Response to referees

We thank both reviewers for thoroughly examining our work and giving constructive comments and suggestions. Below are our responses to all comments in blue text, while the original referee comments are in black. The changes to the manuscript or supplement text are indicated in bold (added to the text) and overstrike (removed from the text).

On behalf of all authors,

Katariina Jussinmäki (nee Kylämäki)

Referee #1

Summary:

The authors present an informative comparison of the secondary organic aerosol produced after photochemical aging of various passenger cars in two different oxidation flow reactors (OFR). This work is important for better understanding the results and validity of data produced by OFR experiments and furthers our understanding of the aerosols generated by a variety of different types of passenger vehicles. The manuscript is well written, the topic relevant to the community, and the experimental methods are clearly described and well thought out. Some parts of the results could be further elaborated on and some small technical points could improve the manuscript. Therefore, I recommend this manuscript undergo minor revisions before the final publication, as described in the specific comments below.

Specific comments:

Pg. 11 Figure 5: Please include the x-axis title "Cycle Index" for clarity. Were measurement errors calculated for the EF shown in this figure? It would be useful to understand which measurements were within the measurement uncertainty and which ones represent significant differences in the EF.

The missing axis title and error bars have been added to Fig. 5a in the revised manuscript. The error limits consider the measurement accuracy of the ELPI+ instruments as well as the error caused by the "convolution method" used in this study to account for the residence time distribution distortion.

Changes (pg. 12, lines 311–318)

"Figure 5. Secondary particle mass EFs (a) for all cycles. The cycles are grouped by vehicle and the cycle indexes on the x-axis correspond to Table S2. The mass concentrations measured by ELPI+ were corrected for DR, standard temperature, background concentration and particle losses on OFR walls. Parking was not included in the EF calculation. **Calculation of error limits is explained in Sect. S2.** Average OH exposure (Eq. 1) is presented on the right y-axis. Ambient temperatures of -9, +23 and +35˚C are denoted with blue, white and red background, respectively.

The correlation coefficient R between the PAM-OFR and the DOFR EFs (b) is calculated from all data, but separate linear fits are shown for gasoline (G) and diesel (D) car cycles. One outlier was excluded in diesel linear fit calculation, and no linear fit is presented for CNG car cycles due to few repetitions."

Changes (pg. 3 of supplementary material, line 32)

"**Error limits for the secondary EFs (Fig. 5a) consist of three different error sources: 1) the measurement accuracy of the aged ELPI+ instruments, 2) the measurement accuracy of the fresh ELPI+ instrument and 3) the error of the convolution method that was used to correct the distortion caused by the residence time distribution. For the first two points, the error of the total particle mass was calculated from the comparison measurement of the three ELPI+ instruments (see Fig. S5) as percentage difference from the average, which was then applied to get ranges of aged and fresh EFs. Since secondary EFs were calculated by subtracting the fresh EFs from the aged EFs, the lower limit of aged EF and upper limit of fresh EF were used to get the lower limit for the range of secondary EF, and vice versa. For the convolution method (point 3), Simonen et al. (2024) found that the PAM-OFR EFs were 81.9 % of the reference during a cold-start NEDC (new European driving cycle), while for the DOFR the number was 86.1 % (see Fig. 5b in Simonen et al. (2024)). In that study, the reference was calculated by multiplying real hydrocarbon time series from a passenger car exhaust measurement with SOA yield and RTD function to get the theoretical maximum SOA production factor. We want to highlight that the reference was not calculated from the data of this campaign. The errors were summed together to get the error bars in Fig. 5a.**"

Pg. 13 Lines 357 – 365: It would be interesting to see the temperature dependent results visualized. Would it be possible to plot these results?

Figure S6 has been added to revised supplementary material, and the ambient temperature was also added to the legend in Fig. 5. To clarify, the temperature dependence seems to be caused by the usage of the electric motor in the PHEV-G-Euro 6d car. In cold conditions, the electric motor is used more. Cycles were started with both empty and half-full battery, which affects the number of combustion engine startups.

Changes (pg. 13 lines 357–361)

"With the PHEV-G-Euro 6d car, the differences seem to be connected to ambient temperature, which affects **usage of electric motor and consequently** primary and fresh emissions (**Fig. S6**). At +23˚C and +35˚C, PAM-OFR EFs exceeded DOFR EFs in all cycles, and at +35˚C the differences were especially high. The electric motor was used more at +23˚C and +35˚C (66.1 % and 78.6 %, respectively) compared to -9˚C (43.6 %), leading to lower fresh particle and SecA precursor emissions."

