

## ***Interactive comment on “Observations of SO<sub>2</sub> and NO<sub>2</sub> by mobile DOAS in the Guangzhou Eastern Area during the Asian Games 2010” by F. C. Wu et al.***

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We would like to thank the referee for taking the time to read the paper carefully and provide helpful suggestions to improve the paper. We have revised the paper according to the referee's comments carefully, where the revised parts are indicated by red font. The detailed revisions are described as follows: General comments: The authors ignore in the data analysis and interpretation that NO<sub>2</sub> has a strong diurnal cycle. These variations result in a spatial variance just due to the fact that the measurements at different locations are taken at different times. Also the estimation of NO<sub>2</sub> flux should better be based on a NO<sub>x</sub> flux. In the DOAS data analysis the HCHO reference is

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missing which may have a significant influence on the data results. Additionally a sufficient error estimation is often missing. E.g. how large is the error if wind direction is used from street level? Response: With respect to the effects of the strong diurnal cycle of NO<sub>2</sub> on the data analysis, we have made some modifications and interpretations in section 3.1.2. The NO<sub>x</sub> emissions have been estimated in section 3.2.1 instead of NO<sub>2</sub>. The HCHO reference has been added to the DOAS data analysis. And we re-retrieve spectra for SO<sub>2</sub> and NO<sub>2</sub> analysis. The results have small changes after including HCHO absorption, as shown in Fig.2. Furthermore, the estimation of the error caused by uncertainties of the wind field was added in section 3.2.1. Specific comments: 1. p. 262 Abstract: A statement that the mobile DOAS is a passive DOAS is missing, and that measurements are performed during daylight (specify time of day) is missing. Response: We have emphasized the “passive DOAS” and specified the measurements time in the abstract (Page 1, Line 15-19). 2. The sentence: “NO<sub>2</sub> is an important trace gas in the atmosphere because it readily undergoes photochemical reactions with other air pollutants.” is not absolutely correct, as it also react with non- air pollutants. Response: The reviewer is correct. The “air pollutants” have been replaced by “other atmospheric constituents” in the introduction (Page 2, Line 35) 3. It is worth to mention here that SO<sub>2</sub> has not necessary to increase with higher energy consumption if according filters are used in power plants. Response: The reviewer is correct. A corresponding statement has been added to the sentence. (Page 2, Line 49-50) 4. p. 264 l.12 Clarify that it is “passive” Differential Optical Absorption Spectroscopy p. 265 l. 4: Which time of day do these data represent? p. 266 l. 12: specify the field of view of the telescope. Response: We have clarified this technique as “passive Differential Optical Absorption Spectroscopy” on Page 4, Line 87-89. The detailed measurement time has been presented on Page 4, Line 110-111. The field of view of the telescope is 0.1° (Page 6, Line 151) 5. What does “has a stable temperature” mean? Please specify. Response: The phrase “has a stable temperature” means the spectrometer is stored in a miniature refrigerator to maintain a stable temperature of +25°C (Page 6, Line 152-153). 6. Please specify that the meteorological data are at street level. But

