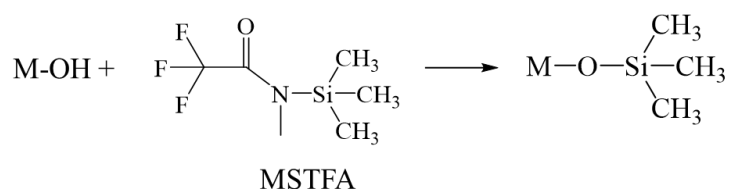


This work collected the particulate intermediate-volatility and semi-volatile organic compounds (I/SVOC) from heavy-duty diesel vehicles (HDDVs) by conducting chassis dynamometer tests. They analyzed the particulate I/SVOCs using two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC-ToF-MS), speciated the unresolved complex mixtures (UCMs), and reported the emission factor (EF) distribution under diverse driving conditions. Besides, they examined the gas-particle (g-p) partitioning of different compound categories and addressed how the sampling artifacts would affect the quantification of organic compounds. On the overall, I think the paper is worth of publication and meets the interest for the reader of this journal. Suggestions and comments are provided as below:

We thank the reviewer for the positive comments and the recommendation for publication. In the revised manuscript, we rephrase the main text based on the reviewers' suggestions where appropriate. Below please see the point-by-point responses to the individual comments.

1. We know that oxygenated groups, i.e., hydroxyl and carboxylic groups, are not well detected in GC-MS without derivatization with MSTFA. How would you detect those oxygenated compounds without the derivatization and guarantee the recoveries in particular.

Basically, oxygenated groups are not well detected in GC-MS without derivatization especially carboxylic acids when using liquid injection auto sampler. In this way of measuring oxygenated organic compounds, active H atom is substituted with trimethyl-silyl (TMS) reagent, (n-methyl-n-(trimethylsilyl) trifluoroacetamide (MSTFA) (He et al. 2018), as shown in the following figure:



The derivatization reaction decreases the polarity of the targeted compound and increases the desorption efficiency in the hot inlet liner (usually held at 275°C). In this work, samples are thermally desorbed in an automated thermal desorption system (TD100-xr, Markes International), which is connected to the GC × GC system instead of using a liquid injection auto sampler. Parameters in the thermal desorption system have been throughout optimized to increase the desorption efficiency and the quality control and quality assurance have been well addressed. For details, please see answer to Q5.

2. In section 3.3, when addressing the I/SVOC distribution, the criteria of O:C ratio of 0.3, 0.4, and 0.5 are deployed. Could you explain why the specific numbers are used.

The O:C ratio of the bulk organics with oxygenated functional groups ranges between 0.2 to 0.5 and the that of the highly oxygenated molecules (HOMs) is much higher. For example, the abundant organic compound, terephthalic acid (C₈H₆O₄), a significant tracer for anthropogenic emissions (He et al. 2018), has a O:C ratio of 0.5. Besides, it was reported that O/C from ambient urban organic aerosol ranges from 0.2 to 0.8 with a diurnal cycle, and that from

biomass burning OA ranges from 0.3 to 0.4 (Aiken et al. 2008). The average molecular weight of the atmospheric aerosol was reported to be 200 amu and bearing one or two oxygenated functional groups would generate O:C ratio in the particular range.

3. Line 101, it is mentioned that three replicated experiments are conducted. What is the repeatability of the measurements, e.g., reporting the standard deviation. Readers may be interested in the repeatability to confirm the robustness of the methods.

Thanks for the comments. We conducted duplicated experiments for each vehicle and driving conditions. Generally, the repeatability of China VI vehicles is better than that of China IV vehicle.

We now add the standard deviation in the revised manuscript.

Updated text (lines 176-193):

“...The average HDDV-emitted particulate I/SVOCs EFs of cold-start and hot-start driving cycles are 147.2 ± 68.3 and 1.7 ± 0.3 mg kg⁻¹·fuel⁻¹ for non-(DPF + DOC) vehicles, 1.6 ± 0.3 and 0.9 ± 0.1 mg kg⁻¹·fuel⁻¹ for (DPF + DOC) vehicles...

...The EF of alkane derived from non-(DOC + DPF) vehicles under the cold-start condition averages to 92 ± 42.8 mg kg⁻¹·fuel⁻¹, which is two order...

...Alkene and cycloalkane show commensurate EFs, with the average values of 2.4 ± 1.1 and 1.8 ± 0.9 mg kg⁻¹·fuel⁻¹ for cold-start and 0.04 ± 0.01 and 0.05 ± 0.02 mg kg⁻¹·fuel⁻¹ for hot-start driving...

