the temperature-dependent expression by Riipinen et al. (2007), based on the method of Macleod-Sugden. σ = 0.058592 - 0.083x10⁻³x(T(K)) in N/m. The adipic acid molar weight of 146 g mol⁻¹ and the liquid phase density of 1085 kg m⁻³ were used. This information has been added in section 2.2. Model description and in a new table, Table2.

  Table 2. Physical properties of the condensable vapours. COVₛ was used in AEROFOR whereas COVₛ and COVᵢ were used in MAFOR.

<table>
<thead>
<tr>
<th></th>
<th>p²(298 K) (Pa)</th>
<th>molar weight (g/mol)</th>
<th>surface tension (298 K) (N/m)</th>
<th>hygroscopic nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COVₛ</td>
<td>1.63x10⁻⁵ᵃ</td>
<td>146</td>
<td>0.34ᵇ</td>
<td>yes</td>
</tr>
<tr>
<td>COVᵢ</td>
<td>5.0x10⁻¹ᶜ</td>
<td>478</td>
<td>---</td>
<td>no</td>
</tr>
</tbody>
</table>
- P. 4227 line 12: if adipic acid is assumed to participate in heterogeneous nucleation and growth from 1.5 nm on, what is the difference between it and ELVOC? Furthermore, ELVOC is a term, which is typically used for highly oxidized C10 or C20 species. It also sounds that ELVOC would be more volatile than condensable organic vapour (COV). I suggest to use another term instead of ELVOC, e.g. COV with some sub-index.

We have now used two types of condensable organic vapours: semivolatile called COV_s and low-volatile called COV_l. The text concerning this was rephrased in Section 2.2 and a new table (Table 2) summarizing the physical properties of these vapours was added.

p. 8, lines 18-32: “The condensable organic vapours that contribute to particle evolution in diesel exhaust are not yet identified. However, based on measurements, Arnold et al. (2012), Kawamura and Kaplan (1987) and Zervas et al (2001) have observed condensable dicarboxylic acids in the exhaust of vehicles. 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_{24–32} range, which were derived almost entirely from unburned oil. Although there may be thousands of different low and semi-volatile condensable organic vapours we have used in AEROFOR a semi-volatile organic compound called COV_s 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_{34}H_{70} (constituent of the engine oil) called COV_l was used in MAFOR.

In addition to condensation, COV_s was assumed to participate in heteromolecular nucleation. The thermodynamical properties for COV_s were adopted from literature, i.e. temperature-dependent expressions for the saturation vapour pressure from Bilde et al. (2003) and for the surface tension by Riipinen et al. (2007) (Table 2). The molecular weight of 0.146 kg mol^{-1} and the liquid phase density of 1085 kg m^{-3} were used.

And later on p. 9, lines 21-31 for MAFOR: “Further aerosol processes are condensation of H_2SO_4, H_2O, COV_s and an extremely low-volatile non-hygrosopic vapor COV_l (Table 2), as well as Brownian coagulation, and mixing with the particle-free dry diluted air. COV_s has the properties of adipic acid (same as in AEROFOR) but different water uptake since the hygroscopic properties of COV_s in MAFOR were that of sodium succinate (Peng and Chan, 2001), i.e. COV_s starts to take up water at RH>48%, and has a growth factor of 1.85 from 10% to 90% RH. The saturation vapour pressure for COV_s was adopted from Lemmon and Goodwill (2000). Due to its extremely low vapour pressure, COV_s 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 COV_s. Since n-alkanes do not form hydrogen bonds with sulfuric acid, it is further assumed that COV_s is not a nucleating compound.”

-P. 4228 line 5: is the final exhaust temperature equal to dry air temperature, 303 K? Yes, 300-303 K. However, this is an assumption because exact exhaust temperature at the end of the ageing chamber was not measured.

- P. 4228 line 9-10: either “Similarly to Lemmetty et al., dilution is modelled: : :” or “According to Lemmetty et al., dilution can be modelled: : :” The sentence was changed to “Similarly to Lemmetty et al., dilution is modelled.”

- P 4228 line 15: either “all” or “only” to be removed We removed the word “all”.

- P. 4231 line 10: “The activation coefficient and COV concentrations were varied”. Wasn’t the case that the coefficients A and K as well as COV concentration were taken as free parameters to find the best correspondence between measurements and the model? At least this is what P4231 line 21 looks like: “obtained coefficients A and K vary strongly” together with P4233 line 14-15, where the COV concentration becomes quite constant.
Yes, the coefficients A and K as well as COV concentration were taken as free parameters to find the best agreement between the modelled and measured particle size distributions at the end of the ageing chamber. This is now clearly mentioned on p. 13, lines 22-23.

- **P4231 line 12-14:** “height of the nucleation mode” would be better as “nucleation mode particle concentration”
  Corrected.

- **P4231 line 27-28:** some reference is needed if the difference between measurement and model is suggested to result from the underestimation by SMPS. Do the authors suggest that all SMPS-measurements underestimate the concentrations of 3-7 nm particles by roughly an order of magnitude, which is the difference between the measurement and the model in Figs. 4 and S3?
  In the studies reported by Arnold et al. (2012) and Rönkkö et al. (2013) the SMPS was the only instrument capable to measure the size distribution of smallest particles. The model of this study predicts that the concentrations of the smallest particles are higher than the measured concentrations. After this result, the authors have continued the work (but with different engine and other parameters) by comparing SMPS measurements to a particle size magnifier (PSM, manufactured by Airmodus Ltd). The results have not yet published, but the paper containing preliminary results (Kuuluvainen et al., 2015) have been accepted to the European Aerosol Conference and also journal article will be done. In general, the comparison of the PSM data and SMPS data leads to similar results: the SMPS measurement seems to significantly underestimate the nanoparticle concentrations.

We modified the text on p. 14 lines 8717: “As seen from Fig. 4, the model predicts higher concentration for the smallest particles of the nucleation mode than the measurements, thus indicating that the SMPS might underestimate the concentration of the particles smaller than 10 nm. According to the manufacturer, the uncertainties in the SMPS measurement may be caused by the uncertainties in voltage and flow accuracy, scan time, bi-polar charge distribution, CPC efficiency curve, DMA transfer function, working gas, diffusion losses, and sampling and conditioning issues. Unfortunately, in the studies reported by Arnold et al. (2012) and Rönkkö et al. (2013) the size distribution of smallest particles was not measured by other methods than by the SMPS, and thus experimental evidence on uncertainties in SMPS measurements of vehicle exhaust nanoparticles is an issue for future studies (see e.g. Kuuluvainen et al., 2015).”

- **P4232 lines 4-5:** “It is not expected that the activation coefficient A was not constant but varied in range: : :”? Does this mean that the authors believe it is constant in reality, but varied the value in model to see the effect in the model output?
  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, [H2O], 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 in order 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.

We also refer to our reply in Specific comment 2) above.

- **P4234 line 7:** does “other organic vapours” now refer to other than the nucleating vapour?
  The sentence was changed to “…or condensation of organic vapours other than the nucleating vapour.”

- **P4234:** are both COV and ELVOC in MAFOR capable to nucleate as in HET mechanism?
Only COVs (old COV) is capable to nucleate according to the HET mechanism. COV₁ (=ELVOC) does not participate in nucleation. Table 2 was added to show the properties of the organic vapours.

- **P4235 lines 1-2**: Is this based on previous measurements? If so, please give the reference. The classification of the initial aerosol as “core mode” and “soot mode” follows Rönkkö et al. (EST, 2013; in particular measurements shown in Figure 4 of that paper).

- **P4236** some terms and sentences are unclear: lines 20-22; line 24 “volatile nucleation mode”;

  We have now clearly defined the concepts “volatile and non-volatile nucleation modes” in Introduction lines 24-29. 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).

- **P4237 line 5**: nucleation drops -> nucleation rate drops

  Corrected.

- **P4237**: here is applied a term “non-volatile nucleation mode”, earlier “core mode”, in figure captions “non-volatile core mode”. Please, harmonize.

  “non-volatile nucleation mode” whenever it exists was changed to “core mode”.

- **P4239**: line 8: cDPF? Previously pDPF is mentioned.

  The misprint was corrected.

- **P4240, line 15**: the time at the end of the simulation, 2.7 s, should be mentioned

  Added.

- **P4240, line 18**: CCN has not been mentioned earlier.

  “cloud condensation nuclei (CCN)” was added.

- **P4240, line 20**: the proxy?

  The word “proxy” was removed, and “adipic acid” was replaced by “the semivolatile organic vapour COVs.”

