We greatly appreciate the review's constructive feedback on our manuscript. In response to the insightful comments, we have thoroughly revised the manuscript. Below, we provide a detailed point-by-point reply to the review's comments. We believe these revisions have significantly improved the clarity and quality of our work, and we have updated the manuscript accordingly. For further details, please refer to the revised version.

Referee 1#

Specific Comments:

The manuscript presents novel findings concerning ship emissions, with a focus on intermediate and semi-volatile organic compounds. The results reveal the enhancement of organic compounds following the transition from high-sulfur to low-sulfur fuels. The manuscript is well written and provides meaningful information to our knowledge. However, there are several questions and comments that require attention:

(1) Lines 63-66: This sentence is ambiguous in terms of the contribution proportion of SO_2. It is suggested to be revised.

Reply: The sentence has been verified against the original reference and revised in lines 64-67 in the improved manuscript as follows:

Specifically, the consumption of heavy fuel oil constitutes 70% of total ship fuel usage (International Maritime Organization, 2016), which is primarily responsible for the majority of SO_2 emissions associated with global shipping. This has considerable effects on coastal regions and the marine environment.

(2) Line 87: Does PM refer to mass or number? It needs to be made clear.

Reply: Thank you for your comment. We have explicitly stated that 'PM' refers to mass in line 89 in the revised version of the manuscript, as shown below:

Previous studies have indicated that the low-sulfur fuel regulation is an effective measure for reducing SO_2 and PM mass emission in many countries.

(3) Line 98: The aging of VOCs to form intermediates is equally important for SOA. Examination of long-time aging process on volatile organic compounds emitted from solid fuel combustion in a rural area of China. Chemosphere 333 (2023) 138957.

Reply: Thanks for your reminding. The aging process of VOCs is not only closely related to SOA formation, but also plays a significant role in ozone formation and its impact on climate and air quality. Additionally, the intermediates formed during VOCs aging are key precursors for SOA formation. This content has been added to the lines 101 -104 of the manuscript:

VOCs have been getting lots of interests due to their crucial role as common precursors of secondary organic aerosols (SOAs) and ozone (O_3) (Shen et al., 2023;Hui et al., 2019). Additionally, the aging process of VOCs and the resulting intermediates also play pivotal role in SOA formation (He et al., 2023; Srivastava et al., 2022).

(4) Line 108: Provide the full name of “WRF-Chem”

Reply: Thank you for the suggestion. We have now provided the full name of "WRF-Chem" (Weather Research and Forecasting model coupled with Chemistry) in lines 112-113 in the revised manuscript.

(5) Line 118 and 102: The emission of IVOCs from various sources are important for the SOA production. It is recommended to enrich the expression, and the following study can be referred to： Emission of Intermediate Volatile Organic Compounds from Animal Dung and Coal Combustion and Its Contribution to Secondary Organic Aerosol Formation in Qinghai-Tibet Plateau, China. Environmental Science & Technology 2024 58 (25), 11118-11127.

Reply: Thank you for your suggestion. We have enhanced the expression to provide a more comprehensive explanation in lines 117-120 in the revised manuscript.

Clarifying the contribution of I/SVOCs from different sources to SOA formation is crucial for a comprehensive understanding of their role in atmospheric processes and their impact on air quality (He et al., 2024; Srivastava et al., 2022).

(6) Section 2: In this study, some data statistical analyses were involved. It is necessary to add the methods used in the statistical analyses mentioned in the text, such as significance tests, etc.

Reply: We appreciate the reviewer’s insightful comment. The data statistical analyses involved in this study, such as significance test, have been explained in the relevant caption of Figure 2 in lines 430-434 in the revised manuscript.

Figure 1 Box-whisker plots of total $EF_{I/SVOCs}$ for the tested ships under (a) different fuel types, (b) different operating modes, and (c) different engine types. N represents the number of samples. Significant differences between samples were determined using an independent samples T-test. The error bars represent the standard deviation of the measured values, while *** indicates a significance level of $p < 0.001$.

