Author’s response (amt-2021-43)

Anonymous Referee #1

Dear reviewer,

Thank you for your comment. Your comment is in the grey lines (1). The response is given below in the white lines (2). It is followed by the changes which have been made in the manuscript (3).

(1) Comment from referee

One of my comments concerned the need for more information regarding how well different correction methods agreed. The revised paper said agreement was on the order of 95-97%, and gave an equation in a new Appendix E to calculate the average relative difference. However, according to Equation (E1) 0% would be perfect agreement and 95-97% would be almost a factor of 2 discrepancy. The text either needs to be revised to be consistent with Appendix E or this discussion needs to be clarified.

(2) Author’s response

The equation of Appendix E was meant to compute the error between results of both steps. From this error, the average agreement was also computed, as 100 % - error, and given in the text. This computation was not explicitly mentioned and therefore unclear. To correct this confusion, the equation in Appendix E was modified to directly give the agreement which is mentioned in the text.

(3) Changes in the manuscript

Modification of Equation E1 and its description in the text.	P38	L1114-1116

Anonymous Referee #2

Dear reviewer,

Thank you for your detailed comments. Your comments are in the grey lines (1). Responses are given below each of them, in the white lines (2). They are followed by the changes which have been made in the manuscript (3).

(1) Comment from referee

The authors performed more data analysis and provide further information on the experiments. The answers to the reviewers are often general and interpretation of data still remain fairly speculative. There are two main issues.

(1) Comment from referee

1) From the new Figure H1 it is obvious that there is a strong growth of the particle size distribution over time. However, their “new method” to determine size dependent wall loss requires a stable size distribution. Otherwise, the change of mass concentration in a size bin does not only depend on wall loss, but also heavily on growth. Thus, the eddy diffusivity coefficient and size dependent wall loss coefficient depend on both, wall loss and growth. The loss rate of BC is not affected by this. The reason that kBC and Beta(Dp) correlate is only due to the fact that Beta(Dp) is fit to kBC. The size dependent wall loss rate method is not independent of kBC and would also not work without the knowledge of kBC. The huge scatter of ke may be due to the inappropriate application. In conclusion, this method development does not provide what it is claimed for.

The authors also claim that the discrepancy in calculated ke between ammonium nitrate and vehicle emission experiments could be attributed to the nature of particles. What is the physics behind this statement? What factor in equation (3) should lead to such a pronounced effect?

(2) Author’s response

Thank you for your comment, which underlines a lack of clarity in the manuscript. The method is, as you say, dependent on the knowledge of k_{BC}. Black carbon is used as a tracer for total losses (leakage + wall losses), as has been done in several studies (Grieshop et al., 2009; Hennigan et al., 2011; Platt et al., 2013). From that, k_e is optimized until corrections of steps 1 and 2 match. This is equivalent to forcing the correlation between the coefficients $\alpha+\beta^{mean}$ and k_{BC}. Therefore, fitting $\alpha+\beta^{mean}$ to k_{BC} guarantees that $\alpha+\beta^{mean}$ accurately represents total losses, such as k_{BC} does. Once $\alpha+\beta^{mean}$ is fitted, the size-dependent coefficients $\alpha+\beta_i(D_p)$ can be applied to the distribution, with the optimized value of k_e. It allows to correct each diameter bin, accounting for the fact that particles have different loss coefficients depending on their size (Crump and Seinfeld, 1981).

Moreover, the distribution cannot be stable, because the concentration in a size bin is affected by both losses and growth (both size-dependent). However, since $\alpha+\beta^{mean}$ (average of $\alpha+\beta_i(D_p)$ of each diameter) is fitted to k_{BC}, which is not affected by growth, the distribution is only corrected for total losses. Therefore, potential effects of growth (coagulation or condensation for instance) are preserved. This is the goal of this method, which is meant to correct total losses (leakage and wall losses), in order to better show the physical processes. Some discussion regarding those aspects has been included in the manuscript.

Regarding the discrepancy and scatter of k_e values, a hypothesis explaining lower loss rates for ammonium sulphate particles could be the effect of charge. Particle charge and electric field can have a dominant effect on wall deposition (McMurry and Rader, 1985; Nah et al., 2016). This factor is not included in the theory of Crump and Seinfeld (1981), and doesn't appear in Equation (3). Perturbations near a chamber can easily induce a buildup of charges on the walls, thus impacting loss rates (Wang et al., 2018). Perturbations can be due to friction of the walls, motion near the chamber, touching the walls, air flows. The ammonium sulphate experiments took place outside of exhaust campaigns, with less motion/people/instruments near the chamber. Also, the injection and sampling flows were lower for ammonium sulphate experiments, inducing lower turbulence. These parameters can reasonably explain the lower values of k_e for ammonium sulphate experiments. Even though ammonium sulphate experiments took place in different conditions as exhaust experiments, their characterization was important to compare results obtained with the method as those found in literature. Also, such results are useful as many experiments of photochemistry are conducted with preexisting ammonium sulphate seeds. Finally, the fact that perturbations are easily induced on a chamber can also explain the scatter of k_e values found for exhaust experiments. Some discussion has been added in the manuscript to emphasize the impact of the experimental conditions instead of the nature of particles.

