

Corrigendum

Gas phase carbonyl compounds in ship emissions: Differences between diesel fuel and heavy fuel oil operation



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ABSTRACT

Gas phase emission samples of carbonyl compounds (CCs) were collected from a research ship diesel engine at Rostock University, Germany. The ship engine was operated using two different types of fuels, heavy fuel oil (HFO) and diesel fuel (DF). Sampling of CCs was performed from diluted exhaust using cartridges and impingers. Both sampling methods involved the derivatization of CCs with 2,4-Dinitrophenylhydrazine (DNPH). The CCs-hydrazone derivatives were analyzed by two analytical techniques: High Performance Liquid Chromatography–Diode Array Detector (HPLC–DAD) and Gas Chromatography–Selective Ion Monitoring–Mass Spectrometry (GC–SIM–MS). Analysis of DNPH cartridges by GC–SIM–MS method has resulted in the identification of 19 CCs in both fuel operations. These CCs include ten aliphatic aldehydes (formaldehyde, acetaldehyde, propanal, isobutanal, butanal, isopentanal, pentanal, hexanal, octanal, nonanal), three unsaturated aldehydes (acrolein, methacrolein, crotonaldehyde), three aromatic aldehyde (benzaldehyde, *p*-tolualdehyde, *m,o*-molualdehyde), two ketones (acetone, butanone) and one heterocyclic aldehyde (furfural). In general, all CCs under investigation were detected with higher emission factors in HFO than DF. The total carbonyl emission factor was determined and found to be 6700 and 2300 $\mu\text{g kWh}^{-1}$ for the operation with HFO and DF respectively. Formaldehyde and acetaldehyde were found to be the dominant carbonyls in the gas phase of ship engine emission. Formaldehyde emissions factor varied from 3870 $\mu\text{g kWh}^{-1}$ in HFO operation to 1540 $\mu\text{g kWh}^{-1}$ in DF operation, which is 4–30 times higher than those of other carbonyls. Emission profile contribution of CCs showed also a different pattern between HFO and DF operation. The contribution of formaldehyde was found to be 58% of the emission profile of HFO and about 67% of the emission profile of DF. Acetaldehyde showed opposite behavior with higher contribution of 16% in HFO compared to 11% for DF. Heavier carbonyls (more than two carbon atoms) showed also more contribution in the emission profile of the HFO fuel (26%) than in DF (22%).

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1. Introduction

Ships and marines emissions make a considerable contribution to both gaseous and particulate air pollutants in the atmosphere,

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particularly on the ports and coastal regions (Miola and Ciuffo, 2011). These toxic pollutants have been associated with serious adverse health effects, including premature death and respiratory symptoms (Corbett et al., 2007; Song, 2014). Carbonyl compounds (CCs) are well known to be critically important in atmospheric chemistry (Sawant et al., 2007) and they attract immense attention due to their adverse health effects on humans (Weng et al., 2010). Certain CCs such as formaldehyde, acetaldehyde and acrolein are known to be toxic, mutagenic or carcinogenic and thus have been

identified as hazardous air pollutants. (Bhattacharya and Tulsawani, 2008), (IARC, 2006). A summary of health hazards associated with carbonyl compounds are listed Table 1 (Karavalakis et al., 2010). The primary emission sources of CCs are diverse and include: motor vehicles (Pang and Mu, 2007), incomplete combustion of hydrocarbon fuels in industrial processes (Liu et al., 2006), cigarette smoke (Pang and Lewis, 2011), biomass burning (Seco et al., 2007), the frying process as a by-product of vegetable oil degradation (Katragadda et al., 2010), wine production (Culleré et al., 2009) and urban incineration (Dai et al., 2012). CCs can also be produced as secondary airborne pollutants via the photochemical oxidation of atmospheric hydrocarbons (Moussa et al., 2006).

Sampling and analysis of CCs started in the middle of the fifties during the last century. Earliest measurements were performed for CCs in cigarette smoke by (Touey, 1955), who used a precipitation method to assess the total aldehyde content by their reaction with (5,5-dimethyl-1,3-cyclohexanedione) in gas-absorption flasks to form dimedon. Later techniques resolved CCs in tobacco smoke using liquid chromatography based on their 2,4-dinitrophenylhydrazine derivatives (Houlgate et al., 1989). Recently, different methods were used to analyze CCs in different sources. High performance liquid chromatography (HPLC) represent the most convenient method for the analysis with

conventional UV–VIS detectors (Feng et al., 2011; Karavalakis et al., 2011). Moreover, on-line capillary liquid chromatography (Prieto-Blanco et al., 2011) and gas chromatography mass spectrometry (GC–MS) (Pang and Lewis, 2011) were employed in the investigation of the CCs. Most of these analytical methods depend on the same principle of sampling, which involves the derivatization of CCs with 2,4-dinitrophenylhydrazine (DNPH) to produce stable CCs-hydrazone derivatives. Carbonyl compounds emission from heavy-duty diesel engines have been intensively investigated recently using different fuel blends such as ethanol–diesel blends (Song et al., 2010) or biodiesel blends (Karavalakis et al., 2011). These studies revealed that the use of biodiesel or ethanol–diesel fuels led to significant increases in the emission of most carbonyl compounds due to the high oxygen containing additives. To our knowledge there is no any study discussing the carbonyl compounds in the emissions of ship engines operated with heavy fuel oil or distillate oils. In this study we investigated carbonyl compounds emission in the gas phase of a ship diesel engine fueled with heavy fuel oil (HFO) and standard diesel fuel (DF, contained 3.2% biodiesel) respectively. The study was carried out as part of a project of the Helmholtz Virtual Institute for Complex Molecular System in Environmental Health (HICE). CCs were collected using 2,4-dinitrophenylhydrazine (DNPH) cartridges and impingers. The

Table 1
Health hazards associated with carbonyl compounds emissions.

