1 Monitoring compliance with sulphur content regulations of

2 shipping fuel by in-situ measurements of ship emissions

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Abstract

In 1997 the International Maritime Organisation (IMO) adopted MARPOL Annex VI to prevent air pollution by shipping emissions. It regulates, among other issues, the sulphur content in shipping fuels, which is transformed into the air pollutant sulphur dioxide (SO₂) during combustion. Within designated Sulphur Emission Control Areas (SECA), the sulphur content was limited to 1 %, and on January 1st, 2015, this limit was further reduced to 0.1 %. Here we present the setup and measurement results of a permanent ship emission monitoring site near Hamburg harbour in the North Sea SECA. Trace gas measurements are conducted with in-situ instruments and a data set from September 2014 to January 2015 is presented. By combining measurements of carbon dioxide (CO₂) and SO₂ with ship position data, it is possible to deduce the sulphur fuel content of individual ships passing the measurement station, and thus, facilitating monitoring compliance of ships with the IMO regulations. While compliance is almost 100 % for the 2014 data, it decreases only very little in 2015 to 95.4 % despite the much stricter limit. We analysed more than 1400 ship plumes in total and for months with favourable conditions up to 40 % of all ships entering and leaving Hamburg harbour could be checked for their sulphur fuel content.

1 Introduction

- 28 Shipping is a major part of the global transportation sector and its importance is still growing.
- 29 According to the United Nations Conference on Trade and Development's Review of

Maritime Transport, in 2013 a total of 9.6 billion tons were transported via ships. This 1 2 corresponds to a growth rate of this sector of 3.8 % per year. (UNCTAD, 2014) Despite being the most efficient and least emitting mode of transportation per ton of cargo compared to land 3 based or airborne transport, shipping emissions nevertheless are a considerable fraction of 4 5 total anthropogenic emissions and have a significant impact on air quality of coastal areas. 70 6 % of shipping emissions are produced within 400 km off the coasts (Corbett et al., 1999) and 7 can cause severe health and environment problems to these regions (Corbett et al., 2007, 8 Eyring et al., 2010). 9 The International Maritime Organisation (IMO), an agency of the UN with 171 Member States, has decided on measures to limit the impact of shipping emissions by adopting on the 10 MARPOL Annex VI protocol in 1997. One part of these measures and the one, on which this 11 12 study focuses, is the reduction of sulphur in ship fuel in order to reduce sulphur dioxide (SO₂) 13 emissions. When oxidised, SO₂ forms small sulphate particles, which have an effect on cloud properties and change their reflectivity and lifetime (Lauer et al., 2007). SO₂ emissions by 14 15 ships lead to an enhanced sulphate concentration of 10 - 50 % in coastal areas (Matthias et al., 2010), which increases acidification by acid rain (Endresen et. al., 2003). Gaseous SO₂ as 16 17 well as sulphate particles have health effects on humans, when inhaled. SO₂ is produced during the combustion process by burning sulphur that is contained in the fuel. Ship engines 18 19 have been developed to be able to burn Heavy Fuel Oils (HFO) that have a very high sulphur 20 content of up to several percent and are basically a waste product of oil refineries and thus 21 very cheap. 22 The IMO regulations concerning sulphur content came into force in 2005 and were revised in 23 2008, the revision came into force in 2010. On all oceans worldwide, the allowed sulphur 24 content in HFOs was capped at 4.5 %, and after 2012 this limit was reduced to 3.5 %. In 25

The IMO regulations concerning sulphur content came into force in 2005 and were revised in 2008, the revision came into force in 2010. On all oceans worldwide, the allowed sulphur content in HFOs was capped at 4.5 %, and after 2012 this limit was reduced to 3.5 %. In addition, so called "Sulphur Emission Control Areas" (SECA) were established with an even further reduced sulphur limit. One SECA is along the North American Coast, and another one comprises the Baltic Sea and the North Sea up to the Shetland Islands and to the western entrance of the English Channel. Within these SECAs the sulphur limit was initially set to 1.5 %, which was reduced to 1.0 % in 2010 and has now reached its current reduction step in January 2015 with a limit of 0.1 %.

