Response to the reviewer's comments

"Dramatic increase in reactive VOC emissions from ships at berth after implementing the fuel switch policy in the Pearl River Delta Emissions Control Area" *by* Zhen-Feng Wu et al.

Reviewer #1

Ship emissions as important sources of air pollution at the coastal cities have raise widespread attention and their emission characteristics have been consistently studied by many researchers. Wu et al. presents the changes of VOC emissions from ships at berth after implementing the fuel switch policy at the ECA. They find that the apparent increase of reactive species in the VOC emissions due to the strategy and their second formation potentials including O3 and SOA are also estimated. This study is well motivated for the effect evaluation of emission control strategies. However, despite the potential meaning of results from this study, the presentation of this study needs be improved to a large extent, especially for the writing.

Major Comments

1. Description of VOCs. The author measured 68 VOC species used by GC-MS/FID, but the author is very chaotic for the description of VOC species in this manuscript, using the term NMHCs or VOCs in different sentences. Which one is the accurate expression? Generally, NMHC concentrations are determined by subtracting the amount of CH4 constituents from the THC measured by FID. The samples collected in canisters and analyzed by a preconcentrator coupled to GC-MSD/FID are speciated VOCs. Could the PEMS system measure THC and CH4 concentrations?

Reply: Thanks. Yes, generally NMHC concentrations are determined by subtracting the amount of CH_4 constituents from the THC measured by FID. In this study, we collected samples in canisters and measured 68 VOC species by a preconcentrator coupled to the GC-MSD/FID. We further measured CH_4 in the canister samples by a gas chromatograph (Agilent 6980GC, USA) with a flame ionization detector and a packed column (5A molecular sieve 60/80 mesh, 3m × 1/8 in.). We did not report CH_4 in the manuscript since our concern is focused on photochemically reactive species. As the 68 VOC species we determined are C2-C12 hydrocarbons, sometimes we just used the term "NMHC" when referring to the 68 VOCs in our manuscript. To avoid confusion, in the revised manuscript we have replaced all "NMHCs" with "VOCs".

2. More information about sampling and analysis is needed, such as sampling flow, sampling time, sampling temperature, the auxiliary load, the devices used for conventional pollutants, and the standard gas for VOC measurement.

Reply: Thanks. As suggested, in the revised manuscript we have added more information about sampling flow, sampling time, devices used for conventional pollutants and standard gas for VOCs measurement as below:

"The ship exhaust first entered a Dekati® ejector dilutor (DI-1000, Dekati Ltd., Finland) from the sampling nozzle and then was spilt into four parts after being diluted with clean air: one part was for air sampling with 2 L canisters and 4 L Teflon bags for 3-5 min after passing through a filter; two other parts were for collecting $PM_{2.5}$ samples with 47 mm Teflon filters (Whateman, Mainstone, UK) and 47 mm quartz fiber filters (Whateman, Mainstone, UK), respectively, at a flow of 16.7 L min^{-1} for 20-30 min, after the diluted exhaust was mixed well in a stay cabin, and then passing through a $PM_{2.5}$ separator; and the last part was the vent. Before dilution, the concentrations of CO_2, CO, SO_2 and NO_x in the ship exhaust were directly measured by a flue gas analyzer (F-550, WOHLER, Germany) while air samples were also collected simultaneously by a 2L canisters and a 4L Teflon bags." (lines 120-127 in the revised manuscript).

We have added more information about the VOCs standards. "The calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 NMHCs including 15 AHs) and TO-14 standard mixture (39 compounds) from Spectra Gases Inc., NJ, USA to 0.5, 1, 5, 15 and 30 ppbv. More details about the analysis are described elsewhere (Zhang et al., 2013; 2015; Yang et al., 2018)." Line 131-138.

Besides, we have also added sampling temperature and the auxiliary load in Table S1 in the supporting information as showed below:

Table S1. More information during sampling.

NO	Auxiliary engine

	Sampling temperature (℃)	Power（kW）	Amount	Condition	Engine loads (%)	Fuel consumption rate(t*d^{-1})
Coastal vessels (before IFSP)						
A	17	1760	2	Off	-	-
		1320	1	On	53	3.0
B	32	2045	2	Off	-	-
		2045	1	On	40	4.1
C-1	34	1760	2	Off	-	-
		1320	1	On	55	4.0
D-1	29	660	1	Off	-	-
		660	2	On	34	2.2
Coastal vessels (after IFSP)						
E	25	200	1	Off	-	-
		200	1	On	39	0.4
F	21	200	2	Off	-	-
		200	1	On	50	0.5
C-2	29	1760	2	Off	-	-
		1320	1	On	52	3.5
G	31	500	2	Off	-	-
		500	1	On	65	1.8
D-2	31	660	1	Off	-	-
		660	2	On	37	2.4
River vessels						
H	25	76	1	Off	-	-
		144	1	Off	-	-
		144	1	On	40	0.3
I	32	73.5	2	On	40	0.3
J	38	58	1	Off	-	-
		58	1	On	32	0.1
K	35	58.8	1	Off	-	-
		58.8	1	On	35	0.1

Reference

Yang, W. Q., Zhang, Y. L., Wang, X. M., Li, S., Zhu, M., Yu, Q. Q., Li, G. H., Huang, Z. H., Zhang, H. N., Wu, Z. F., Song, W., Tan, J. H., and Shao, M.: Volatile organic compounds at a rural site in Beijing: influence of temporary emission control and wintertime heating, Atmos. Chem. Phys., 18, 12663-12682, https://doi.org/10.5194/acp-18-12663-2018, 2018.

Zhang, Y. L., Wang, X. M., Barletta, B., Simpson, I. J., Blake, D. R., Fu, X. X., Zhang, Z., He, Q. F., Liu, T. Y., Zhao, X. Y., and Ding, X.: Source attributions of hazardous aromatic hydrocarbons in urban, suburban and rural areas in the Pearl River Delta (PRD) region, J. Hazard. Mater., 250, 403-411, https://doi.org/10.1016/j.jhazmat.2013.02.023, 2013.

Zhang, Y. L., Wang, X. M., Zhang, Z., Lv, S. J., Huang, Z. H., and Li, L. F.: Sources of C_2-C_4 alkenes, the most important ozone nonmethane hydrocarbon precursors in the Pearl River Delta region, Sci. Total Environ., 502, 236-245, https://doi.org/10.1016/j.scitotenv.2014.09.024, 2015.

3. As mentioned by the author, the fuel composition is a very important factor for VOC profiles, which is a possible reason for the different VOC compositions of the tested ships with the previous results. Then, is there apparent difference of VOC compositions for tested ships using four different fuels? What is the trendy of the VOC emissions when correlating the diesel composition?

Reply: We simply measured solvent-extractable fraction of the oils by GC-MSD as some fuels are very sticky residue oils before the fuel switch policy. Nonetheless, as showed in Figure S1, we could see that after the implementing the fuel switch policy, there is a tendency to have more factions of low molecular weight hydrocarbons (or hydrocarbons having lower carbon numbers). As for ship C, the residual oil used before the fuel switch policy was mainly composed of saturated C_{11}-C_{36} alkanes; after implementing the new policy, however, the residue oil used by ship C was replaced with diesel oil with no peaks after heptacosane (C27) in its total ion chromatographs. For ship D, before implementing the fuel switch policy it used residual oil slightly different from that used by ships A, B and C in its compositions, particularly in relative high fractions of naphthalene and methylnaphthalenes apart from saturated alkanes. After implementing the fuel switch policy, ship D instead used low-sulfur heavy oil. Although the responses of the most hydrocarbons did not change very much, the responses of low carbon number species, including naphthalene, tridecanes and methylnaphthalenes, became relatively higher, and lower carbon number species such as indene (C8) were also detected. As a result, we found the mass percentages of $< C_6$ VOCs (VOCs with carbon numbers below 6) in the total VOCs in ship exhaust increased from 8.5%-27.3% to 44.4%-86.6% after implementing the fuel switch policy. As described in the manuscript, we noticed that the fuel used by the ships became more abundant in low molecular weight fractions, but we did not conduct a comprehensive analysis of the fuel compositions and we do not know if the fuels we samples are representative enough, so we feel it would be inappropriate to go further saying more in this aspect. As a matter of fact, after we report our results to local administrations, they determined to start a full-scale survey about fuels used by ships.

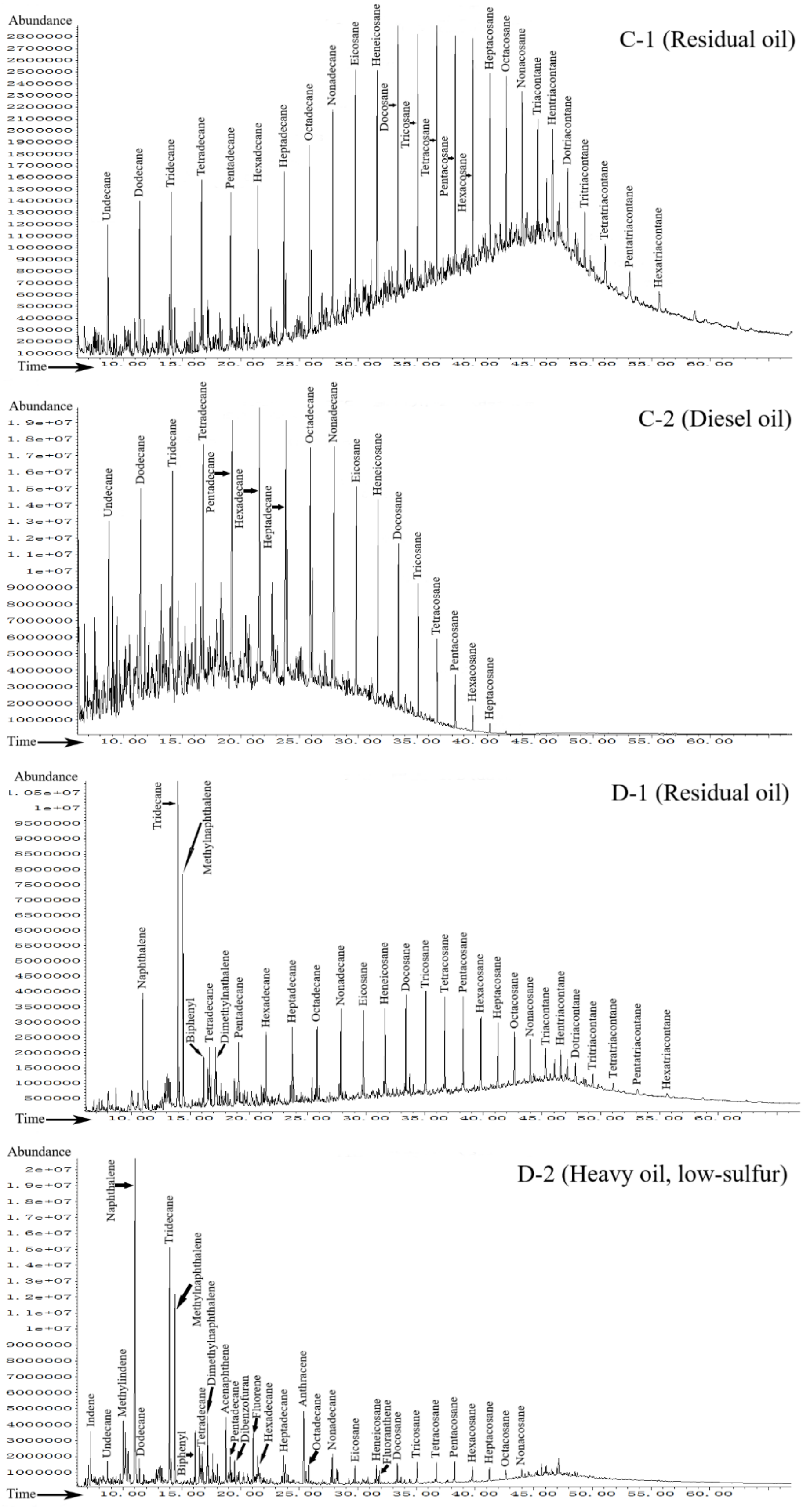


Figure S1. Typical total ion chromatographs of VOC species in fuel oils.

4. More concise. Academic writing is a big question for this manuscript. There are many simple mistakes appeared in substantial sentences, which are mostly summarized in minor comments. Polishing the language is strongly suggested.

Reply: Really sorry for making so many simple mistakes. Thanks a lot for your hard work in carefully checking the manuscript. We have also requested an academic editing service “SPRINGER NATURE Author Services (SNAS)” to improve the English language, grammar, punctuation, spelling, and overall style by one or more of the highly qualified native English speaking editors at SNAS. The verification code is 04C9-9B0B-7E9B-561C-1839.

