

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 2#

In this study, the authors estimated the emission factors of speciated and unspecified I/SVOCs from ocean-going vessels and inland cargo ships with different fuel types, engine types and operating conditions. They found that the emission factors of I/SVOCs increased as the sulfur content in fuels decreased. Although the methods, analysis, and results are not particularly novel which was built on previous studies of IVOCs emissions from vehicles (Zhao et al., 2015, 2016), the measurement data presented in this study are very helpful for estimating SOA formation from ship exhausts. I recommend the publication of this work after the authors could address my comments below.

Major comments:

(1) My major concern lies in the representation of volatility distributions. Though I totally understand that the authors classified volatility based on carbon numbers (Lines 188-194), following the methods in Zhao et al. (2015, 2016), I strongly recommend the authors can plot volatility distributions using the volatility basis set (VBS) framework (Donahue et al., 2006), similar to Figure 2 in Zhao et al. (2015) and Figure 4 in Zhao et al. (2016). The VBS framework is widely used in air quality models for simulating SOA formation. Representing volatility distribution within this framework would provide essential information for inputting the measured data into chemical transport models in future studies.

Reply: We sincerely appreciate your constructive comments regarding the representation of volatility distributions in our manuscript. Based on the recommendations, we utilized the effective saturation concentration (C^*) of n-alkanes in each bin as a proxy for the volatility of intermediate and semi-volatile organic

compounds (I/SVOCs) to derive their volatility distribution. The improved Figure 6, generated using the VBS framework, is presented below. The associated text has also been updated in lines 601-625 in the revised manuscript. The pertinent revised content is outlined as follows:

In order to figure out the volatility distributions of detailed chemical compositions of I/SVOCs from different fuels. The average volatility distributions of UCM, b-alkanes, n-alkanes, PAHs, acids and hopanes based on the volatility basis set (VBS) framework are given in Figure 6. Results revealed that the volatility distributions of UCM exhibited distinct bimodal characteristics, with peak values occurring at $\log C^* = -3$ to -2 and $\log C^* = 3$ to 4 . Notably, the concentration was more pronounced in the low-volatility region. Moreover, the bimodal characteristic of UCM in 0# diesel was more pronounced compared to HFO and MGO. Additionally, HFO exhibited a higher proportion of low-volatility UCM relative to 0# diesel and MGO. The volatile distributions of n-alkanes exhibited a bimodal structure, with peaks occurring at $\log C^* = -4$ to -2 and $\log C^* = 5$ to 6 , respectively. Furthermore, from HFO to MGO and finally to 0# diesel, the VBS peak of n-alkanes progressively shifted towards the higher volatility range. This shift could be attributed to the distinct characteristics of these fuels, where MGO and 0# diesel had lower boiling points and contained fewer carbon atoms in their hydrocarbon chains compared to HFO (Liu et al., 2022). The volatility distributions of other specific I/SVOCs were consistent with their molecular sizes. (O)PAHs emitted from ships were predominantly small molecules with high volatility, primarily enriched in the $\log C^*$ range of 4 to 5 . Acids were mainly concentrated in the higher volatility bins ($\log C^* = 0$ to 5), whereas hopanes exhibited a primary concentration in the lower volatility intervals. 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.