- **P4240, line 28**: 2007 is not too recently any more

  The word “recently” was removed.

- **P. 4235**: Figure and caption, EJ = ED?

  Corrected.

- **P. 4257 on**: the nucleation mechanism applied for the figures from here on, apparently HET, should be mentioned in the legend.

  Added.
Reply to RC C1712, Anonymous Referee #2

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. COVs and COVl 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
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 semi-volatile 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 COVs. 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 (COVs) and/or low-volatile (COVs) 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_{24}–C_{32} 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 COVs 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_{34}H_{70} (constituent of the engine oil) called COV_l 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. \( \sigma = 0.058592 - 0.083 \times 10^{-3} \times T(K) \) in N/m. The adipic acid molar weight of 146 g mol\(^{-1}\) and the liquid phase density of 1085 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 adipic acid vapour pressure was calculated according to Bilde et al. (2003), and for example at 300 K it was 2.46x10\(^{-5}\) Pa (=5.95x10\(^{-9}\) 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. COV\(_s\) was used in AEROFOR whereas COV\(_s\) and COV\(_l\) were used in MAFOR.

<table>
<thead>
<tr>
<th></th>
<th>( p^0(298\ K) ) (Pa)</th>
<th>molar weight (g/mol)</th>
<th>surface tension (298 K) (N/m)</th>
<th>hygroscopic</th>
<th>nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COV(_s)</td>
<td>1.63x10(^{-5})(^a)</td>
<td>146</td>
<td>0.34(^b)</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>COV(_l)</td>
<td>5.0x10(^{-11})(^c)</td>
<td>478</td>
<td>( -^d )</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

\(^a\) Bilde et al., 2003  
\(^b\) Riipinen et al., 2007  
\(^c\) Lemmon and Goodwill, 2000  
\(^d\) Kelvin effect not considered: 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 \( \mu \)m diameter. Effective density of 1200 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\(^3\) and of 1000 kg/m\(^3\) (Park et al. (2003) for 50 nm particles).

A sentence “The tests with 1000 and 1500 kg m\(^{-3}\) 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 2.5x10-5 – 2x10-1 s-1 as the initial GSA concentration varied from 2.8x109 to 2x1012 cm-3 (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, [H2O], 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 K1 and K2 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 \( K_{[\text{GSA}]}^2 = K_1^2 [\text{GSA}]+ K_2^2 \), 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 3.8x10^{-17} and 5.6x10^{-17} cm^3 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 COV\(\text{s} \) in MAFOR are that of sodium succinate (Peng and Chan, 2001), i.e. COV\(\text{s} \) starts to take up water at 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 (p0 (298 K) = 5.0x10-11 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 \( \text{H}_2\text{SO}_4, \text{H}_2\text{O}, \text{COV}\text{s} \) and an extremely low-volatile non-hygroscopic vapor \( \text{COV}\text{s} \) (Table 2), as well as Brownian coagulation, and mixing with the particle-free dry diluted air. \( \text{COV}\text{s} \) has the properties of adipic acid (same as in AEROFOR) but different water uptake since the hygroscopic properties of \( \text{COV}\text{s} \) in MAFOR were that of sodium succinate (Peng and Chan, 2001), i.e. \( \text{COV}\text{s} \) starts to take up water at RH>48%, and has a growth factor of 1.85 from 10% to 90% RH. The saturation vapour pressure for \( \text{COV}\text{s} \) was adopted from Lemmon and Goodwill (2000). Due to its extremely low vapour pressure, \( \text{COV}\text{s} \) 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 \( \text{COV}\text{s} \). Since n-alkanes do not form hydrogen bonds with sulfuric acid, it is further assumed that \( \text{COV}\text{s} \) 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, \( \text{COV}\text{s} \) 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, \( \text{COV}\text{s} \) was not included as well, and in addition \( \text{COV}\text{s} \) 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 \( \text{COV}\text{s} \) 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 1010 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 1010 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 $10^{10}$ 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.
Model studies of volatile diesel exhaust particle formation: Organic vapours involved in nucleation and growth?

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Abstract

A high concentration of volatile nucleation mode particles (NUP) formed in the atmosphere when the exhaust cools and dilutes has hazardous health effects and it impairs the visibility in urban areas. Nucleation mechanisms in diesel exhaust are only poorly understood. We performed model studies using two sectional aerosol dynamics process models AEROFOR and MAFOR on the formation of particles in the exhaust of a diesel engine, equipped with an oxidative after-treatment system and running with low fuel sulphur content (FSC) fuel, under laboratory sampling conditions where the dilution system mimics real-world conditions. Different nucleation mechanisms were tested. Based on the measured gaseous sulphuric acid (GSA) and non-volatile core and soot particle number concentrations of the raw exhaust, the model simulations showed that the best agreement between model predictions and measurements in terms of particle number size distribution was obtained by barrierless heteromolecular homogeneous nucleation between the GSA and a semi-volatile organic vapour combined with the homogeneous nucleation of GSA alone. Major growth of the particles was predicted to occur by the similar organic vapour at concentrations of \((1-2) \times 10^{12} \text{ cm}^{-3}\). The pre-existing core and soot mode concentrations had an opposite trend on the NUP formation, and the maximum NUP formation was predicted if a diesel particle filter (DPF) was used. 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.
1 Introduction

Regardless of many improvements in vehicle technology exhaust particles emitted from traffic constitute major air pollutants in urban environments (e.g. Pey et al., 2009). Although the mass emissions of diesel particles have been reduced due to the tightened emission regulations, the number emission of exhaust nanoparticles has been reported to be significant (Rönkkö et al., 2013, Lähde et al., 2010). These non-regulated particles can penetrate deepest into the human pulmonary and blood-vascular systems having hazardous health effects (Pope and Dockery, 2006, Sioutas et al., 2005, Kettunen et al., 2007, Su et al., 2008, Alföldy et al., 2009). Exhaust particles also affect the climate by scattering or absorbing solar radiation and participating in cloud formation (Charsson, et al., 1992, Bond et al., 2013).

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). These particles are formed in the combustion process and are composed of non-volatile carbonaceous soot agglomerates, onto which semi-volatile vapours can condense (e.g. Kittelson, 1998, Tobias et al., 2001). The Euro 6 level diesel vehicles are equipped with diesel particle filters (DPF) or partial diesel particle filters (pDPF) (Heikkilä et al., 2009) which remove totally or partly soot particles. The oxidative after-treatment systems such as diesel oxidising catalyst (DOC) reduce exhaust hydrocarbon concentrations but simultaneously increase SO$_2$ to SO$_3$ conversion enhancing gaseous sulphuric acid (GSA) formation (Arnold et al., 2006, 2012, Maricq et al., 2002). 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 (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). These particles are suggested to be formed by fuel aliphatic hydrocarbons (Filippo et al., 2008) or lubricant oil metal compounds (Kittelson et al,
2008, Rönkkö et al., 2013, Karjalainen et al., 2014) coated by condensing volatile hydrocarbon and sulphur compounds (Rönkkö et al., 2007, Rönkkö et al., 2013).

Although the measurements indicate that sulphuric acid participates in the production of volatile exhaust particles, the nucleation mechanism is not known. Numerous different nucleation theories involving sulphuric acid such as homogeneous binary nucleation (BHN) (Kulmala et al., 1998, Vehkamäki et al., 2002, 2003), ternary nucleation (Napari et al., 2002, Merikanto et al., 2007), activation nucleation (Kulmala et al., 2006), kinetic nucleation (Weber et al., 1997), ion-induced nucleation (Raes et al., 1985, Arnold et al., 1999, Yu and Turco, 2000), and recently sulphuric acid-amine nucleation (Almeida et al., 2013) as well as sulphuric acid along with oxidized organic vapours (e.g. Riccobono et al., 2014) have been proposed to explain nucleation bursts under atmospheric conditions. Since vehicle exhaust includes similar species as in the atmosphere, the NUP formation might occur in the same way. Arnold et al. (1999) have actually made mass spectrometric measurements of chemi-ions present in the exhaust of combustion engines, including car engines and aircraft gas turbine engines. On the other hand, Ma et al. (2008) reported that ion-induced nucleation did not play an important role in the NUP formation of diesel exhaust. Ion-induced nucleation is not considered in this study.

Recently published models simulating the formation and growth of exhaust particles can be divided into two groups. Some of them are process models (Shi and Harrison, 1999, Voutsis et al., 2005, Lemmetty et al., 2008, Hu and Yu, 2006, 2008) as is also the model considered in this study, whereas some are computational fluid dynamics (CFD) models coupled with aerosol dynamics (Uhrner et al., 2007, Albriet et al., 2010, Liu et al., 2011) and with the major turbulent mixing processes as well (Wang and Zhang, 2012).

