

## Response to comments by referee # 2

### General comments:

The study by Liu et al. reports long term measurements of surface SO<sub>2</sub> and NO<sub>x</sub> from a background measurement site in North China. I consider the data suited for publication in ACP, the manuscript is well organized and well written. However, concerning the data analysis, presentation and interpretation I have a few concerns detailed in the specific comments below that should be accounted in the revised version. Please consider making your data publicly available.

We appreciate the referee's valuable comments. We have addressed each comment as below and revised the manuscript accordingly. We have also made our data publicly available as described in "Data availability: The data in this study can be publicly accessed via <https://doi.org/10.7910/DVN/YFVLHV> (Liu et al., 2022)."

### Specific comments:

#### 1. I8-9: Are the differences in diurnal cycle of SO<sub>2</sub> and NO<sub>x</sub> due to sources or chemistry?

Response: The differences in diurnal cycle of SO<sub>2</sub> and NO<sub>x</sub> were attributed to emissions and chemical and meteorological processes. However, the major reason for the differences in all seasons in this study should be ascribed to apparent different emission sources of these two trace gases and meteorological effects on their concentrations. The diurnal cycle of NO<sub>x</sub>, with higher values during night and lower ones during daytime, can easily be explained by accumulation of NO<sub>x</sub> in the shallow nocturnal boundary layer and dilution and chemical removal during daytime. The diurnal cycle of SO<sub>2</sub>, with a clear peak around noon, seems to be less understandable. However, SO<sub>2</sub> is mainly emitted by power plant stacks and other coal-burning sources (normally with higher stacks), unlike NO<sub>x</sub>, which is mainly emitted by vehicles and other lower height sources. The elevated emission height makes big difference in the diurnal cycle of SO<sub>2</sub> under the influences of boundary layer evolution, transport and other processes. According the study by Xu et al. (2014), the SO<sub>2</sub> noontime-peak phenomenon could be attributed to four processes, i.e., down-mixing, plume transport, mountain valley breeze and fog/severe haze. For the SDZ site, mountain valley breeze is most important, followed by down-mixing.

Xu, W., Zhao, C., Ran, L., Lin, W., Yan, P., and Xu, X.: SO<sub>2</sub> noontime-peak phenomenon in the North China Plain, *Atmos. Chem. Phys.*, 14, 7757-7768, <https://doi.org/10.5194/acp-14-7757-2014>, 2014.

#### 2. I32-34: Please explicitly state the difference between regional and local/suburban pollution.

Response: Local/suburban pollution is closely associated air pollutants emitted locally. The pollution is limited on a smaller scale such as a town, a city or an urban area. Primary air pollutants exhibited a diurnal variation mainly following the diurnal pattern of emissions and containing the signature of diurnal differences of vertical mixing and chemical consumption. Regional pollution occurs over the whole region and is usually associated with large-scale

emissions and significantly influenced by transport and accompanying processes, such as chemical reactions, deposition, etc. In China, city clusters have been formed for decades, air pollution often shows regional characteristics.

We have added some information in Line 35-39.

**3. I36: What are "typical regional characteristics"? Please provide this information.**

Response: The typical regional characteristics of SO<sub>2</sub> as observed at different types of sites in this region in previous studies was a seasonal maximum in winter and minimum in summer and a daytime peak throughout the year. The typical regional characteristics of NO<sub>x</sub> was a seasonal maximum in winter and minimum in summer and a daytime valley in the diurnal pattern.

We have added some information in Line 42-43.

**4. I43: Please provide examples for the few studies (references).**

Response: We have added a reference as below.

Bai, J. H., Wu, Y. M., Chai, W. H., Wang, P. C., Wang, G. C.: Long-term variation of trace gases and particulate matter at an atmospheric background station in North China, *Advances in Geosciences*, 5, 248-263, <http://dx.doi.org/10.12677/ag.2015.53025>, 2015.