Pg. 14 Lines 403 – 405: The authors note that sampling lines, OFR walls and tail pipe history can affect observed concentrations. It is clear how the authors came to this conclusion regarding the OFR walls given the data in Fig. 4 while the cars were parked. However, sampling line and tail pipe history would affect both OFRs used here. Do the authors have other data to support the claims regarding sampling line and tail pipe history?

The Referee is correct that the kind of storage-release phenomenon described would affect both the OFRs, at least to the point where the sampling line to the PAM-OFR and the DOFR split. This explanation was related to the differences between the repetitions (i.e. cycles with the same car, the same ambient temperature and similar OH exposure), which were relatively high for the two oldest cars. The authors compared other emission species than SecA from the comparable cycles and found differences that could be related to events that are not repeatable. The authors did not however find any differences that would systematically explain the SecA EF differences between the cycles or differences between the OFRs.

Changes (pg. 14, lines 395–405)

"Figure 5a also shows significant variability between the repetitions, which was not completely unexpected considering how complex the studied phenomena were. The variability could be caused by differences in SecA precursor or in fresh particle emissions**, which were examined by comparing cycles with the same car and the same ambient temperature**. With the old cars (G-Euro 6b and D-Euro 4), variability between repetitions was high, even though the LVOC fate model or OH exposure did not indicate any uncertainty. Karjalainen et al. (2014) stated that the storage and release phenomena of sulfur and hydrocarbon compounds in the EAS might affect nucleation mode formation in fresh exhaust and, in principle, that kind of phenomena can affect also PM_{aged}. It is also possible that certain driving conditions or changes in the exhaust temperature might trigger a sudden release of SecA precursors. The history of the sampling lines and OFR walls but also the history of EAS and tailpipe surfaces can affect the observed concentrations of emitted compounds. It is important to note that this kind of storage-release phenomena can affect real-world emissions, i.e., they should not be considered measurement artefact. **They can still introduce differences to the SecA, SecA precursor or fresh exhaust emissions of otherwise comparable cycles.**"

Pg. 17 Lines 487 – 499: The authors note that too high NO_x can consume all OH radicals and lead to an underestimation of secondary aerosols. Could this be mitigated by changing the OH radical concentration in scenarios with high NO_x?

The method proposed by the Referee is viable, and adjusting the OH radical concentration before each cycle would have yielded more similar OH exposures throughout the campaign. The decision to keep the initial OH exposure the same was made due to cold start: measuring the OH exposure before each cycle would have ruined the cold start, in addition to being time-consuming. Adjusting the OH exposure in predicted high NO_x situations without measuring it would have led to another source of uncertainty.

Changes (pg. 17, lines 485–494)

"As discussed for the DOFR, low fresh particle concentrations, i.e., too much dilution, did not allow equilibrium between gas and particle phase for the LVOCs, leading to potential underestimation of SecA. This can be a problem especially for modern diesel vehicles with DPFs. However, diesel vehicles also produce more NO_x than gasoline vehicles, and too high NO_x concentration consumes all OH radicals, potentially also leading to underestimation of SecA. **Increasing OH exposure in high-NO_x situations combined with decreased dilution could**

produce the best outcome, although measuring both the DR and the OH exposure with exhaust sample is recommended. In this experiment, the OH exposure was not adjusted because measuring it before the cycle would have affected the cold start. Transient driving adds another layer of difficulty to adjusting dilution. As observed from Fig. 4 and other studies (Kuittinen et al., 2021; Simonen et al., 2019), cold starts produce a significant amount of SecA for gasoline cars, but TWC will decrease the concentrations as it warms up. Therefore, it is challenging to estimate a level of dilution that would be suitable for all parts of the driving cycle. Lastly, the detection limit of the instruments after the OFR is another thing to consider when adjusting dilution."

Technical corrections:

This manuscript uses a large number of abbreviations some of which are non-standard or may have different meanings in different fields. I frequently found myself scrolling back in the document to find definitions in order to fully understand the writing. Therefore, I would encourage the authors to reduce the use of non-standard abbreviations to improve readability. For example, SecA, DOFR, TSAR, ED, RTT, DR, CS, EAS

The authors went through the usage of abbreviations. In cases where the abbreviation was used only a couple times, we changed to the opened term (e.g. ED, RTT, DR, EAS). TSAR was not used without opening the abbreviation. As DOFR is central and essential to the topic of the manuscript and the name of the instrument, we opened it in each chapter. SecA was used as a generic term instead of SOA because there was likely also secondary inorganic aerosol (SIA) formation, but the data did not allow comparisons of the OFRs in this sense. We modified the text so that SecA was opened in each chapter.