5. The unified expression. The author wrote several types of phases to express the implementation of the fuel switch policy, such as after implementing the fuel switch policy, after the new policy, after implementing the policy, after the fuel switch, and after the implementation of the fuel switch policy. Choose a suitable phrase for this expression.

Reply: Thanks for the suggestion. In the revised manuscript, we use “the implementation of the fuel switch policy” to unify the expression.

Minor Comments

1. Line 24 The unit of EF is not unitized, mg/kg and mg kg-1.

Reply: As suggested, we have unitized the unit of EF in mg kg^{-1}.

2. Line 26 more rich… is it not richer?

Reply: As suggested, we have replaced “more rich” with “richer”.

3. Line 34 The number of PM2.5 should be subscripted.

Reply: As suggested, we have replaced “PM2.5” with “$PM_{2.5}$”.

4. Line 34 “may threatens”? It doesn’t need the plural form for the term “threaten”.

Reply: As suggested, we have replaced "threatens" with "threaten".

5. Line 46 ECAs?

Reply: As suggested, we have replaced "ECA" with "ECAs".

6. Line 54 ship emissions?

Reply: As suggested, we have replaced "ship emission" with "ship emissions".

7. Line 57 Is it suitable using the word "combat"?

Reply: As suggested, we have replaced "combat" with "control".

8. Line 78 reveals?

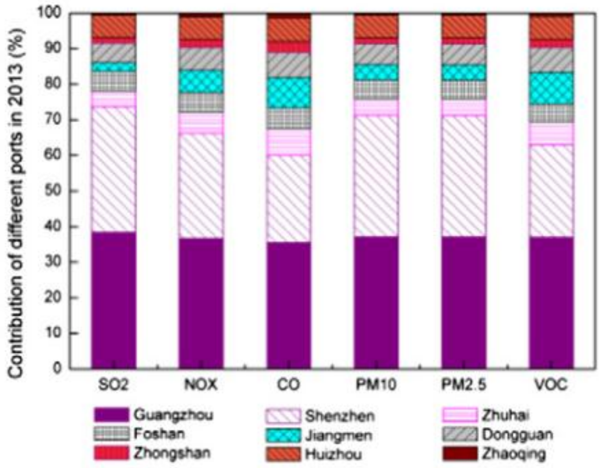
Reply: As suggested, we have replaced "reveal" with "reveals".

9. Line 84 emissions from ships?

Reply: As suggested, we have replaced "emissions from ship" with "emissions from ships".

10. Line 99 Are all the pollutant emissions accounted for 40%?

Reply: Yes, all the pollutant emissions, including SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$ and VOCs accounted for nearly 40%, as shown below (Li et al., 2016a):



a) Ports

Reference

Li, C., Yuan, Z. B., Ou, J. M., Fan, X. L., Ye, S. Q., Xiao, T., Shi, Y. Q., Huang, Z. J., Ng, S. K. W., Zhong, Z. M., and Zheng, J. Y.: An AIS-based high-resolution ship emission inventory and its uncertainty in Pearl River Delta region, China, Sci. Total Environ., 573, 1-10, https://doi.org/10.1016/j.scitotenv.2016.07.219, 2016a.

11. Line 113 What is a PM2.5 cutting head? Please give an accurate description.

Reply: As suggested, we have replaced “$PM_{2.5}$ cutting head” with “$PM_{2.5}$ separator”.

12. Line 120 Is the mass selective detector MSD? What about the mass spectrometer detector?

Reply: Here MSD represents mass selective detector. Both mass selective detector and mass spectrometer detector are often abbreviated as MSD.

13. Line 105 have already used?

Reply: As suggested, we have replaced “already used” with “have already used”.

14. Line 133 The EF of CO2 is calculated not determined. As follows not as following.

Reply: As suggested, we have replaced “determined” with “calculated”.

15. Line 136 Is the unit of Cf (g ·kg-1)

Reply: It is C_F instead of Cf. In the revised manuscript, we have changed the expression in line 154 as "C_F is the carbon content per kg of fuel (g kg^{-1});"

16. Line 140 concentration?

Reply: As suggested, we have replaced "concentrations" with "concentration".

17. Line 151-153 Why is the explanation of VOC composition change placed in this section?

Reply: As suggested, we have moved this part to line 200-202.

18. Line 161 The number of C6 should be subscripted.

Reply: As suggested, we have replaced "C6" with "C_6".

19. Line 156 What is NMHCs? Is the measured VOC species?

Reply: Yes, it refers to the measured VOC species. We have replaced "NMHCs" with "VOCs".

20. Line 158 limited…

Reply: As suggested, we have replaced "limit" with "limited".

21. Line 160 The EFs of CO2

Reply: As suggested, we have replaced "The EF of CO_2" with "The EFs of CO_2".

22. Line 160 Is it right "before to"?

Reply: We have deleted "before".

23. Line 159-163 It should give a summary rather than displaying the tested results of every ship.

Reply: Because ships C and D were tested both before and after the implementation of the fuel switch policy, the changes in emissions for the two ships would be more convincing in reflecting the influence of the fuel switch policy. This is why we particularly display the tested results of ships C and D.

24. Line 166 The term "that" should be "those".

Reply: As suggested, we have replaced “that” with “those”.

25. Line 168 What is the carbonaceous aerosol? Does that mean OC and EC?

Reply: Yes, carbonaceous aerosol included OC and EC.

26. Line 169 “As shown” is the correct form, please revise all of the forms in this manuscript.

Reply: As suggested, we have replaced “As showed” with “As shown” in the whole manuscript.

27. Line 172 the EFs of?

Reply: As suggested, we have replaced “the EF of” with “the EFs of”.

28. Line 176 by marine gasoline?

Reply: The “marine gasoil” was mentioned in Copper et al. (2003) and it referred to a kind of diesel.

Reference

Cooper, D. A.: Exhaust emissions from ships at berth, Atmos. Environ., 37, 3817-3830, https://doi.org/10.1016/S1352-2310(03)00446-1, 2003.

29. Line 178 TVOCs? Does TVOCs denote the measured VOC species?

Reply: Yes, TVOCs denoted the total measured VOC species.

30. Line 180 the emissions?

Reply: As suggested, we have replaced “emission” with “emissions”.

31. Line 191 NMHCs?

Reply: As suggested, we have replaced “NMHCs” with “VOCs”.

32. Line 199 and 214 individual NMHCs?

Reply: As suggested, we have replaced “NMHCs” with “VOCs”.

33. Line 206 the fuel switch?

Reply: We have replaced “after the fuel switch” with “after the implementation of the fuel switch policy”.

34. Line 208 the only alkynes?

Reply: Yes, we only measured acetylene in this study.

35. Line 212 “were” should be revised to “was”.

Reply: As suggested, we have replaced “were” with “was”.

36. Line 217 might played?

Reply: We have replaced “might played” with “might play”.

37. Line 217 their emission are?

Reply: We have replaced “their emission are” with “their emissions are”.

38. Line 223 emission from ship

Reply: We have replaced “emission from ship” with “emissions from ships”.

39. Line 230 Ozone Formation Potentials (OFPs) is?

Reply: We have replaced “Ozone Formation Potentials (OFPs)” with “Ozone formation potential (OFP)”.

40. Line 245 ship-emitted VOCs at berth…

Reply: As suggested, we have replaced “ship-emitted VOCs” with “ship-emitted VOCs at berth”.

41. Line 247 Please give the literature for the calculated method of SOAFPs.

Reply: As suggested, we added “(Zhang et al., 2018a)” in line 283.

Reference

Zhang, Y. L., Yang, W. Q., Simpson, I., Huang, X. Y., Yu, J. Z., Huang, Z. H., Wang, Z. Y., Zhang, Z., Liu, D., Huang, Z. Z., Wang, Y. J., Pei, C. L., Shao, M., Blake, D. R., Zheng, J. Y., Huang, Z. J., and Wang, X. M.: Decadal changes in emissions of volatile organic compounds (VOCs) from on-road vehicles with intensified automobile pollution control: Case study in a busy urban tunnel in south China, Environ. Pollut., 233, 806-819, https://doi.org/10.1016/j.envpol.2017.10.133, 2018a.

42. Line 247 normalized secondary organic aerosol reactivity?

Reply: As suggested, we have replaced "normalized secondary organic aerosols (SOA)" with "normalized secondary organic aerosol reactivity (R_{SOA}, g SOA g^{-1} VOCs)".

43. Line 250 Like Zhang et.al reported?

Reply: We deleted "Like Zhang et.al reported".

44. Line 258-260 What is the problem told by the SOAFP difference under the high NOx and low NOx conditions?

Reply: In this method, Y_i is the SOA yield of VOC species i, as determined by chamber studies (Ng et al., 2007; Lim and Ziemann, 2009; Loza et al., 2014). SOA yields of VOCs depend on nitrogen oxide (NO_x) (Ng et al., 2007). Thus, we calculated the SOAFPs under high-NOx and low-NOx conditions, respectively.

Reference

Lim, Y. B., and Ziemann, P. J.: Effects of molecular structure on aerosol yields from OH radical-initiated reactions of linear, branched, and cyclic alkanes in the presence of NOx, Environ. Sci. Technol., 43, 2328-2334, https://doi.org/10.1021/es803389s, 2009.

Loza, C. L., Craven, J. S., Yee, L. D., Coggon, M. M., Schwantes, R. H., Shiraiwa, M., Zhang, X., Schilling, K. A., Ng, N. L., Canagaratna, M. R., Ziemann, P. J., Flagan, R. C., and Seinfeld, J. H.: Secondary organic aerosol yields of 12-carbon alkanes, Atmos. Chem. Phys., 14, 1423-1439, https://doi.org/10.5194/acp-14-1423-2014, 2014.

Ng, N. L., Kroll, J. H., Chan, A. W. H., Chhabra, P. S., Flagan, R. C., and Seinfeld, J. H.: Secondary

organic aerosol formation from m-xylene, toluene, and benzene, Atmos. Chem. Phys., 7, 3909-3922, https://doi.org/10.5194/acp-7-3909-2007, 2007.

45. Line 256 This decline of RSOA?

Reply: As suggested, we have replaced "This decline in RSOA" with "This decline of R_{SOA}".

50. Line 262 What is the NMHCs?

Reply: We have replaced "NMHCs" with "VOCs".

51. Line 266-267 How about the comparison of Huang et al. results and this study results?

Reply: Huang et al. (2018a) also measured the emissions of VOCs from ship at berth using low-sulfur fuels, so we could directly compare with the coastal vessels after the implementation of the fuel switch policy. We have changed the expression in line 304-307 as below:

"As shown in Fig. S4, based on the VOCs emissions from ship at berth reported in Huang et al. (2018a), we calculated a RSOA of 0.080 g SOA g-1 VOCs under high-NOx conditions and 0.228 g SOA g-1 VOCs under low-NOx conditions for a coastal vessel also using low-sulfur fuels. This relatively higher RSOA under low-NOx conditions was related to the higher fractions of aromatics in the VOC emissions."

52. Line 268 What is the reason for the lower RSOA of Xiao's results?

Reply: The reason for lower R_{SOA} of Xiao's results was that they adopted another method in Gentner et al. (2012) using another set of SOA yield for hydrocarbons as shown in Table R1-1. In the revised manuscript we added explanations for this in line 307-309 "Using another method in Gentner et al. (2012), Xiao et al. (2018) reported an average R_{SOA} of 0.017 g SOA g^{-1} VOCs under high-NO_x conditions, which was close to a R_{SOA} of 0.015 g SOA g^{-1} VOCs calculated by the same method for the coastal vessels after IFSP.

Table R1-1. Average high-NOx SOA yields in Gentner et al. (2012)

Carbon number	Straight-chain alkanes	Branched alkanes	Cycloalkanes (single straight alkyl chain)	Cycloalkanes (branched or multiple alkyl chain (s))	Bicycloalkanes	Tricycloalkanes	Aromatics	Polycyclic aromatics compounds
1	-	-	-	-	-	-	-	-
2	-	-	-	-	-	-	-	-
3	-	-	-	-	-	-	-	-
4	-	-	-	-	-	-	-	-
5	-	-	-	-	-	-	-	-
6	-	-	0.0004	-	-	-	0.14	-
7	-	-	0.0007	0.0001	-	-	0.083	-
8	0.0006	0.0001	0.0015	0.0002	-	-	0.048	-
9	0.0012	0.0002	0.0031	0.0005	0.0005	-	0.077	-
10	0.0026	0.0004	0.0059	0.001	0.001	-	0.12	0.17
11	0.0053	0.0008	0.01	0.0018	0.0018	-	0.15	0.23
12	0.01	0.0017	0.016	0.0034	0.0031	0.0032	0.19	0.28
13	0.019	0.0035	0.026	0.0062	0.0056	0.0057	0.26	0.4
14	0.033	0.007	0.041	0.011	0.0097	0.0098	0.33	0.49
15	0.055	0.013	0.064	0.019	0.016	0.017	0.39	0.62
16	0.089	0.024	0.099	0.031	0.026	0.027	0.43	0.7
17	0.14	0.042	0.16	0.053	0.044	0.045	0.46	0.75
18	0.23	0.073	0.24	0.088	0.072	0.073	0.51	0.79
19	0.37	0.12	0.36	0.14	0.12	0.12	0.56	0.82
20	0.56	0.2	0.5	0.22	0.19	0.19	0.61	0.82
21	0.77	0.32	0.66	0.33	0.29	0.3	0.65	0.82

22	0.96	0.47	0.82	0.45	0.43	0.43	0.67	0.82
23	1.08	0.61	0.94	0.57	0.56	0.57	0.68	0.82
24	1.14	0.7	1.03	0.67	0.66	0.67	0.68	0.82
25	1.16	0.75	1.09	0.73	0.74	0.74	0.68	0.82

Reference

Gentner, D. R., Isaacman, G., Worton, D. R., Chan, A. W. H., Dallmann, T. R., Davis, L., Liu, S., Day, D. A., Russell, L. M., Wilson, K. R., Weber, R., Guha, A., Harley, R. A., and Goldstein, A. H.: Elucidating secondary organic aerosol from diesel and gasoline vehicles through detailed characterization of organic carbon emissions, Proc. Natl. Acad. Sci. U. S. A., 109, 18318-18323, https://doi.org/10.1073/pnas.1212272109, 2012.