**5. I98 & I100-104: Does "heating season" mean winter? Please disentangle the season = winter and the cause for the high NO<sub>x</sub> values = heating. What is mainly used for heating in China? Coal, wood, oil, gas, electricity? Are your conclusion that the high NO<sub>x</sub> and SO<sub>2</sub> concentrations are caused by higher emissions in combination with the meteorological conditions that slow down the reduction by less transport and slower chemical reactions?**

Response: As mentioned in the manuscript, the heating season in North China was from November to March (officially from 15 November to 15 March). So, "heating season" is not an accurate expression. We have changed it to "heating period". During the heating period, a large amount of air pollutants such as SO<sub>2</sub>, NO<sub>x</sub>, and particles are released from burners of centralized and domestic heating facilities. Before 2013 coal was dominantly burned for heating in the NCP, but it has been gradually substituted by natural gas since then in urban areas. In rural areas, however, burning of coal or wood has been a common practice for heating. The high levels of NO<sub>x</sub> and SO<sub>2</sub> were partly due to strong emissions during the heating period and partly due to meteorological conditions that favored the accumulation of air pollutants due to less transport and slower chemical processes.

We have added some information in Line 115-119.

**6. I106-113: What causes the diurnal cycles? Please explain.**

Response: The diurnal cycle of SO<sub>2</sub>, showing a daytime peak, was mainly resulted from mountain valley breeze and downward mixing of SO<sub>2</sub> emitted by elevated sources (Xu et al., 2014). The

diurnal cycle of NO<sub>x</sub>, showing a daytime valley, was mostly due to the active photochemical reactions and vertical mixing during the day and accumulation in the shallow nocturnal boundary layer. We discussed the causes in Section 4.3 and only described the result here.

Xu, W., Zhao, C., Ran, L., Lin, W., Yan, P., and Xu, X.: SO<sub>2</sub> noontime-peak phenomenon in the North China Plain, *Atmos. Chem. Phys.*, 14, 7757-7768, <https://doi.org/10.5194/acp-14-7757-2014>, 2014.

**7. 1141-145: Could the significant peak of SO<sub>2</sub> concentrations in 2008 be correlated with the (preparations for) the Olympic summer games 2008?**

Response: Control measures have been gradually taken a couple of years before the Olympic Games. Particularly, very strict measures started from July 2008. The concentration of SO<sub>2</sub> during September-October and November-March in 2008 was actually lower than that in previous years as a result of the effective control measures. A higher SO<sub>2</sub> in the early half year of 2008 was observed, and the higher emission before the Olympics is believed to be due to more activities in preparing the Olympic game (Lin et al., 2012).

Lin, W., Xu, X., Ma, Z., Zhao, H., Liu, X., and Wang, Y.: Characteristics and recent trends of sulfur dioxide at urban, rural, and background sites in North China: Effectiveness of control measures, *J. Environ. Sci.*, 24, 34-49, [https://doi.org/10.1016/S1001-0742\(11\)60727-4](https://doi.org/10.1016/S1001-0742(11)60727-4), 2012.