Referee #2

This manuscript compares two oxidation flow reactors (PAM-OFR and DOFR) for assessing secondary aerosol formation from the exhaust of seven passenger vehicles representing gasoline, diesel, CNG, and plug-in hybrid technologies. While the manuscript shows that two reactors show comparable secondary EF's it also highlighted the key differences, especially in the background emission factors that could bias the measurements.

Overall this is a very well written manuscript coming from a well thought out study design. A significant number of measurements were performed assuring the statistical significance of the findings. The conclusions are also well justified.

Given the growing recognition that secondary aerosol formation can contribute substantially to the overall air quality and health impacts of vehicle emissions, this work provides important insights for the interpretation, harmonization, and future standardization of OFR-based emission measurements.

Overall I have no major comments and have some minor questions, so the manuscript should be published after some really minor corrections.

Minor questions:

OH generation and background particle formation:

Comment: Could the differences in background particle formation between the OFRs be related to the different OH generation mechanisms? Does the PAM-OFR produce higher ozone concentrations than those used in the DOFR, and could this contribute to the observed differences in background aerosol formation?

The ozone concentrations were added to the materials and methods section, and while they are not directly comparable, it seems that the O_3 in the DOFR was not lower than in the PAM-OFR. The O_3 concentration in the DOFR is controlled by adjusting the mixing of ozone concentrated air to the sample and is normally set so high that ozone is not a restricting reagent. There are definitely differences in the reactor conditions, some by design of the reactors, some measurable and some immeasurable, but the authors did not find any mechanisms connecting them to the background particle formation.

Changes (pg. 6, lines 157–170)

"The PAM-OFR was used in OFR185 mode, according to Li et al. (2015) terminology, in which ozone (O_3) is generated inside the OFR from the photolysis of O_2 at 185 nm. O_3 undergoes photolysis at 254 nm to produce OH. **The reactor-out O_3 concentration was (14.7±0.9) ppm on average.** To get the water necessary for the formation of OH radicals, compressed air humidified with a bubbler was mixed into the sample flow before the reactor. The relative humidity (RH) inside the PAM-OFR during the experiments was on average (44.0±2.1) % and the reactor flow was 8.6 lpm.

The Dekati OFR (DOFR; Dekati, Finland) was used parallel to the PAM-OFR. The DOFR (Fig. 2b) has a similar design to the Tampere secondary aerosol reactor (TSAR), which was developed to measure vehicle emissions in transient driving by Simonen et al. (2017). Compared to the PAM-OFR, the DOFR quartz glass reactor was smaller in size (approx. 3.3 L) and had a conical inlet. Two or three of the twelve 254 nm UV lamps were used for the measurements, so the DOFR is classified as an OFR254. In the DOFR setup, the lamps were positioned just outside the reactor, whereas in the PAM-OFR, they were placed inside the aluminum reactor. The DOFR has a separate O_3 generator, **and the reactor-in O_3 concentration was (29.9±0.7) ppm on average**. **Note that since some of the ozone was consumed in the reactor, the DOFR reactor-in concentration is not directly comparable to the PAM-OFR reactor-out concentration.** The RH inside the DOFR was on average (26.2±5.4) %, and the humidity was created with a similar bubbler than for the PAM-OFR."

Changes (pg. 16–17, lines 456–460)

"For the PAM-OFR, there was a moderate correlation between time since last cleaning and PM_{bg}, whereas for the DOFR, the correlation was weak. Moreover, Fig. 6 ~~shows~~ **indicates** that on some days PAM-OFR PM_{bg} increased during the day while DOFR PM_{bg} stayed relatively stable, which

supports the results from Table 2. **Differences in the reactor conditions, e.g. ozone concentration, did not seem to explain the different PM_{bg} concentrations.**

There are three ways to diminish the uncertainty caused by the background: 1) cleaning the OFR frequently, 2) subtracting the background concentrations or 3) decreasing dilution."

l.345 "*Fig. S4f shows constant particle formation at <20 nm size range in the PAM-OFR, even when the vehicle (PHEV-D-Euro 6d) was parked. These particles seem to have increased the CS allowing easier LVOC condensation to particle phase. Since particle formation continues when engine is turned off, the particles were likely formed from compounds released from the PAM-OFR walls. Therefore, wall interactions seem to have affected SecA formation processes in the PAM-OFR, partially explaining higher EFs compared to the DOFR.*"

Comment: Did the authors attempt to estimate the actual condensation sink (CS) provided by these <20 nm particles and compare it with the CS contributed by soot particles (typically around 100 nm) that are normally emitted by these vehicles? Given their very small size, it is unclear whether these particles would provide a sufficiently large condensation sink to significantly affect LVOC condensation and, consequently, SecA formation.

