Referee 2#

Thanks very much for your constructive comments. So far, we have revised the manuscript accordingly. Our point-by-point responses (in black) to each comment are listed below. And the manuscript also has been improved. Please see the manuscript for details.

Major comments

The discussion does not make a connection between the 106 VOCs measured in this study and the ozone and SOA FP. The manuscript needs to answer the questions:

a) Why measure these specific 106 VOCs? Does this subset of VOCs cover the major species observed in previous mass balances?

b) Why assume that these VOCs can explain the ozone and SOA FP? If the SOA FP of 5 unmeasured VOCs was 100x larger than these 106, then the results of the study would not be representative.

c) How do different environmental conditions influence the accuracy of the SOA and ozone formation?

These are questions which have been considered by previous studies, and the authors should be able to address them relatively easily by adding citations and comments in the introduction, methods, and discussion sections.

Reply: Thanks for your comment.

a) There are thousands of VOC species emitted from exhausts. We can't identify and quantitate all the VOCs. However, the measured VOCs in this study can be considered as the main VOC components and basically reflect the emission conditions of ship exhaust. These specific 106 VOCs, including 11 oxygenated volatile organic compounds (OVOCs), 17 aromatics, 29 alkanes, 11 alkenes, 35 halohydrocarbons and 4 other species were tested according to comprehensive consideration of literatures and determination standards of VOCs, which are showing as follows:

Firstly, alkanes, alkenes, aromatics, and OVOCs are mainly concerned from previous studies from ship exhausts, such as 29 alkanes, 19 alkenes, acetylene, 16 single-ring aromatics, and 23 OVOCs from Huang et al. (Huang et al., 2018), 13 OVOCs, 16 aromatics, 11 alkanes and 6 C4-C8 HCs from Agrawal, H., et al. (Agrawal et al., 2010), 29 alkanes, 21 alkenes, 1 alkyne and 17 aromatics from Wu et al. (Wu et al., 2020). These VOCs have been proved and recognized as the main VOC species from ship exhausts. Our measured VOCs contain almost all of these VOC species, which are also easy to be compared and cited for peers. Even though we can't give

accurate proportion of the measured VOCs to total VOCs, results from previous studies about motor vehicles show that the identified 57 VOCs (28 alkanes, 15 alkenes, 11 aromatics, and 5 OVOCs) could explain more than 62% of the total nonmethane hydrocarbons (NMHC) (Hung-Lung et al., 2007), and the identified 53 individual VOCs accounted for similar to 80% of the NMHCs from light-duty vehicles, with the most abundant VOCs were ethene (13.8%), acetylene (9.0%), isopentane (7.1%), toluene (5.6%), and n-butane (5.5%)(Araizaga et al., 2013). Therefore, the measured 106 typical VOCs in this study are the major species and have been covered almost all of previous observed VOC species.

Secondly, the detection method used in this study is from USEPA TO-15. This method documents sampling and analytical procedures for the measurement of subsets of 97 VOCs that are included in the 189 hazardous air pollutants (HAPs) listed in Title III of the Clean Air Act Amendments of 1990. These 106 VOCs are measured by Gas Chromatography/Mass Spectrometry (GC/MS) according to USEPA TO-15, which is a very mature and accurate method. Almost half of the 97 VOCs are included in our measurement, especially for halohydrocarbons and aromatics, which can reflect the emission of hazardous VOCs to a certain extent. Besides, VOCs involved in measurement standard for source emission that of most concern in China are also included in this study.

