Dear reviewer,

Thank you for your detailed comments. Your comments are in the grey lines. Responses are given below each of them, in the white lines.

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.

Response:

I do agree that information about validity and effects of correction method should be presented. We added several points in appendices, as well as some modifications in the main text, to assess your undermentioned concerns.

Regarding the magnitudes of the corrections, they were computed for each cycle, using the average ratio of corrected PM divided by measured PM. For the neutralized wall experiments, corrected PM is on average (1.5 ± 0.4) times higher than measured PM. For the charged wall experiments, corrected PM is on average (2.8 ± 1.5) times higher than measured PM. For the ammonium sulphate experiments, corrected PM is on average (1.3 ± 0.2) times higher than measured PM. Moreover, Platt et al. (2013) found particle half-life between 3.3 and 4 hours. This is equivalent to having BC decay coefficients of 3.5×10^{-3} and 2.9×10^{-3} min^{-1} respectively. Over a 10-hour long experiment, this would give corrected PM 3.4 and 2.7 times higher than measured PM (respectively). The corrections applied in our study therefore appear to be in a reasonable range. Some discussion was added in the text to address your comment.

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.

Response:

Regarding the lack of information on the PM correction using BC, two graphs were added in Appendix D, showing 2 evolutions of BC. The first one is well represented by a 1st order exponential decay. It shows that the fit is in very good agreement with measurement data. The second one is not well fitted by a 1st order exponential decay. The exponential decay clearly doesn't match the measured values, and induces for instance a 46 % error on the initial concentration. However, the simulation using a 2nd order decay is in very good agreement with measurements. Those graphs show the importance of using in some cases a 2nd order decay. The use of a 2nd order decay has no effect on the 1st step of the correction. In both cases, $[PM]_{measured}$ is multiplied by $[BC]_{t0}/[BC]_t$. The only difference is that this term can be written as $\exp(k_{BC} \times t)$ (in Eq. (2)) when the BC evolution is well fitted by a 1st order exponential. It can however induce some bias during steps 2 and 3 (as described below).

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.

Response:

Regarding the assumption that the size distribution of the BC particles is the same as those of the other PM, we relied on several studies which also assume that aerosols are internally mixed. Even though this assumption can induce uncertainties when the loss rates are size-dependent (Wang et al., 2018), it is used in many chamber studies (Grieshop et al., 2009; Hennigan et al., 2011). Moreover, it was used in a chamber study focusing on particles from vehicle exhausts (Platt et al., 2013). We therefore considered this assumption to be reliable enough to be used in the new correction method. Some discussion about this point was added in the updated manuscript.

How close could they get the step 1 and step 2 corrected PM to agree?

Response:

To verify how well PM corrections from steps 1 and 2 agree, the relative difference between both corrections was computed. For cycles with BC correctly fitted by a 1st order decay, both PM corrections agree with an average of (97.2 ± 2.5) %. For cycles with BC correctly fitted by a 2nd order decay, both PM corrections agree with an average of (94.7 ± 2.6) %. This shows that for the cycles with a 2nd order decay, the bias induced during step 3 in slightly higher than that of cycles with a 1st order decay. However, in both cases, the associated error remains acceptable (5.3 % and 2.8 % for 2nd order and 1st order respectively). The calculation equation was added in Appendix E, and some results were added in the main text

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 ~10^-3 to ~30 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 sec-1 have been rejected?

Response:

Over all the chamber experiments, we obtained k_e values ranging over 4 orders of magnitude. Among those experiments, there were the ones using ammonium sulphate particles instead of exhaust particles. These are the experiments for which k_e were of the order of 10^{-3} to 10^{-2} sec^{-1}. We agree with the reviewer that these values are particularly low. This could be attributed to the nature of the particles. These ammonium sulphate experiments have be done to be compared with the results found in literature (Nah et al., 2017). Moreover, the values of the order of magnitude 10^1 sec^{-1} were all found for experiments associated to highly electrostatically charged walls (e.g. with high wall losses). We therefore considered that is was reasonable to obtain extreme values of k_e for those experiments. Over all, without considering those specific conditions (ammonium sulphate and highly charged wall experiments), the values of k_e range over 2 orders of magnitude. In the simulations of particle wall deposition made by Charan et al. (2018), the values of k_e which were used in the model also range over 2 orders of magnitude (from 0.015 to 8.06 sec^{-1}). The values we found in standard conditions are in a similar range (from 0.04 to 3.23 sec^{-1}). Some discussion was added in the text.

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.

Response:

Thank you for this comment which rises a very interesting question. It seems reasonable to assume that under charged wall conditions, the electrostatic forces should dominate the other forces making the wall deposition size-independent. However, since larger particles have higher kinetic energy, they shouldn't deviate from their path to deposit onto the electrostatically charged walls as easily as smaller particles. This interpretation correlates with a mathematical analysis of the problem. Indeed, high electrostatic charges induce greater turbulence near the walls. This results in much higher difference between deposition coefficients of small and large particles, as shown in Figure 3. Therefore, it appears that under charged conditions, it is particularly important to use the size-dependent deposition coefficient of Eq. (3). This is confirmed by Nah et al. (2017), who explains that particle wall loss rates are enhanced if the chamber walls are charged.

