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. Fuel-based average emission 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 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\(_2\)e for GHGs combining CO\(_2\), CH\(_4\) and N\(_2\)O 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\(_2\)e) 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
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), 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 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 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\textsubscript{x}, carbon monoxide (CO), sulfur dioxide (SO\textsubscript{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\textsubscript{2}, NO\textsubscript{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\textsuperscript{-1} fuel, respectively, and 0.2–6.2×10\textsuperscript{16} particles kg\textsuperscript{-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\textsubscript{x} and SO\textsubscript{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\textsubscript{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. 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, 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 therefore, 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 (CO₂), SO₂, NOₓ, 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 NOx 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

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 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 and 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$_2$O, CO, CO$_2$ and SO$_2$ (Detection parameters for the gaseous matters are shown in Table 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:

\[
C_F = R_{FG} \times (c(CO) + c(CO_2) + c(PM) + c(TVOC))
\]  

(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 \(c(CO)\), \(c(CO_2)\), \(c(PM)\), and \(c(TVOC)\) 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:

\[
EF_{CO_2} = R_{FG} \cdot c(CO_2) \cdot M_{CO_2}
\]  

(2)

where \(EF_{CO_2}\) is the EF for CO\(_2\) (g kg\(^{-1}\) fuel), \(c(CO_2)\) is the molar concentration of CO\(_2\) (mol m\(^{-3}\)), and \(M_{CO_2}\) is the molecular weight of CO\(_2\) (44 g mol\(^{-1}\)).

The remaining EFs were calculated as follows:

\[
EF_X = \frac{\Delta X}{\Delta CO_2} \cdot \frac{M_X}{M_{CO_2}} \cdot EF_{CO_2}
\]  

(3)

where \(EF_X\) is the EF for species X (g kg\(^{-1}\) fuel), \(\Delta X\) and \(\Delta CO_2\) represent the concentrations of X and CO\(_2\) with the background concentrations subtracted (mol m\(^{-3}\)), and \(M_X\) 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:

\[
EF_{XA} = \sum_{i} EF_i \times P_i
\]  

(4)

where \(EF_{XA}\) 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:

\[ \text{EF}_{X,P} = \text{EF}_x \cdot \text{FCR} \]  

where \( \text{EF}_{X,P} \) 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\(_2\)O 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\textsubscript{x}. NO\textsubscript{x} emissions mainly depend on the combustion temperature of the engines. More powerful combustion systems operate at higher temperatures, thereby producing more NO\textsubscript{x} (Corbett, 1999). However, the NO\textsubscript{x} emissions were much lower than for the inland vessels studied by Fu et al. (Fu et al., 2013), particularly in cruise mode (NO\textsubscript{x} concentrations of ~1,000 ppm).

SO\textsubscript{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\textsubscript{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\textsubscript{2}, CO, NO, NO\textsubscript{2}, N\textsubscript{2}O, and TVOCs and for PM based on the carbon balance method were determined. In addition, SO\textsubscript{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 S4 and detailed EFs for PM and its chemical compositions are shown in Table S5).

CO\textsubscript{2} emissions from vessels primarily depend on the carbon content of the fuel (Carlton et al., 1995). Accordingly, the EFs for CO\textsubscript{2} in the present study should theoretically be 3177, 3168, and 3171 g kg\textsuperscript{-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$_2$O 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\textsubscript{x}. Besides, with the increasing of air-fuel ratios, concentration of NO\textsubscript{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\textsubscript{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\textsubscript{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\textsubscript{2} depended solely on the sulfur content of the fuels and were 1.6, 0.9, and 2.6 g kg\textsuperscript{-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 S5. OC and EC were the main components of PM, followed by SO\textsubscript{4}^{2-}, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{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 $OC \times 1.2$ (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,, 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 cruise 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 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 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 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 $45.0 \times n^{0.2} \text{ g kWh}^{-1}$ (n, rated speed, $130 < n < 2000 \text{ rpm}$). 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 low sulfur content in fuels reduces PM formation (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\textsubscript{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\textsubscript{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\textsubscript{x} emission factors compared with common diesel trucks. Besides, one interested thing should be mentioned that Chinese diesel engines always have higher NO\textsubscript{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\textsubscript{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\textsubscript{2}. HH also had significantly higher EFs for CO and NO\textsubscript{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\textsubscript{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 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