53. Line 271 Ships?

Reply: We have replaced “Ships” with “Ship”.

54. Line 273 one the three?

Reply: We have replaced “one the three” with “one of the three”.

55. Line 278 the EF of VOCs and Line 281 the EF of NMHCs? Which one is right?

Reply: We have replaced “NMHCs” with “VOCs” in the whole manuscript.

56. Line 281 Why explained the unit of fuel-based EF here?

Reply: We have deleted “for VOCs emitted per kilogram fuel burned”.

57. Line 287 are not affected?

Reply: We have changed “For river vessels unaffected” to “For the river vessels were not affected”.

58. Table 2 g kg-1 fuel?

Reply: This shows the unit of the emission factor in the table.

59. Figure 5 before and IFSP?

Reply: We have changed “before and IFSP” as “before and after the implementation of the fuel switch policy”.

60. Figure 4 The figure needs add the standard error bar. IFSP is the first appearance. Spell out all acronyms on first use in the abstract and in the body of the article.

Reply: Thanks for the suggestion. We have added the standard error bar in Figure 4 and spell out the acronyms of IFSP on its first use in the abstract and in the body of the article in line 21 and line 86.

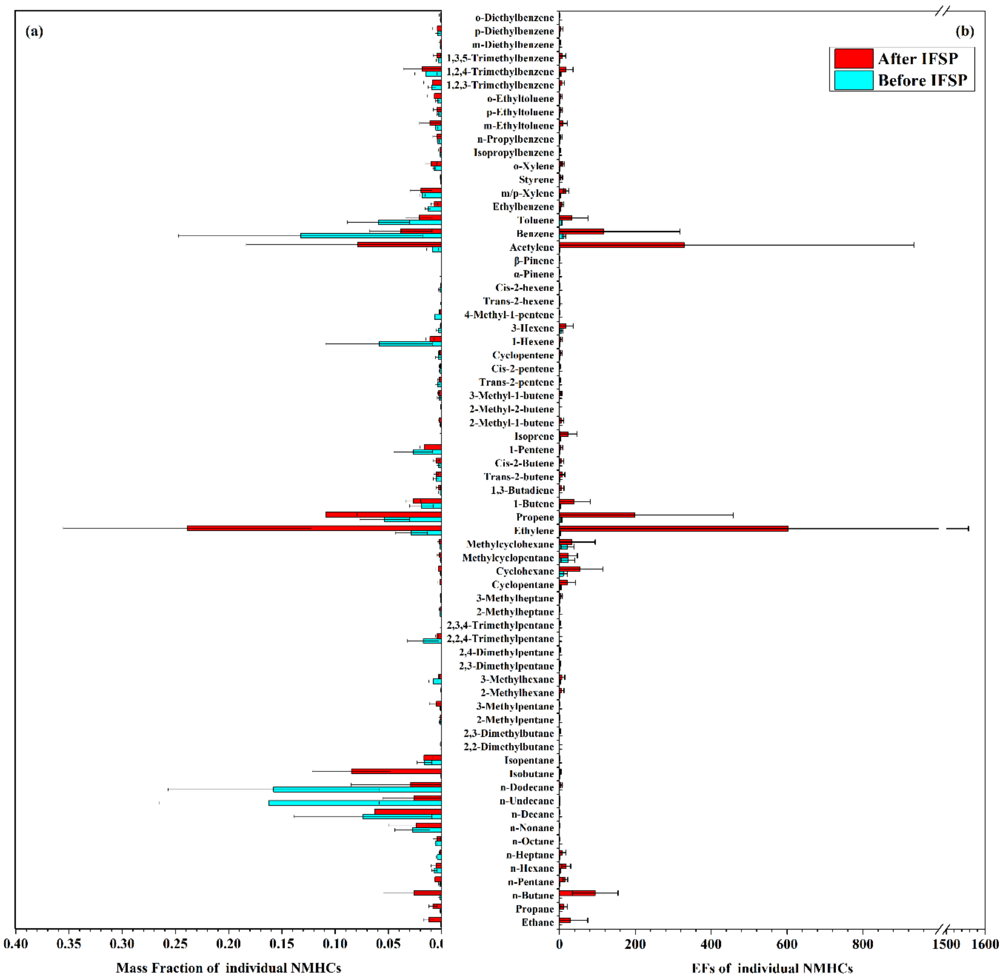


Figure 4. Comparison of VOCs emission factors before and after IFSP for coastal vessels.

61. Figure 2 diagrams?

Reply: We have replaced “diagrams” with “diagram”.

Reviewer #2

The manuscript of Wu et al. with the title of “Dramatic increase of reactive VOC emission from ships at berth after implementing the fuel switch policy in the Pearl River Delta Emission Control Area” characterized the emissions of PM2.5, SO2 and VOCs from ships at berth before and after implementing the fuel switch policy with a FSC limit of 0.5% in the Pearl River Delta ECA in south China. After implementing the fuel switch policy, the EFs of SO2 and PM2.5 for coastal vessels dropped 23 by 78% and 56%, however, the EFs of NMHCs increased by a factor of 15 times before implementing the new policy. The reactive alkenes overtook alkanes to become the dominant group, which led to the sharp increase of ozone formation potential. The results showed that this change may threatens ozone pollution control in the harbor cities. This is a well-written manuscript. The results could help to improve our understanding of another side of fuel switch policy and raised the concerns for reactive VOCs emissions from ships, and found river vessels might had even larger emissions of VOCs and NOx than coastal vessels. I highly recommend this manuscript to be accepted by the journal.

Minor revisions

line 18, change “to reduce” to for reducing”;

Reply: Revised as suggested, Line 18, replaced “to reduce” to “for reducing”.

line 19, change “matters” to “matter”;

Reply: Revised as suggested, Line 19, replaced “matters” to “matter”.

line 19, change “emission” to “emissions”;

Reply: Revised as suggested, Line 19, replaced “emission” to “emissions”.

line 20, change “south” to “southern”;

Reply: Revised as suggested, Line 21, replaced “south” to “southern”.

line 21, change “a” to “an”;

Reply: Revised as suggested, Line 21, replaced “a” to “an”.

line 21, delete “in south China”;

Reply: Revised as suggested, Line 22, deleted “in south China”.

line 22, change “emission” to “emissions”;

Reply: Revised as suggested, Line 23, replaced “emission” to “emissions”.

line 22, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 23, replaced “coastal vessels” to “the coastal vessels”.

line 22, change “dropped” to “decreased”;

Reply: Revised as suggested, Line 23, replaced “dropped” to “decreased”.

line 23, change “the EFs of non-methane hydrocarbons (NMHCs), however, reached” to “however, the EFs of the nonmethane hydrocarbons (NMHCs), were”;

Reply: Revised as suggested, Line 24, replaced “the EFs of non-methane hydrocarbons (NMHCs), however, reached to” to “however, the EFs of the VOCs were”.

line 24, change “about” to “approximately”;

Reply: Revised as suggested, Line 25, replaced “about” to “approximately”.

line 24, change “emission” to “emissions”;

Reply: Revised as suggested, Line 26, replaced “emission” to “emissions”.

line 25, change “NMHCs” to “the NMHCs”;

Reply: Revised as suggested, Line 26, replaced “NMHCs” to “the VOCs”.

line 26, change “more rich” to “richer”;

Reply: Revised as suggested, Line 27, replaced “more rich” to “richer”.

line 28, change “the new policy” to “the new policy was implemented”;

Reply: Revised as suggested, Line 29, replaced “the new policy” to “IFSP”.

line 28, change “reactive alkenes” to “the reactive alkenes”;

Reply: Revised as suggested, Line 30, replaced “reactive alkenes” to “the reactive alkenes”.

line 29, change “for per kilogram of fuel burned, emitted NMHCs” to “the emitted NMHCs per kg of fuel burned”;

Reply: Revised as suggested, Line 30, replaced “for per kilogram of fuel burned, emitted NMHCs” to “the emitted VOCs per kg of fuel burned”.

line 29, change “about” to “approximately”;

Reply: Revised as suggested, Line 31, replaced “about” to “approximately”.

line 30, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 32, replaced “coastal vessels” to “the coastal vessels”.

line 30, change “river vessels” to “the river vessels”;

Reply: Revised as suggested, Line 32, replaced “river vessels” to “the river vessels”.

line 31, change “their EFs of NMHCs” to “the EFs of their NMHCs”;

Reply: Revised as suggested, Line 34, replaced “their EFs of NMHCs” to “the EFs of their VOCs”.

line 35, change “coastal or ocean-going vessels” to “the coastal or ocean-going vessels”;

Reply: Revised as suggested, Line 38, replaced “coastal or ocean-going vessels” to “the coastal or ocean-going vessels”.

line 35, change “along with” to “in addition to”;

Reply: Revised as suggested, Line 38, replaced “along with” to “in addition to”.

line 35, change “river vessels” to “the river vessels”;

Reply: Revised as suggested, Line 39, replaced “river vessels” to “the river vessels”.

line 38, change “total world merchandise trade” to “the total global merchandise trade”;

Reply: Revised as suggested, Line 42, replaced “total world merchandise” to “the total global merchandise trade”.

line 39, change “it is no surprise that” to “unsurprisingly”;

Reply: Revised as suggested, Line 44, replaced “it is no surprise that” to “unsurprisingly”.

line 42, change “would give rise to” to “can cause”;

Reply: Revised as suggested, Line 46, replaced “would give rise to” to “can cause”.

line 42, change “areas,” to “areas”;

Reply: Revised as suggested, Line 46, replaced “areas,” to “areas”.

line 42, change “environmental burden” to “the environmental burden”;

Reply: Revised as suggested, Line 47, replaced “environmental burden” to “the environmental burden”.

line 46, change “more” to “a more”;

Reply: Revised as suggested, Line 51, replaced “more” to “a more”.

line 47, change “brought about” to “resulted in”;

Reply: Revised as suggested, Line 52, replaced “brought about” to “resulted in”.

line 49, change “resulted” to “has resulted”;

Reply: Revised as suggested, Line 54, replaced “resulted” to “has resulted”.

line 50, change “aerosols” to “aerosols, respectively,”

Reply: Revised as suggested, Line 55, replaced “aerosols” to “aerosols, respectively”.

line 51, change “revealed” to “has revealed”;

Reply: Revised as suggested, Line 56, replaced “revealed” to “has revealed”.

line 55, change “reduce” to “be reduced”;

Reply: Revised as suggested, Line 60, replaced “reduce” to “be reduced”.

line 56, change “emission sources” to “emissions sources”;

Reply: Revised as suggested, Line 62, replaced “emission sources” to “emissions sources”.

line 67, change “VOCs” to “the VOCs”;

Reply: Revised as suggested, Line 73, replaced “VOCs” to “the VOCs”.

line 68, change “north” to “northern”;

Reply: Revised as suggested, Line 74, replaced “north” to “northern”.

line 69, change “As a matter of fact, previous” to “Previous”;

Reply: Revised as suggested, Line 75, replaced “As a matter of fact, previous” to “Previous”.

line 70, change “Meanwhile” to “In addition”;

Reply: Revised as suggested, Line 77, replaced “Meanwhile” to “In addition”.

line 75, change “January 1, 2017 to December 31, 2019” to “1 January, 2017, to 31 December, 2019”;

Reply: Revised as suggested, Line 83, replaced “January 1, 2017 to December 31, 2019” to “1 January, 2017, to 31 December, 2019”.

line 76, change “estimiated” to “estimated”;

Reply: Revised as suggested, Line 83, replaced “estimiated” to “estimated”.