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.

Response:

Thank you for underlying this aspect, as it is true that when the walls are charged, particles start depositing on them during the injection phase. It can therefore have an impact on initial particle mass, and thus on the emission factors computed using initial concentrations. The charged walls affected all cycles of the vehicle D4, as well as the MW cycle of the vehicle D2. None of the box plots of Figure 6 was covering experiments with both neutral and charged walls conditions. Therefore, the box plots representing charged walls experiments were clearly specified on Figure 6, and the legend was adapted. Moreover, comparison with particle number emission factors from Louis et al. (2016) with similar Euro 5 diesel vehicles show very similar results, thus indicating that potential wall effects are negligible. Some discussion was added in the main text to clarify this aspect.

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 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.

Response:

The characterization of primary particle emissions is performed right after the chamber is well mixed. At that moment, no corrections for dilution and wall losses have yet been applied to the concentrations. It is directly the measured concentrations which are taken for the estimation of the emission factors. As your comment indicates, this is not clearly described in the text. The manuscript was modified so that this aspect appears clearly.

The range of values for the loss rated due to dilution (alphas) should be presented so we can compare them in magnitude with the loss rates due to wall deposition (betas), 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 NH4SO4 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 NH4SO4 experiments?

Response:

The dilution rates are almost all similar (vary with a factor 3, between 11.25×10^{-4} and 3.75×10^{-4} min^{-1}), and represent only 7 to 24 % of the total loss rate (alpha+beta) for exhaust experiments. For the ammonium sulphate experiments, they represent on average 45 % of the total loss rate. I agree that it is important to explain this in the manuscript, to emphasize the importance of the wall deposition process depending on the conditions. Figure 4 was changed in the updated manuscript to address your comment, and highlight the predominance of the wall losses over leakage by separating the box plots to show vales of alpha, beta, and alpha+beta separately.

Regarding your remarks on ammonium sulphate experiments, they do have similar dilution rates as exhaust experiments. However, since wall loss rates are smaller for those experiments, the share of dilution is higher than for exhaust experiments. It represents on average 45 % of the total losses. This was added in the updated manuscript.

Figure 5 shows that, except for two gasoline exhaust runs that are very different from all the others, the kPM values from the NH4SO4 experiments are quite a bit lower than the kBC 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 NH4SO4 experiments carried out with electrostatic charged walls?

Response:

It is true that for ammonium sulphate particle the slope of k_{PM} vs alpha+beta is a little bit lower than the slope of the fit showed on Figure 5. However, when taking the ratios of k_{PM}/(alpha+beta) for ammonium sulphate, the average over the 5 experiments is 1.04. This indicates that the average difference is about 4 % between both coefficients for ammonium sulphate particle experiments. This is consistent with the general trend observed on Figure 5. However, as the graphic representation doesn't really represent this result, the main text was modified to clearly make it appear.

Regarding BC, it enters in the composition of exhaust particles as one of the main species (Kostenidou et al., 2021). Therefore, when particles deposit onto the walls, BC does too. The wall loss rates can be different if BC is not homogeneously distributed in all particle sizes. However, the particle internal mixing assumption has been made in many studies, considering BC to be a good tracer for exhaust particles (Grieshop et al., 2009; Hennigan et al., 2011; Platt et al., 2013).

Finally, the ammonium sulphate experiments were all carried out when the walls were assumed to be neutralized. The goal of these experiment was to be carried out without organic material, and in conditions as similar as possible to our standard experimental conditions (e.g. without high electrostatic charge on the wall). The parameter that was changed between each ammonium sulphate experiment was the initial concentration, as it can cover a wide range of values during exhaust particle experiments.

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.

Response:

Thank you for this comment on the fact that plotting PM increase versus initial mass PM or initial surface PS would be more adequate than versus initial PN. We decided to plot the PM increase against initial particle surface PS instead, since it makes more sense with regards to the theory (as explained in your comment). The general trend is similar to that obtained when plotted against initial PN. The best fit obtained here is logarithmic. It reflects the fact that PM increase is limited, and will at some point stop increasing even though initial PS increases. We interpreted it as the fact that above a certain threshold ($\sim 10^4$ $\mu m^2.cm^{-3}$), PM increase is limited by certain factors. A limiting factor could be the concentration of available organic material. This result is interesting, and is in good agreement with other studies. Namely, Charan et al. (2020) found that above ~ 1800 $\mu m^2.cm^{-3}$, initial seed surface area becomes insignificant in terms of SOA yield, partly due to initial precursor concentrations. The different value of the threshold between this study and ours could be explained by the differences in chamber size, experimental conditions, particle nature, and composition of the gas phase. Figure 8b was changed to have initial particle surface PS on the x-axis, and this discussion was added in the main text and in the conclusion.

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.

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