Thirdly, generally speaking, alkanes, alkenes, aromatics and carbonyls with carbon number > 6 in VOCs can form SOA (Grosjean, 1992;Grosjean and Seinfeld, 1989). Previous studies find that aromatics and alkanes contribute most to SOAFP from diesel exhaust, with single-ring aromatics such as toluene, benzene and xylene et al. are the most contributors (Gentner et al., 2012;Che et al., 2023). As for O_3, alkenes, aromatics and OVOCs contribute most to OFP (Che et al., 2023). Wang et al. point out that naphthalene, butene, toluene, benzene, and dodecane etc. are the most contributors to OFP from exhausts of diesel trucks (Wang et al., 2020). Almost all of these VOC species have been identified in our study.

b) To be honest, these measured VOCs in this study couldn’t explain the actual OFP and SOAFP from VOCs. Some potential OFP and SOAFP precursors such as formaldehyde, acetaldehyde and benzaldehyde were missing that could led to underestimate of OFP and SOAFP. However, as mentioned above, the measured VOCs can be considered as the main ozone and SOA precursors and basically reflect the OFP and SOAFP conditions of ship exhaust. These data can also be used for comparison

with other studies due to the similar detected VOC species. What's more, based on the typical concerned VOCs, it is intuitive to figure out the impact of the implementation of ship emission control policies on OFP and SOAFP, which is meaningful for further policy formulation.

c) In this study, OFP is estimated using the maximum incremental reactivity (MIR) coefficient method, which represents the maximum contribution of VOC species to the underground O_3 concentration under optimal conditions. (Carter, 1994;Carter, 2010) While SOAFP is calculated using the SOA yields under both high-NO_x and low-NO_x conditions. (Ng et al., 2007) OFP and SOAFP given here are the direct estimated contributions of VOCs from ship exhausts, just like other studies to figure out the effect of fuel switching (Wu et al., 2019;Wu et al., 2020). However, unfortunately, we can't evaluate the accurate contributions of VOCs to SOAFP and OFP in actual atmospheric environment here because they are affected by complicated conditions, such as local temperature, lighting condition, other precursors, atmospheric oxidation, etc., which usually needs to further simulate with air quality models. (Fu et al., 2023)

Relevant contents have been added in lines 219-222 in the revised manuscript.

Minor comments

The abstract summarizes results for CCS and OGVs but not ICS. Please add ICS to the abstract, which will help readers better anticipate the contents of the work.

Reply: Thanks for your comment. ICS has been added in the abstract, showing as follows:

Results showed that emission factor of VOCs (EF_{VOCs}) varied largely from 0.09 to 3.01 g kg^{-1} fuel, with domestic coastal cargo ships (CCSs) had the highest level, followed by inland cargo ships (ICSs) and ocean-going vessels (OGVs).

I find Figure S1 quite valuable and recommend moving the information to the manuscript. However, please find a way to add error bars (or some other measure of variability, like a second Y axis of "standard deviation") to the plot. Please modify the figure caption to explain how the data from different ships were summarized -- it looks like the authors are plotting the mean values? Please comment on the variability between ships? (In contrast, Figure S2 appears to be a summary of Figure S1 and I would leave it in the SI.)

Reply: Thanks for your comment. Figure S1 has been updated with adding the error bars as follows and moved to the manuscript as Figure 2. What needs to be explained to the review is that due to the consideration of costs of the VOCs testing and difficulty of ship exhaust sampling, only 15% of the samples were parallel sampled. Results of the parallel samples showed that the average ratio of Standard Error of Mean (SEM) to the total EF_{VOCs} was 20.8%, which was thought to be acceptable. Then error bars were added in Figure 2 according to both actual standard deviation and this average ratio. These detailed data were also given in Table S5 as sampling errors.

Updated Figure 2 presents the detailed EFs of VOC components for all the test ships under different operating conditions with different fuels. They are not the mean values. While updated Figure S1 are average EFs of VOCs components and their mass fractions for different ships with different fuels. These average EF_{VOCs} were calculated through unweighted average of different actual operating modes.

Brief variations of the total EF_{VOCs} for all the test ships are given in the second paragraph, Section 3.1. Because the EF_{VOCs} is influenced by multiple factors, such as ship type, engine type, operating mode and fuel type, then more detailed discussions about the differences under these factors are presented in Section 3.2.

