

***Interactive comment on “Ship emissions of
SO₂ and NO₂: DOAS
measurements from airborne platforms” by
N. Berg et al.***

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Anonymous Referee #3

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The manuscript by Berg et al. describes a novel application of differential optical absorption spectroscopy by using ocean reflected stray light as light source to measure SO₂ and NO₂ columns in ship plumes. The columns are then converted into emission values taking relative wind speed and light path length into account. The conducted measurements are evaluated as feasibility study for potential future use of this tech-
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nique to monitor ship emissions in emission controlled areas. The novelty of the approach is appealing and fits well within the scope of AMT. However, the manuscript falls short in the discussion of some relevant points, particularly in dealing with uncertainties that arise from radiative transfer and with respect to comparing this approach to other possible monitoring techniques.

General comments: Radiative Transfer: The geometric approximation of the AMF depends, a.o., on solar zenith angle, on the local aerosol profile and in a rather complex fashion on the reflection on the water surface as well as on the optical density and spatial distribution of the ship plume. The error estimation is not complete without at least performing some basic radiative transfer model case studies. Even though the authors state that this is beyond the scope of the paper, its omission leaves the conclusion on the feasibility questionable. The discussion in Section 6.1 on light being reflected on the plume directly is too short. Depending on the optical density of the plume as well as on the single scattering albedo of the aerosol, photons could be multiple scattered inside the plume or be reflected off the plume, thus either de- or increasing the measured slant column. Looking only at the intensity is not sufficient to properly quantify this effect.

Answer: We agree with the referee that there is need to carry out radiative transfer modeling but in our mind this has been pointed very clearly in the paper, discussing the impact of waves and direct scattering in the plume as main error sources and the fact that we don't entirely understand these. For instance in the abstract, section 3.2, section 6.1 and 6.2 and section 7. We clearly state that our assumption corresponds to wind free conditions and then the discussion is a discussion about the magnitude of the uncertainties. We realize that the discussion has caveats and simplifications AND MAYBE WE SHOULD SIMPLY REMOVE MOST OF THE DISCUSSION AT THIS STAGE, NOT TO PRETEND WE UNDERSTAND THE PROBLEM, PLEASE ADVICE.

Ray trace modeling for our application is a complex problem with the largest uncertainty corresponding to the reflection in the water, (specular or diffuse on water particles) combined with plume scattering properties taking into account the solar position and its relative strength compared to the diffuse sky. To our knowledge there are no good models working directly on this today and therefore it will not be possible to carry out any descent modeling within the next 6-8 months. In an ongoing project we have just started preparing for this type of work by collecting particle content and refractive index of ship plumes through particle measurements. We hope in the next year be able to write a second improved paper on this topic.

However, in our mind, this paper describes a feasibility study with several qualities that makes it suitable for publishing, even though we have not theoretically solved the uncertainty problem.

First of all, this is the first time the DOAS method has been used in this type of application, measuring gas emissions from a ship by using ocean scattered solar light. The results shows that the sensitivity is enough to detect SO₂ and NO₂ observing the plume only for a few seconds. The trick here is that we have optimized the system for photons by using a 30° angle of the telescope and a very large liquid guide fiber (5 mm) together with a UV sensitive spectrometer.

Secondly, the paper also, for the first time describes an approach how to obtain gas fluxes from a travelling ships by optical measurements from the air. Important here is that one need to calculate the apparent wind (vector sum of wind speed and ships speed and their direction).

Thirdly, the paper shows a validation study, comparing on board measurements with the one obtained by DOAS measurements from a helicopter, table 4. It shows an agreement within 30-40% which is consistent with a rough error analysis made in the paper. In our mind this replaces some of the lack with the uncertainty budget calculation.

Fourthly we also show a comparison of a ship emission model and DOAS measure-

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ments onboard an airplane, Figure 14, 15. The comparison shows that the so₂ emission measurements and SO₂ model results correlate reasonably well. By combining SO₂ measurements and modeling of CO₂ emissions it seems possible to discriminate between ships having 1% sulfur in their fuel from ships having 0.1% (new legislation on the baltic sea 2015). Again, this study indicates that the DOAS approach may roughly indicate whether a ships is a gross polluter or not which is encouraging for the idea that airborne DOAS measurements could be used for first alert measurements. WE WILL ADD SOME MORE ON THIS.

