

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.

The authors investigate the emissions of 6 diesel passenger cars from Euro 3 to Euro 6 under 2 different driving cycles. They determine emission factors of particle number, particle mass, black carbon, NMHC and IVOC. They present a method to correct the evolution of particle mass concentration for dilution and wall loss of particles in the chamber. They claim that under dark conditions particle mass concentration (PM) increases over time as a function of initial particle number or particle surface concentration. Below a particle number concentration of (8-9)E4 cm⁻³ the particle number concentration (PN) increases, while above it decreases.

The experiments and the data analysis are well described. However, there is much speculation regarding the interpretation of the data and a lack of proof of their claims.

The authors interpret their observation of a sustained increase of particle mass and number concentrations by condensation and nucleation, respectively. However, to have continuous condensation or nucleation a constant production of condensable or nucleating vapors need to occur. Otherwise, vapors will rapidly condense on particles and on the wall and condensation or nucleation stops. In their small chamber the lifetime of such vapors will be less than ten minutes. Therefore, the claim that PM increases over many hours could be due to condensation of IVOCs is not plausible. The authors may also check if the saturation vapor pressure of IVOCs is low enough to partition to the particle phase at the particle mass concentrations of their experiments.

Response:

The partition of IVOCs and SVOCs has been studied to check the potential role of IVOCs in particle evolution. Briefly, the effective saturation concentrations of n-alkanes up to C32 is obtained with the method described in Lu et al. (2018), for VOCs (C>12), IVOCs (C12-C22) and SVOCs (C23-C32). Using Equation (14.43) from Seinfeld and Pandis (2016), the fraction in particle phase is computed, for 2 conditions of initial [PM] typical of significant [PM] increase observed on Figure 9 (200 µg.m⁻³ and 2500 µg.m⁻³). The organic aerosol concentration [OA] is estimated to range roughly between 2 and 80 % of [PM], based on studies giving the ratio [PM]/[OA] or the ratio EC/OC (Kostenidou et al., 2021; May et al., 2014). The wide range is caused by several parameters, such as measurement technique, experimental conditions, driving conditions, vehicle type (motorization and aftertreatment technologies). In this study, the [OA] fraction of [PM] is estimated to be in the range 2-80 %. This is based on the difference between [PM] and [BC], which indicates that the share of organic aerosol could go up to 69 % for the Euro 3 and Euro 4 vehicles.

For the condition with initial [PM] = 200 µg.m⁻³, the percentage of n-alkanes IVOCs present in the particle phase ranges from 0.8 % to 13.7 %, for [OA] estimated as 2 % and 80 % of [PM] respectively. The percentage of n-alkanes SVOCs in the particle phase ranges from 85.5 % to 98.7 % respectively. For the estimation with [OA] = 69 % of [PM], 12.7 % of n-alkanes IVOCs and 98.5 % of n-alkanes SVOCs are in the particle phase.

For the condition with initial $[PM] = 2500 \mu\text{g.m}^{-3}$, the percentage of n-alkanes IVOCs present in the particle phase ranges from 6.7 % to 34.0 %, for [OA] estimated as 2 % and 80 % of [PM] respectively. The percentage of n-alkanes SVOCs in the particle phase ranges from 96.5 % to 99.9 % respectively. For the estimation with $[OA] = 69\%$ of $[PM]$, 32.7 % of n-alkanes IVOCs and 99.9 % of n-alkanes SVOCs are in the particle phase.

These results indicate that at such high particle concentrations, significant fractions of IVOCs and SVOCs could be present in the particle phase. It indicates that IVOCs can participate in the [PM] evolutions observed on Figure 8 and Figure 9, due to high PM concentrations and presence of IVOCs (Figure 6d) for the Euro 3 and Euro 4 vehicles.

This part was added and discussed in Appendix G.

I agree that the growth over several hours cannot be explained solely by the presence of organic material, which would deposit onto the walls or partition in the particle phase. Other interpretations must be discussed. One of them is the possibility that the walls would play the role of a source of organic material. This hypothesis relies on several studies, which showed that vapor wall deposition was a reversible process (Matsunaga and Ziemann ‡, 2010; Yeh and Ziemann, 2015; Zhang et al., 2015). Walls could therefore play a role of sink as well as a role of source of gas-phase pollutants during chamber experiments (Kaltsonoudis et al., 2019). Zhang et al. (2015) observed evaporation of organics from the walls when the temperature went from 25 to 45 °C. Even though the temperature increase in our experiments is not as high (5 °C on average, due to heat created by instrumentation), the role of walls as a source of organic material might be part of the explanation of PM increase. This is only a hypothesis, and it is not likely to explain alone the PM increase. It might still play a role in the observed evolutions by inducing continuous condensation. Some discussion was added in the updated manuscript.