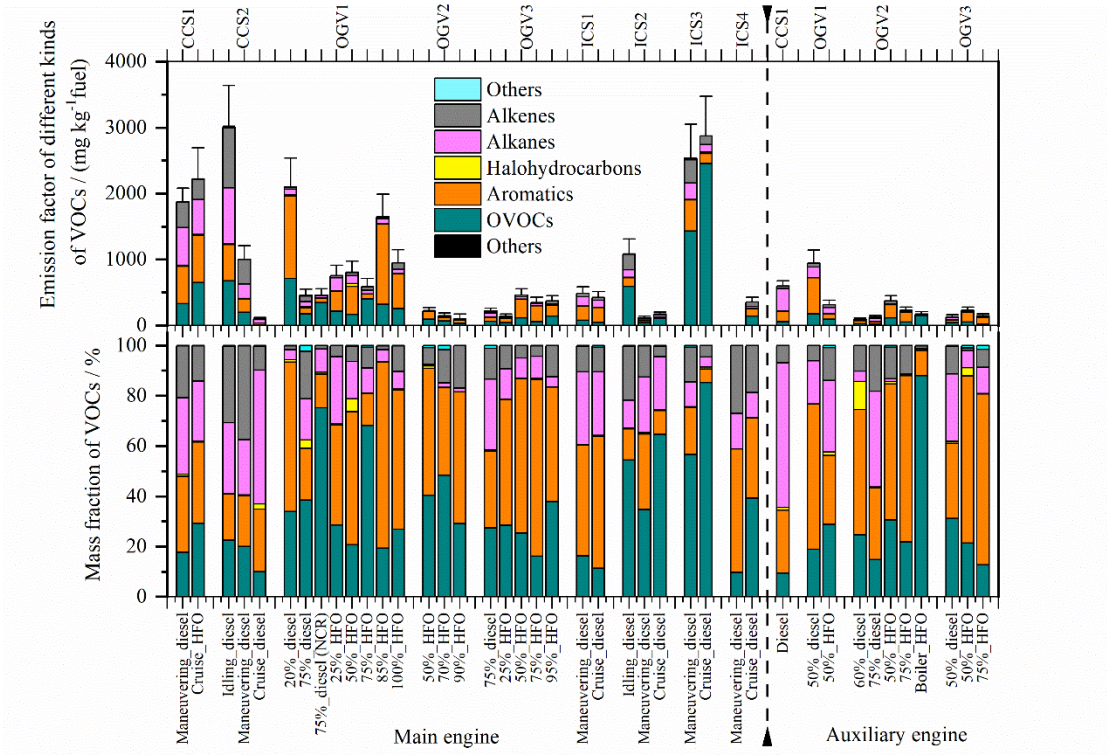

Figure 2 EFs of VOC components and their mass fractions

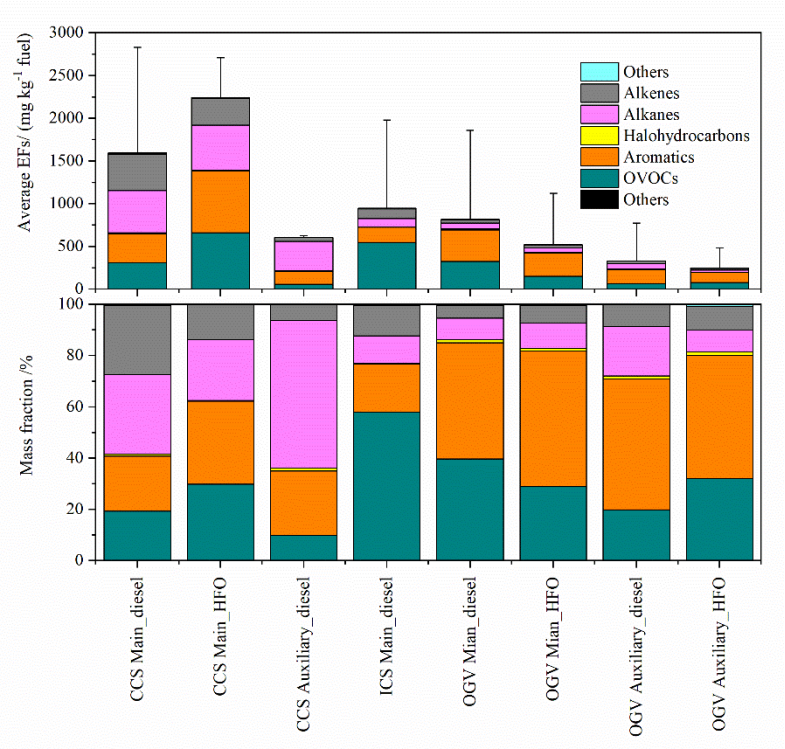

Figure S1 Average EFs of VOCs components and their mass fractions under different ships with different fuels. (These average EF_{VOCs} were calculated through unweighted average of different actual operating modes)

