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

F. Zhang[1,4], Y. Chen[1,2], C. Tian[1], J. Li[3], G. Zhang[3], and V. Matthias[5]

[1]Key Laboratory of Coastal Environmental Processes and Ecological Remediation, Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences (CAS), Shandong Provincial Key Laboratory of Coastal Environmental Processes, YICCAS, Yantai, Shandong 264003, China
[2]Key Laboratory of Cities' Mitigation and Adaptation to Climate Change in Shanghai (China Meteorological Administration), College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China
[3]State key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou Guangdong 510640, China
[4]University of Chinese Academy of Sciences, Beijing 100049, China
[5]Helmholtz-Zentrum Geesthacht, Institute of Coastal Research, Max-Planck-Straße 1, 21502 Geesthacht, Germany

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Correspondence to: Y. Chen (yjchentj@tongji.edu.cn) and C. Tian (cgtian@yic.ac.cn)

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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 than for the two higher engine power vessels. 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. The fuel-based average emissions factor 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.

ACPD

15, 23507–23541, 2015

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 9200 and 5200 $t\,yr^{-1}$ 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 $> 200\,mg\,S\,m^{-2}\,yr^{-1}$ 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). 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.

ACPD
15, 23507–23541, 2015

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. 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, 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), use of bunker oil (fuel meeting the GB/T 17 411–1998 standard, which is less stringent than the ISO 8217–2010 international standard), age of vessels (Chinese commercial vessels have an average age of 19.2 yr compared with 8.0 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

ACPD
15, 23507–23541, 2015

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. 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). Even more stringent limits have been laid down in some national or regional regulations. For example, the EU environment ministers had limited the use of fuels of 1.5 % sulfur (by mass) by all ships in the Baltic Sea, North Sea and English Channel in June 2004 (Eyring, 2005), and the ships operating in the Baltic Sea must use reduced-sulfur fuels (fuel sulfur content less than or equal to 1 % by mass) since 1 July 2010, and even lower sulfur fuels of 0.1 % in January 2015. Additionally, in some ports such as EU ports, seagoing ships at berth are required to switch into using fuels of under 0.1 % sulfur (European Union, 2012). But 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.

Average EFs are often used for shipping emissions inventories on large scales or in regional areas (Tzannatos, 2010; Eyring, 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

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. Results of fuel analyses are presented in Table 2. All of these fuels had relatively low sulfur contents ($\leq 0.13\,\%$ 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. 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 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

ACPD
15, 23507–23541, 2015

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. There were four main components of the system: a flue gas analyzer, three particulate samplers, an eight-stage particulate sampler, and a TVOC analyzer (see Supplement 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. 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 TVOC 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 $\mu g\,C\,cm^{-2}$ 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 1 mL 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 %.

ACPD
15, 23507–23541, 2015

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:

$$C_F = R_{FG} \times (c(C_{CO}) + c(C_{CO_2}) + c(C_{PM}) + c(C_{TVOC})) \quad (1)$$

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 $c(C_{CO})$, $c(C_{CO_2})$, $c(C_{PM})$, and $c(C_{TVOC})$ 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:

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

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:

$$EF_x = \frac{\Delta X}{\Delta CO_2} \cdot \frac{M_X}{M_{CO_2}} \cdot EF_{CO_2} \quad (3)$$

where EF_x is the EF for species X ($g\,kg^{-1}$ fuel), X and 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:

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

ACPD
15, 23507–23541, 2015

Emissions factors of pollutants from offshore vessels in China

F. Zhang et al.

where $EF_{X,A}$ 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.

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. A1. 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. A1). Again, nearly all of these concentrations were

ACPD
15, 23507–23541, 2015

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 ~ 1000 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 B1 and detailed EFs for PM and its chemical compositions are shown in Table B2).

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,

ACPD
15, 23507–23541, 2015

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 high combustion efficiencies with 92.5–97.8, 98.5–99.7 % and 97.8–99.7 % 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

ACPD
15, 23507–23541, 2015

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. 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 B2. 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).

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). However, they were higher than that of automobile diesel soot, in which EC comprises 75–80 wt % of the total PM (Clague et al., 1999).

