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## Comment on amt-2021-43

Anonymous Referee #1

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Referee comment on "Evolution under dark conditions of particles from old and modern diesel vehicles in a new environmental chamber characterized with fresh exhaust emissions" by Boris Vansenant et al., Atmos. Meas. Tech. Discuss.,  
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This paper discusses use of an environmental chamber to characterize particles in primary exhaust emissions, and discusses a new method to correct for particle loss on chamber walls. This method is applied to measurements of total particle number, mass, and VOC levels in various volatility ranges from representatives of various types of gasoline and diesel vehicles used in Europe, using two different driving cycles. The exhausts are injected into the chamber whose contents are monitored in the dark for several hours.

I have several concerns and questions about this study and I think more information needs to be given in the manuscript before it is suitable for publication. Since the primary objective of the paper seems to be describing the method to correct for particle wall losses, more information is needed concerning how well the data are fit by the conceptual model used, and also the magnitudes of the corrections on the reported results.

The method used to estimate particle loss rates is based on several assumptions that are not validated by the data that they present, or are not applicable to all experiments. It is assumed that the BC loss rate can be fit by a unimolecular decay, but it is stated that there are some experiments where the BC data are not fit by this model. This is attributed to the walls being charged in some experiments, which is a reasonable explanation. No data are shown concerning how well or poorly the BC decay are fit by a unimolecular loss curve for representative experiments, nor is there any discussion of the implications of the non-unimolecular decay in some experiments on the validity or possible biases of the corrections. The size correction (steps 2 and 3) are based on the assumption that the size distributions of the BC particles are the same as the other PM from the exhaust, but no information or argument is presented to support this assumption. One might think that BC is physically different from condensed low-volatility organics that form most of the other PM so it is not unreasonable to expect that their size distributions might be quite different. Finally, no figures or data are presented to show how well the "step 3" optimization worked for various types of experiments. How close could they get the step 1 and step 2 corrected PM to agree?

In Section 3.1.3 they state that the magnitudes of the optimized values of the eddy diffusion coefficient,  $k(e)$ , they obtained for their experiments ranged over 4 orders of magnitude from  $\sim 10^{-3}$  to  $\sim 30 \text{ sec}^{-1}$  for the different experiments. This wide variability in diffusion and mixing in experiments in the same chamber and comparable operating procedures gives me concerns about the credibility and validity of the correction method. Shouldn't the experiment with the anomalously low  $k(3)$  value of  $10^{-3} \text{ sec}^{-1}$  have been rejected?

It is stated that about a third of the experiments cannot be fitted by exponential decays, and this is attributed to electrostatic charge on the walls. But is it appropriate to use Equation (3) to predict how wall loss rates depend on size under electrostatic charge conditions? I would think the loss rates would be less size dependent if it were dominated by electrostatic forces, and that maybe only using Step 1 would be more appropriate.

Are data from runs with "charged walls" excluded from the averages on Figure 6? If so, this should be clearly stated. If not, different symbols or bars should be used for data obtained from such experiments, or data should be presented that there are statistically the same.

While the loss of particles to the wall in an environmental chamber can significantly affect results of environmental chamber experiments where the objective is to study the evolution of particles over time in well-mixed air masses, it is less clear whether such elaborate corrections are needed when characterizing primary particle emissions from vehicles. Wouldn't just using the initial measurements after the chamber is well mixed, maybe with extrapolating back to  $\text{time}=0$ , be sufficient for characterizing primary emissions? Would it give similar results? There is no indication of the magnitude of the wall loss corrections in affecting the primary emissions results summarized in Figure 6.

The range of values for the loss rate due to dilution ( $\alpha$ s) should be presented so we can compare them in magnitude with the loss rates due to wall deposition ( $\beta$ s), and show that the dilution rates in all the runs are in the expected range. One way to do this would be to separate "whisker" plots for  $\alpha$  as part of, or on conjunction with, Figure 4. Are the dilution rates similar in the  $\text{NH}_4\text{SO}_4$  experiments, or are they a factor in the lower  $\alpha+\beta$  values shown for those experiments in Figure 4? Is particle loss to the walls important compared to dilution in the  $\text{NH}_4\text{SO}_4$  experiments?

Figure 5 shows that, except for two gasoline exhaust runs that are very different from all the others, the  $k_{\text{PM}}$  values from the  $\text{NH}_4\text{SO}_4$  experiments are quite a bit lower than the  $k_{\text{BC}}$  values from the exhaust experiments, and also the slope of the  $k$  vs  $\alpha+\beta$  line is lower. Since BC is also chemically different from exhaust particles, couldn't it also have different wall loss rates or different effects of rates on size? Were any of the  $\text{NH}_4\text{SO}_4$  experiments carried out with electrostatic charged walls?

The increase in particle mass with time during most of the experiments are explained by

low-volatility gases condensing onto existing particles. Equilibrium partitioning theory predicts that the equilibrium fraction in the particle phase increases with the total particle mass, and is not dependent on particle number. Likewise, the condensation rate would depend on particle surface area, which I think should correlate somewhat better with mass than number. Nevertheless, Figure 8b shows a plot of data related to particle mass increases against particle number, not particle mass or surface area. Is the correlation not as good if plots are against particle mass or surface area instead? If this is the case, it should be pointed out and attempts to explain this should be offered (though I can't think of any explanation if this indeed were the case.) If number, mass and area are highly correlated then the plots would look the same, but in that case plots against particle mass would be more appropriate since it corresponds more directly to the explanation you are giving and existing theories.

In conclusion, I think the paper needs to give more data and information about the validity and performance of the correction method, and the effects of these uncertainties on the corrections to the data that they present, before it is accepted for publication.