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.

This manuscript investigates the gaseous and particulate I/SVOC emission factors (EFs) of high-mileage vehicles (HMVs) and low-mileage vehicles (LMVs) under varying ambient temperatures using TD-GC×GC-MS. The authors provide a comprehensive analysis of the variations in emission factors and their chemical components, identifying a linear correlation between I/SVOC EFs and the modified combustion efficiency (MCE). The experimental methodology is thorough and reliable, and the findings present a significant advancement in understanding I/SVOC emissions from heavy-duty diesel vehicles (HDDVs). The results have practical implications, particularly for researchers developing I/SVOC emission inventories and secondary organic aerosol (SOA) prediction. Overall, I recommend accepting this manuscript following minor revisions.

Response:

Sincerely thanks for the positive comments. We have carefully revised the manuscript according to the specific comments.

Specific comments:

1. In section 2.1, the authors describe the information of the four in-use HDDVs. But the vehicle brand and the engine model of the HDDVs, which are closely related to the vehicle emission are not given. The related information should be given, and some discussion about the uncertainty caused by these differences and the aging of the engine should be included in the manuscript.

Response:

Thanks for the suggestion. We have modified Table 1 in the main text, which offers more information including the brand, the engine model, and the in-use duration to represent the aging of the engine. Also, the uncertainty caused by them has been discussed.

“**Table 1. Information on the test fleet**

Vehicle ID	**D1**	**D2**	**D3**	**D4**
Emission Standard	China V	China V	China V	China V
Aftertreatment Devices	SCR	SCR	SCR	SCR
Brand	DONGFENG	SINOTRUK	DELONG	DELONG
Engine Model	dCi450-51	MC13.54-50	WP10.310E53	WP10.310E53
In-use Duration	7 months	8 months	32 months	32 months
Cumulative Mileage ($\times 10^3$ km)	22.21	34.84	169.50	188.33

Gross Combined Weight Rating (GCWR, t)	48.8	48.8	41.8	41.8
Rated Power (kW)	309	397	228	228
Displacement (L)	11.12	12.42	9.73	9.73

…

…It should be noted that existing research primarily focuses on diesel vehicles with cumulative mileage below 200,000 km. Further experiments are necessary to determine whether I/SVOC emissions from designated HDDVs with over 200,000 km of mileage continue to increase linearly or stabilize. Also, the brand, engine models, GCWR, and displacement of the four HDDVs were slightly different (Table 1), which might bring some uncertainty to the emission analysis results (Zeng et al., 2024; Tolouei and Titheridge, 2009; Aosaf et al., 2022). Future studies should further consider the uncertainties brought by these factors."

Please refer to lines 88 and 226-229 in the main text for details.

2. In Section 2.1, it is better to give the dilution ratio of the exhaust. In addition, was the temperature of the sampling pipe maintained as a certain level to reduce thermophoretic and condensational losses?

Response:

Thanks for the comment. The dilution ratio of the exhaust was about 40 of the exhaust. CVS is a constant temperature dilution system that stabilizes the airflow within the sampling channel at 25°C to reduce thermophoretic and condensational losses.

"Each CHTC-TT lasts 1800 seconds, with an average speed of 46.6 km·h^{-1} and a maximum speed of 88 km·h^{-1} (Fig. S1). When the vehicles were driven at the speed specified by the CHTC-TT on the dynamometer, the emitted exhaust from tailpipes was diluted in the constant volume sampler (CVS). The exhaust dilution ratio was about 40. The CVS system maintains the airflow of the diluted exhausts at 25°C to avoid thermophoretic and condensational losses. CO_2, CO, total hydrocarbons (THC), and NO_x from the diluted exhaust were detected by the real-time gas analyzer module (MEXA-7400HLE, HORIBA, Japan) provided by the CATARC, and a series of offline sampling test samples were also collected from the CVS."

Please refer to lines 91-92 in the main text for details.

3. In Section 2.2, the authors describe the method to remove effects of absorption on the quartz filter when calculating the total I/SVOCs. The gas phase of I/SVOCs are collected after a PTFE filter, but the separation of gas and particle I/SVOCs after the PTFE may break the equilibrium of gas/particle I/SVOCs and lead to evaporation of particle I/SVOCs, which may overestimate the Qgas. It is better to provide some discussion on the uncertainty of this method.

