

Review of “Long-term changes in lower tropospheric baseline ozone concentrations at northern mid-latitudes”, by D. D. Parrish, K. S. Law, J. Staehelin, R. Derwent, O. R. Cooper, H. Tanimoto, A. Volz-Thomas, S. Gilge, H.-E. Scheel, M. Steinbacher, and E. Chan, *Atom. Chem. Phys. Disc.*, 12, 13881, 2012.

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Parrish et al. present a review of trends in ozone at selected surface sites in the northern mid-latitudes, expanding on work presented in the HTAP report (2010), and in previous publications by the authors (Parrish et al., 2009; Cooper et al., 2010; Tanimoto et al., 2009; Gilge et al., 2010), and by others (see below). Thus there is not a lot that is new in this work, and its main purpose is to present an analysis of data from various sites in one paper, sometime updating the published records by a year or two. In terms of scientific results, the paper is adequate for publication in *Atmos. Chem. Phys.* as a summary of the authors’ own work on trends at the selected sites, except for the analysis of data for Japan (discussed below). However, in its present form it does not meet conventional standards for a scientific paper, and it requires significant improvement before being acceptable for publication.

The first major problem with the paper is that it does not give a summary of previously published work on trends in tropospheric ozone in the Introduction, so the reader can see the context for the current work, and see what may be new. There is a body of literature on changes in tropospheric ozone, often using the same data as in this work. As far as I can tell, the overall results in this paper are not new: ozone doubled from the 1950s to around 1990 in Europe; there are seasonal differences in the ozone trends; ozone has leveled off and started to decrease in summer over Europe; ozone has increased in spring over western North America. The leveling off at Mt. Lassen in California is new, as far as I know. The lack of references to prior work on ozone trends continues throughout the paper (except for occasional references to papers by the co-authors). However, the paper contains a reasonable amount of citations the literature on all other areas (model studies, trends in precursors, etc), so the lack of citations to the prior literature on ozone trends, the focus of the paper, is all the more strange, and unacceptable.

The paper requires a paragraph early in the introduction that states, at a minimum:

1. Ozone doubled in the Swiss Alps from the 1950s to the early 1990s (Staehelin et al., 1994). The results of Feister and Warmbt (1987) on the increase at Arkona should also be discussed.
2. Ozone sonde data show increases in ozone over Europe from the 1970s to the 1990s, although the details of the increase differ among the three stations (Logan, 1994; Logan et al., 1999).
3. Ozone at Mace Head increased from 1987 to the late 1990s with no increase thereafter (Derwent et al., 2007).

4. Data from alpine sites in Europe show ozone increased from 1978 until around 2000 and then stabilized (several papers summarized in the Introduction to Logan et al. (2012), as well as the latter paper). The synthesis of data for central Europe by Logan et al. (2012) shows that ozone has decreased since 1998 in sonde, MOZAIC, and alpine site data, with the largest decrease in summer, and no increase in ozone in summer since 1990. The alpine data show increases in the decades before 2000, except summer. The paper also shows similar behavior at Mace Head and the alpine sites.
5. Studies by Parrish et al. (2009) and Cooper et al. (2010) found increases in spring in ozone on the west coast of the U.S., but had to rely on much sparser data records than available for Central Europe. Earlier work on trends in this region by Oltmans et al. and Jaffe et al. should also be acknowledged. While these authors are cited, their results are not discussed.
6. Tanimoto et al. (2009) showed large increases in spring at Happono, the only mountain site in Japan, that are larger than increases at sea-level sites by factors of 2-3.

Instead of this, the paper merely says:

p. 13885. l. 9-10 “During the latter half of the 20th century O<sub>3</sub> concentrations increased markedly at northern midlatitudes. This increase has been documented by a variety of observational studies, ...”  
(*Note lack of citations*).

l. 23-25. “Nevertheless, it does appear that concentrations were lower up to the 1950s with mixing ratios (strictly speaking mole fractions) around 10-20 ppbv, for example, over Europe [Volz and Kley, 1988; Staehelin et al., 1994].”

p. 13886. l. 7-8. “Several recent summaries of changes in tropospheric O<sub>3</sub> have been published [e.g. Vingarzan, 2004; Oltmans et al., 2006].” *Note, no comment on the results in these papers.*

Until this paper summarizes the results of previous work on trends in the Introduction, it is not acceptable for publication. The summary should start where the well-known increase in tropospheric ozone is first mentioned, p. 13885, line 10. The paper must also comment on previous work at appropriate points throughout the paper and in the Conclusions.

