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Interactive comment on “Monitoring shipping emissions in the German Bight using MAX-DOAS measurements” by André Seyler et al.

Anonymous Referee #2

Received and published: 11 April 2017

General comment: This paper describes a 3 year series of multi axis DOAS measurements carried out from the German island Neuwerk, just south of the entry to the river Elbe. This is in the main ship channel of the port of Hamburg and the main aim of the measurements was to study these by observing UV and visible light horizontally towards the ship channel. The paper is well written, with good language and instructive graphs. The paper is a nice combination of measurements methodology and results paper. It shows the methodology to measure mixing ratios in a coastal places, together with ship plume measurements and some results about the effect of new IMO legislation. However, the OBJECTIVE and AIM should be declared more clearly in the text. The paper is also rather long, and I would recommend to shorten it, by removing sections which are outside the main scope of the paper. Forinstance merging and shortening sect 4.5 and 4.6 corresponding to mixing ratio measurements and comparisons. All in all, I believe the paper should be published, with some minor improvements, based on answering my specific comments below:

First, we would like to thank Anonymous Referee #2 for his/her helpful comments. Below, we reply point-by-point to the specific comments . As far as possible, we have considered the suggestions in the revised manuscript.
We tried to shorten the manuscript and omitted unnecessarily repeated information. Section 4.5 was shortened and two plots have been deleted and the remaining ones merged to a common figure. Also 40% of the pieplots in Figure 18 have been removed. At several places paragraphs have been rewritten to make the text more precise and shorter.

Specific comments:

Row 71, p 2: It is claimed that 25% of the NOx emerges as NO2 from the stack, but usually 10% is assumed from fluegas stacks; please give more details: I assume you also assume some titration?

The relevant text passage (Row 71) reads: "The emitted NO_x comprises mainly NO, with less than 25% of NO_x being emitted as NO_2 (Alföldy et al., 2013).” We are referring here to results from a study of Alföldy et al. from the year 2013[1]. In this study, the chemical composition of the plumes of 497 seagoing ships was measured in the port of Rotterdam in September 2008 and a statistical evaluation of emission factors was provided. For the scope of our study, especially the results shown in Figure 17 are interesting:

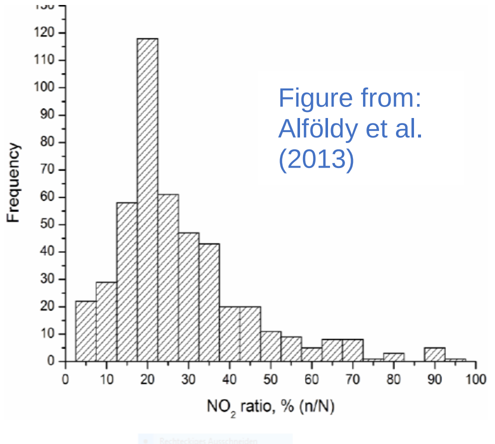

Figure from: Alföldy et al. (2013)

Fig. 17. Distribution of the NO_2/NO_X molar ratio among the studied ships. The total molar ratio range was divided into 19 bins. Frequen-

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[1] Alföldy, B., Lööv, J. B., Lagler, F., Mellqvist, J., Berg, N., Beecken, J., … Hjorth, J. (2013). Measurements of air pollution emission factors for marine transportation in SECA. *Atmospheric Measurement Techniques*, *6*(7), 1777–1791. http://doi.org/10.5194/amt-6-1777-2013

The conclusion of the authors:

“The molar NO2-to-NOx emission ratio, calculated from the mixing ratios of the two components in the plume (%, n/N), is presented in Fig. 17. As can be seen, nitrogen oxides are mostly emitted as NO, the ratio of NO_2 emission is less than 25% at the majority of the ships.”

In Row 71 we are simply referring to this result as background knowledge on the NO/NO_2 ratio in ship plumes, being important for our own study. We are not doing any assumptions here.

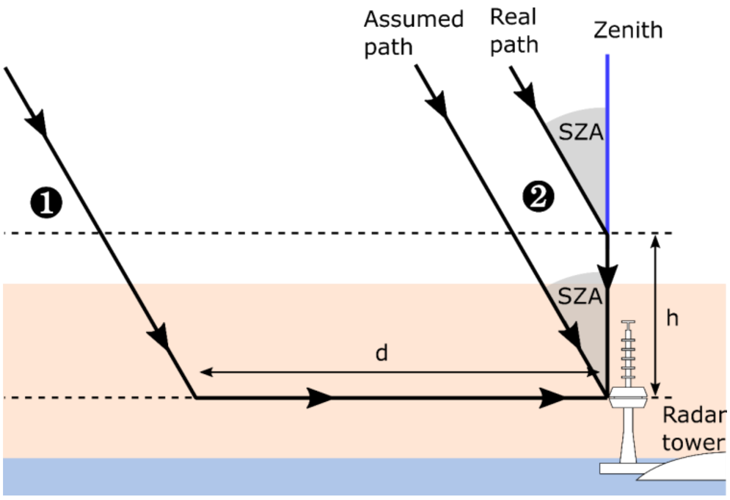
Row 278, p 9: IN the equation do you fit differential absorption cross sections or the absolute ones? Since you are using prime I assume you mean the differential ones; IN row 336 I however get the impression that you use the absolute ones.

