

Interactive comment on “Technical note: Emission factors, chemical composition and morphology of particles emitted from Euro 5 diesel and gasoline light duty vehicles during transient cycles” by Evangelia Kostenidou et al.

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Referee 2:

The manuscript acp-2020-842 by Kostenidou et al. presents a relatively comprehensive analysis of emissions from Euro 5 diesel and GDI vehicles. The work is well done, thoroughly discussed, and presents useful data. However, the manuscript is possibly more suited to a journal focused on emissions and air quality, as it represents incremental progress. However, ACP has published similar work before. This decision is

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ultimately the Editor's. However, considering the thorough analysis and useful data, I would recommend publication in ACP after the following revisions.

Major comments

1. The manuscript is not a technical note in my opinion. The analysis and literature discussion are thorough. There are no new technical advances. The label does not seem appropriate.

The authors fully agree with the reviewer, this is a research article, and indeed we sent it to ACP as a research paper. The categorization as "technical note" has been suggested by an Executive Editor of ACP, we could not do much about it.

2. The abstract, manuscript, and figures do not emphasize enough that the diesel engines used DPFs while the gasoline engines did not. Of course, particulate emissions were lower after the DPFs.

Line 14 should be changed to "BC ... emission factors varying from 0.2 to 7.1 mg/km for gasoline cars and 0.003 to 0.08 mg/km for diesel vehicles with DPF". Every other statement comparing the two should include "with DPF". Scientifically, the manuscript is effectively reporting the efficacy of the DPF by comparison with the gasoline case. However, this does make sense since the vehicles were all commercially available.

We did not emphasize the presence of the DPF on the diesel cars and the absence GPF in the gasoline cars, because in our study we examined EURO 5 vehicles only. By default, diesel EURO 5 cars are equipped with a DOC+DPF while gasoline EURO 5 vehicles are not equipped by any particle filtration system. These information are provided in Table 1.

We modified section 2.1. about vehicles description as follows: "We tested three GDI cars and one PFI vehicle all equipped with three-way-catalysts (TWC), while all diesel cars were equipped with a Diesel Oxidation Catalyst (DOC) and a Diesel Particulate Filter (DPF); two were catalyzed (CDPF) and one was fuel borne catalyst (FBC-DPF)".

We think that this would help the reader to remind that gasoline cars are equipped with TWC only and not DPF.

In the introduction we have this additional sentence talking about recent reduction of diesel sales: “This trend continues despite the very efficient PM (and BC) reduction achieved by diesel cars, due to the combination of DOC and DPF (Gordon et al., 2013; Platt et al., 2017)”.

The authors do not think that they should repeat that diesel had DPF along the entire article, but it is true that we can stress it in the discussion and conclusion.

Furthermore, it is worth to keep in mind that if the DPF has some issues, as this work highlights with the D3 diesel car, then its emissions can be as high as those observed for GDI cars (Figure 7). Thus, the presence of the filter alone cannot characterize the level of the emissions, DPF (or GPF) has to work properly.

3. This manuscript relies heavily on the methodology of Herring et al. (2015) to estimate speciated PAH concentrations. However, the Herring et al. (2015) methodology is not analytically reliable. The authors did not use any laboratory standards, and had no way of knowing whether PAHs had fragmented prior to their identification. Therefore, major potential issues, such as the relative sensitivity of the method to PAHs with different functional groups (which are extremely likely to fragment during electron ionization) were not explored. Herring et al. (2015) only presented validation data from a photoelectric aerosol sensor, which is another indirect method of PAH quantification. If assumed accurate, the validation data from the photoelectric sensor imply that the accuracy of the AMS technique is at best 210% (calculated from their correction factors of 67 and 208). Therefore, the published mass spectral interpretation of Herring et al. (2015) should not be taken as an analytical standard and should not be used in routine engine emissions analysis until further validation work is completed. The current manuscript presents misleading results, as most readers will assume that the authors used reliable methods such as GCMS when seeing the present manuscript.

