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Atmospheric Measurement Techniques Discussions

Field test of available methods to measure remotely SO_2 and NO_x emissions from ships

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Abstract

Methods for the determination of ship fuel sulphur content and NO_x emission factors from remote measurements have been compared in the harbour of Rotterdam and compared to direct stack emission measurements on the ferry Stena Hollandica. The methods were selected based on a review of the available literature on ship emission measurements. They were either optical (LIDAR, DOAS, UV camera), combined with model based estimates of fuel consumption, or based on the so called "sniffer" principle, where SO_2 or NO_x emission factors are determined from simultaneous measurement of the increase of CO_2 and SO_2 or NO_x concentrations in the plume of the ship compared to the background. The measurements were performed from stations at land, from a boat, and from a helicopter. Mobile measurement platforms were found to have important advantages compared to the landbased ones because they allow to optimize the sampling conditions and to sample from ships on the open sea. Although optical methods can provide reliable results, it was found that at the state of the art, the "sniffer" approach is the most convenient technique for determining both SO_2 and NO_x emission factors remotely. The average random error on the determination of SO_2 emission factors comparing two identical instrumental set-ups was 6 %. However, it was found that apparently minor differences in the instrumental characteristics, such as response time, could cause significant differences between the emission factors determined. Direct stack measurements showed that about 14 % of the fuel sulphur content was not emitted as SO_2. This was supported by the remote measurements and is in agreement with the results of other field studies.

1 Introduction

Since the beginning of the 20th century, when coal steamers replaced sail ships, the atmospheric impact of ship emissions increased almost continuously. According to Endresen et al. (2007), the global fuel consumption, between 1925 and 1980 increased

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from 60 to 150 Mt (megatonne, equivalent to 1 Tg, 10^{12} grams), while between 1980 and 2007 (according to IMO, 2009) it increased to 270 Mt.

If on one side shipping plays a fundamental role in world economy moving 80–90 % of world trade by volume (European Commission and Entec UK Limited, 2005), on the other side the negative effects related to its atmospheric emissions have been neglected for a long time. The related combustion process releases into the atmosphere several products and by-products (Lloyd's, 1995): carbon dioxide (CO_2), nitrogen oxides (NO_x), sulphur dioxide (SO_2), particulate matter (PM), volatile organic compounds (VOCs), black/elemental carbon (BC/EC), and organic carbon (OC). Eyring et al. (2010), comparing different studies for the year 2005, found an average yearly emission of 960 Tg of CO_2 for 2005, 6.6 Tg for NO_x, and 6.7 for SO_2. While the overall contribution of shipping to the total CO_2 anthropogenic emission is estimated to be around 2.7 % (IMO, 2009), the contributions to the total anthropogenic emissions of SO_2 (4–9 %) and NO_x (15 %) (Eyring et al., 2010) are more important. NO_x emissions from shipping are relatively high because of the actual design of marine engines, operating at high temperatures and pressures without effective reduction technologies. SO_2 emissions are high because of high average sulphur in marine heavy fuels. Emissions from ships are characterized by their distribution along typical shipping routes, connecting the network of world ports. According to different studies (e.g. Endresen et al., 2003; Eyring et al., 2005), 70 % or more of emissions by international shipping occur within 400 km off land and they can consequently be transported hundreds of kilometres inland. This pathway is especially relevant for deposition of sulphur and nitrogen compounds, which cause acidification/eutrophication of natural ecosystems and freshwater bodies and threaten biodiversity through excessive nitrogen input (Isakson et al., 2001; Galloway et al., 2003). At local and regional-scale, the impact on human health occurs through the formation and transport of ground-level ozone, sulphur emissions and particulate matter. In cities with large ports, ship emissions are in many cases a dominant source of urban pollution. Corbett et al. (2007) demonstrated that PM emissions from ocean-going ships could cause approximately 60 000 premature mortalities

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annually from cardiopulmonary disease and lung cancer, particularly in Europe and Southeast Asia. In addition, ship emissions will have an impact on climate change both as positive radiative forcing due to greenhouse gases like CO_2 and the secondarily formed ozone (O_3) but also of Black Carbon, and negative radiative forcing due to aerosol formation, resulting from the oxidation of SO_2 to sulphate. According to Eyring et al. (2010), the climatic trade-off between positive and negative radiative forcing is still a research topic and a simple cancellation of global means is inappropriate as the warming effect of CO_2 lasts for centuries, while the climate response to sulphate is at a much shorter time scale and thus offers only temporary benefits.

The International Maritime Organization (IMO), in order to limit the hazards related to SO_x and NO_x emissions from ships, prepared an international agreement, adopted in 1997, known as the 1997 MARPOL Protocol, which includes the Annex VI "Regulations for Prevention of Air Pollution from Ships". The regulation entered into force in 2005, after being received by appropriate laws by the signatory States (at European level it was received with the directives 1999/32/EC and 2005/33/EC), and introduces limits to marine fuel sulphur content and engine performance to reduce SO_x and NO_x emissions.

Fuel sulphur content (FSC) is normally given in units of percent sulphur content by mass; in the following written as % (m/m). Globally, the limit for FSC was reduced from 4.5 to 3.5 % (m/m) in 2012. A further reduction to 0.5 % (m/m) in 2020 is planned if the refineries will be able to meet the demand for low sulphur fuel. More stringent limits are in force for Emissions Control Areas (ECAs). The main purpose of ECAs is to preserve peculiar ecosystems and currently they cover SO_x emissions in the Baltic and the North Sea (the discussion about NO_x emissions is ongoing). In 2012 also the waters within 200 miles from the coast of North America became an ECA for both SO_x and NO_x. Within ECAs, the limit for FSC was, until July 2010 and thus during this study, 1.5 % (m/m); thereafter the limit has been 1 % (m/m) and it will be lowered further to 0.1 % (m/m) at the beginning of 2015. Ships at berth in European ports are already obliged from January 2010, according to European regulations, to use fuel with an FSC

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lower than 0.1 % (m/m) during their stay in the harbour. As an alternative to the use of fuels with low FSC, ships are allowed to use an approved SO_2 abatement system (e.g. scrubbers) to reduce sulphur emissions to meet the regulation limits.

NO_x emissions have to respect certain tiers in order to obtain the required Engine International Air Pollution Prevention (EIAPP) certificate for sailing. The emissions can be reduced through modifications of the engine design or through specific abatement systems (e.g. Selective Catalytic Reduction, Humid Air Motor). The different tiers depend on the construction year of the ship: all the ships built within and after the year 2000 have to respect Tier I; more stringent limits are applied for ships build during and after 2011 (Tier II), and for ships build during and after 2016 and operating inside ECAs Tier III applies. The implementation data for Tier III is presently being renegotiated within IMO. Given the long average lifetime of a ship (typically more than 20 yr) a delay can be expected before it will be possible to observe substantial NO_x reductions.

While for NO_x emissions the regulations are implemented through the periodical release of the EIAPP certificates, the effective implementation regarding SO_x emissions is more complicated. The latter, being dependent on the FSC used at a particular time and location, require effective sampling controls in order to verify the implementation. Because of the important price difference between fuel with low and high FSC, there is an economical advantage in ignoring the regulation. The Signatory States should take enforcement action to vessels under their flag, and additionally to vessels of all flags while in their ports. These checks should be performed during Port State Control (PSC) inspections by every Signatory State. According to the United Nations Convention on the Law of the Sea (UNCLOS, 1982) and the MARPOL code, a ship, whenever not in internal waters (e.g. inside a port), can be boarded only if there are clear grounds to suspect that the ship is not respecting the regulations: the only way to collect *a priori* these proofs is by "remote sensing" techniques. In addition, on international waters it is not possible to board any vessels and instead a complaint to the flagstate has to be made.

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The available techniques were therefore reviewed by the European Commission's Joint Research Centre and tested in September 2009 during a measurement campaign in the Rotterdam harbour (SIRENAS-R: "Ship Investigation Remotely about NO_x and SO_2-Rotterdam").

2 SIRENAS-R campaign

The SIRENAS-R campaign goals were evaluation and review, in the field, of the available "remote sensing" techniques (provided by several research groups), which can be used for the estimation of the FSC of a ship. Other air pollutants, NO and NO_2, regulated in MARPOL Annex VI, were also measured. These techniques can be divided into two major groups because of the different principles involved and the different parameters measured:

- The "sniffing" method is based on simultaneous measurement of the elevated concentrations of CO_2, SO_2 and/or NO_x in the exhaust plume of a ship. The measurement of CO_2 allows relating the measurement of SO_2 to the amount of fuel burned at a given time and therefore to calculate the FSC directly (Duyzer et al., 2006; Mellqvist et al., 2008, 2010). This method was used by the Joint Research Centre (JRC) of the European Commission, Chalmers University of Technology (CHA), and The Netherlands Organization for Applied Scientific Research (TNO).