Response:

Suggestion taken. We added the following text in line 105-110 to address this issue in the revised manuscript:

"…the total I/SVOC results in this paper were gaseous I/SVOCs collected by TA tubes plus particulate I/SVOCs collected by quartz filters after deducting artifacts (total I/SVOCs = TA + (1 - 32%) × Q_{total}). Notably, the gas phase of I/SVOCs was collected after passing through a PTFE filter, and the separation of gas and particle I/SVOCs beyond the PTFE filter may disrupt the equilibrium between them. Cheng et al. (2010) evaluated the collection artifacts of organic carbon using various quartz filter sampling methods and found that about 10% of the Qgas derived from volatilized particulate organic carbon by the sampling method used in this study. Therefore, the Qgas in this study may be slightly overestimated. The TA tubes were prebaked at 320°C for 2 hours…"

4. The sentence "…by He et al. (2022b)" in line 132 is missing a period at the end. Please correct this.

Response:

Thanks for pointing this out. The error here has been corrected. Please refer to line 131 in the main text.

5. Some phrases should use standard abbreviations. For instance, the phrase "...as shown in Figure 1" in line 177 should be revised to "...as shown in Fig. 1." Ensure consistent abbreviation usage throughout the manuscript.

Response:

Thanks for pointing this out. Figure 1 in the original manuscript has been removed based on the opinion of Referee #1 and has been revised as Fig. S4 in SI. Therefore, the sentence has been revised to "… as shown in Fig. S4.". Please refer to line 175 in the main text. The abbreviation in the context has been rechecked.

6. In line 227, the "2" in "R2=0.9" is not in superscript. Please adjust the formatting for accuracy.

Response:

Thanks for pointing this out. The error here has been corrected. Please refer to line 223 in the modified manuscript.

7. The steps for qualitatively identifying organic compounds using mass spectrometry principles require further elaboration. Could the authors provide a detailed description of these procedures in the methods section?

Response:

Thanks for the comment. Taking alkanes as an example, compounds containing hydrocarbon chains give rise to a series of ions separated by 14 Da (-CH2-), as shown in Fig. 1. As a result, the top ions to identify alkanes would be m/z = 43, m/z = 57, m/z = 71, and m/z = 84. Due to the stability of chemical groups, generally, the abundance of m/z = 57 is highest, followed by m/z = 43 and m/z = 71. When incorporating these rules into the data treatment software (Canvas, version 2.5, J&X Technologies), a few steps need to be taken, as shown in Fig. 2. Four built-in features can be deployed. ABUND (X) returns the normalized abundance of the input ion mass; HASMASS (X) returns the value to indicate if the input ion exists; ORDER (X) returns the order of the input ion mass; MASS (X) returns the mass of the input ion's order. Additionally, the function allows two logical operators, "And" and "Or". Then, the cluster of alkanes can be extracted by the following rules:

((MASS(1)=43 && (MASS(2)=57 || MASS(2)=71 || MASS(2)=41)) || (MASS(1)=57 && (MASS(2)=43 || MASS(2)=71 || MASS(2)=41)))

where "&&" and "||" refer to the logical operators "And" and "Or", respectively. Paste the rules in Ion Extractor Editor and the cluster of alkanes can be filtered, as shown in Fig. 3.

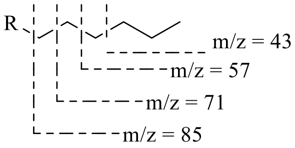
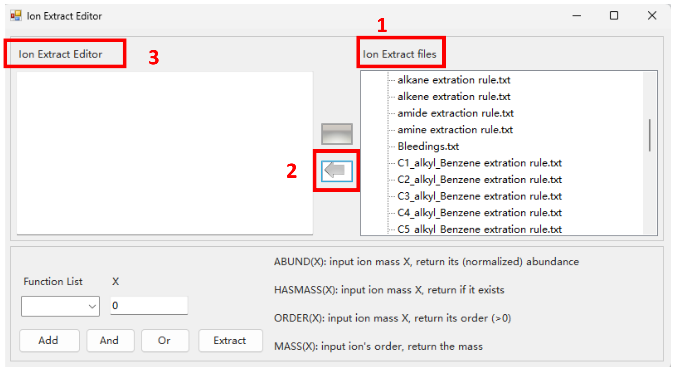


Figure 1. The common fragmentation patterns of n-alkanes.