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The reviewer is right about the need of an intercomparison with GC-MS analysis or other reference methods. Unfortunately, due to an overlapping of issues (COVID lockdown, shutdown of instrumentation in the laboratory) we were not able to finalize the work before the deadline and we did not have many filters available taken at the same time of the on-line analysis (AMS). Once we got access to the laboratory again, we used few quartz filters sampled during one campaign and we compared GC-MS analysis for GDI3 car with AMS results.

Results about this intercomparison are summarized in table S3 in the supplementary material. GC-MS calibration was carried out using the following standards (phenanthrene, fluorine, fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and benzo[a]pyrene, methyl-naphthalene and anthraquinone).

Higher concentrations are detected by AMS (following Dzepina et al. (2007) and Herring et al. (2015) methods) with respect to GC-MS analysis for light unsubstituted PAHs and alkyl-PAHs good agreement for Oxy-PAHs and underestimation is observed for heavy unsubstituted PAHs (as benzopyrene and isomers). NitroPAHs were not analyzed by GC-MS.

We remind that the sampling line was heated at 80-120°C to avoid losses of semi-volatile VOCs (paper in preparation). For particle phase we did use a split of the main line in the last section (3 meters) which was at room temperature. The AMS has a sampling flow below 100ml/min and this distance was enough to get a cold sample. The particles collected on the filters were sampled at 20 l/min, and we are not sure that room temperature was achieved when the flow impacted the filters. The authors think that some volatilization issue for these samples may have occurred.

Some explanation about the methods. Herring et al. (2015) method is based on the paper of Dzepina et al. (2007), which showed that the AMS has the capability to quantify particle bound PAHs in real time in the ambient atmosphere. Dzepina et al. (2007), showed that unsubstituted and methyl-PAHs undergo little fragmentation during

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ionization in the AMS, and that the AMS results agreed well both with photoelectric aerosol sensor (PAS) measurements and also GC-MS offline filter samples for several PAHs and few methyl-PAHs. The results of the intercomparison gave an uncertainty of +35% and –38%. More recently Hartikainen et al. (2020) applied Herring et al. (2015) method to PAHs in fresh and aged residential wood combustion emissions. It is true that for alkyl- and nitro-PAHs more fragmentation is expected.

The authors consider that Herring et al. (2015) is a quite reliable method for PAHs identification and estimation with the advantage of being an online technique, issue remains for nitro-PAHs and some alkyl-PAHs. The authors will be careful and will rather use the term estimate and identification instead of quantification.

A recent work from Yang et al. (2018) measured PAHs and functionalized PAHs both in the gas phase and particle phase emitted from GDI cars. The authors used Teflon filters for particle bound PAHs and used GC/MS. For NO₂-PAHs they used CI negative mode GC-MS. Their results are discussed in the EFs PAHs and are, in general, in good agreement to what found in our work. Surprisingly low NO₂-PAHs were found by Yang et al. (2018) for GDI vehicles (1% of the total PAHs).

The authors should delete Figure 4 and simplify Figure 5 to represent only "PAH" and "functionalized PAH" from the AMS data sets. If the authors wish to keep Figure 4 in the SI, they should add a comment to the caption to emphasize that the results are only estimated.

The authors prefer to keep both Figure 4 and Figure 5 in the main paper as they show the fraction and the profile during the cycles (two different messages). We explained in each figure caption that these results are based on the method of Herring et al. (2015).

Minor comments

Line 42: Dallmann et al. 2014 also belongs in this list.

We added Dallmann et al. (2014) in this list.

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Line 90: Please briefly mention why 3 different dilution systems were used, and what differences could be expected as a result.

There were three different dilution systems used because the data presented in this paper were taken from 4 different campaigns conducted in different years and thus each set up was different. We have already mentioned this in section 2.2 (Instrumentation). However, we added a sentence in this place also in order to emphasize it. We do not expect to see any differences in our results, using those 3 different systems regarding the pollutants we measured (mass concentration of organics, sulfate, ammonium, nitrate, PAHs and BC).

Line 142: Is conductive silicone really present in the tailpipe, or in the sampling system? The Timko citations did not discuss tailpipe tubing.