The lack of information on previous work on ozone changes is particularly noticeable given the detail that is included on factors that may influence ozone changes on p 13885-6.

### **Comments on the results section.**

The authors include figures for all the sites as seasonal time series in a Supplement, while showing figures in the main body of the paper for only a few sites: Hohenpeissenberg and Mace Head for Europe, a composite of sites along the coast (2 year update of Parrish et al., 2009) and Mt. Lassen for the west coast of the U.S., and Mt. Happono for Japan. They also compare time series from various sites for spring (Figure 5). I recommend they add a figure like Figure 5 for other seasons, at least for summer, into the paper (include Figure S12). At present these figures are in the supplement. This paper would be much improved by including a focus on summer, the most photochemically active

season, as well as on spring. Most exceedances of ozone air quality standards are in summer, with serious effects on human health, crop yields, and vegetation in general.

The paper also shows comparison of trends, for varying time periods depending on the start date of the record (Figures 7 and 8). This figure should include the differing time periods for which the trends were computed. It would very be useful also to compare trends for identical time periods, which would restrict the analysis to 1991-2009. This is an interesting period, as trends in emissions in Asia are diverging from those in Europe and North America. I recommend that the authors compute such trends, and make plots similar to Figures 7 and 8 for this period. For Japan they should use data from Ryori, Japan, which has data for 1990 onwards.

The choice to focus on Hohenpeissenberg is rather odd, as it is the least likely to be a baseline station, compared with the high altitude sites of Zugspitze or Jungfraujoch. The site is only 300 m above the surrounding countryside, it is within 50 km of the center of Munich, and within 10 km of several towns with a populations of 10,000-20,000. It is well within the boundary layer. The diurnal variation at the site is not discussed, and should be. The reason for showing this site should be given, as it can only be considered as a regional central European site, rather than a baseline site.

Linear trends are run for 1970 to 2000, and the text comments that a linear increase was observed for the first 30 years, yet it is obvious from Figure 1 that the increase in summer had stopped by 1990. One can see by eye that there is no increase in summer after 1988, and Figure S12 shows the decrease at all the European sites except Mace Head from at least the mid-1990s if not earlier. This must be discussed.

Logan et al. (2012) noted the ozone maxima in July 1994, August 2003, and July 2006 caused by heat-waves. We also commented on the slow-down in the growth of ozone at alpine sites from the 1980s to the 1990s. It is not a new result that the ozone increase over Europe has stopped, as discussed by Logan et al. (2012) and papers cited therein. This should be made clear, as it is seen at all the other alpine sites.

### **Ozone changes at sites in Japan.**

The authors did not pick the most suitable sites for analysis, and more careful analysis of the Japanese surface data is needed. Logan et al. (2012) showed that it is easy to identify problems with particular data sets by examining time series of monthly mean differences of sites within a few hundred kilometers of each other. I include such a plot (Figure 1) for the EANET sites used here, Rishiri Island, Sado Island, and Cape Tappi, as well as data from Oki (EANET) and Ryori. The site locations are shown in Figure 2. (The Ryori data are available at <http://ds.data.jma.go.jp/gmd/wdcgg>, and the EANET data for 2000-2009 at <http://www.eanet.cc> ). The data for the other sites before 2000 are not publically available. Parrish et al. averaged ozone at Rishiri, Tappi, and Sado.

Figure 1 shows that the ozone values at Tappi dropped by 20-25 ppb relative to the other three sites in mid-2008, and clearly should not be used in trend analyses. The Sado site also has (smaller) inconsistencies relative to the other sites (particularly the low values in the first half of 2002), while Rishiri and Ryori are the most self-consistent. I shared Figure 1 with one of the authors of this paper in December, 2011, so I am surprised that the data from Cape Tappi were used.

The data at Ryori start in 1990, so this site should have been selected for trend analysis for the longer period, particularly since the Haplo data was analyzed for 1991-2007.

I compare the seasonal time series for the various sites in Figure 3, and compare trends for 2000-2009 for Rishiri, Ryori, Sado, and Oki to those for Haplo for 2000-2007 in Figure 4. Clearly, the trends at Haplo for those 8 years are much larger than the trends at the sea-level sites, except in autumn. The data for Haplo after the gap in mid-2007 appear to be suspiciously low, as noted in the paper, and the data for the first 7 months of 2007 appear to be unusually high (not commented on in the paper). Until the measurement issues are resolved at Haplo, it is far from an ideal site to rely on for trends downwind of Asia.