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While the 1 % limit could still be met with sulphur reduced HFO, the new regulation forces ships to either use more expensive alternatives such as Marine Gas Oil (MGO), or Ultra low

sulphur HFO, or consider reconstruction to enable the use of alternative fuel such as liquefied natural gas (LNG) or methanol. As an alternative technology, the operation of exhaust gas cleaning systems (scrubbers) is also permitted, as long as it provides the same level of protection against sulphur dioxide emissions as the use of low sulphur fuel. These alternative options have been deployed to some ships and first studies have documented their effectiveness and economic efficiency (Reynolds, 2011, Jiang et al., 2014), but they are still under development and not very widespread, and for the vast majority of ships the only option to meet the regulations is to use desulphurised fuel.

With the regulations in place, the question remains on how to efficiently verify compliance of the ships. To date, compliance is checked by inspection authorities who enter ships at berth, review fuel log books and fuel quality certificates and, when suspicion was raised, take a fuel sample to be analysed at certified laboratories. With the results of these analyses, it is possible to verify compliance and if needed, take legal actions. However, these controls can check just a minor number of ships. It is also not possible to evaluate the performance and compliance of scrubber technology by sulphur prediction in bunker oil samples which would be problematic if this method becomes more popular and common in future. Another problem is to control ship fuel of ships on the open sea.

For these reasons, several studies have suggested the implementation of air quality measurement systems especially aiming at the surveillance of ship emissions. One simple but efficient method is direct and simultaneous measurements of pollution trace gases with in-situ instruments. These instruments can quite easily be adapted to measurement conditions on airplanes, research vessels and trucks and have been used in a variety of campaigns in recent years (Sinha et al., 2003, Schlager et al., 2006, Agrawal et al., 2009, Williams et al., 2009, Diesch et al., 2013, Balzani Lööv et al. 2014, Beecken et al., 2014b). Based on the experience from those studies, we have established a measurement station near the harbour of Hamburg to monitor ship emissions, to estimate sulphur contents of fuel on board of passing individual ships. Our ship emissions dataset from September 2014 to January 2015 documents the quality of implementation of the MARPOL VI regulation with respect to compliant sulphur content in shipping fuel used in SECAs and follows the recent strong tightening of the regulation on January 1st 2015.

2 Measurement Site and Methods

- 2 The measurements reported here were conducted as part of the Mesmart project, a
- 3 cooperation between the University of Bremen and the German Federal Maritime and
- 4 Hydrographic Agency.

2.1 Measurement Site

- 6 Hamburg harbour is the third largest harbour in Europe and the 14th largest worldwide. In
- 7 2014, it had a 20-foot standard container throughput of 9.7 billion containers according to
- 8 Hamburg port statistics. On average there are 800 calls per month, of which more than half
- 9 are container vessels, and the other half consists mainly of Reefer vessels, tankers and bulk
- 10 carriers. The harbour is located at the mouth of the river Elbe about 110 km inland, see Figure
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- 12 Measurements were conducted next to the river Elbe in the town of Wedel, which is near
- 13 Hamburg, on the property and with the support of the Waterways and Shipping Office
- Hamburg. The instruments were set up right at the northern banks of the Elbe, with an
- approximate line of sight distance to ships leaving and entering Hamburg harbour of 0.3 and
- 16 0.5 km respectively. The average main wind direction at this location is with a southerly
- 17 component, so that most of the time within the measurement period, the exhaust plumes of the
- ships were blown to the instruments. The area in the main wind direction south of the
- measurement station and the Elbe River is rural and sparsely populated with no significant
- sources of air pollution. Thus the location of the monitoring site is optimal for relatively low
- background concentrations of nitrogen oxides (NO_x) and SO₂.