We are fitting the differential absorption cross sections together with a low order polynomial to the measured optical depth. We have changed the sentence to make this point more clear:

“Multiple *(differential)* trace gas absorption cross sections obtained from laboratory measurements, as well as a low-order polynomial, are then fitted simultaneously to the optical depth.”

Row 311, p 10: It is claimed that the vertical paths cancels out between path 1 and 2 in Fig 5; I agree with the stratospheric portion but for the tropospheric part there should be a cos (SZA) difference, even if NO2 is homogenously distributed in the troposphere?

That is a good objection. It is in fact true that this is only an assumption. To make things more clear we show a more detailed sketch below. The presented approach of using the O_4 column to estimate the effective horizontal light path length assumes single-scattering geometry. For the vertical paths in a layer of homogenously distributed NO_2 in the troposphere, like it is shown in the first sketch, to cancel out, the reference measurement must have the “assumed path”. This means, it is assumed that the scattering point for the zenith reference is at the altitude of the instrument. In reality, of course, this is not the case. The real scattering altitude for light measured in zenith direction will be in an effective scattering height *h*, as it is shown in the sketch.



As can be seen from the figure, this leads to an underestimation of NO_2 in the reference and therefore to an overestimation of the NO_2 concentration. However, not only the NO_2 is overestimated, but also the O_4 path length is overestimated in a similar way.

Gomez et al. (2014)[2], applying this approach to MAX-DOAS measurements from a high mountain site, did a thorough error analysis in Section 3.2 of their publication. They showed that first, this scattering height *h* is nearly constant up to an SZA of 75°. Secondly, the path error depends only on the vertical distribution of the NO_2 (or SO_2) and on the differences in air mass factors (AMF) of NO_2 and O_4. By assuming a homogeneous layer, like it is shown in the sketch, the error comes from differences in the

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[2] Gomez, L., Navarro-Comas, M., Puentedura, O., Gonzalez, Y., Cuevas, E., & Gil-Ojeda, M. (2014). Long-path averaged mixing ratios of O3 and NO2 in the free troposphere from mountain MAX-DOAS. *Atmospheric Measurement Techniques*, *7*(10), 3373–3386. http://doi.org/10.5194/amt-7-3373-2014

AMF. The SZA dependence of the error of the approach has been plotted by the authors in the following figure:

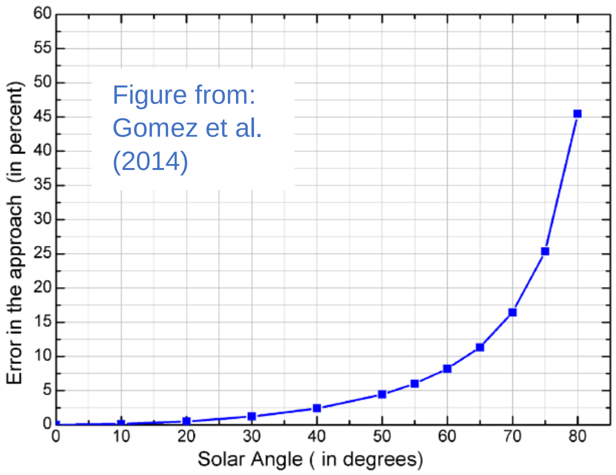


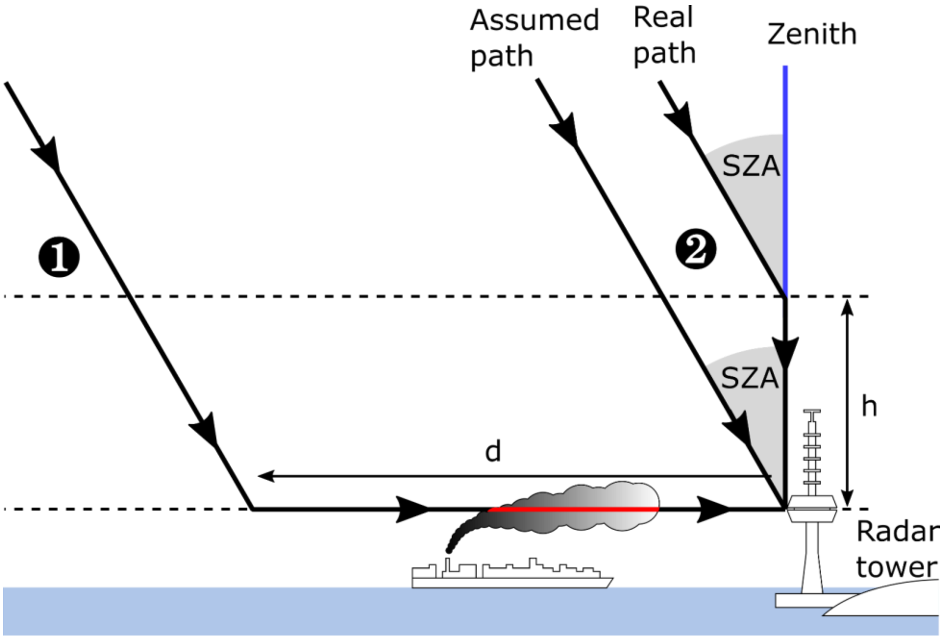
Figure from: Gomez et al. (2014)

