Field test of available methods to measure remotely SO$_x$ 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 based on 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, Differential Optical Absorption Spectroscopy (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 land-based ones because they allow optimizing the sampling conditions and sampling from ships on the open sea. Although optical methods can provide reliable results it was found that at the state of the art level, 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 from 60 to 150 Mt (megatonne, equivalent to 1 Tg, 10^{12} g), while between 1980 and 2007 (according to the International Maritime Organization, 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 Register of Shipping, 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 Tg 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 the local and regional scales, 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 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), as well as 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.

In 1997, the International Maritime Organization (IMO), in order to limit the hazards related to SO_x and NO_x emissions from ships, extended the MARPOL 73/78 International Convention for the Prevention of Pollution From Ships with the Annex VI: Regulations for Prevention of Air Pollution from Ships (MARPOL, 1997). The regulation went into effect in 2005, after being received by appropriate laws by the signatory states (at the European level it was received with the directives 1999/32/EC, 1999, and 2005/33/EC, 2005), and introduces limits to marine fuel sulphur content and engine performance to reduce SO_x and NO_x emissions. Further amendments to Annex VI were adopted in 2008 and entered into force in 2010.

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 North seas (the discussion about NO_x emissions is ongoing). In 2012 the waters within 200 miles from the coast of North America also 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 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 Tier III applies for ships build during and after 2016 and operating inside ECAs. The implementation data for Tier III is presently being renegotiated within the IMO. Given the long average lifetime of a ship (typically more than 20 years) 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 these proofs a priori is by "remote sensing" techniques.

In addition, it is not possible to board any vessels on international waters; a complaint to the flag state has to be made instead.

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 harbour of Rotterdam (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 and Berg, 2010; Mellqvist et al., 2008; Beecken et al., 2014). 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 (DOAS) used by Chalmers, 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 the 17 and 30 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 Alföldy 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 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 gross tons (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

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.

assigned to all ships by the company IHS Maritime on behalf of IMO 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 they can be obtained from a public website at the time of the measurements (e.g. www.marinetraffic.com), or they 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 orientation. This can result in the 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 Chalmers "sniffing" system was tested on ground-, water- and airborne platforms. Installing the instruments on a ship allows targeting particular ships approaching 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
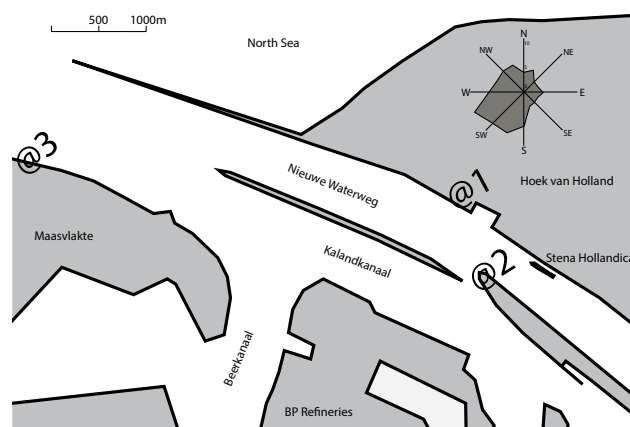

Figure 1. Scheme of the entrance of the port of Rotterdam and the three measurements points used during the SIRENAS-R campaign (@1 = Hoek van Holland, @2 = Landtong, @3 = Maasvlakte). The berth position of *Stena Hollandica* and the average wind direction (years 1999–2011) are also indicated.

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, which allows measuring plumes closer to the sea surface and repeated measurements, the airplane allows reaching 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, for 1 day ship-based and for 5 days helicopter-based mobile platforms were used.