Compound	NOAEL ^a	LOAEL ^b	Health hazard	Reference(s)
Formaldehyde	15 mg/kg day	82 mg/kg day	Recognized: suspected: Carcinogen Gastrointestinal or liver toxicant Immunotoxicant Neurotoxicant Reproductive toxicant Respiratory toxicant Skin or sense organ toxicant	(Til et al., 1989; EPA-HEN, 1994) (ATSDR, 2004) (EEC, HAZMAP) (RTECS) (Frazier and Hage, 1998) (EPA-HEN, 1994; ATSDR, 2004) (EEC, EPA-HEN, 1994) (EPA-HEN, 1994) (Jankovic and Drake, 1996) (HAZMAP) (RTECS) (RTECS) (HAZMAP, EPA-HEN, 1994) (HAZMAP, EPA-HEN, 1994)
Acetaldehyde	8.7 mg/m ³	16.9 mg/m ³	Recognized: suspected: Carcinogen Developmental toxicant Immunotoxicant Kidney toxicant Neurotoxicant Respiratory toxicant Skin or sense organ toxicant	(EPA-HEN, 1994) (ATSDR, 2004) (Jankovic and Drake, 1996) (M. J. Malachowski, 2013) (RTECS) (ATSDR, 2004) (HAZMAP, ATSDR, 2004) (Richard and Lewis, 2007)
Acrolein	0.05 mg/kg day	–	Recognized: suspected: Carcinogen Cardiovascular or blood toxicant Developmental toxicant Gastrointestinal or liver toxicant Neurotoxicant Respiratory toxicant Skin or sense organ toxicant	(EPA-HEN, 1994) (ATSDR, 2004) (Jankovic and Drake, 1996) (M. J. Malachowski, 2013) (RTECS) (ATSDR, 2004) (HAZMAP, ATSDR, 2004) (Richard and Lewis, 2007)
Methacrolein	4.99 ppm	15.3 ppm	Recognized: Highly irritating to the eyes, nose, throat and lungs. Epithelial inflammatory, atrophic and metaplastic changes in the dorsal meatus	(CCOHS)
Acetone	900 mg/kg-day	1700 mg/kg day	Recognized: Inhalation: can irritate the nose and throat. Skin contact: may cause mild irritation. EYE IRRITANT. Causes moderate to severe irritation. Effects of long-term (chronic) exposure: can cause dry, red, cracked skin (dermatitis) following skin contact	(CCOHS)
Propanal	8 mg/m ³	–	Recognized: suspected: Neurotoxicant incidence of atrophy of the olfactory epithelium in male rats	(RTECS)
Crotonaldehyde	0.23 µg/m ³	–	Recognized: suspected: Carcinogen Respiratory toxicant Skin or sense organ toxicant	(EPA-TRI, 1994) (HAZMAP) (HAZMAP)
Benzaldehyde	200 mg/kg day or 26 mg/m ³	400 mg/kg day	Recognized: Forestomach lesions, kidney toxicity Necrotic and degenerative lesions of the brain, renal tubular necrosis and epithelial hyperplasia, hyperkeratosis of the forestomach (in rats)	(Kluwe et al., 1983)

^a No-observed-adverse-effect level.

^b Lowest-observed-adverse-effect level.

CCs were analyzed using a sensitive and versatile analytical GC–SIM–MS method. Multiple repetitions were performed for each fuel type according to the ISO 8178-4 E2 method. The differences in the emission factor and emission profile for each fuel type were investigated and evaluated. The results were compared to recent studies concerning the emission profile of CCs in DF operation in diesel engine.

2. Experimental part

2.1. Engine description, fuel properties and test cycle

Experiments were carried out at the Institute of Piston Machines and Internal Combustion Engines in the University of Rostock, Germany during a sampling campaign between November 12th and November 30th 2012. A single-cylinder diesel research engine (Bank et al., 2013; Etzien et al., 2013) was used to perform these experiments. The engine was able to operate with both standard DF and HFO, mimicking the common dual fuel use HFO for open sea cruising and DF for harbor times or cruising in sulfur emission control areas (SECA's) such as in the Baltic sea, and has a common rail injection system with system pressures up to 1300 bar. Further details regarding the engine are listed in Table 2. Almost all of the operating parameters -including the injection parameters-could be adjusted within the physical ranges of the engine.

Two different fuels were used for the operation. Heavy fuel oil HFO 180 was used as a representative fuel for ship operation in SECAs. On the other hand, a distillate Diesel Fuel DF according to DIN EN 590 was used as a light fuel operation standard. The used DF contained 3.2% rapeseed oil-methyl ester as biodiesel component. The properties of both fuels are listed in Table 3.

The emission testing was performed in these experiments with the engine operating on a test bench. In order to obtain the representative pattern under operating conditions, the engine was run at four different operating load points of 100%, 75%, 50%, 25% loads at nominal speed of 1500 min⁻¹. The duration of each operation point was set according to the weighting factors in ISO 8178-4 E2, starting with 100% engine load for 20 min then reduced to 75% load for 60 min and reduced again to 50% and 25% load for 10 min each respectively. The total cycle duration was 2 h with two cycles run per experiment and two experiments per day. Furthermore, 8 and 7 repetitions were performed for DF and for HFO operation respectively. Some of the repetitions were discarded either due to changes in sampling conditions or due to sampling problems. Therefore, the results shown in this study were derived from 6 to 5 replicate samplings for DF and HFO operation respectively.

2.2. Sample collection and preparation

Emission samples were collected with a different dilution ratio (DR) from the main engine stack depending on the fuel type. A gas

Table 3

Fuel properties used in the sampling campaign.

Parameter	Test specification	Diesel	HFO 180
Cetane index	EN ISO 4264	51	n.d.
Flash point [°C]	ISO 2719	67	n.d.
Density at 15 °C [g/L]	DIN EN ISO 12185	842.5	968.7
Viscosity at 40 °C [mm ² /s]	DIN 53015	3.3	n.d.
Viscosity at 50 °C [mm ² /s]	ASTM D 7042	n.d.	188.83
Lubricity [μm]	DIN EN ISO 12156-1	165	n.d.
Heating value [kJ/kg]	DIN 51900-1,-2,-3	42,848	38,759
CFPP [°C]	EN 116	–10	n.d.
Ru content [mg/kg]	ICP-method	n.d.	n.d.
Ash content [w%]	EN ISO 6245	<0.001	0.06
Vanadium content [mg/kg]	–	n.d.	76
Sodium content [mg/kg]	–	n.d.	8
Aluminum and silicon content [mg/kg]	ISO 10478	n.d.	15
Sulfur content [w%]	DIN 51400-10	n.d.	1.6
Carbon residue [w%]	ISO 10370	n.d.	7.87
Water content [mg/kg]	EN ISO 12937	80	n.d.
Carbon content [w%]	DIN 51732	86.5	83.47
Hydrogen content [w%]	DIN 51732	13.4	11.08
Oxygen content [w%]	DIN 51732	0.0	n.d.

phase sampling line was assembled directly after aerosol sampling system consisting of a porous tube and ejector diluter (Venacontra, DAS, Finland) as shown in Fig. 1A. The final applied dilution ratios were approximately 40 for the DF repetitions and 12 for HFO repetitions. To collect the gas phase, quartz fiber filters were used to remove the particles from the gas phase sampling line. To achieve a stable sampling flow rate during the experiments, critical nozzles were used with a fixed flow rate of 0.2 L min⁻¹. The total sample volume collected was around 48 L per repetition. Two sampling techniques of DNPH cartridges and impingers were used to collect CCs in the gas phase. Both sampling techniques depend on the derivatization of the carbonyl group in CCs with DNPH in acidic media which is known as Brady's test (Kadam et al., 2012). Samplings of CCs were obtained using both sampling techniques in parallel as shown in Fig. 1B.