line 76, change “atmosheric” to “atmospheric”;

Reply: Revised as suggested, Line 84, replaced “atmosheric” to “atmospheric”.

line 77, change “south” to “southern”;

Reply: Revised as suggested, Line 84, replaced “south” to “southern”.

line 81, change “bring about” to “result in”;

Reply: Revised as suggested, Line 89, replaced “bring about” to “result in”.

line 82, change “shut down” to “shut down,”;

Reply: Revised as suggested, Line 90, replaced “shut down” to “shut down,”.

line 82, change “emission” to “emissions”;

Reply: Revised as suggested, Line 90, replaced “emission” to “emissions”.

line 88, change “like” to “such as”;

Reply: Revised as suggested, Line 96, replaced “like” to “such as”.

line 92, change “in comparison” to “for a comparison”;

Reply: Revised as suggested, Line 100, replaced “in comparison” to “for a comparison”.

line 97, change “the fifth” to “fifth”;

Reply: Revised as suggested, Line 106, replaced “the fifth” to “fifth”.

line 98, change “the seventh” to “seventh”;

Reply: Revised as suggested, Line 107, replaced “the seventh” to “seventh”.

line 98, change “contribute near 40%” to “account for nearly 40% of”;

Reply: Revised as suggested, Line 107, replaced “contribute near 40%” to “account for nearly 40% of”.

line 99, change “nine” to “the nine”;

Reply: Revised as suggested, Line 108, replaced “nine” to “the nine”.

line 101, change “FSC” to “the FSC”;

Reply: Revised as suggested, Line 111, replaced “FSC” to “the FSC”.

line 101, change “be lower” to “have been less”;

Reply: Revised as suggested, Line 111, replaced “be lower” to “have been less”.

line 102, change “that” to “in that”;

Reply: Revised as suggested, Line 112, replaced “that” to “in which”.

line 147, change “on average decreased from 2.2 ± 0.5%” to “decreased from 2.2 ± 0.5% on average”;

Reply: Revised as suggested, Line 167, replaced “on average decrease from 2.2 ± 0.5%” to “decreased from 2.2 ± 0.5% on average”.

line 148, change “though” to “although”;

Reply: Revised as suggested, Line 168, replaced “though” to “although”.

line 150, change “hydrocarbons” to “hydrocarbons,”;

Reply: Revised as suggested, Line 171, replaced “hydrocarbons” to “hydrocarbons,”.

line 151, change “chromatograms” to “chromatograms, than those of coastal vessels before the policy”;

Reply: Revised as suggested, Line 171, replaced “chromatograms” to “chromatograms, than those of coastal vessels before IFSP”.

line 157, change “performance of combustion system” to “the performance of the combustion system”;

Reply: Revised as suggested, Line 178, replaced “performance of combustion system” to “the performance of the combustion system”.

line 185, change “, and also larger” to “and higher”;

Reply: Revised as suggested, Line 211, replaced “and also larger” to “and larger”.

line 185, change “engineering vessel” to “engineering vessels”;

Reply: Revised as suggested, Line 211, replaced “engineering vessel” to “engineering vessels”.

line 185, change “crusing condition” to “cruising conditions”;

Reply: Revised as suggested, Line 212, replaced “crusing condition” to “cruising conditions”.

line 186, change “the maximum” to “a maximum”;

Reply: Revised as suggested, Line 212, replaced “the maximum” to “a maximum”.

line 199, change “individual” to “the individual”;

Reply: Revised as suggested, Line 229, replaced “individual” to “the individual”.

line 199, change “remain” to “remained”;

Reply: Revised as suggested, Line 229, replaced “remain” to “remained”.

line 210, change “before” to “before implementing the new policy”;

Reply: Revised as suggested, Line 232, replaced “before” to “before IFSP”.

line 242, change “after implementing the policy, respectively” to “, respectively, after implementing the policy”;

Reply: Revised as suggested, Line 242, replaced “after implementing the policy, respectively” to “respective, after IFSP”.

line 212, change “NMHCs from river vessels were” to “the NMHCs from the river vessels was”;

Reply: Revised as suggested, Line 243, replaced “NMHCs from river vessels were” to “the VOCs from the river vessels was”.

line 212, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 243, replaced “coastal vessels” to “the coastal vessels”.

line 213, change “showed” to “shown”;

Reply: Revised as suggested, Line 244, replaced “showed” to “shown”.

line 213, change “dominated the emission of NMHCs with a share of” to “were dominant in the emissions of the NMHCs at”;

Reply: Revised as suggested, Line 244, replaced “dominated the emission of NMHCs with a share of” to “were dominant in the emissions of the NMHCs at”.

line 214, change “individual” to “the individual”;

Reply: Revised as suggested, Line 246, replaced “individual” to “the individual”.

line 223, change “had a share up to 70.9%” to “accounted for up to 70.9% of those emissions”;

Reply: Revised as suggested, Line 254, replaced “had a share up to 70.9%” to “accounted for up to 70.9% of those emissions”.

line 223, change “variety of the” to “variation in”;

Reply: Revised as suggested, Line 255, replaced “variety of the” to “variation in”.

line 224, change “big” to “large”;

Reply: Revised as suggested, Line 256, replaced “big” to “large”.

line 224, change “compositions of VOC emissions” to “the compositions the VOC emissions”;

Reply: Revised as suggested, Line 256, replaced “compositions of VOC emissions” to “the compositions of the VOC emissions”.

line 225, change “only restricted” to “restricted only”;

Reply: Revised as suggested, Line 256, replaced “only restricted” to “restricted only”.

line 225, delete “can be”;

Reply: Revised as suggested, Line 257, deleted “can be”.

line 226, change “diesels” to “diesel fuels used”;

Reply: Revised as suggested, Line 258, replaced “diesels” to “diesel fuels used”.

line 226, change “sampling might also lead” to “the sampling might have also led”;

Reply: Revised as suggested, Line 258, replaced “sampling might also lead” to “the sampling might have also led”.

line 228, change “potentials” to “potential”;

Reply: Revised as suggested, Line 260, replaced “potentials” to “potential”.

line 229, change “OFPs of VOCs from ship exhausts” to “OFP of the VOCs from ship exhaust”;

Reply: Revised as suggested, Line 261, replaced “OFPs of VOCs from ship exhausts” to “OFP of the VOCs from ship exhaust”.

line 230, change “Formation Potentials (OFPs)” to “formation potentials (OFP)”;

Reply: Revised as suggested, Line 262, replaced “Formation Potentials (OFPs)” to “formation potential (OFP)”.

line 231, change “ships emission” to “ships emissions”;

Reply: Revised as suggested, Line 263, replaced “ships emission” to “ships emissions”.

line 232, change “reactivity,” to “reactivity”;

Reply: Revised as suggested, Line 264, replaced “reactivity,” to “reactivity”.

line 237, change “rise of” to “increase in”;

Reply: Revised as suggested, Line 270, replaced “rise of” to “increase in”.

line 237, change “like” to “such as”;

Reply: Revised as suggested, Line 271, replaced “like” to “such as”.

line 240, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 274, replaced “coastal vessels” to “the coastal vessels”.

line 241, change “OFPs” to “OFP”;

Reply: Revised as suggested, Line 275, replaced “OFPs” to “OFP”.

line 241, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 276, replaced “coastal vessels” to “the coastal vessels”.

line 245, change “suggests” to “suggest”;

Reply: Revised as suggested, Line 279, replaced “suggests” to “suggest”.

line 246, change “SOAFPs of VOCs from ship exhausts” to “SOAFP of the VOCs from ship exhaust”;

Reply: Revised as suggested, Line 281, replaced “SOAFPs of VOCs from ship exhausts” to “SOAFP of the VOCs from ship exhaust”.

line 250, change “Like” to “Similar to”;

Reply: Revised as suggested, Line 286, replaced “Like” to “Similar to”.

line 251, change “SOAFPs” to “SOAFP”;

Reply: Revised as suggested, Line 287, replaced “SOAFPs” to “SOAFP”.

line 252, change “to interpret” to “in interpreting”;

Reply: Revised as suggested, Line 288, replaced “to interpret” to “in interpreting”.

line 252, delete “(IVOCs)”;

Reply: Revised as suggested, Line 288, deleted “(IVOCs)”.

line 261, change “higher” to “higher than that of the other ships,”;

Reply: Revised as suggested, Line 298, replaced “higher” to “higher than that of the other ships”.

line 262, change “has: to “had”;

Reply: Revised as suggested, Line 299, replaced “has” to “had”.

line 262, change “river vessels” to “the river vessels”;

Reply: Revised as suggested, Line 299, replaced “river vessels” to “the river vessels”.

line 262, change “test ships” to “the tested ships”;

Reply: Revised as suggested, Line 300, replaced “test ships” to “the tested ships”.

line 262, change the value” to “a value”;

Reply: Revised as suggested, Line 300, replaced “the value” to “a value”.

line 273, change “one the three ECAs newly established” to “one of the three newly established ECAs”;

Reply: Revised as suggested, Line 315, replaced “one the three ECAs newly established” to “one of the three newly established ECAs”.

line 280, change “of EFs” to “in the EFs”;

Reply: Revised as suggested, Line 322, replaced “of EFs” to “in the EFs”.

line 280, change “more” to “the more”;

Reply: Revised as suggested, Line 323, replaced “more” to “the more”.

line 288, change “did bring about largely” to “resulted in substantially”;

Reply: Revised as suggested, Line 332, replaced “did bring about largely” to “resulted in substantially”.

line 289, change “for” to “due to”;

Reply: Revised as suggested, Line 334, replaced “for” to “due to”.

line 290, change “coastal vessels” to “the coastal vessels”;

Reply: Revised as suggested, Line 334, replaced “coastal vessels” to “the coastal vessels”.

line 290, change “is” to “was”;

Reply: Revised as suggested, Line 334, replaced “is” to “was”.

line 290, change “use” to “had used”;

Reply: Revised as suggested, Line 335, replaced “use” to “had used”.

line 290, change “all along and thus” to “the entire time and thus were”;

Reply: Revised as suggested, Line 335, replaced “all along and thus” to “the entire time and thus were”.

line 291, change “much higher” to “high”;

Reply: Revised as suggested, Line 336, replaced “much higher” to “high”.

line 291, change “larger emission” to “high level of emissions”;

Reply: Revised as suggested, Line 336, replaced “larger emission” to “high level of emissions”.

line 292, delete “would”;

Reply: Revised as suggested, Line 337, deleted “would”.

line 292, change “how to further lower the emission” to “and further lowering the emissions”;

Reply: Revised as suggested, Line 337, replaced “how to further lower the emission” to “and further lowering the emissions”.

Dramatic increase in reactive VOC emissions from ships at berth after implementing the fuel switch policy in the Pearl River Delta Emissions Control Area

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Zhenfeng Wu[1,3], Yanli Zhang[1,2,*], Junjie He[4], Hongzhan Chen[4], Xueliang Huang[1,5], Yujun Wang[4], Xu Yu[1,3], Weiqiang Yang[1,3], Runqi Zhang[1,3], Ming Zhu[1,3], Sheng Li[1,3], Hua Fang[1,3], Zhou Zhang[6], Xinming Wang[1,2,3]

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[4]Guangzhou Environmental Monitoring Center, Guangzhou 510640, China
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Abstract. Limiting fuel sulfur content (FSC) is a widely adopted approach for reducing ship emissions of sulfur dioxide (SO_2) and particulate matter (PM), particularly in emissions control areas (ECAs), but its impact on the emissions of volatile organic compounds (VOCs) is still not well understood. In this study, emissions from ships at berth in Guangzhou, southern China, were characterized before and after the implementation of the fuel switch policy (IFSP) with an FSC limit of 0.5% in the Pearl River Delta ECA. After IFSP, the emissions factors (EFs) of SO_2 and $PM_{2.5}$ for the coastal vessels decreased by 78% and 56% on average, respectively; however, the EFs of the VOCs were 1807 ± 1746 mg kg^{-1}, approximately 15 times that of 118 ± 56.1 mg kg^{-1} before IFSP. This dramatic increase in the emissions of the VOCs might have been largely due to the replacement of high-sulfur residual fuel oil with low-sulfur diesel or heavy oils, which are typically richer in short-chain hydrocarbons. Moreover, reactive alkenes surpassed alkanes to become the dominant group among the VOCs, and low carbon number VOCs, such as ethylene, propene and isobutane, became the dominant species after IFSP. As a result of the largely elevated EFs of the reactive alkenes and aromatics after IFSP, the emitted VOCs per kg of fuel burned had nearly 29 times larger ozone formation potential (OFP) and approximately 2 times greater secondary organic aerosol formation potential (SOAFP) than those before IFSP. Unlike the coastal vessels, the river vessels in the region used diesel fuels consistently and were not affected by the fuel switch policy, but the EFs of their VOCs were 90% greater than those of the coastal vessels after IFSP, with approximately 120% greater fuel-based OFP and 70-140% greater SOAFP. The results from this study suggest that while the fuel switch policy could effectively reduce SO_2 and PM emissions and thus help control $PM_{2.5}$ pollution, it also will lead to greater emissions of reactive VOCs, which may threaten ozone pollution control in the harbor cities. This change for the coastal or ocean-going vessels, in addition to the large amounts of reactive VOCs from the river vessels, raises regulatory concerns for ship emissions of reactive VOCs.

