

## ***Interactive comment on “Variations of O<sub>3</sub> and CO in summertime at a rural site near Beijing” by Y. Wang et al.***

**Y. Wang et al.**

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Comments: In the Introduction please begin with a couple of paragraphs reviewing what is already known about surface ozone variability in China. Also highlight the limited measurements in comparison to Europe and North America, and the much shorter data records. Furthermore, please discuss the rapidly increasing emissions in China and the implications these have for the global ozone budget. Then go on to describe how the Miyun site fits into the picture. I8217;m assuming that: 1) this site fills a gap in our knowledge of summer ozone formation downwind of Beijing; and 2) understanding the factors that control ozone at this site can help constrain regional and global scale chemical transport models, which are important for quantifying the impact of China on the regional and global ozone budgets. It is fine to also state that the results will be beneficial for local ozone control strategies but this needs to be a

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Interactive Discussion

Discussion Paper



secondary point.

– We thank Dr. Cooper for the well thought and very constructive comments on the introduction. The introduction was rewritten.

Comments: The following paper by Wild et al is relevant to your study. Chemical transport model ozone simulations for spring 2001 over the western Pacific: Regional ozone production and its global impacts Author(s): Wild O, Prather MJ, Akimoto H, et al. Source: JOURNAL OF GEOPHYSICAL RESEARCH-ATMOSPHERES Volume: 109 Issue: D15 Article Number: D15S02 Published: MAY 21 2004. Their springtime study shows how stagnation events allow for strong ozone production over east Asia, but these conditions tend to keep the ozone over Asia. In contrast, cloudy frontal systems don't produce as much ozone over Asia, but export the precursors downwind where ozone is formed, having a greater impact on global ozone. In light of this study it would be very useful if you can use GEOS-CHEM to determine if the cloudy monsoonal conditions have large quantities of ozone precursors that can easily produce ozone once the cloudy air mass is exported from China. For example, under cloudy conditions is there still a lot of NO<sub>x</sub> available for future ozone production or has most of it already been converted to HNO<sub>3</sub> or other oxidized species? This analysis will help to make your study more relevant to the broader scientific community.

– We compared the NO<sub>x</sub> to NO<sub>y</sub> ratio during the two-day case-study period 18-19 July (Section 4.3). On 18 July, the Miyun region was under heavy cloud cover and precipitation, and surface O<sub>3</sub> levels were greatly reduced. On the following day (19 July), the area was clear with low relative humidity and surface O<sub>3</sub> levels were high. We have added the following discussion in Section 4.3:

Wild et al. (2004), using a global chemical transport model, examined the influence of different regional meteorological processes on regional ozone production over East Asia in spring time and its global impact. Their work demonstrated in detail that cloudy, cyclonic weather systems unfavorable for boundary layer ozone production over East

Full Screen / Esc

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Interactive Discussion

Discussion Paper



Asia typically allow for efficient lifting of precursors into the free troposphere where ozone is formed downwind, having a great impact on global ozone. In contrast, they found that stagnant, anticyclonic events conducive to strong ozone production over East Asia tend to keep ozone and precursors within the boundary layers, having relatively small impacts on global ozone. In light of their study, we examined the variation in NO<sub>x</sub>, an important ozone precursor, during the two-day period. Although measurements of NO<sub>x</sub> are not available, we adopted model fields as the GEOS-Chem model was found to reproduce the observed variation of O<sub>3</sub>, RH, and COD between 18 and 19 July. The NO<sub>x</sub> to NO<sub>y</sub> (reactive nitrogen family, the sum of NO<sub>x</sub> and its oxidation products) ratio in the boundary layer at Miyun as predicted by the GEOS-Chem model is 0.7 on 18 July (cloudy day with low mixing ratio of surface O<sub>3</sub>) as compared to 0.4 on 19 July (clear day with high O<sub>3</sub>). Simulated mixing ratios of NO<sub>x</sub> in the boundary layer are also higher on 18 July than on 19 July, partly because of an increase in the chemical lifetime of NO<sub>x</sub> below clouds. Consistent with Wild et al. (2004) springtime study, our analysis suggests that although local photochemical production of ozone is suppressed below the optically thick clouds, there is still a lot of NO<sub>x</sub> available for future ozone production when the polluted air mass is exported downwind (toward northeast in summer) or lifted to the free troposphere by convection with implications for global ozone production.

Comments: My final recommendation for making the paper more appealing is to provide some context for the very high pollution levels found in rural China. For example your statement on line 11 of page 10406 describing a "modest peak" of 800 ppbv of CO comes as a surprise to someone accustomed to studying pollution episodes at rural sites in North America. A modest CO peak at a rural site in the eastern USA would be 200 ppbv, with 300 ppbv being very high. The pollution levels in China far exceed what is commonly found in the rest of the world and you need to make this point clear. I would like to see a figure comparing the CO percentiles (like your Figure 2) of ozone and CO at Miyun for June, July and August, averaged over the years 2005-2007 and compared to a rural site in eastern North America. Harvard Forest would be a good

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choice seeing as it is at a similar latitude (although I8217;m not sure if the Harvard Forest data are measured from the top of a tall tower which will make it difficult to compare the ozone data, but should be fine for CO, during well mixed daytime conditions).