Shi and Harrison (1999) concluded that the BHN predicted several orders of magnitude lower nucleation rates than those measured even though the fuel sulphur content (FSC) was as high as 300-500 ppm, and no sink processes such as condensation and coagulation were taken into account. The simulation results reported by Vouitsis et al. (2005) showed that the barrierless nucleation scheme, where clusters are always stable against evaporation (Clement and Ford, 1999), could predict the NUP concentration rather well for low sulphur fuel (FSC=10 ppm), whereas the nucleation rate proportional to the square of sulphuric acid saturation vapour pressure was more appropriate for high sulphur fuel (FSC=250 ppm). Lemmetty et al. (2008)
discovered that by assuming the high SO$_2$ to SO$_3$ conversion ratio of 90% BHN nucleation reproduced the measured size distributions opposed to barrierless nucleation. Du and Yu (2006) concluded that by using their kinetic BHN model for the vehicles running on the fuel with the FSC of 330 ppm, the BHN scheme could not predict the measured NUP concentrations if the SO$_2$ to SO$_3$ conversion ratio was 1%, but that it was appropriate for the ratios greater than 4% even though FCS was less than 50 ppm. If the FSC was 15 ppm, the BHN was the main source of NUP only for vehicles equipped with continuously regenerating particle filters (Du and Yu, 2008).

All of these studies indicate that other low or semi-volatile condensable vapours than GSA are required to explain the measured particle number size distributions. However, all of the previous model studies suffer from the lack of GSA measurements. It is well-known that even a small change in the GSA concentration can cause several orders of magnitude difference in the binary nucleation rate.

**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$_3$) and/or low-volatile (COV$_1$) condensable organic vapours needed to explain the diesel particle evolution in an ageing chamber under laboratory conditions which mimic well the atmospheric dilution conditions. For the first time the applicability of nucleation between an organic compound and sulphuric acid in diesel exhaust was investigated. The other objective is to investigate how changes in vehicle after-treatment technologies, fuel and lubricant oil affect exhaust particle nucleation and growth.**

The model simulations were performed by an aerosol dynamics model AEROFOR (e.g. Pirjola, 1999, Pirjola and Kulmala, 2001, Lemmetty et al., 2008, Arnold et al., 2012). The GSA and particle concentrations in the raw exhaust were adopted from the measurements by Arnold et al. (2012) and Rönkkö et al (2013). The first model simulations by AEROFOR for the same engine equipped with the DOC and DPF have already been described in Arnold et al. (2012). Since AEROFOR produces only the time evolution of the particle number size distributions and concentrations, some of the simulations were repeated with another aerosol dynamics model MAFOR (Karl et al., 2011) which is able to produce the mass and composition size distributions of a multicomponent aerosol.
Both models, AEROFOR and MAFOR, are Lagrangian type box models which are well 
established and evaluated. Although these models are not able to give a spatial distribution of 
temperature and aerosol scalars in the sampling system (Olin et al., 2015), they were able to 
achieve the goals of this study, and subsequently increase our understanding on the formation 
and transformation mechanisms in diesel exhaust under laboratory and atmospheric 
conditions.

2 Methods

2.1 Sampling system and measurements

Since the detailed description of the measurements and instrumentation can be found in 
Arnold et al. (2012) and Rönkkö et al. (2013), only a short description relevant to modelling 
is given here. The emission measurements of a Euro IV standard heavy duty diesel engine 
were performed on an engine dynamometer. Four steady-state conditions with engine loads of 
100%, 75%, 50% and 25% were studied. The FSC was 36 ppm, additionally the FSC of 6 
ppm and biofuel (FSC < 1 ppm) were used in some experiments. Different after-treatment 
systems were used, however, this research mainly deals with the cases when the engine was 
equipped with DOC and pDPF.

The particle sampling and dilution system was a modified version of partial flow sampling 
system (Ntzhiachristos et al. 2004). The system consisted of a porous tube type primary 
diluter followed by an ageing chamber and an ejector type diluter (Fig. 1). Although it is clear 
that the system simplifies the real-world vehicle exhaust dilution process and thus does not 
completely reproduce all the details of the real-world process, it has been shown to reproduce 
the real-world exhaust nucleation particle formation and growth relatively well (Gieschaskiel 
et al., 2005; Rönkkö et al., 2006; Keskinen and Rönkkö, 2010). Therefore, the system has 
been used especially in laboratory studies focusing on vehicle exhaust nanoparticles (e.g. 
Vaaraslahti et al., 2005; Rönkkö et al., 2006; Arnold et al., 2012; Rönkkö et al., 2013).

The ageing chamber was used to ensure adequate residence time for the condensational 
growth of the nucleation mode particles in the cooled and diluted aerosol sample. The 
following ejector diluter was used to bring the sample into the ambient pressures and to
ensure that the particle number concentration was in the measurement range of particle measurement equipment, without significant effects on particles formed during exhaust dilution and cooling (Giechaskiel et al. 2009). In the primary diluter, the dilution air temperature was 30 °C, the relative humidity was close to zero and the dilution ratio was adjusted to 12. The dilution ratios were calculated from the measured CO₂ concentrations of the diluted exhaust sample and the raw exhaust. Based on the constant exhaust flow rate in the dilution and sampling system (55 lpm) and the measurements mentioned in Fig. 1, the residence time of the exhaust in the tube between the PD and AC was 0.1 s and in the ageing chamber 2.6 s. Furthermore, exhaust temperature was measured at two points marked in Fig. 1.

Particle number size distributions of the exhaust were measured using two scanning mobility particle sizers (SMPS) measuring the particle diameters 3-60 nm and 10-430 nm. Also the size distributions for all engine loads were measured using a thermodenuder TD in which the volatile material was evaporated at 265 °C temperature. The size distributions were corrected for particle losses in both SMPS and thermodenuder (Heikkilä et al., 2009).

The gaseous sulphuric acid GSA was monitored by a CIMS (Chemical Ion Mass Spectrometer) whose setup consists of a flow tube reactor through which the exhaust plume is passed. Details of the instrument can be found in Fiedler et al. (2005) and Arnold et al. (2012). In addition, the acidic trace gases were measured in a way analogous to GSA. 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 (Arnold et al., 2012).

### 2.2 Model descriptions

The model simulations were performed by a slightly updated version of an atmospheric chemistry and aerosol dynamics box model AEROFOR (e.g. Pirjola, 1999, Pirjola and Kulmala, 2001, Pirjola et al., 2004, Arnold et al., 2012). The model includes gas phase chemistry, formation of thermodynamically stable clusters by different nucleation mechanisms, condensation of H₂SO₄, H₂O and an organic vapour onto particles (Fuchs and Sutugin, 1970) taking into account molecular dimensions (Lehtinen and Kulmala, 2003), Brownian coagulation of particles (Fuchs, 1964), temperature and cooling profiles (Lemmetty et al., 2006), wall losses (Voutsis et al., 2005) as well as mixing with the particle-free dry
diluted air. The Kelvin effect was taken into account in the condensation processes of organic vapour and sulphuric acid. The saturation vapour pressure of sulphuric acid was calculated according to eq. (8) in Vehkamäki et al., 2003, and surface tension as explained in Vehkamäki et al., (2003), valid at least up to 360–400 K.

In this study, four nucleation mechanisms were used: 1\(^ \text{st} \) classical binary homogeneous \( \text{H}_2\text{SO}_4–\text{H}_2\text{O} \) nucleation (BHN) (Vehkamäki et al., 2003), 2\(^ \text{nd} \) activation theory (ACT) (Kulmala et al., 2006) where under the steady state nucleation rate the number of activated clusters is linearly proportional to the sulphuric acid concentration, i.e. the nucleation rate \( J = A[\text{H}_2\text{SO}_4] \) (\( A= \text{activation coefficient} \)), 3\(^ \text{rd} \) kinetic nucleation (KIN) (McMurry and Friedlander, 1979, Weber et al., 1997, Sihto et al., 2006), where homogeneous homomolecular nucleation occurs involving two sulphuric acid molecules and thus the nucleation rate \( J \) is proportional to the square of the sulphuric acid, i.e. \( J = K[\text{H}_2\text{SO}_4]^2 \) (\( K= \text{kinetic coefficient which includes the collision frequency and the probability of formation of a stable particle after the collision} \)), 4\(^ \text{th} \) homogeneous homomolecular nucleation of sulphuric acid along with homogeneous heteromolecular nucleation between sulphuric acid and organic vapour molecules (HET) (Paasonen et al., 2010), i.e. \( J = K_1[\text{H}_2\text{SO}_4]^2 + K_2[\text{H}_2\text{SO}_4][\text{org}] \). The diameter of the nucleated particle was assumed to be 1.5 nm (Kulmala et al., 2007).

