Reply to Editor

Thanks very much for your comments. We would like to ask you if we can change the authors and the relevant affiliates because of the change of supporting project.

Our replies are given as following according to your comments:

Both reviewers supported the measurement methods and data quality. However, one reviewer mentioned the need to consider the dilution when evaluating organic carbon, and to present more standard emission measures. The other reviewer requested a better treatment of uncertainties.

Thanks for your comment, and the reply is given as following:

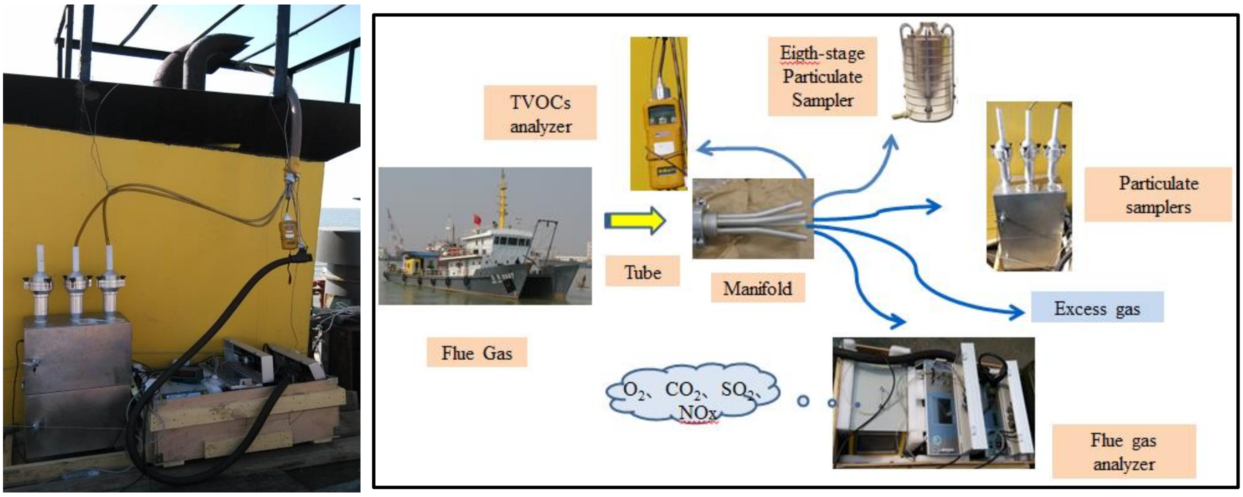
The residence time of soot particle in the pipe could affect the formation of PM, which led to the different composition of PM. The dilution sampling was not used in this study that might be one reason of the lower OC to EC ratio. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods because of the different definitions of OC and EC. They are shown in the revised manuscript (Line 30, Page 15 and Line 1-8, Page 16) as following.

The non-dilution sampling was the main reason of the lower OC to EC ratio in this study. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods (such as TOT) because of the different definitions of OC and EC (Khan et al., 2012). Compared with other diesel engines,, the ratios of OC to EC in this study were higher than that of automobile diesel soot, in which EC comprises 75–80 wt% of the total PM (Clague et al., 1999), and also higher than heavy heavy-duty diesel trucks (HHDDT) with OC to EC ratios below unit for cruse and transient modes even though higher in cold-start/idle and creep modes (Shah et al., 2004).

The real-world measurement system for vessels including on-board test picture and schematic diagram of the portable measurement system has been added in Figure S1. Detailed instruction of the sampling system also has been added in Supporting information, shown as following:

Real-world Measurement System for vessels

Detailed compositions and procedure of the on-board measurement system were given as follows: The whole measurement system was placed on deck next to the exhaust pipe of the vessel. A slender tube was placed into the vessel exhaust pipe to lead out the flue gas. Then it was divided into five subsamples through a manifold for different analyses and evacuation of the excess gas. The on-board test picture (Figure S1, a)) and schematic diagram of the portable measurement system (Figure S1, b)) are shown in Figure S1.



a b

Figure S1 Real-world measurement system for vessels: a) on-board test picture, b) schematic diagram of the portable measurement system

The detection parameters for the gaseous matters have been added as an accessory in Table S3, including the detection method, range, resolution and accuracy etc. We can see that all the detection uncertainties are within the relative error of 5%. During our sampling, 3 to 5 replicate samples for each operating mode were collected, which could give the total error shown in Table S4 and Table S5, including the detection error and the artificial error.

Table S3 Detection parameters for the gaseous matters

Component	Method	Range	Resolution	Accuracy	Time (T$_{90}$)	Conformity
O_2	Electrochemical sensor	20.95%	0.01%	±5% rel.	45 s	ISO 12039, CTM-030

CO_2	NDIR	5%	0.01%	±3% rel.	45 s	ISO 12039, OTM-13
CH_4	NDIR	5%	0.01%	±3% rel.	45 s	
NO	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 10849, Method 7E
NO_2	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 10849, Method 7E
SO_2	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 7935, Method 6C
N_2O	NDIR	2000ppm	1ppm	±3% rel.	45 s	ISO 21258
VOCs	PID	10000ppm	0.1ppm	±5% rel.	-	

NDIR, Non-dispersive Infra-red

PID, Photo Ionization Detectors

Both reviewers indicate a need for context in this manuscript. That context will need to improve to make the manuscript publishable. Simply stating that one needs Chinese emission factors won't be sufficient. While China is a large and important country, especially with regard to shipping, this manuscript does not contain an understanding of WHY Chinese ships might be different. China's fleet probably contains a wide range of ships and fuels. In that case, the emission factors presented here may not be representative of the Chinese fleet. Other emission factors, not measured in China, also may or may not be representative. Without an understanding of what causes a difference in emissions, one can't discuss whether measurements are representative.#

Thanks for your comment, and the reply is given as following:

The estimated contribution of shipping emissions on port cities, the type composition of offshore vessels in China, the fuel consumption and the latest policy made by Chinese Ministry of Environmental Protection aiming to limit the emissions from marine engines have been added in the revised manuscript (Line 5-7, Page 4, Line 14-17, Page 8, Line 8-22, Page 6).

It was estimated that 8.4% of SO_2 and 11.3% of NO_x were emitted from ships in China in 2013 with port cities were the worst effect areas (http://news.xinhuanet.com/politics/2015-06/08/c_127890195.htm). Conditions in

China differ substantially from those in other countries, such as in vessel types (more small motor vessels and the type composition of offshore vessels is shown in Table S1), different fuel standards compared with other countries (fuel meeting the GB/T 17411-2012 standard with sulfur contents of less than 3.5% m/m; however, the ISO 8217-2010 international standard has the maximum sulfur content according to the relevant statutory requirements that always have lower values, such as less than 0.1% in emission control areas), age of vessels (Chinese commercial vessels have an average age of 19.2 yr compared with 8.0 yr and 8.9 yr for Japan and Germany, respectively).

According to statistical data, the total oil consumption of vessels in China was 20.99 million tons in 2011, including 10.99 million tons bonded oil and 5.93 million tons domestic trade oil, with light fuel oil account for 40% of the domestic trade oil and 25% of the total consumption (shown in Table S2).

But because of the serious air pollution these years in China, emission limits for the main sources such as vehicle exhaust, coal combustion, biomass combustion and raise dust have becoming more and more stringent. A draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection, which is named Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ, Ⅱ), is on soliciting opinions. It has set the limits of CO, HC, NOx and PM for different kinds of vessels, which mainly based on the Directive 97/68/EC set by EU and 40 CFR part 1042 set by EPA. Besides, an implementation plan has released by Ministry of Transport of the People’s Republic of China in December 2015 aiming to set shipping emission control areas to reduce SO2 emissions in China (Ministry of Transport of the People’s Republic of China, 2015). All the regulations were set mostly based on other directive and regulations. And therefor, detailed measurement data in China are in urgent need for the further policy making that more fit current situations of vessels.

Initially, it was hoped that the choice of measurement ships would reflect the shipping fleet in general, i.e. in terms of engine type (engine speed and power output), fuel used, engine age and mode of operation, with more than 10 vessels planned to test. However, consideration was given to the practicalities involved with the measurements, i.e. installation of sampling systems, external conditions, etc. Besides, time and economic constraints weighed heavily and only several shipowners willing to participate in the project. Thus, the chosen vessels of different engine powers with diesel used represent a compromise.

Three offshore vessels with different total tonnage and engine power were tested in our study. We inferred that the engine type was the most important influence factor on shipping emissions. All the three vessels are high-speed and medium-speed engines. Statistics have reported that high-speed and medium-speed engines could account for more than 95% of the latest produced vessel engine since 2008 in China, with most of which used in inland vessels and offshore vessels. So, the test vessels have a certain degree of representativeness from this point.

We may not fully understand what causes a difference in emissions. But the simple fact that these ships are measured in China is not the cause of a difference in emissions. These results may be applicable beyond China, and other emission measurements may be valid for Chinese ships. Both reviewers ask for a discussion that relies on physical factors, such as fuel or ship type. Even a simple breakdown for Chinese ships or usage in Chinese waters would be helpful. When comparing with previously published results, comparison with regard to the type of ship would be more instructive. I suggest that authors provide discussion to help readers understand how these measurements, as well as other measurements, would best be used to develop an emission inventory. This could be accomplished, in part, by comparing with a wider range of measurements, as the first reviewer requests. The second reviewer also suggests that authors update their understanding of how measurements are typically presented. Both of these improvements would provide a better context for the potentially useful measurements presented here.#

Thanks for your comment, and the reply is given as following:

Influence factors such as engine type and fuel type have been discussed in the revised manuscript (Line 13-27, Page 18). We inferred that engine type could have more impact on the emission factors.

In order to compare the differences of emission factors from vessels in this study and other non-road diesel engine vehicles, fuel-based emission factors for CO, NO_x and PM were given in Table S7, including military non-road heavy duty diesel vehicles, excavator and wheel loader and other diesel trucks. It could be deduced that engine types have significant impact on emission factors such as non-road heavy duty diesel vehicles always have much higher NO_x emission factors compared with common diesel trucks. Besides, one interested thing should be mentioned that Chinese diesel engines always have higher NO_x and PM emission factors which may be caused by the less strict emission standard applied for diesel vehicles in China. Similarly, the engine type might be an important cause of the different emissions, such as HH had much higher pollutants emissions with an engine produced in China and yet DFH's engine produced in Germany. Besides, emission test for a high-speed marine diesel engine with different kind of diesels showed that, diesel type had limited influence on emissions such as NO_x, CO and CH, but a significant impact on PM emission (28.9-41.5%) because of the different sulfur content in fuel (Xu, 2008).

Because there is no public data of the distribution of engine types in China, we could not give official statistics. But through personal relationships of Marine Affairs Bureau, we got the distribution of vessels through gross tonnage in 2014 in offshore area of Yangtze River Delta that is one of the three largest shipping areas, which is shown in the following table. Unfortunately, we are not allowed to public the data in the manuscript. The gross tonnage of our test vessels are 307, 3235 and 602, respectively, accounting for 34.7% of the total vessels, which could has certain degree of representation.

Distribution of vessels through gross tonnage in 2014 in offshore area of Yangtze River Delta

Gross tonnage (t)	Percentage (%)
10000-49999	3.7
3000-9999	12.7
1000-2999	50.3

500-999	13.8
100-499	8.2
<99	7.0

More power-based emission factor data are added in the revised manuscript in Table 4, including data from US EPA, Khan et al., Agrawal et al.(2008), Moldanova et al.(2009), Celo et al.(2015) and so on.

Besides, detailed calculation method about average EFs for each vessels, converting power-based emission factor to fuel-based emission factor and Carbon balance method have been added and explained in the revised manuscript.

Average EFs for each vessel were calculated based on actual operating conditions, as shown in Formula (4) (Line 3-6, Page 11):

$$EF_{\mathrm{X,A}} = \sum\nolimits_{\mathrm{X},i} EF_i \times P_i \qquad (4)$$

where $EF_{\mathrm{X,A}}$ is the average EF for species X, EF_i is the EF for operating mode *i* for species X, and P_i is the percentage of time spent in operating mode *i* during the shipping cycle.

The converting power-based emission factor to fuel-based emission factor was added as Formula 5 in the revised manuscript (Line 7-11,Page 11), shown as following:

$$\mathrm{EF}_{\mathrm{X,P}} = EF_{\mathrm{x}} \cdot \mathrm{FCR} \qquad (5)$$

where $\mathrm{EF}_{\mathrm{X,P}}$ is the power-based emission factor for species X (g kW h^{-1}), FCR is fuel consumption rate for each vessel (kg fuel (kW h)$^{-1}$).

