

## ***Interactive comment on “Nanoparticle formation in the exhaust of vehicles running on ultra-low sulfur fuel” by Hua Du and Fangqun Yu***

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The authors appreciate the Reviewer8217;s thoughtful and constructive comments, which helped to improve the paper. The responses to the comments accompanied by the original comments (in Italic) are given below.

*8220;Many of the conclusions appear to depend critically on input data whose values are not sufficiently justified. For example, a range of SREF values is assumed with little justification. This should be discussed more fully. Similarly, the result relating to non-volatile cores depends on the assumed number concentration. While a reference is given for their assumed size distribution, the assumed number concentration should be justified. Also, it needs to be made clear at what point the quoted concentration refers. In some cases, additional sensitivity simulations are warranted.8221;*

While it is true that there exist large uncertainty or variability in the SREF and non-volatile core concentration, the authors tend to disagree with the referee that the values of input data used in present study are not sufficiently justified. In the case of SREF values, as pointed out in the manuscript, no direct measurements are currently available, however, the derivation of values of SREF are based on the real gaseous phase H<sub>2</sub>SO<sub>4</sub> concentration measurements in exhaust (Arnold et al., 2006). This make the selected values of SREF more or less justified. The assumed number concentration of non-volatile cores in the manuscript is calculated based on the given reference (Ronkko et al., 2007). One can easily integrate the provided size distribution of non-volatile cores to get the particle number concentration. In reality, both SREF values and non-volatile core concentrations may vary significantly, depending on a number of factors as pointed out in the manuscript. The assumed non-volatile particle concentration is the one before the dilution. We will make these points clearer in the revised paper.

*8220;Equation 1 appears to have terms that account for evaporation to smaller size bins as well as coagulation. Condensation does not appear (there is no term for growth from bin  $i-1$ ), yet it is clear that condensation of organics (and H<sub>2</sub>SO<sub>4</sub>?) are important. How is this treated mathematically?8221;*

Equation 1 accounts for the H<sub>2</sub>SO<sub>4</sub> condensation by considering the coagulation of H<sub>2</sub>SO<sub>4</sub> monomers with larger clusters/particles. Organic condensation is accounted for by Equation 3.

*8220;Equation 3 partly answers the question about condensation of organics. However, the formulation seems not grow particles from bin  $i$  to bin  $i+1$ . Why not and how does this impact the model predictions?8221;*

In order to simulate the aerosol dynamic processes (i.e. nucleation, coagulation and condensation) covering from gas phase molecules with diameter of 0.6 nm to big particles having hundreds of nanometers in diameter, we employed the Discrete-Sectional bin structure in our aerosol dynamic model. For details, please refer to Yu (Atmos.

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Chem. Phys.,6, 5193-5211, 2006). With this type of bin structure, particles don't necessarily have to grow from bin  $i$  to bin  $i+1$ . Due to organic condensation, the particles may fall between  $i$  and  $i+1$  bin. Then the number concentration of the particles will be partitioned into bin  $i$  and bin  $i+1$  considering the mass balance (also see Fundamentals of Atmospheric Modeling; by Mark Z. Jacobson).

*Are shape effects expected to influence the coagulation rates? Are these accounted for in the model (it appears no)? Is this justifiable? How will it impact the results?*

Shape effects of diesel soot particles on their coagulation kernels are not considered in this manuscript. However, their impacts on the results are small, given the time scaled considered in the manuscript. For details, please refer to our reply to comments of referee 1.

*Somewhere early in the methods, there should be a comprehensive list of species treated. The closest I can find is P. 2720, line 13: H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, and other species including organics, soot and refractory cores. Please confirm whether this list is comprehensive of all species treated. Later it appears that organics is separated into a low-volatile and semi-volatile components. It would be better to have a complete list of species in one single place rather than have the reader piece it together from different parts*

In the revised paper, we will specify the all the species considered in our model at P. 2720 line 13. All the species considered are H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O, organics (low-volatile and semi-volatile), diesel soot particles and refractory cores.

*Please write out mathematically how mixing and dilution are treated in the model*

We will write out mathematically how mixing and dilution were treated in the model in the revised paper.

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*8220;Please clarify the size distribution of background aerosol used. Page 2721 line 19 gives a mean size and number concentration, but this does not specify the full size distribution. Is it assumed to be lognormal? If so, what is the sigma value for the distribution?*

The background aerosol size distribution is lognormal. The sigma value is 1.6. This will be clarified during revision.

*8220;It appears that only one background aerosol size distribution is used. How sensitive the results to this size distribution?8221;*

The background aerosol size distribution has nearly no impacts on the nanoparticle formation in exhaust because of its low number concentration and short time scale for nucleation to happen ( $< 1$  s). This is supported by our previous results (see Fig. 8, Du and Yu, 2006).