- Optical methods analyse the variation of the light properties after interaction with the exhaust plume and allow, if the local wind field is known, to determine the emission rate of SO_2. The simultaneous measurement of CO_2 and SO_2 or NO_x emissions at a routine basis with these systems is unrealistic at the moment. Thus the amount of fuel burned at the time of measurement is unknown and has to be estimated by modelling for the calculation of the FSC. The optical methods are currently not suitable for the measurement of NO. Three different optical methods were used during the campaign: differential Optical Absorption Spectroscopy

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(DOAS) used by CHA, Light Detection And Ranging (LIDAR) used by the National Institute for Public Health and Environment (RIVM), and the Ultraviolet Camera (UV-CAM) technique used by the Norwegian Institute for Air Research (NILU).

Measurements were performed in the period between 17 and 30 of September 2009. An overview of the dates in which each instrument was running is given in Table 1. In order to get additional information on the performance of the remote sensing methods the stack emissions of the Stena Hollandica ferry were measured between the 22 and 30 September. The STEAM model from the Finnish Meteorological Institute (FMI) was used to calculate fuel consumption.

Further details about the "sniffer" measurements performed during this campaign and their results are given by Alfoldy et al. (2013).

2.1 Measurement locations and meteorological conditions

The measurements were performed in Hoek van Holland (the Netherlands) at the entrance of the Port of Rotterdam. This location was considered the most suitable because of the high volume of daily traffic, the Port of Rotterdam being the busiest harbour in Europe. Furthermore, facing the North Sea, it allowed testing the instruments in meteorological and light conditions characteristic of the European ECA zones (the Baltic and the North Sea). Within these ECAs, at the time of the measurement campaign, the FSC limit was 1.5 % (m/m).

Figure 1 shows the positions of the instruments during the campaign. Depending on the terminal they are heading for or coming from, the ships have to follow one of the two main channels: the Nieuwe Waterweg or the Calandkanaal. Mainly two sites were used for the measurements (Hoek van Holland and Landtong) to sample the largest possible number of ships transiting in the Nieuwe Waterweg; the choice of site was depending on the wind direction. A third site (Maasvlakte), located close to the outer entrance of the channel, was used only once. On selected days it was possible to install the instruments on-board moving platforms: a fire brigade vessel of the Rotterdam

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Port Authorities and a helicopter. Figure 1 shows also the position of the Stena Lines terminal: during the campaign it was possible to measure the emissions on-board the Stena Hollandica, a roll on/roll off passenger ferry (ROPAX) operated daily between Hoek van Holland (NL) and Harwich (UK).

The fair weather and the strong wind offered reasonable conditions on land for 7 days out of 13 for both optical and "sniffing" methods. Measurements were not successful on the 19 and 24 September because of the wind direction being almost parallel to the channel and on the 27th because of gusty winds. Measurements were only partially successful on the 23rd and 29th because of almost parallel wind and on the 26th because of very low wind speed.

2.2 Identification of target vessels

In order to assess the compliance of a ship with the existing fuel regulations, it has to be unambiguously identified. The majority of the merchant ships of 100 GT and above (there are exemptions for e.g. fishing vessels) are identified by a unique IMO ship identification number made of the three letters "IMO" followed by the seven-digit number assigned to all ships by IHS Fairplay when constructed. When the IMO number is not clearly visible, it is possible to have a precise identification through the Automatic Identification System (AIS, obligatory on ships above 300 GT). AIS is an automated tracking system used on ships and by Vessel Traffic Services (VTS) for identifying and locating vessels by electronically exchanging data with other nearby ships and VTS stations. These data can be recorded by an AIS receiver, or it can be obtained from a public website at the time of the measurements (e.g. http://www.marinetraffic.com), or it can be made available by the coastguards of the respective member states.

The identification of the plume of a particular vessel is based on the apparent wind, the resultant of the created wind from the speed of the boat, and the true wind. The ship exhaust follows the apparent wind as shown in Fig. 2 (Berg et al., 2012). Direction as well as speed of the apparent wind can be significantly changed by changing the ship speed, in the figure the apparent wind changes by 90° for a ship with opposite

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orientation. This can result in overlapping of plumes of two ships with very different positions. For this reason measurement of wind speed and direction is essential for ship identification.

2.3 Measurement platforms

Fixed land based monitoring stations offer the advantage of lower costs and the possibility of being fully automatic. However the probability of sampling the ship plume is related to its transport towards the measurement point (function of the wind direction), and the mixing state of the air parcel. Using a mobile (ground-, water-, or airborne) station it is possible to maximize the sampling probability by positioning the instrument downwind of the emission source and by moving closer to it. During the SIRENAS-R campaign, the CHA "sniffing" system was tested on ground-, water- and airborne platforms. Installing the instruments on a ship allows targeting particular ships approaching them from the downwind direction. However, it is not possible to perform measurements in shallow wind conditions when the plume upraises quickly above 50 m, not allowing measurements at sea level. Airborne measurements, despite the high costs for rental of helicopters/planes, allow for fast checks on target ships also at tens of miles from the coast and considering the large area that can be covered this makes the measurements cost effective, compared to other options. While the helicopter is easier to manoeuvre, allowing to measure plumes closer to the sea surface and to do repeated measurements, the airplane allows to reach locations far off the coast more rapidly and the hourly cost is also considerably less for the latter platform.

During the SIRENAS-R campaign mostly land based measurement platforms were used that were chosen according to the wind direction. In addition, one day ship based and five days helicopter based mobile platforms were used.

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2.4 Sniffing systems

So-called "sniffer systems" have been used by JRC, CHA and TNO in order to measure the SO_2, CO_2, NO and NO_x concentrations of the ship plumes, which are transported from the ship exhaust to the mobile laboratories on the shore site.

The sniffer systems were composed of three commercial air quality analysers, one for the measurement of SO_2, one for the measurement of NO and NO_x, and another one for the measurement of CO_2. The JRC set up comprised two NO / NO_x analysers, to improve the response time by avoiding switching between NO and NO_x measurement.

The measurement of sulphur dioxide is based on fluorescence spectroscopy principles. SO_2 exhibits a strong ultraviolet absorption spectrum between 200 and 240 nm, when it absorbs UV from this, emissions of photons occur (300–400 nm). The amount of fluorescence emitted is directly proportional to the SO_2 concentration. The instruments used were all from Thermo Electron, model 43i-TLE in the case of CHA, 43A in the case of TNO and 43C-TL in the case of the JRC. The instruments are equipped with a hydrocarbon kicker to prevent inaccuracies due to interferences from aromatic VOCs. In order to increase the flow to reduce the response time, CHA had removed this hydrocarbon kicker; the increased flow (5 L min^{-1}) allowed to reach a response time (t90) of 2 s, which is needed for the flight operation (Mellqvist and Berg, 2010). T90 is defined as the time it takes to reach 90 % of the stable response after a step change in the sample concentration (EN 14 626). The critical orifice inside the JRC instrument has been modified to a larger diameter because this was found to reduce the response time. In order to reduce the response time to a t90 of about 15 s the time constant of the JRC instrument was set to 1 s. The TNO instrument had a response time of 19 s and had the hydrocarbon kicker inserted. For calibration, a reference gas mixture of about 100 ppbv SO_2 in synthetic air and SO_2 free synthetic air for the zero calibration have been used.

The NO-NO_x measurements were performed by Thermo Scientific 42C instruments in the case of the JRC while CHA used a Thermo 42i-TL instrument and TNO used

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an Ecophysics 600 CLD instrument. These instruments measure NO by chemiluminescence light, being emitted from the reaction of NO with ozone. The instruments measure NO_x (i.e. the sum of NO and NO_2) when the air passes through a heated Mo-converter (converting NO_2 to NO), while only NO is measured when the Mo-converter is bypassed. Other oxidized nitrogen compounds, in particular PAN and HNO_3, are also (at least partially) converted to NO by the Mo-converter and can thus interfere with the measurement of NO_x. For calibration, a reference gas mixture cylinder of around 200 ppbv NO in nitrogen and NO_x free synthetic air for the zero calibration were used.

The CHA system was running with a more powerful pump and had a time response (t90) of 1 s. However, due to a malfunctioning converter only NO was measured with this instrument.

The CO_2 measurement is performed by a LI-COR LI-7000 optical instrument that measures infrared absorption in two wavelength bands around 5 µm using a broadband light source and bandpass filters. In these wavelength bands, the species H_2O and CO_2 absorb strongly. The instrument has two measurement cells, one sample cell and one reference cell containing known concentrations of CO_2 and H_2O. The concentration in the sample cell is obtained by calculating the light absorption due to CO_2 and H_2O by comparing the intensities in the two cells. The flow through the LI-COR instrument is around 6 L min^{-1}, while the flow for the reference gas is of 150 mL min^{-1}. This instrument responds faster than the SO_2 and the NO/NO_x analyzer; the response time (t90) is <5 s, depending on the pump speed. The calibration curve has been checked by a span gas calibration with at least two known CO_2 gas concentrations in the measurement range (e.g. 370, 395, 420 ppmv).

JRC provided gas standards for CO_2, SO_2, NO, and zero air, that were used by all participants for calibration of their instrumentation. Further, the JRC implemented two independent sniffer systems, one sampling at 15 m height above the mobile laboratory, another at 5 m height. The difference between the results achieved by the lower and higher sampling point were negligible, within the uncertainties of the measurements.