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

ACPD
15, 23507–23541, 2015

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, average EFs for the three vessels in the present study 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 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

ACPD
15, 23507–23541, 2015

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 $45.0 \times n^{-0.2}$ $g\,kWh^{-1}$ ($130 < n < 2000$ rpm). Thus, the emissions limits for HH, DFH, and XYH would be 54.5, 57.5, and 56.5 $g\,kg^{-1}$ fuel, respectively, based on the engine parameters. The average fuel-based EFs for NO_x of ship HH was > 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). Low sulfur content in fuels reduces PM formation, which also could be one reason for the low PM EFs (Lack et al., 2011). 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.

3.4 Power-based emissions factors

Based on the engine power and fuel consumption rates of the vessels, power-based EFs were calculated 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 S2). Therefore, com-

ACPD
15, 23507–23541, 2015

bustion 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 NO_x 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

ACPD
15, 23507–23541, 2015

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,

ACPD
15, 23507–23541, 2015

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.

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.

Supplement

Supplement includes the details of the concentrations of main gaseous matters and PM in shipping emissions (Fig. S1), the fuel-based EFs for the gaseous pollutants (Table S1), PM and the chemical compositions in PM (Table S2) for different operating modes.

ACPD
15, 23507–23541, 2015

The Supplement related to this article is available online at doi:10.5194/acpd-15-23507-2015-supplement.

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ACPD
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Emissions factors of pollutants from offshore vessels in China

F. Zhang et al.

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ACPD
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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^{-1})
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

ACPD
15, 23507–23541, 2015

Table 2. Results from the fuel analysis.

	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

ACPD
15, 23507–23541, 2015

ACPD
15, 23507–23541, 2015

Emissions factors of pollutants from offshore vessels in China

F. Zhang et al.

Table 3. Fuel-based average EFs in the present study and previous studies ($g\,kg^{-1}$ fuel) (NONE = No treatment of emissions, SRC = Selective catalytic reduction).

Vessel ID	CO_2	CO	NO	NO_2	N_2O	NO_X	TVOCs	PM	SO_2	
HH	3071	30.2	98.2	15.5	1.28	115	23.7	9.40	1.60	
DFH	3153	6.93	30.2	5.09	0.38	35.7	1.24	0.72	0.92	
XYH	3151	9.20	26.6	4.71	0.30	31.6	4.18	0.16	2.60	
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	
Diesel engine (Haglind, 2008)	–	7.4	–	–	–	87	–	7.6	54	
Ocean-going ships (Sinha et al., 2003)	3135	19.5	–	–	–	22.3	–	–	2.9	Distillate fuel
Ocean-going ships (Sinha et al., 2003)	3176	3.0	–	–	–	65.5	–	–	52.2	Residual fuel
Cargo and passenger ships (Endresen, 2003)	3170	7.4	–	–	0.08	57–87	2.4	1.2–7.6	10–54	
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
Ships operating in Port (Diesch et al., 2013)	–	–	16	37	–	53	–	–	7.7	

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	635	6.92	20.4	3.24	0.25	23.9	4.27	2.01	0.36
DFH	631	1.39	6.04	1.02	0.08	7.14	0.17	0.14	0.18
XYH	697	2.01	5.87	1.04	0.07	6.97	0.92	0.04	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