(7) Lines 151-152: The parameters of fuels are the most important information in this study. It is suggested that the Table S2 be placed in the main text.

Reply: Thank you for the suggestion. We agree that the fuel parameters are crucial to this study and have moved Table S2 into the manuscript as Table 1 for better accessibility. See details in line 164 in the revised manuscript.

(8) Line 167: A total of 64 sets of gas-phase and particle-phase I/SVOCs samples were collected in this study, involving various engine types, fuels, and operating modes. Please add a table detailing exactly in what fuel, what type of engine, and under what operating modes, etc. these samples were collected.

Reply: Thank you for your valuable advice. The details of specific fuels, engine types, operating modes, and other relevant conditions under which these samples were collected have been added as Table S3 of the supplementary materials.

Table S3 Engine type, operating mode, and fuel type of each ship for each measurement

Ship ID	Engine type	Operating mode	Sampling duration	Ship ID	Engine type	Operating mode	Sampling duration
OGV1	Main engine	20%_MGO[a]	20 min	OGV3	Auxiliary engine	50%_MGO	20 min
		75%_MGO	20 min			50%_HFO	20 min
	Auxiliary engine	75%_MGO (NCR)	27 min			75%_HFO	20 min
OGV2	Main engine	25%_HFO	20 min	ICS1	Main engine	Maneuvering_0#diesel	20 min
		50%_HFO	20 min			Cruise_0#diesel	20 min
		75%_HFO	20 min	ICS2	Main engine	Maneuvering_0#diesel	20 min
	Auxiliary	85%_HFO	20 min			Cruise_0#diesel	20 min

	engine	100%_HFO	20 min	ICS3	Main	Maneuvering_0#diesel	20 min
		50%_MGO	25 min		engine	Cruise_0#diesel	20 min
		50%_HFO	70 min	ICS4	Main	Maneuvering_0#diesel	20 min
OGV3	Main	75%_MGO	40 min		engine	Cruise_0#diesel	20 min
	engine	25%_HFO	20 min				
		50%_HFO	10 min				
		75%_HFO	40 min				
		95%_HFO	40 min				

[a], means percentage of engine load under what type of fuel

(9) Line 202: In formula (1), when calculating EF, has the influence of organic carbon in gaseous phase been considered? How large is the error?

Reply: Thank you for your valuable comment. Unfortunately, the concentration of hydrocarbons (HC) was not quantified in this study and thus was excluded from the calculation of the emission factor. We recognize that incorporating organic carbon in the gaseous phase may introduce a degree of uncertainty into our analysis. It is important to note that in our previous research (Zhang et al., 2018), HC was included in the emission factor calculations. However, based on earlier data, the contribution of gaseous carbon (C) was relatively insignificant. Additionally, we have quantified the contribution of carbon from VOCs to the total emitted carbon in this study (Zhang et al., 2024a). The average emission factor of carbon from VOCs is 0.025% ± 0.020% of that of CO_2, indicating a relatively minor contribution. Considering the limited availability of HC data in this study and its minimal impact, it is reasonable to infer that the uncertainty associated with carbon in gaseous organic matter has a negligible effect on the overall results.

(10) Lines 312-319: Here reveals a very interesting research result that high-quality fuel leads to higher organic matter emissions. What do you think are the reasons for the increase in SVOCs/IVOCs emission factors after the switch from high-sulfur oil to low-sulfur fuel?

Reply: Thank you for your question. The increase in I/SVOCs emission factors after switching from high-sulfur to low-sulfur fuels is a multifaceted phenomenon primarily attributable to alterations in combustion efficiency and changes in the chemical composition of the fuel. A detailed analysis of these factors is provided in the latter part of the second paragraph of Section 3.2 (lines 369-376). Specifically, low-sulfur fuels tend to exhibit reduced combustion efficiency, which can lead to increased formation of I/SVOCs. Moreover, the production process of lower sulfur content fuels can also alter the relative proportions of other fuel components (Liu et al., 2022; Zhang et al., 2024b), potentially leading to a higher propensity for the formation of I/SVOCs under certain combustion conditions, which may account for the observed increase in emission factors.