Figure 5. Estimated error of the MGA versus the SZA.

As can be seen from the figure, the error of the approach is less than 10 percent for typical daytime SZAs.

To keep the approach simple, this amount of uncertainty has to be accepted.

More important for this study is of course the measurement of ship emission plumes. When the wind is coming from the open North Sea, there is negligible background NO_2 and SO_2 in the lower troposphere. When a ship plume is in the horizontal path of the off-axis measurement, like it is sketched below, the difference between assumed and real reference path is irrelevant, introducing no additional error.



Row 387, p 13: Is it assumed that the wavelength difference in O4 signal is linear; if so what are the uncertainties involved?

We changed our method from a simple linear extrapolated scaling factor to using the empirically determined (from RTM simulations) formula from Wang et al. (2014)[3] to improve this source of uncertainty:

$$L_{310} = 0.136 + 0.897 \times L_{360} - 0.023 \times L_{360}^2. \qquad (6)$$

Which was determined from RTM simulations for a variety of aerosol conditions, which results are shown in the following figure:

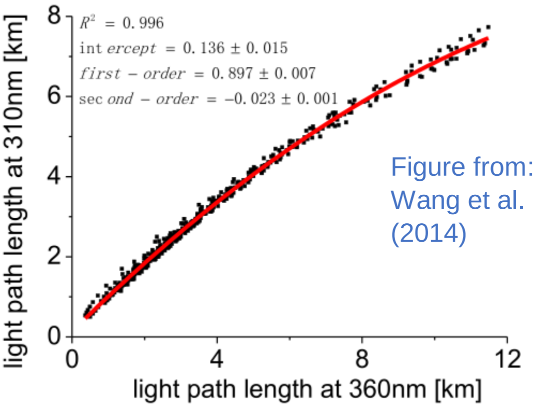


Figure from: Wang et al. (2014)

Figure 1. Scatter plot of light path lengths at 310 nm against light path lengths at 360 nm for 60 aerosol scenarios and combinations of three SZAs and RAAs. The statistical parameters derived from a second-order polynomial fitted to the simulation results are also shown.

Row 406, p 14: It is claimed that the conditions at the Neuwerk radar tower is similar to measurements from high mountains; please motivate better.

This section was completely rewritten to make our motivation clearer:

"This approach has been applied successfully by Sinreich et al. (2013) and Wang et al. (2014b) for measurements in urban polluted air masses over Mexico City and the city of Hefei (China) using MAXDOAS measurements in 1° and 3° (Sinreich et al., 2013) and only in 1° elevation (Wang et al., 2014b), respectively. Gomez et al. (2014) applyed this approach to measurements on a high mountain site at the Izana Atmospheric observatory on Tenerife (Canary Islands), Schreier et al. (2016) at Zugspitze (Germany) and Pico Espejo (Venezuela). Due to the low aerosol amounts in such heights the latter two studies applied the approach without using correction factors. The fact that our instrument is located on a radar tower in a height of about 30m above totally at surroundings (the German Wadden Sea) allows an unblocked view to the horizon in all feasible azimuthal viewing directions. This led to theidea of trying to apply this approach to our shipping emission measurements on Neuwerk."