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Sampling, maintenance and operation of the instruments are performed according to standard operating procedures based on the EN standards (EN 14211 for NO_x and EN 14212 for SO_2), the "Guide to Meteorological Instruments and Methods of Observation "(WMO, 2008)" and the recommendations in the manuals of the different instruments.

Whenever a ship plume arrived to the sniffing system, the peak areas of the SO_2 and CO_2 measurements were determined and the background was subtracted. For the land-based instruments, the duration of a peak (i.e. the time period where the plume was intercepted by the instruments) was typically in the range between 30 and 90 s.

Applying the equations below, the sulphur content can be calculated.

Considering the molecular weight of carbon (12 g mol^{-1}) and sulphur (32 g mol^{-1}); and the carbon mass percent in the fuel (87 ± 1.5 %; Cooper et al., 2005; EPA, 2010), the sulphur mass percent of the fuel can be expressed as:

$$\mathrm{SFC(\%m/m)} = \frac{[SO_2]\,(\mathrm{ppb})32}{[CO_2]\,(\mathrm{ppb})12}0.87 \cdot 100 = \mathrm{SFC(\%m/m)} = \frac{[SO_2]\,(\mathrm{ppb})}{[CO_2]\,(\mathrm{ppb})}0.232$$

where c is the measured net volume mixing ratio (over the background) of the components.

The fuel mass weighted NO_x emission rate can be calculated from the NO_x/CO_2 ratio. Considering the molecular weight of carbon (12 g mol^{-1}), nitrogen (14 g mol^{-1}) and oxygen (16 g mol^{-1}) and the carbon mass percent in the fuel (87 % (m/m) ± 1.5 % (m/m)) (Cooper, 2003), the fuel mass weighted NO_x emission can be calculated (in g kg^{-1}). This value can be converted to engine power weighted NO_x emission applying the typical specific fuel efficiency that varies from 160 g kWh^{-1} to 210 g kWh^{-1} depending on the engine type (Cooper, 2005; Dalsoren et al., 2009).

The engine power weighted NO_x emission rate (E/P) can be formulated:

$$\frac{E}{P}[\frac{g}{\mathrm{kWh}}] = \frac{c(NO_x)[\mathrm{ppb}]}{c(CO_2)[\mathrm{ppb}]} \cdot \frac{46}{12} \cdot 0.87 \cdot e[\frac{g}{\mathrm{kWh}}] = 3.33 \cdot \frac{c(NO_x)[\mathrm{ppb}]}{c(CO_2)[\mathrm{ppb}]} \cdot e[\frac{g}{\mathrm{kWh}}],$$

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where c is the measured net volume mixing ratio of the components, while $e[g\,kWh^{-1}]$ is the fuel efficiency.

Consideration and subtraction of the background is also necessary for NO and NO_x; this can be accomplished in the same way as described for the calculation of the sulphur content. In the case of NO_x, the background, which is subtracted before calculation of the emission factors, can be influenced by interference from other oxidized nitrogen species as mentioned above. However, these species are generally not emitted directly from the combustions source in significant amounts but formed by (photo-) chemical processes taking place in the atmosphere so the measurements of NO_x emissions are unlikely to be influenced by interfering oxidized nitrogen species. At the time scale of a few minutes for the residence time of the NO_x emitted from a ship in the atmosphere before it is measured by the NO_x-analyser, the conversion of NO and NO_2 to other oxidized nitrogen species such as PAN or HNO_3 can be considered as being negligible.

2.5 Optical systems

Optical systems, when the wind field is known, allow to measure emission rates for several substances. During the SIRENAS-R campaign, three different optical instruments were used to determine the SO_2 emission rates of several ships: DOAS, LIDAR, and UV-CAM. The DOAS unit used was also able to measure NO_2 emission rates.

2.5.1 DOAS

The DOAS technique (Platt et al., 1979) is widely used for many applications. During the campaign a DOAS unit was operated by CHA from a Dauphin helicopter (Berg et al., 2012).

The system consists of a UV/visible spectrometer operating either around the 300 nm region or around 430 nm for measuring SO_2 and NO_2, respectively. The spectrometer is connected to an optical telescope via a liquid guide fiber.

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During land/ship based measurements, the telescope points upwards, intercepting above it the plume of a ship passing by. During air based measurements, the telescope point downwards with 30° angle from the horizon. In this case, since the measurements are made by intersecting the plume perpendicularly to the aircraft heading with the telescope looking on the side of the air platform, the plume is intersected twice.

From the measurement of the spectra, the integrated column of the gas across the plume can be derived, and then recalculated to an absolute emission in kg/s by multiplication with the wind speed. An upper limit to the overall uncertainty has been roughly estimated as 30–45 % while the repeatability was about 20 % during sequential measurements (Berg et al., 2012).

2.5.2 LIDAR

The LIDAR technique is an active optical method where a short laser pulse is sent into the atmosphere. Part of the laser light is scattered back towards the instrument, this light is collected and analysed. The time delay between the emission of the light and its return to the instrument determines the distance to the source of the scattering. A Differential Absorption LIDAR (DIAL) is capable of measuring the concentration of a gas in the atmosphere. It does so by sending out pulses of two or more different wavelengths, chosen so that one wavelength is absorbed stronger by the gas to be measured than the other(s). The distance information along the path of the laser beam is still available, so the instrument determines the concentration at a known place in the atmosphere.

The RIVM mobile LIDAR system sends out laser pulses at 300 094 nm that are absorbed by SO_2 and pulses at 299 752 nm that are not absorbed. The pulses at the two wavelengths are sent out alternately; a total of 30 pulses are sent out each second. Usually, 200 pulses are averaged for a single concentration measurement. The system can scan through the plume allowing to retrieve a bi-dimensional concentration distribution. The optimal measuring conditions occur when it is possible to scan per-

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pendicularly to the wind direction. The ship emissions, in $g\,s^{-1}$, are given by the product of the wind profile and the concentration profile.

The instrument was designed and built by RIVM. It is extensively described in Volten et al. (2009) and Berkhout et al. (2012). The standard deviation for individual measurements was calculated by Berkhout et al. (2012) as 38 %. In most of the cases it is possible to carry out repeated scans of the same plume. In this case the standard deviation for the average of four scans is 19 %.

2.5.3 UV-CAM

A new approach based on UV imaging has been tested by the Norwegian NILU institute (Prata et al., 2008). The SO_2 imaging camera (UVGasCam) exploits a strong absorption feature of the SO_2 molecule in the UV region (between 280–320 nm) and is composed by a highly sensitive (between 280–320 nm) CCD array (1344 × 1024 pixels) manufactured by Hamamatsu Photonics and a UV transparent lens objective.

The SO_2 molecules, being in the field-of-view of the camera, causes attenuation of the recorded light intensity. By calibrating the camera using gas cells containing known amounts of SO_2, the recorded light intensity can be related directly to the path concentration. Because the camera can sample rapidly (several images per second), features in the images can be tracked and the "in plume" wind speed and gas flux can be derived. The compact size of the instrument, the relatively low costs and the easiness of operation would make the instrument potentially attractive for routine monitoring of ship emissions of SO_2. So far, the data evaluation and treatment is done manually and requires lots of experience and expertise of the operator.

The technique was previously tested in several cases by volcano measurements (Bluth et al., 2007).

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2.6 Emission model

An alternative to direct emission measurement is the possibility to model the fuel consumption and the associated emissions knowing the main ship information, the speed, and the meteorological data. This is possible using for example the model STEAM (*S*hip *T*raffic *E*mission *A*ssessment *M*odel), developed by FMI (Jalkanen et al., 2009). The modelling work combines vessel water resistance calculations, technical information on ship properties, and fuel consuming systems with activity data from the Automatic Identification System (AIS). If a vessel cannot be identified at all, it is assumed to be a small vessel. The program uses engine rpm (revolutions per minute) data to assign NO_x emission factors, which are based on the IMO Tier I emissions factors (IMO, 1998). Sulphur emission factors are based on the fuel sulphur content and predicted instantaneous fuel consumption of main and auxiliary engines. During the SIRENAS campaign, it was possible to compare the fuel consumption registered on board of Stena Hollandica with the modelled data which showed an agreement within 10 % when the ship was travelling at the designed speed. There is a recent update of STEAM (Jalkanen et al., 2012), which facilitates studies of CO and PM, which were not included in the model version used in the SIRENAS work.

2.7 Stena Hollandica on-board stack measurements

In order to gain detailed information on real ship emissions, measurements have been performed on-board of the ship Stena Hollandica. SO_2 and O_2 were measured by a Fisher Rosemount multiple component analyser, GE 2418, based on IR absorption and a paramagnetic sensor, respectively. Another multiple component analyser (Fisher Rosemount 2419) measured NO, CO_2 and CO from their IR absorption, NO_2 from UV absorption and, again, O_2 by a paramagnetic sensor. Analysers were connected by a 10 m heated line at 180 °C, 6 mm inner diameter (PTFE coated) to a stainless steel probe with glass wool particle filter (in-stack). The sampled gas was conditioned using a portable gas cooler with membrane-gas pump. A critical point was to measure the

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flow of the exhaust gases. Unfortunately, the absence of sufficiently long sections of the exhaust pipes (more than 5 m in this case) did not allow a precise measurement of the flow and therefore calculations based on fuel consumption data have been used instead. The fuel consumption data have been collected directly from the ship computers together with the GPS information. Previous stack emission measurements have been reported in several studies (e.g. Petzold et al., 2007; Moldanova et al., 2009).