2.2 Instrumentation

- 23 The concentrations of SO₂, NO_x, CO₂, and Ozone (O₃) were measured continuously with
- 24 individual instruments, which are combined in a temperature stabilised box to ensure stable
- 25 measurement conditions and at the same time provide a compact and transportable set-up.
- Data are stored in an integrated data logger with the time resolution of one minute. Despite
- 27 different time resolutions of the instruments, we used data normalised to one minute, which is
- sufficient for the analysis of emission events with a duration in the order of several minutes.
- NO_x, SO₂ and O₃ were measured with instruments from the Horiba AP-370 series, which are
- 30 certified instruments according to EU directives (EN14211 for NO_x, EN 14212 for SO₂, and

- 1 EN14625 for O₃) used by German authorities for standard air pollution measurements. CO₂
- 2 was measured with a Licor 840A analyser. The O₃ measurements were not used for this study
- 3 and are just mentioned for completeness.
- 4 SO₂: The Horiba APSA-370 is based on the UV-fluorescence method, using the excitation of
- 5 SO₂ molecules by UV light and measuring the fluorescence which is a function of SO₂
- 6 concentration. The response time of the instrument is specified to be less than 120 s.
- 7 Calibration was carried out with a standard gas mixture from Air Liquide with a concentration
- 8 of 99.7 ppb SO₂ with an accuracy of 5 %. In addition, a daily control was obtained by the
- 9 measurement of zero gas produced with a scrubber, and span gas from an internal permeation
- source with 175 ppb SO₂. There is a NO cross sensitivity for SO₂ which gives for 0.8 % of the
- NO signal an SO₂ signal. We have determined this value of 0.8 % via a set of 6 calibration
- measurements of different NO concentration between 100 and 470 ppb.
- 13 NO_x: The Horiba APNA-370 measures the chemiluminescence of NO molecules reacting
- 14 with O₃. To obtain information about the NO₂ concentration, the device contains a
- deoxidation converter to transfer NO₂ molecules to NO. The NO₂ concentration is calculated
- by the difference of total NO_x, representing NO + NO₂, and NO without conversion. The
- 17 response time for measurement of both gases is 90 s. The instrument is calibrated with an Air
- Liquide standard gas mixture with a concentration of 216.0 ppb NO and an accuracy of 5 %.
- 19 A daily control with scrubber produced zero gas and a NO₂ span gas of 105 ppb is also
- 20 implemented.
- 21 CO₂: The Licor 840A is a non-dispersive infrared gas analyser. It has a response time of 1 s
- and was calibrated with two Air Liquide standard gas mixtures with 306.6 ppm and 990.0
- ppm CO₂ with an accuracy of 2 %.
- 24 The trace gas measurements were complemented with measurements of wind, temperature, air
- 25 pressure and precipitation by a compact weather station (Lufft WS600). With an AIS
- 26 (Automatic Identification System) receiver the information transmitted by passing ships was
- 27 collected, which includes identification number, name and type of the ship as well as position,
- 28 course, and speed.

3 Data analysis

- 30 To obtain the sulphur content of ship fuel in use, the enhancement of SO₂ and CO₂ in
- 31 measurements affected by exhaust gases is measured, and the ratio of these SO₂ and CO₂

1 peaks is used to calculate the fuel sulphur content. The combination of the trace gas peak

2 time, the wind direction, and the AIS information enables the identification of the peak related

3 ship.