(11) Section 3.2: How do the influencing factors such as fuel type, engine type and operating conditions interact to affect the final combustion process and I/SVOCs emissions? Give more explanations.

Reply: Thank you for your insightful question. The interaction between fuel type, engine type, and operating conditions plays significant roles in influencing the combustion process and the emissions of I/SVOCs. These factors affect both the combustion efficiency and the chemical composition of the emissions. Here, we provide a more detailed explanation of how each factor interacts to influence the final emissions:

The chemical composition of the fuel directly affects the types and amounts of I/SVOCs generated during combustion. Fuels with higher aromatic content tend to produce more semi-volatile and particulate-bound organic compounds (Zhao et al., 2015). In contrast, fuels with higher aliphatic content generally produce fewer semi-volatile species (Huang et al., 2018b). The presence of oxygenates in some fuels can alter the combustion temperature and the oxidation pathways, leading to different emission profiles for I/SVOCs. Moreover, the fuel type also influences its vaporization and mixing behavior with air during combustion, which subsequently affects the combustion efficiency (Liu et al., 2022; Zhang et al., 2024). The design and operational characteristics of the engine play a critical role in the combustion process. For example, in internal combustion engines, the air-fuel mixture, combustion chamber design, and fuel injection timing can significantly influence the temperature and pressure during combustion (Sayin and Canakci, 2009). These factors affect the thermal decomposition of hydrocarbons and the subsequent formation of I/SVOCs. Moreover, engine speed and load can influence combustion efficiency, with poor combustion typically leading to higher emissions of I/SVOCs. The operating conditions of the engine, including load, speed, and temperature, also influence the emission characteristics (Rajendran et al., 2023). Under low-load or idle conditions, incomplete combustion often results in higher emissions of I/SVOCs, as fuel is not fully vaporized or oxidized (Liu et al., 2022). High temperatures generally promote more complete combustion, but may also lead to the formation of more highly reactive intermediate species, which can contribute to I/SVOC formation in certain scenarios. The air-to-fuel ratio is another important factor—leaner mixtures (excess air) can result in lower I/SVOC emissions, while richer mixtures (more fuel) may increase the formation of unburned hydrocarbons and intermediate compounds. In summary, fuel type determines the primary chemical composition of the emissions, engine type influences the combustion efficiency and reaction pathways, and operating conditions dictate the degree of combustion completeness and the formation of intermediate compounds. These factors interact in such a way that they lead to varying degrees of incomplete combustion, resulting in the formation of a complex mixture of I/SVOCs.

(12) Lines 353-357: Incomplete combustion is regarded as an important reason for the increase of I/SVOCs with low-sulfur fuel. Can more convincing evidence, such as combustion efficiencies of the engines with different types of fuels, be provided in this study to support the conclusion given here?

Reply: Thank you for highlighting this important aspect. As you suggested, we have calculated the modified combustion efficiencies (MCE) with different fuel types (as shown below). It can be observed that the MCE values decrease significantly as the sulfur content of the fuel decreases. By comparing MCE values across different fuels, we can more robustly establish the relationship between incomplete combustion and the observed increase in I/SVOC emissions. These calculations offer compelling evidence to further support and reinforce the conclusions drawn in this study. This supplementary analysis has been integrated into the manuscript, with detailed information provided in lines 372-376 of the revised version:

To further elucidate the impact of reduced sulfur content on combustion efficiency, we calculated the modified combustion efficiencies (MCE) for various fuel types (Figure S2). The results indicated a notable decline in MCE values as the sulfur content decreased, suggesting that incomplete combustion was a key factor contributing to the elevated levels of I/SVOCs in low-sulfur fuels.