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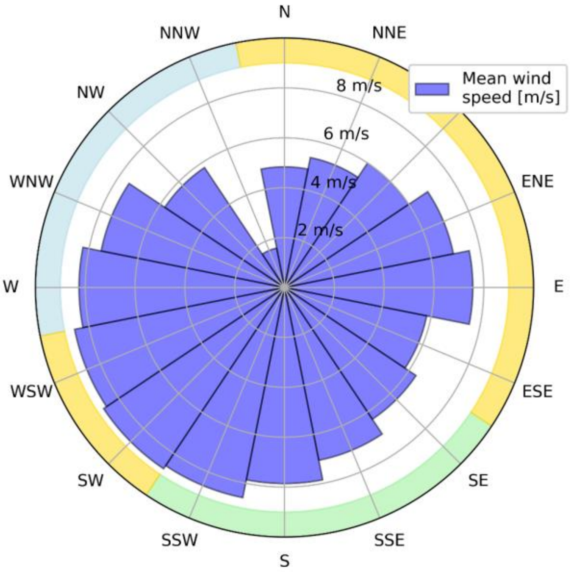
[3] Wang, Y., Li, A., Xie, P. H., Wagner, T., Chen, H., Liu, W. Q., & Liu, J. G. (2014). A rapid method to derive horizontal distributions of trace gases and aerosols near the surface using multi-axis differential optical absorption spectroscopy. *Atmospheric Measurement Techniques*, *7*(6), 1663–1680. https://doi.org/10.5194/amt-7-1663-2014

Eq 4, p 13: It is difficult to follow how you get the expression in eq 4.

We deleted this equation and focus now on the approach which was actually applied to the data (the O4-scaling method).

Row 464 p 16: On this place, and some others, its is claimed that the differential slant columns are higher for SSE and ESE and (more elevated). But part of this should be wind speed effect since I would imagine that the wind speed will be higher from the sea and this will dilute the slant columns more. Has this been investigated ?

We have looked into this: The following polar plot shows the mean wind speed depending on wind direction. Wind speeds from the land sector (light green) are not substantially lower than wind speeds from the open Sea sector (light blue), so such a dependence has not been observed.



Row 470 p 16: Graph 7 is not totally clear. If I understand right the plot correspond to overlayed windroses for different elevation angles rather than that the area of each color represents the wind rose information. I interpreted the latter and I think this should be clarified forinstance in the figure text.

The former is correct. We changed the figure caption to make it clearer:

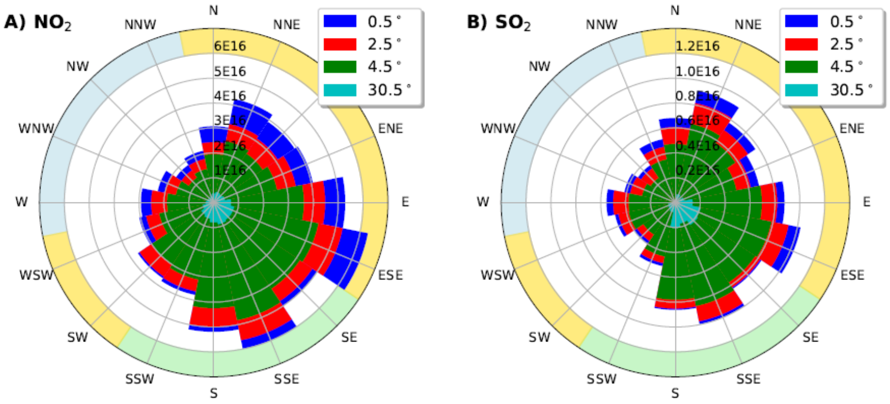
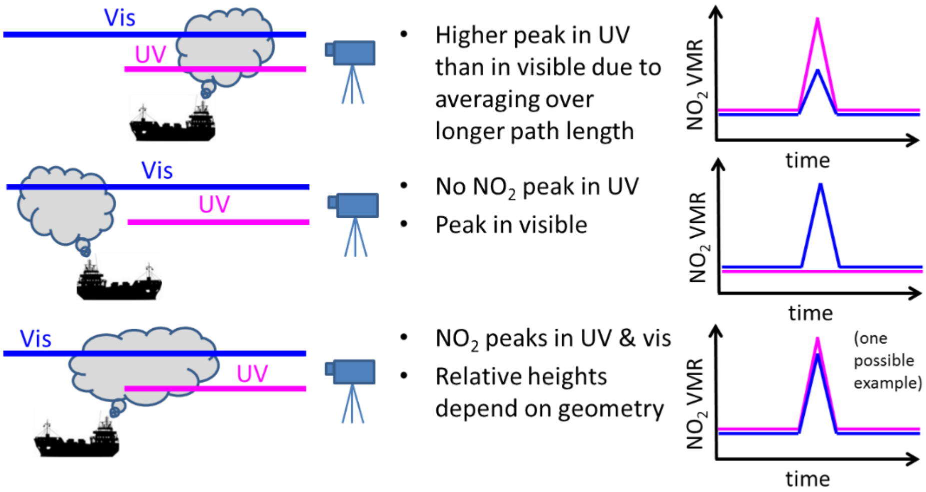


Figure 7: Overlayed wind roses for different elevation angles showing the wind direction distribution of the UV NO_2 (A) and SO_2 (B) differential slant column densities measured in the main viewing direction in 0.5°, 2.5°, 4.5° and 30.5° elevation in the years 2013 and 2014. The wind roses are plotted on top of each other, i.e. the highest values were measured in the lowest elevation angle (blue bars). The colored sectors show directions with wind from land (green), open North Sea (blue) and mixed origin (yellow).

