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Atmospheric Measurement Techniques Discussions

Interactive comment on "Studies of the horizontal inhomogeneities in NO_2 concentrations above a shipping lane using ground-based MAX-DOAS and airborne imaging DOAS measurements" *by* André Seyler et al.

Anonymous Referee #2

Received and published: 4 January 2019

This paper presents measurements of NO2 from ship emissions in the German Bight using MAX-DOAS instrument, and shows that horizontal information on the NO2 distribution can be derived using an onion peeling method with NO2 slant columns derived separately in the UV and visible, which are observing slightly different air masses. The authors show two case studies of different wind directions, and use coincident airborne remote sensing observations of plume extents to derive mixing ratios from the MAXDOAS measurements.

The paper is concisely written, well-organized and logical. The figures are very clear and easy to follow. Overall I found the paper interesting and recommend it be eventually published. I did find it somewhat lacking in a description of motivation for the work and its possible application. The method for deriving horizontal information from MAXDOAS using onion peeling was previously demonstrated for an urban area, and this paper is now applying it to ship emissions. This seems useful in theory, but it's not clear how the information would be used. Without plume extent information, the VMRs are derived over a long path in Section 4. Section 5 uses the airborne information to derive more precise VMR inside the plume, but these airborne measurements are rare and not regular. What would be the purpose of the MAX-DOAS measurements over a long time period? Would they be useful for trends, emissions estimates, monitoring etc? How can this be accomplished without plume width information, and are there other sources of this information? Can better modeling of ship plumes and NOx chemistry improve the estimates?
Also, aerosols, plume height and a few other sources of errors are quickly mentioned in Section 3.1, and clouds are quickly mentioned in Section 4.1. However, there is no thorough quantitative error assessment. I think the error sources need to be discussed and quantified in more detail. If you don't want to get into clouds, at least mention that for now you will only consider and draw conclusions about clear days.

Also, error sources for the the AirMAP measurements should be described. There is an uncertainty given, but it is not clear from where it is derived. There are many possible error sources (fitting uncertainty, surface albedo, profile shape, aerosols etc).

First, we would like to thank Anonymous Referee #1 for his/her helpful comments, particularly concerning the suggestion for the inclusion of ship plume modeling.

We updated and enhanced the described method by incorporating ship plume modeling using a simple Gaussian plume model and combining it with the plume forward trajectories. The information about plume width and height retrieved from the model is then used to derive in-plume volume mixing ratios of NO_2 from the MAX-DOAS measurements without the need for the airborne imaging DOAS measurements. In the new version, the AirMAP measurements are now only used for validation. As a consequence, the structure and aim of the paper was adapted. Section 5 was completely rewritten (now: Section 4.4) and contains two parts: The first part contains a technical demonstration of the method to derive in-plume NO_2 VMRs from MAX-DOAS measurements for ships passing the instrument in a distance of several km. We decided to demonstrate the method on the measurements during the NOSE campaign shown in Fig. 10 (new: Fig. 8), as AirMAP measurements for validation are available for this day.

In the second part of Section 4.4, the AirMAP measurements are used for validating both the plume modeling and the MAX-DOAS results. The modeled plume location and shape (including the plume width) is compared to the AirMAP measurements. The vertical plume extent from the model is compared to the estimation from the MAX-DOAS vertical scan, which was already included in the previous version. As before, the approximate plume position retrieved with the onion peeling MAX-DOAS approach is compared to the AirMAP measurements. The in-plume NO_2 VMR derived from the MAX-DOAS measurements is now compared to the in-plume VMR computed for the AirMAP measurements with help of the modeled plume height.

We kept the general structure, as we think the order of the results facilitates comprehension by enabling the readers to go step-by-step from the more basic time-series plots to the complex map figures which contain a lot of information. Starting with the time-series showing the relation between DSCDs and path-averaged VMRs, then taking the step from the time-series to the map figures with colored lines representing the VMRs and path lengths (for northerly and southerly wind directions) and finally the step to the figures additionally including the AirMAP measurements showing two completely different quantities: for AirMAP vertical columns of NO_2, for MAX-DOAS path-averaged NO_2 VMRs.