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the DOAS data are a vertical column density (VCD). Response: We have clarified that the meteorological data are at street level on Page 6 Line 156. 7. The statement that airborne measurements cover a limited spatial area is not correct, but difficult to achieve on a regularly basis. Response: The reviewer is correct. We have made corresponding modifications on Page 8, Line 201-202. 8. Offset correction is missing. Is this performed? Response: We performed offset correction. Actually, we started with background correction, which includes dark current and offset corrections (Page 8, Line 220). 9. Differential slant column densities are DSCD not SCD and the description has to be corrected. Response: The reviewer is correct. This correction has been made on Page 8, Line 223-226. 10. 269 l. 4-6: A description of how the reference spectra are adapted to the instrument resolution is missing. p. 269 l. 11: A description of how the wavelength calibration with the solar spectrum is performed is required, as the question arise if the authors used an instrument function or not. Response: The reference spectra were acquired with the same instrument as the measurement spectra. All absorption cross sections are convoluted with instrument's slit function to adapt to the instrument resolution during the fit process (text added on Page 9, Line 241-242). The wavelength calibration is performed using a highly resolved solar spectrum which is convoluted with the instrument's slit function (text added on Page 9, Line 246-248). 11. For both evaluations, SO<sub>2</sub> and NO<sub>2</sub>, the references of HCHO are missing. Response: For SO<sub>2</sub> and NO<sub>2</sub> evaluations, the HCHO absorption should be included. The variations of retrieval result included HCHO or not are less than fit uncertainties approximately over high pollutant area (such as GEA). So we didn't include the HCHO absorptions for the retrieval originally. However, in order to obtain reasonable retrieval results we re-retrieved all the spectra considering HCHO absorptions for NO<sub>2</sub> and SO<sub>2</sub> now, as specified on Page 9, Line 238,246. 12. The DSCD derived with the MAX-DOAS are averaged over a measurement distance of several km, as this is the typical viewing length of these instruments. If these measurements are directly compared to the mobile measurements, no strong spatial variations over the averaging path should exist. Else the value of the MAX-DOAS is not necessary

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representative for the instrument location. This has to be shown, e.g. By looking at the variability of the mobile DSCD values within a typical averaging length of the MAX-DOAS in this specific area. Please specify "in order to eliminate the reference" → "in order to eliminate the NO<sub>2</sub> and SO<sub>2</sub> VCD in the reference" Response: Your suggestion is very valuable. We have looked at the variability of the mobile DSCD values within a typical averaging length of the MAX-DOAS in the specific area as now shown on Page 10, Line 259-272. For most days, the standard deviation of mobile DSCDs is small. The phrase "in order to eliminate the reference" has been replaced by "in order to eliminate the NO<sub>2</sub> and SO<sub>2</sub> VCD in the reference" (Page 10, Line 259-260). 13. The Lidar and LP-DOAS measurements used for the radiative transfer calculations are taken at very different locations than the MAX-DOAS measurements. How much do possible variations in the concentration affect the retried results? Please estimate an error. Response: The Lidar and MAX-DOAS measurements are taken at the same location. They are located at Shilou (SL) site, as shown in Fig.1. The LP-DOAS and MAX-DOAS are at different locations. The LP-DOAS is located at Guangzhou University Town (GU) site, 15km northwest of SL. We have estimated the error caused by possible variations in the concentration. The errors are less than 5% for NO<sub>2</sub> and SO<sub>2</sub> by varying the concentration of NO<sub>2</sub> and SO<sub>2</sub> of  $2.5 \times 10^{11}$  molec./cm<sup>3</sup>,  $6.25 \times 10^{11}$  molec./cm<sup>3</sup> and  $1.25 \times 10^{12}$  molec./cm<sup>3</sup> within the boundary layer. (Page 11, Line 293-295) 14. please specify: that the wind data are: "measured wind speed at ground level..." Response: We have now made this clearer on Page 14, Line 361. 15. The SO<sub>2</sub> peak irrespective of wind direction can not be seen in the Fig. 6, maybe if plot type/ quality are improved. Response: We have changed this figure to make this point clearer. 16. please add to SO<sub>2</sub> source "(without dominant NO<sub>2</sub> emission)" Response: We have added the "(without dominant NO<sub>2</sub> emission)" to SO<sub>2</sub> source. (Page 14, Line 371-372) 17. Specify which mobile DOAS data are used for the comparison. The ones during the OMI overpass at the same location? Or average data of the day. In this section especially the strong diurnal cycle of NO<sub>2</sub> is ignored. As this is typically much stronger than the spatial variability, a comparison of the mobile measurements taken over a day

