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 4#

In this study, the authors evaluated the impact of the transition from high-sulfur to low-sulfur on intermediate/semi-volatile organic matters (I/SVOCs) from ocean-going vessels and inland cargo ships. An increase of I/SVOCs has been found as the sulfur content decreased. This novel finding is very helpful for future oil policies. Although this is an interesting paper, certain clarification and revisions are needed. I recommend the publication after the authors address my comments below.

Major comment:

My major concern lies in the measurement. Section 2 should provide further details about the measurement. What is the clean air used in the sampling system, is it the same as zero air where there is no particle? It is important that the system isolates particles and gases originating exclusively from the ship exhaust, minimizing the potential for contamination from external sources. What measures have been taken to ensure this? Besides, is there a cutoff size of the aerosol or is it total suspended particles (TSP)? What is the uncertainty of the measurement? How long is the sampling time? How many samples were collected? It is beneficial to include a table giving an overview of all the samples, including the ship, engine type, fuel type, and operating mode, similar to Table S2 in Zhang et al. (2024). It can be put in the supplement.

Reply: Thank you for your question. In our sampling system, the clean air refers to ambient air that has undergone filtration through a clean air system equipped with dual particle filters, effectively eliminating particulate matter. This differs from the rigorously defined "zero air," which is purified air devoid of both particulate matter and aerosol precursors. Given the substantial demand for clean air in field sampling and the considerable cost associated with preparing zero air, this study utilized filtered ambient air as an alternative. Despite the potential presence of trace gaseous interferences, preliminary measurements confirmed that their concentrations (CO < 1 ppm, SO_2 < 10 ppb, NO_x < 5 ppb, VOCs < 1 ppb) were significantly lower than those in ship exhaust emissions (CO > 50 ppm, SO_2 > 1 ppm, NO_x > 50 ppm, VOCs > 50 ppb), with an uncertainty of less than 2%. Consequently, their influence on the experimental results is considered negligible.

To ensure that the sampling system exclusively captures particles and gases from ship exhaust while minimizing interference from external pollution sources, a sampling pipe (about 3 m) was used to route emissions from stack of ships. Then, the probe of a flue gas analyzer was placed into the vessel exhaust pipe to test the gaseous matters directly. Particulate matter was directly sampled after being diluted by the clean air mentioned above. This ensures that the collected gases and particles are exclusively from the ship's exhaust. The sampling tube was designed with a tightly sealed connection to isolate it from the outside air, preventing the entry of external pollutants. Additionally, to prevent interference from external gases, the dilution system is equipped with specially designed closed pipelines and splitters. The system is regularly cleaned and calibrated to guarantee that only ship exhaust is analyzed. These measures guarantee that the collected samples precisely represent the composition of ship exhaust emissions, while simultaneously minimizing interference from external air pollution sources.

In our study, the aerosol collected from the ship exhausts was total suspended particles (TSP), encompassing particles of all size ranges. This has been clarified in lines 174-175 of the revised manuscript. In this study, a total of 64 samples were collected. Detailed information for each sample, including sampling time, vessel type, engine type, fuel type, and operational mode, has been provided in Table S3.

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 engine	85%_HFO	20 min			Cruise_0#diesel	20 min
		100%_HFO	20 min	ICS3	Main engine	Maneuvering_0#diesel	20 min
		50%_MGO	25 min			Cruise_0#diesel	20 min
		50%_HFO	70 min	ICS4	Main engine	Maneuvering_0#diesel	20 min
OGV3	Main engine	75%_MGO	40 min			Cruise_0#diesel	20 min
		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

Specific comments:

(1) Line 57-58. "shipping emissions are responsible for 25% of fine particulate matter" globally? Please clarify.

Reply: We sincerely apologize for any confusion arising from the typesetting issues in the original manuscript, which led to ambiguity in the reported values. The correct statement should be as follows:

" Results show that shipping emissions are responsible for 2%-5% of fine particulate matter ($PM_{2.5}$)"

(2) Line 358-366. It seems that when analyzing the impact of operating mode (Fig. 2b), all the OGVs and ICSs, fuel types, and engine types are used. Will the result be

different if we investigate samples with the same fuel and engine types to exclude their impact?

