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## Comment on acp-2022-638

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Community comment on "A new insight into the vertical differences in NO<sub>2</sub> heterogeneous reaction to produce HONO over inland and marginal seas" by Chengzhi Xing et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2022-638-CC1>, 2022

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### Comments to the manuscript by Xing et al.:

In the manuscript by Xing et al. MAX-DOAS measurements during ship cruises and on two land stations (inland and coast) were used to measure vertical gradients of HONO and NO<sub>2</sub> to identify potential source mechanisms. Gradient measurements are of significant importance to distinguish between near ground (e.g. direct emissions, heterogeneous NO<sub>2</sub> conversion, etc.) and volume sources (e.g. on particles) of HONO. Only when the vertical HONO structure is known, the impact of HONO on the oxidation capacity of the whole boundary layer can be described, in contrast to typical near surface measurements by in-situ instruments, which overweight the contribution of HONO. Also, when using a path averaging spectroscopic method the risk of overestimation of HONO levels by interferences and sampling artefacts in the instrument's inlets are minimized. Thus, such measurements are of general high importance.

However, I could not follow all the evaluations and arguments in the manuscript caused by missing information. The following comments could be considered to improve the manuscript.

### Major comments:

#### 1) Section 2.1: Missing information to CAMS and SUST sites:

Besides the ship measurements, MAX-DOAS measurements were also performed in parallel in two stations, which were defined as "inland" (CAMS) and "coastal" (SUST). Here I am missing more information to both sites. Especially, where are they? E.g. for the Chinese Academy of Meteorological Science (CAMS) I found Beijing (?), which would be far away from the ship measurements and would make any comparison highly uncertain...

#### 2) Sea- vs. land-oriented measurements:

The ship data was divided in sea- and land-oriented measurements. But isn't that both sea data? To answer this question, two important information are missing: a) How far away were the ship tracks on average from the coastline? b) what is the typical distance for the

light-path of the MAX-DOAS (only the horizontal vector is of importance)? I expect that the distance of the ship from the coast (some km?) was larger than the "horizontal view" of the instrument (horizontal distance between the average scattering point and the instrument). From my experience for Chinese conditions the visibility is often significantly smaller than 1 km... In this case the instrument is only evaluating sea influenced air masses and the observed differences reflect only some undefined horizontal gradient between sea and land, but not any "sea" or "land" data.

### 3) Direct HONO/NO<sub>x</sub> emission ratio

In section 3.2. it seems that HONO/NO<sub>x</sub> ratios from direct emission were determined by the measurement data for CAMS and SUST. However, it is unclear how this has been done? In the present study, only daytime data could be used (light source of the MAX-DOAS = sun...). But one filter to determine the HONO/NO<sub>x</sub> ratio of direct emissions from field data - besides others - is to use only night-time data, caused by the fast photolysis of HONO!? In addition, because of strong vertical gradients and the vertical resolution of the MAX-DOAS the combined use of path averaged HONO and NO<sub>2</sub> data in comparison to in-situ NO ground data cannot be recommended (apples and oranges...). The method used is completely unclear and should be further explained. E.g. how was the direct emission ratio of 0.46% (line 216) of Sun et al. considered ("used to understand...")?

### 4) Unrealistic HONO/NO<sub>x</sub> data:

If the HONO/NO<sub>x</sub> ratio for direct emissions of 0.82 % (CAMS) and 0.79 % (SUST) are true, then the slopes of all HONO against NO<sub>2</sub> data shown in Fig. 5 (a) 0.8 % for CAMS and b) 0.5 % for SUST) are not possible. Even if one assumes the absence of any NO in the atmosphere (very unreasonable) the slopes when using all data should be by definition larger than only the direct emission ratio!? Typically, that should be a few % for field data (cf. ratio of the average ship data of ca. 2.5 %, which I get from the data in lines 191-192) for which 0.8 % (lower limit during daytime, see below) may be direct emissions. But here for SUST all data show a lower HONO/NO<sub>2</sub> ratio (and the HONO/NO<sub>x</sub> ratio would be even much lower...) than the direct emission ratio. Please check the data.

In addition, during daytime a measured HONO/NO<sub>x</sub> ratio (e.g. from sharp plumes) will be lower than what is directly emitted. This can be explained by the different lifetimes of HONO (10-20 min during daytime) and NO<sub>2</sub> (typically some hours). Thus, depending on the time between emission and measurements the contribution of direct emitted HONO will decrease (this is the reason why the "night-time filter" is used to measure direct emission from field data...). For details I recommend the paper by Xue et al. (<https://doi.org/10.5194/acp-22-3149-2022>).

### 6) Unrealistic HONO/NO<sub>2</sub> gradient data:

In figures 9-11 vertical gradient data of the HONO/NO<sub>2</sub> ratio are shown. Here increasing ratios are observed with altitude, which is in contrast to most gradient data, which I know (cf. e.g. our gradient data on a 190 m tall tower, Kleffmann et al., 2003 doi: 10.1016/S1352-2310(03)00242-5). While this may be explained by any unusual chemistry over sea surfaces, the absolute numbers of the HONO/NO<sub>2</sub> at higher altitude of up to 45 % (see Fig. 10) are impossible, independent of how strong any HONO source - e.g. particle nitrate photolysis - may be. The photolysis of HONO is a source of NO. In a