The first sampling technique was the acidified impingers of DNPH, similarly as described in (Parmar et al., 2004). Three impingers were connected in series using 6 mm glass tube connectors. Each impinger vial was filled with 15 ml DNPH-HCl solution and 5 ml of toluene to the impinger stems. The impingers were placed in a rack and connected to the sampling pump. The bubbling action of the air sampling breaks the toluene layer into small droplets, which help to extract the hydrazones from the aqueous phase during sampling, thereby protecting them from decomposition or acid attack. After the sampling was finished, the toluene layer (the extract) was removed to dark vials and capped with a Polytetrafluoroethylene (PTFE) caps and stored at 5 °C until analysis.

For the analysis of the impinger extract, the toluene was evaporated under nitrogen and replaced with 1 ml acetonitrile (ACN). 10 μL and 1 μL aliquots were injected in both HPLC and GC, respectively for analysis.

The second sampling technique was using the DNPH cartridges 'ORBO/555' Sigma Aldrich (Germany) with high sample volume capacity. These cartridges were with 6 mm outer diameter and 110 mm length fueled with dual-bed DNPH supported on silica gel. The first bed contains 300 mg of DNPH in the front section and 150 mg in the back section. After the sampling was finished the cartridges were removed immediately from the sampling line and capped with PTFE caps and stored at 5 °C until analysis.

For the analysis of DNPH cartridges, each cartridge was eluted with 1 ml ACN and immediately analyzed by injection of 10 μL and

Table 2

Experimental parameters used for the ship engine.

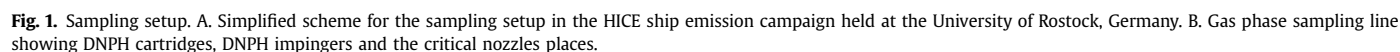
Engine model	1 VDS 18/15
Method of operation	Four stroke diesel, direct injected, compressor charged
Amount of cylinders	1
Valves	4
Stroke	180 mm
Bore	150 mm
Length of connecting rod	332 mm
Nominal speed	1500 min ⁻¹
Compression ratio	13
Maximum power	80 kW
Nominal power	60 kW

2.3. Chemical and materials

2.4. Analytical methods

conditions were as follows: Synergi™ 4 μ m Max-RP 80 A° LC Column (30 mm $\times$ 4.6 mm) produced by Phenomenex Germany; gradient mobile phase: starting with 38% ACN to H₂O at 0 min and rising to 100% ACN in 60 min, then back again to 38% ACN at 62 min and kept it stable until the end of the injection at 70 min; mobile-phase flow rate: 0.5 mL min⁻¹; detector: UV at 360 nm. Column oven temperature was 63 °C.

The second method applied was gas chromatography–mass spectrometry with selective ion monitoring (GC–SIM–MS). The enhanced method was conducted using the Shimadzu GCMS-QP2010 system. A BPX5 (SGE™, Ringwood Victoria, Australia) capillary column (25 m × 0.25 mmid × 0.25 μmfilm) containing 5% phenyl and 95% methyl polysiloxane was used for the chromatographic separation. 1 μl sample solution was injected in split-less mode at an injector temperature of 200 °C. A programmed oven temperature was applied, starting at 70 °C with a rate of 18 °C min⁻¹ up to 200 °C for 20 min, and then increased to 25 °C min⁻¹ up to the final temperature of 330 °C for 5 min. The total analysis time was 37.42 min using helium as carrier gas at a constant flow of 4 mL min⁻¹. The mass spectrometer was operated with electron ionization at 70 eV and the transfer line temperature was set to 260 °C, while the ion source temperature was operating at 220 °C.



3. Results and discussion

3.1. Sampling techniques selection

As it was mentioned in the experimental part of this study, the emission testing was carried out with a ship engine operating on a test bench for a period of two weeks. Therefore, the sampling techniques to be chosen should have the possibility to follow the whole sampling period with reliability in collecting the CCs in the gas phase. Previous studies have indicated that DNPH impingers and cartridges were the most reliable and available sampling methods (Guariero et al., 2008; Lü et al., 2010), therefore both of these sampling techniques were used in the beginning to collect the emission samples. The first sampling technique applied was the acidified DNPH impingers. Unfortunately, the performance of this sampling method has encountered some problems which triggered questions about the reliability of results, such as: i) strong matrix effects in both HPLC and GC–SIM–MS analysis methods, ii) contamination by other carbonyls from the extracting solvent, iii) problems associated with the solvent extraction step after the sampling. Due to lack of reliability in the results obtained from the impinger method, these results were excluded from further analysis in this study.

The second sampling technique involved the employment of DNPH cartridges. The dual-bed DNPH layer cartridges showed more reliable results with high sample volume ability. The back section (second bed layer) functions as a back-up bed in case of breakthrough as sometimes occurs in higher concentration environments. This layer was analyzed separately and showed no breakthrough. Therefore, all the results of this study were derived from the DNPH cartridge analysis. HPLC chromatogram for the impingers and DNPH cartridges extract injection are shown in Fig. 1S.

3.2. Choosing of analysis method

Recently, HPLC has been used to analyze CCs-hydrazone compounds (Lü et al., 2010; Zhao et al., 2010; Ochs et al., 2011). Therefore, in the beginning the HPLC with Diode array detector DAD was adopted to analyze the emission samples collected in this sampling campaign. The HPLC–DAD method was enhanced using chromatography modeling software called 'DryLab[®]', this software improved the efficiency and the quality of the separation with time (Krisko et al., 2006). To make use of this software, different data sets must be obtained from individual injection of the CCs-hydrazone standards. The software showed the best separation using HPLC–DAD method at 63 °C column temperature and 360 nm detector wave-length for 70 min injection time. The HPLC–DAD method indicates very good results with the separation of 23 CCs-hydrazone standards as shown in Fig. 2S.

In contrast, measurement of the real samples using the HPLC method has suffered obvious limitations with the separation and quantification of CCs with more than five carbon atoms and also with the aromatic CCs. Furthermore, the method showed a base line drifting, especially with formaldehyde, one of the most important CCs to be investigated as shown previously in Fig. 1S.

This drawback in the performance of the method could be due to the matrix effect or the complexity of the samples produced by the engine emission. Therefore, we were enforced to figure out another method to analyze the emission samples.