Row 500 p 17: You here discuss the results in Fig 8. The differences in the UV and visible are explained from the penetration length, but should the Visible not in general be higher since it gives the chance of penetrating plumes further away, rather than the opposite which appears to be the case for all plumes here? You explain that the UV should be stronger for close by plumes since a higher fraction of the photons are then affected by absorption. Is is not so that the O4 can only simulate slow variations? Please elaborate..

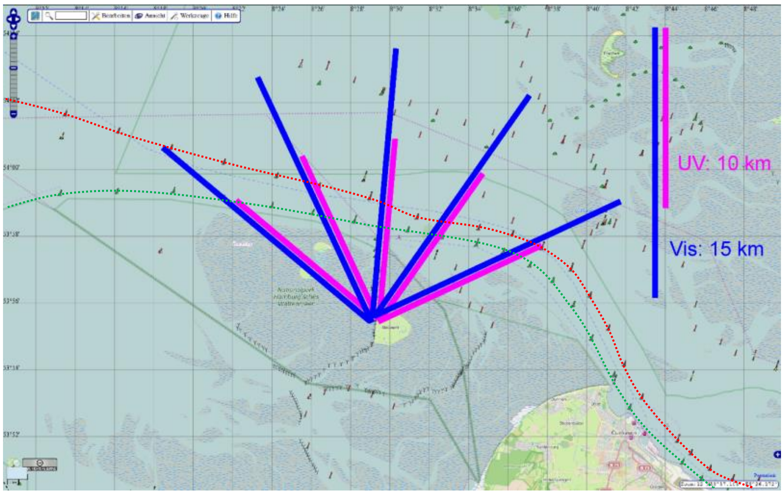
The relevant point here is the position of the ships relative to the measurement site. On average, the measured NO2 slant column densities are higher in the visible than in the UV due to the longer horizontal light path. However, the data shown in Figure 8 are path-averaged mean volume mixing ratios. Typical path lengths are 10 km in the UV and 15 km in the visible. If the measured ship exhaust plume is closer to the instrument than 10 km, which is usually the case for all northerly wind directions since the ships pass the instrument in a distance of 6 to 7 km, the path averaged volume mixing ratio on the visible path will be lower due to the longer averaging distance. We have included two sketches below to make things clearer:



- Higher peak in UV than in visible due to averaging over longer path length

- No NO_2 peak in UV
- Peak in visible

- NO_2 peaks in UV & vis
- Relative heights depend on geometry



Map showing the azimuthal viewing directions and the typical averaging path lengths. The green and red dotted lines highlight the boundaries (line of buoys) of the main shipping lane.

Row 614 p 25: You claim that fig 12/fig 13 shows good agreement between MAX DOAS and in situ, but in my mind this is the case for Fig 13 but not for fig 12, where there appears to be rather big difference in he averages of the two sensors with factor 2-3?

In this Section we do not claim a good agreement in absolute values (which due to the characteristics of both measurement techniques and different measurement geometries is also not expected), but a good agreement in the shape (or course) of the curves. This means that apart from a scaling factor, the day-to-day trends in both time series of daily means are well reproduced.

Row 665 p 27: You suddenly refer to fig 20, without having mentioned fig 17-19 yet in the text. You should consider reordering.

This reference has been deleted.

Row 891 p 35: As concluded here and discussed in section 4.9, the ratio of SO2/NO2 gives an indication of sulfur fuel content in ship plumes. Are you aware that SO2/NO2 ratio measurements from airborne DOAS is used operationally since 2015 by Beecken and Mellqvist (Chalmers University) in the CompMon project and surveillance around Denmark and that this has been presented on several official workshops last year?

Thank you very much for that hint. The methodology presented in the CompMon Report "Best Practices Airborne MARPOL Annex VI Monitoring" (Van Roy, 2016)[4] is very interesting. We added the following paragraph to the chapter on SO_2/NO_2 ratios:

"By comparing SO_2 to NO2 ratios from different ships it is possible to roughly distinguish whether a ship is using fuel with high or low sulfur content (giving a high or low SO_2 to NO_2 ratio). *Beecken and Mellqvist from Chalmers University (Sweden) use this relationship for airborne DOAS measurements of ship exhaust plumes on an operational basis in the CompMon project (Compliance monitoring pilot for MARPOL Annex VI) (Van Roy, 2016). Following the ships and measuring across the stack gas plume they can discriminate between low (0.1 %) and high (1 %) fuel sulfur content ships with a probability of 80-90% (Van Roy, 2016)."*

You mention that the +2015 measurements are biased by noise since you don't really observe any SO2 then. I don't think it then makes sense to show the green data (+2015) in figure 5 since these histograms then only represent noise? Secondly you don't mention when comparing to other measurements that the amount of NO to NO2 titration is very important for the ratio, and this will depend on the distance to the plume, whether you are over land or sea etc. Please add some discussion on this.