**8. 1146-152: Please explain the cause for the changes in NO<sub>x</sub>.**

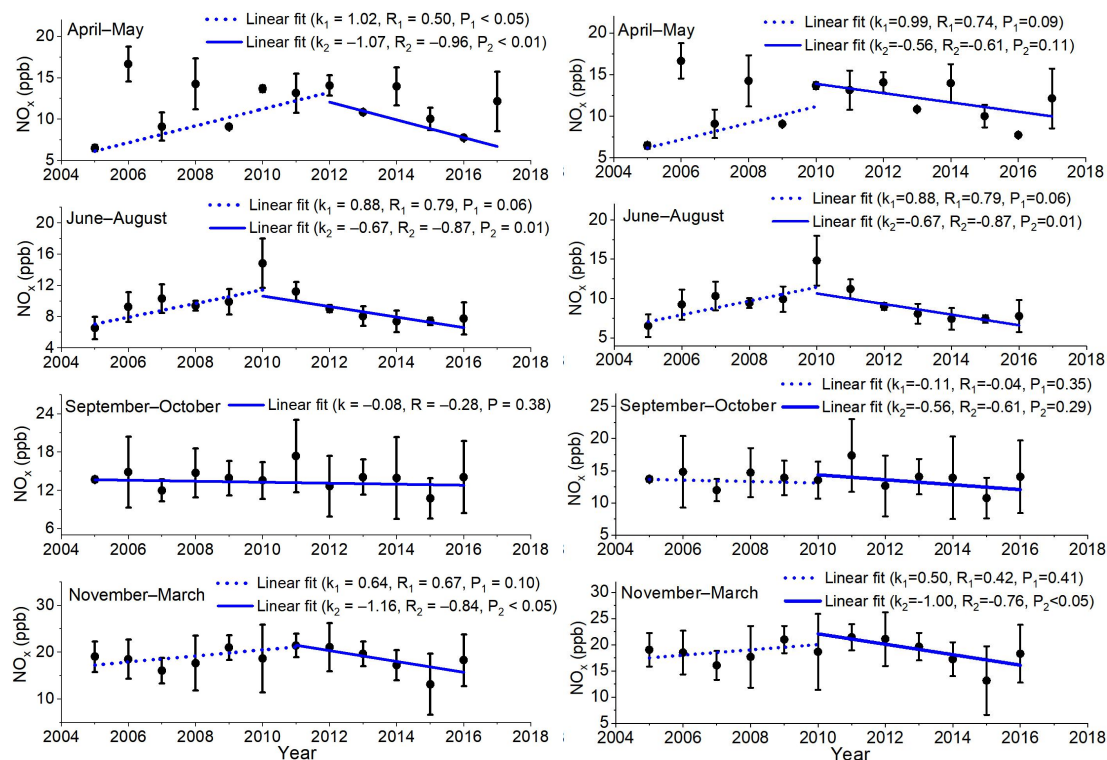
Response: Here we just presented the changing result of NO<sub>x</sub> and we discussed the causes in Section 4.1.

**9. Fig 6: Which months are shown for November-March? Jan, Feb, Mar, Nov, Dec of e.g. 2008, or Nov 2007 - Mar 2008, or Nov 2008 - Mar 2009?**

Response: The period November-March 2008 was November 2008 to March 2009.

**10. Fig 6b: The splitted fits should be consistently covering the same time periods: 2005-2010 and 2010-2017. What caused the change in NO<sub>x</sub> trends 2010/2011?**

Response: Thanks for the suggestion. We refitted the plots by splitting the same time periods: 2005-2010 and 2010-2017, and the result is shown in Figure R1. For April-May, the new split presents an insignificant trend from the old one. Since the peaks of seasonal NO<sub>x</sub> appeared in different years, we kept the previous splits in order to find the significant downward trend years.



**Figure R1. Figure 6b (left) and the revised Figure 6b (right).**

According the analysis by Krotkov et al. (2016) and Duncan et al. (2016),  $\text{NO}_2$  pollution over Northeast China has reached its peak in 2011, and there have large decreases over Beijing, Shanghai, and the Pearl River Delta, which were likely associated with local emission control efforts. Since January 1, 2011, Beijing has adopted the policy of "new car purchase restriction" lottery number purchase. Since August 1, 2011, Beijing has implemented the plan for further promoting the elimination and renewal of old cars. New glass emission standard for air pollutants from the flat glass industry (GB 26453-2011) was also implemented in this year.

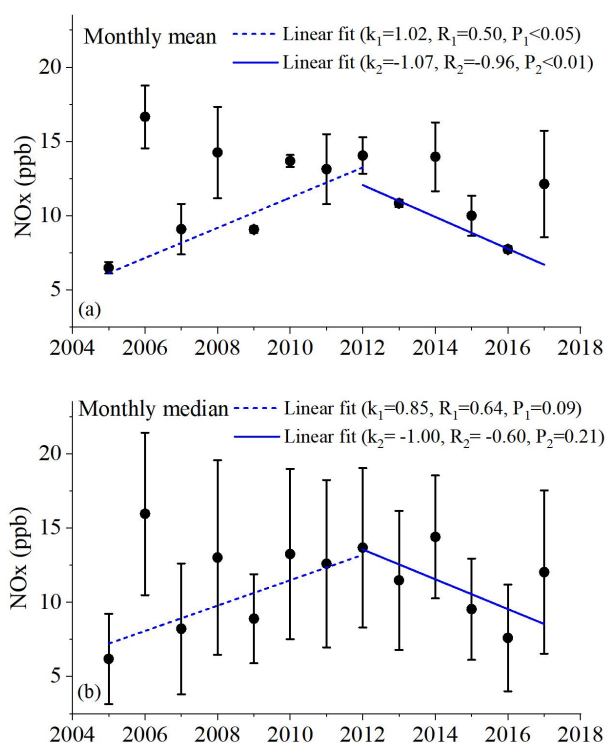
We discussed it in Section 4.1, see Line 213-218.