Reply: We sincerely appreciate the reviewer for raising this important question. Indeed, our current analysis of operating modes (Fig. 2b) encompasses all ship types, fuel types, and engine types, which may introduce variability from these factors. However, upon re-examination of the original data, we discovered that the initial figure (Fig. 2b) displayed trend discrepancies attributable to misclassification errors in the data. We have now revised both the figure and the manuscript accordingly.

After revision, even if the analysis is limited to a subset of samples with the same fuel type and engine type (See in Fig. 3 (A)), the trend of the impact of operating modes on I/SVOC emissions remains relatively consistent with the comprehensive analysis presented in Figure 2 (b). This study primarily aims to examine the overall impact of various aspects of ships from an integrated perspective. Additionally, due to the insufficient sample size for individual variables, which limits representativeness, we included all OGVs and ICSs in the analysis. Incorporating the aforementioned updates, we have thoroughly revised the manuscript to provide a more comprehensive and robust interpretation of the findings (lines 385-406 in the revised manuscript). We appreciate your valuable suggestions once again, which have significantly enhanced the clarity of our analysis.

It could be seen from Figure 2 (b) that the average emission factors (EFs) of I/SVOCs in this study followed a relatively ascending order across operating modes: 1098 ± 305 mg (kg fuel)$^{-1}$ in low, 1542 ± 465 mg (kg fuel)$^{-1}$ in medium and 1457 ± 276 mg (kg fuel)$^{-1}$ in high operating modes, respectively in this study, revealing significantly elevated emissions at both medium and high loads compared to low-load conditions. This trend was consistent with PM emission patterns reported by Zhang et al. (2021), but notably diverged from the characteristics of ship-emitted IVOCs, which reached its lowest value under medium-load conditions in prior studies (Zhao et al., 2014;Huang et al., 2018b). This discrepancy could be attributed to the dominance of SVOCs over IVOCs in this study. Operating modes affect the combustion state in engines and the air-fuel ratio during the combustion process, thereby influencing exhaust emissions (Shrivastava and Nath Verma, 2020). The air-fuel ratio exhibits a decreasing trend with increasing engine load, which induces more pronounced incomplete combustion within the cylinder, thereby establishing a direct causative relationship with elevated total I/SVOC emissions. (Zhang et al., 2021; Watson et al., 1994). The high operating mode is associated with reduced fuel diffusion and combustion time, leading to a partial oxygen deficiency within the cylinder, thereby resulting in an increased generation of I/SVOCs (Zhao et al., 2016;Liu et al., 2022). The investigation of methodologies for optimizing engine design and control systems to achieve enhanced combustion efficiency under different operating conditions, thus reducing emissions, is of great significance.

