Atmos. Chem. Phys. Discuss., 9, C3141–C3153, 2009
www.atmos-chem-phys-discuss.net/9/C3141/2009/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Increasing surface ozone concentrations in the background atmosphere of southern China, 1994–2007" *by* T. Wang et al.

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Received and published: 23 July 2009

Reply to co-editor and referees' comments

First, we thank Dr. Owen Cooper and the two anonymous referees for their helpful comments and suggestions. The main comments are on (1) the relatively large values of p in the linear fits of the seasonally and air-mass averaged data and the use of additional trend analysis method, (2) the contribution of ship emissions to the observed ozone changes at Hok Tsui, and (3) the interpretation of the ozone change at the background site and an urban site. Below we give reply to the above major issues, which is followed by itemized responses to each referee's comments.

On the trend analysis: we have used two additional methods: the linear fitting of de-

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seasonalized monthly ozone and CO and conducting a variance analysis of the means in year 1994-2000 and 2001-2007. For the seasonally and air-mass averaged data, the variance analysis of the data for the above two periods have been carried out.

Applying the linear fit to de-seasonalized monthly data yielded similar results as in the case of original data ($p < 0.01$; slope: 0.57 versus 0.58 ppbv/yr). For CO, it has improved the statistical significance for CO (p: <0.01 versus 0.15), while giving a similar rate of change (slope: 0.34 versus 0.35 pbbv/yr).

The large p value in the linear fit of the seasonal and air-mass grouped data is in part due to a small sample size (14 points) in which case the p value may not be the sole criteria for testing the level of significance. Following the co-editor's suggestion, we divided the data into two periods (1994-2000 and 2001-2007) for four seasons and for four air mass groups. It shows that the later period had significantly higher values (at the 95% confidence level) for ozone in all the seasons and the "East China", "Aged continental", and "Central China+PRD" air masses groups, but not in the "Marine" group. This suggests the ozone levels have increased in the more recent years in continent-influenced air masses. CO did not show a significantly greater value in the later period in any of the above air mass groups.

On ship emissions: we have examined satellite NO2 data along the main shipping routes in the South Sea and East Sea of China, no positive trend has been indicated. The emission data show that land-based sources in China dominate the total NO2 emissions. The results seem to support the contention that the increasing land-based emission is the main cause in the ozone trend measured at Hok Tsui.

On point 3, we think it makes sense to estimate the contribution of background air to the local ozone trend by comparing the rate of change in the upwind and urban sites. We would like to retain this part.

The itemized responses to each referee's comments are given below.

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(1) Co-editor's comments

"This review is by Owen Cooper, co-editor of this manuscript. I am posting my comments now to stimulate the discussion of this paper. My comments are made without the benefit of having read the reviews of the anonymous referees and their assessments will have a major influence on my decision as to whether the paper will be published in ACP. The anonymous referees are free to disagree with any of my comments when they write their reports.

Overall I find the findings to be very interesting and the paper is generally well written and organized. Several issues need to be addressed and/or corrected as outlined in my review below. My main concern is that the p values for seasonal ozone and annual CO rates of increase are fairly high (> 0.05) but the results seem to be treated as highly significant. Clarification of which rates of increase are significant needs to be made. In these cases, analysis of variance tests can be used to determine if ozone or CO increased significantly between 1994-2000 and 2001-2007 (as discussed below)."

Response: We conducted variance tests for the ozone data in the two periods. The results show that the seasonally averaged ozone in the later period is significantly greater (at the 95% confidence level) than that in the earlier period. For CO, a linear fit of the de-seasonalyzed monthly data showed a significant upwind trend (3.4 ppbv/yr, $p<0.01$), but the t-test did not indicate significant larger value in the later period. We will integrate these results into the revised version.

"Main concerns: Throughout the manuscript the word trend needs to be replaced with something like "rate of change" or "increase". Fourteen years is not really long enough to establish a true trend, but is long enough to talk about changes in ozone."

Response: We will change the term as suggested.