Given the consistency of the Rishiri and Ryori for the period of overlap, it appears that Ryori is the most reliable site for assessing trends in the marine boundary layer in Japan. Ryori has used UV light absorption for the entire record.

The linear trends for the Ryori data for 1990-2011 are (with 2 standard errors):

	ppb year <sup>-1</sup>	% year <sup>-1</sup>
DJF	0.22±0.10	0.60±0.28
MAM	0.20±0.10	0.40±0.21
JJA	0.29±0.10	0.88±0.31
SON	0.14±0.10	0.38±0.28
Annual	0.21±0.05	0.54±0.13

These trends were calculated by linear regression using an approach that accommodates missing months of data by fitting the annual cycle and four seasonal trends simultaneously to the time series of monthly means (Eqn. 1 in Logan et al., 2012).

The Ryori trends in winter, spring and autumn are factor of at least 6 smaller than those at Haplo for 1991-2007, and a factor of two smaller in summer.

For the shorter period of 2000-2009 (Figure 4), the trends at Ryori and Rishiri are most self-consistent, and much smaller than those at Haplo for 2000-2007. The trends at Oki are generally consistent with those at Ryori and Rishiri, while those at Sado are larger, influenced by the anomalous looking lower values early in the 2000s.

In summary, Parrish et al. should use the data from Ryori as their marine boundary layer Japanese site, and include it in Figure 7 (their summary plot of trends are the various sites). Ryori fits their criteria of being relatively long, and my analysis shows the data appears robust (Figure 1), it is as close to baseline as there is for Japan, and it uses a UV absorption technique. Ryori has the lowest trends of any of the sites analyzed in winter and spring, and is also among the lower trends in summer and autumn. This should be discussed.

**Other comments:**

Abstract. The text states that “the rate of increase has slowed” at most European sites. This is a strange way of saying the increase has stopped, or in some cases, turned around to a decrease. Clarify.

p. 13884.

l. 3. Give a more recent reference as well for the source of ozone from STE.

l. 10. Levy’s paper is not about ozone, so drop the citation here, and include the Chameides and Walker (1973) reference here.

l. 17-20 Insert a reference for the lifetime of ozone towards chemical loss, such as Fusco and Logan (2003), which shows this in their Figure 5. The ozone lifetime is considerably longer than the quoted 20-30 days in the middle and upper troposphere.

p. 13885

The cartoon in Figure 1 showing processes affecting transport of ozone and PM across the Pacific was fine in the HTAP report, intended for a broader (and perhaps less informed) audience, but it is not needed for this article in ACP. And this article is not focused on transport across the Pacific.

l. 15 Variability in the stratospheric flux of ozone has been proposed as a cause of the increase in tropospheric ozone in the 1990s (after the minimum attributed to the aerosol loading from Pinatubo) in the cited papers, as well as by Tarasick et al. (2005) and Terao et al. (2008). It has never been suggested that this has influenced the doubling of ozone since the 1950s.

p. 13888-13889.

The paper argues that it is about “baseline” sites, but the authors can compare “baseline” and “non-baseline” ozone at only 3 of their 11 sites. They should remove “baseline” from the title of their paper.

They also argue that for global models a comparison to baseline selected data is useful for evaluation of simulated trends, but ignore the fact that this is never done (in the literature to date), as it is far from straightforward to duplicate the methods used to separate the data into baseline and non-baseline, in part because of the larger spatial scales at which global models are run.

line 17. Downwind of the Asian continent, surely. Japan is in Asia.

p. 13891

l. 9-10, 17-18. It is interesting that the authors are so negative about the sonde data, when they describe the early Arkona data as being from “well calibrated, well characterized” wet chemical methods. In fact the sonde and Arkona techniques both relied on the oxidation reduction reaction of KI with ozone, and SO<sub>2</sub> interferes quantitatively (negatively) with the measurement of ozone. Winter-time concentrations of SO<sub>2</sub> may have been high enough to interfere with the ozone measurements in the early years, and the published paper only comments on annual mean SO<sub>2</sub> being low in 1969-1971. It is interesting that there was essentially no increase in ozone in the 1970-1980s following the installation of a filter for SO<sub>2</sub>, until the higher values in 1989.

Table 1 must include which measurement technique was used for which period, for all data sets used. The reader needs to know when earlier, and often less reliable, methods were used. For example, which technique was used at Mt Happon before 1998? The Tanimoto et al. analysis starts in 1998.

l. 13. Derwent et al. (2007) did not use the dispersion model to filter the data from 1989 on, they used halocarbon and CO data up to 1997, and the dispersion model after that.