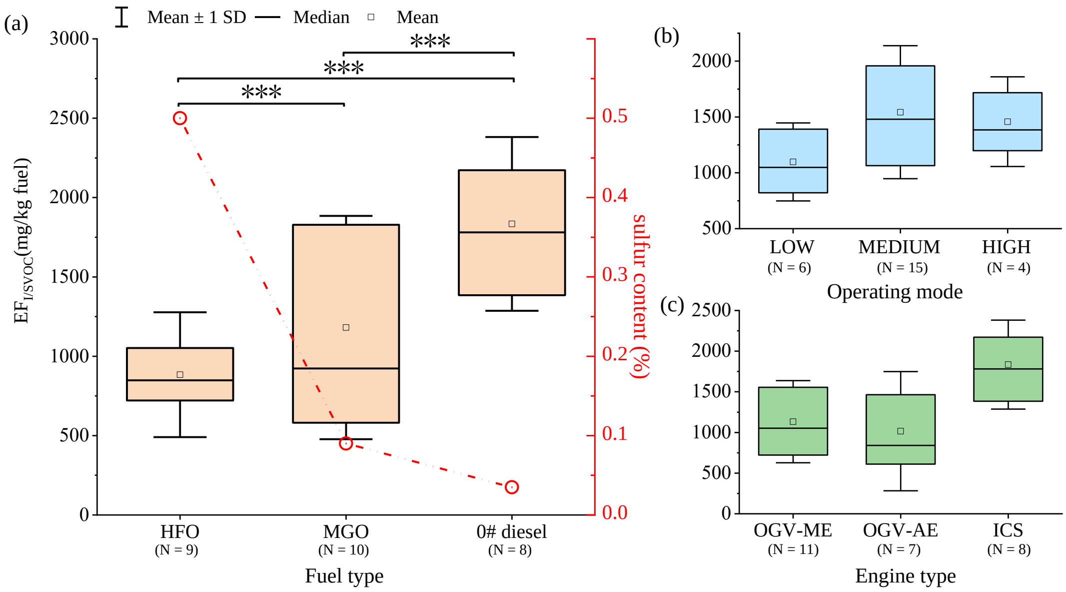

Figure 2 Box-whisker plots of total EFI/SVOCs for the tested ships under (a) different fuel types, (b) different operating modes, and (c) different engine types. *N* represents the number of samples. Significant differences between samples were determined using an independent samples T-test. The error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

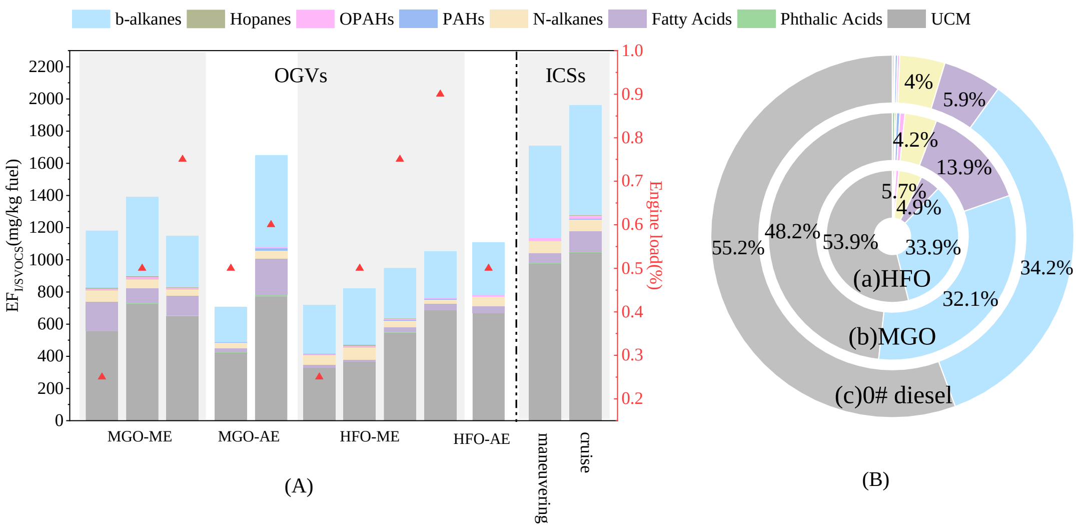

Figure 3. Chemical compositions of I/SVOCs from the tested ships, (A) emission factors (mg (kg fuel)$^{-1}$) and (B) fractional contributions (%). The red triangles represent the engine load.

(3) Figure 2 in line 402. I would suggest replacing the x-axis label with the figure title. More details are needed in the figure caption. The elements of boxplots need to be added. Besides, I do not see error bars. By error bars, the authors might mean whiskers. How many samples are there in each box, it will be more robust if the amount of samples could be shown.

Reply: Thank you for your valuable feedback. We have thoroughly reviewed your suggestions and implemented the necessary revisions. Specifically, we have incorporated elements of a box plot and added error bars to enhance clarity. These modifications have been incorporated into the revised manuscript to improve the clarity and accuracy of the figure. Thanks again for your helpful suggestions.