...2-ring PAHs are detected at abundant concentration of 33.8 ± 15.7 mg kg⁻¹·fuel⁻¹, whereas 3-ring, 4-ring, and 5-ring PAHs are detected at much less concentration of 1.5 ± 0.7 , 1.3 ± 0.6 , and 0.3 ± 0.1 mg kg⁻¹·fuel⁻¹, respectively...”

4. For many categories, such as O-I/SVOCs categories, it seems that they do not have authentic standards. How are these I/SVOCs identified and quantified? The authors should explicitly address the identification of these compound categories in the main text or in the supporting information.

The I/SVOCs emitted by HDDVs are quantified (semi-quantified) by the “three-step” approach. In step one, the compounds of which the authentic standard are available are accurately quantified. However, the portion of accurately quantified mass is relatively small (< 5%). During step two and three, the I/SVOCs are classified by their mass spectrum pattern and semi-quantified by the surrogates. Taking PAHs_{4ring} as an example, all isomeric 4 ring PAHs exhibit the same fragment pattern: m/z 228 ion has the highest relative intensity and the relative intensity of the m/z 228 fragment ion is three times greater than the ensuing high intensity fragments, i.e., 226, 227, 228. The species are identified into PAHs_{4ring} only if their rules of mass spectrum are in accordance with above-mentioned condition.

For most of the species detected in the GC × GC chromatogram space, no authentic standard is available. In this case, they are semi-quantified using surrogate standards. For peak X (X denotes any peak that is not quantified) to

be semi-quantified, the first and second retention time are recorded as (t_{x1} , t_{x2}). The first and second retention times of a series of authentic standards are (t_{A1} , t_{A2}), (t_{B1} , t_{B2}), ..., and (t_{N1} , t_{N2}). The distance between peak X and authentic standard A is computed as:

$$s_A = \sqrt{(t_{x1} - t_{A1})^2 + (t_{x2} - t_{A2})^2}$$

Optimal surrogate is the authentic standard of which the distance between peak X and the standard is the minimum of the array (S_A , S_B , ..., and S_N). Then the calibration curve of the optimal surrogate is applied to peak X to semi-quantify the compound. The quantification approach is addressed in greater detail in He et al. (2022) and summarized in lines 147-156.

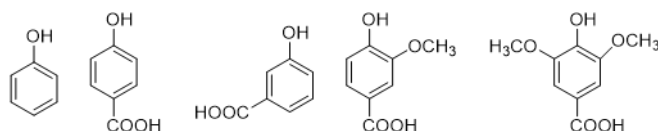
5. The uncertainty assessment of the emission factors should be presented to convince reader of the quantification method, either in the main text or the supporting information.

Thanks for the valuable suggestion. The uncertainty assessment could be derived from the four aspects. First, the peak area or height of internal standards among different samples are highly reproducible. The repeatability of the internal standard signals reveals that the analytical method could be well duplicated. Second, the calibration curves for all the target compounds, including the hydrocarbons and the functionalized standards, are well established (R^2 ranges from 0.950 to 0.999), demonstrating the solidity of this method. Third, the instrument blank tests were conducted throughout the whole experiment, and we did not see observable blank contamination. Duplicated samples were tested randomly, and less than 1% signal intensity of the previous sample was recorded, confirming that the carry-over effect was not a concern. Forth, uncertainties of quantifying individual compounds using surrogates were reported to be 24% and 28.1% (Alam et al. 2018, Huo et al. 2021), which gives an idea of the overall confidential level of the quantification. We give a detailed assessment of the uncertainty of the analytical method and revise the conclusion section based on the reviewer's suggestions.

Updated text in the supporting information (lines 44-51):

"The uncertainties of the emission factors are assessed. First, the peak area or height of internal standards among different samples are highly reproducible, which reveals that the analytical method could be well duplicated. Second, the calibration curves for all the target compounds are well established. Third, the instrument blank tests were conducted throughout the whole experiment, and no blank contamination is observed. Forth, less than 1% signal intensity of the re-test sample was observed, confirming that the carry-over effect was not a concern. Last, it was reported that using surrogates would introduce an uncertainty of approximate 24% and 28.1%, which gives an overall idea of the uncertainty level of the quantification (Huo et al. 2021, Alam et al. 2018).

6. From Fig 2, it seems like the "phenol benzylic alcohol" is the most abundant O-I/SVOC species. Could you give some example compounds of this category and what are the implications with abundant emission of these compounds? Some typical "phenol benzylic alcohol" species are phenols with different functional groups as shown in the figure below.



They are a group of aromatic compounds which contribute to secondary organic aerosol (SOA) formation significantly in both gas-phase and aqueous-phase (George et al. 2015, Yee et al. 2013). Their aerosol yields as a function of organic aerosol mass ranges from 0.1-1 (Yee et al. 2013).

7. Line 340, please check throughout the main text and keep “GC × GC” uniform.

Thanks, and revised.

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