We think that the inclusion of plume modeling allowing derivation of in-plume NO_2 VMRs from MAX-DOAS measurements without the need of airborne measurements makes the paper scientifically more relevant and the described method much more quantitative and the main purpose of the measurements becomes clearer.

Adding NO_x chemistry to the plume model would certainly improve the results but would also be more challenging. As the plumes measured in the study are mostly rather old (plume age usually > 10 minutes), we expect most of the NO to be already converted to NO_2. Some unpublished measurements performed at another site under roughly similar conditions indicate that already after a few minutes, the fraction of NO_2 in the overall NO_x is quite high. After 1 minute, the NO content on the overall NO_x is below 60% for most ships (but up to 96 % for some), after 3 minutes it drops to values below 40% for most ships (but up to 70-80% for some). After 5 minutes it is below 25% for most ships and after 8-10 minutes it is below 20-30% for all ships. Of course, this depends on the ambient ozone concentration.

Middleton et al. (2007)[1] modeled the NO to NO_2 conversion in plumes at short ranges, depending on the O_3 concentration:

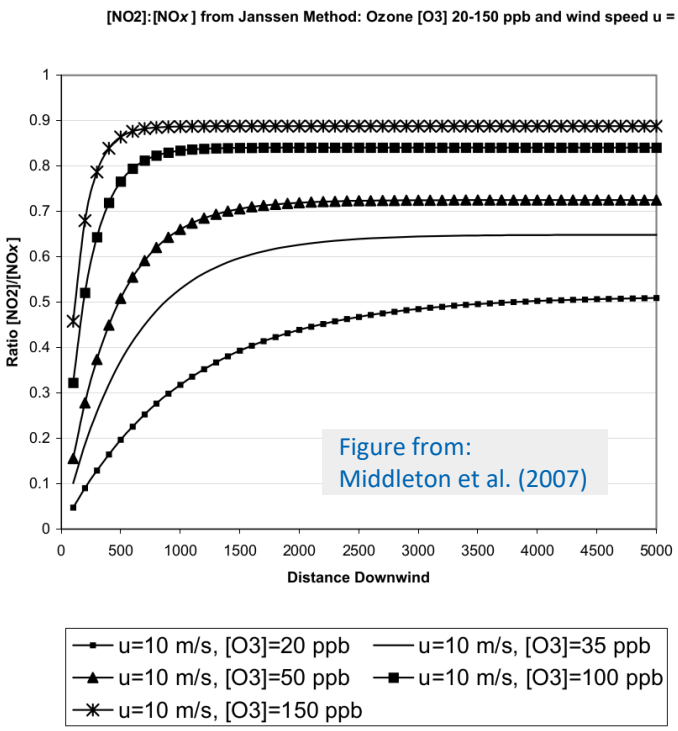


Figure 1
Plot of results for the yield or ratio $[NO_2]$:$[NO_x]$ using the Janssen (Janssen 1986, Janssen *et al*. 1988) method of near-source diffusion-limited O_3, which soon becomes asymptotic to the photostationary state further from the source, after approximately 200 seconds of travel time (2 km downwind here). The effect of changes in O_3 concentration is shown. The wind speed alters the choice of curve according to travel time (distance/speed). (In these curves distance is plotted on the x-axis; empirical curves later in this report show NO_x on the x-axis.)

The figure shows that both the steady state value of the NO_2 to NO_x ratio as well the time until the steady state is reached depend on the O_3 concentration.