This argument referred to the PHEV-D-Euro 6d car and was used also for the D-Euro 6d, the PHEV-G-Euro 6d, and the CNG-Euro 6d-TEMP cars. Apart from the CNG car, they all had a particulate filter, which led to the low soot particle emissions in the fresh exhaust. Fresh particle number size distributions have been shown only for the PHEV-D-Euro 6d car (Fig. 3b and Fig. S4b) as an example of a low-emission car, but the results were similar for the other cars mentioned. The fresh particle number at 100 nm was ~10^4 # cm^{-3}, while after the PAM-OFR the particle number at 10 nm was ~10^8 # cm^{-3}. This translates to condensation sink values of 37.1 m^{-2} at ~10 nm in the PAM-OFR (calculated with an average of number concentrations before and after the PAM-OFR) and 0.051 m^{-2} at ~100 nm in fresh exhaust, calculated with the Palm et al. (2016) LVOC fate model. This indicates that the condensation sink caused by the <20 nm particles in the PAM-OFR was significant.

Changes (pg. 13, lines 345–349)

"Fig. S4f shows constant particle formation at <20 nm size range in the PAM-OFR, even when the vehicle (PHEV-D-Euro 6d) was parked. These particles seem to have increased the CS allowing easier LVOC condensation to particle phase. **With PN concentrations roughly four orders of magnitude greater compared to fresh soot particles, the CS caused by these <20 nm particles was significant.** Since particle formation continues when engine is turned off, the particles were likely formed from compounds released from the PAM-OFR walls. Therefore, wall interactions seem to have affected SecA formation processes in the PAM-OFR, partially explaining higher EFs compared to the DOFR."

l.435 Table 2.

Comment: Table 2 occupies considerable space and could be moved to the Supplementary Material. In addition, several of the reported correlations are based on AMS measurements that were only

available downstream of the PAM-OFR. Therefore, it is not possible to assess whether similar relationships would have been observed for the DOFR, which limits the interpretation of the comparison between the two reactors.

The table has been moved to supplementary material as Table S3 and key values have been added to the main text. The Referee is correct that the SP-AMS results in the table cannot be used for comparison purposes. We wanted to include them because they could provide insight into the composition of the PM_{bg} from the PAM-OFR. The text analyzing the table has been rearranged in order to avoid indicating that the OFRs can be compared based on the SP-AMS results.

Changes (pg. 16, lines 447–456)

"On the other hand, fresh NH_3 ~~and aged NH_4 emissions~~ of the previously measured car correlated moderately with the PAM-OFR PM_{bg} **(R = 0.446) but with**~~. With~~ the DOFR, there was **essentially** no correlation **(R = 0.072)** ~~with fresh NH_3, and aged NH_4 emissions after the DOFR were not measured~~. **BTEX or other VOCs were not found to correlate with PM_{bg} from either of the OFRs (R 0.071 for the PAM-OFR and R -0.113 for the DOFR).**

The SP-AMS results can provide clues about the PM_{bg} formation in the PAM-OFR. Concentrations of sulfate (SO_4), nitrate (NO_3), ammonium (NH_4) and organics correlated equally strongly with the PAM-OFR PM_{bg} (R 0.655, 0.636, 0.646 and 0.776, respectively). It seems that ~~more~~ **NH_3, which is known to adsorb on surfaces easily, was deposited on the PAM-OFR** ~~than on the DOFR~~ **walls, leading to formation of NH_4NO_3 or $(NH_4)_2SO_4$ particles during background measurements**. ~~The PAM-OFR PM_{bg} correlated most strongly with organics out of all species measured by the SP-AMS during the driving cycle, but BTEX or other VOCs were not found to correlate with PM_{bg} from either of the OFRs. This indicates that there was background organic aerosol formation in the PAM-OFR, and that the BTEX were not important precursors to it.~~ **Since the correlation between PM_{bg} and BTEX concentration was weak, the BTEX were not important precursors to the background organic aerosol formation in the PAM-OFR.** ~~We want to note that this data does not allow comparison of the OFRs in this sense.~~"