The ferry has 4 main engines, which are coupled 2 by 2 (Main Engine 1 + 2 and Main Engine 3 + 4). Additionally other 5 auxiliary engines are found, Aux 1, 2, and 3 are usually run on Heavy Fuel Oil (HFO), while Aux 4 and 5 run on Marine Diesel Oil (MDO). Aux 4 and 5 are mainly operated only during departure and arrival (close to the land measurement location during SIRENAS-R) for the ship thrusters. It was possible to perform measurements only on one stack at a time. This implies that the total emissions had to be calculated scaling the measured engines with the fuel consumption charts collected on board. Also the total flow had to be calculated similarly because it was not been possible to have a connection to the main stack for the flow meter. Unfortunately, the fuel consumption of auxiliary engines 4 and 5 were not recorded continuously. The consumption of MDO was only 7.3 % of the total fuel consumption during the period of the measurements; however, the share of MDO is likely to be higher during the manoeuvring phase when leaving and entering the harbour.

A further uncertainty source has been added because it was not possible to have a digital file of the fuel consumption readings. The only way to obtain these was to print screens manually every few hours. The average deviation between the integrated fuel consumption readings and the actual fuel consumption on each leg according to the ships' computer was 8 %. We estimate that the uncertainty on the fuel consumption readings on the open sea is approximately 10 %, higher during manoeuvring.

The use of the fuel consumption plot and the stack measurements allowed retrieving emissions plots, not including MDO consumption, for several journeys of Stena Hollandica.

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3 Field comparison

During the campaign it was possible to measure the vessels using different techniques at the same time. As Table 2 shows, while a large number of parallel data was collected for "sniffing" systems, which were continuously operated, only in a few cases this was possible for the optical systems. This happened primarily because DOAS and LIDAR are limited by wind conditions: to be able to measure the plumes, steady wind orthogonal to the ship movement is needed. Furthermore, the two instruments, as shown in Fig. 3, measure the same ship in two different points at a minimum of 1 km distance, with a time delay of 1–2 min. In our case, the fact that the ship was accelerating and decelerating in the channel did not allow for a real comparison of the different systems. This is true also for modelling because the STEAM model (Jalkanen et al., 2009) was not able to model the acceleration or deceleration to predict the emissions. The UV-CAM, although more flexible in terms of ideal wind conditions during the campaign, was still in development and suffered of lack of spectral selectivity and a tendency of overestimating the SO_2 concentration because of interferences.

Better conditions to evaluate the DOAS system were found during the helicopter measurements in the open sea. In this situation, the speed of the ship is constant, allowing also to compare the results to model predictions, and to perform replicated measurements. In two of these occasions, Stena Hollandica was also measured in the open sea.

3.1 Stena Hollandica

On-board stack measurements (SO_2, CO_2, NO_x, CO, O_2) were performed between 22 and 30 September with the goal of gaining additional quantitative information on the ship emissions. The average sulphur content of HFO determined from the stack measurements during the journeys was of (1.2 ± 0.1) % (m/m) if only the precision (one standard deviation) of the measurement devices is taken into account. This value has to be compared with the previous 5 bunker delivery notes (1.39 ± 0.03) % (m/m)

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values, and the reanalysis of the MARPOL samples (1.40 ± 0.06) % (m/m) measured by the Det Norske Veritas (DNV) laboratory. The MARPOL samples are small portions of the bunkered fuel, which have to be stored in a sealed container in case of Port State Control inspection.

A discrepancy between the actual sulphur fuel content and that determined by plume measurements has also been found in several other studies (e.g. Schlager et al., 2008; Eyring et al., 2010; Lack et al., 2011), including a study performed subsequently on Stena Hollandica (Moldanova et al., 2013) and seems thus to be a commonly observed phenomenon. Partially this can be caused by the fact that also SO_3 and sulphuric acid are formed by the combustion of sulphur containing fuels. During emission studies this has been found to account for between 1 and 8 % of the total sulphur content (Moldanova et al., 2009; Agrawal et al., 2008; Lack et al., 2009; Alfoldy et al., 2013). During the SIRENAS-R campaign 4.8 % of the measured sulphur was present as particle sulphate (Alfoldy et al., 2013) and consequently it cannot fully explain the observed difference. Thus one possibility is that part of the oxidized sulphur is not being measured because it is deposited before the sampling points; in fact, it is known that the acidity of lubrification oil can increase because of sulphur contamination (ABS, 1984). In addition, there is accumulation of material in the boilers of ship engines and this material regularly has to be removed.

3.2 Land based measurements

3.2.1 Sniffing instruments

Generally three simultaneous sniffing measurements were undertaken during the SIRENAS-R campaign (JRC upper and lower sampling points; and TNO). The JRC measurement van was equipped with the two sampling points at 5 and 15 m height, in order to test the influence of the sampling height on measurements. On the 17th and the 18th, CHA was also measuring on the same location as the others. On 16 to 21

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September, the TNO SO_2 analyzer was not operational due to technical problems, so only the days from the 22nd onwards could be used for the comparison.

The measurements have been compared by orthogonal linear regression, using the software RTOOL_v4.1.7 (Beik, 2011). We have chosen to force the regression lines through zero because the distribution of the measurement points in some cases made the evaluation of a possible bias very uncertain. Each point represents a determination of the FSC of a ship at a certain moment. Further, we found it reasonable to assume that there would not be any relevant systematic deviation of the measurements from (0,0) at zero emissions, and, in fact, the regression analysis did not show significant biases for any of the comparisons. Outliers have been eliminated, applying the criterion that an outlier deviates by more than two standard errors from the regression line.

The JRC upper and lower sampling points were found to give results in excellent agreement (Fig. 4): the regressions coefficients for lower versus the upper sampling point is 1.02 with a standard error of 0.01. Applying a 95 % confidence interval ($t\times$ standard error) this means that the regression coefficient lies in the interval 1.02 ± 0.02. In the following analyses, the average JRC values have been used for the comparisons with CHA and TNO and the uncertainty ranges given are 95 % confidence intervals.

Due to instrumental problems, the TNO group did not have any SO_2 measurements for the first days of the comparison, so a comparison of the TNO and CHA observations could not be performed. The comparisons between the JRC measurements and those performed by TNO and CHA for the 17th and the 18th on the Landtong are shown in Fig. 4. The regression coefficient for the comparison of JRC with Chalmers is 1.22 ± 0.08. The difference between the JRC and the TNO measurements is more pronounced: the regression coefficient with confidence interval is 1.64 ± 0.14. This relatively large error was found to be due to the fact that TNO tended to measure higher values of SO_2 as well as lower values of CO_2, compared to the JRC.

The NO_x concentration was measured only at the lower sampling point by JRC. In addition, TNO was measuring NO_x at the same location. Chalmers measured the

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species NO on this location during the first measurement day only. Consequently there were only two parallel NO_x measurements during the major period of the campaign. The measured NO_x-to-CO_2 ratios calculated from the measurement data of the two groups is correlated, but systematic differences were observed between them (Fig. 5). The regression coefficient for the plot of TNO vs. JRC measurements is 1.27 ± 0.04 (95 % confidence interval).

The measurement differences above are not well understood and they are not caused by calibration issues, since all instruments used the same calibration gases. Nevertheless, one problem with sniffers measurements on the shore side, especially in a busy harbour such as Rotterdam, lies in the fact that the background of CO_2 and occasionally SO_2 is quite variable, due to influence of for instance parked ships, power stations and the refineries emitting VOCs in addition to SO_2 and NO_x. This makes the baseline correction quite challenging and for instruments with slow response, the interfering background will influence the measurements. It was found, in fact, that the measurement differences showed a day-to-day variability that may be explained with changing meteorological conditions. For instance, during the Landtong measurements on 18 and 19 September, the Stena Hollandica blew into the sniffer systems quite frequently and this had to be compensated for. We have worked to homogenize the baseline correction but it was not possible to correct for the fact that the instruments all had different time responses.

An estimate of the random error is obtained by comparing the two values of FSC obtained by the JRC with sampling at the upper and the lower inlets: these are two independent sets of measurements, however with all details of the experimental set up, apart from the sampling points, being the same, thus we can assume that the differences between the instruments are due to random error. If each of the two setups is seen as an instrument to measure FSC, the uncertainty between the two instruments

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can be estimated as (Beijk et al., 2008; Kendall, 1969)

$$u^2 = \frac{\sum_{1}^{n} (Ya_i - Yb_i)^2}{2n}$$

where Ya_i and Yb_i are the FSCs of ship i measured by instrument a and b, respectively, and n is the number of measurement pairs. The absolute value of the uncertainty on the FSC (expressed as percent mass of sulphur in the fuel divided by total mass of the fuel) calculated in this way is 0.06 % (m/m), thus corresponding to 6 % relative uncertainty for an FSC of 1 % (m/m) but to 60 % relative uncertaintyfor an FSC of 0.1 % (m/m).