We used the Timko citations in order to explain how the polydimethylsiloxane ($\text{SiO}(\text{CH}_3)_2$) contaminations are interfering to the AMS spectrum. We add a reference (Lamma, 2017) that shows the presence of such compounds in the car exhaust. (PhD Thesis (in French): Mise au point d'une méthode de mesure des siloxanes méthyliques volatils dans le biogaz et dans l'air ambiant et étude de leur impact sur les systèmes photocatalytiques, Dr Lina Lamaa, December 2017, Univ. Lyon, France.)

Line 215: "we conclude that both GDI5 and D4 emitted randomly oil droplets". Surely the emissions are not random, and surely the authors understand a little more than they are saying here. Do the authors mean that the lubrication oil emissions were not correlated with engine load, cycle period, etc.? Please improve the statement to represent a better scientific discussion.

What we want to state here is that the oil droplets were present in the exhaust emissions of GDI5, and D4, (or GDI3 and D3 with the new numeration) during the first minutes of the cycle but also later on the cycle. TEM grids are collected for few minutes, it is not an on-line technique able to identify the effect of acceleration/deceleration. In any case, we are not able to identify a correlation found between the oil droplet emissions

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and the engine load or the speed or the cycle period. We modified the text as: “. . .we concluded that both GDI3 and D3 cars emitted some oil droplets (see also section 3.2 for TEM images), but we did not observe any evident correlation between the oil droplet emissions and the engine load or the speed or the cycle period.”

Table 2: Define theta. $R = \cos(\text{theta in degrees})$. The text suggests that theta is a different parameter to R, when it is not.

The angle theta is described in detail in Kostenidou et al. (2009) and it is an independent parameter of the correlation coefficient R. For the angle theta calculation, the two mass spectra are considered as vectors with x m/z dimensions (equations 2, 3 and 4 of Kostenidou et al. (2009)). The angle θ is a more sensitive metric for AMS mass spectra comparison that are often quite similar to each other. After the publication of Kostenidou et al. (2009) the angle theta has been used in many other publications (e.g., Kaltsonoudis et al., 2017 ACP, Florou et al., 2017 ACP, Paciga et al., 2016 ACP, etc.), for AMS mass spectra comparisons. We have already stated in the Table 2 caption the reference of Kostenidou et al. (2009) and that: “The angle θ provides a better comparison for small differences in the mass spectra (when R^2 is less than 0.97).” However, we expanded this sentence: “. . .as this method treats the mass spectra as vectors. More details about this method are given in Kostenidou et al. (2009).”

Figure 4: OPAH is not readable in light yellow text.

We changed the color in dark yellow.

Figure 6: Add interpretation to the caption. I also suggest adding one of the micrographs from Figure S9 which show the tiny metallic particles, since this is a rare observation.

We transferred 3 micrographs from Figure S9 to Figure that 6 show the tiny metallic particles. The caption has been modified as follows: “Figure 6: TEM images of samples collected during Artemis urban cold cycle. The images show soot particles as fractals,

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as agglomerated, details of primary soot particles and some oil droplets: (a-c) GDI1 vehicle (dilution ratio 40), the sample was collected during the first 120 sec of the cycle; (d-f) GDI3 vehicle (dilution ratio 46), the sample was collected during the first 120 sec of the cycle; (g-i) D1 vehicle (dilution ratio 40) the sample was collected during the first 300 sec of the cycle; D3 sampling the first 45 sec of the motorway cycle, dilution ratio 2, tiny metallic inclusion are observed in (l)”.

Data availability: I recommend that the authors upload a table with the data of Figure7 instead of stating that the data are available on request.

The data of Figure 7 are provided in the supplement in Table S6 and it is already mentioned in the main text (Table S6 summarizes these EFs in $\mu\text{g km}^{-1}$).

We updated this revised version adding the BC EFs of the PFI and the D3 vehicles as a co-author decided to give us these data after we submitted the manuscript in ACPD. We added some parts in the text where we discuss and compare these new EFs.

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