'Secondary organic aerosol formed by EURO 5 gasoline vehicle emissions: chemical composition and gas-to-particle phase partitioning', Kostenidou et al.

Referee #2

The authors applied for the first time PTRMS equipped with a CHARON device to the photooxidation products of gasoline vehicle exhaust and measured the molecular distribution of precursor gases, product gases, and product particles. The detected gas and particle products were consistent with the results of previous chemical analyses of aromatic hydrocarbon chamber experiments. The saturation concentrations of selected products were estimated from the gas-to-particle ratios. The average saturation concentration of secondary organic aerosol (SOA) particles was evaluated to be higher for lower organic aerosol concentrations, consistent with the gas/particle partitioning model. The saturation concentrations evaluated by present experiments were compared with theoretical predictions. A novel aspect of this study is the quantitative evaluation of gas particle distribution at the molecular level with respect to the subject gasoline vehicle SOA. However, the current manuscript does not adequately discuss the uncertainties in the sensitivity ratios of gas and particle analytes that may interfere with the evaluation results. There could be a more in-depth discussion of fragmentation as well. Therefore, this manuscript can be expected to be published but needs to be revised.

(1) Line 24 (abstract). What is "theoretical estimations"? Could you add explanations?

We modified the sentence in: "… the theoretical estimations for saturation concentrations…"

(2) Lines 48-50. Morino et al. (2022) should be added as a recent paper that experimentally discussed photooxidation products in gasoline vehicle exhaust.

Ref. Morino, Y., Li, Y., Fujitani, Y., Sato, K., Inomata, S., Tanabe, K., Jathar, S.H., Kondo, Y., Nakayama, T., Fushimi, A., Takami, A., Kobayashi, S. Secondary organic aerosol formation from gasoline and diesel vehicle exhaust under light and dark conditions, Environ. Sci.: Atmos., 2, 46-64, 2022.

We have added the proposed reference to the revised manuscript.

(3) Lines 163-164 and 417-428: Does the statement in lines 163-164 mean that there is a maximum uncertainty of about 100 in the ratio of the CHARON-PTRMS signal to the PTRMS signal? Is it correct that there is an error of ±2 in the logC* measured in this case? If the experimental error is ±2, many experimental results agree with theory within the error range, and discussion described at lines 417-428 might be too much detailed. Other than the cited reference, is there any experimental evidence that would allow a specific discussion regarding the uncertainty of the ratio of the CHARON-PTRMS signal to the PTRMS signal for present measurement subject compounds?

The sentence in Lines 163-164: "*The OA mass concentrations of HR-ToF-AMS and CHARON may differ between each other up to a factor of 2 as mentioned in Müller et al. (2017) due to fragmentation of analyte ions in PTR-ToF-MS*" means that the mass concentration measured by CHARON could be up to two times lower than the mass concentration measured by AMS. For example, if HR-ToF-AMS measures 3 µg m^{-3} then CHARON measures 1.5 µg m^{-3} (not 0.03 µg m^{-3}). In our study the organic HR-ToF-AMS mass concentration was 1.1-1.5 times higher than the organic CHARON mass concentration. This difference could be due to the fragmentation in PTR-ToF-MS but also because of the different cut of size at the low size range for each instrument (100-150nm for CHARON and 50-70nm for HR-ToF-AMS). For this reason, we scaled up organic CHARON concentration based on organic AMS mass concentration, to "correct" CHARON concentration. This is stated in a sentence just before: "…*while the corresponding particle phase (Cp,i) concentration was measured by CHARON, after normalizing the total OA CHARON mass concentration to the total HR-ToF-AMS OA mass concentration.*" However, we modified these sentences to be better understandable.

To our knowledge a direct mass concentration comparison between HR-ToF-AMS and CHARON for specific compounds and any linkage to fragmentation has not been performed. The fragmentation in PTR-ToF-MS differs for each compound and is more intense as E/N increases (e.g., Müller et al., 2017; Leglise et al., 2019). Leglise et al. (2019) showed that the fragmentation of certain compounds at E/N 100 Td could be that high, that zero signal is left at the parent m/z. However, most of the tested compounds in Leglise et al. (2019) are not related to our study. Using standard compounds expected to be produced in our experiments, we examined their fragmentation in both CHARON and PTR-ToF-MS modes, and we concluded that the signal at the parent m/z may vary between 12 and 100 % of the total signal. In the table below we present the % of the total signal at the parent m/z compounds expected to be found in formed gasoline SOA (at E/N =100 Td):

Compound	Parent m/z	% of the total signal PTR-ToF-MS	% of the total signal CHARON
Maleic anhydride	99.01	95.9	91
Hydroquinone	109.03	88.6	87.2
5-Methylfurfural	111.04	88.4	86.2
Benzoquinone	109.03	88.6	100
Nonanal	143.3	50.8	51.9
Heptanal	115.2	15.7	21.8
Hexanal	101.2	11.9	15.6
Pentanal	87.1	12.2	16

The $C_{g,i}$ concentration is linked to the PTR-ToF-MS measurement uncertainty, which depends on the compound and could be up to 30-40%. The $C_{p,i}$ concentration depends on all possible uncertainties of PTR-ToF-MS detection as the compound was in the gas phase and in addition to any uncertainties related to transmission in the aerodynamic lens of CHARON and the error in vaporization (up to 50% depending on the compound and the particle size). We assume that the fragmentation in PRT-ToF-MS and CHARON (i.e., CHARON + PTR-ToF-MS) for a compound does not differ substantially. TS (total aerosol mass concentration) is provided by the HR-ToF-

AMS and so its uncertainty it's the HR-ToF-AMS measurement uncertainty (up to 30-40%). Thus, the logC* uncertainty is a function of the two instruments measurement uncertainties.