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with the OMI data taken at a fixed time of the day is insufficient. A better correction of the diurnal cycle is necessary. Response: The mobile DOAS data are used for the comparison have now been specified on Page 15 Line 388-395. In the revised section, we compare the results from both instruments in two ways. First, the comparison was performed within a specific satellite ground pixel (113.50E–113.75E, 22.75N–23.00N) for all days with mobile DOAS and OMI data available. Second in order to explore the spatial patterns, all the NO<sub>2</sub> VCDs along the measurement path of mobile DOAS are used for comparison to OMI values within pixels of the higher (0.1° x 0.1°) resolution grid obtained from re-gridding the OMI data again for all days. We also have attempted to estimate the influence of the diurnal variations of NO<sub>2</sub> on these two comparisons. The corresponding discussions are now on Page 16 Line 416-425 and 430-442. 18. The statement "while low NO<sub>2</sub> VCDs were likely overestimated" by OMI, seems to be wrong, as I can not see this in Fig. 8. Response: The statement "while low NO<sub>2</sub> VCDs were likely overestimated by OMI" means the NO<sub>2</sub> VCDs overestimated by OMI observation over the clear area for spatial distribution as shown in Fig. 9. The similar finding is also found in Shaiganfar, R., et al (Estimation of NO<sub>x</sub> emissions from Delhi using Car MAX-DOAS observations and comparison with OMI satellite data, *Atmos. Chem. Phys.*, 11, 10871–10887, doi:10.5194/acp-11-10871-2011, 2011.) We have removed the expression in the paper in order to avoid misunderstanding. 19. p. 273 l. 19: Including here the NO<sub>2</sub> and SO<sub>2</sub> surface concentration does not give additional used information and is more confusing than helpful. p. 273 l.20: Please clarify the sentence which instrument underestimate NO<sub>2</sub> VCD. Response: In order to avoid confusion, we have removed the corresponding passages. 20. The correlation of the spatial distribution of NO<sub>2</sub> from OMI and mobile DOAS is difficult (or not) visible. Please give a correlation plot. The bad correlation may be due to the ignored diurnal cycle of NO<sub>2</sub>. Response: We have added a correlation plot in Fig. 10 and a discussion of the diurnal cycle of NO<sub>2</sub> as remarked in response to comment 17 on Page 16 Line 416-425 and 430-442. What does "constant vertical wind" means? First I guess you mean a vertically constant wind. Second what is the margin for constant? Response: "constant

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vertical wind" here means that the wind field, especially the wind direction, is relatively stable and constant from ground to 400 m height. Wind directions at ground and 400 m height generally agree, with a relative deviation of ~30°. (see Page 17, Line 457-459) 21. p. 274 l.11: The wind field shown in Fig. 12 for ground and 400m measurements seems to vary on some days significantly. Please clarify which day you select as constant wind within the boundary layer and what are for these days the differences. p. 275 l.20 Using 20% for the error of the wind field seems to be optimistic, as wind speed in Fig. 12 vary by almost a factor of 2. How does this factor 2 is estimated? Response: We consider 14 days shown in Fig. 4b as days with constant wind within the boundary layer. For these days, the wind direction at ground and 400 m height up to ~30° in most cases. Resulting uncertainties are estimated to be 20% based on standard deviation of these wind directions. The wind speed varied by almost a factor of 2 from ground to 400m height. However, we don't consider the variations of wind speed between surface and the height of 400m in this paper because they are measured at very different locations which can cause significant changes of wind speed. The ratio of wind speeds at 400 m to that at ground level was estimated to be 1.2-1.3 in (Shanshan Wang et al., Remote sensing of NO<sub>2</sub> emission from the central urban area of Shanghai (China) using the mobile DOAS technique. *JOURNAL OF GEOPHYSICAL RESEARCH*, VOL. 117, D13305, doi:10.1029/2011JD016983, 2012). So the emission errors caused by wind speed are estimated to be 20%-30% due to wind speed at ground level instead. (Page 17, Line 457-466) 22. NO<sub>2</sub> feature a strong diurnal cycle due to photochemical reactions. An emission of NO<sub>2</sub> thus strongly depend on the time of day, solar radiation etc.. The NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions would be a much better value. Response: We have estimated NO<sub>x</sub> emission instead of NO<sub>2</sub> as shown on Page 12, 18; Line 311-326, 467-478. 23. The comparison of the estimated SO<sub>2</sub> emission to the inventory seems to be inconsistent, as the encircled measurement area is much smaller than the whole Guangzhou area and thus the estimated SO<sub>2</sub> emission should be much smaller. Response: The SO<sub>2</sub> emission is 84.60 × 10<sup>3</sup> tons per year from emission inventory in 2010. If SO<sub>2</sub> emission from GEA derived from this emission inventory directly, this