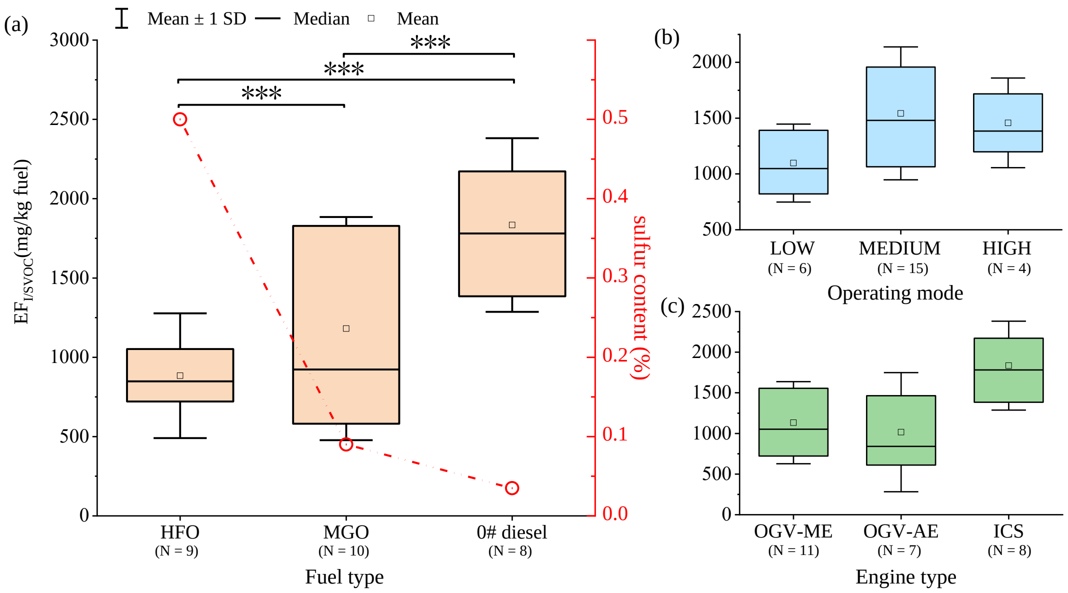

Figure 2 Box-whisker plots of total EFI/SVOCs for the tested ships under (a) different fuel types, (b) different operating modes, and (c) different engine types. N represents the number of samples. Significant differences between samples were determined using an independent samples T-test. The error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

(4) 372-374. This sentence needs to be revised. Is an “and” missing?

Reply: Thank you. Indeed, the sentence would benefit from the addition of "and" to enhance clarity and readability. We have revised the sentence in lines 395-397 in the improved manuscript to ensure proper coherence and fluidity.

<u>“Operating modes affect the combustion state in engines and the air-fuel ratio during the combustion process, thereby influencing exhaust emissions.”</u>

Thank you for pointing this out.

(5) Figure 3 in line 453. Why Fig. 3b is called “distributions”? Do the authors mean fractions? I would suggest the same as Fig. 2 that more details need to be added in the figure caption.

Reply: We sincerely appreciate your insightful suggestions. In response, we have revised the figure title from "distributions" to "fractional contributions (%)" to eliminate potential ambiguity. The figure caption has also been improved accordingly.

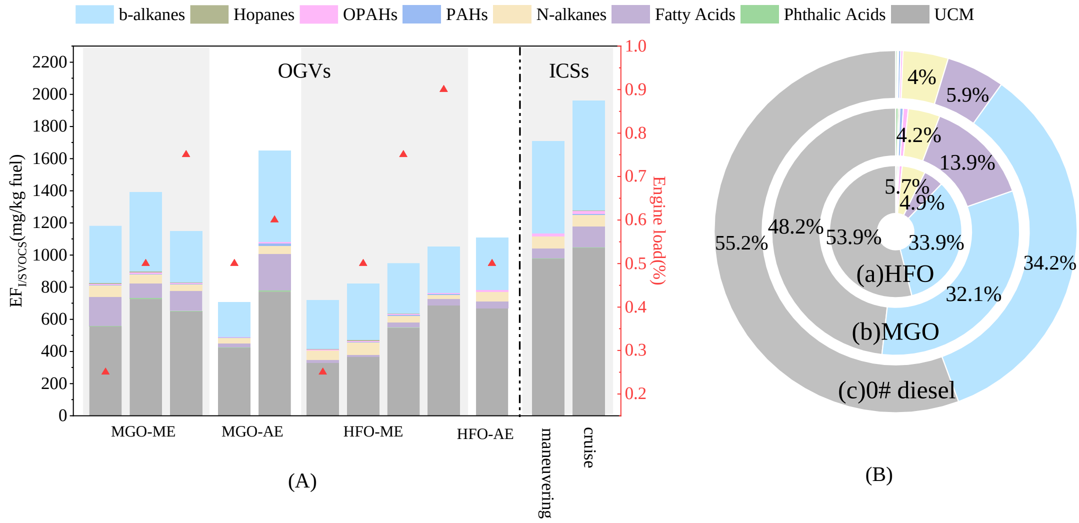

Figure 3. Chemical compositions of I/SVOCs from the tested ships, (A) emission factors (mg (kg fuel)$^{-1}$) and (B) fractional contributions (%). The red triangles represent the engine load.