Krotkov, N. A., McLinden, C. A., Li, C., Lamsal, L. N., Celarier, E. A., Marchenko, S. V., Swartz, W. H., Bucsela, E. J., Joiner, J., Duncan, B. N., Boersma, K. F., Veefkind, J. P., Levelt, P. F., Fioletov, V. E., Dickerson, R. R., He, H., Lu, Z., and Streets, D. G.: Aura OMI observations of regional  $\text{SO}_2$  and  $\text{NO}_2$  pollution changes from 2005 to 2015, *Atmos. Chem. Phys.*, 16, 4605-4629, <https://doi.org/10.5194/acp-16-4605-2016>, 2016.

Duncan, B. N., Lamsal, L. N., Thompson, A. M., Yoshida, Y., Lu, Z., Streets, D. G., Hurwitz, M. M. and Pickering, K. E.: A space-based, high-resolution view of notable changes in urban  $\text{NO}_x$  pollution around the world (2005-2014), *J. Geophys. Res. Atmos.*, 121(2), 976-996, <https://doi.org/10.1002/2015JD024121>, 2016.

**11. 6b April-May: Why is the fit put through the lowest values and does not seem to account for the high values in 2006, 2008, 2010, 2012, 2014, 2017? I'm not fully convinced by the increasing and then decreasing trend. Do the median values support these trends?**

Response: We checked the fitting curve and the median values fit similar trend (R). We fitted the curve not only based on the mean (median) values but also considering their uncertainties as weighting factors.



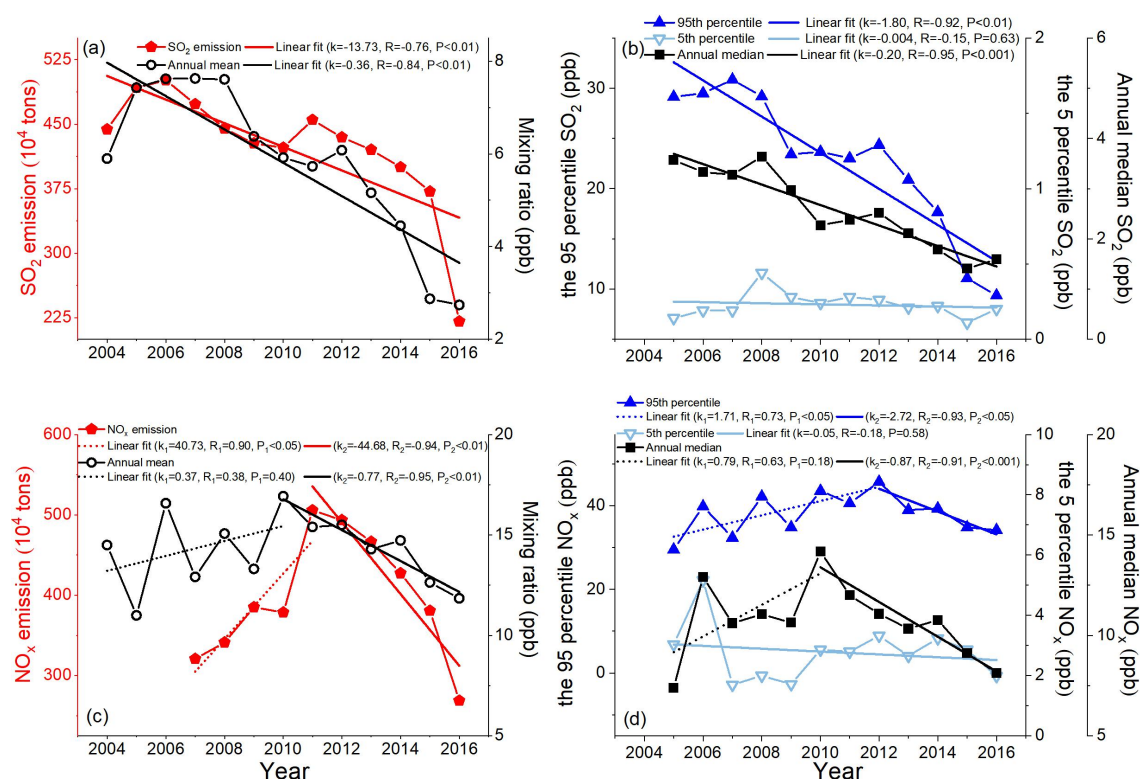
**Figure R2.** Long-term variations in (a) monthly mean and (b) monthly median NO<sub>x</sub> mixing ratios with 1-sigma for April–May in different year at SDZ.