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1 Introduction

World seaborne trade volumes are estimated to account for over 80% of the total global merchandise trade (UNCTAD, 2016). The controls on ship emissions, however, are far less stringent than those on land emissions sources, and unsurprisingly, ship engines are among the world's highest polluting combustion sources in terms of per ton of fuel consumed (Corbett and Fischbeck, 1997). As a large amount of marine ship emissions occur within 400 km of coastlines (Fu et al., 2017), ship emissions can cause air pollution in coastal areas and thus contribute substantially to the environmental burden of disease (Corbett et al., 2007; Lv et al., 2018; Feng et al., 2019; Ramacher et al., 2019; Wang et al., 2019a). Therefore, global efforts have been implemented to regulate and prevent health risks from ship emissions particularly in harbor cities.

An important intervention policy by the International Maritime Organization (IMO) to reduce ship emissions is the designation of emissions control areas (ECAs) where a more stringent limit of fuel sulfur content (FSC) is implemented (IMO, 2017). This ECA approach has resulted in significant improvements in ambient air quality for coastal areas (Lack et al., 2011; Tao et al., 2013; Contini et al., 2015; Zetterdahl et al., 2016). In the North Sea regions, for example, the new policy

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restricting FSC below 1.5% since 2007 has resulted in reduction rates of 42%, 38% and 20% for ambient concentrations of sulfur dioxide (SO_2), sulphate aerosols and ammonium aerosols, respectively, which were related to ship emissions (Matthias et al., 2010); monitoring in U.S. coastal states has revealed significant reductions in ambient $PM_{2.5}$ (particulate matter with an aerodynamic diameter less than 2.5 μm) from residual fuel oil (RFO) combustion due to marine vessel fuel sulfur regulations in the North American Emissions Control Area (NA-ECA) (Kotchenruther, 2017). In the Marmara Sea and the Turkish Straits, ship emissions of SO_2, $PM_{2.5}$ and PM_{10} (particulate matter with an aerodynamic diameter less than 10 μm) were projected to be reduced by 95%, 67% and 67%, respectively, if FSC was restricted to below 0.1% (Viana et al., 2015). Consequently, with the increasingly stringent control over land-based emissions sources, limiting ship emissions has gradually stood out as an effective measure to control air pollution in coastal zones.

Intervention measures for ship emissions, however, are mostly targeted at SO_2 and PM, and much less attention has been paid to other pollutants from ship emissions, such as nitrogen oxides (NO_x) and volatile organic compounds (VOCs), although they are also important precursors to ozone and secondary aerosols (Chameides et al., 1992; Odum et al., 1997; Atkinson, 2000; O'Dowd et al., 2002). Cooper et al. (1996) found that many reactive VOCs, such as ethylene, propylene and isobutylene, were found in emissions from passenger ferries in the Skagerak-Kattegatt-Öresund region; Agrawal et al. (2008) reported emissions of VOCs including carbonyls, 1, 3-butadiene, aromatics and n-alkanes from the main engine, auxiliary engine and boiler of a Suezmax class vessel; Agrawal et al. (2010) and Murphy et al. (2009) further calculated their emissions factors based on shipboard platform measurements and aircraft-based measurements for the main engine of a PanaMax Class container ship. Recently, Huang et al. (2018a) tested a handysize-class bulk carrier under at-berth, maneuvering and cruising conditions, and found that single-ring aromatics accounted for 50-74% of the VOCs with toluene as the most abundant species. Xiao et al. (2018) tested 20 ships at berth in the Jingtang Port in northern China and found that alkanes and aromatics were dominant in the VOC emissions. Previous studies have already demonstrated that ship emissions impact ambient ozone formation in coastal cities (Wang et al., 2019b). In addition, ship emissions could contribute substantially to NO_x in the oceans and coastal areas (Song et al., 2010; Tagaris et al., 2017). Therefore, even in terms of for lowering ambient ozone levels, there is a growing concern about ship emissions as ozone precursors, including NO_x and VOCs.

China has many of the world's busiest ports, sharing approximately 10% of global ship emissions (Fu et al., 2017). To reduce ship emissions, China has also designated three ECAs, namely, the Pearl River Delta (PRD), the Yangtze River Delta and the Bohai Rim, where ships have been required to gradually switch to fuels with an FSC limit of 0.5% from 1 January, 2017, to 31 December, 2019. As estimated by Liu et al. (2018), this fuel switch policy could lower atmospheric concentrations of SO_2 and $PM_{2.5}$ by 9.5% and 2.7%, respectively, in the coastal region of the PRD in southern China. A recent field observation campaign in Jingtang Port also demonstrated that due to the implementation of the fuel switch policy (IFSP), ambient levels of SO_2 dropped from 165.5 ppb to 67.4 ppb, while particulate vanadium (V), a marker of ship PM emissions (Agrawal et al., 2009; Pey et al., 2013; Perez et al., 2016; Tao et al., 2017), decreased drastically from 309.9 ng m^{-}

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^{3} to 9.1 ng m^{-3} (Zhang et al., 2019). However, it is still unknown whether the fuel switch policy will result in changes in ship emissions of VOCs.

For ships at berth, their main engines are shut down, and auxiliary engines become the only emissions source. Because a ship is usually at berth for one day or more and the place where its auxiliary engine discharges pollutants is usually closer to densely populated areas, emissions from ships at berth could have a large impact on coastal areas (Cooper et al., 2003). In the present study, we conducted shipboard platform measurements of air pollutants emitted from coastal vessels at berth in Guangzhou Port in the PRD region in southern China in 2017 and 2018 after IFSP, and we compared the results with those from a similar campaign previously conducted by the authors in 2015 and 2016 before IFSP. Apart from the emissions of pollutants such as $PM_{2.5}$ and SO_2, in this study, we focus on emissions of VOCs and aim to investigate changes in composition profiles and emissions factors of VOCs from ships at berth and to assess the potential influence on the formation of ozone (O_3) and secondary organic aerosol (SOA) due to the fuel switch policy. In addition, river vessels, which commonly use diesel oil as fuel and did not need to implement the fuel switch policy, were also tested in 2017 for a comparison with the coastal vessels that had implemented the policy.

2 Experimental section

2.1 Study area

Guangzhou Port is located in the estuary of the Pearl River and the centre of the PRD region, adjacent to Hong Kong and Macao (Fig. 1). In 2017, cargo throughput of Guangzhou Port was 590 million tons, ranking fifth in China and sixth in the world, and the container throughput in Guangzhou Port was 20.37 million TEU, ranking fifth in China and seventh in the world (China Port Press, 2018). In 2013, Guangzhou Port was estimated to account for nearly 40% of ship emissions of SO_2, NO_x, CO, PM_{10}, $PM_{2.5}$ and VOC from the nine port groups in the PRD bay area (Li et al., 2016a).

2.2 Test ships and fuel types

As required, the FSC for ships at berth should have been less than 0.5% since 1 January, 2017. In the PRD, measures are even more stringent in which ships at berth should use diesel oil that conforms to Chinese national standard GB252-2015 (Standards Press of China, 2015). Table 1 presents the basic information for the 11 tested ships (more information during sampling was presented in Table S1), among which ships C and D were tested both before and after IFSP. According to the classification of ships as by Li et al. (2016a), ships H, I, J and K were river vessels, which were not regulated because they have already used diesel oil as fuel before IFSP, and the others were coastal vessels. No ocean-going ships were tested in this study.

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2.3 Ship exhaust sampling and laboratory analysis

The ship exhaust sampling system is composed of a flue gas dilution system, flue gas analyzer, particulate matter sampler and air sampler (Figure 2). The ship exhaust first entered the Dekati® ejector dilutor (DI-1000, Dekati Ltd., Finland) from the sampling nozzle and then was spilt into four parts after being diluted with clean air: one part was for air sampling with 2 L canisters and 4 L Teflon bags for 3-5 min after passing through a filter, two other parts were for collecting $PM_{2.5}$ samples with 47mm Teflon filters (Whateman, Mainstone, UK) and 47mm quartz fiber filters (Whateman, Mainstone, UK) at a flow of 16.7 L min^{-1} for 20-30 min, after the diluted exhaust was mixed well in a stay cabin, and then passing through a $PM_{2.5}$ separator, and the last part was the vent. Before dilution, the concentrations of CO_2, CO, SO_2 and NO in the ship exhaust were directly measured by a flue gas analyzer (F-550, WOHLER, Germany), while air samples were also collected simultaneously by a 2L canisters and a 4L Teflon bags. The dilution ratios of the flue gas dilution system were then more accurately calculated by comparing the CO_2 concentrations in the samples before and after the dilution. In addition, 500 ml of the fuel oil used by each ship was collected in brown glass bottles to determine its carbon and sulfur contents and to analyse the C_{11}-C_{36} hydrocarbon species.

VOCs in the air samples collected in the canisters and Teflon bags were analyzed by using a preconcentrator (Model 7100, Entech Instruments Inc., USA) coupled to an Agilent 5973N gas chromatography-mass selective detector/flame ionization detector (GC-MSD/FID, Agilent Technologies, USA). The calibration standards were prepared by dynamically diluting the 100 ppbv Photochemical Assessment Monitoring Stations (PAMS) standard mixture (57 NMHCs including 15 AHs) and TO-14 standard mixture (39 compounds) from Spectra Gases Inc., NJ, USA to 0.5, 1, 5, 15 and 30 ppbv. More details about the analysis are described elsewhere (Zhang et al., 2013; 2015; Yang et al., 2018). Besides measured by the flue gas analyzer, the CO_2/CO concentrations were also analyzed by gas chromatography (Agilent 6980GC, USA) with a flame ionization detector and a packed column (5A molecular sieve, 60/80 mesh, 3 m × 1/8 in.) (Liu et al., 2015). The particulate samples collected by quartz filters were analyzed by a DRI Model 2015 multi-wavelength thermal/elemental carbon (OC/EC) analyzer (Li et al., 2018). The carbon contents of the ship fuels were analyzed by an elemental analyzer (Vario EL III, Elementar, Germany), and the sulfur contents were analyzed by the conversion to sulfate with an oxygen bomb combustion (IKA AOD1, IKA, Germany) followed by the determination of sulfate with an ion chromatography (883 Basic IC plus, Metrohm, Switzerland) (Li et al., 2016b). The C_{11}-C_{36} hydrocarbons in the fuels were analyzed with an Agilent 7890/5975C gas chromatography/mass spectrometer detector (GC/MSD) equipped with a HP-5MS capillary column (30 m in length, 0.25 mm I.D., 0.25 μm film thickness) (Yu et al., 2018) after dissolving 50μl fuel oil in 1ml n-hexane and removing the insoluble material through filtration.

2.4 Calculations of emission factors

The emissions factors (EFs) were calculated by a carbon balance approach, which assumed that the carbon in fuel was transformed into the carbon in CO_2, CO, PM and VOCs, and the EF of CO_2 was calculated as follows (Liu et al., 2014):

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$$EF_{CO2}=\frac{C_F \cdot \Delta[CO_2]}{\Delta C_{CO2}+\Delta C_{CO}+\Delta C_{PM}+\Delta C_{VOCs}}, \quad (1)$$

where EF_{CO2} is the emissions factor of CO_2 in unit of g kg^{-1}; C_F is the carbon content per kg of fuel (g kg^{-1}); $\Delta[CO_2]$ is the incremental concentrations of CO_2; ΔC_{CO2}, ΔC_{CO}, ΔC_{PM} and ΔC_{VOCs} represent the carbon mass concentrations of CO_2, CO, PM and VOCs, respectively, after subtracting their background concentrations.

The EF of a pollutant *i* was calculated by:

$$EF_i=\frac{\Delta[i]}{\Delta[CO_2]}\times EF_{CO2}, \quad (2)$$

where $\Delta[i]$ is the incremental concentration of pollutant *i*.

According to the standard method ISO 8178-1, the sulfur in fuel is assumed to be fully transformed into SO_2, so we used Eq. (3) to calculate the EF of SO_2 (Zhang et al., 2018a):

$$EF_{SO2}=S\%\times\frac{64}{32}\times10^3, \quad (3)$$

where EF_{SO2} is the EF of SO_2 in g kg^{-1}, and S% represents FSC.

