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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Nanoparticle formation in the exhaust of vehicles running onultra-low sulfur fuel" *by* Hua Du and Fangqun Yu

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The authors thank the referee for constructive comments that are useful to improve the manuscript. Our point-to-point replies to the comments (in Italic) are given below.

1. *8220;Specifically, the model does not treat Raoult8217;s law in the condensational growth equation; thus it does not account for this aspect of organic gas growth or evaporation that has been accounted for previously in nanoparticle evolution studies (e.g., Zhang et al., 2004; Jacobson et al., 2005; both cited in the manuscript).8221;*

A significant fraction of this manuscript deals with nanoparticle (NP) formation in the exhaust of vehicle running on ultra-low S fuel and equipped with diesel particulate filters. As we pointed out in the paper, sulfate dominates the mass of the observed nucleation mode (Kittelson et al., 2006), and hence it is H2SO4, not organics, which

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dominates the growth of nucleation mode. Raoult8217;s law is not an issue in such cases.

For the vehicles not equipped with diesel particulate filters, organics clearly dominate the growth of nucleation mode particles. We did not consider the Raoult8217;s law in such cases (Fig. 3b, Fig. 5) because of complexity of photochemical aging of semi-volatile organics in the exhaust (Robinson et al. 2007), the large uncertainties in the concentrations and saturation vapor pressures of semi- and low volatile organics, and simplified treatment of these organics (i.e., divided into two categories) in the current simulations. In order to properly take into account the effect of Raoult8217;s law on particle condensation growth, we need more accurate information on the concentrations and vapor pressures of various types of semi and low-volatile organics, more detailed representation of different organics and more importantly their possible photochemistry pathways. Since this manuscript focuses mainly on the NP formation mechanisms, not including Raoult8217;s law in condensation growth will not affect the main conclusions of this paper. Nevertheless, we are aware of the previous study focusing on the evolution of nucleated nanoparticles near highway in which the role of organics has been investigated in detail (e.g., Jacobson et al., 2005). We will emphasize the uncertainty in our treatment of organics in the revised paper.

2. *8220;the model does not account for van der Waals forces or fractal geometry in the coagulation equation, so it underestimates the rate of coagulation in small particles, particularly those smaller than 10 nm. This results in Mode 1 concentration higher than they should be 45 s after emissions in Fig. 3a/3b. Jacobson and Seinfeld (2004, Atmospheric Environment, 38, 1839) found the coagulation due to these kernels may be important not only in reducing the mode but also in speeding the rate of reduction of the mode. At a minimum, the authors should acknowledge these shortcomings and perform a sensitivity test where they increase the coagulation kernel for small particles due to van der Waals forces, using, for example, enhancement factors provided in the study above.8221;*

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The van der Waals forces and fractal geometry can enhance coagulation rates by up to a factor of $\sim$ 10 (Jacobson and Seinfeld, 2004). Our sensitivity test and analysis indicates that the effect is small for the cases considered in this manuscript.

We performed a sensitivity test where we considered van der Walls force and fractal geometry of soot particles. The change in particle size distribution at plume age of 45 s is small. The reason is that the coagulation-scavenging lifetime of nucleation mode particles by soot (and ambient) particles is much longer than the time scale ($< \sim$ 45 s) considered in this study (See below).