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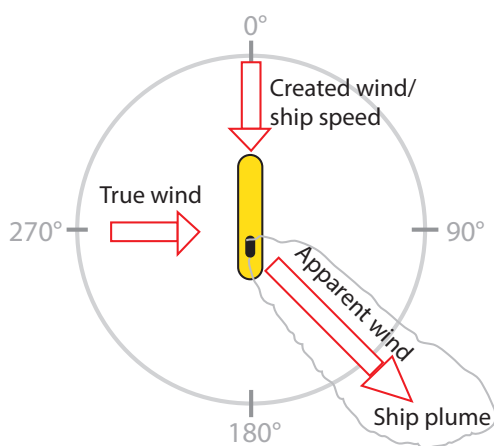
Figure 2. The apparent wind is the resulting wind from the created wind from the speed of the boat and the true wind. The ship exhaust plume follows the apparent wind (figure from Berg et al., 2012).

concentration 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. While the response time is not expected to have an influence of the integrated peak signal caused by the passage of a ship, it is likely to have an influence on the uncertainty of the measurements: a high response time broadens the peak and reduces the height and will thus increase the influence of noise and make the determination of the baseline more uncertain.

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 sulphur dioxide 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 interfering absorptions 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 14626 : 2012). 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 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 has a time response (t90) of 1 s. However, due to a malfunctioning converter only NO was measured with his instrument.

The CO$_2$ measurement was performed by a LI-7000 optical instrument from LI-COR 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$_2$O 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$_2$O. The concentration in the sample cell is obtained by calculating the light absorption due to CO$_2$ and H$_2$O 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 instrumentation. Furthermore 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.

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" (World Meteorological

Organization (WMO), 2008) and the recommendations in the manuals of the different instruments.

Whenever a ship plume arrives 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.

The sulphur content can be calculated by applying the equations below.

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

$$\text{FSC (\% m/m)} = \frac{[\text{SO}_2] \text{ (ppb)} 32}{[\text{CO}_2] \text{ (ppb)} 12} 0.87 \cdot 100$$
$$= \text{FSC (\% m/m)} = \frac{[\text{SO}_2] \text{ (ppb)}}{[\text{CO}_2] \text{ (ppb)}} 0.232,$$

where [...] 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; Dalsøren et al., 2009).

The engine power weighted NO$_x$ emission rate (E/P) can be formulated as follows:

$$\frac{E}{P} \text{ [g kWh}^{-1}] = \frac{c(\text{NO}_x) \text{ [ppb]}}{c(\text{CO}_2) \text{ [ppb]}} \cdot \frac{46}{12} \cdot 0.87 \cdot e \text{ [g kWh}^{-1}]$$
$$= 3.33 \cdot \frac{c(\text{NO}_x) \text{ [ppb]}}{c(\text{CO}_2) \text{ [ppb]}} \cdot e \text{ [g kWh}^{-1}],$$

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 combustion source in significant amounts, but rather formed by (photo-) chemical processes taking place in the atmosphere, so the measurements of NO$_x$ emissions is 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 used for measuring 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 Chalmers from a Dauphin helicopter (Berg et al., 2012; Beecken et al., 2014).

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.

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 points downwards with 30° angle from the horizon. In this case, since the measurements are made by intersecting the plume perpendicularly with the telescope looking on the side of the air platform, the plume is intersected twice because the light reaching the telescope has already passed through the plume before being reflected from the sea surface.

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/h 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 2-dimensional concentration distribution. The optimal measuring conditions occur when it is possible to scan perpendicularly to the wind direction. The ship emissions in kg h^{-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 and Bernardo, 2008; Prata, 2014). 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 cause 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).

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 (Ship Traffic Emission Assessment Model), 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 was 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 onboard 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 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 were reported in several studies (e.g. Petzold et al., 2008; Moldanová et al., 2009).

The ferry has four main engines, which are coupled two by two (main engines 1 + 2 and main engines 3 + 4). Additionally other 5 auxiliary engines (aux) 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 have 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 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*.

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 few cases were possible for the optical systems. This happened primarily because DOAS and LIDAR are limited by wind conditions, to be able to measure the plumes, i.e. steady wind orthogonal to the ship movement. Furthermore, the two instruments, 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. On 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 the 22 and the 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 (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 five bunker delivery notes values with an average of (1.39 ± 0.03) %(m/m), 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 a 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* (Moldanová 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 (Moldanová et al., 2009; Agrawal et al., 2008; Lack et al., 2009; Alföldy et al., 2013). During the SIRENAS-R campaign 7 % of the measured sulphur was present as particle sulphate (Alföldy 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 heights of 5 and 15 m, in order to test the influence of the sampling height on measurements. On the 17th and the 18th Chalmers was also measuring on the same location as the others. On 16 to 21 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 (Beijk, 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. Furthermore, 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

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 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.