3 Results and discussion

3.1 Changes in EFs for ships at berth

The FSC for the tested coastal vessels decreased from 2.2 ± 0.5% on average before to 0.4 ± 0.5% after IFSP, although there were some ships, such as ship G, which violated the regulation with an FSC still above the limit of 0.5% (Table 1). In fact, the ship fuel was transferred from residual fuel oil to diesel oil or heavy oil (Fig S1), and the compositions of the fuels used by the coastal vessels tended to have more low-carbon number hydrocarbons, as demonstrated by their total ion chromatograms, than those of coastal vessels before IFSP (Fig S2).

As shown in Table 2, the EFs for SO_2, which were independent of the combustion system (Corbett et al., 1999), decreased by 78.0% from 44.0 ± 10.5 g kg^{-1} to 9.66 ± 7.97 g kg^{-1} on average. Fuel-based EFs for CO_2, CO, NO_x ($NO+NO_2$), VOCs, $PM_{2.5}$, OC and EC, however, were more complex because they are not only related to the properties of the fuels but also heavily influenced by the performance of the combustion system. The comparison before and after IFSP was also challenged by the fact that the tested coastal vessels during the two campaigns were not the same and that we tested a limited number of ships. Nevertheless, ships C and D had been tested both before and after IFSP and we compared them. The EFs of CO_2 for ships C and D slightly increased from 3025 g kg^{-1} and 3069 g kg^{-1} to 3131 g kg^{-1} and 3196 g kg^{-1} after IFSP; the EF of CO for ship C increased from 3.80 g kg^{-1} to 6.16 g kg^{-1}, but that for ship D decreased from 14.6 g kg^{-1} to 6.41 g kg^{-1}; the EF of NO_x for ship C slightly decreased from 19.9 g kg^{-1} to 19.0 g kg^{-1}, while that for ship D decreased from 51.5 g kg^{-1} to 31.1 g kg^{-1}.

Similar to the EFs of SO_2, the EFs of $PM_{2.5}$ also decreased significantly after IFSP. For example, the EFs of $PM_{2.5}$ for ship C decreased by 45.1% from 1.02 g kg^{-1} to 0.56 g kg^{-1} and that for ship D decreased by 64.3% from 2.44 g kg^{-1} to 0.87 g kg^{-1};

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similar to that of $PM_{2.5}$, the EF of OC for ships C and D decreased by 28.7% and 60.5%, but no significance change occurred in the EF of EC. Therefore, after IFSP, the changes in the EFs of CO_2, CO, NO_x and EC were not significant for the coastal vessels, but the EFs of SO_2, $PM_{2.5}$ and OC decreased.

Compared to SO_2 or other pollutants, the VOCs from coastal vessels shown more dramatic changes in their EFs. As shown in Table 2, the EFs of the VOCs ranged from 60.7 mg kg^{-1} to 197 mg kg^{-1} with an average of 118 ± 56.1 mg kg^{-1} before IFSP, and they ranged from 292 mg kg^{-1} to 5251 mg kg^{-1} with an average of 1807 ± 1746 mg kg^{-1} after IFSP. For ships C and D that were tested both before and after IFSP, the EFs of the VOCs for ship C increased approximately 6 times from 106 mg kg^{-1} to 706 mg kg^{-1}, and that for ship D also increased approximately 4 times from 60.7 mg kg^{-1} to 292 mg kg^{-1}. This substantial change in our study was consistent with that based on shipboard platform measurements by Copper et al. (2003), who also found that the EFs of hydrocarbons from a passenger ferry at berth increased from 0.29-0.57 g kg^{-1} to 1.71 g kg^{-1} after replacing the residual oil (FSC=0.53%) with marine gasoil (FSC=0.09%) (Table 3).

There are only a few previous studies available on air pollutants from coastal vessels at berth (Table 3). The ranges for the EFs of CO_2, PM, VOCs and SO_2 in our study were similar to those determined by Cooper et al. (2003), but our EFs of CO were much higher and our EFs of NO_x were much lower.

River vessels sail in inland rivers and many studies have investigated the emissions from river vessels under cruising conditions (Fu et al., 2013; Peng et al., 2016; Zhang et al., 2016), but no studies are available about their emissions at berth. In this study, river vessels used diesel as fuel, and they were not affected by the fuel switch policy. As shown in Table 3, for the tested river vessels (ships H, I, J and K), the EFs of CO_2 (3014 ± 99.0 g kg^{-1}) and NO_x (28.1 ± 24.5 g kg^{-1}) were close to those for coastal vessels; the EF of CO (77.9 ± 62.5 g kg^{-1}), however, was nearly 4 times higher than that of coastal vessels after IFSP, and larger than that reported for engineering vessels and research vessels under cruising conditions with a maximum of 30.2 g kg^{-1} (Zhang et al., 2016); their EF of SO_2 was as low as 0.69 ± 0.36 g kg^{-1}, while the EF of the VOCs was as high as 3.36 ± 2.77 g kg^{-1}, 85.6% larger than that reported for coastal vessels after IFSP but within the range for research vessels (1.24-4.18 g kg^{-1}) as reported by Zhang et al. (2016).

3.2 EFs of grouped and individual VOCs

The data on the EFs of grouped and individual VOCs are sparse (Cooper et al., 1996; Murphy et al., 2010; Agrawal et al., 2008; 2010), especially for ship emissions at berth. In this study, 68 species of VOCs, including 29 alkanes, 21 alkenes, 1 alkyne and 17 aromatics, were determined. As shown in Fig. 3 and Table 4, for coastal vessels before IFSP, alkanes dominated the emissions among the VOCs at 49.4 ± 24.1% and an EF of 66.0 ± 48.3 mg kg^{-1}, while aromatics and alkenes accounted for 27.9 ± 12.3% and 21.9 ± 11.9% of the VOCs with EFs of 29.2 ± 8.6 mg kg^{-1} and 21.9 ± 4.5 mg kg^{-1}, respectively. However, there were dramatic changes in the compositions of the VOCs after IFSP. Alkenes overtook alkanes to become the most abundant group at 43.1% ± 12.8% and an EF of 924.6 ± 1314.9 mg kg^{-1}, followed by alkanes (33.0 ± 17.5%, 339.2 ± 176.6 mg kg^{-1}) and aromatics (16.1 ± 4.1%, 247.3 ± 236.4 mg kg^{-1}). In addition, the mass percentages of <

Deleted: the EFs of OC and EC for ship C decreased by 28.7% and 56.1%, and that for ship D decreased by 60.5% and 63.0%, respectively. Therefore, after implementing the new policy, the changes in EFs of CO_2, CO and NO_x were not significant for coastal vessels, but the EFs of SO_2, $PM_{2.5}$ and carbonaceous aerosols did become lower.

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C_6 VOCs (VOCs with carbon numbers below 6) in the total VOCs in ship exhaust increased from 8.5%-27.3% to 44.4%-86.6% after IFSP (Fig S3), which indicated more low carbon number VOCs were emitted from ships at berth.

For the EFs of the individual VOCs, the top 25 species remained unchanged after IFSP, but their rankings changed (Table S2). As shown in Fig. 4 and Table 4, n-undecane and n-dodecane were still among the dominant species, although their percentages decreased substantially. Their EFs did not change to the same degree and were 22.5 ± 18.2 mg kg^{-1} and 21.5 ± 17.1 mg kg^{-1} before IFSP and 22.5 ± 24.6 mg kg^{-1} and 32.1 ± 62.1 mg kg^{-1} after IFSP, respectively. In addition, the EF of isobutane increased from 0.06 ± 0.07 mg kg^{-1} to 94.3 ± 62.2 mg kg^{-1}. A Striking increase in EFs was also observed for alkenes. Ethylene overtook 1-hexene to become the most abundant alkene, with its EF increasing from 2.8 mg kg^{-1} to 602 mg kg^{-1} on average. Propene, with an EF of 5.5 ± 1.5 mg kg^{-1} before IFSP, had the second largest EF of 198 ± 260 mg kg^{-1} after IFSP, an increase of over 30 fold. The alkene 1-hexene, which ranked first among alkenes with an EF of 5.9 ± 3.8 mg kg^{-1} before IFSP, also increased 1.9 times to 17.3 ± 19.4 mg kg^{-1}. The mass percentages of acetylene, the only alkynes detected, increased from 0.9 ± 0.6% to 7.5 ± 7.6%, with its EF increasing from 0.9 ± 0.6 mg kg^{-1} to 328.7 ± 605.4 mg kg^{-1}. Benzene and toluene were the dominant aromatic species before and after IFSP. Their EFs increased from 11.9 ± 4.6 mg kg^{-1} and 6.0 ± 1.2 mg kg^{-1} to 116.5 ± 200.8 mg kg^{-1} and 33.3 ± 42.5 mg kg^{-1}, respectively, after IFSP.

The composition of the VOCs from the river vessels was similar to that of the coastal vessels after IFSP. As shown in Fig. 3 and Table S2, alkenes also were dominant in the emissions of the VOCs at 45.1 ± 5.9%, while aromatics and alkenes accounted for 33.7 ± 4.8% and 14.3 ± 4.1%, respectively. For the individual VOCs, the most abundant species were ethylene, isobutene, propene, acetylene, n-decane and benzene. However, the EFs of the VOCs for the river vessels were 1.9 times those of the coastal vessels after IFSP (Table 2), suggesting that VOCs emissions from the river vessels might have played an important role as their emissions are closer to populated areas and thus should be regulated.

Recently, both Xiao et al. (2018) and Huang et al. (2018a) carried out VOC emissions tests on ships at berth in China's ECA. Xiao et al. (2018) reported that aromatics and alkanes dominated the VOCs emissions from the ships at berth. Furthermore, the most abundant alkane species were n-heptane, methylcyclohexane, n-octane, n-nonane, n-decane and n-undecane, and benzene and toluene accounted for 9% of the VOCs emissions; Huang et al. (2018a) also investigated the VOC emissions from ships at berth, but aromatics accounted for up to 70.9% of those emissions, while alkenes only accounted for 6.7%. The variation in ship fuels might be one of the key reasons for the large differences in the compositions of the VOC emissions among the available studies. The fuel switch policy restricted only the FSC below 0.5%, so many types of fuels could be used in ships, as seen from the four types of diesels fuels used by the tested ships (Fig. S1). Nonetheless, engine designs, performance and loads during the sampling might have also led to the differences (Cooper et al., 1996).

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3.3 Ozone and SOA formation potential

3.3.1 OFP of the VOCs from ship exhaust

Ozone formation potential (OFP) is the approach that uses maximum incremental reactivity (MIR) to represent the maximum contribution of VOCs to near-surface ozone formation under optimal conditions (Carter, 2009). With ships emissions data in this study, the normalized ozone reactivity (R_{O3}, g O_3 g^{-1} VOCs) and OFP (g O_3 kg^{-1} fuel) were calculated as:

$$R_{O3} = \sum_i w_i \times (MIR)_i \ , \quad (4)$$

$$OFP = \sum_i EF_i \times (MIR)_i \ , \quad (5)$$

where w_i is the mass percentage of the total VOC emissions for *i* species.

As described in Fig. 5, the R_{O3} of the tested coastal vessels increased by almost 70% from 3.19 ± 0.82 g O_3 g^{-1} VOCs to 5.41 ± 0.69 g O_3 g^{-1} VOCs. The main reason for the increase in R_{O3} is that shares of highly reactive alkenes (such as ethylene and propene) increased among the VOCs emitted, and the contribution percentages of alkenes to R_{O3} increased from 56.4% ± 13.3% to 75.7% ± 13.3%. OFP increased 28.7 times from 0.35 ± 0.11 g O_3 kg^{-1} fuel to 10.37 ± 13.55 g O_3 kg^{-1} fuel.

For the river vessels, their average R_{O3} was 5.55 g O_3 g^{-1} VOCs, which was close to that of the coastal vessels after IFSP, but their average OFP (22.98 ± 16.59 g O_3 kg^{-1} fuel) was more than double that of the coastal vessels. As shown in Fig. S4, the R_{O3} (4.22 g O_3 g^{-1} VOCs) reported by Huang et al. (2018a) for ship emissions after IFSP was approximately 20% lower than the R_{O3} (5.41 g O_3 g^{-1} VOCs) from this study, and the R_{O3} of 2.63 O_3 g^{-1} VOCs reported by Xiao et al. (2018) was even lower than the R_{O3} before IFSP in this study. These results also suggest that there is great diversity in ship-emitted VOCs at berth, even in different regions of China.

3.3.2 SOAFP of the VOCs from ship exhaust

Similarly, normalized secondary organic aerosols reactivity (R_{SOA}, g SOA g^{-1} VOCs) and SOA formation potential (SOAFP, g SOA kg^{-1} fuel) can also be calculated as (Zhang et al., 2018a):

$$R_{SOA} = \sum_i w_i \times Y_i \ , \quad (6)$$

$$SOAFP = \sum_i EF_i \times Y_i \ , \quad (7)$$

where Y_i is the SOA yield of VOC species *i*. We could calculate the SOAFP under high-NO_x and low-NO_x conditions (Ng et al., 2007). However, we should be cautious in interpreting the results because intermediate volatile organic compounds were not measured in this study, which may lead to underestimation of SOA yields (Huang et al., 2018b; Lou et al., 2019).