Carbon balance method was used in this study to give the emission factors, which assumes that all carbon in the fuel was emitted as carbon-containing gases (CO, CO2, and TVOC) and carbon-containing particulate matter. So Formula 1 was given as shown below:

$$C_{\mathrm{F}} = R_{\mathrm{FG}} \times (c(\mathrm{C_{CO}}) + c(\mathrm{C_{CO_2}}) + c(\mathrm{C_{PM}}) + c(\mathrm{C_{TVOC}}) \qquad (1)$$

R_{FG} could be calculated according to this formula since all the other parameters could be measured during or after the sampling.

The correction for CO_2 has been implemented in the carbon balance equation.

Background CO_2 concentration (the CO_2 concentration of ambient air) was subtracted to ensure all the carbon was transformed from the carbon in the fuel. In the same way, when other emission factors were given, background concentrations had also been subtracted, such as CO, NO_x, etc.

Other minor revisions made will be shown in the revised manuscript.

Thanks again.

Best regards,

Fan Zhang, Representative of all the authors

Reply to Referee 1#

Thanks very much for your comments. Our replies are given as following according to your comments:

#I had difficulty in understanding what place these results had in the picture of the ship emissions measurement community. There does not appear to be a well-defined focus for the work. If the goal is to claim the Chinese ships are somehow different then there must be extensive comparison to available literature, as well as assessment of ship type distribution from available inventories. If the goal is to add measurements of three ships to the database of measurements, then this can be done in a simpler way. If the goal is to suggest that current Chinese inventories are incorrect then there was no re-assessment based on the refined emission factors, even a course re-calculation. Please consider what your focus is and ensure this message is shared effectively. #

Thanks for your comment, and the reply is given as following: This study has given the on-board measurement of pollutants from different vessels in China, and also the impact of engine speed on NO_x emission. We are focused on adding the measurement database of shipping emissions in China, because the engine type, fuel and vessel type are very different of Chinese vessels compared with other countries (such as Chinese commercial vessels have an average age of 19.2 yr compared with 8.0 and 8.9 yr for Japan and Germany, more small motor vessels are used in China (type composition of offshore vessels in China is shown in Table S1), and diesel is very common fuel used in offshore vessels (see more detailed information in Table S2) but with no fuel stands), which makes the ship emissions unknown in China. When ship emissions inventory was calculated or contribution of ship emissions on environment was estimated in China, emission factors always need to adopt to other countries (Song, 2014;Yang et al., 2015;Ng et al., 2013;Zhou et al., 2007). We aim to give detailed emission factors data to establish the system local emission factor database in China, and also provide some data base for the policy making of emission stands of vessels in China (A draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection, which is named Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ, Ⅱ), is on soliciting opinions). Though the number of test vessels in this study was small, it could reflect the real exhaust condition of offshore vessels with diesel used in China. And this measurement is just a beginning, more number and more type of vessels' test will be carried out in our next work (two fishing vessels' measurement has been finished up to now).

The discussion of emission factors with load should be compared much more thoroughly to available data. Only a limited number of references were chosen to compare to. There is a significant amount of data in the Lloyds register, Europe and elsewhere that can be compared to, and this should be done to place the results in appropriate context. (Marine Exhaust Emissions Research Programme, Lloyd's Register of Shipping, London, United Kingdom, 1995, http://ec.europa.eu/environment/air/pdf/marine_exhausts.pdf)#

Thanks for your comment, and the reply is given as following: More power-based emission factor data are added in the revised manuscript in Table 4, including data from US EPA, Khan et al., Agrawal et al.(2008), Moldanova et al.(2009), Celo et al.(2015) and so on.

#Do these results really represent a different sub-population of emission factors due to location, maintenance etc, or are they just within the standard deviation of the current data?#

Thanks for your comment, and the reply is given as following: According to the comparison among this study and previous studies, significant differences do exist for different vessels, such as the NO_x and PM emission factors. As we mentioned in the Introduction section, the reported emissions factors for CO, NO_x, PM are in the range of 0.5–16, 2.9–44, 22–109, 0.3–7.6 g kg^{-1} fuel from previous studies, compared to 30.2, 115, 9.4 g kg^{-1} fuel of vessel HH, a typical high-speed engine vessel in China.

Besides, because there is no measurement data of shipping emissions in China except several inland ships now, we have no idea of the current condition. The most important purpose of our study is to achieve the basic data of shipping emissions in China which could have comparison with other measurement data.

The authors claim that the majority of ships in use in China are of the type investigated in this study, however it would be informative to see a breakdown of slow speed, medium speed and high speed engines (and sources) to understand the distribution of engine types.

Thanks for your comment, and the reply is given as following: Because there is no public data of the distribution of engine types in China, we could not give official statistics. But through personal relationships of Marine Affairs Bureau, we got the distribution of vessels through gross tonnage in 2014 in offshore area of Yangtze River Delta that is one of the three largest shipping areas, which is shown in the following table. Unfortunately, we are not allowed to public the data in the manuscript. The gross tonnage of our test vessels are 307, 3235 and 602, respectively, accounting for 34.7% of the total vessels, which could has certain degree of representation.

Distribution of vessels through gross tonnage in 2014 in offshore area of Yangtze River Delta

Gross tonnage (t)	Percentage (%)
10000-49999	3.7
3000-9999	12.7
1000-2999	50.3
500-999	13.8
100-499	8.2
<99	7.0

The manuscript refers to studies that are quite old. For example, the global PM burden for ships is a 2000 reference that likely uses data that is 20 years old. The most recent IMO greenhouse has study would provide a much more appropriate reference. There are a number of studies referenced where more recent studies are available. These should be sought out.#

Thanks for your comment, and the reply is given as following: New references about the shipping emissions have been added in the revised manuscript (Line 21-25, Page 3)

According to estimates from IMO (http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Pages/Greenhouse-Gas-Studies-2014.aspx), international shipping emissions for 2012 are estimated to be 796 million tonnes CO_2 and 816 million tonnes CO_2e for GHGs combining CO_2, CH_4 and N_2O. International shipping accounts for approximately 2.2% and 2.1% of global CO_2 and GHG emissions on a CO_2 equivalent (CO_2e) basis, respectively.

Other studies about characteristic of gaseous species and PM and emission factors are also added in the manuscript in the revised manuscript (Line 21-23, Page 5).

Besides, characteristics of gaseous species and PM have attracted more attention recently (Anderson et al., 2015;Celo et al., 2015;Mueller et al., 2015;Reda et al., 2015).

Estimated contribution of shipping emissions to port cities has been added in the revised manuscript (Line 5-7, Page 4).

It was estimated that 8.4% of SO_2 and 11.3% of NO_x were emitted from ships in China in 2013 with port cities were the worst effect areas (http://news.xinhuanet.com/politics/2015-06/08/c_127890195.htm).

Moreover, the updated information about standards set by IMO, EPA or EU has been added in the revised manuscript (Line 25-30, Page 5 and Line 1-6, Page 5).

Ships operating in the emission control areas (ECAs) (the Baltic Sea, the North Sea, the North America and the Caribbean of US) should use fuels with sulfur less than 0.1% m/m since January 2015. Even more stringent limits have been laid down in some national or regional regulations. For example, in some EU ports, seagoing ships at berth are required to switch into fuels of under 0.1 % m/m sulfur since 2010 (The Council of the European Union, 1999); both marine gas oil and marine diesel oil used in water area within 24 nautical miles of coastline in California should have sulfur content less than 0.1 % m/m since 2014 (California Code of Regulation Titles 13 and 17). Emission standard of Tier II for NO_x set by MARPOL VI has been executed since January 2011 in ECAs, and more stringent rules of Tier III will be executed from January 2016.

The latest policy made by Chinese Ministry of Environmental Protection aiming to limit the emissions from marine engines also has been added in the revised manuscript (Line 8-22, Page 6).

But because of the serious air pollution these years in China, emission limits for the main sources such as vehicle exhaust, coal combustion, biomass combustion and raise dust have becoming more and more stringent. A draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection, which is named Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ,Ⅱ), is on soliciting opinions. It has set the limits of CO, HC, NO_x and PM for different kinds of vessels, which mainly based on the Directive 97/68/EC set by EU and 40 CFR part 1042 set by EPA. Besides, an implementation plan has released by Ministry of Transport of the People's Republic of China in December 2015 aiming to set shipping emission control areas to reduce SO_2 emissions in China (Ministry of Transport of the People's Republic of China, 2015). All the regulations were set mostly based on other directive and regulations. And therefor, detailed measurement data in China are in urgent need for the further policy making that more fit current situations of vessels.

Uncertainties (labeled as 'error' in the manuscript) are not death with appropriately. There is no discussion on uncertainties of the gas phase measurements. There is no discussion on how the uncertainties are propagated which are then shown on the bar charts.

Thanks for your comment, and the reply is given as following: The detection parameters for the gaseous matters have been added as an accessory in Table S3, including the detection method, range, resolution and accuracy etc. We can see that all the detection uncertainties are within the relative error of 5%. During our sampling, 3 to 5 replicate samples for each operating mode were collected, which could give the total error shown in Table S4 and Table S5, including the detection error and the artificial error.

Table S3 Detection parameters for the gaseous matters

Component	Method	Range	Resolution	Accuracy	Time (T_{90})	Conformity
O_2	Electrochemical sensor	20.95%	0.01%	±5% rel.	45 s	ISO 12039, CTM-030
CO_2	NDIR	5%	0.01%	±3% rel.	45 s	ISO 12039, OTM-13
CH_4	NDIR	5%	0.01%	±3% rel.	45 s	
NO	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 10849, Method 7E
NO_2	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 10849, Method 7E
SO_2	NDIR	1000ppm	1ppm	±3% rel.	45 s	ISO 7935, Method 6C
N_2O	NDIR	2000ppm	1ppm	±3% rel.	45 s	ISO 21258
VOCs	PID	10000ppm	0.1ppm	±5% rel.	-	

NDIR, Non-dispersive Infra-red

PID, Photo Ionization Detectors

There are minor reference issues. Many of the large strings of references are put mid sentence and can go at the end. The reference to Lack and Corbett 2010, should actually refer the Lack et al 2008 study on light absorbing carbon from ships. Some references have the name twice (e.g. Cooper et al. (Cooper, 2003))

Thanks for pointing out the incorrect references in the manuscript. All the reference mistakes have been revised in the new manuscript.

P23521: The discussion on OC/EC ratios does not consider that dilution, which was not used of this study, can significantly affect the amount of OC measured. Dilution will contribute to different OC/EC ratios.

Thanks for your comment, and the reply is given as following: The residence time of soot particle in the pipe could affect the formation of PM, which led to the different composition of PM. The dilution sampling was not used in this study that might be one reason of the lower OC to EC ratio. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods because of the different definitions of OC and EC. They are shown in the revised manuscript (Line 30, Page 15 and Line 1-8, Page 16) as following.

The non-dilution sampling was the main reason of the lower OC to EC ratio in this study. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods (such as TOT) because of the different definitions of OC and EC (Khan et al., 2012). Compared with other diesel engines,, the ratios of OC to EC in this study were higher than that of automobile diesel soot, in which EC comprises 75–80 wt% of the total PM (Clague et al., 1999), and also higher than heavy heavy-duty diesel trucks (HHDDT) with OC to EC ratios below unit for cruse and transient modes even though higher in cold-start/idle and creep modes (Shah et al., 2004).

Thanks again.

Best regards,
Fan Zhang, Representative of all the authors

Reference:

Agrawal, H., Malloy, Q. G. J., Welch, W. A., Miller, J. W., and Cocker, D. R.: In-use gaseous and particulate matter emissions from a modern ocean going container vessel, Atmos. Environ., 42, 5504-5510, 10.1016/j.atmosenv.2008.02.053, 2008.

Celo, V., Dabek-Zlotorzynska, E., and McCurdy, M.: Chemical Characterization of Exhaust Emissions from Selected Canadian Marine Vessels: The Case of Trace Metals and Lanthanoids, Environmental Science & Technology, 49, 5220-5226, 10.1021/acs.est.5b00127, 2015.