Section 4, on the Analysis approach, largely repeats the same points, and uses exactly the same methods, as Parrish et al. (2009); the present text comes across as pedantic and repetitive, and should be shortened considerably but saying exactly the same approach was used as in the earlier paper. There are differing approaches to deriving seasonal trends in ozone, and the method adopted by the present authors is appropriate when there are no gaps in the time series, so that true seasonal means can be formed. The authors should say what they do when months of data are missing, especially if a season is represented by only one month. There are gaps in some of the datasets they used.

The authors should state how they obtain the confidence intervals for their quadratic fit, and state which statistical package they use, or if they wrote their own software.

p.13895

l. 5. It is unclear if the STE flux of ozone should change only gradually. The change in ozone in the lower stratosphere after the major eruptions of El Chichon and Pinatubo was not gradual, so even if the mass flux of air changes gradually, that of ozone may not have for short periods. And the air mass flux may not change gradually, but have interannual variability.

p. 13896

l. 3. The rate of change of the slope should not be referred to as the acceleration, as it can also be a deceleration. It should simply be referred to as the change in slope, or the quadratic term, with the units as given (ppb year<sup>-2</sup>). To refer to “negative accelerations” is rather like referring to “negative increases” instead of “decreases” and sounds rather silly. This must be fixed throughout the paper, where “negative acceleration” appears quite often.

l. 11-14. Of course the slope and its change (in original units) do not depend on the reference year chosen. This is hardly the place to be giving a tutorial about extremely simple statistics that were used.

p. 13898.

A quadratic fit is not likely to give the same year for maximum ozone as a data set with variability, so this point is rather belabored. There are many papers on the high ozone seen in August 2003 prior to the one cited.

In terms of the comment that the longest record will yield the most precise regression results, this is only because the increase is so large. The precision of a trend depends on the magnitude of the change, and the variability in the time series, as well as on its length. The statement as given (l. 23-24) sounds naïve. The Zingst-Arkona record has precise trends because they are so large compared to the variability in the record.

P. 13899

The discussion of the Mace Head data is a bit vague, “specific transport patterns”, which begs the question of which ones, and why they only affected the late 1990s. The boreal fires that Derwent et al. mention were in August 1998, so cannot explain the high ozone prior to this, and they cannot explain the relatively high ozone in 1999 and 2000. Others have argued for transport anomalies in the extra-tropics after the 1997/98 El Nino, including enhanced STE, but these papers are not cited.

What is abundantly obvious from Figure 3 is that ozone at Mace Head does not appear to have increased since the late 1990s, and this is discussed in several previous papers.

The text is unnecessarily confusing in saying that there are differences in seasonal cycle (and trends) between Mace Head and Arkona-Zingst. Why not just say that the former has a summer minimum, and the latter a summer maximum, as is well known and well understood (with citations of course). (Photochemical sink in summer for baseline Mace Head (low NO<sub>x</sub>), photochemical production giving a summer maximum over mainland Europe (with attendant emissions of precursors), also give reasons for differences in winter, etc.) The only proper way to compare trends between the two sites is to first compute trends for identical time periods, and compare them. This should be done.

p. 13900.

l. 9-10. The alpine sites used in the supplement (and in other papers as noted above) do not cover a particularly large part of Europe, mostly just the Alps. Logan et al. (2012) show that there has been no increase in ozone in summer in central Europe since 1990, and this is apparent in the figures in this paper. However it is not mentioned explicitly, instead only commenting on the quadratic fit. The Zingst data also show this lack of increase since 1991 when that data start. Discuss this.

p. 13901-13902.

A comparison is made of trends for filtered and unfiltered data for Jungfraujoch, but the authors did not do this the correct way, as they did not use the same time periods for each. In a record of ~20 years, the addition of 2 years of data will inevitably change the trends, so they should have used 1990-

2008 for both filtered and unfiltered data for deriving trends with the quadratic fit (Figure S16 used 1990-2008 and 1990-2010 respectively), to show if filtering the data makes any difference.

p. 13903

There is discussion of the difference in trends for the filtered and unfiltered data from Mace Head. The reason for this (which the authors should point out) is that there is a jump in the offset between the two time series in 1997 (see Figure 1). It is not because there is a monotonic trend in the difference between the two. The change in the offset suggests that the filtering changed around 1997. This should be discussed.