The condensable organic vapours that contribute to particle evolution in diesel exhaust are not yet identified. However, based on the measurements, Arnold et al. (2012), Kawamura and Kaplan (1987) and Zervas et al (2001) have observed condensable dicarboxylic acids in the exhaust of vehicles. 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 \( \text{C}_{24}–\text{C}_{32} \) range, which were derived almost entirely from unburned oil. Although there may be thousands of different low and semi-volatile condensable organic vapours we have used in AEROFOR a semi-volatile organic compound called COV\(_2\) 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 \( \text{C}_{34}\text{H}_{70} \) (constituent of the engine oil) called COV\(_1\) was used in MAFOR.

In addition to condensation, COV\(_2\) was assumed to participate in heteromolecular nucleation. The thermodynamical properties for COV\(_2\) were adopted from literature, i.e. temperature-dependent expressions for the saturation vapour pressure from Bilde et al. (2003) and for the
surface tension by Riipinen et al. (2007) (Table 2). The molecular weight of 0.146 kg mol$^{-1}$ and the liquid phase density of 1085 kg m$^{-3}$ were used. The vapour concentration is a free parameter. Pure adipic acid is insoluble in water. Hämeri et al. (2002) have measured that the organic fraction of the mixtures containing adipic acid and ammonium sulphate does not contribute to water uptake. However, Yeung et al. (2009) found out that adipic acid can have effects similar to those of more water-soluble organic species. Since AEROFOR assumes that the particles are in balance with the ambient water vapour concentration it might overestimate the wet diameters of the particles.

To minimise the effect of numerical diffusion typical for sectional models, 100 size sections turned out to be sufficient. The fixed sectional presentation for aerosol size distribution was used since the sectional representation is more advantageous for the treatment of simultaneous nucleation and particle transformation than the modal aerosol representation. Especially in diesel exhaust, the rapid formation of volatile particles may lead to size distribution peaks that do not have a lognormal shape.

The set of stiff differential equations describing the time evolution of particle number concentrations in each section as well as the vapour concentrations was solved using Numerical Algorithms Group, Ltd. library FORTRAN-routine D02EJF (1990). The time step was set to 0.01 second.

Some of the cases simulated by AEROFOR were repeated by a Multicomponent Aerosol Dynamic model MAFOR (Karl et al., 2011). The model describes aerosol formation by different nucleation processes (details on nucleation options in Karl et al., 2012a), here only the HET nucleation option was used. Further aerosol processes are condensation of H$_2$SO$_4$, H$_2$O, COV$_s$ and an extremely low-volatile non-hygroscopic vapor COV$_l$ (Table 2), as well as Brownian coagulation, and mixing with the particle-free dry diluted air. COV$_s$ has the properties of adipic acid (same as in AEROFOR) but different water uptake since the hygroscopic properties of COV$_s$ in MAFOR were that of sodium succinate (Peng and Chan, 2001), i.e. COV$_s$ starts to take up water at RH>48%, and has a growth factor of 1.85 from 10% to 90% RH. The saturation vapour pressure for COV$_l$ was adopted from Lemmon and Goodwill (2000). Due to its extremely low vapour pressure, 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 COVs. Since n-alkanes do not form hydrogen bonds with sulfuric acid, it is further assumed that COVj is not a nucleating compound.

The mass transfer of gas molecules to particles is calculated using the Analytical Predictor of Condensation scheme (Jacobson, 1997). The composition of particles in any size bin can change with time due to multicomponent condensation and/or due to coagulation of particles. Thus, the size-segregated chemical composition of the generated particulate matter can be tracked at high temporal resolution. MAFOR has been evaluated with chamber data (Karl et al., 2012b), particle number measurements at a motorway (Keuken et al., 2012), and it has been shown to compare well with AEROFOR (see Karl et al., 2011). In this study, 120 size bins were used to represent the aerosol size distribution ranging from 1.5 nm to 10 μm diameter. An effective density of 1200 kg m\(^{-3}\) (Virtanen et al., 2002) was used for soot particles. The tests with 1000 and 1500 kg m\(^{-3}\) showed that the results were not sensitive to the applied density value.

2.3 Input values based on the measurements

In the model simulations with AEROFOR and MAFOR the raw exhaust dilutes rapidly by dry air (T = 303 K) so that the final dilution ratio DR\(_f\) is 12. Since it is very difficult to mathematically analyse the dilution and cooling processes they are described in simple parameters as in Lemmetty et al. (2006). A detailed simulation of cluster and particle formation during cooling in a porous diluter is out of the scope of this study (see e.g. Pyykönen et al., 2007, Olin et al., 2015). According to Lemmetty et al. (2006), the temperature was assumed to follow the exponential curve of the Newtonian cooling

\[
T(t) = T_{\text{fin}} + (T_1 - T_{\text{fin}}) \exp\left(-\frac{t}{\tau_c}\right)
\]

where \(T_1\) is the raw exhaust temperature and \(T_{\text{fin}}\) the final exhaust temperature. The parameter \(\tau_c\) is the time constant for cooling, and it refers to the time when the remaining excess temperature is \(\sim 37\%\) (=1/e %) of the original value. In this study, \(\tau_c\) was determined based on the temperature measurements at two points shown in Fig. 1, and a value of 0.03 s was obtained at all engine loads. Similarly to Lemmetty et al. (2006), dilution is modelled by using an exponential equation
The dilution time constant $\tau_d$ is the time in which the system has achieved the final dilution ratio, and no dilution occurs after this. In this study $\tau_d$ is a free parameter. Its value was assumed to be 0.12 s; however, sensitivity tests will be presented in section 3.3.1. It should be noted that by assuming that cooling is caused only by dilution, the upper limit for $\tau_c$ is determined by an equation (Lemmetty et al., 2006)

$$\tau_c \leq \frac{\tau_d}{\ln(DR_f)}.$$  

Consequently, $\tau_d$ must be $\geq 0.075$ s.

The initial exhaust particle size distribution (raw exhaust) accounted for two modes, the soot mode and the core mode, both formed in the combustion processes in the engine. The modal geometric mean diameters ($D_g$), number concentrations and standard deviations (Table 1) were adopted from the measurements (Rönkkö et al., 2013).

The initial raw exhaust GSA concentrations were as well adopted from the measurements (Arnold et al., 2012, Rönkkö et al., 2013). During the 100% engine load periods the GSA concentration varied from $2.2 \times 10^9$ to $3 \times 10^{12}$ cm$^{-3}$, during the 75% engine load period from $1.2e10$ to $3e11$ cm$^{-3}$, and during the 50% period it was around $6 \times 10^{10} - 1 \times 10^{11}$ cm$^{-3}$ (Figure 2). 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 onto the walls of the ATS.

Model simulations were performed mainly at the 100% engine load phases even though some simulations were repeated at 75% and 50% engine loads. The models were initiated by the measured GSA and non-volatile particle concentrations given in Table 1.

3 Results and discussion

3.1 Comparison of the nucleation mechanisms

3.1.1 Binary homogeneous nucleation
In the first set of model simulations the BHN mechanism was assumed. Fig. 3a illustrates the evolution of the particle number concentration $N_3$, gas concentrations and nucleation rate, along with the particle number size distribution at the end of the simulation when the initial GSA concentration was $2 \times 10^{12}$ cm$^{-3}$, which was the measured stabilized concentration at the end of the second 100% engine load in Fig. 2. Also shown is the measured particle size distribution at the end of the ageing chamber (Fig. 3b black curve), and time development of the condensation sink CS (Fig. 3c).