(3) Changes in the manuscript

Discussion regarding the use of BC as a tracer.	P9	L267-268
Clarification on the difference between $\alpha+\beta_i(D_p)$ and $\alpha+\beta^{mean}$ and their application.	P11	L330-336
Discussion on the correction of particles in a size bin.	P12	L339-341
Mention of the specific wall losses for ammonium sulphate particles.	P16	L442-443 L449-450
Details on the specific wall losses for ammonium sulphate particles.	P17-18	L473-481
Details on the specific wall losses for ammonium sulphate particles.	P18	L495-499
Discussion on the comparison between $\alpha+\beta^{mean}$ and k_{BC}.	P18	L501-503
Clarification on the use of $\alpha+\beta_i(D_p)$.	P19	L517-519
Discussion on the specific wall losses for ammonium sulphate particles.	P19	L520-524

(1) Comment from referee

2) The authors attribute the measured growth of PM to a prolonged condensation of IVOCs, as outlined in Appendix G. Indeed, IVOCs can partition into PM at given conditions. However, according to Figure 6, IVOC emissions are 10-20 times lower than PM emissions (Euro 3 and Euro 4). The increase in PM mass is 30-120% (Fig F1). Thus, there is no way enough IVOCs to contribute to this PM increase.

The paper does not provide a sound explanation of what the reason for the measured PM increase is. I believe this is an important issue as such a large effect, if real, would have far-reaching implications. For example, there are many studies on SOA formation of vehicle emissions. If primary emissions would show such a behavior, all/most of these studies could be heavily biased. Even emission factors, as determined in this paper, would be incorrect. One should take PM not after injection but at a much later time. This is not even addressed in the paper. I am not aware of chamber studies reporting such an effect. Thus, there is still the option of an instrumental or procedural artefact. One possibility could be an evolving change of particle density with coagulation of primary particles due to a high BC fraction.

(2) Author's response

We agree that IVOCs alone cannot be responsible for the PM increase observed in our study. Their emission and contribution are discussed because they were successfully quantified at emission. This was one of the goals of this study, as many uncertainties exist on IVOC emissions. Also, our results suggest that they could play a significant role in PM increase in some cases, due to their fraction in particle phase (as outlined in Appendix G). This is therefore included in the discussion of PM evolution. However, SVOCs are likely to have a major role on PM evolution in the dark, as they can easily partition between the gas and particle phase (as seen in Appendix G). They are known to be a potential large source of SOA (Kroll and Seinfeld, 2008; Robinson et al., 2007; Zhao et al., 2014). They are likely to participate in the PM evolutions observed in our study, with similar processes as those discussed for IVOCs. This interpretation relies on the assumption that SVOCs were emitted. This assumption seems reasonable, especially for the Euro 3 and Euro 4 vehicles, based on data on SVOCs from diesel vehicles (Lu et al., 2018; Zhao et al., 2015). Also, some SVOCs were measured in our study with sorbent tubes, with emission factors in the same range as IVOCs. However, it is likely that only a small fraction of SVOCs was actually measured with the sorbent tubes (Lu et al., 2018). Their emissions could therefore be higher and explain in part the increase of PM. We agree that the emphasis on IVOC role was too important, with limited discussion on SVOC role. This was modified in the updated manuscript.

Regarding the potential implications on primary emission evolutions, we think that our study could help understand the evolutions in conditions with no processes of photooxidation. As you say, there are many studies on SOA formation with artificial light exposure, and our study could be a complement to describe evolutions without light exposure. Also, we think that emission factors shouldn't be measured after several hours, but right after injection, because the evolutions are due to the partitioning but also to potential interactions in the gas-phase. However, given the important question of dilution conditions when measuring particle emissions (Robinson et al., 2007), it is important to clearly indicate the dilution ratio associated to emission factors of particles. As you suggested, some discussion has been added in the updated manuscript.

Finally, according to Peng et al. (2016), it appears that particle evolution induces an increase of density up to 1.4 g.cm^{-3}, due to deposition of organic material. Applying this density at the end of the evolution in our study would induce a more significant PM increase. The PM increase with a final density of 1.4 g.cm^{-3} would be about 17 % higher than one with the density in our study (1.2 g.cm^{-3}). As density was not measured, we chose to apply a constant value to avoid overestimating PM increase. The value of 1.2 g.cm^{-3} was chosen to be in the range of what is found in several studies (Bahreini et al., 2005; Barone et al., 2011; Hallquist et al., 2009; Totton et al., 2010). Some discussion has been added in the updated manuscript.

(3) Changes in the manuscript

Discussion on the methodology to compute particle emission factors from the chamber.	P20	L537-543
Discussion on SVOC measurements.	P22	L608-610
Discussion on SVOC role in PM evolution.	P23	L648-651
New paragraph for the interpretation of PM evolution.	P23	L654

Discussion on the potential role of a change of particle density on PM evolution.	P24	L677-681
Mention of SVOCs for PM evolution.	P30	L844
Mention of SVOCs for PM evolution.	P41	L1177

Other changes made in the manuscript

(3) Changes in the manuscript		
Misspelling of a word.	P17	L457
Reference list updated according to Copernicus Publications standards.	P31-36	L876-1080

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