(6) Figure 4 in line 545. Please improve the readability.

Reply: Thank you. Figure 4 has been improved as following:

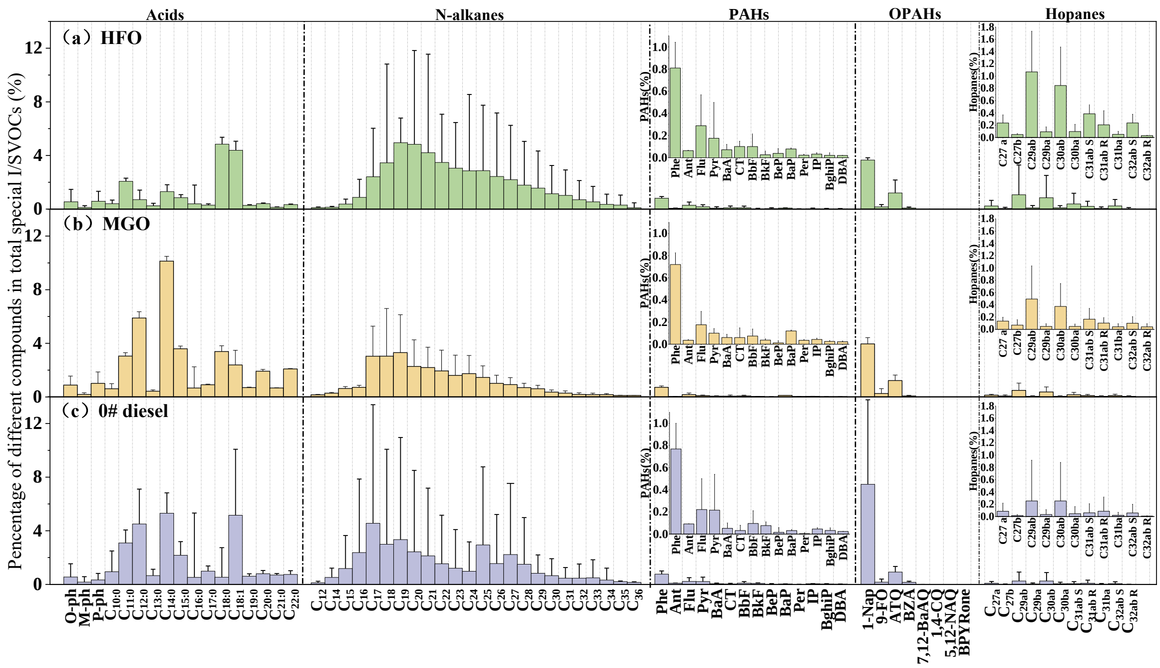

Figure 4 Profiles of I/SVOCs in ship exhausts under different fuels

(7) Line 592: The hopanes is not discernible in Fig. 6.

Reply: Sorry for the ambiguity regarding the hopanes in Figure 6. Due to their significantly lower levels relative to other markers, the hopanes were not easily distinguishable in this figure. Consequently, we have adjusted the color scheme to enhance readability and applied a logarithmic scale to the Y-axis. Moreover, the figure has been revised to illustrate the volatility distributions of I/SVOCs based on the Volatility Basis Set (VBS) framework from different fuels, enhancing its clarity and precision.