"Some of the references in the Introduction are not correctly summarized. For example on page 10432, lines 23-26, previous studies are given credit for attributing past

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changes in ozone above western North America to Asian emissions. However, Jacob [1999] doesn't look at ozone observations, he just used a model to predict future changes of ozone. Jaffe and Ray [2007] speculate that rising Asian emissions could be one of several reasons why ozone is increasing, but they make it clear that they weren't able to identify the source of the ozone increase. The text also implies that Collins et al. [2003] have shown that past changes in ozone in the mid- and upper troposphere are linked to climate change and enhanced transport from the stratosphere. But this paper only compares 1990-94 to 2090-94 and only talks about possible ozone changes 100 years in the future."

Response: we will replace the text in line 21-27, page 10431, by the following: "...In remote areas, changes in emissions in distant and local source regions, wild biomass burning, and atmospheric circulation all play an important role in ozone trends, and it can be of considerable challenge to establish the spatial representativeness of the observed trend and to pin down the underlying cause(s), as highlighted by analyses of the ozone trends in rural/remote western United States (Jaffe et al., 2003; Parrish et al., 2004; Jaffe and Ray, 2007; Oltmans et al., 2008; Parrish et al., 2009)."

"Recent papers relevant to the Introduction are: Increasing ozone in marine boundary layer inflow at the west coasts of North America and Europe, D. D. Parrish, D. B. Millet, and A. H. Goldstein, Atmos. Chem. Phys., 9, 1303-1323, 2009 Tanimoto, H. (2009), Increase in springtime tropospheric ozone at a mountainous site in Japan for the period 1998-2006, Atmos. Environ., 43, 1358-1363."

Response: We will include them in the introduction. For the second reference, we will add it in the following paragraph:

"...In the maritime regions impacted by Asian continental outflow, Chou et al. (2006) reported a positive trend in surface ozone in northern Taiwan for the 1994–2003 period, whereas the ozone data obtained at several Japanese sites indicated no obvious trends during the 1990s in regionally 20 polluted air masses from China (Naja and Akimoto,

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2004). A recent study of the ozone data for 1998-2006 at Mt Happo, Japan, however, showed an increasing springtime ozone of ~1 ppbv/yr (Tanimoto, 2009), and the author suggests the rising emission from East Asia be one of the causes."

"Please provide a little more information on the GOME and SCHIMACHY data. Which "level" of data was downloaded? Did the authors conduct any processing of the retrievals, or apply any cloud screening. Or was this all done by TEMIS?"

Response: We used the level 2 data which are directly downloaded from above TEMIS web site. No additional processing was performed by us. We will clarify this in the revision.

"Figure 3 provides the rate of change of ozone for all four seasons. While the average of these 4 rates is similar to the annual rate in Figure 1, the statistical significance drops from $p<0.01$ for the annual analysis to $p=0.07$-0.18 for the seasonal analysis. None of the seasons are significant at the $p=0.05$ level which is generally considered to be the maximum p-level to indicate a robust and significant rate of increase. This point needs to made clear in the text. Why does p increase when the data are examined seasonally? Is it because the sample size is reduced by a factor of 4 when compared to the annual analysis in Figure 1? What do you get if you take a season and split the data into two groups, 1994-2000 and 2001-2007, and conduct an analysis of variance test? Is the later group significantly greater than the earlier group? It may be that there is a highly significant increase in ozone between 1994-2000 and 2001-2007 (as could be shown by the analysis of variance test), it's just that using a linear fit to describe the increase is not as significant."

Response: The sample size in Fig 3 is actually 1/12 of that in Figure 1, thus a larger p value in Fig. 3 is in part due to a much smaller number of data points. For a small sample size, the p value may not be used as the sole criteria for statistical test (Mitulsky, 1995) because the linear regression assumes that data scatter follows a Gaussian distribution, and this assumption can be violated for cases with small number of samples.

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Following the co-editor's suggestion, we divided the data into two parts: 1994-2000 and 2001-2007 and computed the mean values for ozone in whole as well as for each season and for each air-mass group. A variance test (t-test) was done to check the confidence level for the difference between the means in the two groups. The result shows that the mean ozone in the later period is significantly greater than that in the earlier period (at the 99% confidence level for the all month data with an rate of increase of 0.87 ppbv/yr and at 95% confidence level all four seasons (with an rate of 0.72-1.01 ppbv/yr). Except in the "Marine" group, ozone was higher in other air masses groups affected by continental emissions (East China: 0.94 ppbv/yr; Central China: 1.20 ppbv/yr, Aged Continental: 0.85 ppbv/yr). We will include these results in the revised manuscript.

