

He et al. reported the emission factors of the particulate intermediate and semi-volatile organic compounds by the heavy-duty diesel vehicles, using the two-dimensional gas chromatography time-of-flight mass spectrometry. The authors discussed the volatility distribution of the grouped 21 categories from different driving conditions and discussed the gas and particle phase distribution. The speciated data from the vehicular emission sources is useful for understanding the ambient environmental data, where locational specific source profiles are quite limited. Thus, I would suggest the publication if the author can address my following comments:

We thank the reviewer for the detailed and insightful comments. We provide below a point-to-point response to reviewers' comments. A copy of the manuscript with the changes tracked and a clean copy are submitted together with this response document. The comments from the reviewers are in black type and our response texts are marked in blue.

The abbreviation of ISVOCs and SVOCs in the title should be specified.

Revised as suggested.

Line 30: "EF" should be defined.

Thanks, and revised.

Line 69: it should be "sub-cooled liquid vapor pressure"

Revised as suggested.

Lines 83-84, the sentence "Particulate I/SVOCs at ascending speed stages are collected and analysed separately" is a repeat to line 79-80, please revise the statement.

Thanks for pointing out the mistake. We delete the repeated sentence.

Line 101: revise "duplicated" to "repeated"

Revised as suggested.

Line 106: repeated words of ""monitored collected".

It should be "monitored collocated" instead of "monitored collected"

Line 117: "Field blank samples are collected collocated at the upstream of the emission pipeline". This sentence is grammatically incorrect, please revise.

Thanks for the comment. We delete collocated as suggested.

Line 120: "A total of 36 filter samples plus 3 field blanks were collected..." please specify the detailed sampling information, e.g., how many samples from the non-(DPF + DOC) vehicles, etc.?

Thanks for comments. We already gave the detailed sampling information in the previous published paper He et al. (2022), Table S2. To make it clear for the readers, we revise the texts.

Updated text (lines 125-126):

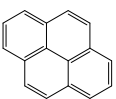
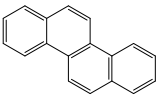
“...A total of 36 filter samples plus 3 field blanks were collected and subjected to the determination of I/SVOCs, among which 1/3 were non-(DPF + DOC) vehicle samples and 2/3 (DPF + DOC) vehicle samples...”

Lines 145 and 146: revise “Nest” to “Next”; “elusion” to “elution”.

Thanks very much for pointing out the mistakes. We revised accordingly.

Line 151-155: the specific molecular information of the quantified species should be specified, maybe in the supporting information. For example, what is the carbon range of the measured alkanes, alkenes, cycloalkanes, and hopanes, etc.? The information is necessary as the g-p partitioning are highly associated with the intrinsic chemical properties of the compounds. Besides, the naming of the 4-ring PAHs₂₀₂ and 4-ring PAHs₂₂₈ looks weird, and it is not consistent in the main text and in the legend of Figure 2.

We fully agree with the comment and list the molecular information and the formula of the quantified species in the supporting information (Table S1). We classify 4-ring PAHs into two subgroups: 4-ring PAHs₂₀₂ and 4-ring PAHs₂₂₈ considering their different benzene structures and mass spectrum patterns.

Structure	Molecular weight
	202
	228

We change the names of 4-ring PAHs in the revised manuscript to keep consistency with Figure 2.

Updated text (line 158):

“...3-ring PAHs, 4-ring PAHs (PAH_{4rings202} and PAH_{4rings228}), 5-ring PAHs...”

There is a negative value of removal efficiency of gas phase data for 4 ring PAHs in Table S2, please check.

Check and revised.

Line 197: what does the “Mono-aromatic compounds” refer to, as it is not within the 21 categories? Is it alkyl benzenes? Please specify.

Monoaromatic compounds are the sum of C₂ alkyl benzene, C₃ alkyl benzene, C₄ alkyl benzene, C₅ alkyl benzene, and C₆ alkyl benzene, of which the latter ones are resolved within the 21 categories. To avoid ambiguity, we revised the text (lines 206-208):

“...Mono-aromatic compounds (i.e., C₂-C₆ alkyl-substituted benzenes), which were measured to take over 10%...”

Figure 1. I'm confused why there are only six data point for each category, while the sample numbers are 36?

The scatter data points are the averaged values of the emission factor from respective driving conditions and/or test vehicles. To make it clear, we add the description in the revised manuscript (lines 211-213).

“...represent different organic species and driving cycles. The scatter points lying in the left side of the bars represent the averaged emission factors measured from different driving conditions or test vehicles. The square...”