It seems highly unlikely that titration of ozone by  $\text{NO}_x$  is an issue at Mace Head, unless the authors are discussing urban air in winter. Are they arguing that undiluted urban air reaches this remote location in winter? Clarify.

p. 13906

l. 5-6. “Observational data” – one is redundant. Observations, or data, you do not need both. There is no ambiguity here that the paper is about observations.

There is the same amount of data in all seasons except for the Cooper et al. study, so this should be made clear.

Figure S12, comparing the time series in summer, should be moved to the main paper and discussed there. This is the most photochemically active season.

This statement should be dropped: “it must be realized that the lack of a statistically significant change (e.g. the Japanese MBL in winter in Fig. 7a) does not necessarily indicate that there has been no change; rather it may indicate that any long-term change that occurred over the period of the data record is too small to be discerned with strong statistical significance given the length of the data record and the interannual variability that is present in the data sets.”

This sounds like a plea for a trend in ozone when the trend analysis says there isn’t one for the period analyzed. The authors should use the Ryori data instead, which does happen to have a small, but significant, increase in winter, as I show above.

p. 13906

It has been known for decades that ozone increases with altitude above the surface, based on profile data (see literature cited in Logan, 1999). This section is rather naïve. It is common practice to show profile trends in percent per unit time (see Logan et al., 1999, and references therein).

p. 13907

The authors average the trend results for nine sites in Europe and North America, but the errors on the mean trends are likely too small. The time series for the alpine sites in Europe are highly correlated, and the results for these sites should not be considered as independent measures of trends for the entire northern mid-latitudes. A more careful approach to computing errors on the mean trend is needed, allowing for correlation among sites within a region.



The text reads as if the trend was the same for 50 years (1950-2000), but the time series show that the leveling off started before 2000 at many sites.

### Comments on the Supplement.

Figure S4. Using the very limited data from Arosa in the 1950s to compute trends when there is a gap of over 30 years is stretching things a lot, especially when the early data are duplicated as 5 identical points. As noted above, the doubling of ozone from the early to the later data is already documented in the paper by Stachelin et al. (1994). A similar comment (to S4) applies to Figure S6. The fit for 1934-2000 in Figure S6 clearly is only for summer, so the legend should be changed. The caption should state that the Jungfraujoch data are available at <http://ds.data.jma.go.jp/gmd/wdcgg/>.

Figure S8. The caption states “Nevertheless, the linear fit includes all years, because the precision of the derived parameters is significantly better, and the data near 2000 appear anomalously high.” Subjective comments such as “*the data near 2000 appear anomalously high*” have no place in this paper as a rationale for anything, especially when the most obviously anomalous points in the figure are in 1994, and are not even mentioned. One cannot say which points are anomalous without doing a lot more analysis.

Figure S11. The data for 2000-2009 are available at the EANET web-site, and are the same as those used by Tanimoto et al. (2009).

Figure S12. Move to the paper and discuss the summer time series as noted above.

Figure S12. left: what are the solid lines? right: The vertical distribution of trends should only be shown if the same time period is used for all sites.