"The revised CO rate of increase is 3.5 ppbv/year with a p value of 0.15. Such a high p value does not give strong evidence that CO is increasing significantly. This analysis includes marine air from the south which isn't expected to have a strong increase in CO. What do you get when you filter the CO by source region or by season? Is the rate of increase more significant when transport is from East China or during autumn? Is it possible that as China's economy becomes more modern with more efficient power plants that CO emissions are increasing at a lower rate than NOx emissions? Also, what about shipping? Do the satellite data show an increase in NO2 along the major shipping lanes of southeast China? Several recent papers show that ships account for at least 13% of global anthropogenic NOx emissions but produce very little CO."

Response: Following the suggestion of referee 1, we computed the trend using de-seasonalized data which gives a rate of change of CO of 3.4 ppbv/yr ($p<0.01$), indicating that de-seasonality can improve the level of significance. However when we examined CO in each air-mass group, neither the linear fit nor the variance test showed a significant trend in CO. The less definitive trend of surface CO may indicate stabilized emission of CO in China due to improved efficiencies in power generation and other industries and/or reduced burning of biomass/biofuel. Recent emission inventory (Zhang

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et al., 2009) also suggests a more rapid increase in NOx than CO during 2001-2006 (55% versus 18%).

As to ship emission of NO2, we examined the rate of change of satellite NO2 along the main shipping routes in southeastern China (see attached figure), but no obvious trend can be detected. It is possible, however, that a small increase in NO2 exists from increased shipping activities over the oceans but cannot be detected by satellite. The contribution of ship emissions to total NO2 in China is much smaller compared to other parts of the world (see Fig. 4 in Dalsoren et al., 2009). By comparing the mean ozone in 2001-2007 and that in 1994-2000, the air mass group "East China", "Central China+ PRD" and Aged Continental" all showed significant higher O3 in the more recent period (with the rate of change of 0.94, 1.20 and 0.85 ppbv/yr, respectively). However the "Marine" air group did not show a significant difference in the two periods. This is consistent with the lack of a positive trend in the satellite NO2 data.

"Page 10441 line 25 It's not clear to me how it is determined that the increase in background ozone accounted for 70% of the increase in the total ozone in Hong Kong. If local NOx emissions are decreasing in an effort to control ozone, then shouldn't locally produced ozone be decreasing? This would imply that all (not 70%) of the total ozone increase in Hong Kong is due to background ozone."

Response: This is an interesting point. The 'extra' increase in total ozone at the urban site could be due to an increased local production of ozone (for example, if NOx is reduced at a faster pace than VOC in the typically VOC-limited urban environment, a warmer urban climate), increased transport of ozone from nearby Shenzhen urban area, and changing freshly emitted NO/NO2 ratios etc.

"In all figures the font size of the text along the axes as well as the text listing the rate of increase and p values needs to be increased."

Response: We will increase the font size in the revision.

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“Minor comments. If no explanation is given please replace the text in the manuscript with the suggested text. page 10430, line 7 increased at an average rate page 10431 line 22 wild fires page 10432 line 29 the major types of air masses influencing the site, and the ozone page 10433 Please make it clear that Hok Tsui is separated from the main urban are of Hong Kong by a ridge page 10434 line 18 against a NIST page 10436 line 26 The 14 years of data give”

Response: We will make the suggested changes in the revision.

(2) Anonymous Referee #1

“This paper presents an analysis of ozone data from the Hok Tsui site in Hong Kong. The analysis uses a variety of techniques to examine trends in ozone including analysis of the seasonal means, use of local winds, CO filtering and segregation using back trajectories. The paper is well written and fairly clear, although I would like to see some additional details e.g. R2 values and N for all calculations.

While the results are interesting, and generally consistent with our “expected” result, I am a bit concerned on the statistical methods and the statistical significance. Of all the “trends” reported in the paper, only the trend in monthly means (Figure 1) is statistically significant at a P value of 0.05 or lower, which is the usual criteria for significance. The authors attempted to look for trends in certain subsets of the data (by season, air flow, etc), however none of these reached a significance level of 0.05 or lower. Obviously our “expectation” is that ozone has increased in the air flow coming out of mainland China. However in the air arriving to Hong Kong from East China (Table 2) the slope is only slightly greater than for the entire dataset (0.64 vs 0.55) and the result is not statistically significant. (P=0.08). Using the CO concentrations as a screening tool might be useful, but if CO is also increasing, then doesn’t this represent a bias in the analysis?”