Open Canvas → Open Browser → File → Load Data (load a sample) → Speciation → Find All Peaks → Mass Spectrum → Extraction Rules



alkane extration rule.txt
alkene extration rule.txt
amide extraction rule.txt
amine extraction rule.txt
Bleedings.txt
C1_alkyl_Benzene extration rule.txt
C2_alkyl_Benzene extration rule.txt
C3_alkyl_Benzene extration rule.txt
C4_alkyl_Benzene extration rule.txt
C5 alkyl Benzene extration rule.txt

ABUND(X): input ion mass X, return its (normalized) abundance
HASMASS(X): input ion mass X, return if it exists
ORDER(X): input ion mass X, return its order (>0)
MASS(X): input ion's order, return the mass

Figure 2. The steps to enable the ion extract function built in Canvas.

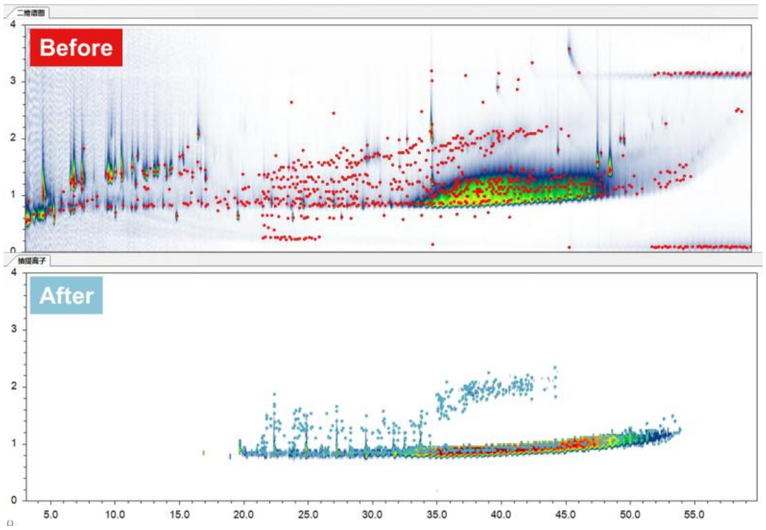


Figure 3. Comprehensive two-dimensional chromatograms before and after screening alkanes. Each red and blue point represents a chromatographic peak.

We have compiled the above explanation in SI. Please refer to line 37-59 in SI for detail.

8. Specify the number of test repetitions conducted for each vehicle. Additionally, indicate the sample sizes used for all calculations involving averages to enhance the transparency and reproducibility of the results.

Response:

Thanks for the comment. Table S1 in SI has been supplemented the number of test repetitions.

“**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 line 61 in SI for detail.

9. In Line 237-238: “The EF ratios across different volatility bins decreased with decreasing volatility, highlighting that the elevated I/SVOC EFs of HMVs were primarily due to a marked increase in organics within the volatility range of bins 2 to 6.”. But according to the Fig. 3, the I/SVOCs EFs of HMVs and LMVs exhibited a rebound within the volatility range of bins 2 to 4. Is there any explanation for this phenomenon?

Response:

In fact, a similar volatility distribution phenomenon has also been found in previous studies on vehicle exhaust I/SVOC emissions. For example, both Zhao et al. (2015) and He et al. (2022) tested the exhaust from diesel vehicles and found an I/SVOC EF rebound around bin 2, as shown in the figure below, but they did not explain such a phenomenon. Liang et al. (2022) compared the I/SVOC volatility distribution in exhaust, diesel, and lubrication oil from an engine, using the Positive Matrix Factorization (PMF), and concluded that the EF rebound around bin 2 was attributed to the lubrication oil. However, we did not analyze the diesel and lubrication oil used in our test vehicles by TD-GC×GC-MS and without other evidence. We will improve in our future research.