In contrast, Figure 3 is very detailed and not really digestible to the reader. I would move this figure to the SI, and report all data as downloadable data files so that readers requiring this level of detail can use it. I cannot read the x axis of Figure 3. Consider plotting this instead as "mass fraction of Alkanes" with subcategories of the measured alkanes (i.e. subdivide Figure S2) instead.

Reply: Thanks for your comment. Figure 3 has been updated as Figure 4 in the revised manuscript and shown as follows. Because halohydrocarbons, tetrahydrofuran, carbon disulfide, and 1,4-dioxaneand only account for very small mass fractions of the total test VOCs (0.55%-3.06% of total VOCs), they are removed from Figure 4 to enhance the readability for reader. While detailed mass fractions of all the test VOC species in this study also have been added in Table S7 as the reviewer suggested. However, profile of VOCs is a very important characteristic of ship exhausts, which can show the differences of VOC mass fractions intuitively among different ships with different fuels, and therefore we still want to keep this figure in revised manuscript.

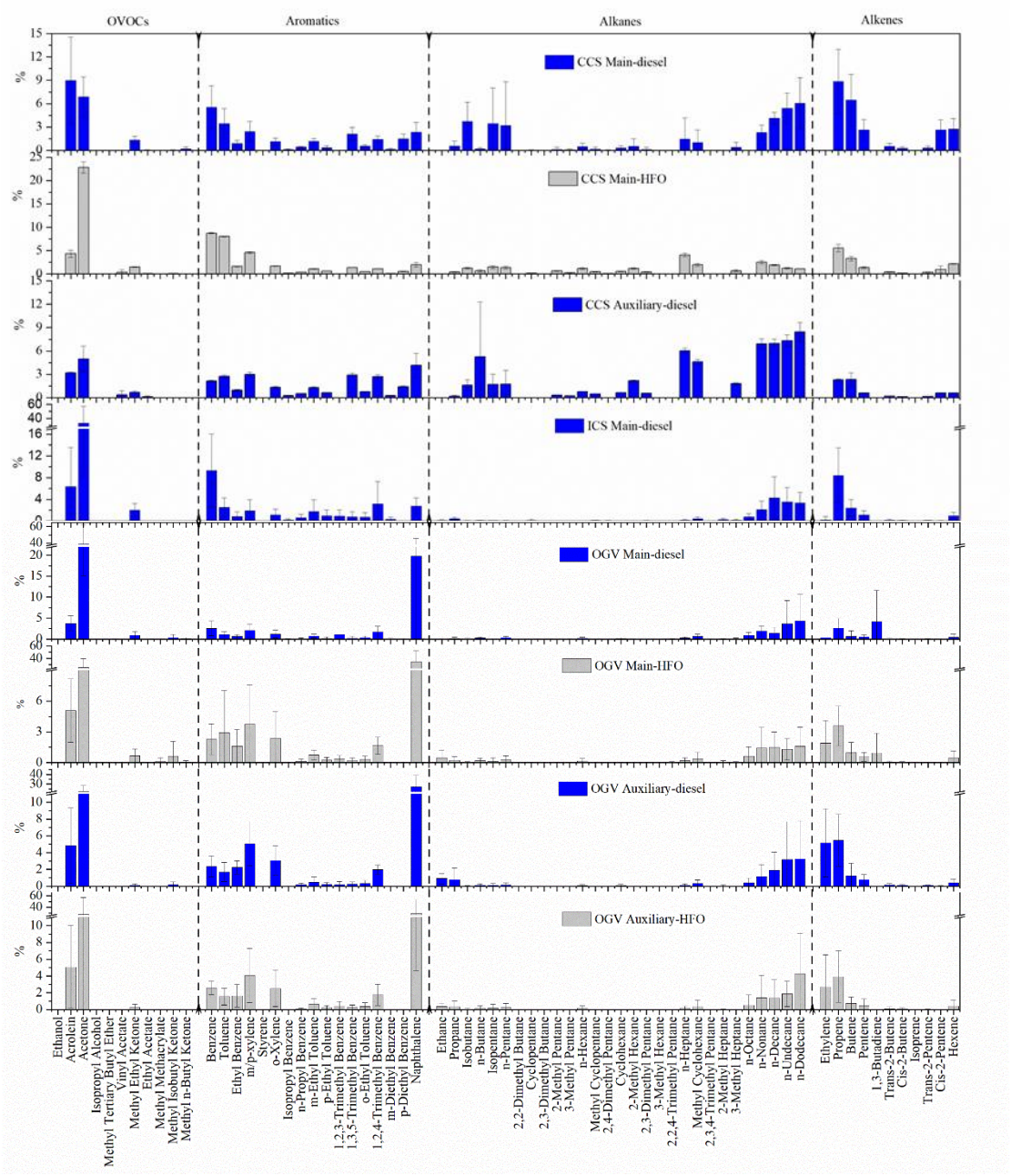

Figure 4 Mass fractions of individual VOCs from test ships under different engine types and fuels (except halohydrocarbons, tetrahydrofuran, carbon disulfide, and 1,4-dioxaneand due to their very small mass fractions)

As noted above, the introduction should mention and cite studies which explain the connection between VOC chemistry and SOA formation potential.

Reply: Thanks for your comment. Relevant contents have been added in lines 70-81 in the revised manuscript as follows:

Generally speaking, alkanes, alkenes, aromatics and carbonyls with carbon number > 6 in VOCs can form SOA (Grosjean, 1992;Grosjean and Seinfeld, 1989).