Gas chromatography mass spectrometry GC–MS has been previously employed for the analysis of CCs. Previous studies used pentafluorophenylhydrazine (PFPH) as derivatization agent (Ho and Yu, 2004; Zapata et al., 2010; Pang et al., 2011). Using DNPH as a derivatization agent for the analysis of CCs by GC–MS was already described more than 30 years ago (Linko et al., 1978; Uralets

et al., 1980), and these studies had reported some obstacles encountered in the GC separation of carbonyl–DNPH hydrazone compounds such as thermal stability at high temperatures, ruggedness of the GC inlet and column, and the formation of syn and anti-isomers. A previous study by (Dong and Moldoveanu, 2004) showed reliable results for the CCs–DNPH hydrazone analysis in cigarette smoke, which also could be considered as complex emission source. Recent studies have used the DNPH as derivatization agent to capture the volatile carbonyl metabolite of flecainid (Prokai et al., 2012) or to collect acrolein in French fries (Osório and de Lourdes Cardeal, 2011) and analyze the extract using GC–MS method.

In this study a gas chromatography mass spectrometry method applying selective ion monitoring technique (GC–SIM–MS) was optimized for the analysis of the emission samples. A standard mixture of 21 CCs-hydrazone was injected in Shimadzu GCMS–QP2010 system as shown in Fig. 2.

Several standard solutions were tested with different system parameters from injection temperature to oven temperature. The results showed that the thermal stability and isomer formation are not only related to the chromatographic conditions of injector temperature and oven programming, but also to the acidity of the sample solution. In fact, the acidity of the sample solution has much more effects than the chromatographic conditions. The isomers' ratio formation depends mainly on the acidity of the derivatization solution. The effect of sample acidity on the performance of HPLC analysis has been previously reported by (Uchiyama et al., 2003) who observed that changing the acidity of the derivatization agent will result in a different ratio of isomers.

Concerning the thermal stability of the CCs-Hydrazone, no measurable effects were detected when high column temperature was applied with the last CCs eluted up to 300 °C and 200 °C of injection temperature. Injection temperature was tested up to 280 °C, and no significant change in the responses was noticed when compared to 200 °C. Moreover, the chromatography showed better potential thermal stability by applying a higher flow rate of the carrier gas, which means reduced retention times during the chromatographic separation (De Graff et al., 1998). To improve the sensitivity of the method, selective ion monitoring mode (SIM) was applied for quantification. Additional fragment monitoring enhanced the correct assignment of co eluted target compounds such as propanal and acrolein which cannot be separated by the total ion chromatogram.

The separation and quantification was performed using four criteria which are significant for each CCs-hydrazone: i) the retention time R_t for each CCs-hydrazone, ii) the target ion mass; Target m/z , iii) reference ion mass; $R_f m/z$ which produced by the hydrazone fragmentation and iv) the ratio between $R_f m/z$ to Target m/z . Table 3 shows the limit of detection (LOD), limit of quantification (LOQ) and the linearity of the method for the 21 CCs-hydrazone analysis using GC–SIM–MS. It was difficult to separate the *m* and *o*-tolualdehyde isomers since both isomers showed the same fragments and R_t with the method conditions. This was also mentioned in other studies (Ochs et al., 2011; Prieto-Blanco et al., 2011) where they forced the same conflicts regarding the separation between the tolualdehyde isomers (*o,m,p*).

In order to further investigate the formation of syn and anti-isomers associated with CCs compounds, in particular with acet-aldehyde and propanal hydrazine, which showed higher isomers' ratio in standards and in real samples in comparison to other carbonyls, individual standards were injected for each compound. The results revealed that no significant difference was observed in the fragment pattern or in the detector response during the analysis. The detector response was inspected by tracking the signal ratio between the target and the reference fragments mass for each

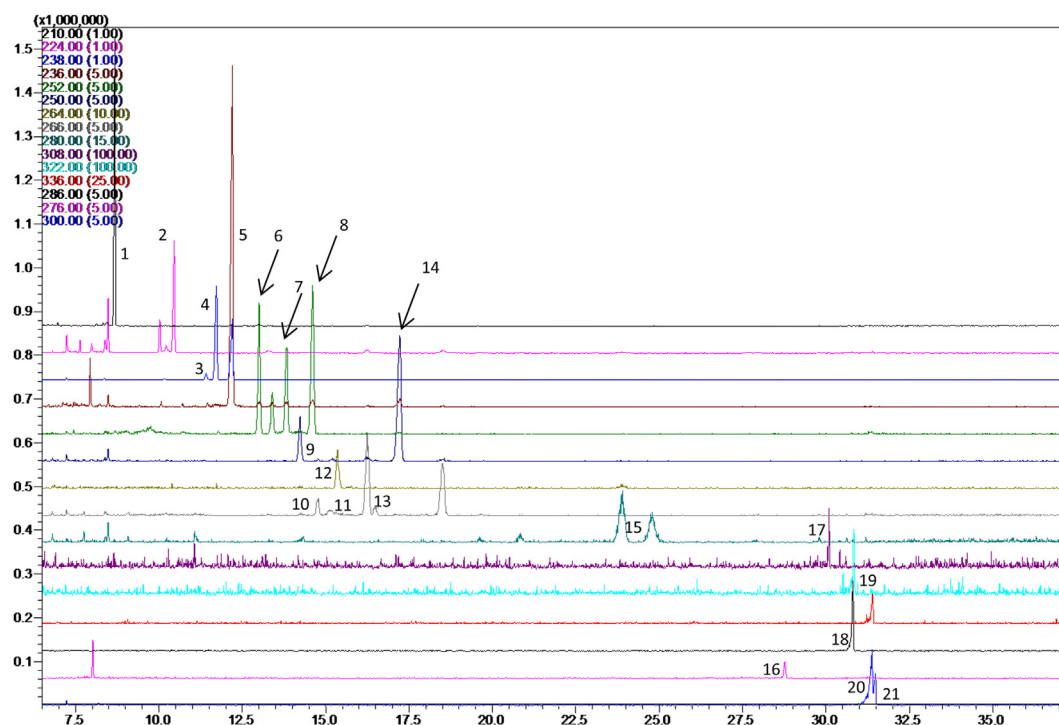


Fig. 2. Separation of CCs-hydrazone standards by GC–SIM–MS method. 1-Formaldehyde 2-Acetaldehyde 3-Propanal 4-Acetone 5-Acrolein 6-Isobutanol 7-Butanal 8-2-Butanone 9-Methacrolein 10-Isopentanal 11-2,3-Butadione 12-Ethyl Vinyl Ketone 13-Pentanal 14-Crotonaldehyde 15-Hexanal 16-Furfural 17-Octanal 18-Benzaldehyde 19-Nonanal 20-*m,o*-Tolualdehyde 21-*P*-Tolualdehyde.

isomer. The ratio was stable with 95% matching between syn- and anti-isomers for both compounds as shown in Fig. 3. This concludes that the detector has the same response for both isomers. Therefore, for the quantitative measurements the sum of both isomers' signal area has been constituted to calculate the total concentration for the compound, which was also applied before by (Dong and Moldoveanu, 2004) to estimate the concentration of CCs with two isomers.