– The point is well taken. We have removed modest from the text and added the following text in Section 4 to compare the CO levels observed at Miyun with those at other Chinese sites and US sites:

At Miyun the mean daytime mixing ratios of CO are 600 ppbv (ppbv = nmol mole<sup>-1</sup>) in summer 2006, higher than the mean summertime CO levels observed at Lin An in the Yangtze River Delta (Wang et al., 2002) and at a coastal site (Tai O) near Hong Kong in south China (Wang et al., 2005) by 220 ppbv and 400 ppbv, respectively. The higher CO levels at Miyun may reflect the influence of CO sources from the Beijing urban area located upwind of the site under the prevailing southwesterly in summer. By comparison, mean summertime CO mixing ratios at rural low-elevation sites in the eastern North America are generally less than 200 ppbv (Chin et al., 1994; Mao et al., 2004).

Minor Comments:

Throughout the paper CO and O<sub>3</sub> are described in units of ppbv, but described as concentrations, which is incorrect. All ppbv values need to be referred to as mixing ratios. Also all instances of ppb need to be replaced by ppbv. Also the brackets around [O<sub>3</sub>] and [CO] are unnecessary and need to be removed.

– We have made changes in the manuscript.

page 10399, line 1 change to "an understanding"

– Corrected.

page 10399 line 9 change to "an elevation of 152 m"

– Corrected.

page 10399 line 11-13 rearrange to: Mountains rise steeply to the north of the site, while the terrain to the south falls off gradually to about 90 m in a region characterized by a mix of agriculture and small villages.

– Corrected.

page 10399 line 15 change to: "between relatively clean continental air"

– Corrected.

page 10399 line 19 change to: "includes a suite"

– Corrected.

page 10400 line 12 When CO is measured, is it concentrations or mixing ratios that are determined by subtracting the zero value from measured voltage. etc?

– It is a mixing ratio. We8217;ve clarified in the text.

page 10401 line 8 change to "and run through 2006"

– Corrected.

page 10402 lines 1-3 change to: "CO levels increased by about 300 ppbv from June to July, monthly mean O3 decreased by 17 ppbv"

– Corrected.

page 10402 line 10 The Chinese air quality standard corresponds to 102 ppbv. Is this determined at standard temperature and pressure, or some other level of temperature and pressure?

– This is determined at 1 atm pressure and 25oC. We have ve clarified in the text.

page 10402 line 20-21 the trend is not increasing, but the CO is increasing, so change this sentence to say: "capturing the increase in CO from June to July"

– Corrected.

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Interactive Discussion

Discussion Paper



page 10402, line 27 Please provide some details of the TRMM data, such as the type of instrument, the platform, orbit frequency and spatial resolution of the monthly average rainfall data.

– The TRMM data we used are 0.5o x 0.5o gridded monthly products comprised of mean hydrometeor profiles from the TRMM Microwave Imager (TMI) instrument on board the TRMM satellite. We have added the details in the text.

page 10403 line 2 change to "East Asian summer monsoon"

– Corrected.

page 10403 line 8 change to: "observations sampled at the site had less than"

– Corrected.

page 1040 line 10 change to: "clean air was encountered only 15"

– Corrected.

page 10403 lines 21-22 are the relative humidity values averaged over all hours, or just daytime hours?

– Just daytime hours. We8217;ve clarified in the text.

page 10403 line 27 change to "influence on photolysis rates"

– Corrected.

page 10404 line 26 change impressive to striking

– Corrected.

page 10405 lines 20-22 How do you know that the model underestimates NO, do you have measurements that you can compare with the model.

– We do not have measurements of NO, but given the coarse resolution of the model and the fact that the model underestimates CO in the plume, we believe the model

Full Screen / Esc

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Discussion Paper



also underestimates NO in the urban plume. We have changed the text as follows to indicate that it is our speculation:

The model, given its relatively coarse resolution, underestimates CO and probably also concentrations of NO<sub>x</sub> in the urban pollution plume reaching the site, underestimating consequently the titration effect of NO on O<sub>3</sub>.

page 10405 line 26 You state that the model demonstrates the significance of the radiative impact of monsoonal clouds on ozone and explains why obs. at other sites in east China do not show an O<sub>3</sub> max. in summer. But how do you know this? Have you, or other researchers actually conducted analyses to see if this really is the case, or is your statement just speculation? Please clarify.

– This is our speculation. As the East Asian summer monsoonal circulation prevails over the whole east China (east of the Tibetan Plateau) during summer, we speculate that the significant radiative impact of monsoonal clouds on ozone demonstrated at the Miyun site is a large-scale regional phenomenon. Indeed, surface observations at other sites in east China do not show an O<sub>3</sub> maximum in summer. We have clarified in the text:

As the East Asian summer monsoonal circulation prevails over the whole east China (east of the Tibetan Plateau) during summer, we expect the radiative impact of monsoonal clouds on ozone to be significant on a regional scale. Consistent with our speculation, previous observations at other surface sites in east China do not show a maximum of O<sub>3</sub> in summer (Wang et al., 2002; Luo et al., 2000).

page 10406 line 22 change to "Large intra-seasonal differences"

– Corrected.

page 10407 line 1 change to "associated with the onset"

– Corrected.

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