At our Neuwerk station, typical background O_3 volume mixing ratios in summer are in the range of 30 to 40 ppb, but can go up to 60-70 ppb or down to 20 ppb as well. Taking a closer look at the curves for 35 ppb and 50 ppb ambient O_3 in the figure, it can be seen that the steady state is predicted to be reached already after 3 to 4 minutes and in the steady state the fraction of NO_2 on the overall NO_x is 65-70%. This fits quite well to our measurements mentioned above.

Meier (2018)[2] shows AirMAP NO_2 measurements during an overflight over a ship and its plume from the NOSE campaign on 21 August 2013. The across−plume integrated NO_2 VCD increases with flown distance from the ship overpass, stabilizing on a plateau at a distance of around 3 km. This 3 km are not the distance since emission, as the plume is moved by the wind during the time from ship overpass to this point. Taking the combination of plume forward trajectories and simple Gaussian plume model, the plume age at this point is estimated to be ~400 seconds or ~6.5 minutes, in which the emitted air parcels traveled a distance of ~1.5 km. This is in the same order of magnitude than the measurements and model results discussed above.

To conclude, after a few minutes, at the latest after 10 minutes, the NO to NO_2 conversion reaches its steady state, depending on the ambient ozone concentration. As the plumes

[1] Middleton, D. R., Luhana, L. and Sokhi, R. S.: Review of methods for NO to NO2 conversion in plumes at short ranges, Environment Agency, Bristol., 2007.

[2] Meier, A. C.: Measurements of Horizontal Trace Gas Distributions Using Airborne Imaging Differential Optical Absorption Spectroscopy, phd thesis, University of Bremen, Bremen., 2018.

considered in the manuscript are usually older than 10 minutes, NO to NO_2 titration should not have a strong influence on the presented results. However, for a potential next step, the derivation of NO_x emission factors, accurate modeling of the NO-to-NO_2-titration would be important.

Regarding clouds: The following sentence was added to the manuscript: "In the following, only clear sky days or measurements under cloud free conditions are considered." and the whole paragraph was moved to Section 3.1.

As requested, a few words on possible error sources for the AirMAP measurements were also added.

Below, we reply point-by-point to the specific comments. As far as possible, we have considered the suggestions in the revised manuscript.

Specific points:

Page 2, Line 5: specify whether these are ship or land based in situ measurements

Both ship-borne and land-based in-situ measurements of shipping emissions are common. There are even airborne measurements, e.g. by Beecken et al. (2014)[3] and Balzani Lööv et al. (2014)[4].

Changed the sentence from

"Most measurements of pollution are performed with in-situ instrumentation, and this includes monitoring of the effect of ship emissions."

to

"Most measurements of **air** pollution are performed with in-situ instrumentation, and this includes monitoring of the effect of ship emissions, **which is usually performed with either land-based or shipborne in situ measurements.**"

Page 3, Section 2.1: Mention temporaral resolution of measurements here

We added the following sentences to Section 2.1:
"The total exposure time (or integration time) per measurement is 10 seconds for off-axis measurements and 20 seconds for zenith sky reference measurements. A new azimuthal measurement in one of the five different directions (see Section 2.2 and Fig. 1) starts about every 30 seconds. The measurement sequence is intermitted by a vertical scan in the main direction (335° azimuth) and a zenith sky measurement, both together taking in total around 90 seconds. The temporal resolution for one viewing direction, i.e. the time until the same azimuthal direction is probed again, is around 4 minutes. "

Page 4, Line 7: Not sure column amount is a concentration?

A column amount is not a concentration, but integrating a concentration along a certain light path delivers a column amount. Changed the structure of the sentence from "The quantity retrieved from DOAS measurements is the concentration of an absorber integrated along the atmospheric light path, the so-called slant column density (SCD)."

to

"The quantity retrieved from DOAS measurements is **the so-called slant column density (SCD), the integrated concentration of an absorber along the atmospheric light path.**"
to make it more precise.

3 Beecken, J., Mellqvist, J., Salo, K., Ekholm, J., and Jalkanen, J.-P.: Airborne emission measurements of SO2 , NOx and particles from individual ships using a sniffer technique, Atmos. Meas. Tech., 7, 1957-1968, https://doi.org/10.5194/amt-7-1957-2014, 2014.