The quantification of the identified compounds was carried out by using analytical curves provided by Shimadzu software "GCMS solution" using nine levels of external standard with concentrations ranging from 0.01 ng ml⁻¹ to 250 ng/ml. The limit of detection (LOD) was considered as 3 times higher than the signal to noise ratio (S/N).

3.3. Emission factors

Nineteen CCs were identified in the emissions from DF and HFO operation including ten aliphatic aldehydes (formaldehyde, acetaldehyde, propanal, isobutanol, butanal, isopentanal, pentanal, hexanal, octanal, nonanal), three unsaturated aldehydes (acrolein, methacrolein, crotonaldehyde), three aromatic aldehyde (benzaldehyde, *p*-tolualdehyde, *m,o*-tolualdehyde), two ketones (acetone; butanone) and one heterocyclic aldehyde (furfural). Fig. 4 shows the average of emission factor variation between HFO and DF fuels.

As it was mentioned in the experimental part, the total valid repetitions for DF operation were 6 repetitions and for HFO operation were 5 repetitions. After combining the replicates, a two tailed Student's *t*-test showed a significant difference between the DF and HFO measurements (*p*-value 0.0334).

The emission factors given in this study were calculated based on the energy output from the engine. The engine efficiency was 42% in DF operation and 38% in HFO operation. For each fuel type a statistical calculation was performed including all repetitions. The

median, average, standard deviation (STDEV) and coefficient of variation (CV) for each fuel type are shown in Table 5. The STDEV for whole measurements in DF repetitions was 0.14 with a CV of 0.39, while for HFO repetitions; STDEV was approximately 0.1 with CV of 0.37. Furthermore, Pearson correlations for repetitions for the same fuel type showed a significant high correlation with *r* = 0.97 in HFO and *r* = 0.99 in DF. That encourages us to discuss the variation between the DF and HFO operation observing the average measurements regardless the variation from one repetition to the other.

In general, all HFO repetitions were observed with higher carbonyl emission factors than in DF repetitions. Formaldehyde was found to be the predominant carbonyl compound in both fuel types operation but with a higher emission factor in HFO repetitions about 3870 µg kWh⁻¹, while in DF repetitions it was 1540 µg kWh⁻¹. For acetaldehyde the emission factor was 1050 µg kWh⁻¹ in HFO repetitions and with 250 µg kWh⁻¹ for DF. The analysis of the aliphatic aldehydes showed that propanal, butanal, isopentanal and pentanal were associated with higher emission factor in HFO than DF operation, while isobutanol has showed a relatively constant emission factor in both fuel, approximately 25 µg kWh⁻¹ and 27 µg kWh⁻¹ in HFO and DF operation respectively. The minimum emission factor in aliphatic aldehyde mentioned above in HFO operation was for isobutanol (25 µg kWh⁻¹), while for DF operation the minimum emission factor was for isopentanal (20 µg kWh⁻¹).

For the aliphatic ketones, a high difference was noticed in acetone emission factor between HFO and DF operation (406 µg kWh⁻¹ vs. 27 µg kWh⁻¹), while the emission factor of the other aliphatic ketone (2-butanone) was 2-fold higher in HFO comparing to DF (50 µg kWh⁻¹ vs. 20 µg kWh⁻¹).

For higher molecular weight aliphatic aldehydes (more than five carbon atoms), hexanal, octanal and nonanal, it was clear that these compounds have a higher emission factor in HFO operation. They were found to have 3–12-fold higher emission factors in HFO than