As shown in Fig. 5, for the coastal vessels, R_{SOA} decreased by ~75% from 0.288 ± 0.114 g SOA g^{-1} VOCs to 0.073 ± 0.079 g SOA g^{-1} VOCs under high-NO_x conditions, while R_{SOA} also decreased by 66.5% from 0.313 ± 0.088 g SOA g^{-1} VOCs to 0.105 ± 0.085 g SOA g^{-1} VOCs under low-NO_x conditions. This decline of R_{SOA} resulted from the decrease in mass percentages of aromatics and alkanes, which have higher SOA yields than those of alkenes (Ng et al., 2007; Lim and Ziemann, 2009; Loza et al., 2014). However, with the dramatically increased EFs of the VOCs, under high-NO_x conditions,

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SOAFP increased 1.6 times from 0.037 ± 0.026 g SOA kg^{-1} fuel to 0.096 ± 0.092 g SOA kg^{-1} fuel, and under low-NO_x conditions, SOAFP increased 2.5 times from 0.040 ± 0.025 g SOA kg^{-1} fuel to 0.137 ± 0.111 g SOA kg^{-1} fuel.

In particular, the R_{SOA} for ship F (Fig. S4) was significantly higher than that of the other ships, largely due to a higher fraction (11.5%) of n-dodecane, which had the highest SOA yield among the VOCs. For the river vessels, the R_{SOA} was the lowest in the test ships, with a value of 0.037 ± 0.017 g SOA g^{-1} VOCs under high-NO_x conditions and 0.069 ± 0.026 g SOA g^{-1} VOCs under low-NO_x conditions. However, their SOAFP was 0.165 ± 0.131 g SOA kg^{-1} fuel under high-NO_x conditions and 0.322 ± 0.267 g SOA kg^{-1} fuel under low-NO_x conditions, which were the largest of the values due to their much higher EFs.

As shown in Fig. S4, based on the VOCs emissions from ship at berth reported in Huang et al. (2018a), we calculated a R_{SOA} of 0.080 g SOA g^{-1} VOCs under high-NO_x conditions and 0.228 g SOA g^{-1} VOCs under low-NO_x conditions for a coastal vessel also using low-sulfur fuels. This relatively higher RSOA under low-NOx conditions was related to the higher fractions of aromatics in the VOC emissions. Using another method in Gentner et al. (2012), Xiao et al. (2018) reported an average R_{SOA} of 0.017 g SOA g^{-1} VOCs under high-NO_x conditions, which was close to a R_{SOA} of 0.015 g SOA g^{-1} VOCs calculated by the same method for the coastal vessels after IFSP.

3.4 Conclusions

Ships emissions control is primarily targeted in terms of PM-related pollution, and designating ECA with a fuel switch policy is a widely adopted approach to control air pollution in harbor cities. In the present study, we measured emissions from coastal vessels at berth in Guangzhou Port in the PRD region, one of the three newly established ECAs since 2017, and we preliminarily investigated the changes in emissions caused by the fuel switch policy, and further compared the results with those measured for river vessels unaffected by the fuel switch policy.

As reported by previous studies, our study also demonstrated that after IFSP, the EFs of both SO_2 and $PM_{2.5}$ for the coastal vessels decreased, as evidenced by the fact that the EFs of SO_2 reduced by ~78.0% and the EFs of $PM_{2.5}$ reduced by ~55.5% on average. However, the EF of the VOCs increased approximately 14 fold from 118 ± 56.1 mg kg^{-1} to 1807 ± 1746 mg kg^{-1}. Moreover, the compositions of the VOCs emitted from the coastal vessels also changed greatly. The mass percentages of alkenes increased from 8.5%-27.3% to 44.4%-86.6%. The sharp increase in the EFs, as well as elevated fractions of the more reactive species, resulted in a much higher OFP for the VOCs than that of the other species, which sharply increased at approximately 29 fold from 0.35 ± 0.11 g O_3 kg^{-1} fuel to 10.37 ± 13.55g O_3 kg^{-1} fuel. The SOAFP also increased by over 50%, although the R_{SOA} was reduced by 66.5%-74.8%.

For the river vessels were not affected by the fuel switch policy, the EFs of the VOCs were measured at value as high as 3358 ± 2771 mg kg^{-1}, which was almost double those for the coastal vessels after IFSP, with the OFP and SOAFP also at approximately 2 times their counterparts for the coastal vessels after IFSP.

In summary, our tests in the Guangzhou Port demonstrated that for coastal vessels at berth, the fuel switch from high-sulfur residual fuel oil to low-sulfur diesel or heavy oil resulted in substantially decreased emissions of SO_2 and $PM_{2.5}$ and

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Data availability

The data used in this publication are available to the community and can be accessed by request to the corresponding author.

Author contributions

ZFW performed data analysis with contributions from YLZ and XMW. JJH, XLH, XY and WQY helped sampling. HZC and YJW helped project coordinating and data interpretation. RQZ, MZ, HF and ZZ helped sample analysis.

Competing interests

The authors declare that they have no conflict of interest.

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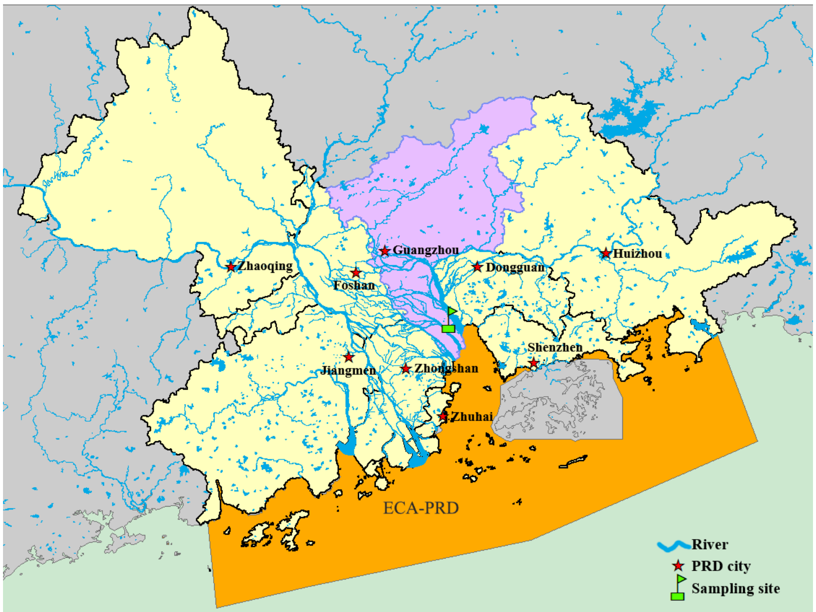

Figure 1. The realm of ECA-PRD and the sampling site.

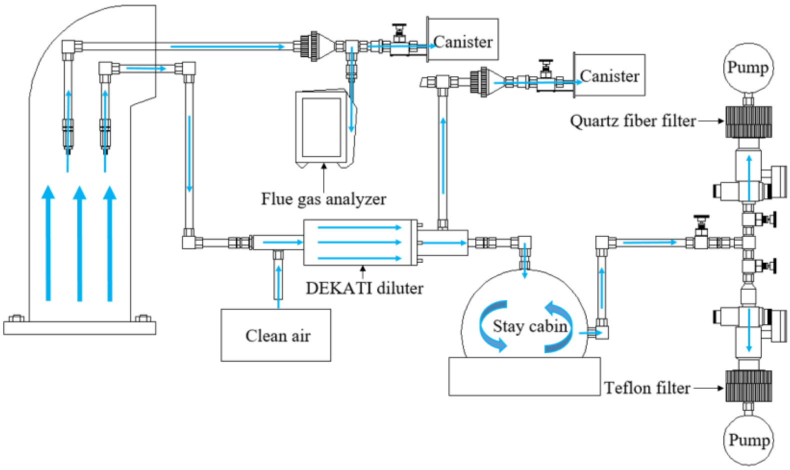

Figure 2. Schematic diagram of sampling setup.

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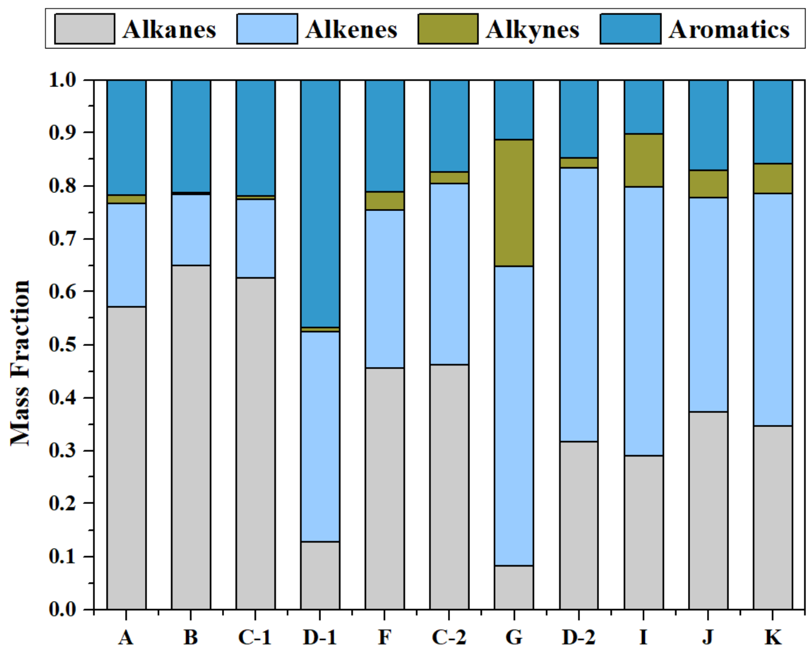

Figure 3. VOCs grouping according to their functional group. A, B, C-1 and D-1 are coastal vessels tested before JFSP, F, G, C-2 and D-2 are coastal vessels tested after JFSP, and I, J and K are river vessels tested.

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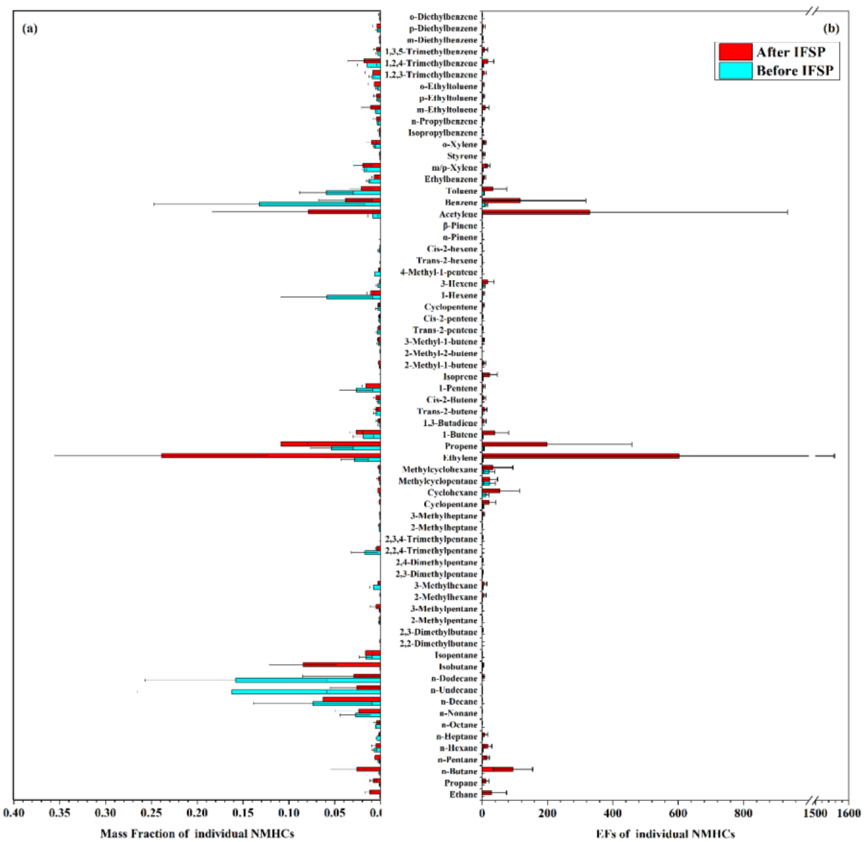
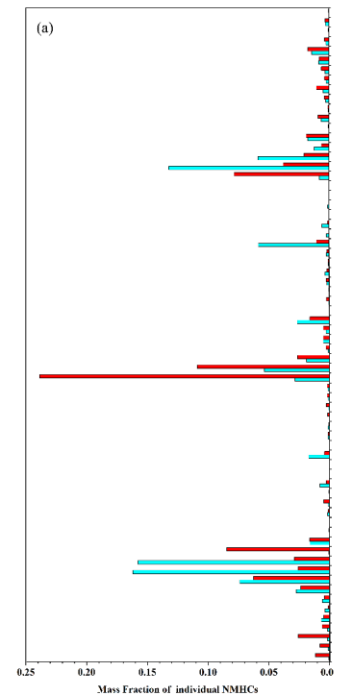


Figure 4. Comparison of VOCs emission factors before and after IFSP for coastal vessels.