When wind conditions are favourable for measurements, the exhaust plumes of ships passing 4 5 the instrument leave a distinctive enhancement of the measured component against 6 background concentrations. Since this enhancement is most significant in NO measurements, 7 and NO is an indicator for recent combustion processes, these NO peaks are used to identify 8 the time stamp of a ship emission event. For these time stamps peaks in CO₂ are then identified, which is more complicated because background concentrations are larger and more 9 10 variable due to the surrounding vegetation. Background signals for each gas are determined 11 via a customized running mean filter. Only for those events for which there was a significant 12 CO₂ peak and a clearly determinable background, are the SO₂ signals analysed. For all peaks the individual peak area above the background concentration is determined. This accounts for 13 14 the difference in peak width for each gas due to different time resolutions of the respective 15 instruments. The peak area value of the SO₂ peaks is corrected with 0.8 % of the peak area value of the NO peaks to account for the cross sensitivity. With the assumption that fuel 16 contains 87±1.5 % carbon (Cooper et al., 2003) and 100 % of the sulphur and the carbon 17 18 content of the fuel are emitted as SO₂ and CO₂ respectively, the sulphur fuel content (SFC) 19 mass percent can be calculated as follows:

$$SFC[\%] = \frac{S[kg]}{fuel[kg]}$$

$$20 = \frac{SO_2[ppm] \cdot A(S)}{CO_2[ppm] \cdot A(C)} \cdot 87[\%]$$

$$= \frac{SO_2[ppb]}{CO_2[ppm]} \cdot 0.232[\%]$$

$$(1)$$

21 where A(S) is the atomic weight of sulphur and A(C) of carbon. Using this formula, it is

relatively simple to calculate the sulphur content for each set of peaks. For a discussion about

23 the uncertainties of this formula see section 3.1.

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The second part of the data analysis is the attribution of the identified emission events to

individual passing ships. Within 30 minutes before each event, which is characterised by the

time the emissions arrive at the instruments, the AIS data is analysed for ship positions close

to the measurement site. In combination with wind information this yields in most cases the

- 1 identification of the individual ships having caused the emission. The time the exhaust plume
- 2 travels from being emitted to being analysed is about 2 to 10 minutes dependent on wind
- 3 speed and direction. However, there are events in which there are two or more ships too close
- 4 to each other, or where no AIS signal was received, such that no single ship can be associated
- 5 to the signal. These events are excluded from the data set.

3.1 Uncertainties

- 7 There are several aspects that influence the accuracy of the calculated values of the sulphur
- 8 content for each ship. The SFC-formula (1) assumes a 100 % conversion from sulphur to SO₂
- 9 during combustion, which is only true for an idealised combustion process. There is a range
- of uncertainty with respect to the amounts of sulphur oxidised and released as particles.
- 11 Studies found that there could be an underestimation of the sulphur fuel content between 1 -
- 12 19 % from assuming complete conversion (Schlager et al., 2006, Agrawal et al., 2008,
- 13 Moldanova et al., 2009, Balzani Lööv et al., 2014).
- 14 The uncertainty or sum of systematic and random error of our measurements is determined
- from a combination of the calibration uncertainty and the uncertainty resulting from the signal
- 16 to noise ratio (SNR). CO₂ values with a SNR of less than five are excluded from the data,
- which leads to an upper limit uncertainty of 20 %. However, the majority of CO₂ values has
- an uncertainty of around 10 %. For SO₂ we do not exclude data with a low SNR because these
- are the zero sulphur content cases. The SNR of SO₂ data for a sulphur content of around 0.1
- 20 % is 10 or better, with a decrease for lower sulphur content values. For an SNR below 5 we
- 21 consider the SO₂ signal as zero. This is only important for the January 2015 data, since the
- measured SO₂ concentrations in 2015 are much lower than for the 2014 data. This is shown in
- Figure 2 as a comparison between one week in December 2014 and one week in January 2015
- 24 with similar weather conditions. While no reduction in NO values can be observed, there is a
- 25 large reduction in SO₂ values as expected.
- 26 All uncertainties added up with the root of sum of squares method, this gives us an
- 27 uncertainty range for the sulphur content calculations of 15 30 %.