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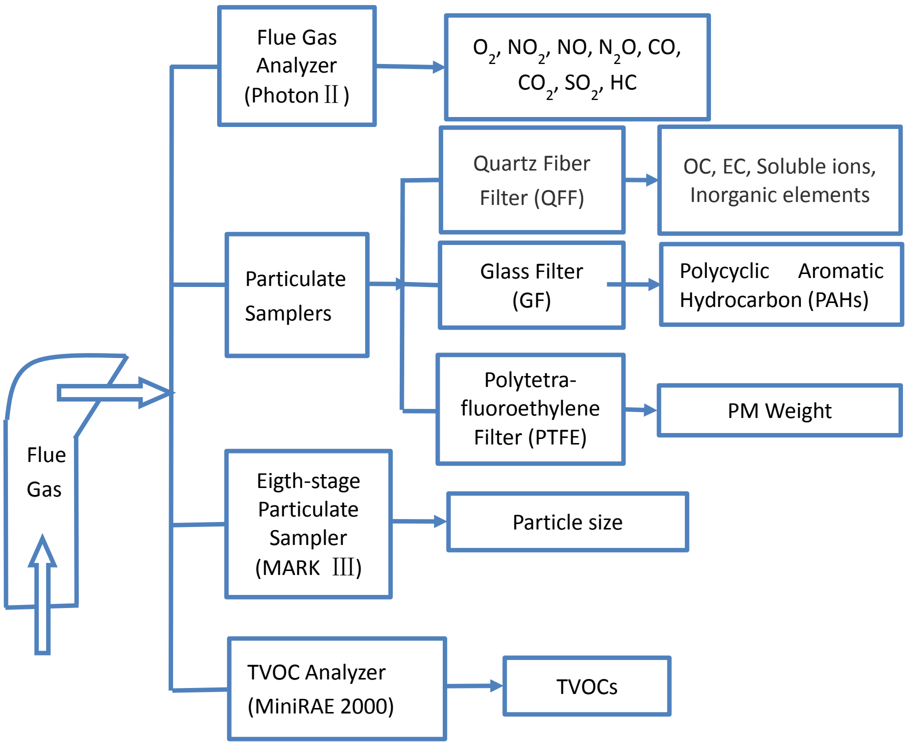

Figure 1. On-board emissions test system and measured analytes.

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15, 23507–23541, 2015

Emissions factors of pollutants from offshore vessels in China

F. Zhang et al.

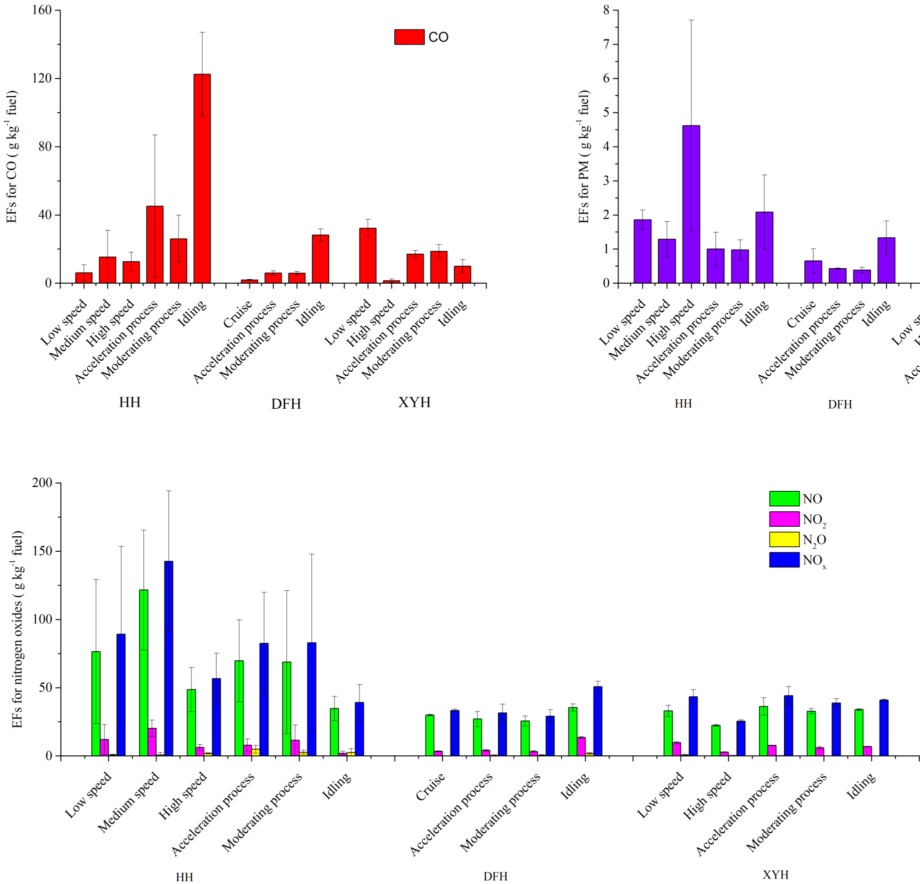

Figure 2. EFs for the typical pollutants in different operating modes.