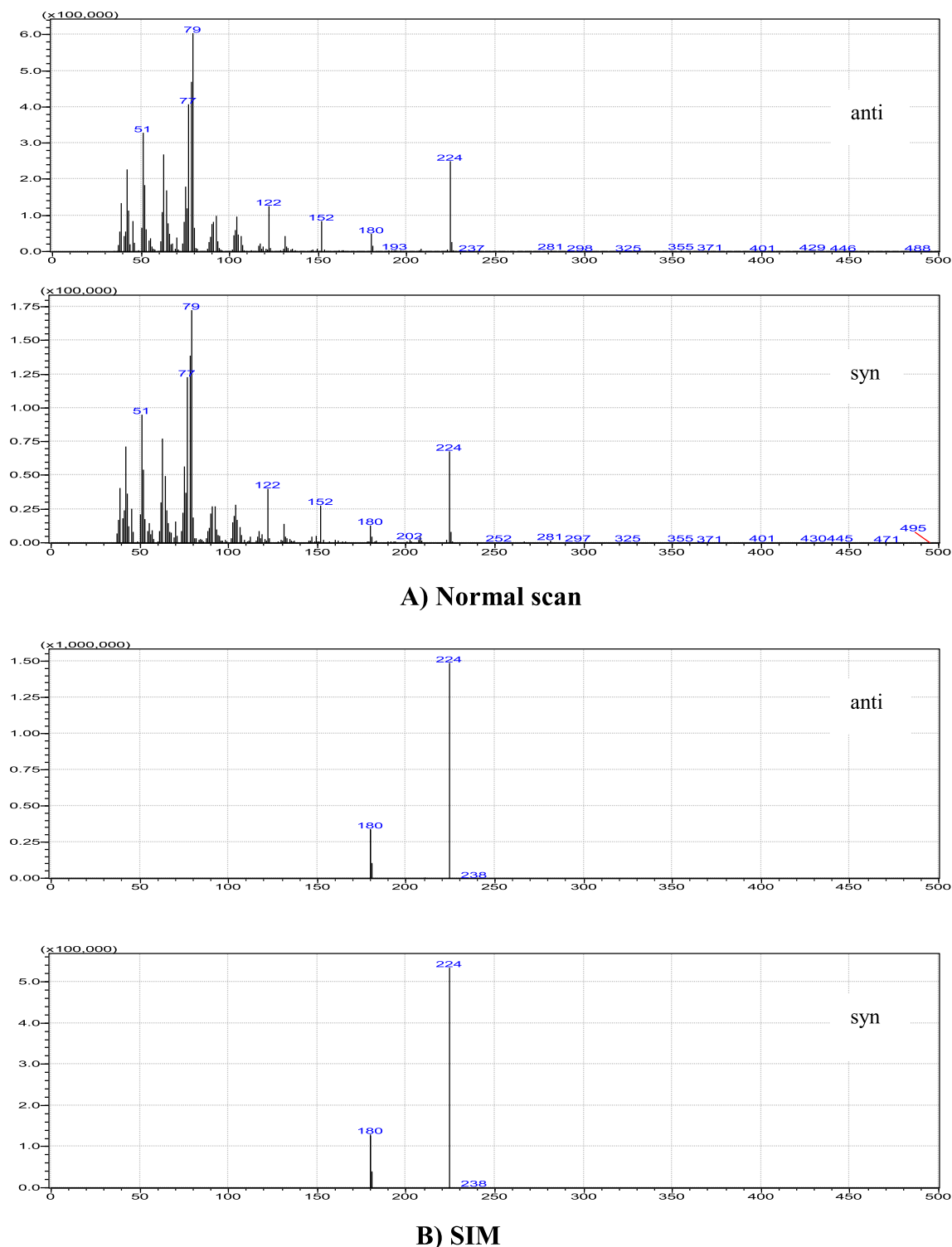


Fig. 3. Mass pattern fragments for anti- (top panel) and syn- (bottom panel) isomers for acetaldehyde. (A) normal mode and (B) SIM mode.

in DF. In HFO operation, hexanal was exhibited a minimum emission factor of $87 \mu\text{g kWh}^{-1}$, while octanal was with the highest of $255 \mu\text{g kWh}^{-1}$. For DF operation nonanal had the minimum emission factor of $10 \mu\text{g kWh}^{-1}$ and the highest was for octanal with about $30 \mu\text{g kWh}^{-1}$.

For unsaturated carbonyls (acrolein, methacrolein and crotonaldehyde), no significant difference was found for acrolein with

$101 \mu\text{g kWh}^{-1}$ in HFO and $76 \mu\text{g kWh}^{-1}$ in DF. The highest emission factor for unsaturated carbonyls was found for methacrolein with $129 \mu\text{g kWh}^{-1}$ in HFO and $61 \mu\text{g kWh}^{-1}$ in DF. Crotonaldehyde was detected with a significant difference and showed a two times higher emission factor in HFO than in DF operation with $48 \mu\text{g kWh}^{-1}$.

For aromatic aldehydes (benzaldehyde, *p*-tolualdehyde and *m,o*-

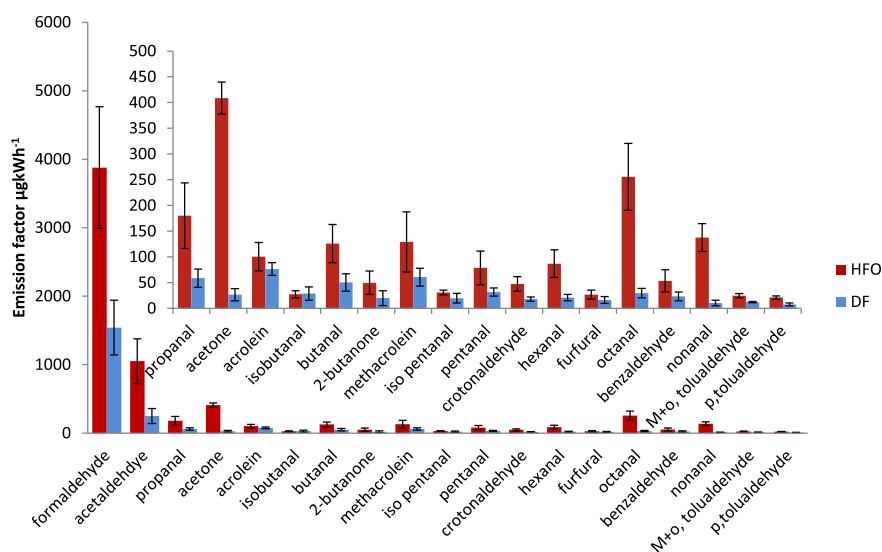


Fig. 4. The average of CCs emission factor ($\mu\text{g kWh}^{-1}$) variation between HFO and DF fuels operation.

tolualdehyde), no significant difference was found for benzaldehyde between HFO and DF operation but it was detected with a higher emission factor of $53 \mu\text{g kWh}^{-1}$ in HFO. Significant differences were found for *m,o*-tolualdehyde and *p*-tolualdehyde between HFO and DF operation. Both compounds showed almost the same emission factor in operation with the same fuel, and they ranged from 21 to $25 \mu\text{g kWh}^{-1}$ in HFO and 8 – $12 \mu\text{g kWh}^{-1}$ for DF operation. The last compound investigated was furfural: No significant difference was found in both fuel types, the emission factor was found to be 27 and $16 \mu\text{g kWh}^{-1}$ in HFO and DF operations respectively.

The total emission factor of aliphatic aldehydes was observed to be almost 3 times higher in HFO operation, while for aliphatic ketones the ratio was much higher (9 times) in HFO than in DF operation. Unsaturated carbonyls, aromatic carbonyls and furfural showed almost the same ratio (almost 2 times higher) in HFO than in DF fuel operation (Fig. 5).

Finally, the total emission factor for the all CCs in HFO operation was found to be $6700 \mu\text{g kWh}^{-1}$ and for DF $2300 \mu\text{g kWh}^{-1}$ as

shown in Table 4. This indicates that the emission of CCs from HFO operation is about 3 times higher than emission in DF fuel operation.

3.4. Emission profiles

Due to the emission factor differences between HFO and DF operation a disparity in the emission profiles was also expected. Fig. 6 shows the contribution of individual carbonyl compounds in the emission profiles for HFO and DF repetitions.

Generally, formaldehyde and acetaldehyde were found to be the predominant carbonyls in the emission profile for both fuel operations. Both compounds make together 74% of the total carbonyl emission in the HFO and 78% in DF. This result was comparable with a previous study reported by (Sawant et al., 2007), which showed that formaldehyde and acetaldehyde contributed with a median of about 70% in the total emission of carbonyls in heavy-duty diesel tractors and also in diesel-powered pucker up generators fueled with ultralow sulfur diesel fuel (ULSDF). Another study by (Ban-Weiss

Table 4
GC–MS method validation data.

