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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term trend of surface ozone at a regional background station ineastern China 1991–2006: enhanced variability" *by* X. Xu et al.

X. Xu et al.

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We would like to thank both anonymous referees for their comments and helpful suggestions. We revised our paper according to their comments and suggestions.

Response to comments by referee 1

1. When based on scattered data stemming from different instruments and time periods as this, the calibration procedures are crucial. The authors write that the instruments were "carefully calibrated". I would like some more details on this. How was the calibration done and how often? Was the field instruments calibrated against a transfer standard, or taken to a lab etc?

Indeed details about the calibrations are important information for this study. We have described the instrument calibrations in a paragraph added to Section 2.

2. In sect. 3.3 the authors write that the existence of a diurnal variation in ozone indicates that photochemical formation of ozone is important "...in all seasons". I disagree with this, and think that the diurnal cycle mainly reflects the diurnal variation in the mixing in the boundary layer. This mixing combined with ozone deposition to the surface and/or titration with NO is the most likely cause for the ozone diurnal cycle in my view and doesnt necessarily indicate any local photochemistry taking place.

Our original words are "The diurnal patterns of surface ozone at Linan, together with the large amplitudes, indicate that in all seasons photochemical formation of ozone is important in the Yangtze Delta region". Here the phrase "in all seasons" is indeed an inappropriate expression. However, we believe that you overestimate the influences of physical processes on the diurnal cycle of surface ozone at Linan. Although some physical processes related to the vertical mixing, e.g., surface deposition and entrainment, may be as important as photochemistry in determining the variation of surface ozone, photochemistry is still one of the important factors contributing to the diurnal cycle of surface ozone, particularly in regions with high pollutants levels (Frost et al., 1998). A numerical study (Yang and Li, 1999) suggests that in some polluted regions in China, such as, the Yangtze Delta, the Sichuan Basin, etc., the variation of surface ozone is mainly determined by photochemistry and the vertical mixing can even lead to a decrease of surface ozone level. A more specific simulation of surface ozone at Linan, using an observation-based box model, indicates that on a clear autumn day photochemical production of ozone is one order of magnitude larger than the loss of ozone (Zhu et al., 2004). The same study also shows that the entrainment causes faster increase of surface ozone concentration in the morning than mere photochemistry and slower increase in the afternoon, implying that surface ozone level in the afternoon would be suppressed by the vertical mixing without photochemical forma-

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tion. Therefore we believe that at least in the warmer seasons the observed diurnal cycle of surface ozone at Linan is mainly caused by photochemistry, not the mixing.

In view of the importance of physical processes, we have changed the original sentence to "The diurnal patterns of surface ozone at Linan, together with the large amplitudes, indicate that photochemical formation of ozone is one of the important factors in the Yangtze Delta region, at least in the warmer seasons".

3. In sect. 3.5 the authors presents the results of in-situ NOx measurements. However, no details are given to these measurements. What kind of NOx monitoring was carried out? Is there any correlation between NOx and O3? Do the data contain NO2 separately or just NOx as a sum? More details on this should be included.

We have included the details about the NO_x measurements in Section 2 and Table 1. Although the dataset contains NO, NO_2, and NO_x concentrations, we only use NO_x data in this paper. There is no simple linear correlation between the hourly/daily mean NO_x and O_3 concentrations. The O_3-NO_x relationship looks like a hyperbolic curve. Least-square fit gives a negative linear correlation between the monthly O_3 and NO_x concentrations (slope = - 0.61, α = 0.05). There are correlations between the monthly lowest/highest 5% of ozone concentration and NO_x concentration. According to the suggestion of referee 2, we have included in the revised paper a figure showing the correlations (Fig. 10).

Response to comments by referee 2

1) In abstract, the authors should list the "Possible causes for the observed trends are discussed". Among these possible causes, it is really due to "the increase of NOx concentration"?

"Possible causes for the observed trends are discussed" is already in the abstract. According to our study, we believed that the increase of NO_x concentration is the most

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likely cause.

2) The authors should give more linkage between NOx change and ozone variations (Fig. 6 and Fig. 8). How about the percentage of regional ozone transport from the surrounding area such as the Yangtze Delta Region? If possible, to use a box model to show how these NOx increase can make daily amplitude of relative diurnal variations?

Giving more linkage between NO_x change and ozone variations is indeed a good idea. We compared the monthly NO_x concentration with the monthly extreme values of ozone. There is certain correlation but with lower significance. Theoretically, the monthly highest ozone value is more influenced by NO_x in the warmer months (due to more intensive photochemistry) than in the colder months and the monthly lowest ozone value is more influenced by NO_x in the colder months (due to stronger titration) than in the warmer months. In view of the different effects of NO_x, we compared the monthly lowest 5% of ozone with the monthly mean NO_x concentration in colder months (November to April) and the monthly highest 5% of ozone with the monthly mean NO_x concentration in warmer months (May to October). We found significant correlations between the extreme values of ozone and the NO_x concentration. We have included a figure (Fig. 10) showing these correlations and added text to Section 3.5.

Although it is interesting to know the relative contribution of regional ozone transport from the surrounding area to Linan and the influence of NO_x increase on the daily amplitude of relative diurnal variation of ozone, we do not make any simulation in the current study. As for the ozone transport from the surrounding area, the study of Ma et al.(2002) provides some valuable information. According to this study, the contribution of lateral boundary import (LBI) is comparable to and at night even larger than the contribution of in-situ photochemical production. To better understand how the NO_x increase can change the daily amplitude of relative diurnal variations and other issues, modeling studies are needed, as already stated in the manuscript. However, these

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studies are out of scope of current paper.

3) Fig.1 should afford high resolution figures, the proportions of different clusters given in the colored boxed are not clear.

Larger fonts are used in the redrawn figure. Higher resolution figure will be submitted.

4) Please list seasonal peak and minimum of ozone in different seasons and years in table 2.

The seasonal maximum and minimum concentrations of ozone have been included in Table 2 in the revised manuscript.

5) Please give monthly mean lines during 1994-1995 and 2005-2006 in Fig. 2.

Monthly mean lines for the periods 1994-1995 and 2005-2006 have been plotted in the figure.

6) Have any datasets to show the VOCs change at Linan? Please discuss the possible impacts of VOCs change on ozone variations.

Although there are some VOCs data from Linan, the dataset is inadequate to show a clear picture of long-term change of VOCs at the site. During the campaigns PEM-West A and B canister samples were collected at Linan by Drs. J.-Z. Zhao and M. Rodgers. The samples were analyzed for hydrocarbons (data available from http://www-gte.larc.nasa.gov/). The total measured non-methane hydrocarbons (TNMHCs) averaged 92 ppbC and 541 ppbC for PEM-West A and B, respectively. Because the samples were few and taken during relatively short periods, these data may not well represent the TNMHCs level of early 1990s. Another two datasets of TNMHCs covers four different seasons and are based on more samples. The first one is for the period from August 1994 to April 1995, showing an average of TNMHCs of about 75 ppbC (Xu et al., 1996), while the second one is for the period from October 2003 to July 2004, showing an average of TNMHCs of about 239 ppbC (Wang et al, 2006). These data show about a factor of two increase of the TNMHCs level at Linan in about ten

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years. In view of the rapid changes in VOCs and other ozone precursors, more studies should be done to better understand the possible impacts of these changes on ozone in the Yangtze Delta region.

In the last paragraph of Section 3.5 the increase of NMHCs concentration and its impact are briefly mentioned. We have made slight changes to the related text without adding more discussions.

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