Point-to–point responses to review comments (egusphere-2024-3290)

Title: Emissions of Intermediate- and Semi-Volatile Organic Compounds (I/SVOCs) from Different Cumulative Mileage Diesel Vehicles under Various Ambient Temperatures

Review of Shuwen Guo et al.

In the current study, gaseous and particulate I/SVOCs emitted from four HDDVs were analyzed using GC×GC-MS. The emission factors as well as the composition of I/SVOCs were reported. Overall, the experiments were nicely done and the data are well analyzed. The current contribution is a welcome addition to the field. There are several places in the paper are a bit obscure as detailed in the comments below. Beyond these, I do not see any major obstacles to publication.

Response:

We thank the reviewer for supporting our work, and we provide below a point-by-point response to the individual comments.

Specific comments:

(1) The experiments were well organized. My general question is the innovation of the current study. The I/SVOC emissions as well as their compositions from heavy diesel vehicles have been widely reported, including the studies from their own group. Any new findings that the authors would like to highlight in the current one?

Response:

Thanks for the comment. We highlight the findings below:

1) This study discussed the differences in I/SVOC emissions of heavy-duty diesel vehicles (HDDVs) with different cumulative mileage and calculated the emission deterioration coefficient, which has been overlooked in previous studies (Chang et al., 2022; He et al., 2022a, b; Liu et al., 2021). We found that overlooking the I/SVOC emission degradation will result in a more than three-fold underestimation of the total I/SVOC emissions of China V HDDVs in China.

2) The low ambient temperatures would lead to more I/SVOC emissions for high-mileage vehicles (HMVs), but no significant impact on low-mileage vehicles (LMVs). This has also been less focused on in the past.

3) We discussed the certain linear correlation ($R^2 = 0.73$) between I/SVOC EFs and modified combustion efficiency (MCE), which reveals the increase of I/SVOC emissions above is caused by a decrease in engine combustion efficiency.

(2) Line 24: “Compounds such as phenol, …. appeared only in HMV emissions”. These are compounds that are widely observed in vehicle emissions. Any reason for their disappearance in LMV emission? Are there any potential artifacts in the sample analysis?

Response:

Thanks for the comment. We did observe chromatographic peaks of phenols from LMV exhaust, but their peak areas were significantly smaller compared to those observed in HMVs and were indistinguishable from those in background samples. Phenols reported in previous studies were also emitted by high cumulative mileage vehicles. For instance, He et al. (2022) investigated HDDVs with a service duration ranging from 2 to 6 years. Zhang et al. (2024) tested I/SVOCs from HDDVs with service duration ranging from 1 to 6 years and found weak phenol signals for newer ones. As vehicle age and mileage increase, engine combustion efficiency decreases, leading to higher organic emissions in I/SVOCs and thus phenol concentrations above background levels to be detected.

(3) Line 179: "Oxy-PAH&Oxy-benzene", I don't think the abbreviations were pre-defined. Also, what compounds specifically do they represent? I noticed the authors also separately classify "phenol" instead of grouping them into "Oxy-benzene".

Response:

Thanks for the comment. Similar abbreviations have appeared in our previous research papers (He et al., 2022a, b 2024), and we apologize for the author's oversight in not specifying the types of organic compounds covered by the abbreviations again in the manuscript of this study. Oxy-PAH & Oxy-benzene represent all organic compounds containing benzene rings and oxygen-containing groups, except for phenols whose hydroxyl group is directly connected to the benzene ring. We supplement a detailed description of all organic category names as SI-1 in supporting information (SI).

"**SI-1. Description of all organic category names.**

Alkane: n-alkane and i-alkane. Alcohol: aliphatic alcohol. Phenol: organics containing one benzene ring and a hydrocarbon group directly attached to the benzene ring. Carbonyls: aliphatic ketone and aliphatic aldehyde. Acid: aliphatic acid. Oxy-PAH & Oxy-benzene: organic compounds containing benzene rings and oxygen-containing groups, except for phenols whose hydroxyl group is directly connected to one benzene ring. PAH_2rings: PAH with 2 benzene rings. PAH_3rings: PAH with 3 benzene rings. PAH_4rings: PAH with 4 benzene rings. Alkene: organics containing carbon double bond(s) without any other function groups. Cycloalkane: organics containing a saturated carbon ring without any other function groups.

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Please refer to lines 27-35 in the SI for details.