To address this shortcoming in our study we have completely redone the SO_2 to NO_2 ratio peak analysis. The baseline determination has improved substantially (using a second running median filterapplied to the lower 50% quartile when necessary) and the positive bias in the measurements since 2015 is now gone. In addition to that, the section has been rewritten taking into account your comments. Also, the importance of NO to NO_2 titration especially for the comparison to other studies is now mentioned in this section.

Updated plots:

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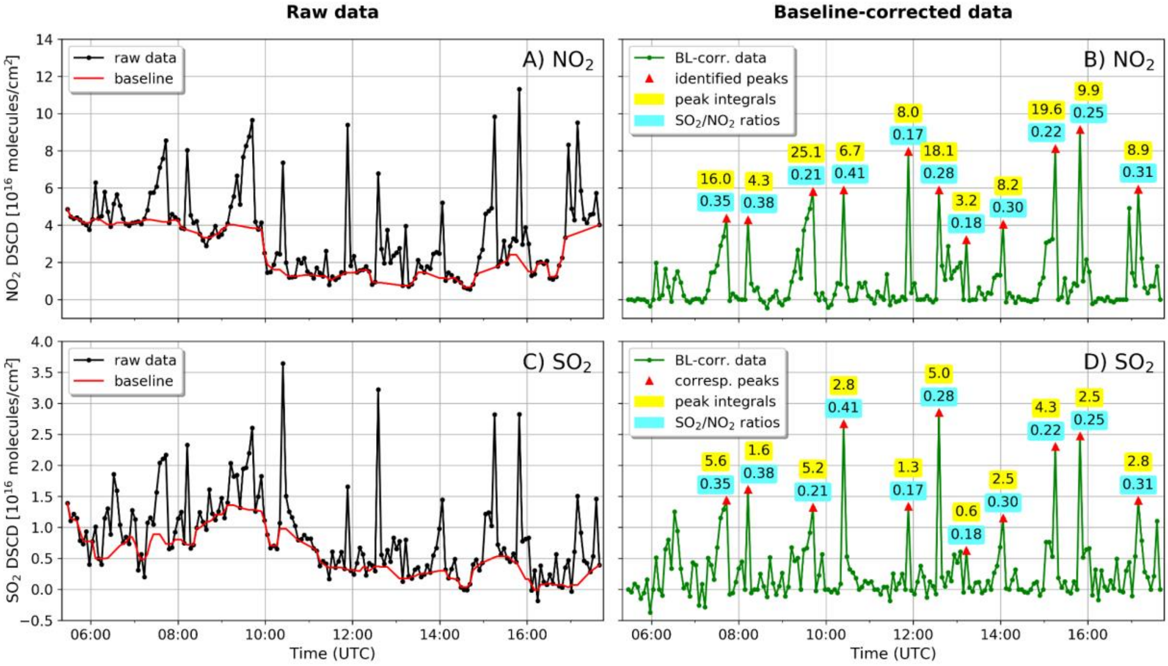
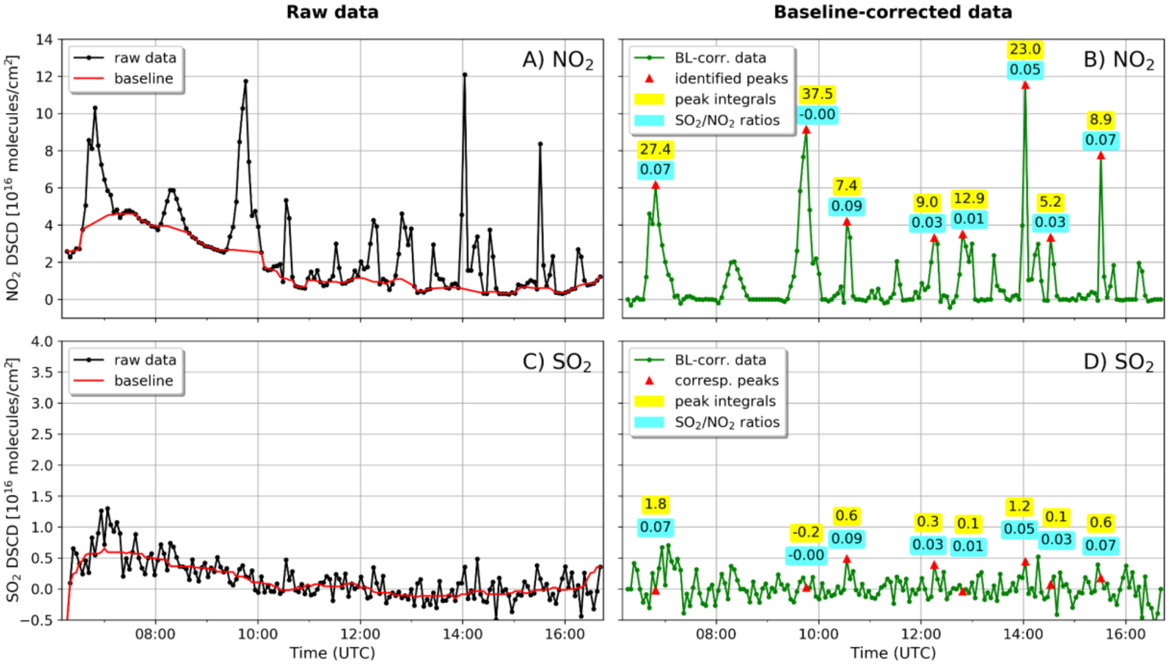
[4] Van Roy, W. (2016). Best Practices Airborne MARPOL Annex VI Monitoring. Retrieved from http://ec.europa.eu/transparency/regexpert/index.cfm?do=groupDetail.groupDetailDoc&id=29311&no=7