**12. I169: Which day or month did the emission control measures for the Olympic games came into effect? Shouldn't this be visible in the seasonal data in Fig. 6?**

Response: Strict emission control measures took effect in July 2008. It can be seen in Fig. 6 that SO<sub>2</sub> concentrations exhibited a large variability during June–August in 2008, also SO<sub>2</sub> concentrations during the two periods of September–October and November–March were apparently lower than that in previous years. Lin et al. (2012) had discussed the changes in SO<sub>2</sub> between the pre-Olympic and the post-Olympic periods.

**13. Fig 5 right column: Please add data for the median. Maybe the NO<sub>x</sub> median fluctuates less than the NO<sub>x</sub> mean? Does the median also show a trend over time? Please add a description of the left and right y-axis to the figure caption. I assume that the 95 percentile refers to the left axis and the 5 percentile to the right axis. Is this correct?**

Response: We have added data for the median in Fig. 5 right column. The NO<sub>x</sub> median shows trends similar to the NO<sub>x</sub> mean. We added a description of the left and right y-axis to the figure caption.



**Figure 5.** Annually variations in (a) SO<sub>2</sub> mixing ratios at SDZ and total SO<sub>2</sub> emissions in North China; (b) the 5th and 95th percentile of the hourly mean and annual median of SO<sub>2</sub> mixing ratios and SO<sub>2</sub> emissions in North China; (c) NO<sub>x</sub> mixing ratios at SDZ and total NO<sub>x</sub> emissions in North China; (d) the 5th and 95th percentile of the hourly mean and annual median of NO<sub>x</sub> mixing ratios and NO<sub>x</sub> emissions in North China. The emission data are from the 2005–2017 Yearbook of National Bureau of Statistics of China and China Statistical Yearbook on Environment provided by Ministry of Ecology and Environment of the People's Republic of China.

#### 14. Fig5c: What caused the steep increase in NO<sub>x</sub> in 2010?

Response: Before 2011, the annual mean NO<sub>x</sub> showed an increasing trend with fluctuation year by year. We also have no clues about this steep increase in NO<sub>x</sub> in 2010, as well as that in 2006. It is worth noting that the motor vehicles in Beijing in 2010 had increased significantly from the previous year (see Figure S2), since the policy of purchase restriction in motor vehicle was implemented in 2011. In addition, NO<sub>x</sub> emissions from power plants and industrial sources were not strictly controlled before 2011. Therefore, more NO<sub>x</sub> would be emitted in years with prosperous economy.

We added information in the revised manuscript, see Line 208-212.



**15. I201: Please provide information on the details of the pollution prevention plans, especially with respect to SO<sub>2</sub> and NO<sub>x</sub>, so that the reader can see how strict the measures were and how they changed over time.**

Response: Details of the pollution prevention plans and its implementation can be found in UN Environment (2019), A REVIEW OF 20 YEARS' Air Pollution Control in Beijing (<http://sthjj.beijing.gov.cn/bjhrb/resource/cms/2019/04/2019041916301550241.pdf>) and in Zheng et al. (2018). Control process and specific measures for coal combustion and motor vehicles in Beijing from 1998 to 2017, and China's clean air policies implemented during 2010–2017 had been reviewed. We added information in the revised paper, see Line 247-249.