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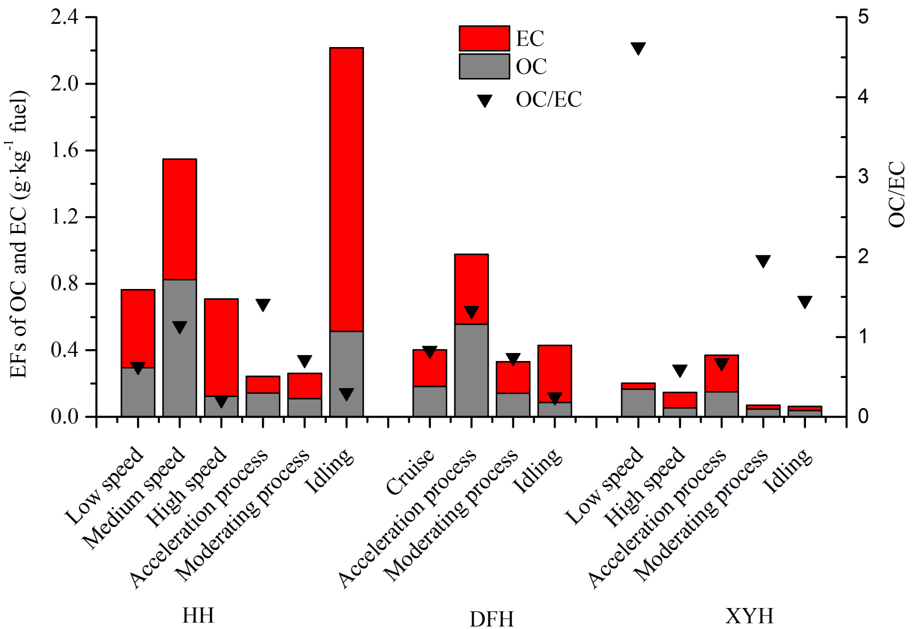

Figure 3. EFs for OC and EC and the ratios between them.

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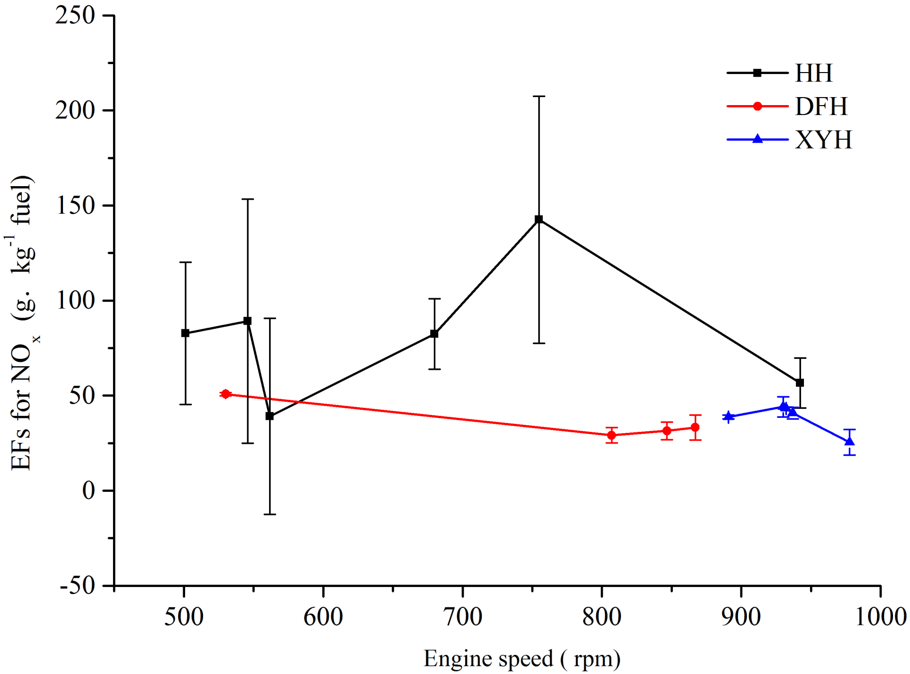

Figure 4. Emissions factors for NO_x at different engine speeds.

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