No.	Compound	Target M/Z	Ref. M/Z	Rt.min	LOQ ng/ml	LOD ng/ml	Correlation coefficient R ²	Calibration curve equation	RSTD%
1	Formaldehyde	210.1	180.1	8.675	12	5	0.9979	$Y = 8442.878X - 80877.12$	2.613
2	Acetaldehyde	224.1	180	10.03	1.2	0.5	0.9959	$y = 0.1963x + 1.1839$	2.264
3	Propanal	238.1	181	11.42	5.5	1.3	0.995	$y = 0.2192x + 4.6547$	2.472
4	Acetone	238.1	181.1	11.73	17	6	0.9988	$Y = 6597.156X - 117993.8$	2.98
5	Acrolein	236.1	189.1	12.21	18	6	0.996	$Y = 5275.893X - 102842.7$	3.01
6	Isobutanol	252.1	180.1	13.01	28	12	0.998	$Y = 2620.216X - 88144.76$	3.7
7	Butanal	252.1	181	13.4	2.6	0.4	0.9967	$y = 0.2846x + 20.069$	4.11
8	2-Butanone	252.1	152	13.83	3	0.5	0.99	$Y = 760.8574X - 3960.012$	5.22
9	Methacrolein	250.1	156.1	14.24	3	0.45	0.991	$Y = 391.2504X - 1836.081$	4.32
10	Isopentanal	266.2	185	14.76	4	0.77	0.9957	$y = 0.4187x + 9.9318$	5.07
11	2,3-Butadione	266.1	181.1	15.11	12	6	0.996	$Y = 85.84549X - 1128.811$	7.3
12	EVK	264.1	181.1	15.36	3	1	0.9936	$Y = 219.8647X - 1010.203$	2.87
13	Pentanal	266.2	181.1	16.48	15	3.1	0.9945	$y = 0.5425x + 21.165$	4.05
14	Crotonaldehyde	250.1	181.1	17.23	3	0.85	0.9961	$Y = 3842.862X - 38282.44$	2.43
15	Hexanal	280.2	181.1	23.9	4	0.9	0.99	$Y = 415.6371X - 1614.999$	5.24
16	Furfural	276.2	155	28.76	2.7	0.76	0.9945	$Y = 279.3622X - 932.2195$	3.89
17	Octanal	308.3	181.1	30.1	17	5	0.9941	$Y = 25.94768X - 474.6966$	6.95
18	Benzaldehyde	286.1	181.1	30.81	3	0.95	0.9979	$Y = 1953.115X - 19964.79$	4.34
19	Nonanal	322.2	181.1	30.84	17	6	0.9961	$Y = 103.2398X - 2203.302$	8.02
20	<i>M + o</i> Tolualdehyde	300.1	181.1	31.39	3	1	0.99	$Y = 1875.717X - 14616.73$	4.85
21	<i>p</i> -Tolualdehyde	300.2	178.1	31.49	3	1	0.9904	$Y = 646.7605X - 4740.397$	2.66

Table 5Median and average emission factor in ($\mu\text{g kWh}^{-1}$) for both HFO and DF repetitions with the statistical calculations.

Variable	DF repetitions				HFO repetitions			
	Median $\mu\text{g kWh}^{-1}$	Average $\mu\text{g kWh}^{-1}$	STDEV $\pm$	CV	Median $\mu\text{g kWh}^{-1}$	Average $\mu\text{g kWh}^{-1}$	STDEV $\pm$	CV
Formaldehyde	1608	1541	400	0.26	3581	3878	888	0.23
Acetaldehyde	202	250	110	0.44	922	1051	327	0.31
Propanal	58	59	18	0.30	177	180	64	0.35
Acetone	28	27	12	0.45	409	406	31	0.08
Acrolein	73	76	12	0.16	93	101	27	0.27
Isobutanal	34	29	13	0.45	27	27	7	0.25
Butanal	54	50	17	0.33	121	126	37	0.30
2-Butanone	19	20	14	0.72	40	50	23	0.46
Methacrolein	61	61	17	0.28	167	129	58	0.45
Isopentanal	19	20	9	0.48	32	31	4	0.15
Pentanal	34	32	8	0.25	88	79	33	0.42
Crotonaldehyde	18	18	4	0.23	49	48	14	0.30
Hexanal	19	21	6	0.30	96	87	27	0.31
Furfural	18	16	7	0.41	30	27	9	0.32
Octanal	27	30	9	0.31	251	255	65	0.25
Benzaldehyde	26	23	9	0.37	58	53	22	0.40
Nonanal	10	10	5	0.53	132	138	27	0.20
M + o- Tolualdehyde	12	12	1	0.10	26	25	4	0.17
p-Tolualdehyde	6	8	3	0.35	21	21	3	0.15
Total carbonyls		2302				6711		
			Average	0.35			Average	0.28
			STDEV	0.14			STDEV	0.10
			CV	0.39			CV	0.37

STDEV = Dard deviation CV = Correlation coefficient.

et al., 2008) showed similar results for diesel-powered motor vehicles fueled with normal diesel fuel (NDF) with 73% contribution for formaldehyde and acetaldehyde in the total emission. That was not the case with another study (Fontaras et al., 2010), which used different biodiesel blends on modern passenger cars and especially with rape-seed biodiesel emission. Both compounds count for almost 40% of the total emission profile contribution as showed in Fig. 7. Therefore, we believe that the 3.2% biodiesel content in the DF used in this study has no influence or impact on emission profile of the DF.

Three significant differences can be counted in the emission profile for both DF and HFO operation. First, formaldehyde was found to have less contribution in the emission profile in HFO operation of about 58%, while it was accounted for about 67% in DF. Second, acetaldehyde was found to contribute less with 16% in HFO emission profile and 11% in DF emission profile. The third significant difference in the emission profile was the contribution of the other heavier carbonyls (more than five carbon atoms), which accounted for 26% in HFO emission profile and 22% in DF emission profile.

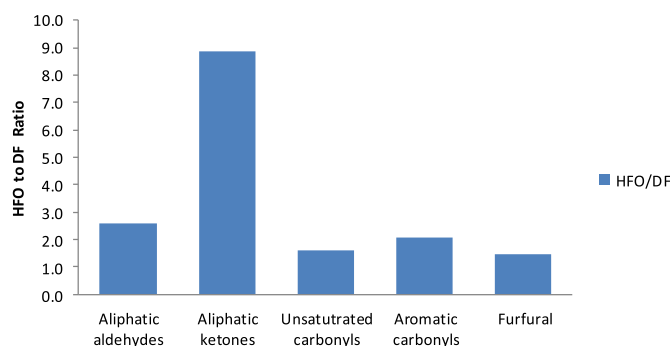
Overall, aliphatic aldehydes were found to have the same contribution with 88% of the total emission as showed in Fig. 8,

while aliphatic ketones accounted for 7% in HFO operation, which is three times higher than in DF operation. This was the main difference in the emission profile contribution between both fuel operations. For unsaturated carbonyls, the contribution was 4% in HFO and 7% in DF. Other CCs, aromatic carbonyls and furfural, showed almost the same contribution in both fuel types.