### References

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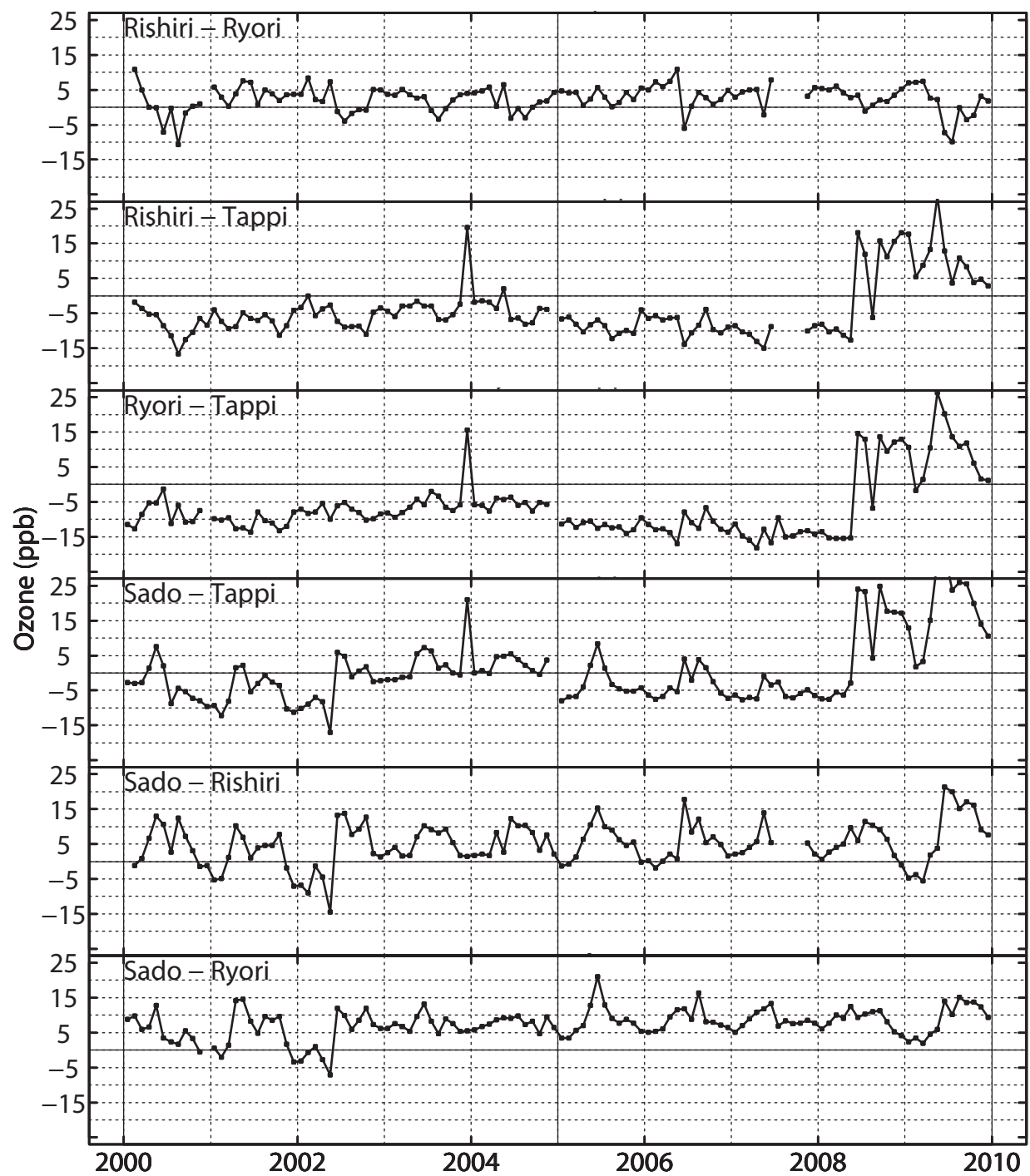


Figure 1. Differences of monthly mean values for ozone for pairs of locations.