As an example, we calculate the lifetimes of a 10 nm particle coagulating with 100 nm particles and a 3 nm particle scavenged by 40 nm particles. The coagulation kernel of a 10 nm particle with a 100 nm particle is 2x10^{-8} (cm^3 particle^{-1} s^{-1}) (spherical, no van der Waals) and 2x10^{-7} (cm^3 particle^{-1} s^{-1}) (fractal, with van der Waals). The enhancement in coagulation kernel is a factor of 10 when considering fractal geometry and van der Waals forces. The lifetime of this 10 nm particle due to scavenging by 100 nm particles will be $\sim$ 5000 s (spherical, no van der Waals) and $\sim$ 500 s (fractal, with van der Waals). In the second example, the coagulation kernel of a 3 nm particle with a 40 nm particle is 4x10^{-8} (cm^3 particle^{-1} s^{-1}) (spherical, no van der Waals) and 1.2x10^{-7} (cm^3 particle^{-1} s^{-1}) (fractal, with van der Waals). The coagulation rate enhancement is a factor of 3. The lifetime of this 3 nm particle due to scavenging by the 40 nm particles will be $\sim$ 2500 s (spherical, no van der Waals) and $\sim$ 830 s (fractal, with van der Waals). The coagulation kernels used here were extracted from Jacobson et al. (2004, 2005) and concentration of big particles is assumed to be 10^4 (particle cm^{-3}). As one can see, for the 10 nm particle and the much smaller 3 nm particle, the lifetimes due to scavenging by bigger particles are much longer than the time scale ($\sim$45 s) in the our simulations. Therefore, the effects of fractal geometry and van der Waals force on reducing the number concentration of nucleation mode during NP evolution near roadway would be small, given the evolution time scale considered in this study.

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It also should be noted that the ambient particles mixed into plume dominate the large particles at plume age of > $\sim$ 5 s and it is not clear what is their fraction dimension. Nevertheless, the van der Waals forces and fractal geometry shall have small effect on the results presented in this study. We will point out in the revised paper that van der Waals forces and fractal geometry are not considered in our calculations and these effects may become important for studying plume at longer time scale.

3. *8220;it is not clear from the simulations whether coagulation or growth is more important in the author8217;s model. The author should run separate simulations isolating the effects of nucleation, coagulation, and condensation.8221;*

Nucleation and growth is a coupled process in our kinetic model and thus cannot be separated. Also, as we pointed out in text, nucleation process happens within the first 0.1 s of plume age. Thereafter, the evolution of nucleation mode particles is dominated by condensation/evaporation and of course mixing. Coagulation plays a small role at the time scale considered in this study (refer to answer in point 2). However, as exhaust plume age increases ($>$100 s), the role of coagulation in reducing the number concentration of Mode I becomes more important as pointed out in other references (e.g. Jacobson et al., 2005). We will clarify the point in the revised paper.

4. *8220;The caption to Fig. 2a states that the conversion efficiency was tuned at each temperature to ensure the model matched the data. This renders the figure relatively useless. In particular, the fit derived appears to cross data from four different studies but not from any data consistently from the same study. The authors should show results in Fig. 2a for fits to each data set given in Fig. 2b and state in the text that the results from the tuned fit are somewhat inconsistent with any of the individual data set measurements.8221;*

The authors do not agree with referee on this. We seek to illustrate two important points in Figure 2. Firstly, we showed that with reasonable selections of sulfur (to sulfuric acid) conversion efficiency (ϵ) at each temperature, our model agree well with observed NP

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number concentration at each temperature and thus can explain the observed temperature dependence of particle formation. Secondly, we also showed that useful information about the temperature-dependent ϵ can be derived by combing measured NP formation and modeling analysis. ϵ is a critical parameter controlling nanoparticle formation in engine exhaust and it is not an easy task to measure its values. It is clear from Fig. 2b that the experimental data on the temperature dependence of conversion efficiency have large uncertainties. The ϵ values we derived from particle number concentrations measured by Kittleson et al. (2006) are within the uncertainty ranges and is very close to the average (black solid curve) of four experimental data sets We will make these points clearer in the revised paper.

5. *8220;How is Equation 1 solved? Is it solved with an ODE solver or operator split? In either case, what is the solution mechanism (provide original reference as well). Does the solution conserve properties (e.g., volume). Is it stable, positive definite?*

The Equation 1 is solved with operator split; the original reference to the solution mechanism is the book entitled 8220;Fundamentals of Atmospheric Modeling8221; by M.Z. Jacobson. The volume in our model is conserved and the scheme is stable.

6. *8220;Section 2.1. 8220;it is important to note that previous theoretical studies considered the latter two processes only and that the nucleation process was excluded from their models8221;; This statement should be clarified. The difference in the present study is primarily that emissions with particle traps are examined and specially attention is paid to conversion of sulfur due to the trap rather than other studies did not consider BHN.8221;*

We will clarify the statements as suggested.