(4) Line 190: the emission factors of ISVOCs between LMV and HMV differs quite a lot according to Figure 2a. And according to Figure 3, the fractional contributions from different components are also different for HMV and LMV. Hence, I'm not sure it is appropriate to present the average volatility distributions of I/SVOCs from the entire fleet. Could Figure 1 be separated into LMV and HMV?

Response:

Suggestion taken. We divided Figure 1 into LMV and HMV results for plotting, rather than taking the average of the two, as shown in the figure below. Figure (a) was the average volatility distribution of I/SVOCs from the LMVs, and (b) from HMVs. Different colored bars represent different organic groups. The highest I/SVOC EFs for LMVs were in bin 3 and bin 2, reaching 5 mg·km^{-1} and 4 mg·km^{-1}; but for HMVs were in bin 6 and bin 5, reaching 37 mg·km^{-1} and 31 mg·km^{-1}, respectively. The I/SVOCs they emitted are mainly IVOCs.

The information in this modified figure overlapped with Figure 3 in the main context (line 253), and thus this modified figure was placed in the SI as Fig. S4. The original Fig. 1 in line 190 of the manuscript has been deleted, and other figure numbers and figure references in the main text have been modified. The SI was modified as follows:

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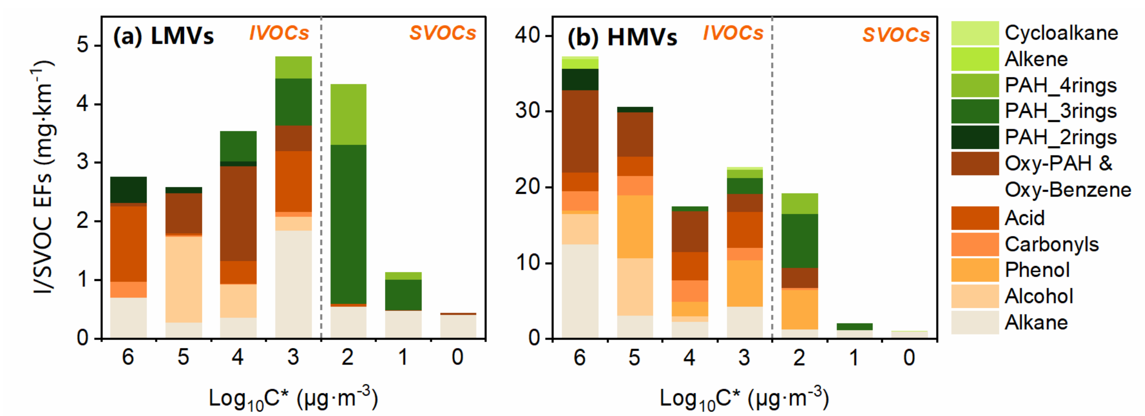

Fig. S4. The average volatility distribution of I/SVOCs from the (a) LMVs and (b) HMVs. Different colored bars represent different organic groups."

Please refer to lines 76-79 in the SI for details.

(5) Line 225: How many sets of the tests were performed? Does each data point on Figure 2b represents the average emission factor for each entire 1800s test cycle? Also, I hesitate to agree that gaseous I/SVOCs show good correlation with THC because the datapoints on Figure 2b concentrates at two ends of the fitted line, which might affect the reliability of the linear regression. Any more evidence on this point? Or any other supporting references?

Response:

Thanks for the comment. We performed ten sets of tests and two or three parallel tests were conducted, as shown in the table below, which has been supplemented in the SI. Each data point on Figure 2b represents the EF for each entire 1800s test cycle.

Previous studies on vehicle exhaust emissions have reported a linear correlation between I/SVOC and THC (or nonmethane hydrocarbons, NMHCs). For example, Zhao et al. (2015, 2016) reported a stronger correlation between total I/SVOCs and NMHCs (R^2 = 0.92-0.98) emitted from motor vehicles. The strong correlation between total I/SVOCs and THC (R^2 = 0.78-0.87) was also found by Tang et al. (2021). Their linear correlation and ratio have also been used to estimate the I/SVOC emission inventory when no detailed I/SVOC measurement data are available (Zhang et al., 2024; Zhao et al., 2022). For instance, Zhao et al. (2022) used the EF ratios of IVOCs to NMHCs of diesel vehicles calculated by previous studies to estimate the IVOC emission inventory for mobile sources in China.