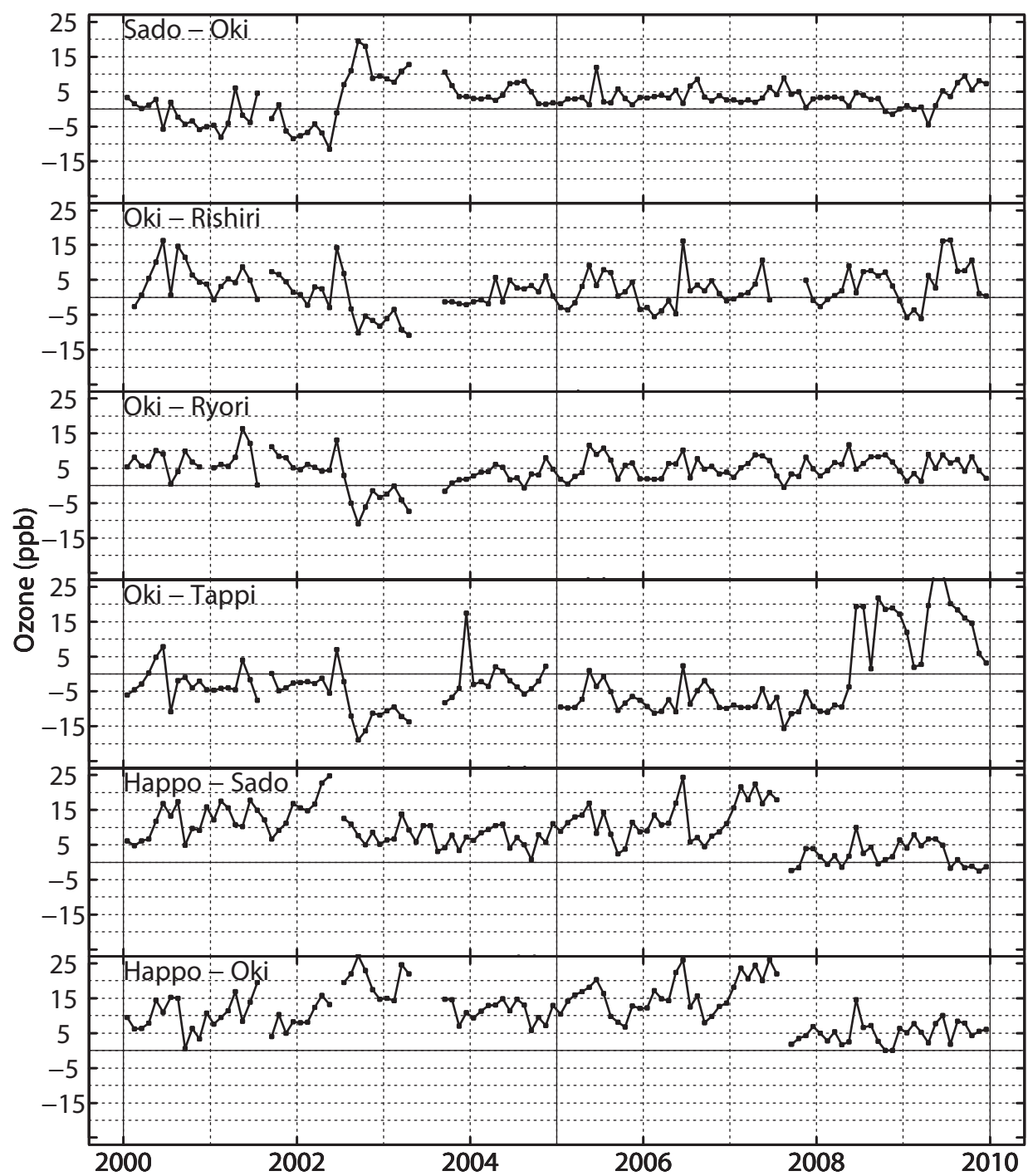


Figure 1. Continued.