Lastly, We believe it is somewhat unfair that the reviewer requires we solve all problems at once before publishing, when compared to other studies. Forinstance the DOAS instrument by Schiamachy and MAX DOAS measurements are fighting airmass factor and in the past many papers have emerged without a perfect solution to this problem.

WE ARE WILLING TO MAKE ADJUSTEMENTS IN THE TEXT TO MAKE CLEAR THAT THIS IS A FEASIBILITY STUDY WITH THE NEED FOR BETTER UNDERSTANDING OF UNCERTAINTIES REGARDING AIRMASSFACTORS BY RAY TRACE MODELLING, WE COULD ALSO REMOVE SOME OF THE DETAILED RESULTS IF REQUIRED. WE HENCE ASK THE REVIEWER FOR MORE SUGGESTIONS ON THIS TOPIC

Measurement setup: Please explain why a telescope viewing angle of 30 degrees was chosen.

Answer: The sea surface reflectance increases strongly with the incidence angle, (Fresnel equation) and 30° below the horizon, i.e. 60° incidence angle was chosen as a good compromise between distance to the ship (optical path of light) and the intensity. WILL ADD THIS IN THE TEXT.

The roll angle of the aircraft/ helicopter will also introduce an error

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Answer: Correct, but during the flights we made certain that the airplane was balanced (not tilted) while transecting the ship plumes. WILL ADD THIS IN THE TEXT. . Discussion of results: An agreement between model and measurement of about 40% seems promising. However, looking at Fig. 16 that shows some rather large discrepancies between optical and in situ measurements raises the question whether the DOAS method would really be sufficiently reliable to not give false positives in the future when ships run on 0.1% SFC only. In fact testing this method on ships that indeed run only on SFC 0.1% seems advised. Also, the instrumental setup seems rather costly, which might speak against the method. A discussion of DOAS vs. other methods would be very interesting.

Answer: To clarify; we have combined DOAS measurements of SO₂ with a ship emission model from FMI which estimates the power consumption of the ship, hence CO₂, based on its speed and type. Most of the variability, in Figure 16, in our mind, comes from uncertainties in the ship emission model which calculated emission. It is today difficult to measure on ships with low sulphur since the larger ships use higher sulfur levels, while the smaller ships emit little to be able to detect them.

Regarding other methods, we have been involved in several studies and are using a sniffer system in addition to the DOAS as described in the introduction. There are presently no other methods for airborne surveillance so therefore it will be difficult to do what the referee asks.

Specific comments: Section 2.1: Please clarify how the operation with 2 spectrometers and 1 telescope works – or are there 2 telescopes? Answer: There is only one telescope and one spectrometer that is used for either SO₂ or NO₂, by changing the wavelength region. WE WILL CLARIFY.

Section 2.1: (1) Since ozone strongly absorbs in the same wavelength range as SO₂, checking the sensitivity of the SO₂ fit to the inclusion of ozone is advised to make sure that ozone is indeed cancelled out by the reference.

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Answer: We have previously included also ozone in the retrieval but with no drastic change of results. It was later removed to minimize the degrees freedom in the fitting procedure, to improve the S/N for the measurement. Consider that the plume is only intercepted during a few seconds, and the time difference between the plume measurements and the reference measurements is very short. Hence will there be no change in the background atmospheric column of ozone, although the background ozone inside the ship plume may be lowered due to titration by NO. If one assumes that all ozone (20-30 ppb at sea) is removed and that the path through the plume is 100 m then the negative ozone value will be -2 ppm*m. This corresponds to a differential optical depth of 2×10^{-5} at 310 nm, which is about 20 times lower than the noise level which is 1×10^{-3} due to short integration time. By sniffer measurements we have also observed that titration at sea is surprisingly slow and most of the NO_x still remains as NO even several kilometers downwind.

(2) The fitting range that is chosen for NO₂ includes a water vapor absorption band. Since emission plumes typically also contain water vapor raises the question of why is no water reference included in the NO₂ fit or why is the NO₂ spectral fitting region not shortened to avoid the water absorption? (3) Please include a NO₂ fit picture.

ANSWER: WE WILL ADD a fit.

The flue gas contains maybe 10% of water, but at the distance of 1 km where we measure this has been diluted by four orders of magnitude based on CO₂ measurements (inside flue gas 10-15%, 1 km downwind 10-20 ppm). The water level will then be 0.1% higher than the typical background water concentration of 10000 ppm Δ water = 100 ppm Assuming a pathlength of 100 m this corresponds to a differential absorption of 2×10^{-6} , which is 400 times smaller than the noise level. Hence water can not be detected.