There are also some issues regarding the PN increase and the particle number concentration threshold. This observation depends on the available instrumentation. The smallest particles they can measure is 14 nm. They do not present the particle size distributions of their different experiments and therefore it is not clear in which cases a nucleation mode is formed. This would happen very fast during injection and there is not a steady nucleation going on as explained above. If an increase of PN occurs, this happens because of coagulation of nucleation mode particles, which produces particles of larger size that become measurable in their SMPS. This is not an increase of PN but the fact, that they did not measure the particles below 14 nm. Thus, the threshold and the time of increase depend on this measurement parameter. The fact, that a growing nucleation mode influences the PN at larger sizes is not a new finding. One should always be aware of it when analyzing such data.

Response:

I agree that continuous nucleation is not a possible explanation for continuous PN increase. Coagulation of nucleation mode particles, initially undetected by the SMPS, is a reasonable explanation. Nucleation mode particles are most likely to be present and have significant impacts when initial concentrations are low (below $[8-9]\times 10^4 \text{ #.cm}^{-3}$). Above that concentration, they might still be present but without observable impacts on PN evolution. Some discussion was added with Figure 10 to discuss the cases for which nucleation mode particles are likely to be present.

Due to this, the interpretation of Figure 11 was thoroughly modified, and the figure was adapted. The PN increase is now clearly presented as an artifact due to the SMPS measurement range. It is not a physical creation of particles, but growth of nucleation mode particles. This enables to discuss the presence of a nucleation mode even though it is not measurable with the current experimental set up. Above the value of $[8-9] \times 10^4 \text{ #.cm}^{-3}$, coagulation of nucleation mode particles might still occur, but with negligible impacts on PN evolution. Coagulation of the particles in the SMPS range is in those conditions the predominant process explaining the decrease of PN. Therefore, the chamber is well adapted to observation and quantification of the process of coagulation for initial concentrations above this value. As your comment says, the threshold and the time of increase don't represent indicators of physical processes. The time of increase was removed since it has no physical interpretation and has no use for the characterization of the chamber. The threshold value is now described as the value below which nucleation mode particles are likely to have significant effects on particle number evolution. It is also given as the value above which the chamber and experimental set up are suitable for quantification and observation of the coagulation process.

We decided to show these results in the text with the modified Figure 11, because one of the main goals of this paper is also to characterize the chamber. Therefore, detailing the most suitable conditions for the study of a physical process (coagulation) appears to be relevant.

At high PN concentrations when “coagulation prevails” the Figures 11c,d,e show first the expected decrease of PN due to coagulation, which is however after 1-2-h followed by an increase of PN. Do the authors have an explanation for this observation? Are these wall loss corrected PN data? If yes, this would mean the newly developed algorithm could eventually not correctly compensate for the losses.

Response:

The slight increase in the second half of the evolutions could in part be explained by the growth of nucleation mode particles. As discussed on Figure 10c and d, nucleation mode particles could be present in those conditions (high initial PN). It would be relatively small compared to total PN, and would grow slowly by coagulation and/or condensation. This slow growth could explain the slight PN increase observed after a few hours. Also, as time increases, the correction becomes more important, with higher error bars. Taking the error bars into account makes the increase less significant.

The authors need to provide more evidence why PM should grow over hours. Condensable vapors are lost to the walls and it is not plausible how an oversaturation is maintained over hours without production. Thus, the wall-loss correction method could induce such an artifact.

Response:

Regarding the possible artifact induced by the correction method, we made some verifications to make sure that the observed PM growth was a real phenomenon. We specifically looked at the cycles with the highest increase rates (3 last points on Figure 8, from Euro 3 MW conditions) and the longest increase durations (points on the upper left corner of Figure 9a, from Euro 3 UC and Euro 4 UC and MW conditions). We performed the verifications using the measured (e.g. uncorrected) PM concentrations. It is presented on Appendix F of the updated manuscript. Briefly, for the “rapid” PM increase experiments, measured data also show high PM increase rates. The increase durations are smaller than for corrected PM. This difference is normal considering the fact that leakage and wall deposition would at some point overtake PM growth even though the latter is still occurring. This corresponds to a slight decrease of uncorrected PM, and an increase of corrected PM. It hereby extends the PM increase duration obtained for corrected concentrations. Moreover, for the “long” PM increase experiments, measured PM concentrations show increase durations going up to 355 minutes (Euro 4 MW conditions). The shorter increases are followed by slight PM decreases, with decrease rates smaller than that of BC (by a factor 2.2 on average), until the end of the experiment. This indicates that processes leading to PM increase are present at all times of the experiments. Moreover, for the longer increases, the increase phases are followed by extremely small decreases or constant concentrations. This indicates that PM increasing processes are present during the whole time of the experiment. Overall, the PM increase rates and durations observed for corrected concentrations appear to be due to actual physical processes, and not artifacts induced by the correction method. The figures and discussion have been added in Appendix F of the updated manuscript and in the main text, before Figure 8, to clarify this aspect in section 3.3

