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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes" *by* D. D. Parrish et al.

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The authors are grateful for the great deal of time and thought that the referee clearly put into the review of our paper [*Parrish et al.*, 2012]. We incorporate most of those comments into our revised manuscript, which has led to substantial improvements. Other suggested changes are not made for the reasons discussed below. Our responses to all comments follow. The original comments from the referee are in *italics* and our responses in plain text.

General comments

The paper brings together long-term surface/free trop. ozone measurements from the Northern hemisphere and presents trend analyses of the data. The analyses are done

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Interactive Discussion

Discussion Paper

in a straight-forward manner and the presentation is mostly done in a clear way. The main findings of the paper are of large interest to the scientific community. Thus, the manuscript is recommended for publication in ACP. Several modifications are suggested before publication, though. Significant parts of the underlying data and analyses are based on previous work published e.g. by Parrish (2009) and Cooper (2010) etc. More details of these studies would improve the clarity of the manuscript. Furthermore, parts of the observational data need more discussions.

Thank you for these evaluations and comments.

Specific comments

p. 13890: A map showing the monitoring stations/areas including the underlying individual stations for the merged data sets would help.

We have added a map of the monitoring stations to the Supplementary Material, and refer to it in our revised draft.

p. 13891: Regarding the measurements at Arkona, the authors state: "These measurements were initially conducted by well-calibrated, well-characterized wet chemical methods". Could the authors provide some more discussion of the general agreement between the old wet chemical method and today's UV monitors? Is there any risk of systematic artifacts due to interference or other analytical pitfalls? The very low concentration levels in the mid 1980s may indicate analytical problems.

Generally speaking the old wet chemical methods agree very well with today's UV monitors. In fact, when UV monitors were introduced in the U.S., the U.S. EPA initially mandated that the UV monitors be "calibrated" by comparison with a standard wet chemical method, although it was not long before UV monitors were accepted as an "Equivalent Method". However, the actual field performance of the wet chemical methods undoubtedly varied with operator and site characteristics.

At Arkona, there are no overlapping measurements with a UV monitor or other tech-

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nique. However, data from this site have been included in previous analyses of early O_3 concentrations [e.g. *Volz and Kley,* 1988]. The relative dip in O_3 seen in all seasons in the 1980s is not understood, and perhaps does indicate analytical problems; however whether those data are included or excluded has little influence on the analysis presented, so this potential problem is of small consequence for our purposes. A discussion of these issues has been added to the description of the data from this site, so that it now reads: "The data from these two sites are combined here to give one continuous record covering 1956-2010, but it must be noted that changes in site and measurement techniques add uncertainty to this data record. For example as discussed by *Feister and Warmbt* [1987], the earlier wet chemical methods suffered from negative interferences from sulfur dioxide (SO_2). However, the SO_2 concentrations at Arkona were so low that this interference was found to be negligible. A CrO_3 filter (for SO_2 removal) was installed in 1972 without detectable change in measurements. The concentration of the reagent solution was doubled in the mid 1970s, which led to a significant increase in observed maximum O_3 concentrations, but there was no indication that the mean concentrations were affected. Finally, a change from four measurements per day (0,6,12,18 h) to continuous recording was made in 1982, again without significant change [see Fig. 8 of *Feister and Warmbt* 1987]. The site change from the Arkona to Zingst does not show significant differences in values, nor in the trend. Nevertheless, the relative dip in O_3 seen at Arkona in all seasons in the 1980s is not understood, and perhaps does indicate analytical problems; however the exclusion of those data have little influence on the following analysis, so this potential problem is of small consequence for our purposes. "

p. 13891: The authors refer to (and use) the measurements from the 1930s and 1950s (Arosa and Jungfraujoch). A short description of the analytical methods together with the expected precision and the general quality of these data should be given (Fig S4 and S6 indicates the importance of these data).

At Arosa and Jungfraujoch O_3 measurements were made both by long-path absorption

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spectrophotometry and by wet-chemical techniques, which compared well with each other as reviewed by *Crutzen* [1988]. This short discussion has been added to the revised draft.

p. 13892: The authors state: "Parrish et al. (2009) have demonstrated that these measurements can be combined into a single record representative of MBL baseline O3 concentrations." How was this done? It's not obvious how it's possible to combine time series from several stations spread over a large area into one single time series. Although this is documented in the original reference it would help the readability of the present manuscript to include some description here.

This statement has been revised to read "By showing that there were no statistically significant differences between monthly average O_3 determinations in onshore airflow when measurements were concurrently available from separate sites, *Parrish et al.* [2009] were able to combine these measurements into a single record representative of MBL baseline O_3 concentrations."

p. 13893: (Similar comment as above). The authors write: "To increase the robustness of the latter data set, measurements from the three northern MBL sites (Rishiri Island, Cape Tappi, and Sado Island, 38–45 N latitude) reported by Tanimoto et al. (2009) are combined into a single data set." Again – how are these three more or less parallel time series "combined" into one? This should be explained.