In the graph below show a typical measurement with a Picarro instrument of CO₂ and water in a ship plume, 1 km downwind the ship. It can be seen that the water level is

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not changing significantly in the plume.

Figure 1. Ship plume measurements with a ins itu instrumnet (picarro). Grey is H₂O , pink and light blue CO₂ is. Note that gas phase water is not changing when inside the ship plume.

p.6274, ln.17 and p.6283, ln.2: why was SO₂ only detected in 60% of the plumes?
Answer: Probably detection limit problem

p.6278, ln.4: cite Grainger and Ring, 1962 when mentioning the Ring-effect, Answer:
WE WILL CHANGE THIS IN THE TEXT.

p.6280, ln.15: typically “AMF” is used for air mass factor. $1/\sin^2(\text{telescope angle})$ is a geometric approximation of the AMF. Its uncertainty does not only depend on the presence of waves, but also changes with e.g. solar zenith angle or the optical density of the plume. These inherent uncertainties should be stated. See also discussion above.

Answer: WE WILL CHANGE THIS IN THE TEXT.

p.6286. ln.10: 3 measurements of the same ship plume are not necessarily probing the same slant columns as the diameter of the plume might change due to dilution and depending on the distance to the ship as well as the radiative transfer of the measurements might not be comparable. It is therefore not a given that the uncertainty of a measurement is reduced by repeating it 3 times.

Answer: In the measurements approach we transect the ship plumes at the same distance from the ship. In the flux calculation the mass across the plume is obtained by summing up the measured slant columns. This value should be about the same each time. To obtain the gasflux the mass is multiplied by wind speed. This value will vary from time to time and averaging will reduce the uncertainty.

Tables 1-3: Though appreciating the work that has gone into collecting the information contained in these tables and its value for a real emission control, most of the informa-

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tion is not relevant for this publication and partially contained in the histograms. The tables could be removed or shortened.

Answer: We disagree that the tables should be removed. The histograms do not contain any ship specific information in contrast to the tables. The tables will put the measurements in better context and make the reader better understand the measurements situation.

Figs 1 and 2: please use wavelength as x-scale instead of channels Answer: Will be changed.

Fig. 6: The background becomes negative over time in an almost systematic fashion. What could be the cause of that? The 3rd peak is larger than the first 2 peaks. Is that caused by measuring the plume closer to the ship? If so, then see also comment above. Answer: The background varies over time since the reference spectra correspond to the first spectrum. But for each ship measurement the area above the nearest baseline points, on either side of the plume, are used. Figure 6 does not correspond to measurements of the same ship but three different ones, as shown in Fig 3. Therefore the peaks are different.

Fig.14: measurement error bars are not visible Answer: the figure text will be changed omitting the word bars.

Technical corrections: p.6276, ln.19: “obey” instead of “obeys” Answer: Will be changed.

p.6281, ln.17: “of the ships” instead of “for the ships” (?) Answer: Will be changed.

p.6285, ln.8: delete “a” after SO₂ Answer: Will be changed. p.6285, ln.24: replace “Fig.9” with the appropriate Fig. number Answer: Will be changed. p.6290, ln.5: “need” instead of “needs” Answer: Will be changed. Fig.3, caption, 2nd line: “outside the” instead of “outsidethe” Answer: Will be changed.

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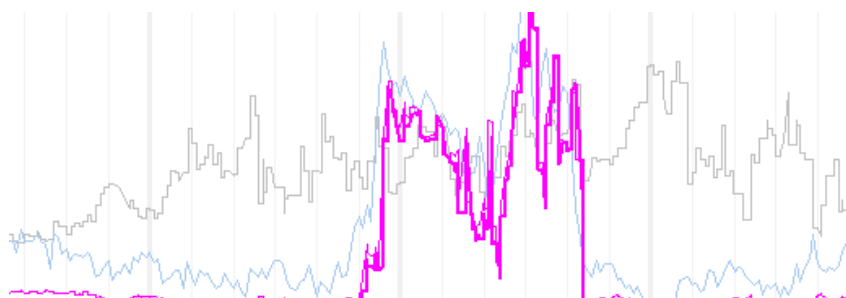


Figure 1. Ship plume measurements with an in situ instrument (Picarro). Grey is H₂O, pink is CO₂. Note that gas phase water is not changing when inside the ship plume.

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