typical atmosphere for which  $[O_3] > [NO_x]$  this is quickly converted to  $NO_2$ . Since in higher layers in a well-mixed atmosphere a PSS can be assumed (far away from any direct sources) the maximum HONO/ $NO_2$  ratio is given by the ratio of the lifetimes of both molecules. For HONO this is around 10 min at noon (check for  $J(\text{HONO})$ ), while for  $NO_2$  this is mainly limited by its reaction with the OH radical during daytime (the Leighton chemistry will not play a role here). Assuming a high OH concentration of  $10^7 \text{ cm}^{-3}$  at 1 km altitude a lifetime of ca. 3 h can be calculated. Thus, a maximum HONO/ $NO_2$  ratio of ca. 6 % should result under steady state conditions. If HONO is measured close to a source, e.g. in near ground measurements in a steep vertical gradient, higher HONO/ $NO_2$  ratios are possible (= no PSS...). But in a homogeneous mixed atmosphere at 1 km altitude (see figures 9-11) such high HONO/ $NO_2$  data is impossible. Please check.

### **Minor comments in the order of the manuscript:**

Line 37-38: There are several "heterogeneous reactions of  $NO_2$ ". Here the authors should distinguish between slower nighttime conversion ( $NO_2 + H_2O$  and  $NO_2 + \text{organic}$ ) and daytime sources ( $NO_2 + \text{organic} + \text{light}$ , see Stemmler et al., 2006; or  $NO_2 + TiO_2 + \text{light} = \text{photocatalysis}$ ). Otherwise some arguments of the authors (with solar radiation, see below) are unclear.

Line 51-53, general comment to this section, but also to the author's own evaluations: These simple correlation studies always bear the risk of a misinterpretation of the results. Typically, trace gases which are emitted or formed near to the ground will anyhow correlate caused by the variable mixing layer height. This is mainly modulated by diurnal surface temperature variation which has also an effect on the relative humidity. Thus, e.g. at the end of the night the temperature and mixing height are low, while the relative humidity is high. Caused by the resulting high S/V ratio under these conditions, heterogeneous HONO formation is faster and the HONO/ $NO_x$  ratio will correlate with the humidity, without any necessary mechanistic link (see also correlation of Radon with HONO...). Also, often at very high humidity the HONO/ $NO_x$  ratio is again decreasing with humidity. This is typically explained by uptake on very humid surfaces. However, the highest relative humidity is often observed close before sunrise, when direct emissions start to increase. Thus, the high HONO/ $NO_x$  air masses from slow nighttime sources (typically 5 %) are "diluted" by fresh low HONO/ $NO_x$  emissions (around 1%), leading to the decreasing HONO/ $NO_x$  ratios at high humidity. Thus, the authors should highlight (and later consider for their own evaluation...) that simple correlation analysis may lead to artificial correlations and misleading conclusions.

Line 77-85: With respect to the main topic of the manuscript, I would expect a more extended summary of the existing gradient data (from towers, and MAX-DOAS), which is normally very different to the present results (see major comment 6).

Line 187-189: This sentence could make sense only if a photolytic  $NO_2$  conversion process is considered (see above). However, even for a photolytic  $NO_2$  conversion process which was found to correlate with  $J(NO_2)$  in lab studies (see Stemmler et al., 2006), the steady state HONO/ $NO_2$  ratio would not change with variable solar radiation, since both,  $J(\text{HONO})$  (sink) and  $J(NO_2)$  (source) show a linear correlation. Thus, the argument is not valid.

Lines 191-192 and 205: Here very different HONO/NO<sub>2</sub> ratios are specified for the same (?) ship data? From the data in lines 191-192 I get values of 2.7 % and 2.4 % ("total averaged"), while in line 205 45 % are mentioned for the "average value"? Check data and/or explain differences.

Line 202: should be "high HONO concentration". A production rate (dHONO/dt) was not determined and you may have a small production rate (slope) at high HONO.

Line 206-207: Check again the argument (see above, sources and sink scale with radiation...).

Section 3.2.1: Check whether the "turning points" (especially the two in Fig. 6c) are significant or just scatter of the data? In addition, possible "artificial correlations" should be discussed, see above.

And can you explain, why only the "six highest values" are shown in Fig. 6 (red data) and not the mean/median? Is that representative or are here only outliers shown?

Line 245, 246, 251: Here continuously increasing or decreasing data is shown and the highest value are specified as "peak". However, the "peak values" were not determined and could be even at lower or higher temperatures...

Paragraph lines 282-295/ figures 10 and 11: What is the difference between both figures? Seems to be the same? Define two cases?

Line 315: Where is that HONO peak at 12:15 in Figure 12c? I see a stronger peak at ca. 14:15...?

Line 330-331: The two RH and especially the two T values are not very different to allow any conclusions to the mechanism.

Line 343-344, Fig. 15: Not the NO<sub>2</sub> concentration is increasing during this period (see color code), but the layer is getting thicker.

Line 347-348. The peaks in HONO at ca. 9:45, 11:00, 11:45 and 12:30 in Fig. 15 are anticorrelated to NO<sub>2</sub> (in contrast to the statement...), which is very unusual? Check data

and sentence.

Line 375: Should be "emission ratio".

Fig. 1: The data shown seems to be not "typical". The DSCDs in the figure are factors higher than the data described in section 3.1?

Figure 3. Check the HONO/NO<sub>2</sub> data. I get 0.027 and 0.024 using the HONO (0.23 /0.27) and NO<sub>2</sub> (8.46/11.31) data?

Figure 6: please show the red/right y-axis scaling in all figures (will be different in a) and b)).

Figure captions 10 and 11. Is "Sea" the average data or "sea/land oriented data"?