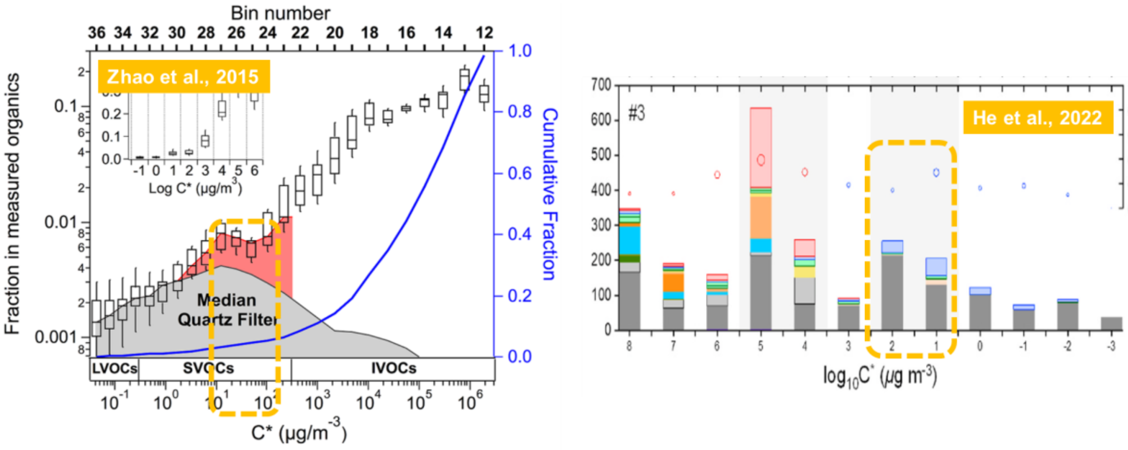


Figure 4. I/SVOC volatility distribution in the study of Zhao et al. (2015) and He et al. (2022).

10. Around line 240, there’s a comparison of the proportions of HMV and LMV organic compounds; was there also a comparison of different component emission factors (EFs) between HMV and LMV? Are all substances higher in HMV?

Response:

Thanks for the comment. The EFs of all organic compounds emitted by HMVs are higher than that of LMVs, but the magnitude of the increase varies. The supplementary figure below has been added to the SI and the main text has been modified as follows:

“

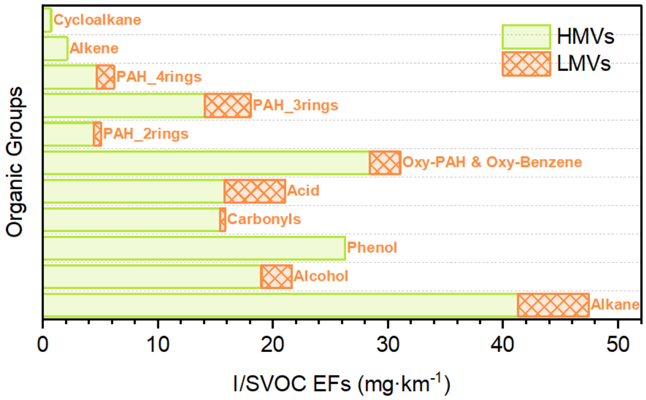


Figure S8. The average organic group distribution of HMVs and LMVs.”

“…To further compare volatility and category distribution, the average EFs of HMVs and LMVs are shown separately in Fig. 2. The EF ratios across different volatility bins exhibited a decreasing trend with decreasing volatility, indicating that the elevated I/SVOC EFs of HMVs were primarily due to a marked increase in organics within the volatility range of bins 2 to 6. Figure 2 further depicts the relative proportion of distinct organic groups present in I/SVOC emissions and their EFs are shown in Fig. S8. The EFs of all organic compounds emitted by HMVs were higher than those of LMVs, but the magnitude of the increase varied. Except for phenol, alkene, and cycloalkane, the organic group with the highest HMV-LMV ratio was carbonyls, up to 34, as shown in Fig. S8. The next highest is oxy-PAH & oxy-benzene, whose HMV-LMV ratio reached 11. The ratios of PAH_2rings, alcohol, and alkane were 7. Overall, the HMV-LMV ratios of O-I/SVOCs were relatively higher, which contributed 65% of the I/SVOCs emissions from HMVs, compared to 42% for LMVs. Since the SOA yields of O-I/SVOCs are lower than those of hydrocarbon-like I/SVOCs in the same bin (Chacon-Madrid and Donahue, 2011), variations in O-I/SVOC proportions directly impacted the SOAFP gap between HMVs and LMVs, which would be further discussed in Sect. 3.5. Alkane and oxy-PAH & oxy-benzene were the dominant contributors to I/SVOCs for both HMVs and LMVs. PAH_3rings contributed 8% of the I/SVOC emissions for HMVs, but 23% for LMVs. Interestingly, phenol, alkene, and cycloalkane were not detected in any of the LMV samples."