For the sniffer measurements, the uncertainty is mainly due to the fluctuations in the baseline concentrations of NO_x, SO_2 and CO_2. These fluctuations determine the "detection limit", i.e. they determine the lower limit of the increase in the concentrations due to the plume passage that can be observed. The response time of the instruments is important because a fast response time increases the height of the peak caused by the plume and the background.

3.2.2 Comparison sniffing – stack measurements

The Stena Hollandica on-board stack measurements can be compared to sniffer and optical measurements downwind the plume of the ship; however in this case also combustion of MDO in the Auxiliary Engines 5 and 6 may influence the average. Particularly during the manouevering in the harbour area, this contribution may be important, and as the MDO has a sulphur content of 0.5 % (m/m) this can significantly reduce the SO_2/CO_2 ratio in the plume compared to what would be found if the fuel was HFO only. The JRC performed measurements in the harbour on the plume of Stena Hollandica at six occasions and found an average FSC of 0.86 % m/m with a standard deviation of 0.23 % m/m. The stack measurements within the harbour gave values of FSC (1.2 % (m/m) with a standard deviation of 0.15 % (m/m)) that were not significantly

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different from those obtained on the open sea, however, the contribution from the two auxiliary engines running on MDO with lower sulphur content. In the harbour area, these auxiliary engines are likely to give a significant contribution to the overall emissions from the ship.

Also the NO_x emission factors for Stena Hollandica, relative to power generation (kWh) or to fuel combustion (kg fuel), will depend on the contribution from the auxiliary engines that typically have higher rotational speeds and thus lower NO_x emission factors than the main engines (Alfoldy et al., 2013) and, in fact, also the few available "sniffer" measurements of NO_x were below the on-board stack measurement.

3.2.3 Optical instruments

The range of the emissions measured, for the different systems, in Rotterdam, is given in Fig. 6. While the emissions from the different vessels can differ significantly (simply due to the sizes of the ships or the respective acceleration or deceleration while leaving or entering the channel) it appears that the range of measurements is rather homogeneous except for the UV-camera, which shows generally higher values. Measurements with the UV camera have been performed for most of the days, but so far only the results of the 17 September have been analysed for a total of 11 ships. No other optical technique measured such high emission rates, as is apparent from Fig. 6. In addition, the measured emission rates are higher than can be expected from ships of the appropriate type sailing at full power on high-FSC fuel. This leads to the conclusion that the UV camera most likely overestimates the emission rate values.

The distribution of SO_2 emission rates of the ships measured by DOAS and LIDAR is shown in Fig. 7. The figure shows the multimodal distribution of the SO_2 emission rate. The first, most frequented, mode of the emission rates measured by LIDAR has a maximum at 20 $kg\,h^{-1}$ emission rate, which is in good agreement with the DOAS results. 78 % of the measured ships are included in this mode. The second mode that contains 15 % of the cases has maximum at 70 $kg\,h^{-1}$. This value is higher than the second maximum of DOAS results by 17 %. The remaining 7 % of the ships are distributed be-

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tween 105, 155 and 205 kg h^{-1} emission rate bins. The corresponding DOAS bins are also at lower emission rates, in addition, the highest emission rate bins are missing at the DOAS measurement.

The differences between SO_2 emission rate distributions given by the LIDAR and DOAS techniques may be due to the different measurement conditions. LIDAR measurements were performed of arriving or leaving ships, during acceleration or deceleration consequently, while DOAS measurements were made on open sea during steady state operation of the ship engines. It is likely, that the first emission rate peak that has same maximum as the DOAS peak contains measurements made on ships with steady state operation condition, while the second, third, fourth and fifths peaks contain the accelerating/decelerating cases.

Comparison of emission rates of a ship measured by LIDAR and DOAS technique is difficult, since there was no common measurement at the same place and same time. The LIDAR was faced to the open sea, looked forward approximately by 1 km, while DOAS looked up vertically from the measurement site. It means that the distance between the two measurements was 1 km and the minimal time delay 1–2 min. Table 3 summarises the three closest measurements by LIDAR and DOAS technique taken on 17 September; Stena Hollandica arriving and leaving and Stena Britannica arriving. The differences between the two techniques are also indicated.

The arrival and leaving of Stena Hollandica were measured three times per case, while Stena Britannica was measured twice. The repeated measurements provide different emission rate values. The standard deviation of the repeated measurements is especially high in the case of Stena Hollandica leaving (43 %). In this case the emission rate increased by a factor of 3.5 in four minutes. This high deviation does not reflect the uncertainty of the method, rather the different conditions of the measurements. Since LIDAR measurements were taken during the launching manoeuvre of the ship, different engine loads can be expected in the time frame of the three measurements which results in different SO_2 emission.

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Figure 8 shows the three sequential LIDAR scans of the leaving Stena Hollandica. It is clearly seen, how the emission rate increases with the time and the distance from the measurement location. Consequently, the standard deviation of the repeated measurements does not reflect the uncertainties on the measurement technique only but also the changing emission rate., Under these conditions, the comparison with the DOAS technique could not be done.

On the contrary to the DOAS measurement, the UV-CAM can be compared with the LIDAR since both looked into the same direction and the measurements were performed at the same time. As shown in Fig. 9, the two measurements agree only in two cases (Stena Britannica and Hollandica), in the other cases the UV-CAM significantly overestimates the SO_2 emission rate compared to the LIDAR results. The scattering of the UV-CAM measurements can be due to the presence of particles in the ship plumes, which reflect and absorb a significant part of the incoming UV light. A new version of the UV-CAM with a co-aligned spectrometer may allow to distinguish the fraction of absorption related to the particles from the one related to SO_2.

Important contributions to the uncertainty on the LIDAR determination of ship emissions come from uncertainty on the wind speed measurements, meandering of the plume and noise on the echo signal received by the instrument.

3.3 Measurements from mobile platforms

3.3.1 "Sniffing" instruments

The SO_2 emission factors for Stena Hollandica were determined by helicopter borne ‚sniffer' measurements by CHA using the same system as applied in the harbour (Berg et al., 2010; Mellqvist, 2010). The 25 measurements on 23, 25 and 27 September of SO_2 and CO_2 gave an average calculated FSC of (1.13 ± 0.18) % (m/m), while the 19 measurements of NO and CO_2 gave an average emission factor of (34 ± 4) g $(\text{kg fuel})^{-1}$ for NO, Noteworthy is, that NO_2 from the helicopter was not measured and this should add about 20 % to the measured NO_x emission factor according to Alfoldy et al. (2013).

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The values above should be compared to the on board stack measurements of SO_2 and NO_x that yielded (1.2 ± 0.1) % (m/m) FSC and $(41 \pm 3\,g)(kg\ fuel)^{-1}$, respectively. As discussed in Sect. 2.1, the fuel analysis showed higher FSC, i.e. 1,4 % (m/m). Part of this is due to the fact that sulfate in particles was not measured.

3.3.2 DOAS

The SO_2 emission factor for Stena Hollandica was also determined by DOAS measurements from the helicopter combined with modelling of the fuel consumption, using the STEAM model (Jalkanen et al., 2009). A detailed discussion of this comparison can be found in Berg et al. (2012). The comparison showed differences of (-30 ± 14) % and (-41 ± 11) %, respectively, between the measurements and the certified fuel sulphur content for two days, with equal measurement precision of about 20 %. The agreement with the on-board stack measurements, 14 % below the certified value, is obviously somewhat better. Main contributions to the uncertainties on the DOAS measurements stem from the evaluation of the optical path of the ocean scattered light due to waves, and direct and multiple scattering in the exhaust plume. Rough estimates of these sources have been accounted for in the total uncertainty, which is estimated to be 30–45 % (Berg et al., 2012).

Stena Hollandica was measured outside the channel with the UV-DOAS installed on a helicopter. The result shows a good agreement with the stack measurements performed on-board Stena Hollandica with only a 5 % difference in one case while in the second case the on-board measurements exceeded the DOAS measurements by more than a factor of two (see Table 4). Figure 10 shows the modelled variation of the SO_2 emission rate for the first two hours of the Stena Hollandica journey from Hoek van Holland to Harwich on 25 September. Measured emission rates determined by onboard stack measurement and DOAS technique are also shown in the figure. The latter was performed from the helicopter when the ship reached the steady state operation. The error bar given by repeated DOAS measurements is also indicated. It can be concluded

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that the modelled value and the two measurement results agree within the error bar of the DOAS measurement.

The uncertainty budget for the DOAS determinations of ship emissions is discussed by Berg et al. (2012). The largest contributions are related to wind speed, influence of waves and plume width.