What is the “O-I/SVOCs”? the definition should be given.

Revised as suggested (line 236).

Figure 5, the babel “>0.3, >0.4 and >0.5” should be presented on the x-axis, current format is not clear.

Revised as suggested.

Line 297: “However, the vapor loss to the Teflon surface has long been a concern, especially in smog chamber community”. Does the author mean Quartz?

Thanks very much for comment. We miswrite the sentence and delete it.

Lines 298-300: “OA concentration in the tailpipe is orders of magnitude higher than that in the ambient air even after the dilution in the CVS system, which would facilitate partitioning to the particle phase.” This statement seems not consistent with the results shown in Figure 6, where most of the measured I/SVOCs are in the gas phase, not in the particle phase.

The freshly emitted OA in the tailpipe is in dynamic partitioning between the gas and particle phases and the OA concentration is orders of magnitude higher than that in the ambient environment. According to the Pankow theory, higher concentration of OA facilitates the g-p partitioning into the particle phase (Pankow 1994):

$$f_{part,T} = \left(1 + \frac{1}{k_{OM} \times C_{OA}}\right)^{-1}$$
$$k_{OM} = \frac{RT}{10^6 P_L^0 \delta MW}$$

where R is the gas constant, T is the temperature, P_L^0 vapor pressure, MW is the molecular weight of the aerosols, and δ is the activity coefficient in organic phase.

Even so, I/SVOCs are still measured to be dominated by the gas phase concentration. One of the main reasons is that diesel particulate filter (DPF) removes the diesel emitted PM efficiently (Chen et al. 2021) for (DPF + DOC) vehicles. For non-(DPF + DOC) vehicles, the g-p partitioning varies among different organic compound groups. For example, the alkanes are observed to reside predominantly in the gas phase while 4-ring and 5-ring PAHs in the particle phase.

Has the author measured the total OA concentration? If you did, you can try to model the g-p distribution using

Pankow absorption theory (Pankow, 1994), and to see if it can explain the gas-phase dominant results for the I/SVOCs. And also, why the phase distribution of hopanes is distinctly different between non-(DPF + DOC) vehicles and (DPF + DOC) vehicles, any particular explanations? Reference: Pankow, J. F. (1994). An absorption model of gas/particle partitioning of organic compounds in the atmosphere. *Atmospheric Environment*, 28(2), 185-188.

We agree with the reviewer that the concentration of total OA is a critical parameter determining the g-p partitioning of I/SVOCs (please see the answers to previous comment where we address the Pankow theory). The monitoring modules connected to the Constant volume sampler (CVS) system include a real-time gas analyzer module (MEXA-7400HLE, HORIBA, Japan) to monitor the transient concentration of CO and CO₂, a temperature and relative humidity sensor, an air filtration system, and a flow control system. Total OA concentration is not available in the current design of CVS system. Given this, we directly measure I/SVOC concentration in the gas and particle phase and estimate the g-p particle partitioning of the resolved compound categories instead of modeling the coefficients using Pankow theory.

The distribution of hopane between non-(DPF + DOC) vehicles and (DPF + DOC) vehicles is distinctly different. Hopane, by nature, partitions predominantly into the particle phase and the statement is confirmed by the results obtained from non-(DPF + DOC) vehicles. For (DPF + DOC) vehicles, hopane (or PM) is captured and removed by DPF efficiently, as a result of which the particle phase concentration of hopane is reduced dramatically.

Reference:

- Chen, H., X. Sun, X. C. Wang, F. Y. Sun, P. Zhang, L. M. Geng & H. F. Wang (2021) Filtration Efficiency and Regeneration Behavior in a Catalytic Diesel Particulate Filter with the Use of Diesel/Polyoxymethylene Dimethyl Ether Mixture. *Catalysts*, 11.
- He, X., X. Zheng, Y. Yan, S. J. Zhang, B. Zhao, X. Wang, G. H. Huang, T. Chen, Y. H. Cao, L. Q. He, X. Chang, S. X. Wang & Y. Wu (2022) Comprehensive chemical characterization of gaseous I/SVOC emissions from heavy-duty diesel vehicles using two-dimensional gas chromatography time-of-flight mass spectrometry. *Environ Pollut*, 305, 119284.
- Pankow, J. F. (1994) AN ABSORPTION-MODEL OF GAS-PARTICLE PARTITIONING OF ORGANIC-COMPOUNDS IN THE ATMOSPHERE. *Atmospheric Environment*, 28, 185-188.