Khan, B., Hays, M. D., Geron, C., and Jetter, J.: Differences in the OC/EC Ratios that Characterize Ambient and Source Aerosols due to Thermal-Optical Analysis, Aerosol Science and Technology, 46, 127-137, 10.1080/02786826.2011.609194, 2012.

Moldanova, J., Fridell, E., Popovicheva, O., Demirdjian, B., Tishkova, V., Faccinetto, A., and Focsa, C.: Characterisation of particulate matter and gaseous emissions from a large ship diesel engine, Atmos. Environ., 43, 2632-2641, 10.1016/j.atmosenv.2009.02.008, 2009.

Ng, S. K. W., Loh, C., Lin, C., Booth, V., Chan, J. W. M., Yip, A. C. K., Li, Y., and Lau, A. K. H.: Policy change driven by an AIS-assisted marine emission inventory in Hong Kong and the Pearl River Delta, Atmos. Environ., 76, 102-112, 10.1016/j.atmosenv.2012.07.070, 2013.

Shah, S. D., Cocker, D. R., Miller, J. W., and Norbeck, J. M.: Emission Rates of Particulate Matter and Elemental and Organic Carbon from In-Use Diesel Engines, Environmental Science & Technology, 38, 2544-2550, 10.1021/es0350583, 2004.

Song, S.: Ship emissions inventory, social cost and eco-efficiency in Shanghai Yangshan port, Atmos. Environ., 82, 288-297, 10.1016/j.atmosenv.2013.10.006, 2014.

Yang, J., Yin, P.-l., Ye, S.-q., Wang, S.-s., Zheng, J.-y., and Ou, J.-m.: Marine Emission Inventory and Its Temporal and Spatial Characteristics in the City of Shenzhen, Huan jing ke xue= Huanjing kexue / [bian ji, Zhongguo ke xue yuan huan jing ke xue wei yuan hui "Huan jing ke xue" bian ji wei yuan hui.], 36, 1217-1226, 2015.

Zhou, F., Guo, H., and Hao, Z.: Spatial distribution of heavy metals in Hong Kong's marine sediments and their human impacts: A GIS-based chemometric approach, Mar. Pollut. Bull., 54, 1372-1384, 10.1016/j.marpolbul.2007.05.017, 2007.

Reply to Referee 2#

Thanks very much for your comments. Before giving our reply, we would like to present several statements to help you understand further about the current shipping emission situations in China, which will be added and explained in the revised manuscript.

Firstly: The measurement data of shipping emissions are in urgent need. Laws and regulations for shipping emissions have already managed to make, which require the basic measurement data very much. Besides, estimating contribution of ships to air and calculating emission inventories of ships based on local emission factors are essential in China because of the differences of ships with other countries. So this study is focusing on adding the measurement database of shipping emissions in China. And to our knowledge, only very limited study has carried on on-board measurement of ocean vessels in China. Even though our work is not comprehensive, it is a start to have a look at the emission conditions of vessels in China.

Secondly: High speed and medium speed engines are the predominant engines used in vessels of offshore and inland rivers in China, which always take light diesel as fuel. Though only three offshore vessels' data were reported in this study, they were typical offshore diesel vessels that could, to some extent, represent the emission conditions from a low level to a relative high level in China.

Furthermore: On-board test is really hard due to the unpredictable of field work, the expensive rent for vessels, unwillingness of vessel owners, and also the lower online operating parameter devices on the ships, etc. We have finished five vessels till now, and is carrying on measurement of heavy fuel vessels now. More accurate data will be provided to scientific research and policy-making in our follow-up work.

Our replies are given as following according to your comments:

p.23509 14-18…low engine power vessel, … higher engine power vessel - this is a bit confusing description of the vessels, especially as also medium-speed and high speed engines and different engine loads are used to describe the experiments. It looks like there are two smaller and one larger vessels, maybe this, or using the vessel abbreviations would make the text easier.

Thanks for your comment, and the reply is given as following: The vessels' abbreviations have been added in the revised manuscript (Line14-17, Page 2).

Observed concentrations and emissions factors for carbon monoxide, nitrogen oxides, total volatile organic compounds, and particulate matter were higher for the low engine power vessel (HH) than for the two higher engine power vessels (XYH and DFH).

p.23512, l. 15 IMO legislation in ECAs is not decided by EU environmental ministers, the same rules apply for the North Sea & English Channel and for the Baltic sea through all years, not only 2004-2010.

Thanks for your comment, and the reply is given as following: The legislations set by IMO that applied in ECAs have been checked and rewritten in the revised manuscript (Line 25-28, Page 5, Line 4-6, Page 6), which are shown as following:

Ships operating in the emission control areas (ECAs) (the Baltic Sea, the North Sea, the North America and the Caribbean of US) should use fuels with sulfur less than 0.1% m/m since January 2015.

Emission standard of Tier II for NO_x set by MARPOL VI has been executed since January 2011 in ECAs, and more stringent rules of Tier III will be executed from January 2016.

Other legislations in EU and USA also have been checked and rewritten in the revised manuscript (Line 28-30, Page 5 and Line 1-4, Page 6), which are shown as following:

Even more stringent limits have been laid down in some national or regional regulations. For example, in some EU ports, seagoing ships at berth are required to switch into using fuels of under 0.1 % m/m sulfur since 2010 (The Council of the European Union: Council Directive 1999/32/EC of 26 April 1999, Official Journal of the European Communities, 13-18); both marine gas oil and marine diesel oil used in water area within 24 nautical miles of coastline in California should have sulfur content less than 0.1 % m/m since 2014 (California Code of Regulation Titles 13 and 17).

Besides, the first draft aimed to limit the emissions from marine engines in China is on soliciting opinions now, and the details are shown in revised manuscript (Line 8-22, Page 6), as shown below:

But because of the serious air pollution these years in China, emission limits for the main sources such as vehicle exhaust, coal combustion, biomass combustion and raise dust have becoming more and more stringent. A draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection, which is named Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ, Ⅱ), is on soliciting opinions. It has set the limits of CO, HC, NO_x and PM for different kinds of vessels, which mainly based on the Directive 97/68/EC set by EU and 40 CFR part 1042 set by EPA. Besides, an implementation plan has released by Ministry of Transport of the People's Republic of China in December 2015 aiming to set shipping emission control areas to reduce SO_2 emissions in China (Ministry of Transport of the People's Republic of China, 2015). All the regulations were set mostly based on other directive and regulations. And therefor, detailed measurement data in China are in urgent need for the further policy making that more fit current situations of vessels.

p.23514, Operating modes – the normal is to express operating modes as % of max engine load and not ship speed which is affected by external conditions as currents, wind-speed e.c.t. The comparison with other data is difficult when using vessel speed when most of the other published factors are based on engine load.

Thanks for your comment, and the reply is given as following: Vessel speed was used in the study to give different operating modes. According to ISO 8178-E3, speed and torque of the test engine need to be measured during the sampling to calculate the effective power, which could give the load rate. But unfortunately, we were not allowed to install any detector for the engine of the vessels, only real-time engine speed could be read through the tachometer. We were more focused on the actual navigation conditions, and more than three samples for each mode were collected to give an average value to reduce the influence form external conditions.

Besides, vessel speed used as a variable to check out the variations of pollutants from ship was applied before, and good results have also been obtained (Cappa et al., 2014). We considered it was also feasible using vessel speed to give different operating modes.

p.23516, Formula 2: The flue gas emission rate R(FG) is essential for the calculation, how was it obtained? Has the correction for CO2 in the engine inlet air been implemented in the carbon balance equation? In formula 3 – What is meant with ‘background subtracted?

Thanks for your comment, and the reply is given as following: Carbon balance method was used in this study to give the emission factors, which assumes that all carbon in the fuel was emitted as carbon-containing gases (CO, CO2, and TVOC) and carbon-containing particulate matter. So Formula 1 was given as shown below:

$$C_{\mathrm{F}} = R_{\mathrm{FG}} \times (c(\mathrm{C_{CO}}) + c(\mathrm{C_{CO_2}}) + c(\mathrm{C_{PM}}) + c(\mathrm{C_{TVOC}}) \qquad (1)$$

R_{FG} could be calculated according to this formula since all the other parameters could be measured during or after the sampling.

The correction for CO_2 has been implemented in the carbon balance equation. Background CO_2 concentration (the CO_2 concentration of ambient air) was subtracted to ensure all the carbon was transformed from the carbon in the fuel. In the same way, when other emission factors were given, background concentrations had also been subtracted, such as CO, NO_x, etc.

p. 23517 Part 3 – what is reason of presentation and comparison of concentrations in exhaust? These vary largely among the different engines and operation conditions and do not allow any general comparison.#

Thanks for your comment, and the reply is given as following: As we mentioned in the Introduction, concentrations in exhaust of inland ships on the Grand Canal of China, the only test vessels reported in China, were also presented and also other studied (Sinha et al., 2003;Corbett et al., 1999;Williams et al., 2009;Berg et al., 2012). Even though there were big differences among different engines and operation conditions, comparison could be done to a certain extent, such as the differences for different power engines. Besides, this study is focused on presenting detailed basic data, initial concentration data was also given for other studies to compare or recheck.

p. 23519 l. 1-3 CO2 emissions – ship HH had actually rather bad and not ‘high’

combustion efficiency with 2-7.5% C emitted as other but CO2. p. 23521 – OC depends very much on dilution of the exhaust analyzed and OC analyzed on PM sampled without dilution cannot be directly compared with OC analyzed on samples from diluted exhaust.#

Thanks for your comment, and the reply is given as following: The sentence was rewritten in the revised manuscript (Line 6-10, Page 13), shown as following:

Under actual conditions, CO_2 emissions were 2940–3106, 3121–3160, and 3102–3162 g kg^{-1} fuel for HH, DFH and XYH, respectively, which means they had combustion efficiencies with 92.5–97.8%, 98.5–99.7% and 97.8–99.7% in terms of CO_2 for these three vessels.

The non-dilution sampling was the main reason of the lower OC to EC ratio in this study. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods (such as TOT) because of the different definitions of OC and EC. We just give the actual OC to EC ratio under undiluted situation. During our later sampling, both samples with and without dilution were collected to give the differences between them. The details are shown in revised manuscript (Line 30, Page 15 and Line 1-8, Page 16), as shown below:

The non-dilution sampling was the main reason of the lower OC to EC ratio in this study. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods (such as TOT) because of the different definitions of OC and EC (Khan et al., 2012). Compared with other diesel engines,, the ratios of OC to EC in this study were higher than that of automobile diesel soot, in which EC comprises 75–80 wt% of the total PM (Clague et al., 1999), and also higher than heavy heavy-duty diesel trucks (HHDDT) with OC to EC ratios below unit for cruse and transient modes even though higher in cold-start/idle and creep modes (Shah et al., 2004).

p. 23522 – Section 3.3 – How were the emission factors for different operation modes averaged? There are standardized methods for averaging, were these applied?#

Thanks for your comment, and the reply is given as following: Average EFs for each vessel were calculated based on actual operating conditions, as shown in

Formula (4) (Line 3, Page 10):

$$EF_{\mathrm{X,A}} = \sum\nolimits_{\mathrm{X},i} EF_i \times P_i \tag{4}$$

where $EF_{\mathrm{X,A}}$ is the average EF for species X, EF_i is the EF for operating mode *i* for species X, and P_i is the percentage of time spent in operating mode *i* during the shipping cycle.

There is no standardized method for averaging emission factors for different operating modes in China. Only a draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection (Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ, Ⅱ)) is on soliciting opinions. Even though other standard such as ISO 8178-4 (Reciprocating internal combustion engines -- Exhaust emission measurement -- Part 4: Steady-state test cycles for different engine applications) has standardized method for the calculation of weighted emission factors, it is calculated as:

$$E_{WM} = \frac{\sum_{i=1}^{i=n}(m_i \times WF_i)}{\sum_{i=1}^{i=n}(p_i \times WF_i)}$$

where E_{WM} is the overall weighted emission factor (g/kW-hr), m_i the emission factor for i mode (g/hr), WF_i the weighted factor for i mode, and p_i the engine load for i mode (Khan et al., 2013). In previous study, weighted emission factor was given for vessels under different engine loads in order to have comparison of measured emission factors with literature data (Agrawal et al., 2008); average emission factor were also given for load conditions of 85-110% from one serial 4-stroke medium-speed marine diesel engine (Petzold et al., 2010). Unfortunately, we have no measurement engine load, so a weighted average emission factor was calculated based on the actual operating modes (added in supporting information as Table S6) in this study.

p. 23523 l. 3-4 – How were the Tier-1 limit emissions calculated in g/kg-fuel? The specific fuel consumption needed for the calculation need to be shown. This is also the case for the power-based emission factors Table 3. Fuel-based emission factors – The table is mostly missing information about fuels used by the vessels and

their sulphur content which is essential for EFs both for SO2 and for PM.#

Thanks for your comment, and the reply is given as following: Another formula that converting power-based emission factor to fuel-based emission factor was added as Formula 5 in the revised manuscript (Line 7-11,Page 11), shown as following:

$$\mathrm{EF}_{\mathrm{X,P}} = EF_{\mathrm{x}} \cdot \mathrm{FCR} \tag{5}$$

where $\mathrm{EF}_{\mathrm{X,P}}$ is the power-based emission factor for species X (g kW h^{-1}), FCR is fuel consumption rate for each vessel (kg fuel (kW $h)^{-1}$).