UN Environment. A Review of 20 Years' Air Pollution Control in Beijing. United Nations Environment Programme, Nairobi, Kenya, 2019.

Zheng, B., Tong, D., Li, M., Liu, F., Hong, C., Geng, G., Li, H., Li, X., Peng, L., Qi, J., Yan, L., Zhang, Y., Zhao, H., Zheng, Y., He, K., and Zhang, Q.: Trends in China's anthropogenic emissions since 2010 as the consequence of clean air actions, *Atmos. Chem. Phys.*, 18, 14095-14111, <https://doi.org/10.5194/acp-18-14095-2018>, 2018.

**16. I207-208: Please add what caused the shift in time of the maximum and what are the implications?**

Response: The daily maximum of SO<sub>2</sub> concentrations was caused by the downward mixing of SO<sub>2</sub> emitted by elevated sources in this region. As strict and effective control measures were continuously implemented, the contribution from such a source largely decreased and finally became negligible. Governed by the development of the planetary boundary layer, the diurnal variation of SO<sub>2</sub> concentrations would peak around noon. Xu et al. (2014) have discussed the implications. We discussed it in Section 4.3, see Line 337-347.

Xu, W., Zhao, C., Ran, L., Lin, W., Yan, P., and Xu, X.: SO<sub>2</sub> noontime-peak phenomenon in the North China Plain, *Atmos. Chem. Phys.*, 14, 7757-7768, <https://doi.org/10.5194/acp-14-7757-2014>, 2014.

**17. I217-220: Please show in how far the changes in NO<sub>x</sub> correlate with the emission control measures in Beijing and/or NCP. I think this is speculative and giving details on the pollution prevention plans could support your conclusion.**

Response: Here, we draw this conclusion based on the opposite trends of the observational NO<sub>x</sub> and SO<sub>2</sub> mixing ratios. The increase of NO<sub>x</sub> and the decreasing of SO<sub>2</sub> in Stage II tells the fact of much more effective of pollution control measures on SO<sub>2</sub> rather than NO<sub>x</sub>. China intensified its acid rain control in the beginning of this century by much more strict control of SO<sub>2</sub> emissions from coal-fired power plants. However, the control of NO<sub>x</sub> emissions remained weak until the introduction of the new Emission Standard of Air Pollutants for Thermal Power Plants (GB13223-2011) (Wang et al., 2019). Such major difference in SO<sub>2</sub> and NO<sub>x</sub> emission control caused an earlier peak for SO<sub>2</sub> (around 2006) and a later peak for NO<sub>x</sub> (around 2011-2012) (Li et al., 2017). Our emission data for North China (Figure 5) nearly resemble the nationwide situation

and the mixing ratio data at SDZ (Figure 7) are consistent with the general trends of SO<sub>2</sub> and NO<sub>x</sub> emissions.

We add information in the revised manuscript, see Line 267-275.

Wang, N., Lyu, X., Deng, X., Huang, X., Jiang, F., Ding, A.: Aggravating O<sub>3</sub> pollution due to NO<sub>x</sub> emission control in eastern China, *Science of the Total Environment*, 677, 732-744, <https://doi.org/10.1016/j.scitotenv.2019.04.388>, 2019.

Li, M., Liu, H., Geng, G., Hong, C., Liu, F., Song, Y., Tong, D., Zheng, B., Cui, H., Man, H., Zhang, Q. and He, K.: Anthropogenic emission inventories in China: a review, *National Science Review*, 4, 834–866, <https://doi.org/10.1093/nsr/nwx150>, 2017.

**18. Fig7.: Do you have an explanation for the small peak at 2 am? Are the differences in SO<sub>2</sub> and NO<sub>x</sub> between the years significant? Please provide uncertainty range, e.g. 1-sigma-range for SO<sub>2</sub> and NO<sub>x</sub>.**

**Again, what are the uncertainty ranges? I assume, that the decreasing trend for SO<sub>2</sub> is robust. However, I'm not convinced that the differences in NO<sub>x</sub> between the different periods are outside the 1-sigma range.**