More interpretation is needed to explain the observed PM increase. The walls being a source of organic material is not likely to be the main reason. Another possible explanation is the growth of small particles, undetected by the SMPS (as seen for the PN evolutions). This is discussed with the measured PN distribution of 2 cycles with long increases (Euro 3 UC and Euro 4 MW). They show that during the whole experiments, small particles (below 20 nm) are present in significant and almost constant concentrations. They could come from the growth of nucleation mode particles (by coagulation or condensation), undetected by the SMPS before their growth. The reason why the concentration of those particles remains quite steady could be that they increase (by growth of nucleation mode particles) and decrease at the same time (by their own coagulation). This would have the effect of bringing more material inside the detection range of the SMPS, therefore increasing total particle mass during the whole course of the experiments. This explanation would mean that the observed PM increase is partially an artifact (due to SMPS measurement range), and that it might induce an overestimation. Some discussion about this was added in the main text.

Overall, the continuous PM increase observed for the Euro 3 and Euro 4 vehicles can be explained by several complementary phenomena (growth of initially undetected particles, condensation of emitted organics, condensation of organics released by the walls). Three figures and some discussions were added in the updated manuscript (Appendix F, Appendix H, main text) in order to more accurately describe the observed PM evolutions.

Although Figure 5 shows a good correlation between the mean loss coefficients and k_{BC} it is also obvious, but not mentioned, that there is a large off-set. Why does this occur and how

does this affect the PM correction? The authors need to show that the PM growth is a real phenomenon and not an artifact from their correction method.

Response:

The off-set of Figure 5 represents the fact that for some cycles the average loss coefficient obtained with the optimized value of k_e , is slightly higher than k_{BC} . It reflects the fact that small particles have a higher loss coefficient than the larger ones, and that it impacts the average loss coefficient $\alpha + \beta_{ke}^{mean}$. In spite of that, the optimized value of k_e that was taken is that for which corrected PM from steps 1 and 2 match the better. Another value of k_e could have been chosen, in order to have $\alpha + \beta_{ke}^{mean}$ coefficients and k_{BC} coefficients as close as possible. Some tests were conducted on 3 experiments to establish the impact of matching the loss coefficients $\alpha + \beta_{ke}^{mean}$ and k_{BC} instead of matching the corrected PM from steps 1 and 2. The tests were conducted on the 2 experiments for which the coefficients $\alpha + \beta_{ke}^{mean}$ and k_{BC} have the worse match (the 2 gasoline on the lower left corner of Figure 5). It results in a PM difference of less than 10 % on average (8.9 and 9.7 % for each test). A test was also conducted on a cycle with higher loss coefficients (the gasoline experiment with the highest value of $\alpha + \beta_{ke}^{mean}$). For this cycle, the impact on corrected PM is 9.8 %. These impacts are not negligible, but don't affect the trends observed in section 3.2. Also, due to the size-dependence of the wall losses, the match of corrected PM from steps 1 and 2 seems to be a better indicator than the match of average loss coefficients $\alpha + \beta_{ke}^{mean}$ and k_{BC} . Some discussion about this was added in the main text, below Figure 5.

By calculating corrected PM do they use the average loss rate or the size dependent loss rates?

Response:

Corrected PM is obtained using the size-dependent loss rate. The “average loss rate” $\alpha + \beta_{ke}^{mean}$ is never actually applied. It is computed using the size-dependent loss coefficients of each diameter range, which are applied to each particle size bin.

Line 27: “Condensation is 4 times faster when the available particle surface if multiplied by 3”. How did the authors calculate this? Is this for a certain particle size?

Response:

This result is obtained using Figure 9a. The group with high initial particle surface has an average initial concentration of $1.57 \times 10^5 \mu\text{m}^2.\text{cm}^{-3}$, with an average time to reach maximum PM of 12 minutes. The other group has an average initial concentration of $2.40 \times 10^4 \mu\text{m}^2.\text{cm}^{-3}$, with an average time to reach maximum PM of 482 minutes. This means that there is a ratio 6.5 between initial surfaces of both groups (instead of 3 as written in the preprint), and a ratio $1/4$ in the time needed to reach maximum PM. The value was modified, and the explanation of the computation was added in the main text of the updated manuscript.

Overall, I do not see much scientific progress in this paper.

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