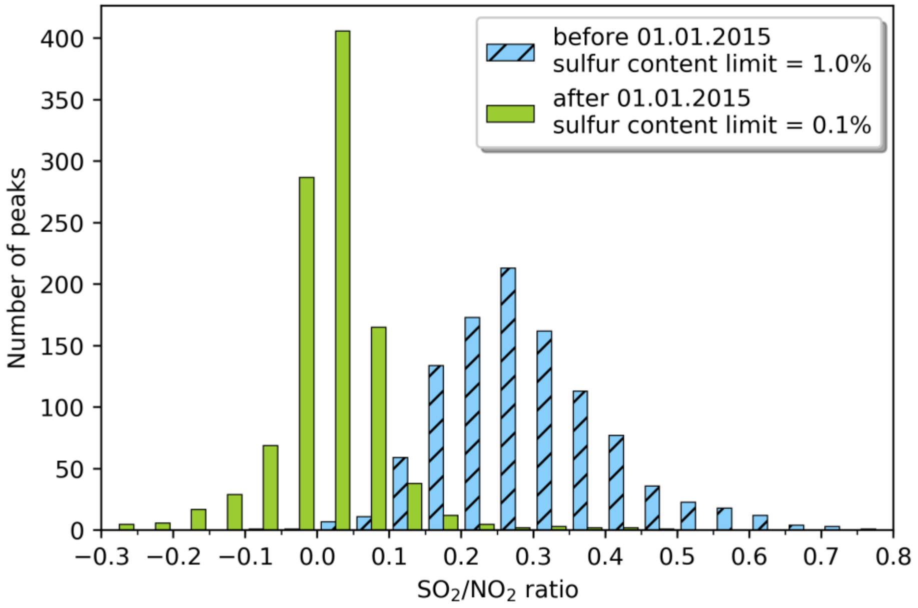
For an example day (23.07.2014) before the change in regulations:



For an example day (03.07.2015) after the change in regulations:



And the updated histogram:



Row 903 p 35: It is mentioned that there are still SO2 coming from land. This is surprising since there are very few SO2 emission sources anymore and power plants generally have abatement equipment. It would be interesting to understand this better
?

SO_2 concentrations in Germany decreased significantly in the last decade (-93% since 1990) due to advanced filter techniques and are now stable on a low level [5]. Still, the most important source is energy production, followed by industry. In Bremen, typical annual mean values are 1 to 2 µg/m³, with short-time peaks (maximum 1-hour-means) of 20 to 80 µg/m³, with the highest values close to industrial sites [6]. The German Federal Environmental Agency (Umweltbundesamt) operates a network of several in-situ air quality measurement stations throughout Germany [7]. The following two plots show SO_2 daily mean concentrations for the last 18 months for five rural stations and five urban stations in Northern Germany. The overall mean value for each station is given in the legend.