So, the error in the logC* is much lower than ±2 and so, the comparison with the theoretical values and logC* values from other studies can be safely discussed. We have added some discussion about the uncertainty of the logC* in the revised manuscript (section 4.3).

(4) Lines 311-324. With respect to nitroaromatics, there may be underestimation due to fragmentation compared to aldehydes and ketones. If available, please discuss any experimental information on fragmentation of nitroaromatics. The authors assume that heterogeneous processes are important for the formation of nitroaromatic hydrocarbons, but there is also a hypothesis that nitrophenols are formed by gas-phase reactions of phenoxy-type radicals with NO_2 (e.g. Harrison et al., 2005). Is there any evidence from the results of this study to support the hypothesis of heterogeneous reactions?

Ref. Harrison, M.A.J., Barrra, S., Borghesi, D., Voine, D., Arsene, C., Olariu, R.I., Nitrated pheols in the atmosphere: a review, Atmos. Environ., 39, 231-248, 2005.

We examined the fragmentation of some pure compounds in CHARON mode. Among them, there were some aldehydes and some nitroaromatics. Specifically, we found that:

for methylglyoxal 86.6% of the total signal was attributed to the parent m/z 73.03,

for 5-methylfurfural 86.2% of the total signal was attributed to the parent m/z 111.04,

for 4-nitrophenol 91.2% of the total signal was attributed to the parent m/z 140.03 and

for nitrocatechol 72.4% of the total signal was attributed to the parent m/z 156.03

4-nitrophenol and nitrocatechol did not fragment significantly and their signal at the parent ion (73-91%) was comparable to those of the functionalized aldehydes such as methylglyoxal (~87%) which had an appreciable contribution in the formed SOA. Thus, nitroaromatics were likely not underestimated compared to the functionalized aldehydes. Nevertheless, to be clear about fragmentation we have already stated in the paper that "Tables 4 and S5 do not account for any fragmentation in the concentration calculations unless it is mentioned." In the revised version we added the same statement for the SVOC (Tables 3 and S3).

From the data of this study, we cannot support whether the nitroaromatics were formed through heterogeneous or gas-phase reactions. Their gas and particle phase concentrations do not differ importantly, thus there are no evidence to support one way or the other.

(5) Lines 382-384. The author discusses the cause of the experimental results, but it is not clear. Do the authors want to write that the experimental results are qualitatively explained by the gas/particle partitioning model?

Yes indeed. According to the gas/particle partitioning model, when the formed aerosol has relatively lower concentration most of the semi-volatile compounds will not reach the corresponding saturation concentration level and thus, they will remain in the gas phase. Increasing the concentration of the formed OA the atmosphere gradually becomes saturated and when the aerosol concentration of an x compound exceeds its saturation concentration this compound will start partitioning between the gas and the particle phase. This behavior characterizes all the semi-volatile compounds that constitute SOA, but each compound has different saturation concentration.

At the same time the existence of pre-existing particles facilitates the condensation of the vapors because particles serve as surface for the vapors to condense on. This is the reason of the ammonium sulfate particles are being used in environmental chamber experiments. In the absence of pre-existing particles, the first semi-volatile products will condense onto the chamber walls, and they will be never measured. Since, there are always pre-existing particles in the ambient, laboratory simulations should include also pre-existing particles (usually ammonium sulfate).

Thus, one reason for the lower volatility of the SOA that Lannuque et al. (2022) reported is probably due to the lower aerosol concentration (toluene SOA and pre-existing ammonium sulfate), which allows a larger fraction of the higher volatility compounds to remain in the gas phase. When the SOA mass concentration increases (as in our work) a larger fraction of the higher volatility compounds is forced to move to the particle phase and so SOA contains a larger part of higher volatility compounds. We now added a sentence clarifying this behavior.

(6) Line 431. There is an end of parentheses, but the beginning of parentheses is unclear.

We added a "(".

References:

Leglise, J., Müller, M., Piel, F., Otto, T. and Wisthaler, A.: Bulk organic aerosol analysis by proton-transfer-reaction mass spectrometry: an improved methodology for the determination of total organic mass, O:C and H:C elemental ratios, and the average molecular formula, Anal. Chem., 91, 12619–12624, 2019.

Müller, M., Eichler, P., D'Anna, B., Tan, W., and Wisthaler, A.: Direct sampling and analysis of atmospheric particulate organic matter by Proton-Transfer-Reaction Mass Spectrometry, Anal. Chem., 89, 10889-10897, 2017.

Lannuque, V., D'Anna, B., Kostenidou, E., Couvidat, F., Martinez-Valiente, A., Eichler, P., Wisthaler, A., Müller, M., Temime-Roussel, B., Valorso, R., and Sartelet, K.: Gas-particle partitioning of toluene oxidation products: an experimental and modeling study, EGUsphere [preprint], https://doi.org/10.5194/egusphere-2023-1290, 2023.