Comparison of UV-DOAS measurements provided by helicopter flights with model calculations for other ships and with the sniffer measurements is shown in Fig. 11. Model calculations were made based on the assumption that main engines of the ships use fuel with fixed 1.5 % (m/m) FSC, while the auxiliaries run with 0.5 % (m/m) FSC fuels. The model calculation can be refined, if the fixed fuel sulphur ratio is replaced by the real ones determined by the sniffing measurements. It can be seen that in most of the cases (from Lion to Endeavor) the corrected model results lie within the error bars of the UV-DOAS measurements. This finding validates the method by which the fuel sulphur ratio is calculated from the combination of optical SO_2 emission measurement and fuel consumption modelling.

4 Conclusions

The "sniffer" principle, with the state of the art of measurement techniques, appears to provide the most convenient approach to determination of FSC and NO_x emission factors for ships by remote measurements. The experimental results showed that two instruments operated under identical conditions had a precision in the FSC determination of 0.06 % (m/m).

Visual inspection of the data (Fig. 4) suggests that the absolute values of the residuals are approximately independent of the value of the observation. This means that the relative importance of random errors will increase with decreasing FSC, in our case from 6 % for 1 % (m/m) FSC to 60 % for 0.1 % (m/m) FSC. It was found by the comparison of the three groups, that the regression coefficient of the straight line between the observed values can significantly differ from 1, which implies that apparently minor

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differences in the instrumental characteristics, particularly in the response times, may have a significant impact on the values of the calculated emission factors.

This relatively high standard deviation for low FSCs is a result of the higher uncertainty on the measurement of lower sulphur concentration, but also the higher uncertainty on measurement of lower CO_2 concentration. In fact, the low sulphur fuel was mainly used by small boats (e.g. port authorities and service boats), with a low fuel consumption. Future regulations of ship emissions will lead to lower FSCs and consequently to higher relative errors on their determination, however, as the CO_2 emissions will not decrease like the sulphur content, the uncertainties are likely to be lower than what appears from the above discussion. In addition, a lower background of SO_2 is likely to improve the detection limit of the sniffer method, as discussed in Sect. 2.2.1.

It was found that also the DOAS and the LIDAR techniques can provide reliable estimates of SO_2 emissions from ships, however, they are influenced by relevant additional error sources because the vertical wind profile is needed for the emission rate calculation. In addition, for compliance control it is necessary to complement these measurements with modelling of fuel consumption in order to calculate FSC and emission factors of NO_x. This is presently being implemented operationally by CHA in a Danish Navajo Piper airplane, combining DOAS and the STEAM method (Beecken et al., 2013; Jalkanen et al., 2009).

The UV camera is the cheapest and easiest optical technique; however, it has proved to be the least reliable method in the tested configuration. It is the consequence of the high particle emission of ships that due to scattering modify the recorded light intensity. After further technical developments, the reliability of the measurement may be improved.

The use of a mobile platform has two important advantages: it can allow to position the measurement devices in a favourable position relative to the ship, in the case of the sniffer technique downwind and close to the stack, which optimizes the precision and accuracy of the measurements. Further, it can allow to measure ship emissions under steady state conditions outside internal waters, which are the most relevant condition

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for evaluation of their environmental impacts and for investigating whether they comply with the IMO legislation.

When the limit of 0.1 % (m/m) FSC comes into force for SECA areas in 2015, it will be important to assure that available monitoring techniques have the necessary accuracy and precision for monitoring compliance with this rule. The results of the present study suggests that further developments may be needed to reach this goal. Although the sniffer techniques presently appear to provide the best option for compliance monitoring, it is worth mentioning that optical techniques may provide the most convenient option for rapid identification of ships using heavy fuel oil with high sulphur content in areas where this is not allowed.

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Table 1. Overview of the measurements, performed in September 2009 during the SIRENAS-R campaign. The table shows the location of the different research groups and their instruments during the measurement days (1: Hoek van Holland, 2: Landtong, 3: Maasvlakte, S: Fire-brigade Ship, H: Helicopter, O: Onboard Stena Hollandica).

	17	18	19	20	21	22	23	24	25	26	27	28	29	30
JRC Sniffer	2	2	2	2	1	1	1	1	1	1	1	1	1	1
TNO Sniffer*	2	2			1	1	1	1	1	1		1	1	
CHA Sniffer/DOAS	2	S	2		1		H	H	H	H	H		1	
NILU UV-CAM	2	2	2	2	1	1	1	1	1	1	1	1	1	
RIVM LIDAR	2	2			1	1	1	1	1					
Stena Stack						O	O	O	O	O	O	O	O	O

* SO_2 was not measured by TNO before the 22nd.

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Table 2. Overview of the number of ships measured by different techniques during the SIRENAS-R campaign. Relative errors observed by repeated measurement are indicated in the last column (Repeatability). Note, this value for sniffing technique reflects the repeatability of fuel sulphur ratio, while in the optical cases it indicates only the uncertainty of sulphur emission rate. Uncertainty of fuel sulphur ratio is increased by the uncertainty of fuel consumption that is generally a high value. * The LIDAR measured on 7 days, the UV camera on 12 days, but not all data was available for comparisons. ** UV-CAM shows the lowest difference between the repeated measurements, however, it has an important significant bias compared to the others.

	Number of targeted ships	Number of days (out of 13)	Repeatability
Sniffing	475	10	30 %
LIDAR	45	2*	29 %
UV-CAM	11	1*	** 18 %
DOAS (ground + ship)	11	2	20%
DOAS (helicopter)	20	3	

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Table 3. Comparison of SO_2 emission rates in kg/h given by DOAS and LIDAR techniques. In the last column, relative differences are presented (DOAS-LIDAR).

	DOAS	LIDAR	Difference
Stena Hollandica, 08:37	91.10 ± 11 %	57.60	37 %
Stena Hollandica, 08:39		66.96	26 %
Stena Hollandica, 08:41		68.40	25 %
Stena Hollandica, average		64.32 ± 9 %	29 %
Stena Hollandica, 15:02	114.6 ± 14 %	31.72	72 %
Stena Hollandica, 15:04		95.04	17 %
Stena Hollandica, 15:06		109.44	4 %
Stena Hollandica, average		78.73 ± 43 %	31 %
Stena Britannica, 16:15	29.70 ± 9 %	73.44	−147 %
Stena Britannica, 16:17		48.96	−65 %
Stena Britannica, average		61.20 ± 28 %	−106 %

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Table 4. SO_2 emission rates provided by helicopter based DOAS measurements between 23 and 27 September 2009 and compared to on board measurements.

Ship name	Time	Velocity, kn	Emission rate, kg h^{-1}	St.Dev. %	On board, kg h^{-1}
Maeris	24/14:40	17	56	40	
Frank	24/15:15	13	19	35	
Taurine	24/15:33	15	12	4	
Sporades	24/15:40	14	20	12	
Altius	24/16:00	14	18	3	
Maersk Ethien	24/16:03	14	23	17	
Lion	25/10:04	15	37	9	
Sloman	25/10:21	14	25	–	
Cap Callisto	25/10:42	16	56	14	
Hyundai	25/11:05	23	129	13	
Deneb J	25/11:25	18	61	17	
Ginga Tiger	25/11:28	16	65	44	
Maas Viking	25/14:20	22	12	16	
St. Hollandica	25/15:02	19	92	19	97
Endevor	27/10:52	18	25	26	
SKS Tugela	27/11:20	16	61	21	
Gennaro	27/11:40	17	29	33	
Genco	27/12:05	17	34	25	
Maersk Fl.	27/14:32	20	32	17	
Katherina B	27/14:50	12	17	31	
St. Hollandica	27/15:06	22	54	18	119

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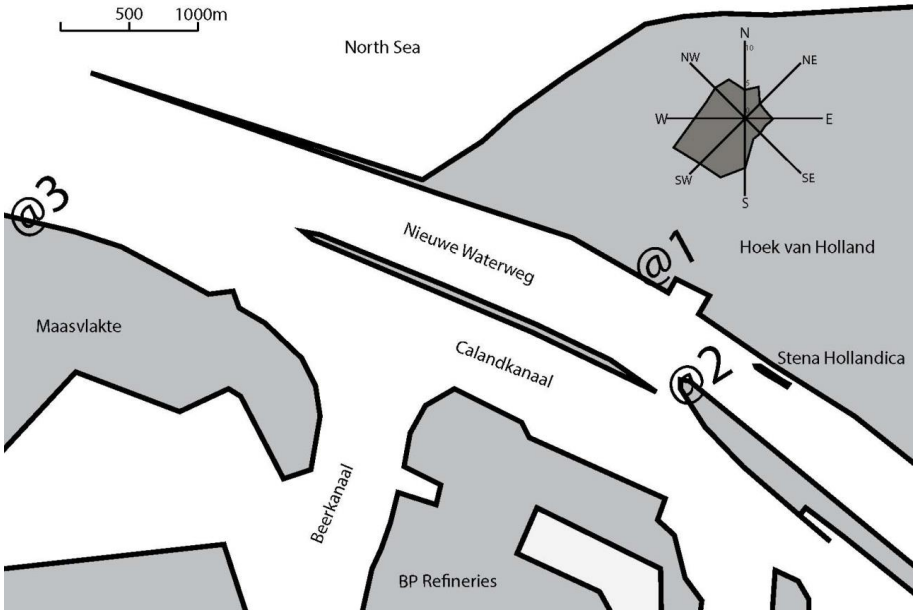

Fig. 1. Scheme of the entrance of the port of Rotterdam and the three measurements points used during the SIRENAS-R campaign (@1 = Hoek van Holland, @2 = Landtong, @3 = Maasvlakte). The berth position of Stena Hollandica and the average wind direction (years 1999–2011) are also indicated.

