

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

Referee #1

This manuscript describes a study on the chemical composition of primary and photooxidation generated-secondary organic species (both gas and particle phases) from a EURO 5 gasoline under Artemis cold urban, hot urban, and motorway cycles. Gas and particle phase chemicals were analyzed by a chemical analysis of aerosol on-line (CHARON) inlet coupled with a proton-transfer-reaction time-of-flight mass spectrometer (PTR-ToF-MS). Gas-to-particle partitioning was presented as volatility distributions. I must admit that I am not an expert on organic aerosols. Therefore, I cannot provide expert opinion on the technical quality or novelty of this study. I do have some specific and technical comments as listed below.

Specific comments:

1. Section 2 Experimental. Page 4 Line 110-111: It will be worthwhile to explain the hypotheses for running the cold urban cycles at three different conditions (Experiments 1 to 3) as well as for using different dilution ratios. The result section then needs to explain if these hypotheses were tested true. Other than listing data in the tables or figures, the authors spent little effort to explain the differences from different cycles, either from the source of the differences or their real-world implication perspectives.

For Exp 2 we inserted the whole cold urban cycle inside the chamber, while for Exp 1 and 3 we inserted only the first 5 minutes of the cycle. The reason for using only the first 5 minutes of the cycle is that most of the VOCs are emitted within this period according to Marques et al. (2022), who studied the fresh VOC emissions of this vehicle.

Multiplying the fresh VOC emissions concentration with the corresponding partial dilution ratio (emissions to initial fresh VOCs into chamber, Table 1) we calculated the real fresh VOC concentrations to 338×10^3 , 110×10^3 and 331×10^3 ppb for the experiments 1, 2 and 3 correspondingly. This result implies that inserting only the first 5 minutes of the cold urban cycle (experiments 1 and 3) the final VOC concentration is higher (approximately 3 times higher) compared to Exp 2, where the whole cold urban cycle was inserted. This is because if we continue inserting more emissions until the end of the cycle (15.3 minutes), the content of the chamber will be diluted, since this part of the emissions is characterized by very low VOCs levels and thus, the injection of a whole cycle will result in lower final VOCs concentrations inside the chamber. Indeed, the VOCs concentrations were lower for Exp 2, where the whole cold urban cycle was injected. However, this was not a hypothesis since we were aware of this from Marques et al. (2022).

Concerning Exp 1 we did not apply any dilution after the emissions entered the chamber (i.e., DR was 1). Due to the high VOC concentrations inside the chamber, the signal of the major compounds at PTR-ToF-MS was saturated, thus we applied a dilution in front of the

PTR-ToF-MS inlet. This experiment indicated that the cold urban emissions in an 8 m³ chamber from this vehicle were quite high to be measured by the PTR-ToF-MS. So, we decided that a dilution was needed for the rest experiments. Thus, for Exp 2 and 3 we applied dilutions of 3.2 and 5.1 respectively inside the chamber (using a pump and inserting purified air at the same moment, with the same volumetric rate) until the PTR-ToF-MS signal of the major VOCs was not anymore saturated. Thus, the different dilution ratios (after the emissions had entered the chamber) were a result of our effort to measure the fresh VOCs without signal saturation in the PTR-ToF-MS. The partial dilution ratio (emissions to initial fresh VOCs into chamber) was calculated by comparing the major emitted VOCs between the online fresh emissions (Marques et al., 2022) and the chamber emissions just after their injection into the chamber (we updated the values in Table 1, they were copied pasted from an old version accidentally).

The O and C distributions (VOCs, SVOCs and SOA) among the three different cycles were generally similar despite the small differences discussed already in the paper. What is significantly different among the cycles, is their emission factor levels. As it has been discussed in Marques et al., (2022) the cold urban emissions levels are approximately one order of magnitude higher than the corresponding motorway emissions. This suggest that the corresponding cold urban SOA will be significantly higher than the rest cycles. To verify this assumption, we calculated the production factors (PF) of the formed SOA (in µg km⁻¹) during each cycle using the equation bellow:

$$PF = SOA \frac{DR*V}{D}$$

where SOA is the mass concentration of the SOA, DR is the total dilution ratio after the vehicle exhaust, V is the volume of the chamber (8 m³) and D is the distance of the injected cycle (4.51 km for a complete Artemis urban cycle, 1.53 km for the first 5 minutes of an Artemis urban cycle and 23.8 km for an Artemis motorway cycle). It must be mentioned that the above calculations do not include any wall-losses corrections. The production factors have been added to Table 1. A whole cold urban cycle produced 2096 µg km⁻¹ while a hot urban cycle resulted in almost the half concentration (982 µg km⁻¹) and a motorway cycle produced an SOA concentration 10 times lower (193 µg km⁻¹). The above demonstrates that the produced SOA in the cities, especially in the morning and in the afternoon, when people use their vehicles starting with a cold engine to drive to their workplaces and back, can be ten times higher compared to those produced by driving to a highway. Thus, the rural or suburban areas located near the highways are less affected by the SOA derived by gasoline GDI vehicles. In the revised version we added a small section: 4.4 SOA Production Factors and a sentence in the conclusions where we discuss all the above.