Response: Due to a small sample size of seasonally or air-mass averaged data (14 points), the p value may not be the sole criteria for testing the statistical significance.

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We applied another method: dividing the data into two time periods (1994-2000 and 2001-2007) and comparing the means, and the result shows significant positive trend for “East China”, “Central China+ PRD” and Aged Continental”, not for Marine air.

We use CO as a tracer of pollution to reduce the impact of local emission, and we think any small inter-annual change in CO should not affect its application for this purpose. We will add number of data points (N).

“I think it is very important that we let the data speak for itself and not jump to preordained conclusions. For example, if the data support the idea that the ozone trend is present IN ALL AIRMASS CATEGORIES (not just East Asian), that what does that tell us? While clearly emissions in China have increased, it is not clear what has happened to other sources over this same time period (eg SE Asian biomass burning emissions). Specifically, if the airflow in summer is generally not from China, then why is the summer trend nearly the same as in other seasons and with nearly the same statistical significance?”

Response: As indicated, the new analysis suggests that ozone did not have a significant trend in the Marine air, while other air-mass groups showed increased concentrations of O3 in the more recent years. Given a less definitive trend of the in-stu CO data, we will modify the original text to make it less assertive about the cause of the ozone trend at Hok Tsui.

“I would like to see the authors do some additional statistical analysis using methods other than Ordinary Linear Regression (OLR). I believe the authors should review some of the past work comparing statistical methods and incorporate other statistical methods. Since each method makes it own set of assumptions, and usually it difficult to verify rigorously these assumptions, conducting the analysis using several methods will result in a more robust analysis. I would encourage the authors to review some past work which has focused on a variety of statistical methods, for example: Hess, A., H. Iyer, and W. Malm, 2001. Linear trend analysis: A comparison of methods. Atmo-

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spheric Environment 35, 5211-5222. Jaffe D. and Ray, J. Increase in Surface Ozone at Rural Sites in the Western U.S. Atmos. Environ., doi: 10.1016/j.atmosenv.2007.02.034, 2007. (compares trends with deseasonalized data and Thiel's method)

Weatherhead, E. C., G. C. Reinsel, G. C. Tiao, X. L. Meng, D. Choi, W. K. Cheang, T. Keller, J. DeLuisi, D. J. Wuebbles, J. B. Kerr, A. J. Miller, S. J. Oltmans, and J. E. Frederick, 1998. Factors affecting the detection of trends: Statistical considerations and applications to environmental data. Journal of Geophysical Research 103(D14), 17,149-17,161."

Response: Following the suggestion, we have applied the trend analysis to deseasonalized ozone (and CO) data, and indeed the level of significance of the fit has improved. We will compare the result with the original method.

"I did not find the satellite discussion helpful. Many others have published these and it is quite clear that Chinese emissions are increasing relatively rapidly. I think the authors should focus on doing the best job they can do explain the data from Hong Kong."

Response: The satellite data are important for the discussion on the changes of NO2 over land and over the oceans. We would like to retain them. In the revised version, more discussions will be added on explaining the Hok Tsui data, especially the summer-time changes.

"A few other minor comments: Pg 10436, line 4: How is winter treated? I assume that the year is plotted based on Jan and Feb and that the previous years December is included in the winter average, correct? Pg 10436, line 26: Define local. I assume you mean direct NO titration, correct? Figures 1, 6 and 7: R2 and P values will improve if the data are deaseasonalized."

Response: The winter data included January, February, and December in the same year, as our dataset covers Jan. 1994 to Dec. 2007. We meant local titration by NO,

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and will clarify this point. As indicated above, using de-seasonalized data has improved the p value for CO, we will show this result.

(3) Anonymous Referee #2

“This paper presents the decadal change of surface ozone at a coastal site in Hong Kong, and suggests that the increase in ozone levels is primarily due to the increased emissions of NOx in the upwind eastern China. Data used in the paper are well documented and I find the results to be very interesting. Several issues need to be clarified as described in my review below.