Two features emerge from the figures. First, nucleation occurs very fast, and it starts after 0.1 s just at the entrance of the ageing chamber, and reaches the momentary maximum value $3.0 \times 10^9$ cm$^{-3}$ s$^{-1}$ after 0.23 s. Nucleation is totally suppressed after one second if no condensable organic vapour is present, and somewhat faster, after 0.6 s, if the condensable organic vapour concentration is present with a concentration of $8 \times 10^{12}$ cm$^{-3}$. Sulphuric acid concentration decreases first mainly by dilution, but after 0.12 s nucleation and condensation are competing processes. The time evolution of the condensation sink (CS) (e.g. Pirjola et al., 1999, Kulmala et al., 2001), whose inverse is a measure of the lifetime of condensable vapour molecules in the exhaust, is presented in Fig. 3c for the simulations with and without organic vapour. The initial CS is 3.5 s$^{-1}$ based on the dry core and soot modes. Due to dilution it decreases during the first 0.17 s but then steeply increases up to a value of 8 s$^{-1}$ as long as nucleation occurs, and after the suppression of nucleation slightly decreases as the number concentration decreases due to coagulation, even though condensation still grows the particles. For comparison, typical atmospheric CS values are in the range of $10^{-4} - 10^{-1}$ s$^{-1}$. It should be noted that in this study the dilution ratio was only 12, whereas in atmospheric conditions it might be even more than 1000 at plume ages of 2.7 s (Kittelson et al., 1998, Du and Yu, 2008). Typically, the nucleation mode has been fully formed at the dilution ratio of approximately 100 (Keskinen and Rönkkö, 2010) or after less than 0.7 s residence time in the atmosphere (Rönkkö et al., 2007). The predicted GSA concentrations at the end of the ageing chamber are $1.2 \times 10^8$ cm$^{-3}$ and $6 \times 10^6$ cm$^{-3}$ without and with the condensable organic vapour, respectively. Unfortunately, these values cannot be compared with observations since only the raw exhaust GSA concentration was measured.

Secondly, the newly formed particles are not able to grow to the measured sizes by sulphuric acid. At the end of the simulation, the modelled geometric mean diameter of the nucleation mode is only 5.5 nm. To reach the measured modal mean value of 13.7 nm the COV,
concentration should be as high as $8 \times 10^{12}$ cm$^{-3}$. Consequently, the concentration of particles smaller than 40 nm covering the grown volatile and non-volatile nucleation mode particles is much higher than the observed one (Fig. 3b), the modelled total particle concentration $N_3$ ($2.9 \times 10^8$ cm$^{-3}$) strongly exceeds the measured value $8 \times 10^6$ cm$^{-3}$.

When the raw exhaust GSA concentration was $4.4 \times 10^{11}$ cm$^{-3}$, AEROFOR predicted the maximum momentary nucleation rate of $3.9 \times 10^4$ cm$^{-3}$ s$^{-1}$ (Fig. S1). Although nucleation continued for 2.2 s, it was not able to produce enough new particles. The final modelled $N_3$ was $6.8 \times 10^5$ cm$^{-3}$, too small compared to the measured $N_3$ of $6.6 \times 10^6$ cm$^{-3}$. The sulphuric acid concentration was not sufficient to grow the nucleated particles to the measured 11.2 nm sizes. When increasing the COVs concentration up to $1 \times 10^{12}$ cm$^{-3}$, the mean diameter of the core mode was close to the measured 21 nm, however, the nucleation mode diameter (9 nm) was still too small. On the other hand, higher COVs concentrations let the core mode particles grow too much.

When the measured raw exhaust GSA concentration was $1.53 \times 10^{11}$ cm$^{-3}$, the model did not predict any newly formed particles. This is inconsistent with the measurements which showed that the volatile nucleation mode was present since the GSA concentration exceeded $1 \times 10^{10}$ cm$^{-3}$ (Fig. S2). Thus, we can conclude that the BHN mechanism cannot explain the measurements.

### 3.1.2 Cluster activation and kinetic nucleation

The second set of simulations was performed by using the ACT mechanism for nine different initial GSA values selected from Fig. 2. The activation coefficient $A$ and the COVs concentration were varied to find the best agreement with the modelled and measured particle size distributions at the end of the ageing chamber. The changes in these parameters affected the particle size distributions at the end of the ageing chamber so that an increase in $A$ increased the nucleation mode particle concentration, whereas an increase in the COVs concentration shifted the nucleation mode to larger sizes and simultaneously slightly decreased the nucleation mode concentration. As an example, Fig. 4 presents the results for all nucleation mechanisms studied in this research for the 100% engine load when the GSA concentration was stabilised to $2.0 \times 10^{12}$ cm$^{-3}$, and COVs = $6 \times 10^{11}$ cm$^{-3}$. Again, in the case
when no condensable organic vapour was present the nucleation mode and even the core
mode did not sufficiently grow.

With the ACT mechanism nucleation is not suppressed but the formation of 1.5 nm clusters
continues during the whole simulation time 2.7 s (Fig. S3). The formed clusters were
activated to grow by sulphuric acid and COVs, however, the growth by sulphuric acid alone
was not sufficient (Fig. S3, dotted line). When the COVs was included, the N₃ at the end of the
ageing chamber was 9.3x10⁶ cm⁻³, close to the measured value 6.6x10⁶ cm⁻³. As seen from
Fig. 4, the model predicts higher concentration for the smallest particles of the nucleation
mode than the measurements, thus indicating that the SMPS might underestimate the
concentration of the particles smaller than 10 nm. According to the manufacturer, the
uncertainties in the SMPS measurement may be caused by the uncertainties in voltage and
flow accuracy, scan time, bi-polar charge distribution, CPC efficiency curve, DMA transfer
function, working gas, diffusion losses, and sampling and conditioning issues. Unfortunately,
in the studies reported by Arnold et al. (2012) and Rönkkö et al. (2013) the size distribution of
smallest particles was not measured by other methods than by the SMPS, and thus
experimental evidence on uncertainties in SMPS measurements of vehicle exhaust
nanoparticles is an issue for future studies (see Kuuluvainen et al., 2015).

For the other initial GSA values, the model was able to predict the measured size distributions
as well. The estimated COVs concentration was close to 10¹² cm⁻³ except in the cases when
practically no nucleation occurred, i.e. for the GSA concentration smaller than around 10¹⁰
cm⁻³. The results by Arnold et al. (2012, open diamonds in Fig. 4) indicate that at the 100%
engine load the lower limit concentrations of all acidic gases (other than GSA) are 3x10¹¹ -
2x10¹² cm⁻³ for the GSA concentrations of 4.4.x10¹¹ - 2x10¹² cm⁻³.

Based on our simulations, as the initial GSA concentration varied from 2.8x10⁹ to 2x10¹² cm⁻³
the activation coefficient A varied in the range of 2.5x10⁻⁵ - 2x10⁻³ s⁻¹ (Table 3 and Fig. 5a).
Two orders of magnitude smaller values for A have been found in the ambient field
measurements (e.g. Sihto et al. 2006, Paasonen et al, 2010) and in the laboratory
measurements (Sipilä et al., 2010). It should be noted that the exhaust GSA concentrations are
much higher than in the atmosphere, and the formation mechanism might be different as well.

As seen from Table 3, the modelled total number concentrations (particles > 3 nm) were in
good agreement with the measurements.
By using the KIN mechanism the kinetic coefficient $K$ and condensable vapour concentration varied (Table 3). As an example, Fig. 4 presents the results for the 100% engine load with $K = 5.5 \times 10^{-17}$ cm$^3$ s$^{-1}$ and $\text{COV}_s = 6 \times 10^{-11}$ cm$^3$. Also with this mechanism nucleation occurred continuously, but the nucleation rate decreased faster than with the ACT mechanism (Fig. S4). The concentrations of particles larger than 3 nm ($N_3$) and size distributions were in good agreement with the measurements (Table 2). However, sulphuric acid alone was not sufficient to grow the particles to the detectable sizes.

As with the ACT mechanism, the nucleation coefficient $K$ varied strongly as a function of the initial GSA concentration (Table 3 and Fig. 5b) with the KIN mechanism. However, during the steady state driving cycle (100% engine load), the measured raw exhaust parameters such as temperature, $\text{H}_2\text{O}$ concentration, RH, core and soot mode particle concentrations, were constant, only GSA varied, probably due to the storage effect in the ATS as mentioned in section 2.3. Therefore, it was expected that the nucleation coefficients $A$ and $K$ should have constant values when simulating the different cases within the same engine load.

### 3.1.3 Heteromolecular nucleation.

Finally, the fourth set of simulations was performed by assuming homogeneous heteromolecular nucleation between sulphuric acid and organic vapour molecules $\text{COV}_s$ along with the homogeneous homomolecular nucleation of sulphuric acid. Paasonen et al. (2010) suggested that, besides organic vapours participate in the initial growth of the nucleated particles, they might also be involved in the nucleation process itself. The idea was recently supported by the results of the chamber measurements (e.g. Dal Maso et al., 2015).