While O_3 is formed from the photochemical interactions of volatile organic VOCs and oxides of nitrogen (NO_x), with alkenes having the highest Maximum Incremental Reactivity (MIR), followed by aromatics and OVOCs (Carter, 1994). Typical aromatics, alkenes, and alkanes are the most concerned VOCs from diesel exhausts. For example, Previous studies find that aromatics and alkanes contribute most to SOAFP from diesel exhaust, with single-ring aromatics such as toluene, benzene and xylene et al. are the most contributors (Gentner et al., 2012;Che et al., 2023). Wang et al. (2020) point out that naphthalene, butene, toluene, benzene, and dodecane et al. are the most contributors to OFP from exhausts of diesel trucks.

The introduction should introduce the concepts of IVOCs and OVOCs, which appeared in line 169 without definition. Especially since these definitions are different from the common IVOC, SVOC, LVOC categories.

Reply: Thanks for your comment. IVOCs is intermediate volatile organic compounds, while OVOCs is oxygenated volatile organic compounds. Since IVOCs and OVOCs reported by Liu et al. (2022) are not the focus of this study. The ambiguous sentence as following has been deleted in the revised version.

I/OVOCs samples were obtained by automatic sampler to get IVOCs and OVOCs samples that had been reported in other study (Liu et al., 2022).

Line 142, for the reader's benefit, please add the range of years meant by "older", based on Table 1, after making this subjective comment.

Reply: Thanks for your comment. The ranges of years have been added in lines 174-176 in the revised manuscript as following:

It's worth noting that the ocean-going vessels were newly constructed ships, while the inland cargo ships had older engines (6 to14 years) compared with other types of ships (less than 10 years).

Table 1, which engines were sampled? Note this in the caption, please.

Reply: Thanks for your comment. VOCs from all the engines listed in Table 1 had been collected in this study. The introduction has been added in lines 206-207 in the revised manuscript.

VOCs samples were collected by summa canister from both main engines and auxiliary engines of all the ships listed in Table 1.