4 Results

- 2 Using the method described above we were able to identify 824 ship plumes of 474 individual
- 3 ships within the months of September, November and December 2014. Unfortunately no data
- 4 are available in October due to instrumentation problems. This data set is the so called pre-
- 5 regulation-change set, where the regulatory allowed sulphur fuel content for the ships of is 1.0
- 6 %. The January 2015 data set consists of 589 ship plumes of 374 individual ships, which since
- 7 the 1st of January 2015 have to comply with the new 0.1 % rule. As shown in Figure 3, the
- 8 difference between these two data sets is remarkably obvious.
- 9 In the pre-regulation-change data set, 99.6 % of all ships complied with the 1 % sulphur limit
- 10 with respect to the measurement uncertainty. This is better than previously published
- 11 compliance rates of 85 % of 174 ship plumes (Beecken et al, 2014a), although it should be
- 12 noted that this study did not describe the uncertainty considerations and was measured by
- airplane on the open sea. The latter may imply that compliance might not be so high when no
- direct control is possible. Compliance rates at other locations for land based measurements
- show values of 90 % of 255 ship plumes and 97 % of 211 ship plumes (Beecken et al, 2014b).
- 16 However, a study of Diesch et al., 2013, that describes measurements with a mobile
- 17 laboratory along the Elbe River near our measurement site, found for 139 ship plumes a
- 18 compliance of nearly 100 %. This could possibly be credited to the special location of
- Hamburg harbour where ships have to go up the Elbe for more than 100 km.
- 20 In accordance with the practice in use that fuel samples analysed in laboratories are
- 21 considered as exceeding the 0.1 % sulphur limit in a legally binding way above the value of
- 22 0.149 %, we suggest to use a corresponding value of 0.15 % as a limit value for discussing the
- compliance of the ships in our January 2015 data set. This is in consistence with the formerly
- stated measurement uncertainties. In Figure 4, a more detailed graph of the January 2015 data
- is shown. The red line shows the 0.1 % limit with the shaded area indicating a conservative 30
- 26 % measurement uncertainty. The blue line indicates the suggested 0.15 % limit for
- compliance discussion. Of all the ships measured in January 95.4 % were complying with the
- 28 new regulation. There are preliminary results for first SFC measurements in January 2015
- 29 presented in Beecken, 2015, which are comparable with our measurements, although with
- 30 slightly higher uncertainty and lower compliance rates.
- 31 Color-coded in the Figures 3 and 4 are the lengths of the ships in 50 m size steps. Even before
- 32 the regulation change ships smaller than 100 m did not use fuel with sulphur values higher

- 1 than 0.2 %, most likely because their engines cannot process such fuels or storage capacity for
- 2 two different kinds of fuels is not available. After the regulation change, those smaller ships
- 3 still do not use the fuels that reach up to the allowed 0.1 % limit. If one considers only those
- 4 ships larger than 100 m that could choose which fuel to use and had to change their way of
- 5 operation, the compliance drops to 93 %.
- 6 The number of ships that can be detected for compliance depends strongly on the wind
- 7 conditions. Assuming the average number of calls in Hamburg harbour according to Hamburg
- 8 port statistics of 800 ships per month means that 1600 emission events happen at our
- 9 measurement station of ships on their way in and out of the harbour. For months with good
- wind conditions like December 2014 and January 2015, we can detect about 30-40 % of those
- events, for month with unfavourable wind conditions like November 2014, this value drops to
- 12 less than 10 %.

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5 Conclusions

- 15 In this study, we have used the method of in-situ measurements of trace gases to implement a
- system to monitor compliance of ships with sulphur fuel content regulations. This has been
- 17 discussed and suggested before (Balzani Lööv et al., 2014). Here we present a suitable
- 18 location for permanent stationary measurements near Hamburg harbour, one of the largest
- 19 harbours in Europe, and demonstrate a measurement approach that successfully characterises
- 20 emissions from passing ships. We describe the method used to identify ship emission events
- and the corresponding ships and present a large data set on fuel usage of ships of altogether
- 22 1413 analysed ship plumes. This includes the one of the first data sets, after the most recent
- 23 regulation change in the North Sea SECA, where fuel sulphur content limits were reduced
- 24 from 1 % to 0.1 % on January 1st, 2015.
- Our data shows that the vast majority (95.4 %) of all the ships we have measured are indeed
- complying with the new regulation of 0.1 % sulphur fuel content. Compliance has dropped
- slightly compared to the value of more than 99 % observed for the 1 % sulphur limit in fall
- 28 2014. It should be noted that the global oil price and thus MGO costs for the needed sulphur
- 29 quality in January 2015 was the lowest since 2009, which could have a positive influence on
- 30 the acceptance of the new regulation.