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value might be smaller than estimated emission from mobile DOAS. However, GEA including the fractions of Dongguan City (Fig. 1), the SO<sub>2</sub> emission estimated by mobile DOAS contain the Dongguan fractional contribution of SO<sub>2</sub>. On the other hand, the major SO<sub>2</sub> sources of Guangzhou located the GEA. And thus we think the results from mobile and local inventory are agreement on order of magnitude at least. 24. Description of back trajectories incl. Fig. 14 + 16 seems not to be very useful for the data interpretation and more confusing. Also the Fig. 17 seems to be redundant. Please shorten this section. Response: We have removed the Fig. 16 and Fig. 17 as well as shortened this section (Page 19, Line 518-522). However, we retained the Fig. 14. We think it help us understand the air mass trajectories directly and visually. 25. Fig. 1 Please indicate LP-DOAS and MAX-DOAS light path/ viewing direction. Also indicate the scales of each map. Fig.2: This figure is redundant. Response: We have changed the Fig. 1 and removed the Fig.2 p. 288 Fig.4 Please clarify for which times the data points are averaged? Are these daily average or averages only for the time if both data are available? p. 289 Fig.5 Please clarify for which time the data are average. To increase the clarity of the plot add a line between the data points. Why is this figure not combines with figure 12? Response: We have made corresponding revisions. If both data are available, we average only for the time. 26. p. 290 Fig.6 The data are displayed in a very unclear way and are not useful. Please change e.g. to 2D plots with colour coded concentrations. p. 291 Fig.7 Please combine with Fig.1 p. 293 Fig.9 If comparing Fig.8 and Fig.9, in Fig. 9 the axis seem to be wrong labeled (switched) p. 297 Fig. 13 Clarify for which time of day the emissions are estimated. Response: We have made corresponding revisions 27. p. 299 Fig. 15 Please indicate in the caption what shaded days mean. Also here are days with very high SO<sub>2</sub> when wind is not from south-east. Please explain. Response: We have added it in the caption. The wind in the days with very high SO<sub>2</sub> on 24 and 28 November and 10 and 12 December are also from south-east as shown on Page 19, Line 518-519. Maybe the SO<sub>2</sub> are slight high on 14 and 15 November and 11 December, but the values are just 10-15ppb, which are smaller than those in the days with southeasterly wind. 28. p. 300 Fig.16 This figure

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seems to be redundant. Response: We have removed it. Technical comments: p. 264 l. 19 Specify the city in Mexico. p. 264 l. 19/20 specify the country for Mannheim and Ludwigshafen p. 266 l.16 "as well as" → and p. 269 l.16 ", these" → the p. 287 Fig 3 In caption: "in the text" → "in section ..." p. 288 Fig.4 Third figure caption: "add Offset" → "mobile DOAS data + add Offset" Response: Thank you for your careful modifications. We have modified the above editorial errors in our revised manuscript according to your suggestions. p. 295 Fig. 11 The track of the mobile DOAS is difficult to see over the OMI map. Please change the display. Response: We have changed the display about this figure. Maybe it is much better for seeing now. Thanks for your opinions and very appreciated your time. If you have any questions about the manuscripts, please let me know.

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