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

$$K[\text{GSA}]^2 = K_1[\text{GSA}]^2 + K_2[\text{GSA}][\text{COV}_s]$$

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 $5.6 \times 10^{-17}$ cm$^3$ 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).
The GSA and COVs concentrations for the HET nucleation (used in Eq. (4)) were the same as for the KIN nucleation given in Table 3. Interestingly, the COVs concentration was almost constant, around 1.7x10^{12} cm^{-3}, except for the two lowest GSA cases in which no nucleation occurred, and with the extremely high GSA concentration in which case the particles could notable grow by the GSA. However, the sensitivity of particle number size distribution against the COVs concentration will be presented in Section 3.3.2.

Although both nucleation and condensation consumed the COVs, its high concentration ensured that the size distribution with the initial GSA=2.0x10^{12} cm^{-3} and COVs = 6.0x10^{11} cm^{-3} remained the same as presented for the KIN mechanism where COVs was consumed only by condensation (Fig. 4). This case is named hereafter the base case.

By using the same K_1 and K_2 values for the other initial GSA values (Table 1) the model was able to predict the size distributions which were in good agreement with the experiments. The modal mean diameters of the volatile nucleation mode coincided with the measured ones even though the model predicted stronger NUP formation than measured if the GSA concentration exceeded 10^{11} cm^{-3} (Fig. 6). In regard to the core mode the model overestimated the growth of particles and slightly underestimated their number concentration. The reason might be too high water content of these non-volatile particles in the model. On the other hand, the SMPS measured mobility diameters which do not grow in spite of substantial condensation occurs if the particles are fractal-like as soot particles. We cannot exclude the possibility of fractal structure of core particles, or condensation of organic vapours other than the nucleating vapour.

The MAFOR model with somewhat different organic condensation processes predicted well the GMDs and number concentrations in the base case but underestimated the NUP concentrations at GSA below 1x10^{11} cm^{-3}. The particle distribution in MAFOR is initially non-hygroscopic (non-volatile core and soot particles) and becomes increasingly hygroscopic through condensation of GSA and COVs.

### 3.2 Mass size distribution

As mentioned above, additional model simulations for the base case (raw exhaust GSA=2x10^{12} cm^{-3}) were carried out by the MAFOR model. With MAFOR it is possible to
track the mass composition of each size bin during the simulation. Fig. 7 shows the time
development of the number size distribution and Fig. 8 the mass and composition size
distributions. The initial raw exhaust particle distribution at t=0.0 s was assumed to be entirely
non-hygroscopic. It was divided into the core mode between 5-15 nm consisting of non-
volatile organic matter (OMnv) and the soot mode consisting of elemental carbon.

During the dilution stage, rapid nucleation of GSA and COVs occurred to form a new volatile
particle mode with GMD at ~2 nm at 0.1 s (red lines in Fig. 7). By condensation of sulphuric
acid and COVs the exhaust particles became more hygroscopic. The growth of the volatile
nucleation mode was promoted by condensation of COVI in the MAFOR simulation. Core
mode composition at 0.1 s (mass fraction in percentage) was 4.5% OMnv, 18.9% sulphuric
acid, 2.1% semi-volatile organic matter (OMs), 32.2% extremely low-volatile organic matter
(OMl), and 41.3% water. In the ageing chamber, the volatile and core modes grew further by
condensation of GSA, COVs, COVI and water. Nucleation by the HET mechanism
continuously produced new particles which were scavenged or grown to larger particles. The
total particle mass increased from 3.5 μg m⁻³ at 0.1 s to 28.2 μg m⁻³ at 0.9 s, and further to
116.8 μg m⁻³ after 2.7 s. At 0.9 s GMD of the volatile mode and core mode increased to 8-9
nm and ~20 nm, respectively. The percentage mass fraction of condensed organic matter
increased to 55.5% while that of water and sulphuric acid decreased to 29.9% and 13.7%,
respectively.

At the end of the simulation (2.7 s) the measured GMDs of the volatile and core modes were
13.1 nm and 24.7 nm, respectively, closely matched by the models. Both models
underestimated particle number concentrations of the core mode. The modelled mass fractions
of the final exhaust particle composition are given in Table 4. According to MAFOR, the final
mode of particles with a non-volatile core consisted of 78.0% condensed organic matter, 6.8%
sulphuric acid and 15.0% water. Initially present non-volatile organic particles formed the
nuclei for the condensation of gas-phase vapours in the core mode. However, OMnv
contributed negligible to the final mass of the core mode. MAFOR probably underestimated
the water content of the exhaust particles by assuming that COVI was non-hygroscopic.

### 3.3 Sensitivity analysis
The sensitivity of particle number size distribution against the dilution time constant, condensable organic vapour concentration, and engine load were tested by AEROFOR for the base case.

### 3.3.1 Effects of dilution time constant

After 0.1 s the exhaust enters into the ageing chamber. If the dilution time constant $\tau_d$ increases from 0.12 s (base case) to e.g. 0.5 s, the dilution of exhaust gases continues further in the ageing chamber than for the base case. It should be noted that dilution only occurs when the simulation time is less than $\tau_d$. Due to the slower momentary dilution rate, the gas concentrations are at first higher leading to stronger nucleation and new particle formation (Fig. 9). However, simultaneously the condensation sink of pre-existing and nucleated particles grows consuming both gases more efficiently, and after 0.4 s from the beginning the gas concentrations and nucleation rate become lower than those of the base case. After that the growth rate of particle number concentration depletes and stabilizes to a somewhat smaller number as in the base case. Fig. 9c shows that in general, the modal sizes of the final distribution are rather close to that of the base case but their concentrations are lower.

When the time constant decreases to 0.075 s, all dilution occurs before the exhaust enters into the ageing chamber. This leads to a very fast reduction of the gas concentrations, and subsequently decreases the nucleation and total condensation. Therefore, the final gas concentrations remain higher unlike the particle concentration and their sizes that are smaller than in the base case. The laboratory studies by Mathis et al., (2005) showed that dilution conditions such as the dilution ratio, temperature and relative humidity of the dilution air strongly affect the formation of volatile nucleation mode.

### 3.3.2 Effects of condensable organic vapour

The used initial COVs concentrations were $10^{10}$ cm$^{-3}$ and $10^{12}$ cm$^{-3}$. Fig. S5 illustrates the number size distribution as a function of COVs concentration. As expected, an increase in COVs concentration increases the nucleation rate and new particle production. Simultaneously, the enhanced condensation of GSA and COVs consumes these vapours, and after 1.2 s the nucleation rate dramatically drops, the particle number concentration stabilizes, but particles still continue growing in size. All in all, the final nucleation mode accounts for
too many particles, around 3-fold compared with the base case, and besides this mode has grown so much that it totally covers the core mode. In fact, the geometric mean diameter of the mode was doubled up to 25 nm. The situation is vice versa, if the COVₜ concentrations is decreased. The nucleated particle concentration remains too low and they do not grow sufficiently to reach the measured sizes.

With MAFOR we tested how much the volatility properties of the condensing organic vapours affect the size distribution (Fig S6). In the first test, COVₜ 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, COVₜ was not included as well, and in addition COVₛ 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 COVₛ 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.

### 3.3.3 Effects of pre-existing non-volatile core particles

The base case simulation was repeated for different concentrations of initial soot and core particles. As mentioned earlier, these non-volatile particles were formed during the combustion process, and engine technology along with combustion optimization, fuel and lubricant oil compositions, after-treatment systems, and engine load affect their formation and concentrations. Lähde et al. (2010) found out that while the non-volatile soot mode concentration decreased, the non-volatile nucleation mode concentration increased for a heavy duty diesel engine. In these simulations the initial non-volatile soot mode concentration varied between 1.1x10⁶ and 6.8x10⁷ cm⁻³, and the soot mode between 2.6x10⁵ and 1.5x10⁷ cm⁻³ (Fig. 10 a) while the geometric mean diameters and standard deviations of the modes remained constant as given by Table 1.

Fig. 10b shows the nucleated particle (NUP) concentration at the end of the ageing chamber as a function of the condensation sink (CS) of pre-existing soot and core particles. The NUP concentration was manually calculated or if possible, determined by fitting three modes on the
final size distribution (Hussein et al., 2005). It is obvious that while the CS decreases the NUP concentration increases. If \( CS \geq 1 \text{s}^{-1} \), the NUP concentrations linearly depend on the logarithm of the CS. This occurs if the initial dry soot mode concentration is larger than \( 1.0 \times 10^6 \text{cm}^{-3} \) and the core mode concentration larger than \( 1.5 \times 10^7 \text{cm}^{-3} \). It should be noted that due to small sizes the effect of the core mode on the CS is small indeed. The maximum NUP concentration is \( 1.7 \times 10^7 \text{cm}^{-3} \) when the CS is zero. This corresponds to cases in which vehicles are equipped with modern diesel particle filters (DPF), the efficiency of those in solid particle number reduction is nowadays even 99.9%. The NUP formation is ceased if the CS is as high as \( 52 \text{s}^{-1} \). This occurs if the soot mode and core mode concentrations at hot exhaust (696 K) are for example, \( 6.8 \times 10^7 \) and \( 2.6 \times 10^5 \text{cm}^{-3} \), respectively, with the modal sizes as given in Table 1.