4 Balzani Lööv, J. M., Alfoldy, B., Gast, L. F. L., Hjorth, J., Lagler, F., Mellqvist, J., Beecken, J., Berg, N., Duyzer, J., Westrate, H., Swart, D. P. J., Berkhout, A. J. C., Jalkanen, J.-P., Prata, A. J., van der Hoff, G. R., and Borowiak, A.: Field test of available methods to measure remotely SOx and NOx emissions from ships, Atmos. Meas. Tech., 7, 2597-2613, https://doi.org/10.5194/amt-7-2597-2014, 2014.

Page 8, Line 9: Not sure what you mean by “instrument measures in wind direction”

The whole sentence was reformulated to: “But as the movement of the ship together with the measured wind can result in an apparent wind direction very different from the measured wind direction, a measurement along the measured wind direction (windward, i.e. pointing anti-parallel to the wind vector) does not in general correspond to a measurement along the plume. ”

Page 8, Line 14: NO2 only increases up to a point…

Yes, of course, thanks for noticing. Corrected to:

“Therefore, the NO_2 signal increases **(up to a point)** with distance from the ship and, depending on the wind direction, with distance from the ship track.”

Page 11, Figure 6/7: In situ value colour saturates. Please mention what is the value in the text if not planning to change the colour scale. Maybe you could include it in Figure 5 as a function of time?

Good suggestion, as the information that the in situ instrument in fact measured two overlapping plumes got lost in the saturated color scale before. We included the measured in-situ values in the text and additionally pointed out that the in situ instrument measured two overlapping plumes.

Adding the in-situ curve to Figure 5, however, does not work, as the in-situ instrument measures much higher values, in this case for example reaching nearly 10 ppb and extending the y-axis range to account for the much higher in-situ values would substantially decrease the dynamics of the MAX-DOAS curves which is needed here for distinguishing the different cases.

Figures 6/7/8/9: I find the forward trajectory of the plumes a bit hard to interpret. What is the timescale on these? Do the black to grey values denote anything?

The lightness of the gray shading denotes the age of the plume. A colorbar showing the relationship between the lightness of the gray shading and the plume age was included in all plots showing modelled plumes.

Figure 10 and discussion in Section 5.3: I find the discussion of plume height a bit confusing and how it is used in the airborne observations. The MAX-DOAS on the tower seems to measure above the ship according to Figure 10, and the plume is not at the surface in the figure. Is there an assumed start height of the plume above the ocean?

As the MAX-DOAS measures down to the sea surface, the plume is assumed to reach down to the surface as well. The plume modelling supports this assumption. We added a hint on this to the text.

We also added the information that the heights are not to scale to the caption of Figure 10.

The AirMAP instrument is measuring the column to the surface. Why is 500 m used for the AMF calculation and not 335 m? Do the 335 m and 500 m height box profiles include a constant VMR to the surface? I don’t think different assumptions will change the results by much, but the description of profiles and relation to the figure could do with some clarity.

A 335m box profile could have been used, but only for this specific ship. The vertical extent of the other plumes in the figure are certainly different from this, probably larger, as the plumes are older. 500m seemed like a good first guess for all the ships. The correction to the measured/modeled plume height (here 335m or 320m, respectively) is done in the computation of the in plume VMR. And yes, the box profile assumes constant NO_2 up to 500m. We added this information to the manuscript and the respective paragraph now reads:

“For the retrieval of NO_2 vertical column densities, air mass factors were calculated for an NO_2 box profile **assuming constant NO_2** in the lowest 500 m, in an atmosphere without aerosols and for a constant surface reflectance of 0.05. **This box profile height is an educated guess on an upper limit for the typical vertical plume extent for older ship plumes, which the plume modeling has proven to be in the right order of magnitude.**”

Figures 11 and 14: Why show VMR and not DSCD for the MAX-DOAS here? Even though the DSCD is very diluted over a large area, it would at least put the measurements in the same units for easier visual comparison.