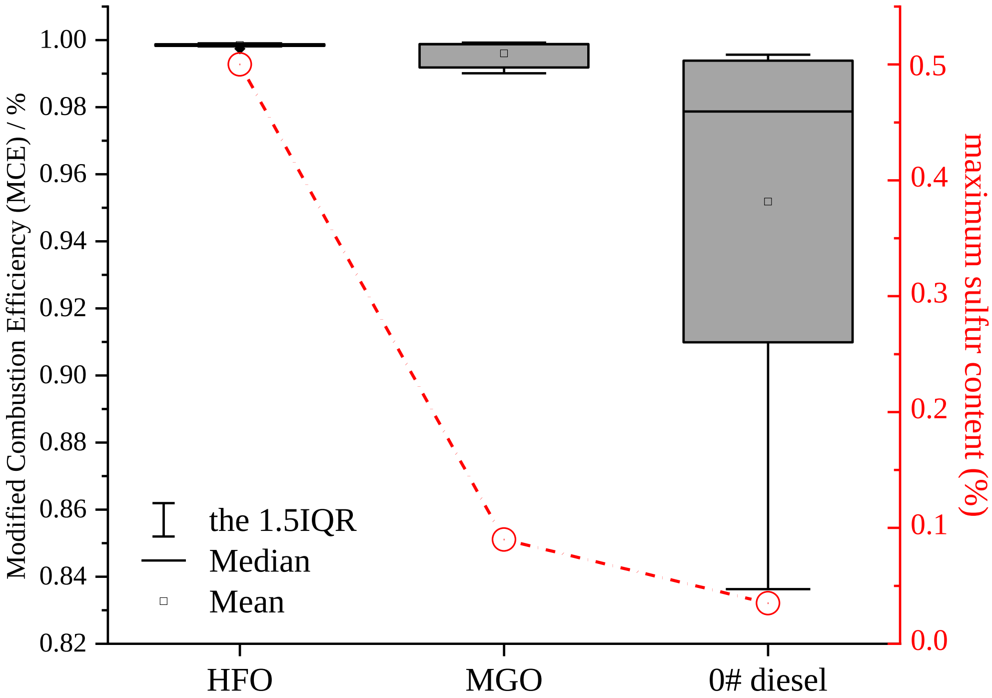

Figure S2 Box-whisker plot of the MCE with different fuel types

(13) Figure 2: Explain the meanings of the different symbols in this box plot, such as which one represents the average value, the median, etc. Besides, what method was used to calculate the P value?

Reply: Suggestion taken. The meanings of the different symbols in the box plot have been added in Figure 2. Significant differences between samples were determined using an independent samples T-test, which is shown in the caption of Figure 2.