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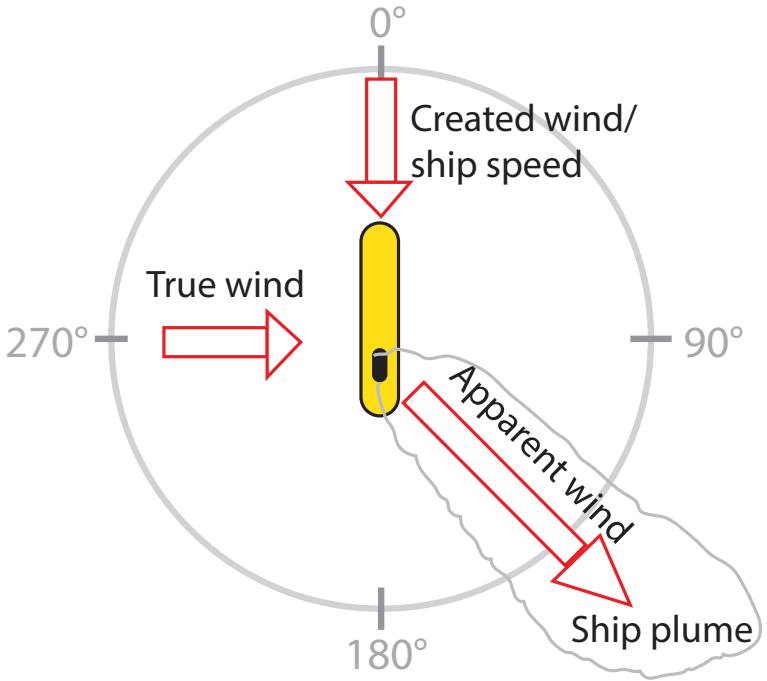

Fig. 2. The apparent wind is the resulting wind from the created wind from the speed of the boat and the true wind. The ship exhaust plume follows the apparent wind (from Berg et al., 2012).

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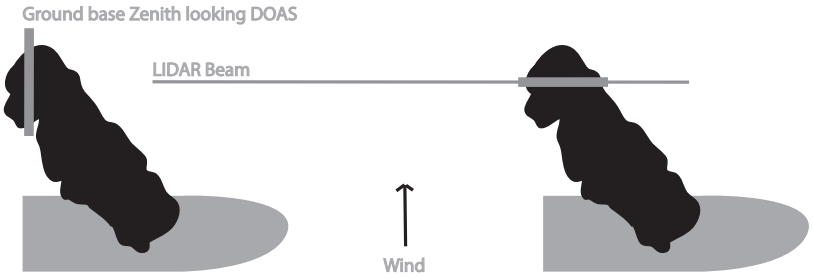

Fig. 3. DOAS and LIDAR work on different optical planes. A land-based upwards looking DOAS, like the "sniffing" system, requires a direct transport of the plume through its field of view. The LIDAR used in this study requires preferentially similar wind conditions as the DOAS (moderate and perpendicular to land), but has to measure at a certain distance because it receives only light that is scattered back from about 400 m distance or more (see also Fig. 8). The DOAS measures in the vertical direction, the wind blows the plume across.

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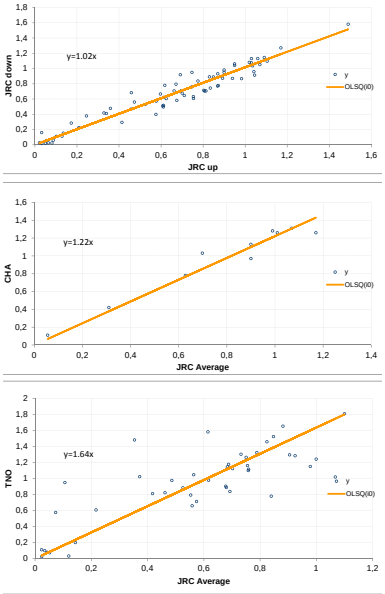

Fig. 4. Comparison of FSC, expressed in percent sulphur by mass in fuel, determined by "sniffer" measurements (see text). "JRC up" and "JRC down" are the two JRC sampling points, "JRC Average" is the average of these two points. "CHA" and "TNO" are the measurements performed at the same time on the same ship. Regression lines, forced through (0,0), have been obtained by orthogonal regressions. The number of outliers removed is 3 in the upper figure, 1 in the middle figure, and 2 in the lower figure.

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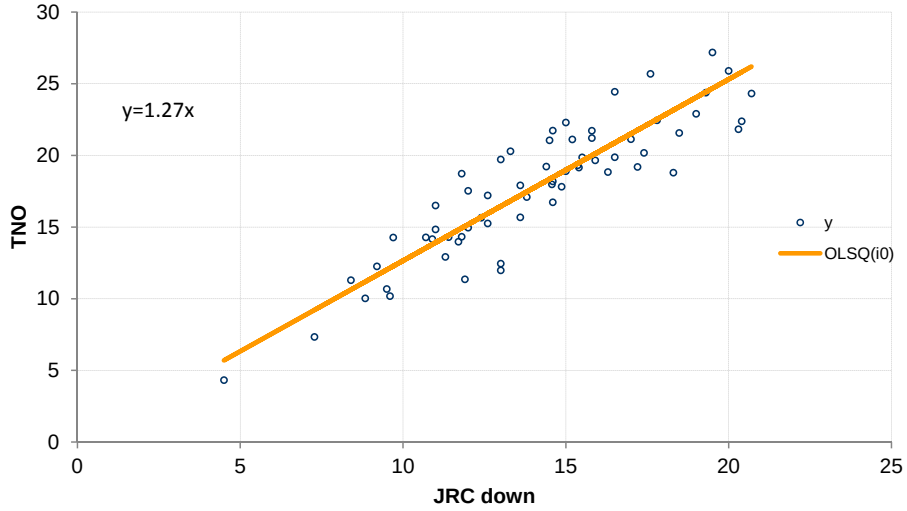

Fig. 5. Comparison of NO_x emission rates (g NO_2 kWh^{-1}) determined by "sniffer" measurements (see text), assuming an engine fuel efficiency of 185 g $kWhl^{-1}$. Regression lines, forced through (0,0), have been obtained by orthogonal regressions. Three outliers have been removed.

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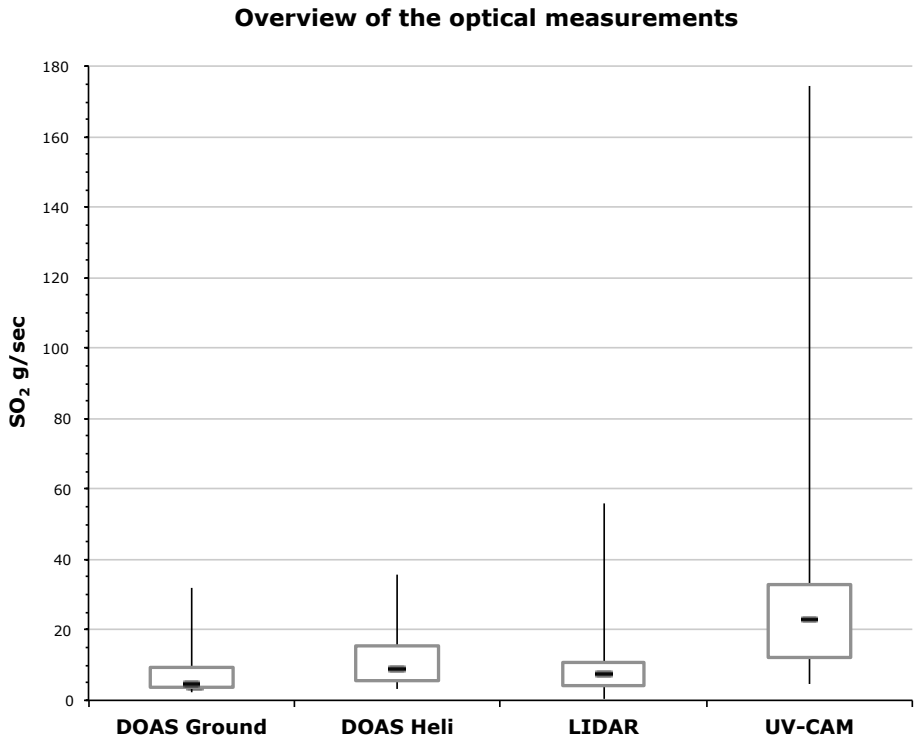

Fig. 6. Emission values observed by the different optical measurement techniques during the SIRENAS-R campaign. The bars indicate the maximum and minimum values, the squares indicate the 25th and 75th percentile, and the dark line is the median of the measurement distribution.