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

[a] The LIDAR measured on 7 days, the UV camera on 12 days, but not all data was available for comparisons. [b] UV-CAM shows the lowest difference between the repeated measurements, however, it has an important significant bias compared to the others.

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. Outliers may be caused by interferences from other emission sources than the ship under investigation, or by measurements with high uncertainty due to low signal intensity.

The JRC upper and lower sampling points were found to give results in excellent agreement (Fig. 3): the regressions coefficient for lower versus the upper sampling point is 1.02 with a standard error (SE) 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 Chalmers 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 Chalmers observations could not be performed. The comparisons between the JRC measurements and those performed by TNO and Chalmers for the 17th and the 18th on the Landtong are shown in Fig. 3. 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 difference 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 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-CO2 ratios calculated from the measurement data of the two groups is correlated, but systematic differences were observed between them (Fig. 4). 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 "sniffer" 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, 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 can be estimated as (Beijk et al., 2008; Kendall and Stuart, 1969)

$$u^2 = \frac{\sum_{1}^{n} (Y_{a_i} - Y_{b_i})^2}{2n},$$

where Y_{a_i} and Y_{b_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
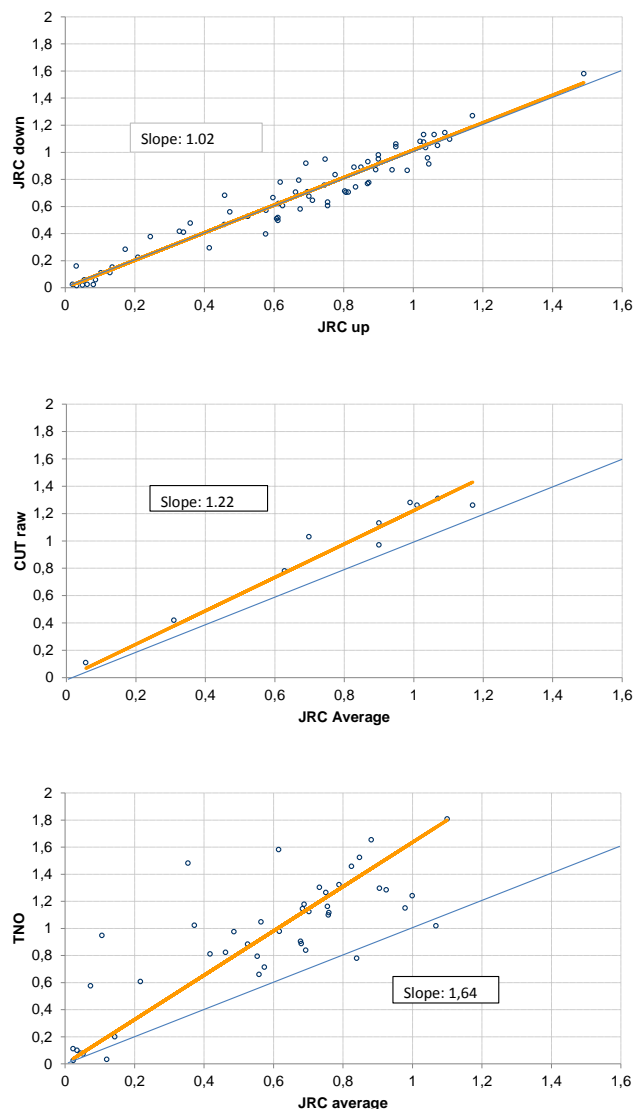
Figure 4. Comparison of NO_x emission rates (g NO_2 kWh^{-1}) determined by "sniffer" measurements (see text), assuming an engine fuel efficiency of 185 g kWh^{-1}. Regression lines, forced through $(0, 0)$ have been obtained by orthogonal regressions. Three outliers have been removed.

for the SO_2 and NO_x emissions factors respectively, found by Beecken et al. (2014) as the square root of the sum of all squared uncertainties due to calibrations and measurements for the respective gas species and CO_2.