According to Formula 5 and the fuel consumption rates that obtained from Engine Performance Curve of each vessel combined with real-time engine speed in each operating mode, power-based emission factors could be calculated, which have been presented in Table 4.

The IMO Tier I emissions limit for NO_x is $45.0 \times n^{-0.2}$ g kWh^{-1} (n, rated speed, $130 < n < 2000$ rpm). The rated speeds n for the vessels were shown in Table 1, so we could get the power-based emissions limit. Fuel-based emissions limit could be calculated combined with fuel consumption rate of each vessel that was also given in Table 1. Thus, the emissions limits for HH, DFH, and XYH would be 54.5, 57.5, and 56.5 g kg^{-1} fuel, respectively.

All the fuel used of the test vessels were diesel. And the fuel analysis results were shown in Table 2, where sulfur content for each kind of diesel could be found. All of these fuels had relatively low sulfur contents (≤0.13%m) and low metals concentrations (V, Al, Si, Pb, Zn, Mn, etc.).

Table 2 Results from the fuel analysis (diesels)

	Units	HH	DFH	XYH
Total calorific value	MJ kg^{-1}	45.44	45.40	45.50
Net calorific value	MJ kg^{-1}	42.51	42.48	42.55
Ash content	%m	0.001	＜0.001	＜0.001
Sulfur (S)	%m	0.0798	0.0458	0.130
Carbon (C)	%m	86.66	86.40	86.49
Hydrogen (H)	%m	13.32	13.22	13.44
Nitrogen (N)	%m	＜0.2	＜0.2	＜0.2
Oxygen (O)	%m	＜0.4	＜0.4	＜0.4

p. 23524 – section 3.5 – Since the Tier is based on power-based EF it would be good to look at these as well, these EFs are usually stable. The variability of the fuel-based EFs is related to the power-based ones through inverse specific fuel consumption which can have similar shape as seen on fig. 4#

Thanks for your comment, and the reply is given as following: Both fuel-based EFs and power-based EFs were given in this study, as different kind of data for different purpose, such as detailed fuel-based EFs are more useful for inventory estimating and power-based EFs are more easier for looking at the emission situation and comparing among different vessels.

The fuel consumption rates have little change in different operating modes for the test vessels, which are queried from the Engine Performance Curve. Power-based emission factor for NO_x would have the similar variability trends of fuel-based emission factor as shown in Fig.4. Furthermore, fuel-based emission factor is calculated directly from the measurement data, which would be closer to the actual condition than power-based emission factor.

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Best regards,
Fan Zhang, Representative of all the authors

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Emissions factors for gaseous and particulate pollutants from offshore diesel engine vessels in China

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Abstract.

Shipping emissions have significant influence on atmospheric environment as well as human health, especially in coastal areas and the harbor districts. However, the contribution of shipping emissions on the environment in China still need to be clarified especially based on measurement data, with the large number ownership of vessels and the rapid developments of ports, international trade and shipbuilding industry. Pollutants in the gaseous phase (carbon monoxide, sulfur dioxide, nitrogen oxides, total volatile organic compounds) and particle phase (particulate matter, organic carbon, elemental carbon, sulfates, nitrate, ammonia, metals) in the exhaust from three different diesel engine power offshore vessels in China were measured in this study. Concentrations, fuel-based and power-based emissions factors for various operating modes as well as the impact of engine speed on emissions were determined. Observed concentrations and emissions factors for carbon monoxide, nitrogen oxides, total volatile organic compounds, and particulate matter were higher for the low engine power vessel (HH) than for the two higher engine power vessels (XYH and DFH). Fuel-based average emissions factors for all pollutants except sulfur dioxide in the low engine power engineering vessel were significantly higher than that of the previous studies, while for the two higher engine power vessels, the fuel-based average emissions factors for all pollutants were comparable to the results of the previous studies, engine type was one of the most important influence factors for the differences. ~~The f~~Fuel-based average emission~~s~~ factors for nitrogen oxides for the small engine power vessel was more than twice the International Maritime Organization standard, while those for the other two vessels were below the standard. Emissions factors for all three vessels were significantly different during different operating modes. Organic carbon and elemental carbon were the main components of particulate matter, while water-soluble ions and elements were present in trace amounts. Best-fit engine speeds during actual operation should be based on both emissions factors and economic costs.

1 Introduction

Gaseous and particulate pollutants emitted from vessels operating in the open ocean as well as in coastal areas and inland waterways have significant adverse impacts on human health, air quality, and climate change (Cappa et al., 2014;Righi et al., 2011;Marmer and Langmann, 2005;Winebrake et al., 2009). It has been estimated that 87,000 premature deaths occurred in 2012 due to burning of marine fuels with high sulfur content. Shipping-related particulate matter (PM) emissions have been reported to be responsible for approximately 60,000 cardiopulmonary and lung cancer deaths annually, with most cases occurring near coastlines in Europe (Viana et al., 2014), East Asia, and South Asia (Corbett et al., 2007). Approximately 9,200 and 5,200 t yr^{-1} of PM are emitted from oceangoing and coastal ships, respectively, in the USA(Corbett, 2000), with most of which are fine or even ultrafine aerosols (Viana et al., 2009;Saxe and Larsen, 2004). Globally, about 15% of nitrogen oxides (NO_x) and 5–8% of sulfur oxides (SO_x) emissions are attributable to oceangoing ships (Corbett, 2000). Shipping emissions affect acid deposition and ozone concentrations, contributing ~~>~~more than 200 mg S m^{-2} yr^{-1} over the southwestern British Isles and Brittany as well as ~~an~~ additional 6 ppb surface ozone during the summer over Ireland (Derwent et al., 2005). Moreover, aerosol emissions from international shipping also greatly impact the Earth's radiation budget, directly by scattering and absorbing solar radiation and indirectly by altering cloud properties (Righi et al., 2011). Besides, according to estimates from IMO (2014), total shipping emissions were approximately 938 million tonnes CO_2 and 961 million tonnes CO_2e for GHGs combining CO_2, CH_4 and N_2O for the year 2012. International shipping emission accounts for approximately 2.2% and 2.1% of global CO_2 and GHG emissions on a CO_2 equivalent (CO_2e) basis, respectively. Because nearly 70% of ship emissions are estimated to occur within 400 km of land (Endresen, 2003), ships have the potential to contribute significantly to air quality degradation in coastal areas. In addition, ports are always the most concentrated areas for ships to berth at, emission reduction measures such as switching heavy fuels to cleaner fuels are required when ships are close to ports or offshore areas, but not all of them can obey the regulations (De

Meyer et al., 2008), which result in significant influence on atmospheric environment of port cities and regions.

Rapid developments of ports, international trade, and the shipbuilding industry in China have negatively affected the ambient air quality of the coastal zone due to shipping emissions. It was estimated that 8.4% of SO_2 and 11.3% of NO_x were emitted from ships in China in 2013 with port cities were the worst effect areas (http://news.xinhuanet.com/politics/2015-06/08/c_127890195.htm). In 2013, there were 0.18 million water transport vessels (Ministry of Transportation, 2013) active in Chinese waters, 8 ports in China were listed among the world's largest 10 ports, and 11 container ports were listed among the world's largest 20 container ports. The number of ports with cargo handling capacity of more than 200 million t yr^{-1} grew to 16 (Ministry of Transportation, 2010). Rapid development of ports in China has resulted in increasingly serious pollution of ambient air, particularly in coastal zones and near ports. Only a few studies have focused on pollution from shipping emissions in China. Rough estimates of the influence of shipping emissions on ambient air in the port of Shanghai, the largest port in China (Zhao et al., 2013), and in the Bohai Rim (Zhang et al., 2014) that have been generated using empirical formulas. One case study of real-world emissions of inland vessels on the Grand Canal of China has been conducted (Fu et al., 2013). Other studies also have developed to the inventories in large ports or delta regions (Zheng et al., 2011;Zheng et al., 2009) by using EFs obtained from other countries or areas. However, there are no systematic studies of vessel emissions in the coastal zone or in ports, nor accurate estimates of shipping emissions to ambient air based on measured emission factors (EFs). Conditions in China differ substantially from those in other countries, such as in vessel types (more small motor vessels and the type composition of offshore vessels is shown in Table S1), ~~use of bunker oil~~different fuel standards compared with other countries (fuel meeting the GB/T 17411-2012 standard with sulfur contents of less than 3.5% m/m; however, the ISO 8217-2010 international standard has the maximum sulfur content according to the relevant statutory requirements that always have lower values, such as less than 0.1% in emission control areas), age of vessels (Chinese commercial vessels have an average age of 19.2 yr compared with 8.0 yr and 8.9 yr for Japan and Germany, respectively). Thus, experimentally determined EFs for vessels in other countries cannot be used directly to estimate shipping emissions and their contribution to ambient air quality in China. Systematical ~~experimental~~ measurement EFs for different kinds of vessels in China is essential.

Numerous studies of shipping emissions based on experimental measurements have been conducted since the International Maritime Organization (IMO) first began to address air pollution from vessels in 1996, particularly in developed countries. Most of these studies have been carried out by performing tests on-board ~~the vessel~~ from the exhaust pipe (Agrawal et al., 2008;Murphy et al., 2009;Fridell et al., 2008;Juwono et al., 2013;Moldanova et al., 2013) or by taking measurements within the exhaust plumes (Sinha et al., 2003;Chen et al., 2005;Lack et al., 2009;Murphy et al., 2009;Berg et al., 2012;Pirjola et al., 2014;Petzold et al., 2008). NO_x, carbon monoxide (CO), sulfur dioxide (SO_2), and PM are the main constituents of shipping emissions (Moldanova et al., 2009;Williams et al., 2009;Agrawal et al., 2008;Poplawski et al., 2011;Endresen, 2003) that have been quantified. In addition, black carbon (BC) (Lack and Corbett, 2012;Sinha et al., 2003;Moldanova et al., 2009;Corbett et al., 2010) and cloud condensation nuclei (CCN) (Sinha et al., 2003;Lack et al., 2011) also have been reported in some studies. Reported emissions factors for CO, SO_2, NO_x, PM, and BC are in the range of 0.5–16, 2.9–44, 22–109, 0.3–7.6, and 0.13–0.18 g kg^{-1} fuel, respectively, and $0.2–6.2 \times 10^{16}$ particles kg^{-1} fuel for CCN. Besides, characteristics of gaseous species and PM have attracted more attention recently (Anderson et al., 2015;Celo et al., 2015;Mueller et al., 2015;Reda et al., 2015).

The IMO has set the emission limits for NO_x and SO_x in the revised MARPOL (Maritime Agreement Regarding Oil Pollution) Annex VI rules (IMO, 1998). Ships operating in the emission control areas (ECAs) (the Baltic Sea, the North Sea, the North America and the Caribbean of US) should use fuels with sulfur less than 0.1% m/m since January 2015. Even more stringent limits have been laid down in some national or regional regulations. For example, in some EU ports, seagoing ships at berth are required to switch into fuels of under 0.1 % m/m sulfur since 2010 (The

Council of the European Union, 1999); both marine gas oil and marine diesel oil used in water area within 24 nautical miles of coastline in California should have sulfur content less than 0.1 % m/m since 2014 (California Code of Regulation Titles 13 and 17). Emission standard of Tier II for NO_x set by MARPOL VI has been executed since January 2011 in ECAs, and more stringent rules of Tier III will be executed from January 2016. ~~But~~ However, in China, no specific policy or limit for shipping emissions has been implemented except in Hong Kong, which is making legislation about the limit of 0.5% sulfur content fuel used when berth in the port from 2015. But because of the serious air pollution these years in China, emission limits for the main sources such as vehicle exhaust, coal combustion, biomass combustion and raise dust have becoming more and more stringent. A draft aimed to limit the emissions from marine engines set by Ministry of Environmental Protection, which is named Limits and measurement methods for exhaust pollutants from marine compression ignition engines (CHINA Ⅰ, Ⅱ), is on soliciting opinions. It has set the limits of CO, HC, NO_x and PM for different kinds of vessels, which mainly based on the Directive 97/68/EC set by EU and 40 CFR part 1042 set by EPA. Besides, an implementation plan has released by Ministry of Transport of the People's Republic of China in December 2015 aiming to set shipping emission control areas to reduce SO_2 emissions in China (Ministry of Transport of the People's Republic of China, 2015). All the regulations were set mostly based on other directive and regulations. And therefor, detailed measurement data in China are in urgent need for the further policy making that more fit current situations of vessels.