Granted, but the DSCD along the path difference, $\Delta DSCD = DSCD_{vis} - DSCD_{UV}$, is smaller than the DSCD along the UV path, $DSCD_{UV}$, and this reverses the situation in the figure: The higher NO_2 value is no longer shown along ΔL, where the plume is located, but close to the instrument along L_{UV}, and much lower NO_2 is shown along ΔL where the plume is. This is rather unintuitive, as shown below, so we would prefer to keep the plotted quantities as is.

Existing figure showing MAX-DOAS **VMR**:

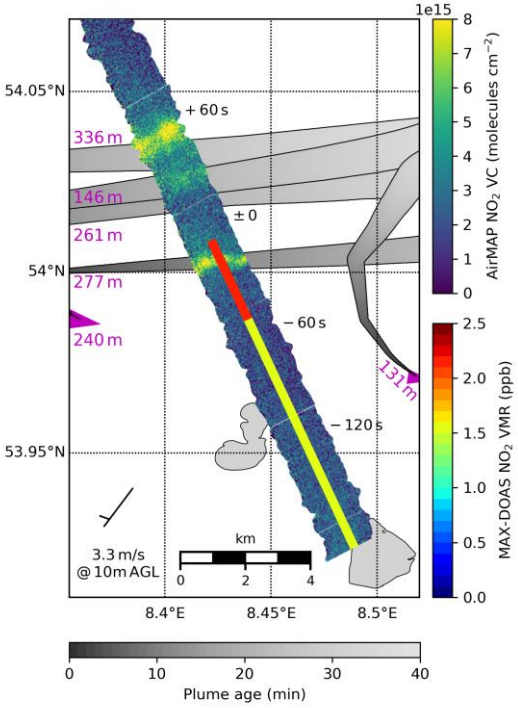
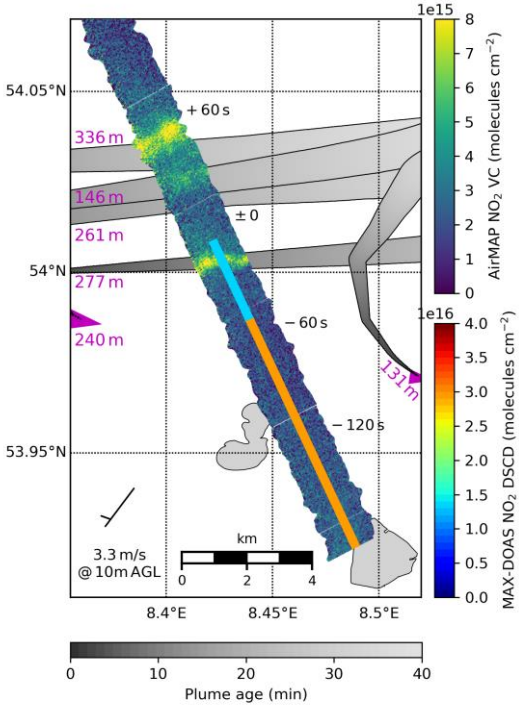


Figure showing MAX-DOAS **DSCD** instead:



To better visually discriminate the two measurements, we changed the color-scale of the AirMAP measurements to *viridis*, one of the new perceptually uniform sequential colormaps introduced with *Python* package *Matplotlib* version 2.

Technical corrections:

Page 2, Line 14: change colon to semicolon

Done.

Page 3, Line 25 and 26: Change “in a” to “at a” in both cases

Done.

Page 13, Line 2: “lightboth” not a word

Changed “concentrations on all lightboth path segments” to

“concentrations on both path segments”

figure 10: change “not up to scale” to “not to scale”

Done.

Page 18, Line 3: change colon to semicolon

Done.

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