These results also indicate that a reduction in non-volatile particle concentrations as a result of modern engines and particle filters actually enhance the nucleation and volatile particle emissions as also discovered by Du and Yu (2006).

### 3.3.4 Effects of engine load

Driving conditions at 100% and 75% engine loads had minor effects on the number concentrations of soot mode and core mode particles (Table 1) whereas at 50% engine load the soot mode concentration was significantly lower and core mode concentration higher than at the higher loads leading to much lower condensation sink of \( 2.5 \text{s}^{-1} \) (Fig. 10b). Additionally, due to lower temperatures at lower loads the \( \text{SO}_2 \) to \( \text{SO}_3 \) conversion in the catalyst is less efficient, and subsequently the GSA concentration remains lower, in the stabilised phase \( 3 \times 10^{11} \text{cm}^{-3} \) (Fig. 2). This, in turn, led to lower NUP formation, in maximum \( 3.4 \times 10^6 \text{cm}^{-3} \) at the end of the simulation. At a 50% engine load no NUP formation was predicted.

### 3.4 Effect of FSC

The aim of the last set of simulations was to find the initial GSA concentration when nucleation is ceased at 100% engine load (\( T=697 \text{K} \)) for the base case (CS=3.5 s\(^{-1}\)) and for the case when all non-volatile particles were filtered (CS=0 s\(^{-1}\)). The highest GSA value of \( 2 \times 10^{12} \text{cm}^{-3} \) was reached when the engine was operated by diesel with the FSC of 36 ppm (Fig. 11).
It should be noted that the GSA concentration depends also on the sulphur content of the lubricant oil. If the DPF was used, the NUP concentration was 1.9x10^7 cm^-3, two times higher than for the pDPF. In both cases, the predicted NUP concentrations decreased with lower GSA concentrations, and ceased when the GSA concentration was around 10^{10} cm^-3. This value corresponds to the usage of biofuel with FSC < 1 ppm as seen from Fig. 3 in Arnold et al. (2012). On the other hand, the GSA concentration of 3x10^{11} cm^-3 was measured by Arnold et al (2012) when the FSC was 6 ppm. As seen from Fig. 11, the NUP formation does not depend linearly on the GSA concentration. For example, when decreasing the GSA concentration by 85% from 2x10^{12} to 3x10^{11} cm^-3 the NUP concentrations decreases only 15-25%.

4 Concluding Remarks

Although our model simulations cover the exhaust particle formation and growth during the laboratory sampling, the results might be generalized to concern the atmospheric conditions as well. It is well-known that nucleation mode formation at the laboratory tests is very sensitive to the dilution conditions (Khalek et al, 2003, Mathis et al., 2004). However, our on-road and laboratory measurements (Rönkkö et al., 2006, 2007) showed that the volatile nucleation mode was already formed in the atmosphere in less than 0.7 seconds, at closer than 10 m distance from the exhaust pipe, and that the dilution system along with the ageing chamber used in these measurements mimics reasonably well the real-world conditions and size distributions measured on-road. The exhaust plume age of 0.4-0.7 s in the atmosphere corresponds to the atmospheric dilution ratio of approximately 200-400 (Kittelson et al., 1998).

The aerosol dynamics models used in this research are process models that describe the main aerosol processes in details. They use sectional representations for particle size distributions with at least 100 size sections to prevent numerical diffusion and are free from assumptions of lognormal particle modes that are used in modal models. Several nucleation mechanisms and their potential to predict particle formation in diesel exhaust were investigated. The best fit with the measurements was predicted by the HET nucleation mechanism in which both sulphuric acid and semi-volatile organic acid molecules participate. Nucleation occurred
continuously in the ageing chamber producing stable clusters of 1.5 nm in size. Due to the
competition of coagulation and condensation, these freshly formed particles were scavenged
or grew to larger sizes. The nucleation rate decreased as a function of elapsed time due to the
increased condensation sink and subsequent reduction of the nucleating vapours. However, at
the end of the simulation at 2.7 s, the model predicted 2.8x10^5 particles per cm^3 in the size
range of 1.5-3 nm at 100% engine load, and 3.0x10^5 cm^-3 at 75% engine load. These results
suggest a hypothesis that diesel exhaust might yield a reservoir of small clusters that might be
activated to grow to even cloud condensation nuclei (CCN) sizes if sufficient amounts of
condensable vapours are present.

According to the model simulations, it was discovered that the semivolatile organic vapour
COVs mostly accounted for the nucleation particle growth since GSA alone was not
sufficient. MAFOR predicted that the aged exhaust particles contained 9-10% COVs and 6-7%
sulphuric acid in terms of mass. The required COVs concentrations in both models were as
high as (0.6-1.8)x10^{12} cm^-3 in the raw exhaust. In that case the modern DOC does not prevent
totally the formation of organic condensable vapours. The COVs concentration at the end of
the simulation was around 1.1x10^{11} cm^-3 at 100% engine load and 6.5x10^{10} cm^-3 at 75%
engine load. This indicates that diesel exhaust also emits precursor vapours for secondary
organic aerosol as reported by Robinson et al. (2007).

Despite the recognized health and climate effects of particle emissions the volatile nucleation
mode particles emitted from diesel engines are not regulated. To fulfill the Euro 6 standards
new diesel vehicles have to be equipped with DPFs which remove core and soot mode
particles. However, based on the model simulations the NUP concentration at high load can
be 1.7x10^7 cm^-3 if the raw exhaust GSA concentration was 2x10^{12} cm^-3. The GSA
concentration depends not only on the sulphur contents of fuel and lubricant oil, but also on
the driving history of the engine. Decreasing the FSC from 36 ppm to 6 ppm the GSA
concentration decreased 85% from 2x10^{12} to 3x10^{11} cm^-3, and the subsequent decrease in the
NUP concentration was 15-25%. The NUP formation was in practice suppressed if the GSA
concentration was below 10^{10} cm^-3. This requires the use of biofuel. Also the development of
lubricant oil additives might reduce their sulphur content and subsequent particle emissions.

Supplementary material related to this article is available online
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Tables

Table 1. Lognormal parameters (number concentration N, geometric mean diameter $D_g$, standard deviation $\sigma$) for non-volatile exhaust particles and GSA concentration in raw exhaust at different engine loads and exhaust temperatures. Index 1 refers to the core mode and index 2 to the soot mode.

<table>
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<th>GSA (cm$^{-3}$ x10$^{10}$)</th>
<th>$N_1$ (cm$^{-3}$ x10$^6$)</th>
<th>$D_{g1}$ (nm)</th>
<th>$\sigma_1$</th>
<th>$N_2$ (cm$^{-3}$ x10$^6$)</th>
<th>$D_{g2}$ (nm)</th>
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<td>1.25</td>
<td>1.96</td>
<td>49</td>
<td>2.15</td>
</tr>
<tr>
<td>100</td>
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<td>8.8</td>
<td>1.25</td>
<td>1.96</td>
<td>49</td>
<td>2.15</td>
</tr>
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<td>657</td>
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<td>8.4</td>
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<td>49</td>
<td>1.98</td>
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<tr>
<td>75</td>
<td>657</td>
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<td>1.53</td>
<td>8.4</td>
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<tr>
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<td>657</td>
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<td>1.53</td>
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<td>1.79</td>
<td>49</td>
<td>1.98</td>
</tr>
<tr>
<td>50</td>
<td>618</td>
<td>11.1</td>
<td>0.427</td>
<td>7.5</td>
<td>1.23</td>
<td>5.34</td>
<td>56</td>
<td>1.87</td>
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</table>

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

<table>
<thead>
<tr>
<th>COV</th>
<th>p$^0$(298 K) (Pa)</th>
<th>molar weight (g/mol)</th>
<th>surface tension (298 K) (N/m)</th>
<th>hygroscopic</th>
<th>nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>COV$_s$</td>
<td>1.63x10$^{-5}$a</td>
<td>146</td>
<td>0.34b</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>COV$_l$</td>
<td>5.0x10$^{-11}$c</td>
<td>478</td>
<td>_d</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

a Bilde et al., 2003
b Riipinen et al., 2007
c Lemmon and Goodwill, 2000
d Kelvin effect not considered: Ke=1 (due to low vapor pressure)
Table 3. Initial condensable organic vapour concentrations (COVs) and activation coefficient (A) as well as the initial COVs and kinetic coefficient (K) as a function of the initial gaseous sulphuric acid concentration (GSA). For heterogeneous nucleation GSA, COVs and $N_{3\text{fin}}$ are as for kinetic nucleation but $K_1=3.8\times10^{-17}$ and $K_2=5.6\times10^{-17}$ cm$^3$ s$^{-1}$ for each case.