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

The NOx 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 NOx EFs for HH differed significantly in different operating modes, ranging from 39.1 to 143 g kg\(^{-1}\) fuel. The NOx EF was highest when the engine speed reached ~750 rpm (Fig. 4). At lower engine speeds, the NOx EFs had fluctuating but lower values. At higher engine speeds closer to the rated speed of 1200 rpm, the NOx EFs were much lower. The NOx 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 NOx 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 NOx 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 NO₂, NO, N₂O, CO, CO₂, TVOCs, SO₂ 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 NOₓ 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 NOₓ was NO, and all the offshore vessels had higher NOₓ concentrations in high speed modes.

Because of the low-sulfur fuels used in this study, SO₂ 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 CO₂ were 2940–3106, 3121–3160, and 3102–3162 g kg⁻¹ fuel for HH, DFH and XYH. 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 NOₓ EFs in low speed than in high speed, but showed higher values when in
acceleration process. EFs for SO\textsubscript{2} were 1.6, 0.9 and 2.6 g kg\textsuperscript{-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\textsubscript{4}\textsuperscript{2-}, NH\textsubscript{4}\textsuperscript{+}, and NO\textsubscript{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\textsubscript{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\textsubscript{x} showed that when the engine speed was close to the rated speed, there would be lower NO\textsubscript{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\textsubscript{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 fuel-based EFs for the gaseous
pollutants (Table S4), PM and the chemical compositions in PM for different
operating (Table S5) modes and the actual operating conditions of vessels (Table S6)
and the emission factors of pollutants from diesel engine vehicles (Table S7).

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products or commercial services mentioned in this publication.
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<tr>
<th>Vessel ID</th>
<th>Vessel type</th>
<th>Displacement (ton)</th>
<th>Ship length × width (m)</th>
<th>Engine power (kw)</th>
<th>Vessel age (year)</th>
<th>Rated speed (rpm)</th>
<th>Fuel consumption rate (g/KWh)</th>
</tr>
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<td>350×2</td>
<td>4</td>
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<td>200</td>
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<td>1600×2</td>
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<td>900</td>
<td>200</td>
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<td>&lt;0.001</td>
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</table>
Table 3 Fuel-based average EFs in the present study and previous studies (g·kg⁻¹ fuel)

<table>
<thead>
<tr>
<th>Vessel ID</th>
<th>CO₂</th>
<th>CO</th>
<th>NO</th>
<th>NO₂</th>
<th>N₂O</th>
<th>NOₓ</th>
<th>TVOCs</th>
<th>PM</th>
<th>SO₂</th>
<th>S content (%m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HH</td>
<td>3071±1565</td>
<td>30.2±16.2</td>
<td>98.2±37.2</td>
<td>15.5±5.45</td>
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<td>115±44.3</td>
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<td>0.08</td>
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<tr>
<td>DFH</td>
<td>3153±176</td>
<td>6.93±1.00</td>
<td>30.2±1.60</td>
<td>5.09±0.42</td>
<td>0.38±0.18</td>
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<td>0.05</td>
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<td>XYH</td>
<td>3151±175</td>
<td>9.20±2.95</td>
<td>26.6±1.63</td>
<td>4.71±0.42</td>
<td>0.30±0.15</td>
<td>31.6±2.20</td>
<td>4.18±0.15</td>
<td>0.16±0.07</td>
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<td>0.13</td>
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<td>60-87</td>
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<td>6-30</td>
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<td>87</td>
<td>-</td>
<td>7.6</td>
<td>54</td>
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<td>-</td>
<td>5.4-17.0</td>
<td>SCR</td>
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(NONE=No treatment of emissions, SCR=Selective catalytic reduction)
Table 4. Power-based EFs in present study and previous studies (g·kWh⁻¹)

<table>
<thead>
<tr>
<th>Vessel ID</th>
<th>CO₂</th>
<th>CO</th>
<th>NO</th>
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<td>HH</td>
<td>699±352</td>
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<td>18.1</td>
<td>-</td>
<td>1.31</td>
<td>10.3</td>
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<td>-</td>
<td>11.4</td>
<td>-</td>
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<td>18.21</td>
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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\textsubscript{x} at different engine speeds