"Table S1. Sets of test cycles.

NO.	Vehicle ID	Ambient Temperature	Cold- or Hot-start Cycle	Repetitions
1	D1	23°C	Cold-start cycle	2
2	D1	23°C	Hot-start cycle	2
3	D2	23°C	Cold-start cycle	2
4	D2	23°C	Hot-start cycle	2
5	D2	0°C	Hot-start cycle	2
6	D3	23°C	Cold-start cycle	3
7	D3	23°C	Hot-start cycle	3
8	D4	23°C	Cold-start cycle	3
9	D4	23°C	Hot-start cycle	3
10	D4	0°C	Hot-start cycle	2

Please refer to lines 61 in the SI for details.

(6) The influence of temperature on emission is interesting. What are the variations of other pollutants with the changes in temperature, i.e., THC, NOx, CO, etc?

Response:

We did find that the emissions of other pollutants from HMV were also affected by low ambient temperature, but this part was not mentioned in the manuscript as it is not related to the title of the article. The low temperature caused the average EFs of THC (NOx, CO) to increase from 289 mg·km^{-1} (2629 mg·km^{-1}, 359 mg·km^{-1}) to 302 mg·km^{-1} (3555 mg·km^{-1}, 404 mg·km^{-1}). However, the reasons for their increase in EFs were different. THC and CO are the by-products of incomplete combustion of diesel, and thus their EFs are directly related to MCE. The EF of NOx is related to the treatment efficiency of the selective catalytic reduction (SCR) system, whose ammonia aqueous solution may partially solidify at 0°C thereby reducing the reaction efficiency of NOx in SCR. The same emission change pattern of these conventional pollutants was found in LMV. The detailed data is shown in the table below, which has been supplemented in SI.

"Table S3. Average THC, NOx, and CO EFs for LMV and HMV, respectively.

Vehicle	Test Cycle	THC (mg·km^{-1})	NOx (mg·km^{-1})	CO (mg·km^{-1})
LMV (D2)	Hot_23°C	35	6951	600
	Hot_0°C	38	8048	657
HMV (D4)	Hot_23°C	289	2629	359
	Hot_0°C	302	3555	404

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Please refer to lines 65 in the SI for details.

(7) The overall presentation is acceptable, but English could do with improvement in places.

Response:

Thanks for the comment. We have polished the English expression of the entire text again. Taking the modifications listed in the table below for example:

Original		**Modified**	
Line	***Text***	***Line***	***Text***
49	These variations underscore the need for a more precise assessment of diesel vehicle I/SVOC emission factors (EFs).	47	These discrepancies highlight the urgent need for a more precise assessment of diesel vehicle I/SVOC emission factors (EFs).
52	Furthermore, many regions in China experience temperatures of 0°C or lower during the autumn and winter. Consequently, HDDVs operating under such low-temperature conditions may exhibit different emission characteristics compared to those under normal temperatures (e.g., 23°C). This underscores the importance of examining the variations in I/SVOC emissions and exhaust component distribution from HDDVs across different temperature conditions.	50	Given that many regions in China experience temperatures below 0°C during winter, evaluating how HDDVs operate under such conditions is critical in I/SVOC emissions and exhaust component distribution across different temperature conditions.
61	In the study of Zhao et al (2015), approximately 80% of I/SVOCs emitted by diesel vehicles remain unresolved by GC-MS, reckoned as UCM. Moreover, due to the variability in the response signals detected by mass spectrometry for different complex organic compounds (He et al., 2022b), the lack of detailed component information introduces significant uncertainties in I/SVOC quantification and prediction of SOA formation potential (SOAFP).	58	For example, Zhao et al (2015) reported that 80% of I/SVOCs emitted by diesel vehicles were classified as UCM. This lack of detailed chemical information introduces uncertainties in I/SVOC quantification and prediction of SOA formation potential (SOAFP) (He et al., 2022b).
182	The alkane proportion was lower but O-I/SVOC proportion was higher than that in previous studies (alkane: 37% to 66%, O-I/SVOCs: 20% to 27%) (He et al., 2022b; Zhang et al., 2024a).	180	The proportion of O-I/SVOCs was notably higher in this study compared to previous research, where alkanes typically accounted for 37% to 66% and O-I/SVOCs for 20% to 27% (He et al., 2022b; Zhang et al., 2024a).

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