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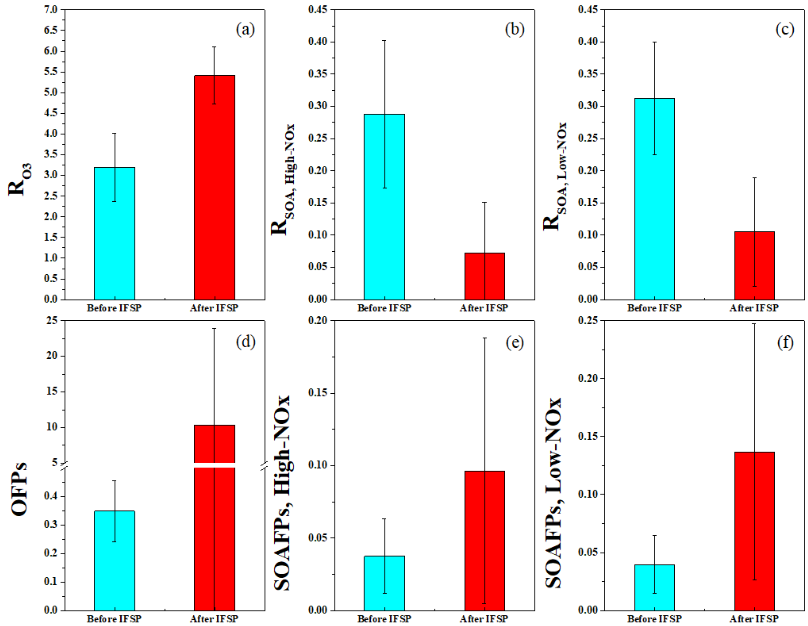

Figure 5. The changes in R_{O3} (g O_3 g^{-1} VOCs), R_{SOA} (g SOA g^{-1} VOCs), OFP (g O_3 kg^{-1} fuel) and SOAFP (g SOA kg^{-1} fuel) for coastal vessels before and after IFSP.

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Table 1. The basic information of test vessels.

NO	Test date	Ship types	Gross tonnage (t)	Vessel age (yr)	Auxiliary engine		Fuel types		
					Power (kW)	Amount	Types	C/%	S/%
Coastal vessels (before JFSP)									
A	2015.12.17	container vessel	47917	3	1760	2	residual oil	84.9	1.60
					1320	1			
B	2016.08.19	container vessel	41482	8	2045	3	residual oil	82.9	2.90
C-1	2016.08.19	container vessel	49437	4	1760	2	residual oil	82.7	2.10
					1320	1			
D-1	2016.11.15	bulk carrier	38384	3	660	3	residual oil	84.4	2.20
Coastal vessels (after JFSP)									
E	2017.03.29	bulk carrier	8376	8	200	2	diesel oil	86.6	0.68
F	2017.12.22	bulk carrier	10716	10	200	3	diesel oil	86.6	0.13
C-2	2018.04.21	container vessel	49437	6	1760	2	diesel oil	85.8	<0.01
					1320	1			
G	2018.05.03	container vessel	25719	19	500	3	heavy oil (low-sulfur)	86.5	1.14
D-2	2018.05.06	bulk carrier	38384	4	660	3	heavy oil (low-sulfur)	87.5	0.47
River vessels									
H	2017.03.29	dry cargo carrier	2445	9	144	2	diesel oil	86.0	0.06
					76	1			
I	2017.09.27	container vessel	1862	7	73.5	2	diesel oil	86.0	0.03
J	2017.09.27	container vessel	1357	15	58	2	diesel oil	86.1	0.03
K	2017.09.27	container vessel	1420	10	58.5	2	diesel oil	85.9	0.02

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Table 2. The emission factors for test vessels (in unit of g kg^{-1}).

Ships	CO_2	CO	SO_2	NO_x	VOCs	OC	EC	$PM_{2.5}$
Coastal vessels (before JFSP)								
A	3097	8.03	32.0	61.7	0.11	0.59	0.15	2.30
B	3029	5.33	58.0	29.1	0.20	0.29	0.05	1.46
C-1	3025	3.80	42.0	19.9	0.11	0.22	0.07	1.02
D-1	3069	14.6	44.0	51.5	0.06	0.16	0.61	2.44
Coastal vessels (after JFSP)								
E	3120	24.2	13.5	56.6	1.68	1.41	2.08	8.46
F	3156	5.50	2.52	13.0	1.11	0.55	1.41	2.17
C-2	3130	6.16	0.06	19.0	0.71	0.16	0.29	0.56
G	3079	41.0	22.8	19.2	5.25	2.05	1.49	5.90
D-2	3196	6.41	9.40	31.1	0.29	0.07	0.22	0.87
River vessels								
H	3087	26.2	1.20	25.0	0.81	0.74	5.21	12.5
I	3055	59.6	0.52	13.3	1.40	-	-	-
J	2865	171	0.68	9.77	6.93	-	-	-
K	3050	55.0	0.36	64.4	4.29	-	-	-

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Table 3. Fuel-based average EFs (g kg^{-1}) from this study in comparison with those reported previously.

Ships	FSC	Condition	CO_2	CO	PM	VOCs	SO_2	NO_x
Coastal vessels or ocean-going vessels								
Coastal vessels-Before IFSP[a]	>0.5%	At berth	3055	7.93	1.81	0.12	44.0	40.6
Coastal vessels-After IFSP[a]	<0.5%	At berth	3136	16.7	3.59	1.81	9.66	27.8
Passenger ferry-α[b]	0.08%	At berth	3080-3297	2.69-4.58	0.99-2.12	0.57-0.99	1.56-1.65	70.3-90.6
Passenger ferry-β-1[b]	0.53%	At berth	3121-3284	4.34-6.99	1.96	0.29-0.57	10.2-11.0	54.4-71.6
Passenger ferry-β-2[b]	0.09%	At berth	3200	-	1.29	1.71	1.67	84.2
Passenger ferry-γ[b]	1.20%	At berth	3125-3226	1.50-2.60	1.37-2.00	0.87-1.14	23.7-24.1	64.7-84.7
Car/truck carrier[b]	0.23%	At berth	3237-3251	4.31-4.59	0.80-0.89	0.89-1.08	4.68	45.0-46.4
Container/ro-ro[b]	2.20%	At berth	3199-3212	3.55-4.17	2.49-3.10	0.79-0.88	44.0-44.2	59.4-70.4
Chemical tanker[b]	0.06%	At berth	3159	3.22-3.41	0.65-0.75	1.36-1.40	1.21	81.8-83.6
PanaMax Class Container[c]	3.01%	Cruising	2805	1.32	10.9	-	52.40	89.9
River vessels								
River vessels[a]	<0.5%	At berth	3134	77.9	12.5	3.36	0.69	28.1
Engineering vessel[d]	0.08%	Cruising	3071	30.2	9.40	23.7	1.60	115
Research vessel-α[d]	0.05%	Cruising	3153	6.93	0.72	1.24	0.92	35.7
Research vessel-β[d]	0.13%	Cruising	3151	9.20	0.16	4.18	2.60	31.6

[a]This study; [b]Cooper et al. (2003); [c]Agrawal et al. (2010); [d]Zhang et al. (2016); [e]Zhang et al., (2018b) with a coefficient of 0.22 kg kWh^{-1} to convert g kWh^{-1} to g kg^{-1}.

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Table 4. Emission factors (mg kg^{-1}) of VOCs for test vessels.

Species	Coastal vessels (before IFSP)				Coastal vessels (after IFSP)				River vessels		
	A	B	C-1	D-1	F	C-2	G	D-2	I	J	K
Ethane	0.1	0.1	0.1	0.1	8.8	5.6	99.0	3.4	17.4	59.4	31.6
Propane	0.1	0.1	0.1	0.1	14.6	3.6	24.5	2.7	2.4	9.0	7.5
n-Butane	0.3	0.1	0.4	0.0	5.6	20.7	15.4	19.3	0.6	2.1	149.3
n-Hexane	0.4	1.7	1.0	0.4	5.0	1.4	2.8	3.6	0.3	3.6	0.6
n-Octane	0.8	1.0	0.7	0.3	9.6	4.5	1.2	0.7	4.9	57.7	26.3
n-Nonane	4.6	4.5	4.1	0.3	43.0	37.3	1.4	0.9	20.5	199.6	144.5
n-Decane	2.4	23.2	15.2	0.8	117.3	97.9	2.2	1.7	32.8	300.5	247.5
n-Undecane	21.0	45.7	22.9	0.3	45.6	42.8	0.7	0.7	24.7	195.9	179.9
n-Dodecane	26.8	42.5	15.5	1.3	127.2	1.0	0.2	0.1	0.7	6.8	57.6
Isobutane	0.2	0.04	0.04	ND[e]	88.5	73.3	180.0	35.2	252.1	1336.5	459.1
Isopentane	2.2	1.1	2.0	1.2	14.5	14.1	35.6	7.6	23.6	171.3	73.4
3-Methylhexane	0.8	1.0	1.5	0.3	3.1	1.4	15.6	1.0	7.0	36.8	35.0
TM224PE[a]	ND	4.1	1.3	2.2	2.8	4.0	18.0	1.4	9.0	73.5	32.8
Other alkanes	1.8	3.0	1.8	0.6	21.2	18.4	34.6	14.4	11.1	129.0	43.2
Sum of alkanes	61.5	128.3	66.5	7.8	506.8	326.2	431.1	92.7	407.1	2581.9	1488.4
Ethylene	2.9	3.2	2.2	3.1	170.5	96.7	2062.7	79.3	401.8	1155.1	1125.2
Propene	7.1	6.3	3.7	4.9	82.8	71.1	595.2	42.8	201.1	969.5	378.3
1-Butene	2.1	0.6	2.6	1.7	23.9	21.1	102.7	10.1	32.0	149.0	105.6
Trans-2-butene	0.6	0.4	0.5	0.5	3.9	5.5	17.6	1.7	5.7	34.0	21.0
1-Pentene	4.1	2.0	1.2	2.9	17.3	14.7	57.9	5.2	24.7	143.1	80.4
1-Hexene	2.5	10.3	2.8	8.1	7.9	11.1	46.6	3.5	18.0	127.1	68.9
M4PE1ENE[b]	0.7	1.1	0.3	0.7	1.4	1.5	10.4	0.6	3.0	26.4	12.6
Other alkenes	1.1	2.7	2.4	2.2	23.1	19.9	82.5	7.2	26.1	206.0	96.8
Sum of alkenes	21.1	26.5	15.8	24.0	330.8	241.6	2975.6	150.4	712.5	2810.3	1888.8
Acetylene	1.8	0.7	0.6	0.5	38.5	15.4	1255.1	5.6	139.1	355.5	241.8
Benzene	9.6	11.6	7.9	18.6	18.3	13.0	423.7	10.9	46.6	191.7	129.5
Toluene	5.4	7.6	4.8	6.3	15.7	7.8	98.2	11.7	22.1	131.3	75.5
Ethylbenzene	1.1	2.5	1.8	0.7	7.4	5.3	13.1	3.0	6.3	61.5	28.2
m/p-Xylene	1.8	3.5	1.7	1.3	24.1	19.4	20.4	7.0	11.5	129.1	57.4
o-Xylene	0.6	1.5	0.7	0.5	14.1	10.1	9.3	2.9	6.3	69.1	31.6
m-Ethyltoluene	0.7	1.5	0.5	0.2	24.8	11.4	2.0	1.4	8.4	100.0	75.9
o-Ethyltoluene	0.3	1.2	0.6	0.1	16.8	6.1	1.7	0.9	5.0	54.2	28.9
TM123B[c]	1.1	2.4	1.1	0.2	19.7	9.5	2.2	0.8	5.5	71.1	43.9
TM124B[d]	1.0	5.3	2.1	0.2	44.1	18.3	3.3	1.6	15.2	167.8	99.7
Other aromatics	1.7	4.6	2.2	0.3	49.1	21.6	15.5	2.8	15.5	206.2	105.2
Sum of aromatics	23.3	41.8	23.2	28.4	234.0	122.6	589.5	43.0	142.5	1182.0	675.7

[a]2,2,4-Trimethylpentane; [b]4-Methyl-1-pentene; [c]1,2,3-Trimethylbenzene; [d]1,2,4-Trimethylbenzene; [e]Not detected.

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