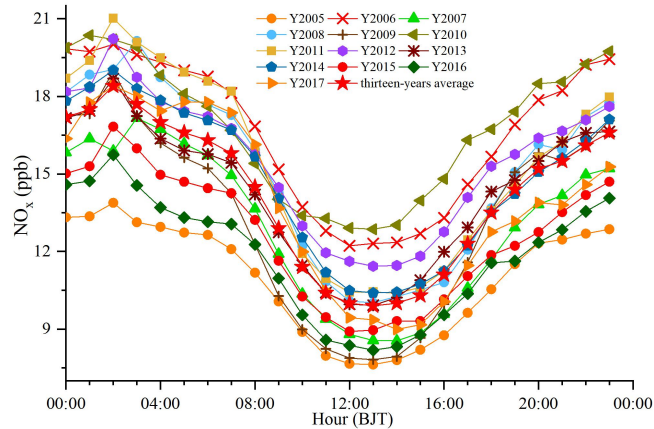
Response: Frankly, we do not have any clues about the small peak at 2 am yet.

In this section, time intervals were divided according to the average diurnal change of SO<sub>2</sub> in different years (see Figure S3 in supplementary material). Although the difference in diurnal change of NO<sub>x</sub> was not as obvious as SO<sub>2</sub> (see Figure R3 here), we applied the same time intervals here.

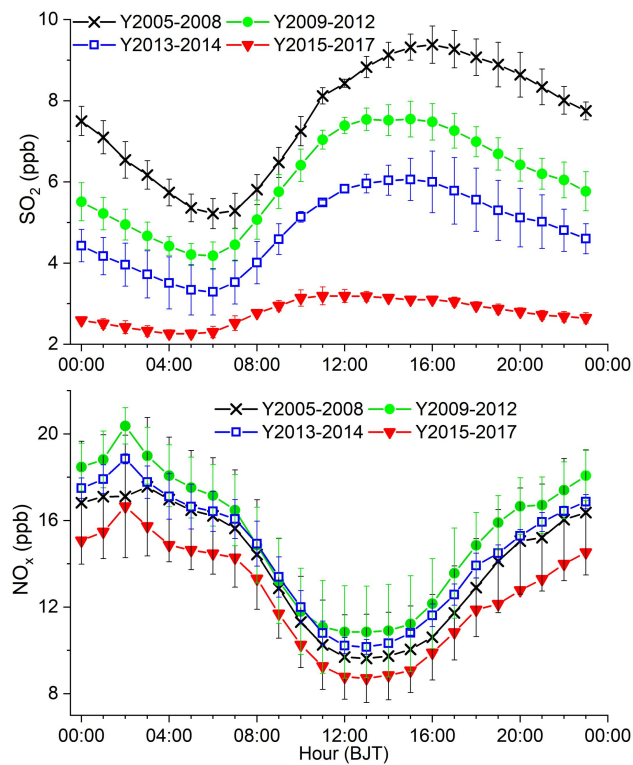
Figure R4 shows the result of adding 1-sigma ranges for SO<sub>2</sub> and NO<sub>x</sub> in Figure 7. For SO<sub>2</sub>, the differences among the 4 different periods are significant ( $P < 0.001$ ) from the One-Way ANOVA test, and the differences between the two groups are also significant ( $P < 0.01$ ) from t-test. For NO<sub>x</sub>, the differences among the 4 different periods are significant ( $P = 0.01$ ) from the One-Way ANOVA test, but the differences between the two groups are only significant ( $P < 0.01$ ) between Y2009-2012 and Y2015-2017 from t-test.

We added information in the revised paper, see Line 253-255 and Line 263-265.





**Figure R3.** The average diurnal variations in NO<sub>x</sub> mixing ratios in different years at SDZ.



**Figure R4.** 1-sigma ranges for SO<sub>2</sub> and NO<sub>x</sub> are added in Figure 7.

**19. I238:** Please detail what you mean with "relatively more difficult in emission control". Are there less regulations with respect to traffic emission control? Are the traffic emission control regulation less strictly adhered to?