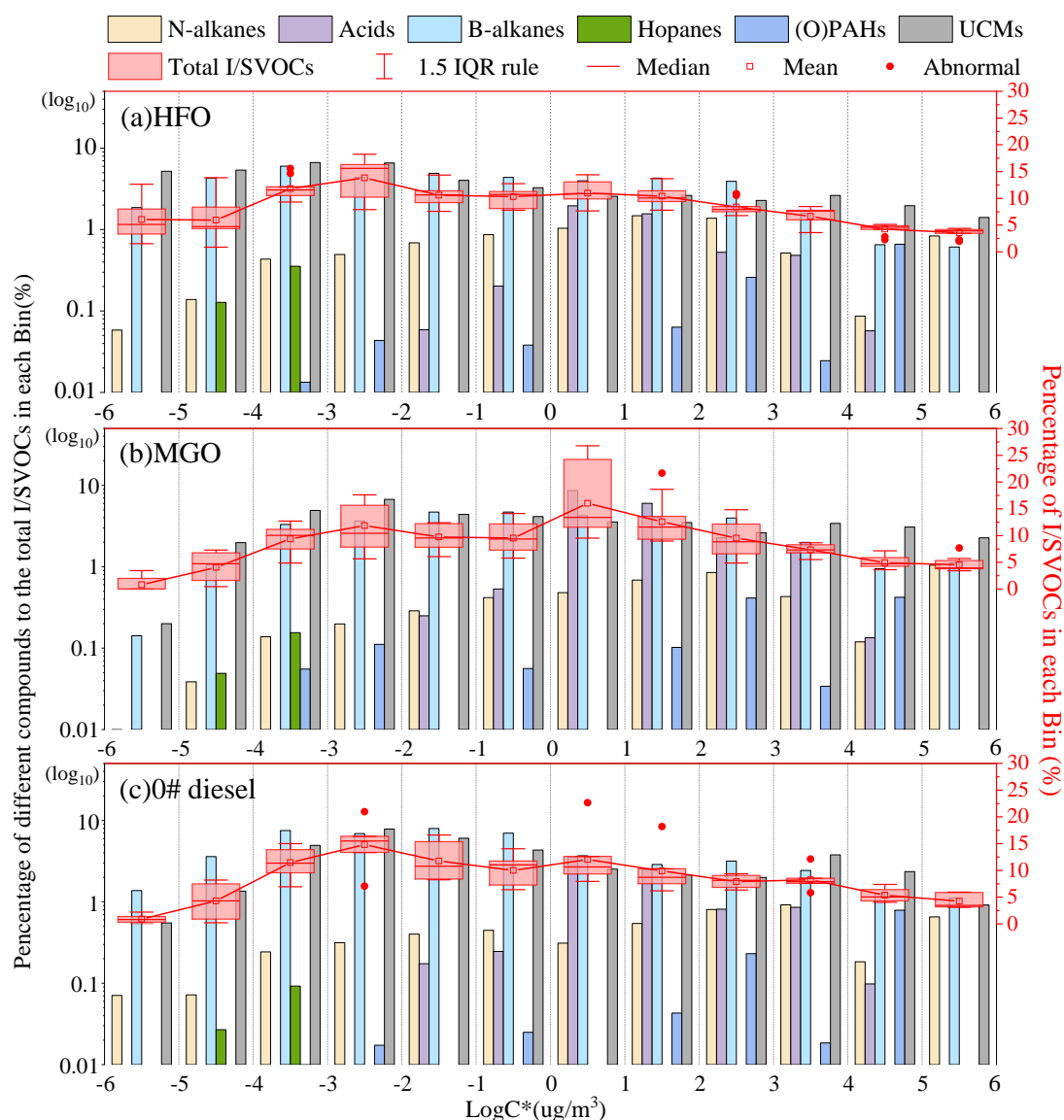


Figure 1 The volatility distributions of I/SVOCs based on the volatility basis set (VBS) framework from different fuels

(2) My second major concern is related to the method used for calculating SOA formation in Section 2.5 and the SOA formation potential (SOAFP) showed in Fig.7. As shown in Eq.3 in Line 218, the formed SOA is a function of reacted precursor concentration [HC], oxidation time, and assumed OH concentrations. I am very confused how the authors derived the SOAFP in Figure 7 without providing details on the amount of precursor reacted, oxidation time, or OH concentrations. Please refer to Figure 5 in Zhao et al. (2016) and include more detailed information on how SOA formation was calculated in this study. Furthermore, it would be helpful to compare the SOA production from ship exhausts with previous studies (Morino et al., 2022; Zhao et

al., 2015, 2016). Is the SOA production from ship exhaust higher or lower than SOA formed from vehicle exhaust?

Reply: Thank you for your insightful comments. We appreciate your attention to the details of the SOA formation calculation in Section 2.5 and the SOA Formation Potential (SOAFP) presented in Figure 7. In response to your concern, we acknowledge that the calculation of SOA in Figure 7 may lack clarity, particularly due to the omission of explicit information on the amount of precursor reacted, oxidation time, and OH concentrations.