7. *8220;Section 2.2. It is probably not correct to say that selecting two distinct categories will have little effect in light of these results. The authors should at least discuss this issue a little more thoroughly in light of the variation of volatility with carbon number and acknowledge possible uncertainties.8221;*

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See our reply 1 above.

8. *8220;Section 3.1. Are you certain that the pathway from SO2 to H2SO4 with a particle trap follows the mechanism given or is this your hypothesis based on what generally happens during ambient oxidation?*

The reaction pathway from SO2 to H2SO4 with particle filters in the manuscript is given in many diesel vehicle NP studies and some of the references are Lehmann and Mohr, Int. J. Vehicle Des. (2001); Maricq et al., Environ. Sci. Technol. (2002); Vogt et al., Environ. Sci. Technol. (2003) and Kittelson et al., CRC E-43 Final report (2002).

9. *8220;Section 3.1. Mode III consists mainly of soot agglomerates and ambient particles; The emitted soot must dominate the ambient. This should be stated8221;.*

The statement that the emitted soot must dominate the ambient is incorrect. Initially when diesel exhaust just emits out of tailpipe, the number concentration of soot particles is $\sim 10^7$ particle cm^{-3} for vehicles without traps. During this stage, soot dominates ambient particles ($\sim 10^4$ particle cm^{-3}) in terms of number concentration in Mode III. But soot particle concentration drops dramatically to $\sim 10^4$ particle cm^{-3} during the initial rapid dilution within $\sim$ 1-3 s of plume age and with a dilution ratio of $\sim$ 1000. Thus the number concentrations of soot and ambient particles in Mode III are on the same level around this plume age. As exhaust further dilutes, the soot concentration continues to decrease. During this time period, the ambient particle dominates soot particles in Mode III. For vehicles with particle filters, the initial soot concentration is much lower and around 10^5 (cm^{-3}) (Kittelson et al., 2006). Thus as exhaust dilutes, it takes less time for ambient particles to dominate in Mode III.

10. *8220;It is not clear in the text what the size distribution of emitted soot particles is. Are the emissions log-normally distributed? If so, what are the lognormal parameters, including the mass emissions? Is the only source of nucleation-mode particles homogenous nucleation, or were some particles emitted as with the soot mode?*

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The assumed soot mode is lognormal distribution. The total soot number concentration is 4x10^5 particle cm^{-3} and 10^7 particle cm^{-3} for vehicles with and without particle filters, respectively. The mean size is 50 nm in diameter. The standard deviation is 1.8. Binary H2SO4-H2O homogenous nucleation is the only source of nucleation mode particles in the case in which vehicles are running on ultra-low sulfur fuel and equipped with particle filters. For vehicles running on low sulfur fuel and without particle filters, the non-volatile cores are the only source of nucleation mode particles. We will clarify these in the revised paper.

11. *8220;A weakness of the present approach when examing results 90 m downwind is that the study does not account for 3-D transport. This shortcoming should be acknowledged relative to other studies that have included such transport.8221;*

This study concentrates on NP formation near the tailpipe and its evolution on the road. Studying NP evolution in the vicinity of roadway is not our focus. Due to its horizontal resolution (15 m X 15 m, Jacobson et al., 2005), 3-D transport model cannot resolve the nucleation process happened near the tailpipe (within 0.1 s of plume age) and NP evolution process on the roadway. For the evolution of particles in the exhaust transported away from roadway, 3-D transport model (Jacobson et al., 2005) clearly has an advantage and this will be pointed out.

12. *8220;Summary and discussion. 8220;A complete physical picture..8221;; The authors need to modify this statement in light of the fact that the model does not account for 3-D effects, Raoult8217;s law, or several coagulation kernel terms8221;.*

The statement will be modified.

13. *8220;Summary and discussion. Please acknowledge that other studies have examined this issue in the absence of particle traps and come to similar conclusions about the important of organics in the nucleation mode.8221;*

We will add some discussions on the previous studies about the role of organics in

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controlling the evolution of nucleation mode particles in vehicles without particle traps.

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