Average EFs are often used for shipping emissions inventories on large scales or in regional areas (Tzannatos, 2010;Eyring V., 2005). However, to evaluate the effects of shipping emissions on air pollution in local areas such as near ports, various ship speeds and operating modes should be considered, including docking, berthing, and departing from ports etc. Previous studies have confirmed that EFs are significantly different under various load conditions (Petzold et al., 2010) or in different operating modes (Fu et al., 2013;Winnes and Fridell, 2010) for individual vessels. Therefore, more detailed measurements of EFs in different operating modes are necessary to better estimate the impacts of shipping emissions on the environment.

In this study, experimental data for three different diesel engine power vessels were collected. All pollutants were measured directly in the stack. Gaseous emissions and PM from the diesel engines were the main targets, including CO, carbon dioxide (CO_2), SO_2, NO_x, total volatile organic compounds (TVOCs), and total suspended particulates (TSP). Fuel-based EFs for the three vessels were calculated using the carbon balance method under different operating conditions. In addition, fuel-based average EFs as well as power-based average EFs to values reported in other studies and for other vessels were compared. Finally, the impacts of engine speed on the EFs of NO_x were evaluated.

2 Experimental

2.1 Test Vessels and Fuel Types

Initially, it was hoped that the choice of measurement ships would reflect the shipping fleet in general, i.e. in terms of engine type (engine speed and power output), fuel used, engine age and mode of operation, with more than 10 vessels planned to test. However, consideration was given to the practicalities involved with the measurements, i.e. installation of sampling systems, external conditions, etc. Besides, time and economic constraints weighed heavily and only several shipowners willing to participate in the project. Thus, the chosen vessels of different engine powers with diesel used represent a compromise.

Three different diesel engine power offshore vessels, including one engineering vessel, Haohai 0007 (HH), with low power and high speed engine, one large research vessel, Dongfanghong 2 (DFH), with high power and medium speed engine, and another research vessel, Xiangyanghong 08 (XYH), with medium power and medium speed engine were selected for this study, whose technical parameters are shown in Table 1. High speed and medium speed engines are the predominant engines used in vessels of offshore and inland rivers in China, which always take light diesel as fuel.

Engineering vessels are designed for construction activities such as building docks in port areas or waterways, dredging, etc. They are common vessels in coastal areas of China because of the heavy demand for oilfield construction and port expansion. The maintenance of engineering vessels is typically poorer than for other types of vessels and as a result, they may have relatively high emissions. On the other hand, research vessels of DFH and XYH from universities and research institutes are generally well maintained and use high-quality diesel fuel but with different engine powers, which might have relatively low emission factors for pollutions. Therefore, these research vessels can reflect the impact of engine power on emissions and also can represent the lower end of expected EFs for Chinese vessels. In all, a general range of EFs for gaseous and PM pollutants emitted from different offshore vessels of China and their influence factors could be given through the on-board measurement.

The fuels used in all test vessels were common diesel fuels obtained from fueling stations near the ports. According to statistical data, the total oil consumption of vessels in China was 20.99 million tons in 2011, including 10.99 million tons bonded oil and 5.93 million tons domestic trade oil, with light fuel oil account for 40% of the domestic trade oil and 25% of the total consumption (shown in Table S2). (Zhu, 2013) Results of fuel analyses are presented in Table 2. All of these fuels had relatively low sulfur contents (≤0.13%m) and low metals concentrations (V, Al, Si, Pb, Zn, Mn, etc.).

2.2 Test Operating Modes

~~As noted above,~~ EFs are significantly different under differing load conditions and operating modes. Vessel speed is also an important influence factor for emissions which has reported by Starcrest Consulting Group, LLC (Starcrest Consulting Group, 2012) that 15-20% of fuel consumption could be reduced by reduce 10% of the vessel speed. In this study, vessel operating modes were classified according to actual sailing conditions. There were six modes of HH: low speed (4 knots), medium speed (8 knots), high speed (11 knots), acceleration process, moderating process and idling, four modes of DFH: cruise (10 knots, medium speed for DFH), acceleration process, moderating process and idling, and five modes of XYH: low speed (3 knots), high speed (10 knots), acceleration process, moderating process and idling. Three to five ~~groups~~ sets of replicate samples were collected for each operating mode.

2.3 Emissions Measurement System and Chemical Analysis of Particulate Matter.

A combined on-board emissions test system (Fig. 1) was used to measure emissions from the coastal vessels under actual operating conditions. There was no dilution in this test system with all the species measured directly from the exhaust~~. Detailed compositions were given as follows: A slender tube was placed into the vessel exhaust pipe to extract flue gas. The sample was then divided into five subsamples through a manifold for different analyses and evacuation of the excess gas.~~ and ~~There~~ there were four main components of the system: a flue gas analyzer, three particulate samplers, an eight-stage particulate sampler, and a TVOCs analyzer. (see Supporting Information for more details). All analytes are also shown in Fig. 1: The flue gas analyzer (Photon II) is aimed to test instantaneous emissions of gaseous pollutions, including O_2, NO_2, NO, N_2O, CO, CO_2 and SO_2 (Detection parameters for the gaseous matters are shown in Table ~~S1~~S3). Three particulate samplers are installed to collect PM using different filters at the same time, including quartz fiber filter, glass filter and polytetrafluoroethylene filter to analyze different chemical components of PM. And the portable TVOCs Analyzer is used to monitor the concentration of total VOCs with isobutylene as correction coefficient gas. Besides, a temperature sensor is installed near the smoke outlet to test the flue gas temperature. A total of 33 sets of samples for HH, 20 sets for DFH and 23 sets for XYH were collected, with 3 to 5 sets for each operating mode.

The OC and EC were measured on a 0.544 cm^2 quartz filter punched from each filter by thermal optical reflectance (TOR) following the IMPROVE protocol with a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA). The measuring range of TOR was from 0.05 to 750 μg C cm^{-2} with an error of less than 10%. Concentrations of water soluble ions in $PM_{2.5}$, such as Na^+, NH_4^+, K^+, Mg^{2+},

Ca^{2+}, Cl^-, NO_3^- and SO_4^{2-}, were determined by Ion Chromatography (Dionex ICS3000, Dionex Ltd. America) based on the measurement method of Shahsavani et al. (Shahsavani et al., 2012). The detection limit was 10 ng ml^{-1} with an error of less than 5%, and 1ml RbBr with concentration of 200 ppm was put in the solution as internal standard before sampling. The concentrations of 33 inorganic elements in $PM_{2.5}$ were estimated using Inductively Coupled Plasma coupled with Mass Spectrometer (ICP-MS of ELAN DRC II type, PerkinElmer Ltd. Hong Kong) following the standard method (Wang et al., 2006). The resolution of ICP-MS ranged from 0.3 to 3.0 amu with a detection limit lower than 0.01 ng ml^{-1}, and the error was less than 5%.

2.4 Data Analysis

Carbon balance formula was used to calculate the EFs for all exhaust gas components. It was assumed that all carbon in the fuel was emitted as carbon-containing gases (CO, CO_2, and TVOC) and carbon-containing particulate matter. So there was a certain equilibrium relationship between the carbon in the fuel and in the exhaust:

$$C_{\mathrm{F}} = R_{\mathrm{FG}} \times (c(\mathrm{C_{CO}}) + c(\mathrm{C_{CO_2}}) + c(\mathrm{C_{PM}}) + c(\mathrm{C_{TVOC}})) \qquad (1)$$

where C_{F} represents the mass of C in per kg diesel fuel (g C kg^{-1} fuel); R_{FG} represents the flue gas emissions rate (m^3 kg^{-1} fuel); and $c(\mathrm{C_{CO}})$, $c(\mathrm{C_{CO_2}})$, $c(\mathrm{C_{PM}})$, and $c(\mathrm{C_{TVOC}})$ represent the mass concentrations of carbon as CO, CO_2, PM, and TVOC (g C m^{-3}) in the flue gas, respectively.

The EF for CO_2 was calculated as follows:

$$EF_{\mathrm{CO_2}} = R_{\mathrm{FG}} \cdot c(\mathrm{CO_2}) \cdot \mathrm{M_{CO_2}} \qquad (2)$$

where $EF_{\mathrm{CO_2}}$ is the EF for CO_2 (g kg^{-1} fuel), $c(\mathrm{CO_2})$ is the molar concentration of CO_2 (mol m^{-3}), and $\mathrm{M_{CO_2}}$ is the molecular weight of CO_2 (44 g mol^{-1}).

The remaining EFs were calculated as follows:

$$EF_{\mathrm{x}} = \frac{\Delta \mathrm{X}}{\Delta \mathrm{CO_2}} \cdot \frac{\mathrm{M_X}}{\mathrm{M_{CO_2}}} \cdot EF_{\mathrm{CO_2}} \qquad (3)$$

where EF_{x} is the EF for species X (g kg^{-1} fuel), $\Delta\mathrm{X}$ and $\Delta\,\mathrm{CO_2}$ represent the concentrations of X and CO_2 with the background concentrations subtracted (mol m^{-3}), and $\mathrm{M_X}$ represents the molecular weight of species X (g mol^{-1}).

In addition, average EFs for each vessel were calculated based on actual operating conditions, as follows:

$$EF_{\mathrm{X,A}} = \sum_{\mathrm{X},i} EF_i \times P_i \quad (4)$$

where $EF_{\mathrm{X,A}}$ is the average EF for species X, EF_i is the EF for operating mode *i* for species X, and P_i is the percentage of time spent in operating mode *i* during the shipping cycle.

Power-based emission factors and fuel-based emission factors could be interconverted with the formula as following:

$$\mathrm{EF}_{\mathrm{X,P}} = EF_{\mathrm{x}} \cdot \mathrm{FCR} \quad (5)$$

where $\mathrm{EF}_{\mathrm{X,P}}$ is the power-based emission factor for species X (g kW h^{-1}), FCR is fuel consumption rate for each vessel (kg fuel (kW h)$^{-1}$).

3 Results and discussion

3.1 Concentrations in Shipping Emissions

Concentrations of CO, NO_x, SO_2, TVOC, and PM from the three vessels are shown in Fig. S1. Nearly all of the concentrations measured in the exhaust of low engine power vessel HH were higher than those of the two higher engine power vessels. Concentrations of CO, SO_2, and NO_x from HH were 10.7–756, 5.34–33.1, and 87.8–1295 ppm, respectively, and 14.3–59.5 mg m^{-3}PM. In contrast, concentrations of CO, SO_2, NO_x, and PM were 50.1–141, 5.27–16.9, 169–800 ppm and 7.06–21.8 mg m^{-3}, respectively, for DFH and 36.0–224, 0.49–35.9, and 235–578 ppm and 0.56–6.31 mg m^{-3}, respectively, for XYH.

A previous study demonstrated that concentrations of CO primarily depend on engine power, with higher CO emissions resulting from vessel engines with lower power (Sinha et al., 2003). There was a similar trend in this study with generally higher concentrations for HH and lower concentrations for DFH. The CO concentrations in the present study were similar but slightly lower than those of inland vessels (Fu et al., 2013), except in the idling mode of HH. In different operating modes, CO concentrations were significantly different. For example, the maximum value was observed in idling mode and the minimum value in medium speed mode for HH. All three ships had the lowest CO concentrations at their economic speeds (medium speed for HH, cruise mode for DFH, and high speed for XYH), demonstrating that their engines are optimized for the most common operating mode.