Main concerns: The p values are used in the paper to assess the statistical significance of ozone or CO increase rates. A large range of p values is presented, e.g. $p<0.01$ for the annual increase and $p=0.07$-0.18 for the seasonal change, and the authors described that both annual and seasonal increase are statistical significant. The referee suggests the authors to add a general description of the statistical concept of the p-value in Section 2 or the beginning of Section 3, and clarify that what level of p values should be generally considered as "statistical significant". This will help future readers to better understand the results presented in this paper.”

Response: as discussed above, we have applied another method for deriving the trend and for testing the level of significance (i.e., variance test). We will add a section 2.4 to describe the three methods for examining the changes and how we treat the level of statistical significance.

“Data obtained at three sites are discussed: the background site Hok Tsui, the WGL site used to examine the impacts different air-mass groups, and the urban site CW. Both Hok Tsui and WGL are very close to the urban center of Hong Kong and the adjacent PRD, but the authors conclude that the increase of surface ozone at Hok Tsui is mainly due to long-range transport from eastern China, instead of local effects of Hong Kong and PRD. To support the conclusion, the authors need to provide the readers a clear geophysical relationship of these sites, the urban HK and PRD. A map

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showing local topography, prevailing winds and locations of these sites along with HK and PRD, will help. This will help future readers of this paper better understand the function of the background site as described in page 10433, and data filtering described in Section 3.2.2."

Response: We will add a map.

"Page 10440, line 5-10, the authors described that "the abnormally high ozone concentrations in 2004 coincided with the highest tropospheric NO2 columns in the PRD and the NCP for that year". But, comparing Fig.1 and Fig.5, I did not find such a relationship. Which season are you indicating? In fact, ozone is maximum in the autumn of 2004, but NO2 columns in the PRD and the NCP are maximum in the spring of 2004. If you are suggesting the autumn, I notice that NO2 columns are actually maximum in the autumns of 2005 and 2006. But, according to Fig.1, we do not see relatively high ozone levels at the study site in the autumns of 2005 and 2006. Wouldn't this somehow imply that the increase of ozone at Hok Tsui might not be directly due to the increase of NOx emissions in upwind eastern China?"

Response: The NO2 column at NCP and PRD is maximum in December 2004, the surface ozone at Hok Tusi is the highest in October 2004. The abnormally high ozone in October 2004 may be due to meteorology more than emission changes. We will remove that sentence.

"Would the increase of shipping emissions in the past decades (Eyring et al., 2005) play a role? The study site is located in the southeastern tip of Hong Kong island. The trajectories analysis shows that 30% of air masses are from the Marine group, and 13% from the Aged Continental group (Fig.4). Both marine and aged continental air masses might be strongly affected by international shipping. Several model analysis (e.g., Dalsoren et al. 2009) suggested that the contribution of shipping emissions to surface ozone and acid deposition is large over some coastal zones."

References: Eyring V. et al., Emissions from international shipping: 1. The last 50

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years. JGR, 2004JD005619 Dalsoren S. B. et al., Update on emissions and environmental impacts from the international fleet of ships: the contribution from major ship types and ports, ACP, 9, 2171-2194, 2009

As indicated in the reply to co-editor's comment, we examined the rate of change of satellite NO2 along the major shipping routes in southeastern China, but no obvious trend can be detected. It is possible, however, that a small increase in NO2 exists due to increased shipping activities over the oceans but cannot be detected by satellite. It is worth noting that the contribution of ship emissions to total NO2 in China is much smaller compared to other parts of the world (see Fig. 4 in Dalsoren et al., 2009). Overall, we think the land-based emission plays a dominant role in the observed changes of ozone at Hok Tsui.

"Page 10441, line 25: It is not clear to me that how the increase in background ozone accounted for 66% of the increase in the total ozone in the urban area of Hong Kong. How did you get the value 66%? Increase at Hok Tsui (0.55)/Increase at CW (0.83)= 66%? The calculation is not defensible, considering the non-linear feature of ozone photochemistry and the complexity of dynamic transport processes."

Response: The rate of change in total ozone in the urban area is 0,83 ppbv/yr, and the upwind site observed an increase rate of 0.58 ppbv/yr. This reveals that the local change in total ozone is largely due to the increased ozone in the air coming into Hong Kong. We think it is reasonable to estimate the outside contribution using the simple method we adopted.

Please also note the Supplement to this comment.

Interactive comment on Atmos. Chem. Phys. Discuss., 9, 10429, 2009.