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Reply on RC1

Xueli Liu et al.

Author comment on "Measurement report: Variations in surface SO₂ and NO_x mixing ratios from 2004 to 2016 at a background site in the North China Plain" by Xueli Liu et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-866-AC4>, 2022

We thank for the constructive comments and suggestions. We revised our manuscript according to the comments and suggestions. The following list the point-to-point response to the comments. The changed texts were highlighted with yellow color.

Response to comments by referee # 1

General comments:

This paper reports on NO_x and SO₂ measurements at a background site in the North China Plain.

The site, the instrumental setup, quality control and the data processing procedures have been described in detail. Data are compared to other data from other measurement sites. The long-term trend of both SO₂ and NO_x, their diurnal and seasonal behavior are discussed and compared to emission data. As publications of long time series of NO_x and SO₂ are rare, the manuscript should be published after these questions have been answered:

Specific comments:

1. Line 66 and following

Here the authors describe the setup of the instrument. For NO_x detection, a chemiluminescence analyzer has been used. Unfortunately, it is not stated how NO₂ is converted to NO for detection.

Has a thermal or a photolytical converter been used? If a thermal converter has been used this would mean that a large fraction of the NO_x would be in fact NO_y, as nitric acid and nitrates would cause significant interferences in the NO₂ channel (Jung et al., 2017, Steinbacher et al., 2007). This interference should be discussed. How frequent was the conversion efficiency determined? Was an NO₂ gas standard used or was it done by gas phase titration?

Response: Thanks. The commercial NO_x analyzer (Model 42CTL) uses a molybdenum NO₂-to-NO converter heated to about 325°C. We have also noticed the drawback of this

technique, but have to accept what has been available since 2004. A favorable and direct NO₂ measurement technique based on cavity ring-down principle could be a choice in the future, but there would be another challenge in the availability of stable and reliable reference standard of NO₂. We discussed the possible interference in another paper (see <https://doi.org/10.5194/acp-22-1015-2022>). We cited the discussion in the revised paper. The following text are added in the revised paper. see Line 72-77.

“In Model 42C-TL NO_x analyzer, NO₂ is converted to NO by a molybdenum NO₂-to-NO converter heated to about 325°C. The conversion efficiency was checked annually using gas phase titration of an NO standard with O₃. The converter was replaced if the conversion efficiency was found lower than 96%. The drawback in this NO₂ converter was known to suffer from the interference of other NO_y compounds such as PAN and HNO₃ (Steinbacher et al., 2007; Jung et al., 2017), which was also discussed in Yin et al. (2022). As it is not possible in our case to remove the interference, the reported NO₂ and NO_x levels should be treated as upper limits.”

Steinbacher, M., Zellweger, C., Schwarzenbach, B., Bugmann, S., Buchmann, B., Ordóñez, C., Prevot, A. S. H., and Hueglin, C.: Nitrogen oxide measurements at rural sites in Switzerland: Bias of conventional measurement techniques, *J. Geophys. Res.-atmos.*, 112(D11), <https://doi.org/10.1029/2006JD007971>, 2007.

Jung, J., Lee, J., Kim, B., and Oh, S.: Seasonal variations in the NO₂ artifact from chemiluminescence measurements with a molybdenum converter at a suburban site in Korea (downwind of the Asian continental outflow) during 2015–2016, *Atmos. Environ.*, 165, 290-300, <https://doi.org/10.1016/j.atmosenv.2017.07.010>, 2017.

Yin, Q., Ma, Q., Lin, W.*, Xu, X., and Yao, J.: Measurement report: Long-term variations in surface NO_x and SO₂ from 2006 to 2016 at a background site in the Yangtze River Delta region, China, *Atmos. Chem. Phys.*, 22, 1015–1033, <https://doi.org/10.5194/acp-22-1015-2022>, 2022.

How was mixing depth determined?

Response: We used a hybrid single-particle Lagrangian integrated trajectory model (Hysplit4.9) from National Oceanic and Atmospheric Administration, USA, with the NCEP–NCAR reanalysis meteorological data set (<https://ready.arl.noaa.gov/archives.php>) to calculate the atmospheric mixed layer heights. We added this information in the revised paper, see Line 86-88.

2. Line 162 and following

The authors state that there is a lag between SO₂ mixing ratios and emissions. What can cause such a lag? Change in meteorology would only lead to a decoupling of emissions and measured SO₂ and NO₂ values but not to a time shift.