The equation utilized for the estimation of SOA production via IVOCs in this study is as follows:

$$\Delta SOA_{IVOCs} = \sum_j [HC_j] \left(1 - e^{-k_{OH,j} [OH] \Delta t}\right) \times Y_j$$

where $[HC_j]$ represents the concentration of IVOCs species involved in the reaction, Y_j is the yield coefficient of IVOCs species, and k_{OH} is the OH reaction rate constant of precursor j at 25°C ($\text{cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$); $[OH]$ is the OH concentration ($\text{molecules} \cdot \text{cm}^{-3}$), which is assumed in this study to be $1.5 \times 10^6 \text{ molecules} \cdot \text{cm}^{-3}$; Δt is the photochemical age (h); and Y_i is the SOA mass yield of precursor j . And the OH reaction rate constants ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) and SOA yields used in this study were the same as Zhao et al. (2016), which reacted (Δt) after 48 h photo-oxidation at the OA concentration of $9 \mu\text{g}/\text{m}^3$, as explained in detail in Table S5 and Table S6.

The refined description of the SOAFP estimation method is presented in lines 229-238 of the revised manuscript.

where $[HC_j]$ represents the concentration of IVOCs species involved in the reaction, Y_j is the yield coefficient of IVOCs species, and k_{OH} is the OH reaction rate constant of precursor j at 25°C ($\text{cm}^3 \cdot \text{molecules}^{-1} \cdot \text{s}^{-1}$); $[OH]$ is the OH concentration ($\text{molecules} \cdot \text{cm}^{-3}$), which is assumed in this study to be $1.5 \times 10^6 \text{ molecules} \cdot \text{cm}^{-3}$; Δt is the photochemical age (h); and Y_j is the SOA mass yield of precursor j . And the OH reaction rate constants ($\text{cm}^3 \text{ molec}^{-1} \text{ s}^{-1}$) and SOA yields used in this study were the

same as Zhao et al. (2016), which reacted (Δt) after 48 h photo-oxidation at the OA concentration of $9 \mu\text{g}/\text{m}^3$, the specific values of Y_j and k_{OH} under different environmental conditions were obtained from the simulation study of smoke chamber (Table S5-S6).

Furthermore, to enhance the comparative analysis, we have incorporated a detailed discussion that contrasts the SOA production from ship exhausts with findings from previous studies (Lines 647-655).

Previously, there has been limited research on SVOCs and their SOAFP, resulting in a scarcity of relevant comparative studies. Compared to diesel vehicles ($430 \pm 574 \text{ mg (kg fuel)}^{-1}$), gasoline vehicles ($39 \pm 79 \text{ mg (kg fuel)}^{-1}$) and nonroad machinery ($424 \pm 138 \text{ mg (kg fuel)}^{-1}$) reported in previous IVOC studies (Zhao et al., 2015; Zhao et al., 2016; Qi et al., 2019), SOA emissions of total I/SVOCs from ships using 0# diesel exhibit significantly higher formation potential ($634 \text{ mg (kg fuel)}^{-1}$). This discrepancy highlights critical knowledge gaps in current assessments, where the scarcity of research on SVOCs and their SOAFP has led to incomplete comparisons.

Specific comments:

The writing quality needs some improvement. Several sentences would benefit from commas instead of periods. For instance, a comma should be used after "detection methods" in Line 449. I also recommend that the authors pay closer attention to the use of conjunctions throughout the manuscript to enhance readability and clarity.

Reply: We appreciate your valuable feedback. We have conducted a thorough review of the manuscript and significantly enhanced its writing quality by refining sentence structures and improving readability. Specifically, we have replaced periods with commas where appropriate, such as after "detection methods" in line 478, to maintain the continuity of sentence. Furthermore, we have revised the use of conjunctions throughout the manuscript to ensure a smoother flow and greater clarity. All these modifications have been integrated into the revised manuscript.

Reference

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Qi, L. J., Liu, H., Shen, X. E., Fu, M. L., Huang, F. F., Man, H. Y., Deng, F. Y., Shaikh, A. A., Wang, X. T., Dong, R., Song, C., and He, K. B.: Intermediate-Volatility Organic Compound Emissions from Nonroad Construction Machinery under Different Operation Modes, *Environ. Sci. Technol.*, 53, 13832-13840, 10.1021/acs.est.9b01316, 2019.

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