More than 80% of the NO_x was NO in this study, with NO_2 and N_2O accounting for <20% in all operating modes (Fig. S1). Again, nearly all of these concentrations were higher in the exhaust gas of HH than in that of the two vessels. In high speed modes, all of the vessels had high concentrations of NO_x. NO_x emissions mainly depend on the combustion temperature of the engines. More powerful combustion systems operate at higher temperatures, thereby producing more NO_x (Corbett, 1999). However, the NO_x emissions were much lower than for the inland vessels studied by Fu et al. (Fu et al., 2013), particularly in cruise mode (NO_x concentrations of ~1,000 ppm).

SO_2 concentrations in the exhaust gas depend on the sulfur content of the fuel and the flow rate of the flue gas. There were significant differences among the three vessels in their flow rates, which could account for the different concentrations of one vessel in different operating modes. But because of the low-sulfur fuels used in these vessels, the SO_2 concentrations were low compared with those in other studies (Williams et al., 2009;Berg et al., 2012).

Much lower concentrations of PM in the exhaust gas were observed in the present study compared to those of inland ships in China (Fu et al., 2013). However, they were similar to those from ships at berth reported by Cooper et al (Cooper, 2003). HH had higher PM concentrations than the two vessels in the exhaust gas. There were significant differences among the different operating modes because of changes in the injection point of the engines (Sippula et al., 2014;Li et al., 2014).

3.2 Fuel-based Emissions Factors

Fuel-based EFs for the gaseous species CO_2, CO, NO, NO_2, N_2O, and TVOCs and for PM based on the carbon balance method were determined. In addition, SO_2 was calculated based on the sulfur content of the fuels. Fuel-based EFs for the typical pollutants such as CO, PM and nitrogen oxides in different operating modes are shown in Fig. 2 (detailed EFs for all the gaseous pollutants are shown in Table ~~S2~~ S4 and detailed EFs for PM and its chemical compositions are shown in Table ~~S3~~S5).

CO_2 emissions from vessels primarily depend on the carbon content of the fuel (Carlton et al., 1995). Accordingly, the EFs for CO_2 in the present study should theoretically be 3177, 3168, and 3171 g kg^{-1} fuel for complete combustion. Under actual conditions, CO_2 emissions were 2940–3106, 3121–3160, and 3102–3162 g kg^{-1} fuel for HH, DFH and XYH, respectively, which means they had combustion efficiencies with 92.5–97.8%, 98.5–99.7% and 97.8–99.7% in terms of CO_2 for these three vessels.

CO emissions of HH were much higher than of XYH, followed by DFH. The power of their respective engines was 350, 600, and 1600 kW. In addition, there were large differences in CO emissions among different modes. All these three vessels had relatively high EFs for CO while accelerating compared with other modes, but the highest EFs were during the idling modes of HH and DFH, and the low-speed mode of XYH. Because CO emissions in diesel engines primarily depend on the excess air ratio (which determines the fuel-air mixture), combustion temperature, and uniformity of the fuel-air mixture in the combustion chamber (D, 2004), ship engines with lower power generally have higher CO emissions (Carlton et al., 1995). Localized hypoxia and incomplete combustion in cylinder were the main reasons for CO emission of diesel engine. CO emissions always had positive relationships with the air-fuel ratio. There was lower air fuel ratio when in low engine load, which resulted in lower CO emission, and vice versa (Ni, 1999).

Much higher NO_x EFs were observed for HH than for the other two vessels. These results were inconsistent with those of Sinha et al. (Sinha et al., 2003), in which emissions of NO_x increased with the power of the ship engine. With increasing vessel speed, NO_x EFs for HH first increased and then decreased. XYH had lower EFs when operating at high speed than at low speed. Nitrogen oxides included NO, NO_2, and N_2O in the present study. More than 70% of the NO_x was in the form of NO for all vessels, because most of the NO_x emissions were generated through thermal NO formation (Haglind, 2008). The primary reasons that slow diesel engines such as the one in HH have higher NO_x emissions include higher peak flame temperatures and the NO formation reactions being closer to their equilibrium state than in other engines (Haglind, 2008). NO_x emissions from vessels are temperature-dependent (Sinha et al., 2003) and also are influenced by the oxygen concentration in the engine cylinder (Ni, 1999). In larger engines, the running speed is generally slower and the combustion process more adiabatic, resulting in higher combustion temperatures and more NO_x. Besides, with the increasing of air-fuel ratios, concentration of NO_x showed a tendency first to increase, then to decrease, which always had the maximum value in the operating mode that close to full load of engine because of the high temperature and oxygen in the engine cylinder (Ni, 1999). Furthermore, there were always higher EFs values in acceleration process and lower in moderating process in this study. When the engines were in transient operating conditions, such as acceleration process or moderating process, concentrations of NO_x always had corresponding changes in the cylinder. Studies about diesel engines showed that when the rotational speed had a sudden increase, there would be a first increasing, then decreasing and last stable tendency for the NO_x concentrations, and vice versa (Tan et al., 2012).

TVOCs emissions from HH were much higher than from the other two vessels; the lowest emissions were observed for DFH. Previous studies (Sinha et al., 2003) have reported that hydrocarbon emissions from vessels depend on engine power, with low-power engines emitting more hydrocarbons. The present results were partially consistent with these previous studies. Besides, hydrocarbon emissions also depend on the percentage utilization of engine power (Sinha et al., 2003). As for various operating modes, TVOCs EFs had large differences. For example, HH had the highest TVOCs emissions in accelerating mode, which was almost three times the high of the lowest value in medium–speed mode. The EFs for SO_2 depended solely on the sulfur content of the fuels and were 1.6, 0.9, and 2.6 g kg^{-1} fuel for HH, DFH, and XYH, respectively in this study. Hydrocarbon could be generated because of the incomplete combustion. For example, in diesel cylinders, there always exist air in wall regions and crevices, as well as when scavenging occurred during the aeration, which could cause the uneven mixing of air and fuel (Ni, 1999).

Fuel-based EFs for PM and its chemical components were shown in Table ~~S3~~S5. OC and EC were the main components of PM, followed by SO_4^{2-}, NH_4^+, and NO_3^-. Metals such as V, Ni, Cr, Fe, As, and Cd made up a proportionately small part of the total PM mass. However, other rare elements such as Tb, Er, Yb, and Lu had higher values than did some of the common elements. PM was an in-process product during the combustion in cylinder, whose forming process included the molecular cracking, decomposition and polymerization results of lack of oxygen. High temperature and oxygen deficiency were the main reasons for the formation in diesel engines, which always had high concentration values in high load operating modes (Ni, 1999). HH had much higher PM emission factors than the other two vessels, in addition to the influence of engine type, sampling condition would be another influence factor according to our deduction. Vessel DFH and XYH had much higher exhaust flue gas stack (10m and 6 m) than HH (2.5 m). Because non-dilution system was used during the sampling, flue gas would through the sampling tube (See in Figure S1) at low temperature and also low flow rate, which could cause the PM deposition on the wall of the tube (Kong et al., 2011;Lee et al., 2004) which caused more PM reduction for DFH and XYH.

EFs for OC and EC and the ratios between them are shown in Fig. 3. EFs for OC and EC for HH were higher than for the other two vessels. Organic matter (OM) is generally calculated as OC × 1.2 (Petzold et al., 2008) to account for the mass of elements other than carbon in the emitted molecules. OM EFs for individual vessels mainly depend on the engine type and the amount of unburned fuel, i.e., the efficiency of combustion. (Moldanova et al., 2013) BC emissions also depend heavily on the engine type (Lack et al., 2009). Therefore, the different types of engines and their levels of maintenance could account for the large differences in OC and EC EFs observed among the three vessels in this study. The ratios of OC to EC in the present study were much lower than those for large diesel ships reported previously (OC/EC = 12) (Moldanova et al., 2009) and also lower than that reported for a medium-speed vessel (Petzold et al., 2010). The non-dilution sampling was the main reason of the lower OC to EC ratio in this study. Besides, TOR was used to measure OC and EC in PM, which always had a lower OC content compared with other methods (such as TOT) because of the different definitions of OC and EC (Khan et al., 2012). Compared with other diesel engines,~~However~~, ~~they~~ the ratios of OC to EC in this study were higher than that of automobile diesel soot, in which EC comprises 75–80 wt% of the total PM (Clague et al., 1999), and also higher than heavy heavy-duty diesel trucks (HHDDT) with OC to EC ratios below unit for cruse and transient modes even though higher in cold-start/idle and creep modes (Shah et al., 2004).

Studies have shown that SO_4^{2-} formed from vessel-emitted SO_2 is a major contributor to CCN and ship track formation (Schreier et al., 2006;Lauer et al., 2007). Sulfate is also an important component of PM emitted from vessels. In the present study, EFs for SO_4^{2-} were much lower than previously reported (Petzold et al., 2008;Agrawal et al., 2008), but similar to those detected by a high-resolution time-of-flight aerosol mass spectrometer in a previous study (Lack et al., 2009). This may be because EFs for SO_4^{2-} are mainly related to the sulfur content of the fuel; SO_4^{2-} is not generally emitted directly from the engines, but forms after release from the stack (Lack et al., 2009). Because PM was collected directly from engine emissions in the present study, the sulfur-to-sulfate ratios were low (<0.6% for vessels). Other ions such as NO_3^- and NH_4^+ accounted for a small percentage of the PM emitted from the vessels compared with SO_4^{2-}, consistent with previous studies (Lack et al., 2009). SO_2 is more easily oxidized to SO_3 in catalytic reaction cycles with metals commonly present in the exhaust gas (V, Ni), while hydroxyl radicals are additional needed to convert NO_x to NO_3^- (Moldanova et al., 2009).

Na^+ and Cl^- were considered to originate from marine air. Their concentrations were highly correlated ($r^2 = 0.78$); the differing air demands of the engines under different conditions might have caused observed variations in the EFs relative to the fuel demand.

The elemental compositions of PM in the present study differed from previous studies showing high elemental contents of S, Ca, V, Fe, Cu, Ni, and Al (Agrawal et al., 2008;Moldanova et al., 2009). V and Ni are typically associated with combustion of heavy fuel oil (Almeida et al., 2005). In the present study, the high-quality fuels resulted in low EFs for V and Ni. In our previous study, PM from shipping emissions was estimated to account for 2.94% of the total $PM_{2.5}$ at Tuoji Island in China, using V as a tracer of shipping emissions (Zhang et al., 2014). Reconsidering the former results based on the EFs obtained in the present study, we determined that the contribution of vessels near Tuoji Island had been underestimated, because the estimate should have included both heavy and other types of fuels. However, some rare elements such as Tb, Er, Yb, and Lu had relatively high EFs compared with those of other elements in the present study, which may be related to the source of the fuels.

3.3 Fuel-based Average Emissions Factors

Based on actual operating conditions (Table ~~S4~~S6), average EFs for the three vessels in the present study (according to formula (4)) along with EFs from previous studies are shown in Table 3. EFs for all of the pollutants except SO_2 were significantly higher for HH than for the other two vessels, potentially due to poor combustion conditions. Most~~F~~ of the EFs for DFH and XYH were within the range of emissions for other vessels due to having well maintained engines and the high quality of the fuels used. The EFs for NO_x, PM, and SO_2 were much lower than reported ~~for vessels~~ in previous studies (other than NO_x for ocean-going vessels). All the sulfur of the fuels in the present study were significantly below the emissions limit of 3.50% established by IMO in the revised MARPOL Annex VI rules, applicable since 2012 (IMO, 1998).

The IMO Tier I emissions limit for NO_x is 45.0 × $n^{-0.2}$ g kWh^{-1} (n, rated speed, $130 < n < 2000$ rpm). The rated speed and fuel consumption rate for each vessel are shown in Table 1. Thus, the emissions limits for HH, DFH, and XYH would be 54.5, 57.5, and 56.5 g kg^{-1} fuel, respectively, calculating combined with formula (5). The average fuel-based EFs for NO_x of ship HH was more than 100% above the IMO standard, while those of the other two ships were below the IMO standard (Table 3). PM emissions for HH were also higher than previously reported, but those for the two research vessels were much lower (Table 3). Fuel type is one of the most important influence factors on pollutant emissions, for example, sulfur content in the fuel not only influence the SO_2 emission directly, but also had impact on PM formation in the flue gas stack with ~~L~~low sulfur content in fuels reduces PM formation~~, which also could be one reason for the low PM EFs~~ (Lack et al., 2011). Vessels with higher sulfur content always had relatively higher PM emissions, which were also shown in Table 3. In addition, different engines and levels of maintenance have a significant impact on all combustion-dependent emissions. Emission reduction measures have been used in some vessels. For example, NO_x emissions can be reduced by measures such as selective catalytic reduction (SCR) and direct water injection (DWI), which had been implemented on some vessels previously studied in a harbor in Finland (Pirjola et al., 2014). The results showed that SCR effectively reduced NO_x emissions, while vessels with DWI had high PM emissions.