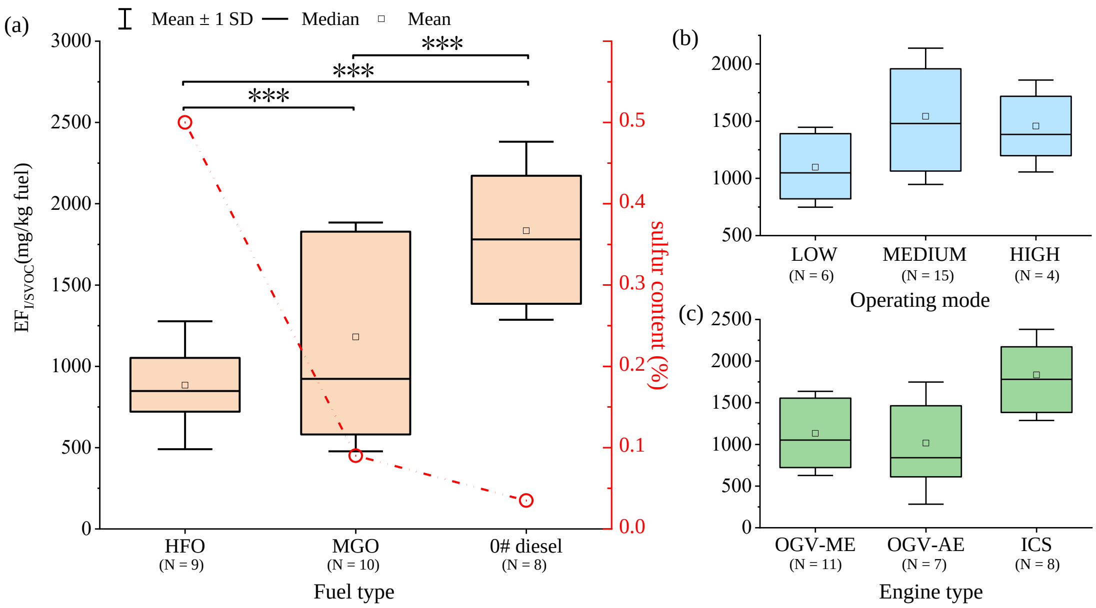

Figure 2 Box-whisker plots of total $EF_{I/SVOCs}$ for the tested ships under (a) different fuel types, (b) different operating modes, and (c) different engine types. N represents the number of samples. Significant differences between samples were determined using an independent samples T-test. The error bars represent the standard deviation of the measured values, while *** indicates a significance level of $p < 0.001$.

(14) Lines 410-412: Given that UCM accounts for a very high proportion of total I/SVOCs, what do you think the future research on UCM should be carried out, and is it necessary to further identify more compounds and what analytical methods should be used?

Reply: Thank you for your insightful question. Given that UCM (Unresolved Complex Mixture) accounts for a significant portion of total I/SVOCs, future research should prioritize refining analytical techniques to better characterize and identify the compounds within UCM. Since UCM is composed of a complex array of compounds that can often overlap in conventional single-dimensional Gas Chromatography (GC), employing Two-Dimensional Gas Chromatography (GC×GC) offers a powerful approach for separating and identifying more components (Tang et al., 2023). GC×GC enhances separation by utilizing two orthogonal columns with different stationary phases, thus allowing for improved resolution of complex mixtures like UCM (Marriott, 2004). Moreover, Orbitrap mass spectrometry provides ultra-high resolution and high mass accuracy, which can significantly improve the identification of individual compounds in the UCM (Kösling et al., 2022). Its capability to differentiate isomeric compounds and identify low-abundance species with high sensitivity is essential for the characterization of complex mixtures. Although GC × GC and Orbitrap MS are individually powerful analytical techniques, their integration with complementary methods such as high-resolution liquid chromatography (HRLC) or high-resolution mass spectrometry (HRMS) would significantly enhance the characterization of UCM. These combined approaches could enhance the detection of a wider range of compounds, including semi-volatile and non-volatile species, which may be more challenging to analyze with GC×GC alone. In conclusion, the identification of more compounds in the UCM and the application of advanced analytical techniques, such as GC×GC and Orbitrap MS, are crucial for advancing our understanding of UCM's role in I/SVOC emissions. These approaches offer superior separation, sensitivity, and resolution, making them invaluable tools for future research on UCM characterization.

Detailed information also has been provided in lines 707-710 in the revised manuscript:

Future research can obtain more comprehensive and accurate organic component emission data by using advanced methods such as comprehensive two-dimensional gas chromatography-mass spectrometry (GC × GC-MS) and Orbitrap mass spectrometry.

(15) Section 3.4: It is reasonable to divide the volatile range with normal alkanes as indicators. However, when discussing the differences in volatile distribution under different fuel types, only the phenomenon was described. How did the differences in fuel composition eventually lead to changes in volatile distribution? Can a summary of this part be made based on the component differences of different fuels?

Reply: Thank you for your insightful comment. The variations in fuel composition indeed play a crucial role in shaping the volatile emissions during combustion. Fuels with different chemical compositions, such as varying carbon chain lengths, aromatic content, and sulfur levels, lead to different combustion behaviors. These differences influence the volatility of the organic compounds released during combustion, which subsequently alters the distribution of I/SVOCs (Liu et al., 2022). Additionally, the sulfur content can also affect combustion efficiency, which may further alter the volatile distribution by influencing incomplete combustion processes.

In summary, the changes in volatile distribution can be attributed to the complex interactions between fuel composition, combustion conditions, and the inherent chemical properties of different fuel types. We have now added a more detailed explanation of these interactions and their impact on volatile emissions in lines 620-625 in the revised manuscript:

The compositions and physicochemical properties of different fuel types vary, leading to differences in the volatile organic compounds they contain. Consequently, the type of fuel played a significant role in determining the distribution of volatile fractions for each individual I/SVOC component. The composition and combustion efficiency of fuel are important factors affecting the emission and distribution of I/SVOCs.