Please refer to line 238-242 in the main text and line 88 in SI for details.

11. The introduction and the section on SOA prediction would benefit from additional supporting references. Consider including following studies that explore the generation and sources of urban particulate matter to provide a more robust foundation for your discussion.

- Jacob M. Sommers, Craig A. Stroud, Max G. Adam, Jason O'Brien, Jeffrey R. Brook, Katherine Hayden, Alex K. Y. Lee, Kun Li, John Liggio, Cristian Mihele, Richard L. Mittermeier, Robin G. Stevens, Mengistu Wolde, Andreas Zuend, Patrick L. Hayes (2022) Evaluating SOA formation from different sources of semi- and intermediate-volatility organic compounds from the Athabasca oil sands. Environmental Science: Atmospheres. DOI: 10.1039/d1ea00053e.
- Qingsong Wang; Juntao Huo; Hui Chen*; Yusen Duan; Qingyan Fu; Yi Sun; Kun Zhang; Ling Huang; Yangjun Wang; Jiani Tan; Li Li*; Lina Wang; Dan Li; Christian George; Abdelwahid Mellouki, &Jianmin Chen (2023) Traffic, marine ships and nucleation as the main sources of ultrafine particles in suburban Shanghai, China. Environmental Science: Atmospheres. DOI: 10.1039/d3ea00096f.
- Ling Huang, Hanqing Liu, Greg Yarwood, Gary Wilson, Jun Tao, Zhiwei Han, Dongsheng Ji, Yangjun Wang, Li Li*. Modeling of secondary organic aerosols (SOA) based on two commonly used air quality models in China: Consistent S/IVOCs contribution but large differences in SOA aging. Science of the Total Environment 2023, 903, 166162. https://doi.org/10.1016/j.scitotenv.2023.166162.
- Yangjun Wang; Miao Ning; Qingfang Su; Lijuan Wang*; Sen Jiang; Yueyi Feng; Weiling Wu; Qian Tang; Shiyu Hou; Jinting Bian; Ling Huang; Guibin Lu; Kasemsan Manomaiphiboon; Burcak Kaynak; Kun Zhang; Hui Chen, &Li Li* (2024) Designing regional joint prevention and control schemes of PM2.5 based on source apportionment of chemical transport model: A case study of a heavy pollution episode. Journal of Cleaner Production. DOI: 10.1016/j.jclepro.2024.142313.
- Sahir Azmi, Mukesh Sharma (2023) Global $PM_{2.5}$ and secondary organic aerosols (SOA) levels with sectorial contribution to anthropogenic and biogenic SOA formation. Chemosphere. https://doi.org/10.1016/j.chemosphere.2023.139195.

Response:

Thanks for the suggestion. We have included these up-to-date relevant papers for reference and the main text has been revised as follows:

"As a major air pollutant, fine particulate matter ($PM_{2.5}$) leads to over three million premature deaths globally each year (Apte et al., 2018), mainly associated with lung cancer, ischemic heart disease, and stroke (Guan et al., 2018; Xue et al., 2021). Secondary organic aerosol (SOA) accounts for 12% to 77% of the total $PM_{2.5}$ mass based on global source apportionment results (Huang et al., 2014; Sun et al., 2020; Zhang et al., 2021). Observation studies have demonstrated that SOA contributions increase with the severity of pollution during haze episodes in megacities in China (He et al., 2020; Ho, 2016; Li et al., 2015; Azmi et al., 2023; Wang et al., 2023; Wang et al., 2024). Among potential SOA precursors, intermediate-volatility and semi-volatile organic compounds (I/SVOCs), with effective saturation concentrations (C^*) between 10^3 to 10^6 and 10^0 to 10^2 $\mu g \cdot m^{-3}$, have been demonstrated to be more effective than volatile organic compounds (VOCs) (Daniel S. Tkacik et al., 2012; Jathar et al., 2013; Morino et al., 2022; Sommers et al., 2022; Huang et al., 2023). …”