Line 323, "emission of EF" change to "the EF" (EF is "emission" already)

Reply: Thanks for pointing it out. The sentence has been revised in the improved manuscript in in lines 377-379.

As mentioned before, fuel type could influence the EF_{VOCs} significantly (Wu et al., 2019;Wu et al., 2020), which also would be one of the most important influence factors in the future under the background of increasingly strict ship oil policy.

Figure 4 caption should point to the section where the source ratios are cited, please.

Figure 4: I do not disagree with the authors that the B:T:E ratios could be used as tracers for ship emissions. But please add a box to highlight the region you are suggesting. Specify the recommended region explicitly in the text for clarity.

Reply: Thanks for your comment. Figure 4 and the caption have been revised and improved as follows.

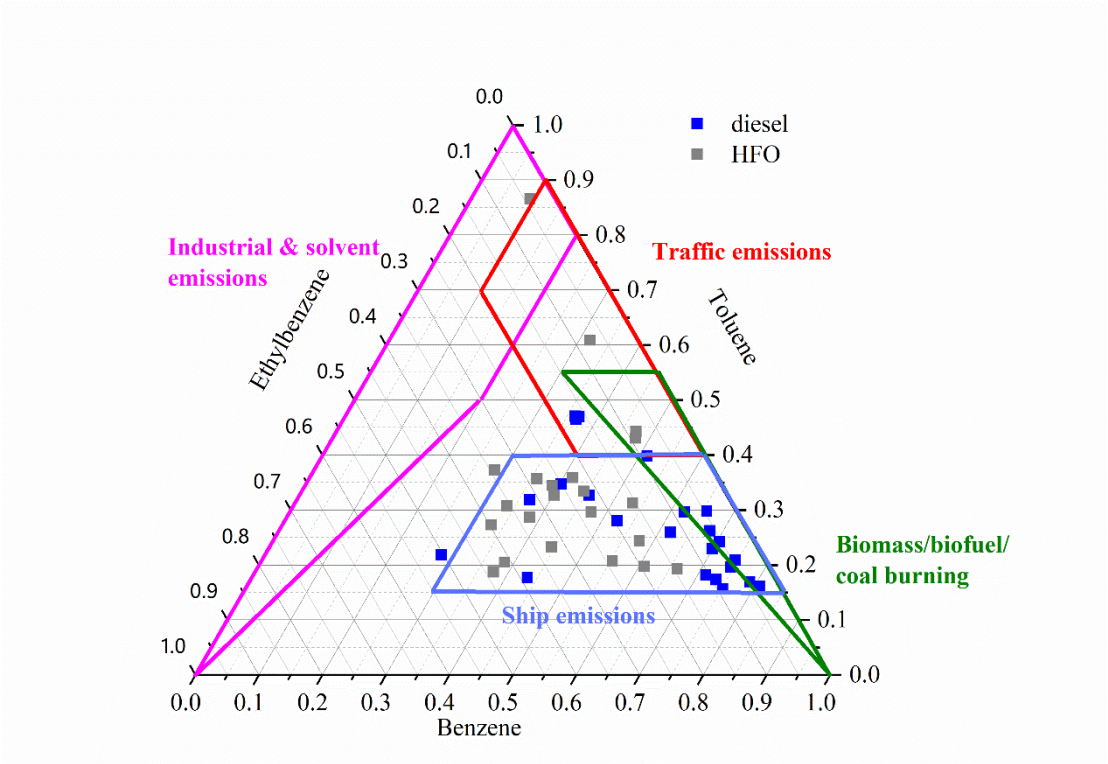

Figure 4 Relative proportions of benzene, toluene and ethylbenzene from the ship exhausts. B:T:E ratios from other sources were cited from Zhang et al. (2016b) that summarized 28 examples from biomass burning, 35 examples from biofuel burning, 17 examples from coal burning, 11 examples from diesel vehicle exhaust, 31 examples from gasoline vehicle exhaust, 24 examples from gasoline evaporation, 25 examples

from roadside or tunnel tests, and 66 examples from industrial processes and solvent applications.

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