<table>
<thead>
<tr>
<th>GSA (cm$^{-3}$)</th>
<th>COVs (cm$^{-3}$)</th>
<th>A (s$^{-1}$)</th>
<th>$N_{3\text{fin}}$ (cm$^{-3}$)</th>
<th>COVs (cm$^{-3}$)</th>
<th>K (cm$^3$ s$^{-1}$)</th>
<th>$N_{3\text{fin}}$ (cm$^{-3}$)</th>
<th>$N_3$ (cm$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.76E+09</td>
<td>6.00E+10</td>
<td>2.00E-03</td>
<td>6.88E+05</td>
<td>4.00E+10</td>
<td>1.00E-12</td>
<td>6.84E+05</td>
<td>7.69E+05</td>
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<tr>
<td>3.41E+09</td>
<td>8.00E+10</td>
<td>2.00E-03</td>
<td>6.93E+05</td>
<td>8.00E+10</td>
<td>5.00E-13</td>
<td>7.52E+05</td>
<td>1.03E+06</td>
</tr>
<tr>
<td>1.36E+10</td>
<td>1.25E+12</td>
<td>1.00E-03</td>
<td>3.54E+06</td>
<td>1.50E+12</td>
<td>5.00E-14</td>
<td>3.16E+06</td>
<td>3.13E+06</td>
</tr>
<tr>
<td>4.17E+10</td>
<td>1.50E+12</td>
<td>5.50E-04</td>
<td>5.97E+06</td>
<td>1.70E+12</td>
<td>4.00E-15</td>
<td>5.08E+06</td>
<td>4.61E+06</td>
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<td>1.53E+11</td>
<td>1.60E+12</td>
<td>2.00E-04</td>
<td>7.34E+06</td>
<td>1.70E+12</td>
<td>7.00E-16</td>
<td>5.79E+06</td>
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<td>2.50E-16</td>
<td>7.10E+06</td>
<td>6.57E+06</td>
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<tr>
<td>2.01E+12</td>
<td>1.00E+12</td>
<td>2.50E-05</td>
<td>1.14E+07</td>
<td>6.00E+11</td>
<td>5.50E-17</td>
<td>9.52E+06</td>
<td>8.03E+06</td>
</tr>
</tbody>
</table>

Table 4. Mass fractions of particle components at 2.7 s obtained from simulation by MAFOR with initial GSA = $2\times10^{12}$ cm$^{-3}$. OM$_s$, OM$_l$ and OM$_{\text{av}}$ refer to semi-volatile, low volatile and non-volatile organic matter.

<table>
<thead>
<tr>
<th></th>
<th>Volatile Mode</th>
<th>Core Mode</th>
<th>Soot Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>0.128</td>
<td>0.150</td>
<td>0.116</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>0.058</td>
<td>0.068</td>
<td>0.053</td>
</tr>
<tr>
<td>OM$_s$</td>
<td>0.104</td>
<td>0.103</td>
<td>0.092</td>
</tr>
<tr>
<td>OM$_l$</td>
<td>0.710</td>
<td>0.676</td>
<td>0.531</td>
</tr>
<tr>
<td>OM$_{\text{av}}$</td>
<td>0.000</td>
<td>0.002</td>
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</tr>
<tr>
<td>SOOT</td>
<td>0.000</td>
<td>0.000</td>
<td>0.208</td>
</tr>
<tr>
<td>TOT</td>
<td>1.000</td>
<td>1.000</td>
<td>1.000</td>
</tr>
</tbody>
</table>
**Figures**

Figure 1. Schematic figure of diluting a ageing exhaust. ATS = after-treatment system, PD = porous diluter (12:1), AC = ageing chamber with the volume of 2.4 dm³, EJ = ejector diluter (8:1). Red circles refer to temperature measurements. Exhaust flow rate through the dilution/sampling system was kept constant 55 lpm.

Figure 2. a) Time series of the concentrations of GSA (black curve) along with standard deviations (light blue shaded area), and particles larger than 3 nm (red crosses) in the raw exhaust as a function of engine load (dotted grey bars) at 1800 rpm. Also shown is the exhaust temperature (blue crosses).

Figure 3. (a) Time evolution of particle number concentration ($N_3$), gaseous sulphuric acid (GSA) and condensable organic vapour (COV$\_s$) in cm$^3$, as well as nucleation rate ($I$) in cm$^3$ s$^{-1}$ by the BHN mechanism,  (b) Measured (black) and modelled (red) particle number size distribution at the end of the ageing chamber. (c) Condensation sink for sulphuric acid. Initial GSA=2x10$^{12}$ cm$^{-3}$, COV$\_s$= 8x10$^{12}$ cm$^{-3}$ and COV$\_s$ = 0.

Figure 4. Comparison of measured and modelled particle size distributions, considering different nucleation mechanisms. Engine load was 100%, initial GSA = 2.0x10$^{12}$ cm$^3$, COV$\_s$ = 6x10$^{11}$ cm$^{-3}$ except for BHN it was 8x10$^{12}$ cm$^{-3}$. The simulation time was 2.7 s. Black squares refer to the measured size distribution by the SMPS after the ageing chamber.

Figure 5. Nucleation coefficients as a function of GSA and COV$\_s$ concentrations when the nucleation mechanism was ACT (a), KIN and HET (b).

Figure 6. Mean diameters (GMD) (a) and number concentration of particles > 3 nm (b) at the end of the simulation for the volatile nucleation mode and the core mode. The nucleation mechanism for these simulations was HET. Also shown are the measured values at the end of the ageing chamber.

Figure 7. Number size distribution ($dN/d\log D_p$ in particles cm$^{-3}$) at different stages of the exhaust ($t$=0.0 s, black lines; $t$=0.1 s, red lines; $t$=0.9 s, green lines; $t$=2.7 s, blue lines) as modelled by AEROFOR (lines with open squares) and by MAFOR (dashed lines) together with the SMPS measurement at 2.7 s (blue open diamonds). Initial size distribution with the
core mode at 10 nm and soot mode at 49 nm. The nucleation mechanism for these simulations was HET.

Figure 8. Mass composition distribution (dM/dlogDp in ng m$^{-3}$) at different stages of the exhaust (initial at t=0.0 s, after dilution t=0.1 s, in the ageing chamber t=0.9 s, and final t=2.7 s) modelled by MAFOR. Includes the total mass concentration (green line) and the mass distributions of non-volatile organic matter (OM$_{nv}$, red dashed line with open circles), soot (black dashed line), sulphuric acid (black dash-dotted line), semi-volatile organic matter (OM$_s$, black dashed line with open circles), extremely low-volatile organic matter (OM$_l$) as well as the mass distribution of water (blue dashed line). The nucleation mechanism for these simulations was HET.

Figure 9. Effects of time constant ($\tau_d$) on time evolution of gases (a), particle number and nucleation rate (b) and number size distribution (c)-(e), where particle number concentration in cm$^{-3}$ is shown by color bar. In a) and b), solid curves refer to $\tau_d = 0.12$ s (base case), dotted curves to $\tau_d = 0.5$ s, and dasdotted curves to $\tau_d = 0.075$ s. The nucleation mechanism for these simulations was HET.

Figure 10. a) Initial soot and core mode concentrations. The legend shows the corresponding condensation sinks in s$^{-1}$. b) Nucleated particle concentration (NUP) at the end of the simulation as a function of initial condensation sink for 100% engine load with GSA = 2x10$^{12}$ cm$^{-3}$ and raw exhaust T= 697 K. Also shown in (b) are the results for 75% engine load with GSA=.3x10$^{11}$ cm$^{-3}$ and raw exhaust T= 657 K. Back dots refer to the base cases.

Figure 11. Nucleated particle concentration (NUP) at the end of the simulation as a function of initial GSA concentration for 100% engine load. The initial core and soot mode concentrations were as in the base case (CS=3.5 s$^{-1}$) or zero (CS=0 s$^{-1}$). The nucleation mechanism for these simulations was HET.
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