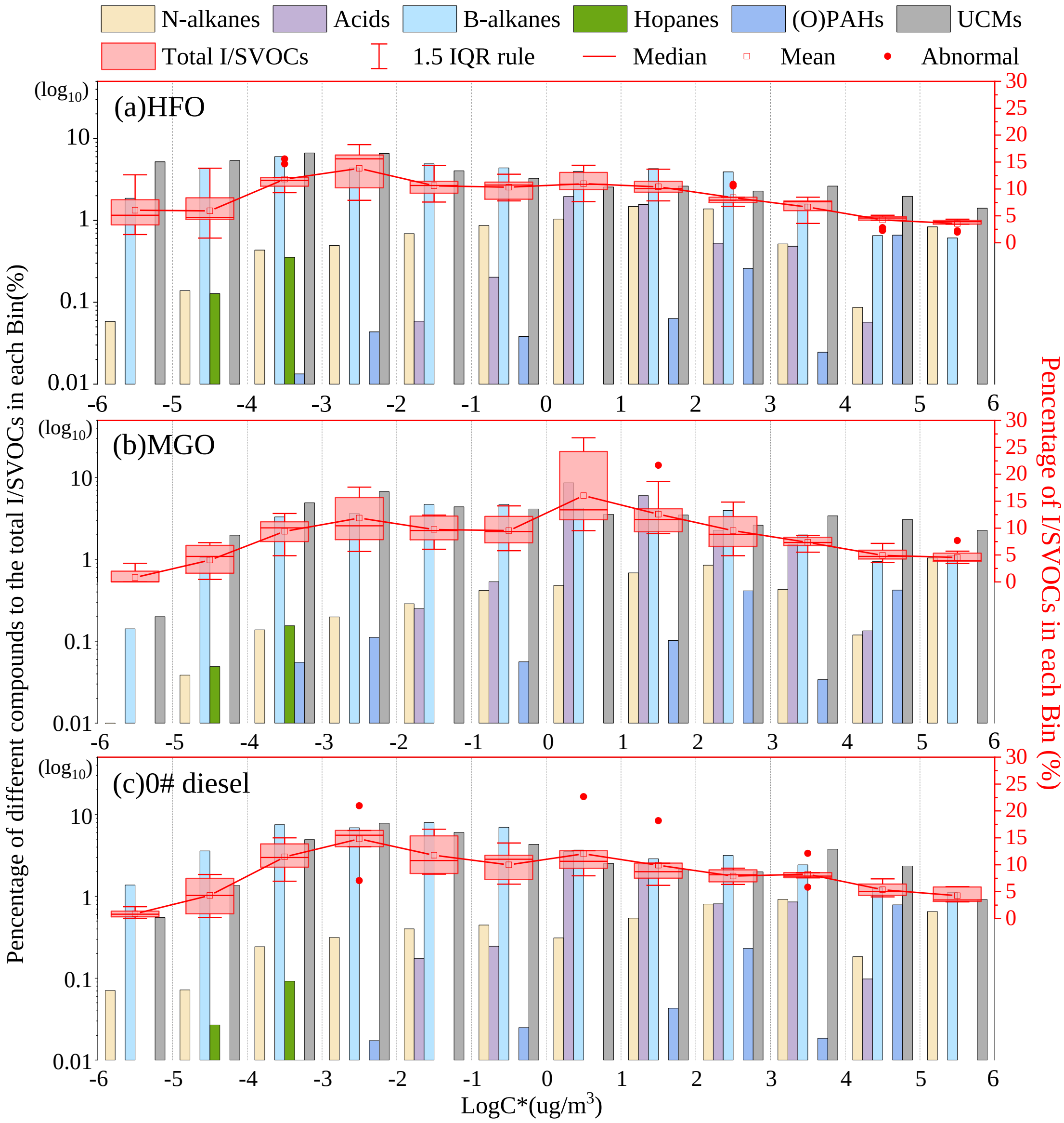

Figure 6 The volatility distributions of I/SVOCs based on the volatility basis set (VBS) framework from different fuels

Figure 6 in line 597. Hapones should be hopanes. It is necessary to improve the readability. The authors can try to use the log scale. More details need to be added in the figure caption as well.

Reply: Thanks very much for your suggestions. The term "Hapones" has been corrected to "hopanes". We recognize the advantages of employing a logarithmic scale for data presentation and have consequently adjusted the Y-axis to adopt a logarithmic scale. Moreover, the figure has been revised to illustrate the volatility distributions of I/SVOCs based on the Volatility Basis Set (VBS) framework from different fuels, enhancing its clarity and precision.

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