*8220;Page 2721 line 20-21: The mean size and concentration of soot particles is assumed to be 50 nm in diameter and  $1e7$   $cm^{-3}$ , respectively. This sentence appears at the end of the paragraph about background aerosols. The number concentration given, however, is surely not meant to represent the ambient background. What does this refer to and how/where does this input to the model? Also, please specify the full size distribution: lognormal? What is the sigma? Are the conclusions sensitive to this assumed value?8221;*

As clearly written in the sentence, 50 nm and  $1e7$  are the mean size and number concentration of soot particle size distribution. This size distribution, inputted to the model at  $t=0$  (i.e., before dilution), was used only in the case that the diesel exhaust after-treatment is not assumed in the simulation (Fig. 3b and Fig. 5a). It is lognormal and sigma is 2.1. The conclusions are not sensitive to this assumed value because 1) Fig. 3b (high FSC and no after-treatment) was presented only as a qualitative comparison to the case of low FSC and with diesel after-treatment which is really the focus of the manuscript; 2) In Fig. 5a, the assumed  $1e7$  of particle number concentration won't

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affect the simulated nucleation mode because the time scale of organic activation of non-volatile cores is much smaller than the lifetime of soot particle scavenging.

*8220;Please give the assumed vapor pressures of each organic component in the model. What value of organic surface tension is used when correcting for the Kelvin effect?8221;*

The vapor pressures of organic components in the model are temperature dependent and adopt the formula of alkenes in Makar (2001) with carbon number 32 (low-volatile) and 24 (semi-volatile). The surface tension is set to 30 dyn/cm for both organics assumed here (a value within  $\pm 10$  dyn/cm of almost all low- and high-molecular weight organics in Lide, D. R. (Handbook of Chemistry and Physics, 2003)

*8220;The treatment of the sulfur conversion efficiency is confusing. On p. 2723, lines 7-9, it says that the treatment of Giechaskiel et al (2007) is adopted by your study. Later, however, you compare the sulfur conversion efficiency used in your simulations with the Giechaskiel results. This must be a contradiction? Shouldn't the treatment of sulfur conversion by the model be discussed in the methods section?8221;*

Except Fig. 2, the sulfur conversion efficiencies in all the other figures used the values in Giechaskiel et al (2007). The purpose of Fig. 2 is to demonstrate the good temperature dependence of predicted nucleation rate in our model by comparing the derived sulfur conversion efficiency with estimated ones in Giechaskiel et al (2007). We will clarify these points in the revised paper.

*8220;A number of different scenarios are run with the model to reach different conclusions. It is difficult for the reader to keep track of which scenario goes with each figure and what are the corresponding input parameters. Much of the input data is scattered in different figure captions or appears scattered throughout the results section. This should be organized into one place more systematically for the benefit of the reader. Table 1 is a good start but documents only a subset of the simulations performed here. I recommend adding a section to the method section that describes all the scenarios*

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*in one place, preferably lays out a table with all the necessary data, and discusses the motivation behind each scenario.*8221;

Just as pointed out by the referee, the necessary information of input data is included in the figure caption and results section. We feel that this may actually facilitate reader8217;s reading because all the necessary information can easily be accessed to the reader instead of constantly referring to a page far away from the page readers are currently reading.

*8220;Page 2728, line 26: non-volatile particles are assumed to be in the range of 1.8 nm 8211; 3nm in diameter. Again, please specify the complete size distribution.*8221;

The mean size is assumed to be 2.5 nm, the number concentration is set to be  $3e08$ , and sigma is assumed to be 1.3.

*8220;Please define briefly in the introduction sulfur storage/release effects*8221;

Yes, we will add a sentence in the Introduction to define the sulfur storage/release effects.

*8220;p. 2719, line 26: dilution ratio at plume age of 5s varies from 5 to 10. Please clarify/confirm that this corresponds to the roadside and therefore, the end of stage 2.*

Dilution ratio (DR2) of 5 to 10 in 5 s in stage 2 means that at the end of stage 2 the total dilution ratio would be  $DR2 \times DR1$  (DR1 is the dilution ratio at the end of stage 1). This will be clarified.

*8220;Section 2.1: Please define precisely the upper and lower size boundaries for the sectional microphysics used as the manuscript currently has the vague from molecular size to several micrometers. How are the size sections spaced?*8221;

The lower and upper size (diameter) boundaries are around 0.6 nm and 1000 nm, respectively. The size sections are spaced using discrete-sectional structure (see Yu, Atmos. Chem. Phys.,6, 5193-5211, 2006).

8220;Section 2.1: How are the  $N_j$  values calculated?8221;

$N_j$  is the ratio of total volume concentration in bin  $j$  to the volume of a single cluster/particle in that bin.

8220;Fig. 1: The logarithmic scale makes it difficult to evaluate the agreement between observation and model. Please discuss in the text the total mass and number concentrations implied by each of these size distributions.8221;

Due to the large variation in the particle number concentrations, we feel that the logarithmic scale is a suitable one to give the whole picture of particle size distribution. Mass is dominated by big particles and is not the focus of the current study. Nevertheless, we will mention the total number concentrations of the nucleation mode.

8220;Fig. 2a and Fig. 3a: the x-axis needs to be labeled and given units8221;

The corresponding changes will be made.

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Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2715, 2008.

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