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.

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 manoeuvering 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 on-board 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 different from those obtained on the open sea, however, the contribution from the two auxiliary engines running on MDO with lower sulphur content was not measured on-board. In the harbour area, these auxiliary engines are likely to give a significant contribution to the overall emissions from the ship.

Figure 3. 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.

of 1 % (m/m) but to 60 % relative uncertainty for an FSC of 0.1 % (m/m).

The average relative standard deviation on the determination of FSC values by the "sniffer" method during this campaign was estimated by Alföldy et al. (2013) to be 23 % by comparing repeated determinations of emissions from the same ship. The uncertainty on the determination of the NO_x emission factor (in g per kg fuel) was found in the same way to be 26 %. These estimates are close to those of 20 and 24 %
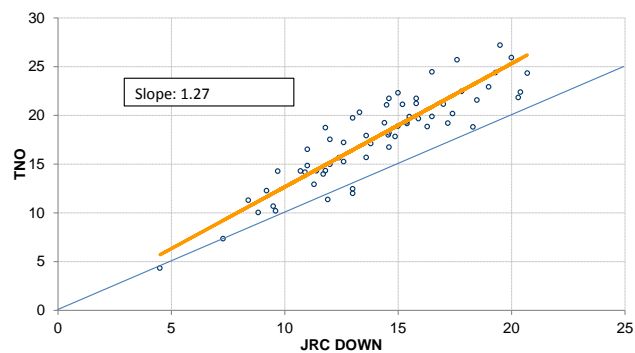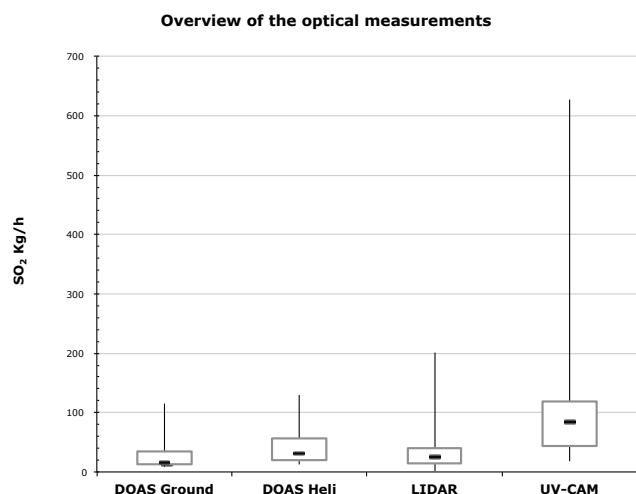
Figure 5. Emission values observed by the different optical measurement techniques during the SIRENAS-R campaign. The bars indicate the maximum and minimum values, the squares indicate the 25th and 75th percentile and the dark line is the median of the measurement distribution.

Figure 6. SO$_2$ emission rate distribution measured by the LIDAR technique. Results of the DOAS technique are plotted by the red line.

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 (Alföldy 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. 5. 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. 5. In addition, the measured emission rates are higher than can be expected of 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 measurements of ship emissions of SO$_2$ performed with the UV camera in this and other campaigns are further discussed by Prata (2014).

The distribution of SO$_2$ emission rates of the ships measured by DOAS and LIDAR is shown in Fig. 6. The figure shows the multimodal distribution of the SO$_2$ emission rate.
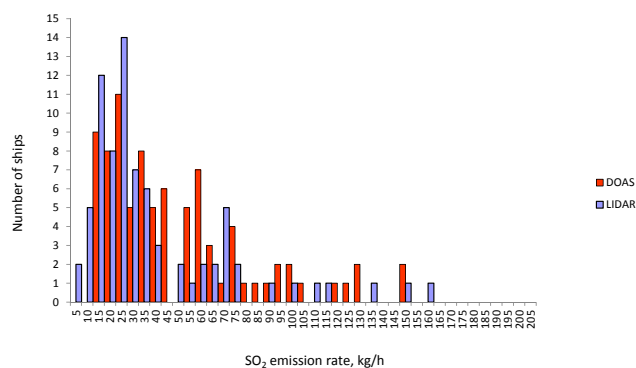
The first, most frequented, mode of the emission rates measured by LIDAR has a maximum at $20\,\mathrm{kg\,h^{-1}}$ emission rate, which is in good agreement with the DOAS results. 78 % of the measured ships are included in this mode. The second mode that contains 15 % of the cases has maximum at $70\,\mathrm{kg\,h^{-1}}$. This value is higher than the second maximum of the DOAS result by 17 %. The remaining 7 % of the ships are distributed between 105, 155 and $205\,\mathrm{kg\,h^{-1}}$ 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 LIDAR and DOAS technique 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 the 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 summarizes the three closest measurements of 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