“**Reference** …

Azmi, S. and Sharma, M.: Global PM2.5 and secondary organic aerosols (SOA) levels with sectorial contribution to anthropogenic and biogenic SOA formation, Chemosphere, 336, 139195, https://doi.org/10.1016/j.chemosphere.2023.139195, 2023.

…

Huang, L., Liu, H., Yarwood, G., Wilson, G., Tao, J., Han, Z., Ji, D., Wang, Y., and Li, L.: Modeling of secondary organic aerosols (SOA) based on two commonly used air quality models in China: Consistent S/IVOCs contribution but large differences in SOA aging, Sci Total Environ, 903, 166162, https://doi.org/10.1016/j.scitotenv.2023.166162, 2023.

…

Sommers, J. M., Stroud, C. A., Adam, M. G., O’Brien, J., Brook, J. R., Hayden, K., Lee, A. K. Y., Li, K., Liggio, J., Mihele, C., Mittermeier, R. L., Stevens, R. G., Wolde, M., Zuend, A., and Hayes, P. L.: Evaluating SOA formation from different sources of semi- and intermediate-volatility organic compounds from the Athabasca oil sands, Environ. Sci.: Atmos., 2, 469–490, https://doi.org/10.1039/D1EA00053E, 2022.

…

Wang, Q., Huo, J., Chen, H., Duan, Y., Fu, Q., Sun, Y., Zhang, K., Huang, L., Wang, Y., Tan, J., Li, L., Wang, L., Li, D., George, C., Mellouki, A., and Chen, J.: Traffic, marine ships and nucleation as the main sources of ultrafine particles in suburban Shanghai, China, Environ. Sci.: Atmos., 3, 1805–1819, https://doi.org/10.1039/D3EA00096F, 2023.

Wang, Y., Ning, M., Su, Q., Wang, L., Jiang, S., Feng, Y., Wu, W., Tang, Q., Hou, S., Bian, J., Huang, L., Lu, G., Manomaiphiboon, K., Kaynak, B., Zhang, K., Chen, H., and Li, L.: Designing regional joint prevention and control schemes of PM2.5 based on source apportionment of chemical transport model: A case study of a heavy pollution episode, Journal of Cleaner Production, 455, 142313, https://doi.org/10.1016/j.jclepro.2024.142313, 2024.

…”

Please refer to line 38-41, 370, 421, 460, and 474-480 in main text for details.

Reference:

He, X., Zheng, X., You, Y., Zhang, S., Zhao, B., Wang, X., Huang, G., Chen, T., Cao, Y., He, L., Chang, X., Wang, S., and Wu, Y.: 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, https://doi.org/10.1016/j.envpol.2022.119284, 2022b.

Liang, Z., Yu, Z., and Chen, L.: Quantifying the contributions of diesel fuel and lubricating oil to the SVOC emissions from a diesel engine using GC × GC-ToFMS, Fuel, 310, 122409, https://doi.org/10.1016/j.fuel.2021.122409, 2022.

Zhang, X., He, X., Cao, Y., Chen, T., Zheng, X., Zhang, S., and Wu, Y.: Comprehensive characterization of speciated volatile organic compounds (VOCs), gas-phase and particle-phase intermediate- and semi-volatile volatility organic compounds (I/S-VOCs) from Chinese diesel trucks, Sci. Total Environ., 912, 168950, https://doi.org/10.1016/j.scitotenv.2023.168950, 2024.

Zhao, Y., Nguyen, N. T., Presto, A. A., Hennigan, C. J., May, A. A., and Robinson, A. L.: Intermediate volatility organic compound emissions from on-road diesel vehicles: chemical composition, emission factors, and estimated secondary organic aerosol production, Environ. Sci. Technol., 49, 11516–11526, https://doi.org/10.1021/acs.est.5b02841, 2015.