In order to compare the differences of emission factors from vessels in this study and other non-road diesel engine vehicles, fuel-based emission factors for CO, NO_x and PM were given in Table S7, including military non-road heavy duty diesel vehicles, excavator and wheel loader and other diesel trucks. It could be deduced that engine types have significant impact on emission factors such as non-road heavy duty diesel vehicles always have much higher NO_x emission factors compared with common diesel trucks. Besides, one interested thing should be mentioned that Chinese diesel engines always have higher NO_x and PM emission factors which may be caused by the less strict emission standard applied for diesel vehicles in China. Similarly, the engine type might be an important cause of the different emissions, such as HH had much higher pollutants emissions with an engine produced in China and yet DFH's engine produced in Germany. Besides, emission test for a high-speed marine diesel engine with different kind of diesels showed that, diesel type had limited influence on emissions such as NO_x, CO and CH, but a significant impact on PM emission (28.9-41.5%) because of the different sulfur content in fuel (Xu, 2008).

3.4 Power-based Emissions Factors

Based on the engine power and fuel consumption rates of the vessels, power-based

EFs were calculated (according to formula (5)) and compared to results from previous studies (Table 4). The EFs for HH were much higher than those for the other two vessels, except for SO_2. HH also had significantly higher EFs for CO and NO_x than previously reported values. On the other hand, most of the EFs for DFH and XYH were within the range of previously reported results. All of the EFs for SO_2 in the present study were lower than those in previous studies, because of the low sulfur content of the present fuels. Generally, PM emissions from marine diesel fuels are dependent on the fuel (sulfate and metal oxide ash constituents) and on combustion conditions (unburned hydrocarbons and carbon residue constituents) (Cooper, 2003). HH had the highest PM emissions, although there were almost no differences among the fuels (Table ~~S3~~S5). Therefore, combustion conditions were likely the determining factor. The PM emissions observed in the present study were within the range previously reported, except for XYH, which had a much lower value.

3.5 Impact of Engine Speed on NOx Emissions Factors

NO_x is formed in the combustion chamber by a combination of atmospheric nitrogen and oxygen under high-pressure and high-temperature conditions. Many factors affect NO_x formation, including engine temperature, injection point, and fuel quality. The IMO emissions limit for NO_x is determined by the rated speed of the engine; however, other factors must also be considered to reduce NO_x emissions.

The NO_x EFs for the test vessels at various engine speeds are shown in Fig. 4. The rated speeds of the vessels were 1200, 900, and 1000 rpm for HH, DFH, and XYH, respectively. The actual engine speeds of HH were much lower than the rated speed, while the two larger engine power vessels operated close to their rated speeds, except during one operating mode of DFH. The NO_x EFs for HH differed significantly in different operating modes, ranging from 39.1 to 143 g kg^{-1} fuel. The NO_x EF was highest when the engine speed reached ~750 rpm (Fig. 4). At lower engine speeds, the NO_x EFs had fluctuating but lower values. At higher engine speeds closer to the rated speed of 1200 rpm, the NO_x EFs were much lower. The NO_x EFs for the two larger engine power vessels changed slightly with engine speed, but also had lowest values when their engine speeds approached their rated speeds. Combined with the diesel propulsion characteristic curve, there were large increases in the fuel consumption rate when the engine speed increased. Therefore, a best-fit engine speed should be determined based on both EFs and economic costs.

Engineering approaches for reducing the NO_x emissions of marine engines may be applied before, during, or after the combustion process (Verschaeren et al., 2014;Habib et al., 2014). In the present study, the NO_x EFs of the two research vessels were below the IMO Tier I emissions limits. However, for EMS, measures should be taken to meet the IMO emissions limit, including increasing the engine speed and applying engineering technologies during or after combustion, such as exhaust gas recirculation (EGR), selective non-catalytic reduction (SNCR), or SCR.

4 Conclusions

Three offshore vessels with different engine power were chosen in this study to collect measured data of gaseous species and particulate matter, including NO_2, NO, N_2O, CO, CO_2, TVOCs, SO_2 and the total suspended particulate. Besides, chemical compositions of the PM were also analyzed to give detailed EFs for OC, EC, water soluble ions and metal elements. Concentrations, fuel-based EFs, fuel-based average EFs as well as power-based average EFs for species of offshore vessels in China were given. Furthermore, impact of engine speed on NO_x EFs was also discussed.

There were higher concentrations of pollutants for low engine power vessel HH than for the other two vessels. CO concentrations for offshore vessels were slightly lower than inland vessels in China, and all the three vessels had the lowest CO concentrations at their economic speeds (the speed of the least vessel operating expenditures during one voyage, they were high speed mode, cruise mode and high speed mode for HH, DFH and XYH, respectively). More than 80% of the NO_x was NO, and all the offshore vessels had higher NO_x concentrations in high speed modes. Because of the low-sulfur fuels used in this study, SO_2 concentrations of these three offshore vessels were lower than that in the literatures. And the PM concentrations were much lower than inland vessels while showing significant differences among different operating modes.

Fuel-based EFs for gaseous species and PM were given based on the carbon balance method. EFs for CO_2 were 2940–3106, 3121–3160, and 3102–3162 g kg^{-1} fuel for HH, DFH and XYH~~ with high combustion efficiencies~~. Because of the combustion conditions such as excess air ratio, combustion temperature and uniformity of the fuel-air mixture, EFs for CO showed high values in idling mode, but low values in economic speed. All the offshore vessels had high NO_x EFs in low speed than in high speed, but showed higher values when in acceleration process. EFs for SO_2 were 1.6, 0.9 and 2.6 g kg^{-1} fuel for HH, DFH and XYH based on sulfur content of the fuels. OC and EC were the main components of PM, with low OC to EC ratios lower than 0.1, followed by SO_4^{2-}, NH_4^+, and NO_3^-. Metals such as V, Ni, Cr, Fe, As, and Cd made up a proportionately small part of the total PM mass.

Fuel-based average EFs as well as power-based EFs for the three different engine power vessels were given. EFs for most gaseous species and PM of HH were much higher compared with the other higher engine power vessels, which was also >100% above the IMO standard for NO_x. Average PM EF of the low engine power vessel, HH was also much higher than that in the literatures. However, average EFs for most species of the two larger engine power vessels were within the range of previously reported results. Engine type was inferred as one of the most influence factors for the differences of emission factors.

The impact of engine speed on EFs for NO_x showed that when the engine speed was close to the rated speed, there would be lower NO_x EFs values. However, combined with the high fuel consumption rate, an optimal engine speed should be determined based on both EFs and economic costs. Emission reduction measures for NO_x for some of the offshore vessels in China are still essential to meet the IMO emission limit.

Given the limits of vessel types and numbers, this study substantially gives the EFs for gaseous species and PM of three different diesel engine power offshore vessels. However, as the development of ports in China, emissions from cargo ships and container ships with large engine power have becoming one of the most important air pollution sources in port cities and regions. Systematical EFs of all kinds of offshore vessels in China are essential in order to give the accurate emission inventory of ships.

Supporting Information

Supporting Information includes the details of the real-world measurement system for vessels (Fig. S1), the concentrations of main gaseous matters and PM of shipping emissions (Fig. S2), the types composition of offshore vessels in China (Table S1), the Chinese market consumption of marine oil in 2011 (Table S2), the detection parameters for gaseous matters (Table S3), ~~the concentrations of main gaseous matters and PM in shipping emissions (Fig. S1), the detection parameters for gaseous matters (Table S1),~~ the fuel-based EFs for the gaseous pollutants (Table ~~S2~~S4), PM and the chemical compositions in PM ~~(Table S3)~~ for different operating modes (Table S5) and the actual operating conditions of vessels (Table ~~S4~~S6)~~,~~ and the emission factors of pollutants from diesel engine vehicles (Table S7).

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Table 1. Technical parameters of test vessels

Vessel ID	Vessel type	Displacement（ton）	Ship length ×width (m)	Engine power (kw)	Vessel age（year）	Rated speed (rpm)	Fuel consumption rate (g/KWh)
HH	Engineering vessel	307	44×13	350×2	4	1200	200
DFH	Research vessel	3235	96×15	1600×2	18	900	200
XYH	Research vessel	602	55×9	600	5	1000	200

Table 2 Results from the fuel analysis (diesels)

	Units	HH	DFH	XYH
Total calorific value	MJ kg^{-1}	45.44	45.40	45.50
Net calorific value	MJ kg^{-1}	42.51	42.48	42.55
Ash content	%m	0.001	＜0.001	＜0.001
Sulfur (S)	%m	0.0798	0.0458	0.130
Carbon (C)	%m	86.66	86.40	86.49
Hydrogen (H)	%m	13.32	13.22	13.44
Nitrogen (N)	%m	＜0.2	＜0.2	＜0.2
Oxygen (O)	%m	＜0.4	＜0.4	＜0.4

Table 3 Fuel-based average EFs in the present study and previous studies (g kg^{-1} fuel)

Vessel ID	CO$_2$	CO	NO	NO$_2$	N$_2$O	NO$_X$	TVOCs	PM	SO$_2$	S content (%m)
HH	3071±1565	30.2±16.2	98.2±37.2	15.5±5.45	1.28±1.70	115±44.3	23.7±21.0	9.40±2.13	1.60	0.08
DFH	3153±176	6.93±1.00	30.2±1.60	5.09±0.42	0.38±0.18	35.7±2.20	1.24±0.04	0.72±0.33	0.92	0.05
XYH	3151±175	9.20±2.95	26.6±1.63	4.71±0.42	0.30±0.15	31.6±2.20	4.18±0.15	0.16±0.07	2.60	0.13
Commercial vessel (Williams et al., 2009)	3170	7-16	-	-	-	60-87	-	-	6-30	
Cargo vessel (Moldanova et al., 2009)	3441	2.17	-	-	-	73.4	-	5.3	39.3	1.9
Diesel engine (Haglind, 2008)	-	7.4	-	-	-	87	-	7.6	54	2.7
Ocean-going ships (Sinha et al., 2003)	3135	19.5	-	-	-	22.3	-	-	2.9	0.1 ~~Distillate fuel~~
Ocean-going ships (Sinha et al., 2003)	3176	3.0	-	-	-	65.5	-	-	52.2	2.4 ~~Residual fuel~~
Cargo and passenger ships(Endresen, 2003)	3170	7.4	-	-	0.08	57-87	2.4	1.2-7.6	10-54	0.5-2.7
Ships operating in harbor areas(Pirjola et al., 2014)	-	-	42-72	-	-	65-86	-	-	4.6-9.8	NONE
	-	-	16-49	-	-	25-79	-	-	5.4-17.0	~~SRC~~SCR
Ships operating in Port(Diesch et al., 2013)	-	-	16	37	-	53	-	-	7.7	

(NONE=No treatment of emissions, ~~SRC~~SCR=Selective catalytic reduction)

Table 4. Power-based EFs in present study and previous studies (g kWh^{-1})