- 1 With the described method it is possible to easily and reliably identify those ships that do not
- 2 comply. It is possible to check 10 40 % of all ships entering and leaving the harbour,
- 3 depending on wind conditions. This should be interesting to government agencies in charge of
- 4 the control of the SECAs.

6 Acknowledgements

- 7 The research project, which facilitated the reported study, was funded in part by the German
- 8 Federal Maritime and Hydrographic Agency and the University of Bremen. The authors thank
- 9 the Waterways and Shipping Office Hamburg and the Institute for Hygiene and Environment,
- 10 Hamburg, for their help and support.

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Figure 1: Location of the measurement station on the northern bank of the river Elbe, near Hamburg harbour. On the right: picture of instrument box. Map source: OpenStreetMap.

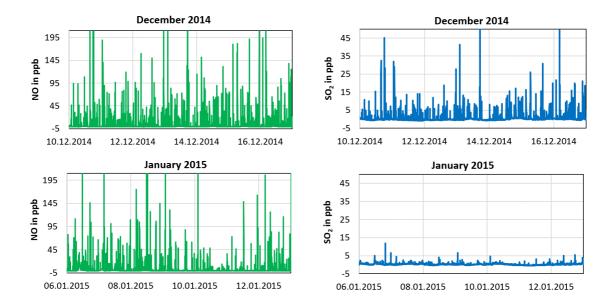


Figure 2: Comparison of absolute NO and SO_2 volume mixing ratio values measured over two weeks, one week in December 2014 and one in January 2015 with comparable wind conditions. Each peak belongs to one emission plume of an individual ship. The reduction in SO_2 in 2015 is obvious, while for NO no reduction can be observed.

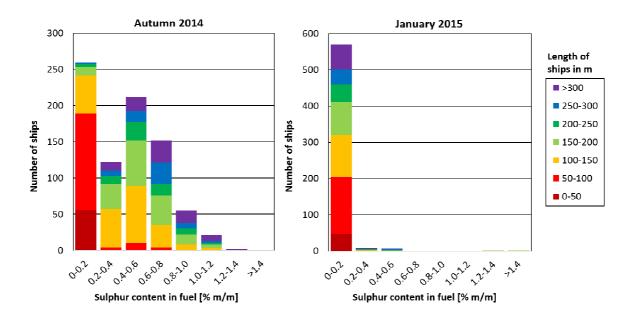


Figure 3. Sulphur fuel content in autumn 2014, and in January 2015, after the change of fuel regulations. Colour-coded is the length of the ships that have been analysed. While in 2014 only small ships had fuel sulphur contents below 0.2%, nearly all ships fell into this category in January 2015.

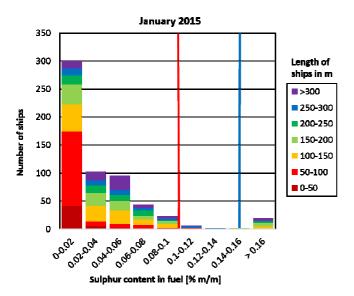


Figure 4: Detailed view of the January 2015 data set. Colour-coded is the length of the ships, the red line indicates the 0.1 % limit with the shaded area representing the upper limit uncertainty of 30 %. The blue line indicates the suggested limit of 0.15 % for flagging ships as exceeding the allowed sulphur fuel content limit.