(16) Figure 4: In the figure involving Hopanes, some error bars are covered.

Reply: Thank you for highlighting this issue. We have adjusted the figure to ensure that the error bars are fully visible and not obscured in the revised version of the manuscript. See details below:

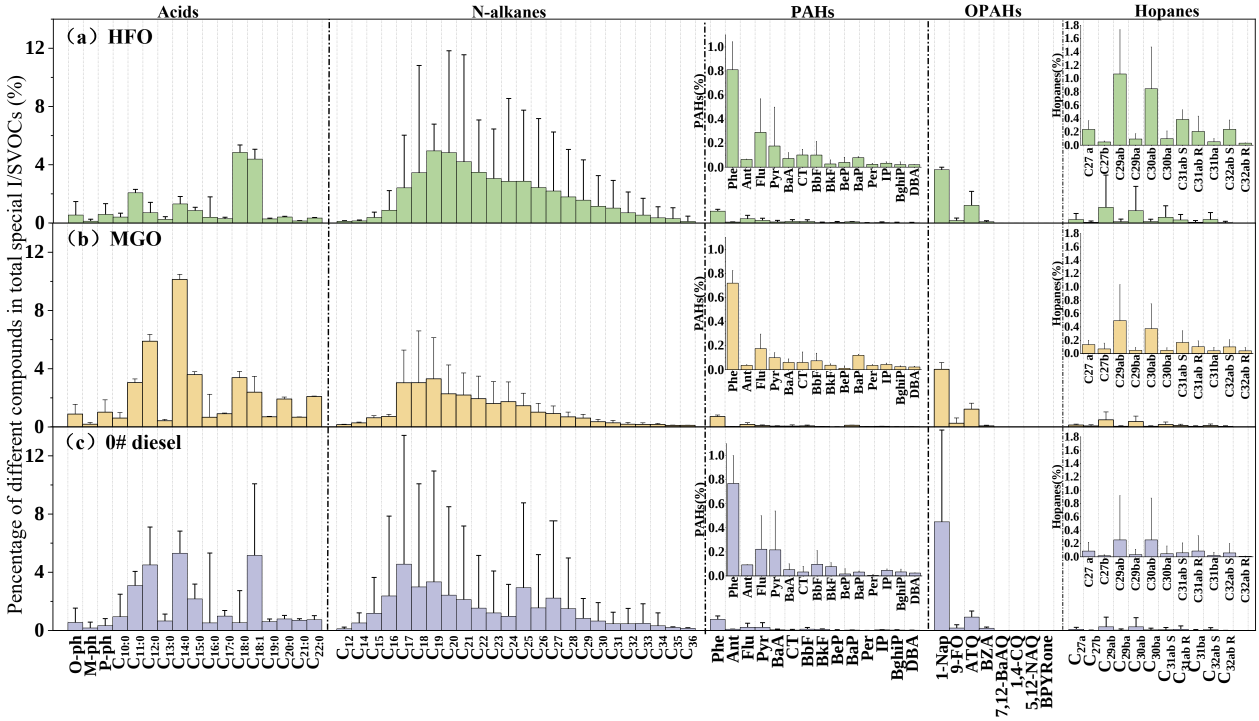

Figure 4 Profiles of I/SVOCs in ship exhausts under different fuels

(17) Figure 5 and Figure 6: The meanings of the Y-axis titles have not been clearly explained.