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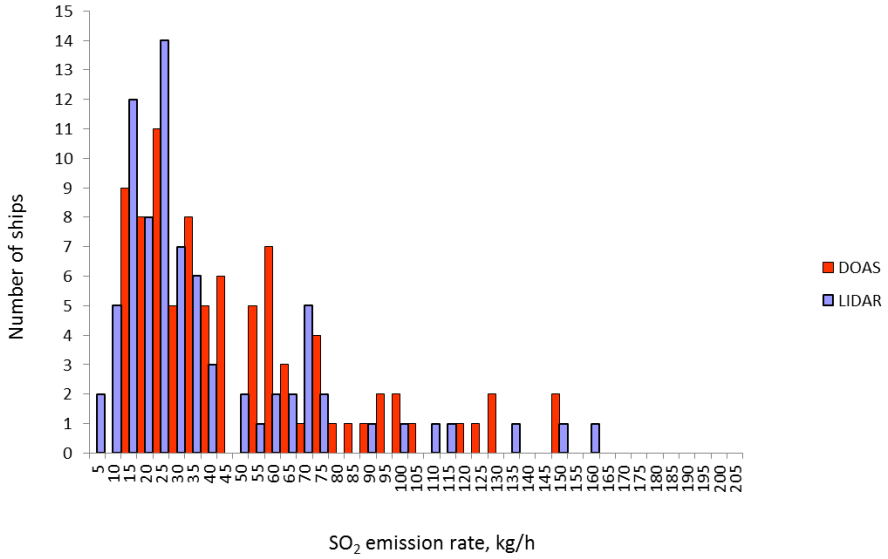

Fig. 7. SO_2 emission rate distribution as measured by the LIDAR and by the DOAS techniques.

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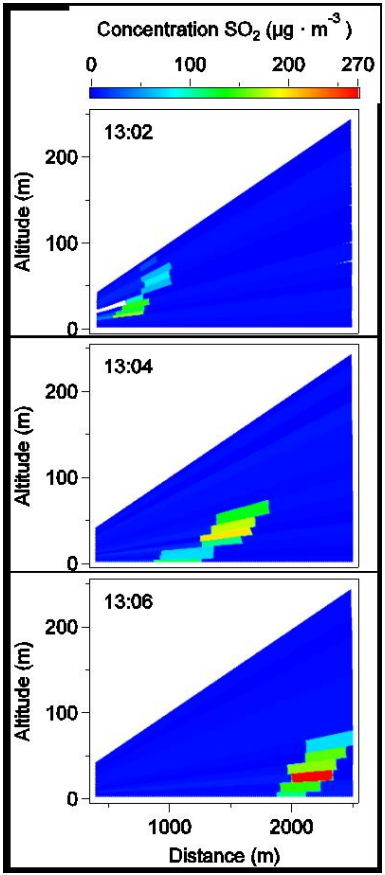

Fig. 8. Three sequential LIDAR measurements during the departure of Stena Hollandica on 17 September 2009. The blue area is the area covered by the LIDAR scans.

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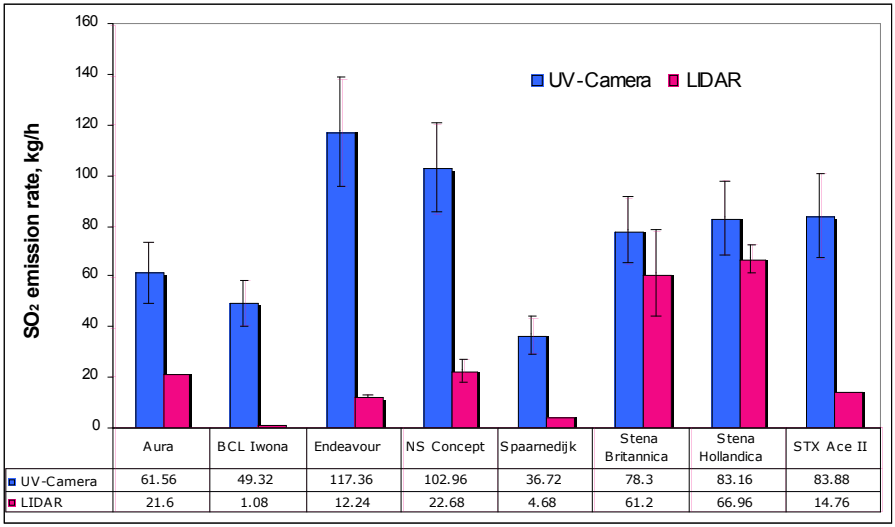

	Aura	BCL Iwona	Endeavour	NS Concept	Spaarnedijk	Stena Britannica	Stena Hollandica	STX Ace II
UV-Camera	61.56	49.32	117.36	102.96	36.72	78.3	83.16	83.88
LIDAR	21.6	1.08	12.24	22.68	4.68	61.2	66.96	14.76

Fig. 9. Comparison of LIDAR and UV-camera measurements of the same ships taken at the same time and location on 17 September.

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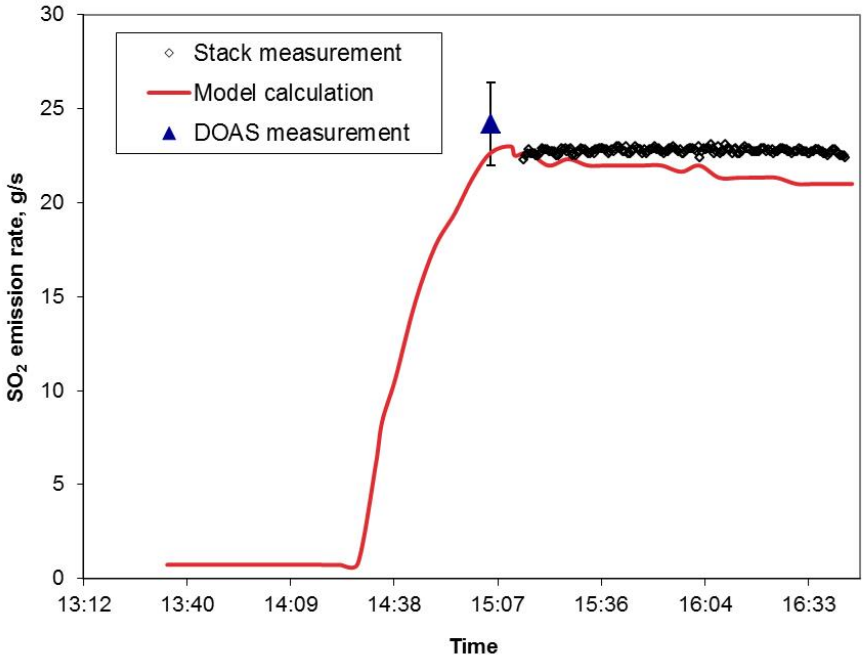

Fig. 10. Comparison of 7 repeated UV-DOAS measurements of Stena Hollandica (blue triangle, mean and standard deviation) performed by helicopter on 25 September 2009, with on-board stack measurements results (black diamonds). The corresponding model simulation is also indicated (red line).

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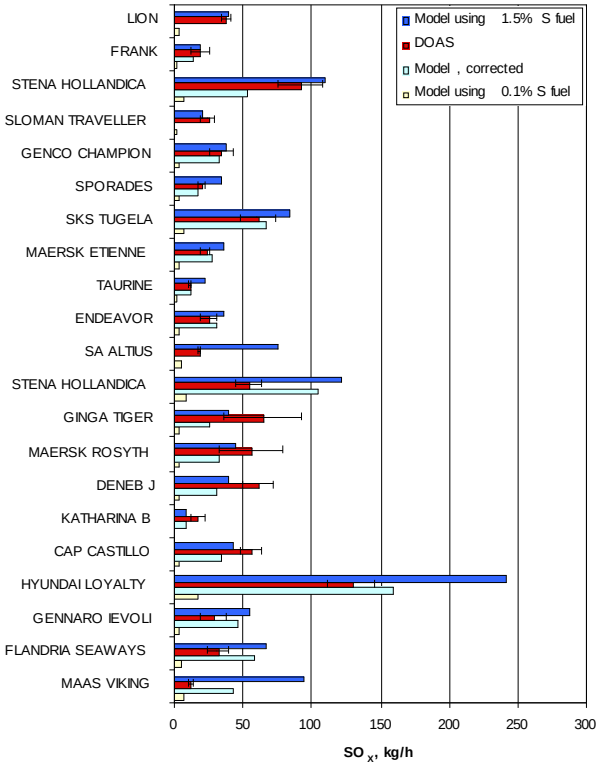

Fig. 11. Comparison of DOAS measurements performed by helicopter (in red), the modelled SO_x emission from the targeted vessel (assuming 1.5 % (m/m) fuel sulphur ratio for main engines and 0.5 % (m/m) for auxiliaries, in blue), the modelled emissions corrected with the sniffing measurement (taken sulphur ratio determined by sniffing), and the model results for a future scenario where ships run with 0.1 % (m/m) sulphur fuel.

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