These differences in the emission factor and profile for both fuels could be related to many reasons; one reason could be the difference in composition of the HFO and DF that could lead to different combustion behavior inside the engine. Another reason could be related to the higher organic contain in HFO exhaust, which had also found by some other techniques used in the sampling campaign such as Photo Ionization–Mass spectrometry (PI–MS) and in the particle analysis.

4. Conclusion

In this study, the detailed carbonyl compounds emission factors and emission profiles in the gas phase emission from a ship engine fueled with heavy fuel oil HFO and distilled diesel fuel DF were identified and determined by enhanced analytical GC–SIM–MS method based on DNPH derivatization. Nineteen carbonyl compounds were characterized in both fuel types' operation which are known to have negative effects on environment and human health. In general, all carbonyls were found to have higher emission factors in HFO operation than in DF operation. Formaldehyde and acetaldehyde were found to be the dominant carbonyls. The total emission factor concentration for HFO operation was $6700 \mu\text{g kWh}^{-1}$ and $2300 \mu\text{g kWh}^{-1}$ for DF. That makes the emissions from HFO operation almost three times higher than in DF operation. Emission profile contribution showed also a different pattern from HFO to DF operation. Formaldehyde showed less contribution in the emission profile of HFO operation than in DF operation. Acetaldehyde showed the opposite behavior with higher contribution in HFO operation than in DF operation. Heavier carbonyls (more than five carbon atom) showed also more contribution in the emission profile of the HFO fuel than in DF. These differences in the emission factors and profiles could be related to the difference in the organic

**Fig. 5.** Total carbonyls emission factor ratio between HFO and DF operation.

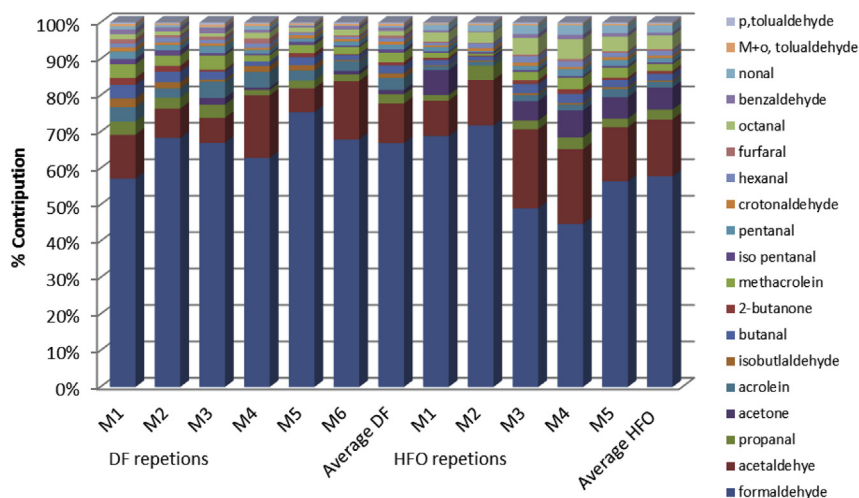


Fig. 6. Emission profile for each fuel type repetitions and the average value.

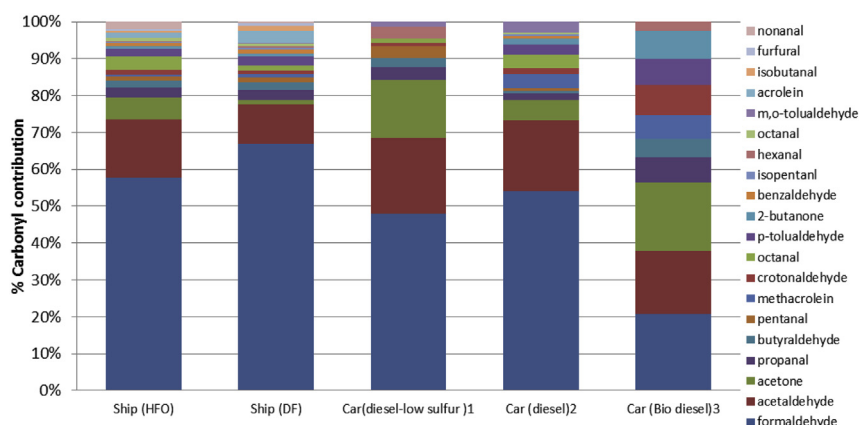


Fig. 7. Comparison of emission profile contribution for carbonyl compounds with other studies .1, (Sawant et al., 2007). 2, (Ban-Weiss et al., 2008). 3, (Fontaras et al., 2010).

composition of HFO compared to DF fuel. The carbonyl emission factors and profiles obtained from the current study are useful in the risk assessment of humans exposed to ship emissions and the study of the toxic effects of the ship emission using uncontrolled HFO fuels. The current study was performed in the framework of the *Helmholtz Virtual Institute of Complex Molecular Systems in Environmental Health* (HICE), which addresses the health effects of anthropogenic combustion aerosols by comprehensive characterization of the chemical composition of the aerosol and the

biological effects on air–liquid exposed human lung cell-cultures. The increased carbonyl compounds emission is in line with an about 2.5 time higher particle emission (PM_{2.5}) in the case of HFO-operation. The emitted particles may act as deep-lung carriers for the hazardous CCs. It can be concluded that the use of distillate diesel fuels is preferable for reduction of health-relevant carbonyls.

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at <http://dx.doi.org/10.1016/j.atmosenv.2015.03.057>.

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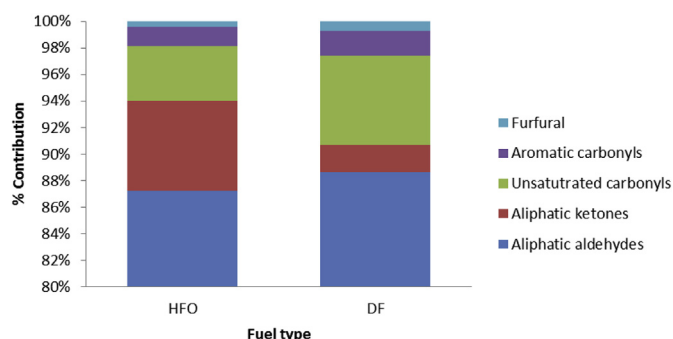


Fig. 8. Emission profile contribution for carbonyl groups in HFO and DF operation.

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