The following sentences have been added to revised draft: "This is accomplished by assuming that a seasonal average O_3 determination at any one of the three sites constitutes an independent determination of the MBL O_3 concentration in this region; the average of all available averages for each season (from either two or all three of the sites) is taken as the best estimate of the regional MBL seasonal average. These two Japanese data sets have been extended through 2011 because of their relatively short temporal extent. Problems were identified in the data at Mt. Happo in 2007 and 2010, which led to their exclusion."

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p. 13893: Authors write: "For the US Pacific Coast MBL, Parrish et al. (2009) utilized a window high, onshore wind to select baseline conditions." What does this mean? Was the screening of data based on local wind measurements at the individual sites – for certain sectors/wind speeds? How good metric is the local wind compared to the general advection (e.g. land/sea breeze effects etc)?

This has been further explained. The revised draft now reads: "For the U.S. Pacific Coast MBL, *Parrish et al.* [2009] selected data collected during a high, onshore local wind window. This wind selection criterion was shown to give comparable results to selection by criteria based upon several continental tracers."

p. 13896: Authors write: "The year 2000 was selected here because that year is well inside the time period covered by all data records; selection of a reference year near one end of the data record would degrade the confidence limits for the intercept determined in the linear regression". That may be true, but for several sites (e.g. Hohenpeissenberg) the linear fit is applied only unto 2000, thus this year is indeed at the end of the record. What possible effect does this have for the results? Should the ref. year be changed to an earlier year for these sites?

We have selected the year 2000 as the reference year to calculate the relative average trends plotted in Fig. 7b, so it is not practical to use an earlier year for some of the sites. In practice the selection of reference year can make about a factor of two difference in the confidence limit of the derived intercepts. For example, at Hohenpeissenberg the derived confidence limits for reference years 2000 and 1985 (the center of the measurement record before 2000) are compared below.

Season, CL 2000, CI 1985
Spring, 2.2 ppbv, 1.1 ppbv
Summer, 3.3 ppbv, 1.7 ppbv
Autumn, 1.7 ppbv, 0.9 ppbv

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Winter, 1.9 ppbv, 1.0 ppbv

However, since the confidence limits for the year 2000 intercept (see error bars in Fig. 6 of *Parrish et al.* [2009]) are relatively quite small, no change has been made in this treatment.

p. 13897 and elsewhere: The authors find the strongest rate of increase in winter. This is somewhat surprising as one could expect the signal of anthropogenic precursors for ozone formation to be stronger in spring and summer. Some discussion of the possible reasons for the seasonal differences in long-term trends would be of interest.

Observed O_3 concentrations are the net result of local and regional O_3 production and destruction, and long-range transport. One major influence of anthropogenic emissions is destruction of O_3 from reaction with emitted precursors (primarily nitric oxide as well as some hydrocarbons), which is most important in winter. Further, the relative influence of photochemical production and destruction has important seasonal differences that do not necessarily lead to spring or summertime peaks. Hence, explanations of seasonal differences in O_3 changes are not clear without detailed model calculations. Our goal in this paper is to define the O_3 changes that have occurred as accurately and precisely as possible from the available observations. We prefer not to speculate further as to the causes of the changes.

p. 13901: Authors write: "After 2007 the traceability system and operational protocol for monitoring ambient O3 in Japan was modified and the instruments of EANET were replaced in 2009, so a systematic error is suspected. Efforts are underway attempting to resolve this discrepancy; until a resolution is reached, the more recent data are not included in the analysis of O3 changes at this site."

The Japanese data are of particular interest in this manuscript because they indicate a very different trend than in Europe and the US. Unfortunately, the two most recent years of data (after the mentioned change in procedures) may indicate a major problem with the previous ozone data and it's not obvious that it's only reflecting a "systematic

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error" as the authors write. A systematic error could either be a fixed or a relative bias which would influence in the estimated trends in different ways. A non-systematic error (e.g. problems linked to procedures for calibration, maintenance etc.) would, however, influence the measurements and trends in a more random manner. The Japanese historical data are an essential part of the manuscript and at the same time the most recent data undermines their reliability. How to deal with that? I think the authors need to give more details about these data, what type of change in procedures etc. were adopted in 2007 and what implications that will have for the data and the estimated trends up to 2007.

We now have more information regarding the Japanese data. We have rewritten this section in the revised manuscript, which we believe addresses these important concerns expressed by the referee.

p. 13902: The authors should give some more information about the North American FT data. Based on Fig S9 they seem to be based on data in 1984 and the years from the mid 1990s and on. Why this large time gap? Is the linear slope significant if 1984 is omitted? Although this presumably is explained in Cooper et al (2010) some key information should be included here as well.

The revised manuscript now has the statement: "This data set does have a long gap between the first year (1984), when a large data set was collected during the NASA CITE-2 study, and 1995, when the MOZAIC program and two sonde series were initiated. The derived slope is still significant if the 1984 data are excluded and does not statistically significantly differ from that derived from the full data set [see *Cooper et al.*, 2010]."

p. 13907. Authors write: "The result is an increase of approximately 1%yr-1 relative to the respective year 2000 intercepts in each season, specifically 1.08±0.09, 0.89±0.08, 0.79±0.12 and 1.22±0.12%yr-1." It's somewhat unclear how these confidence levels were calculated.

