Reply to RC C1113, Anonymous Referee #1

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

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 sˆ-1. The typical atmospheric conditions very rarely reach 0.1 sˆ-1. Are the values in range 2 to 7 sˆ-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-word 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)."

2) **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.

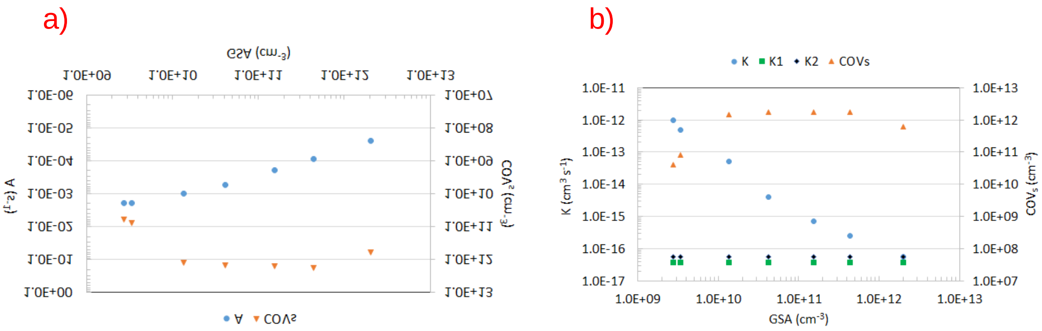

Figure 5. Nucleation coefficients as a function of GSA and COV$_S$ concentrations when the nucleation mechanism was ACT (a), KIN and HET (b).

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, H_2O 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 $2.46\text{x}10^{-5}$ Pa (=$5.95\text{x}10^{9}$ 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. $\sigma = 0.058592 - 0.083\text{x}10^{-3}*T(K)$ 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. COV_s was used in AEROFOR whereas COV_s and COV_l were used in MAFOR.

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

[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)

- P. 4227 line 12: if adipic acid is assumed to participate in heterogenous 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}–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_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-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 COV_s. Since n-alkanes do not form hydrogen bonds with sulfuric acid, it is further assumed that COV_l 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_S 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 COV_s (old COV) is capable to nucleate according to the HET mechanism. COV_l (=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: lines20-22; 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 COV_s.”

- 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.