Vessel ID	CO_2	CO	NO	NO_2	N_2O	NO_X	TVOCs	PM	SO_2	
HH	699 ±352	7.38 ±3.76	22.0 ±8.41	3.45 ±1.24	0.30 ±0.39	25.8 ±10.0	5.44 ±4.84	2.09 ±0.48	0.36	
DFH	631 ±35.2	1.39 ±0.20	6.04 ±0.32	1.02 ±0.08	0.08 ±0.04	7.14 ±0.44	0.17 ±0.01	0.14 ±0.07	0.18 -	
XYH	697 ±38.5	2.01 ±0.65	5.87 ±0.36	1.04 ±0.09	0.07 ±0.03	6.97 ±0.48	0.92 ±-	0.04 ±0.01	0.57	
Tanker(Winnes and Fridell, 2010)	-	1.61	-	-	-	7.82	-	0.58	-	
Berthed ships(Cooper, 2003)	653-699	0.33-1.71	-	-	-	9.6-20.2	-	0.14-0.54	0.4-9.6	
Crude Oil Tanker(Agrawal et al., 2008)	588-660	0.77-1.78	-	-	-	15.8-21.0	-	1.10-1.78	7.66-8.60	
Cruise ships(Poplawski et al., 2011)	-	-	-	14.0	-	-	-	2.91	4.20	
US EPA	621	1.4	-	-	-	18.1	-	1.31	10.3	
Marine Engine(Sippula et al., 2014)	-	1.2	-	-	-	11.4	-	0.72-1.9	-	
Large marine ships(Khan et al., 2013)	600 ±2	-	-	-	-	16.1 ±0.1	-	1.42 ±0.04	9.44	
Ocean going container vessel(Agrawal et al., 2008)	658	0.77	-	-	-	18.21	-	1.64	8.39	
Large cargo vessel(Moldanova et al., 2009)	667	0.42	-	-	-	14.22	-	1.03	10.3	
Ocean going cargo vessel(Celo et al., 2015)	614-628	0.26-0.83	-	-	-	11.3-16.3	-	0.81-1.51	5.8-8.7	IFO180
	609 ±1	1.31 ±0.02	-	-	-	8.4 ±0.03	-	0.37 ±0.01	4.7 ±0.01	IFO60
	605 ±1	0.00	-	-	-	16.7 ±0.1	-	2.2 ±0.2	10.3 ±0.03	IFO380
	622 ±1	1.22 ±0.02	-	-	-	10.7 ±0.04	-	0.30 ±0.03	0.47 ±0.1	MDO

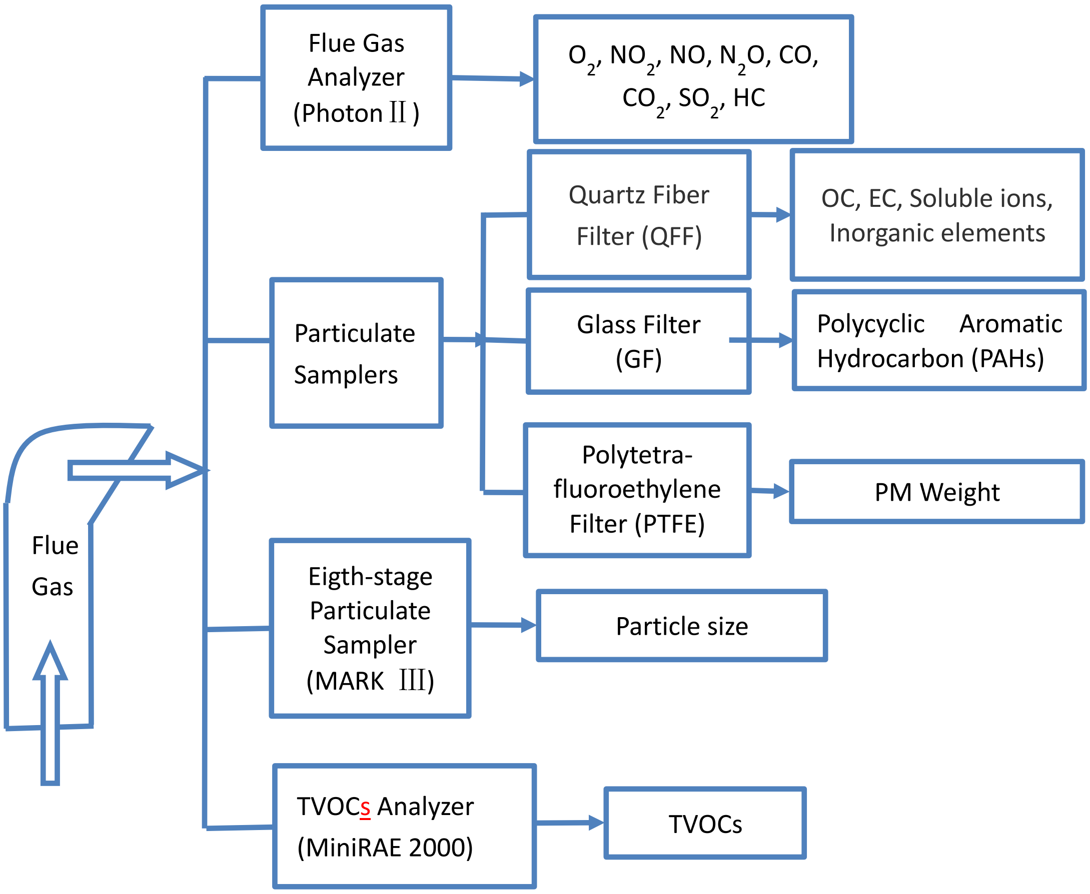

Figure 1. On-board emissions test system and measured analytes.

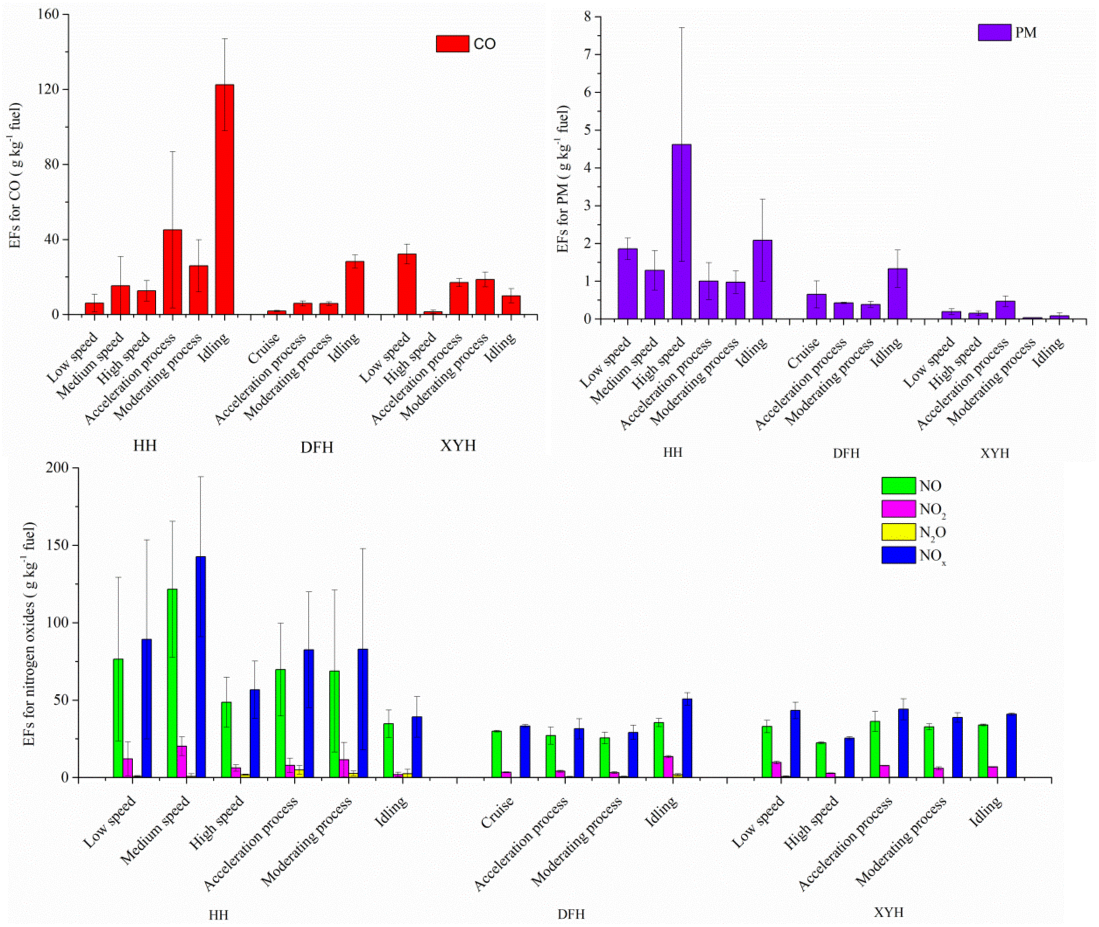

Figure 2. EFs for the typical pollutants in different operating modes

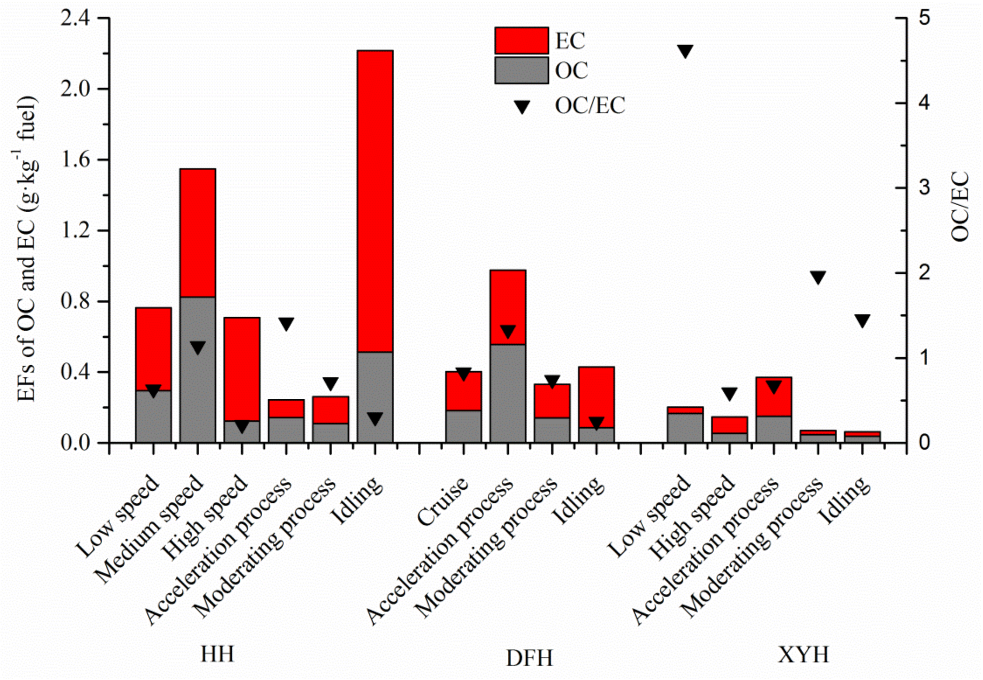

Figure 3. EFs for OC and EC and the ratios between them

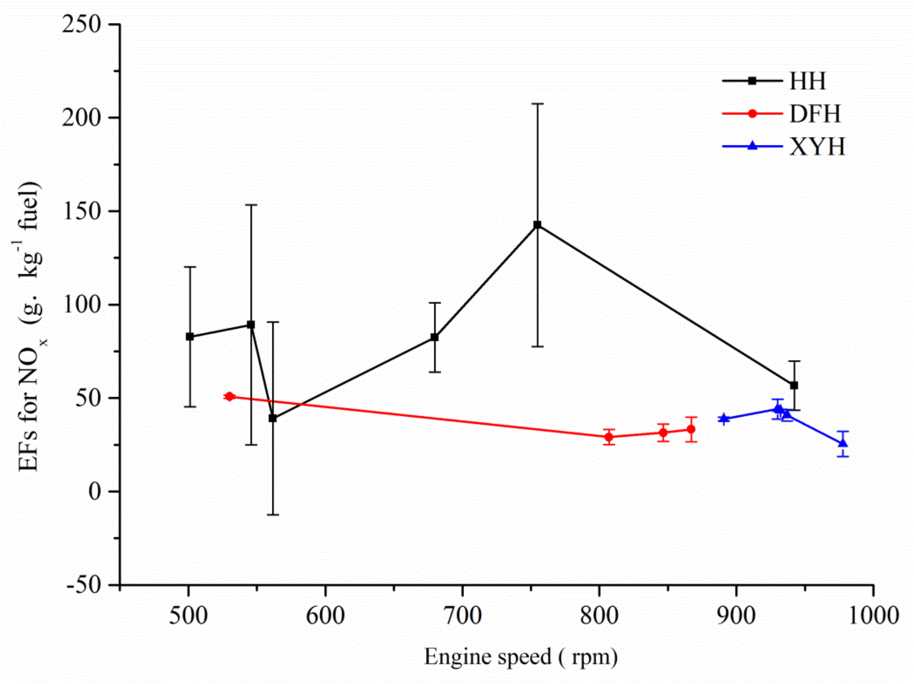

Figure 4. Emissions factors for NO_x at different engine speeds