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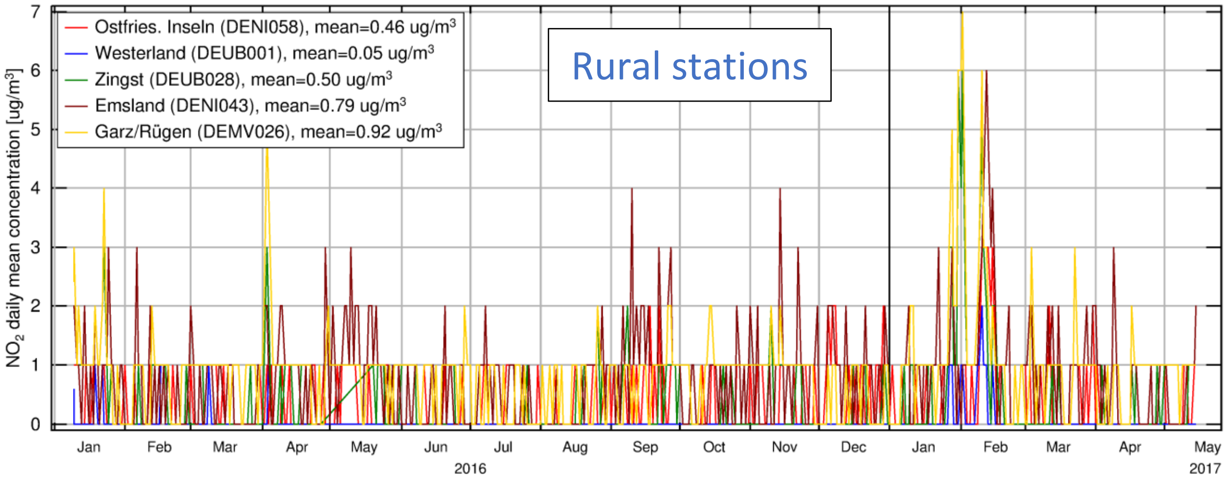
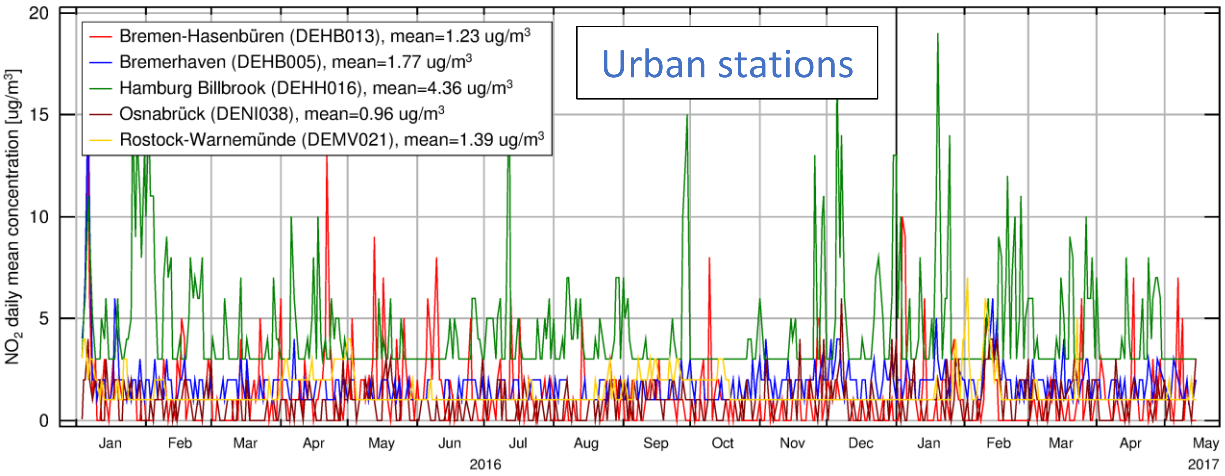
[5] https://www.umweltbundesamt.de/daten/luftbelastung/luftschadstoff-emissionen-in-deutschland/schwefeldioxid-emissionen (16.05.2017)

[6] Der Senator für Umwelt, Bau und Verkehr
Contrescarpe 72, *Das Bremer Luftüberwachungssystem - Jahresbericht 2015*
http://www.bauumwelt.bremen.de/sixcms/media.php/13/BdV_L_2016-08_Jahresbericht_Luftmessnetz_2015_Anhang.pdf (16.05.2017)

[7] https://www.umweltbundesamt.de/daten/luftbelastung/aktuelle-luftdaten (16.05.2017)





The typical average SO_2 concentrations measured by the German Federal Environmental Agency (“Umweltbundesamt”) for rural stations are around 0.5 to1 µg/m^3, corresponding to 0.2 – 0.4 ppbv (Conversion factor: 1 ppb = 2.62 µg/m^3 for SO_2). Measurements in cities and especially close to industrial areas show higher values. Bremerhaven, which is the station closest to our instrument, has a mean concentration of 1.77 µg/m^3, corresponding to 0.67 ppbv.

We measured mean SO_2 mixing ratios from land between 0.3 and 0.4 ppbv since January 2015 (see Figure 17), which in our opinion fits very well to those measurements.

Technical Corrections: Well written in most places.

Row 812 p 31: Change limis to limits

Done.

Row 873 p 33: Change This to These

Done.

Interactive comment on Atmos. Chem. Phys. Discuss., doi:10.5194/acp-2016-1153, 2017.