2. Table 1: Please describe why the VOC and NO_x concentrations for Exp 1-3 are much higher than Exp. 4-5.

The VOC and NO_x concentrations during the cold urban cycles (Exp 1-3) are much higher than those during the hot urban cycle (Exp 4) and motorway cycle (Exp 5) because of the lower catalyst efficiency during the cold urban cycle. Specifically, the first minutes of the

cold urban cycle the engine is still cold and thus the TWC efficiency is low. Online primary emissions measurements of the same vehicle obtained by Kostenidou et al. (2021) and Marques et al. (2022) confirm this behavior for PM, VOCs, NO_x and Total Hydrocarbon (THC) concentrations. We added a sentence in the revised paper at the first paragraph of the Results section, explaining this behavior.

3. Page 5 Line 150. What are the sources for such high concentrations of ammonium nitrate? Section 4.3 mentioned that NH₄NO₃ particles may grow to >600 nm to clog the AMS orifice. It would be good to include size distribution evolution plots in supplemental materials, as the particle lifetime in the chamber as well as transmission efficiencies through inlets would change with particle size. Fig. 4 only shows two instant distributions, not time series.

High concentrations of ammonium nitrate were observed due to the high NH₃ and NO_x amounts emitted by the tested vehicle especially during the cold urban cycles. NO_x is oxidized to HNO₃ which reacts with NH₃ to form NH₄NO₃. Even though we only have NO_x measurements (not NH₃) during this study, we do know that high NO_x and NH₃ emissions is a general characteristic of the GDI vehicles as it is already stated in the manuscript (Page 9, lines 272-273).

However, we now added a clarification on page 5, line 150 and a second clarification on page 9, lines 272-273.

In addition, we added Figure S6 (Supplement) which illustrates the evolution of organics and nitrate mass distributions over Exp 2, where is clearly shown that the formed particles grow larger than 600 nm.

Technical corrections:

1. Abstract Page 1 Line 24, I would revise the sentence to: “Comparing our results to the theoretical estimations **for saturation concentrations**, we observed...”

Done.

2. Page 2 Line 57: Delete “...**the** those...”

Done.

3. Page 3 Line 67: Change “Except for” to “Besides”

Done.

4. Page 3 Line 68: Change “weather” to “whether”

Done.

5. Page 5, Line 129: missing a “)”

Done.

6. Page 5, Line 133: explain acronym “E/N”

E/N is the ratio of the electric field strength to the gas number density. It is now explained in the revised version.

7. 1: should TS include inorganic aerosol?

Yes, TS is the mass concentration of the total suspended particles and should include both organic and inorganic aerosol. Physically the total aerosol mass concentration reflects to the surface available for the semi-volatile organic compounds to condense on. We cannot ignore the inorganic particles (either externally or internally mixed with the organic particles) because they also offer a surface to the semi-volatile organics. The higher the total surface, the more organic material will be transferred to the particulate phase.

8. 2: explain the parameter $K_{p,i}$

The parameter $K_{p,i}$ is the gas-to-particle partitioning coefficient. It is now explained in the revised manuscript.

9. Page 14, Line 431: missing a “(“

We added a “(“.

10. 1-3: the y-axis's are fractions rather than %.

We now change the y-axis names of Figures 1-3 from “%” to “Fraction of”.

References:

Kostenidou, E., Martinez-Valiente, A., R'Mili, B., Marques, B., Temime-Roussel, B., Durand, A., André, M., Liu, Y., Louis, C., Vansevenant, B., Ferry, D., Laffon, C., Parent, P., and D'Anna, B.: Technical note: Emission factors, chemical composition, and morphology of particles emitted from Euro 5 diesel and gasoline light-duty vehicles during transient cycles, *Atmos. Chem. Phys.*, 21, 4779–4796, 2021.

Marques, B., Kostenidou, E., Martinez-Valiente, A., Vansevenant, B., Sarica, T., Fine L., Temime-Roussel, B., Tassel, P., Perret, P., Liu, Y., Sartelet, K., Ferronato, C., and D'Anna B.: Detailed speciation of non-methane volatile organic compounds in exhaust emissions from diesel and gasoline Euro 5 vehicles using online and offline measurements, *Toxics*, 10, 4, 184, <https://doi.org/10.3390/toxics10040184>, 2022.