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The standard approach for calculating the confidence limit of a weighted average is from the inverse of the sum of the inverses of the confidence limits of the numbers averaged [see for example p. 70-71 of *Bevington*, 1969]. In response to a comment of the first referee (Jennifer Logan), these weighted averages have been revised, and a short explanation of the confidence limits has also been added in the revised draft.

p. 13909: The value of the data from Bermuda and Sable Island is questionable, and the authors also state that due to the scattered data coverage "neither of these data sets is ideal". I think these data don't bring much extra value to the manuscript and suggest taking them out unless the authors provide good reasons for having them in.

We agree that these data don't bring a great deal of extra value, but since the Japanese data are from sites directly downwind of Asia, the question arose regarding ozone changes at sites directly downwind of North America. We believe that it is valuable to show what data are available for this region, so we prefer to keep this discussion, which adds only one paragraph to the manuscript and two figures to the Supplementary Material.

p. 13912: This paragraph is somewhat obscure and should be rephrased: "Approximately 85% of the European and North American error bars include the average seasonal O3 changes derived from the nine European and North American data sets. To put this in perspective, if the entire northern mid-latitude region in this longitude range had hypothetically experienced a uniform O3 change at all sites, with differing inter-annual variability superimposed, then 95% of the confidence limits would be expected to include the average seasonal O3 changes. The close correspondence between the actual and the hypothetical inter-site agreement indicates this high degree of uniformity in the average seasonal O3 increases."

Thank you for this comment, as this paragraph is particularly important to our conclusions. We have rewritten this text to occupy its own paragraph: "The baseline O_3 concentration change that has occurred exhibits a high degree of uniformity over lon-

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gitudes at least from the eastern North Pacific, over North America, the North Atlantic and Europe. This can be demonstrated by considering the error bars in Fig. 7b, which indicate the 95% confidence limits of the average seasonal rates of increase at the individual sites. If it were hypothetically assumed that the entire northern mid-latitude region in this longitude range had experienced a uniform O_3 change at all sites, with differing interannual variability superimposed, then 95% of the confidence limits would be expected to overlap the average seasonal O_3 changes indicated by the black plus symbols in Fig. 7b. In actuality, 85% of the European and North American error bars do include the average seasonal O_3 changes derived from the nine European and North American data sets. The close correspondence between the actual and the hypothetical inter-site agreement indicates that there does exist a high degree of longitudinal uniformity in the average seasonal O_3 increases that occurred over the last half of the 20th century at northern mid latitudes."

p.13912: Authors write: "This slowing in the rate of increase has advanced to the point that O3 over Europe has recently begun decreasing." This could be read as a rather political statement. When looking at e.g. exceedances of ozone threshold values, it is presently difficult to see signs of reductions in Europe. I would suggest to rephrase this statement to clarify what is actually decreasing. Is it the baseline mean, the overall seasonal/annual mean etc?

This is an excellent point. The sentence in question has been changed to read "This slowing in the rate of increase has advanced to the point that seasonal average O_3 over Europe has recently begun decreasing at some sites in some seasons, particularly summer."

Further remarks

This manuscript is based on seasonal means. Have the authors looked at other ozone indicators, like percentiles, day-time values, daily max etc? Change in anthropogenic emissions would not only affect the seasonal means, but also the frequency distribution

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of hourly ozone (both the high and low percentiles). In general, the annual or seasonal mean values are less suited for process studies than e.g. the high percentiles (and low percentiles in winter) since the mean values are a mix of all kinds of atmospheric processes. For the present study the mean values may, however, be the most appropriate, as the focus is long-term changes in the background/baseline. Some words on this question would be good to include, though.

We agree that there is a great deal of additional analysis that could be done to facilitate process studies. However, this additional analysis is beyond the scope of this already long paper. Some such work has recently been completed. *Cooper et al.*, [2012] have presented an interesting analysis for North America and *Oltmans et al.*, [2012] have addressed these issues on a global scale. The present study does focus on long-term changes in the background/baseline concentrations, so mean seasonal values are indeed most appropriate.

Do the authors have any explanation why the results for different seasons apparently vary in similar manner for several sites, i. e. that dips and peaks in the 3-months means seem to be reflected in both summer and autumn, summer and winter etc? Seems to indicate a season-to-season dependency?

In our view, the lifetime of O_3 is long enough (in the revised draft we quote between a few to 20-30 days or longer) that O_3 is effectively transported zonally on time scales shorter than its lifetime. Consequently, there is a great deal of similarity in temporal variability among all baseline sites at northern mid-latitudes. However, the lifetime of O_3 is short with respect to seasonal scales, so seasonally average ozone can vary approximately synchronously at all sites at northern mid-latitudes. We prefer to not speculate beyond this rather simple explanation.

References: (References not included here are cited in *Parrish et al.* [2012].)

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