Reply: Suggestion taken. We have revised the explanations for the Y-axis titles in Figures 5 and Figure 6 to ensure greater clarity. These clarifications are now included in the revised manuscript. See details below:

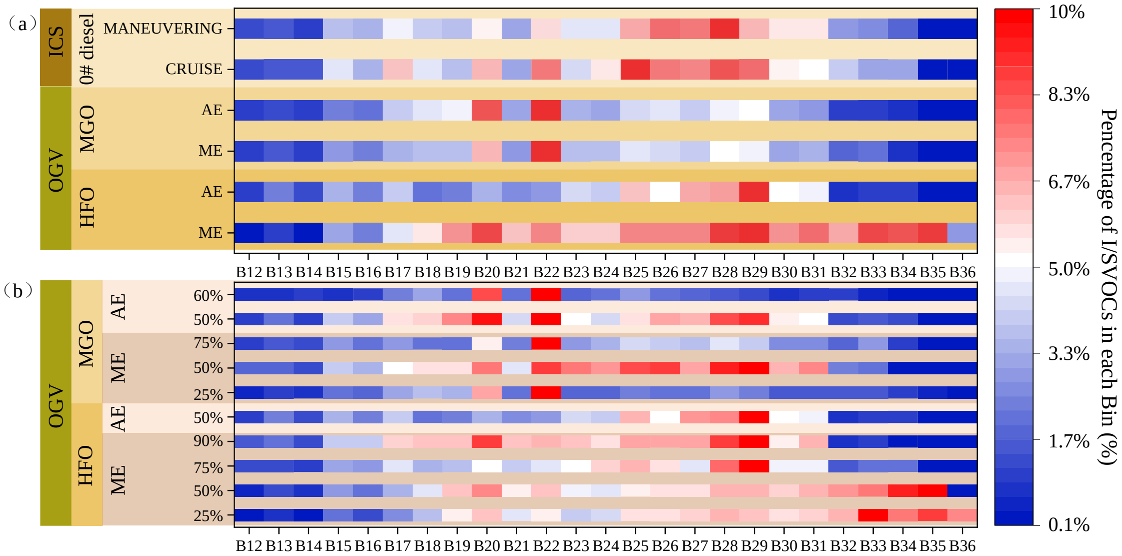

Figure 5 Split-bar heat plot of the I/SVOCs proportions in each volatile bin under (a) different fuel types for different engines, and (b) different operating conditions (25%-90% operating modes) for OGVs

(18) Figure 6: In the legend, the word "Hopanes" is misspelled.

Reply: Thank you for pointing that out. The misspelling of "Hopanes" in the legend has been corrected in the revised version of Figure 6. Moreover, Figure 6 also has been revised as the volatility distributions of I/SVOCs based on the volatility basis set (VBS) framework from different fuels for improved clarity.