Table 3. Comparison of SO_2 emission rates in $kg\,h^{-1}$ given by DOAS and LIDAR techniques. In the last column, relative differences are presented (DOAS-LIDAR).

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

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 4 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 that results in different SO_2 emission.

Figure 7 shows the three sequential LIDAR scans of the *Stena Hollandica* during its departure. 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 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. 8, 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.
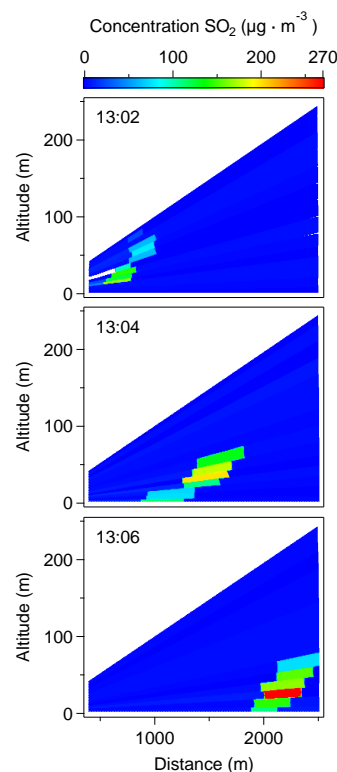
Figure 7. Three sequential LIDAR measurements during the departure of *Stena Hollandica* on the 17 September 2009. The blue area is the area covered by the LIDAR scans.

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 Chalmers using the same system as applied in the harbour (Berg et al., 2010; Mellqvist and Berg, 2010). The
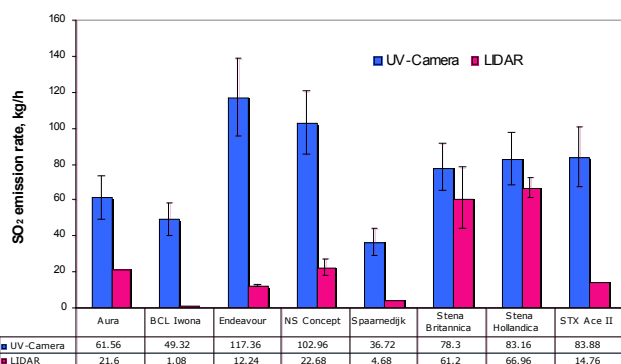
Figure 8. Comparison of LIDAR and UV-camera measurements of the same ships taken at same time and location on the 17 September.

25 measurements on 23, 25 and 27 September of SO_2 and CO_2 gave an average calculated FSC of $(1.13 \pm 0.18)\%$ (m/m), while the 19 measurements of NO and CO_2 gave an average emission factor of $(34 \pm 4)\,\mathrm{g}\,(\mathrm{kg}\,\mathrm{fuel})^{-1}$. Noteworthy is, that NO_2 from the helicopter was not measured and this should add about 20 % to measured NO_x emission factor according to Alföldy et al. (2013).