Response: Yes, there seemed a lag between the variation in mean and the 95% percentile of SO₂ mixing ratios and the emissions. Surface SO₂ mixing ratio in 2012 was evidently inconsistent with the emission trend. China has implemented a series of stringent clean air actions from 2013 to 2017, and the “Beijing 2013-2017 Clean Air Action Plan” was the most comprehensive and systematic pollution control program in Beijing (UN Environment, 2019). Before 2013, there would be some emissions being not

counted for some reasons by local government, as the change in the 95% percentile of SO₂ mixing ratios did not show a similar decreasing trend of the mean SO₂ mixing ratios from 2009 to 2011. Another reason would be the change in SO₂ mixing ratios at the SDZ regional background site was not as obvious as the change in Beijing urban and other polluted areas as Lin et al. (2012) had stated. Changes in meteorology would also lead to a decoupling of emissions and measured SO₂ and NO₂ values, but it cannot be quantified how much the changes contributed to this time shift.

We add the information in the revised paper, see Line 179-190.

3. Line 166 and following

The authors write that the 2008 Olympic games should affect the emissions. However, in figure 5 the measured SO₂ values are highest in 2008 and low in 2009. Is it possible the effect of the worldwide economic crisis in 2009 is larger than the effect of the Olympic games and not well represented in the emission data?

Response: In Lin et al. (2012), we indicated that surface SO₂ mixing ratios in Beijing in the first half year of 2008 before the Olympic game, held in August and September, showed higher values than that in the rest of the year. We believe the higher emission before the Olympics was due to more activities in preparing the Olympic game. Although more reduction in SO₂ was seen in the post-Olympics period, the SO₂ mixing ratio showed a higher annual mean in 2008 than in 2009. Theoretically, the worldwide economic crisis in 2009 might cause a lower level of SO₂ but considering the economic stimulation measures implemented by the government, we do not think the economic crisis played a significant role. Moreover, the higher NO_x emission in 2009 than in 2008 supports our view. The improvement of energy structure has been speeded up in Beijing from 2009, which might be a more important factor.

We added information in the revised paper, see Line 195-203.

4. Line 246 and following

In chapter 4.3. the authors explain the different diurnal features of SO₂ and NO_x. The profile of NO_x coincides with the change in mixing depth while the diurnal profile of SO₂ is opposite to it. The profile of SO₂ is explained by transport from SO₂-rich air from above which originate from remote, not necessarily elevated, sources, which will increase SO₂ concentration during daytime. However, during nighttime an efficient loss process must reduce the SO₂ concentration again. What is the loss process that reduces the concentration of SO₂ reduced during nighttime?

Response: Due to the typical mountain-plain topography, south wind prevails in the daytime and north wind prevails at night in the North China Plain (Lin et al., 2008), similar diurnal wind directions like that in Figure S6. South wind brings polluted air mass and north wind transports clean air to SDZ. This process should be the major cause of the decreasing SO₂ levels during nighttime, since surface SO₂ mixing ratios depend on vertical air exchange. Enhanced relative humidity during nighttime should be also a loss effect since SO₂ is a very soluble gas. In addition, dry deposition of SO₂ in a shallow nocturnal boundary layer might lower the SO₂ level as well.

We added information in the revised paper, see Line 342-347.

5. Line 246 and following

With respect to the daily profile of NO_x it was argued that it is the result of transport processes during noontime. But isn't it more likely that NO_x is emitted from local sources close to the ground, as motor vehicles and small burners This was observed at the background site at Linan (Yin et al., 2022), which showed similar diurnal cycles and similar mean NO_x concentrations.

Response: Since the SDZ station is selected as WMO/GAW regional station, local anthropogenic emissions are well avoided. The station is situated on the south slope of a hill, on the north hill side of a valley with a northeast-southwest orientation. The southwest mouth of the valley is open to Beijing and the south plain. In the valley, motor vehicles running on the roads and dispersing human activities can emit NO_x as well as the transport from the south. As seen in Figure 8, the NO_x rose map showed wider source origins than SO₂. It seems that the diurnal NO_x cycle is not only similar with that at Linan, but also with those in urban areas, which might tell us a truth of regional characteristics of air pollution in eastern China. But these should be carefully studied in the future.

We add information in the revised paper, see Line 350-352.

Technical corrections:

1. Line 91: High values in winter and low values in summer

We have revised the manuscript accordingly.

2. Line 102:lower mixing depth heights

We have revised the manuscript accordingly.

3. Line 112: 27 ppb (ppb is missing)

We have revised the manuscript accordingly.

4. Line 112:I think a one-digit precision of the values is sufficient here

We have revised the manuscript accordingly.

5. Line 238:More difficulties

We have revised the manuscript accordingly.

6. Line 247:high values in winter and low values

We have revised the manuscript accordingly.

7. Line 249:greatly different from each other

We have revised the manuscript accordingly.

8. Line 287:low values in

We have revised the manuscript accordingly.

9. Line 288:exhibited great differences

We have revised the manuscript accordingly.

Please also note the supplement to this comment:

<https://acp.copernicus.org/preprints/acp-2021-866/acp-2021-866-AC4-supplement.pdf>