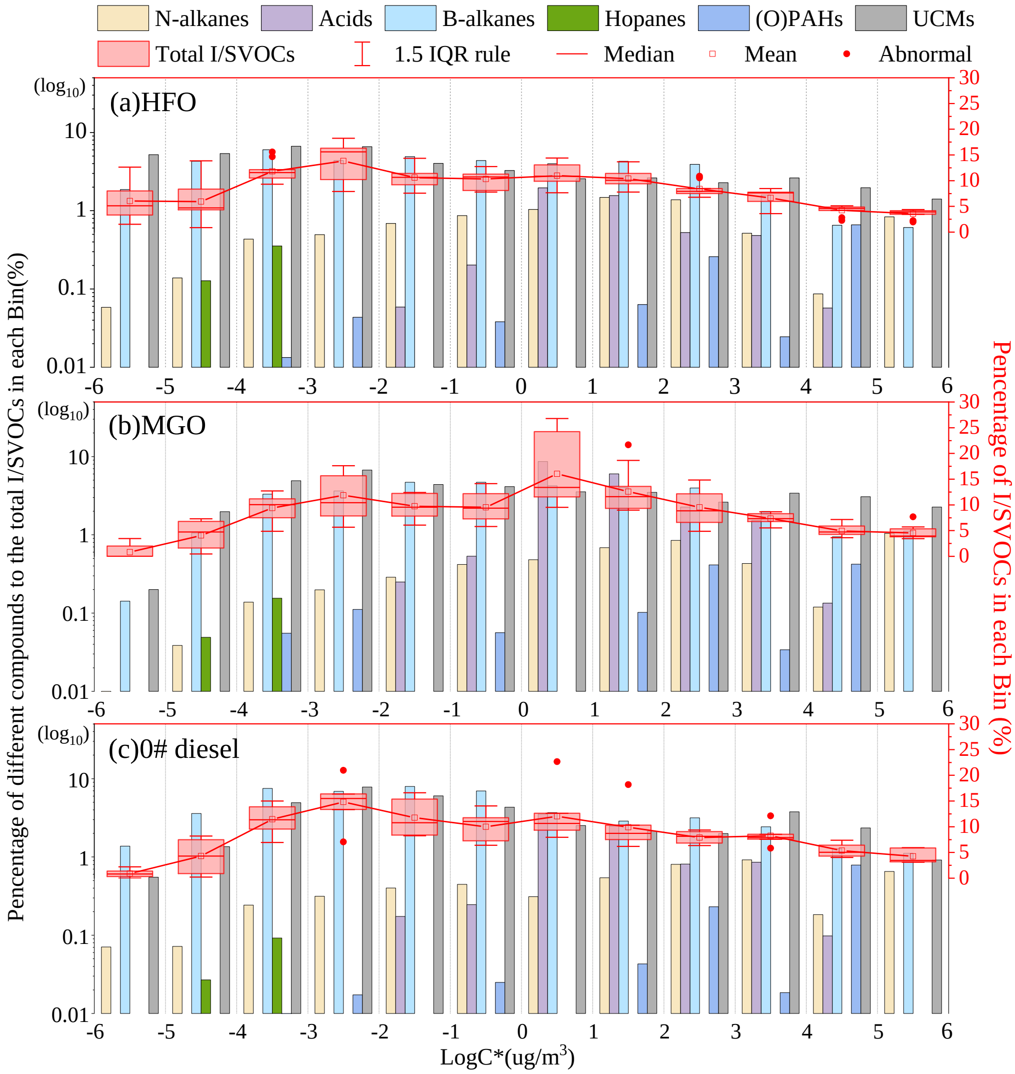

Figure 3 The volatility distributions of I/SVOCs based on the volatility basis set (VBS) framework from different fuels

(19) Figure 7: Could the total error bar of SOAFP be given?

Reply: Suggestion taken. The error bars for SOAFP have been added in the revised Figure 7.

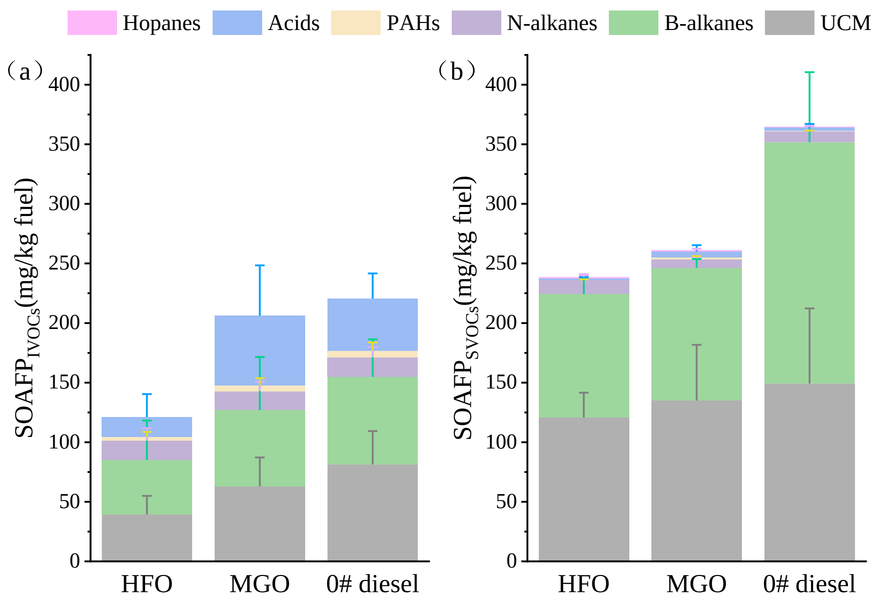

Figure 7. SOAFP from (a) IVOCs and (b) SVOCs

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