Response: Unlike emissions from industries, emissions from automobiles are relatively more difficult to control. The reason that supports this argument is that emissions from industrial plants could be quantitatively measured, thus control measures that require a reduction of a certain percentage in emissions could be implemented. However, the estimation of emissions from automobiles bears large uncertainties in the first place. Though there are also strict control

regulations as to cars with license plates of a chosen number are not allowed to be on road on certain days, the actual reduction in emissions also depends on the usage of other cars.

We added information in the revised manuscript, to see Line 294-299.

**20. 1246-278:** When discussing the differences in the diurnal cycle of SO<sub>2</sub> and NO<sub>x</sub> their different lifetimes also should be considered. With SO<sub>2</sub> lifetimes of ~13-10h in summer and 48-58h in winter [e.g. 1] transport from the NCP to the measurement site certainly has an impact. However, NO<sub>x</sub> lifetimes are shorter and significantly differ between summer (~6h) and winter (~24h) [e.g. 2] and day (29h) and nighttime (6h) [e.g. 3]. Here transport not always may have an impact and the observed NO<sub>x</sub> levels might be more local. Please discuss. Moreover, is there a diurnal cycle in the local emissions of SO<sub>2</sub> and NO<sub>x</sub>?

## References

- [1] Lee, C., Martin, R. V., van Donkelaar, A., Lee, H., Dickerson, R. R., Hains, J. C., Krotkov, N., Richter, A., Vinnikov, K., and Schwab, J. J.: SO<sub>2</sub> emissions and lifetimes: Estimates from inverse modeling using in situ and global, space-based (SCIAMACHY and OMI) observations, *J. Geophys. Res.*, 116, D06304, <https://doi.org/10.1029/2010JD014758>, 2011.
- [2] Shah, V., Jacob, D. J., Li, K., Silvern, R. F., Zhai, S., Liu, M., Lin, J., and Zhang, Q.: Effect of changing NO<sub>x</sub> lifetime on the seasonality and long-term trends of satellite-observed tropospheric NO<sub>2</sub> columns over China, *Atmos. Chem. Phys.*, 20, 1483–1495, <https://doi.org/10.5194/acp-20-1483-2020>, 2020.
- [3] Kenagy, H. S., Sparks, T. L., Ebben, C. J., Wooldridge, P. J., Lopez-Hilfiker, F. D., Lee, B. H., et al. (2018). NO<sub>x</sub> lifetime and NO<sub>y</sub> partitioning during WINTER. *Journal of Geophysical Research: Atmospheres*, 123, 9813–9827, <https://doi.org/10.1029/2018JD028736>.

Response: We thank the referee for this helpful comment. We agree with the referee that a longer lifetime may be more associated with an impact from transport on a regional scale. 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<sub>x</sub> as well as the transport from the south. As seen in Figure 8, the NO<sub>x</sub> rose map showed wider source origins than SO<sub>2</sub>. It seems that the diurnal NO<sub>x</sub> 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.

**Technical corrections:**

**1. l8: and other instances: valley -> minimum**

We have revised the manuscript accordingly.

**2. l16: What is SDZ? Please introduce abbreviations before first usage.**

We have revised “at SDZ” as “at the Shangdianzi (SDZ) background site”.

**3. l91: high value -> high concentrations**

We have revised the manuscript accordingly.

**4. l115,123,132,: showed -> shows**

We have revised the manuscript accordingly.

**5. l205: were -> are**

We have revised the manuscript accordingly.

**6. l221: "is" -> "shows" or "are"**

We have revised the manuscript accordingly.

**7. l232: has -> has been**

We have revised the manuscript accordingly.

**8. l237: should -> could**

We have revised the manuscript accordingly.

**9. l243: were not be > have not been**

We have revised the manuscript accordingly.

**10. l247: high -> high concentrations**

**low -> low concentrations**

We have revised the manuscript accordingly.

**11. l272: Please specify what "YRD" is.**

We have revise “the YRD” as “the Yangtze River Delta”.

**12. 1277: was -> were**

We have revised the manuscript accordingly.

**13. 1285: exhibited greatly different for all > exhibited large differences in all**

We have revised the manuscript accordingly.

**14. 1299-300: "... had weaker influence than SO<sub>2</sub> by the emission reduction..." -> had a weaker response to the emission reduction in ... than SO<sub>2</sub>**

We have revised the manuscript accordingly.