The values above should be compared to the on board stack measurements of SO_2 and NO_x that yielded $(1.2 \pm 0.1)\%$ (m/m) FSC and $41 \pm 3\,\mathrm{g}\,(\mathrm{kg}\,\mathrm{fuel})^{-1}$, 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 were 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 $(-30 \pm 14)\%$ and $(-41 \pm 11)\%$, respectively, between the measurements and the certified fuel sulphur content for 2 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 onboard *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). Direct comparison of Mobile DOAS to direct
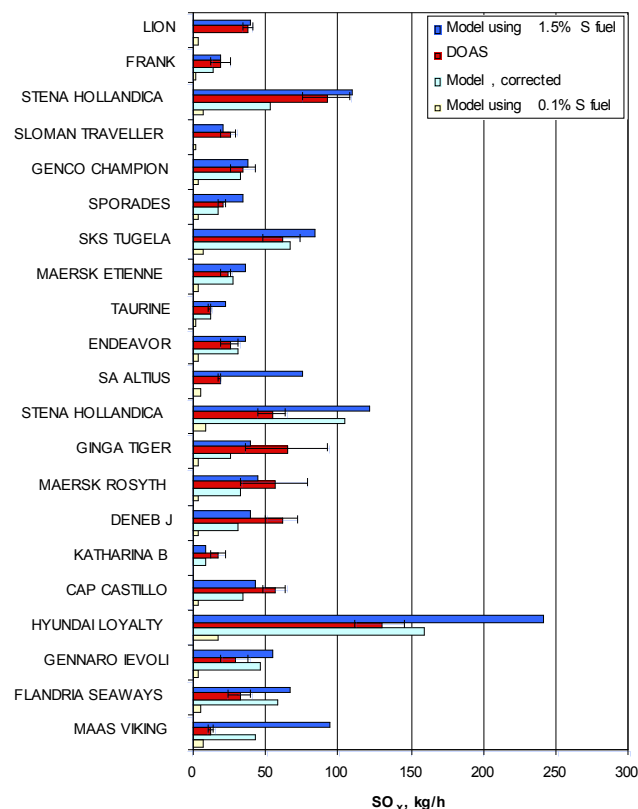

Figure 9. Comparison of DOAS measurements performed by helicopter (in red), the modelled SO_x emission from the targeted vessel (assuming 1.5 % (m/m) fuel sulphur ratio for main engines and 0.5 % (m/m) for auxiliaries, in blue), the modelled emissions corrected with the sniffing measurement (taken sulphur ratio determined by sniffing), and the model results for a future scenario where ships run with 0.1 % (m/m) sulphur fuel.

stack measurements has only been done to a limited extent for measurements of industries; Rivera et al. (2009) did SO_2 measurements on a power plant in Spain for validation purposes and the average determined flux with the DOAS came within 7 % of the values monitored at the plant measurements. Johansson et al. (2014) have compared emission inventories in east Texas to mobile DOAS measurements, with a correspondence within a factor of 2 for large scale industrial conglomorates.

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. 9. 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

Table 4. SO_2 emission rates provided by helicopter-based DOAS measurements between 23 and 27 September 2009. For *Stena Hollandica* (in bold) also on board measurements are available.

Ship name	Time	Velocity, kn	Emission rate, $kg\,h^{-1}$	SD %	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**

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 experimental problems encountered during the campaign were mainly due to the logistical difficulties related to measuring simultaneously on the same air volume by the different techniques ("sniffer" and optical). Furthermore, the fact that most of the measurements took place in a harbour environment caused a relatively high level of "noise" on the measurements due to the many nearby emission sources. It also meant that ships, for what concerns speed and use of auxiliary engines, were often not in the conditions typically found on the open sea. In spite of these difficulties, the results of the campaign allow to draw a series of 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 results of the FSC measurements based on the "sniffer" principle from land ($0.86 \pm 0.23\,\%\,(m/m)$), from stack ($1.2 \pm 0.15\,\%\,(m/m)$) and from a mobile platform: ($1.13 \pm 0.18\,\%\,(m/m)$) showed agreement within the uncertainty limits. 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. 3) 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 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 measurement 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., 2014; Jalkanen et al., 2009).

The UV camera is the cheapest and easiest optical technique; however, it proved to be the least reliable method in the tested configuration. This 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 positioning 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. Furthermore, it can allow to measure ship emissions under steady state conditions outside internal waters which are obviously the typical conditions for the largest part of the ship emissions. As a caveat, it should be mentioned that ship emissions in harbours are likely to be particularly important from a health perspective.

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 suggest 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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