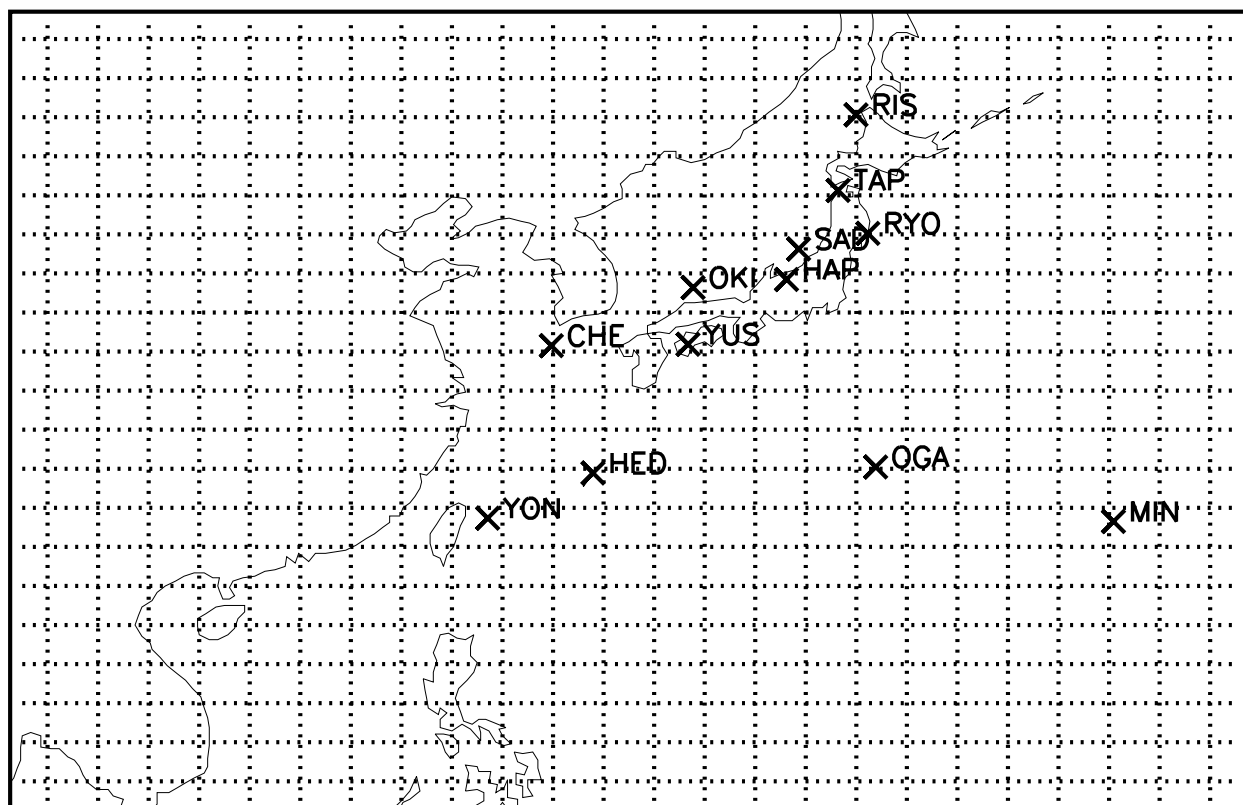


Figure 2. Map of sites with surface ozone data available from <http://www.eanet.cc> (EANET) and <http://ds.data.jma.go.jp/gmd/wdcdg> (World Data Centre for Greenhouse Gases).

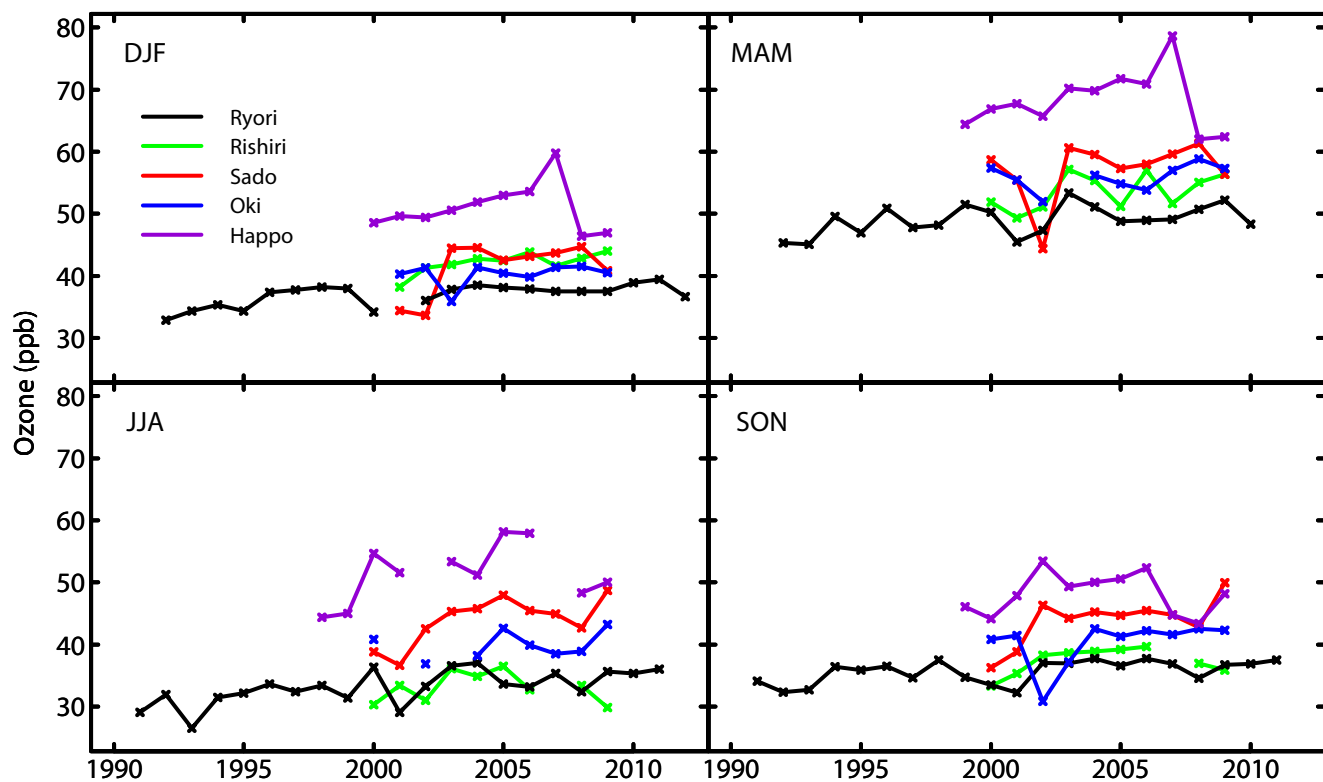


Figure 3. Seasonal mean time series. Means are included only if data for all three months are available.

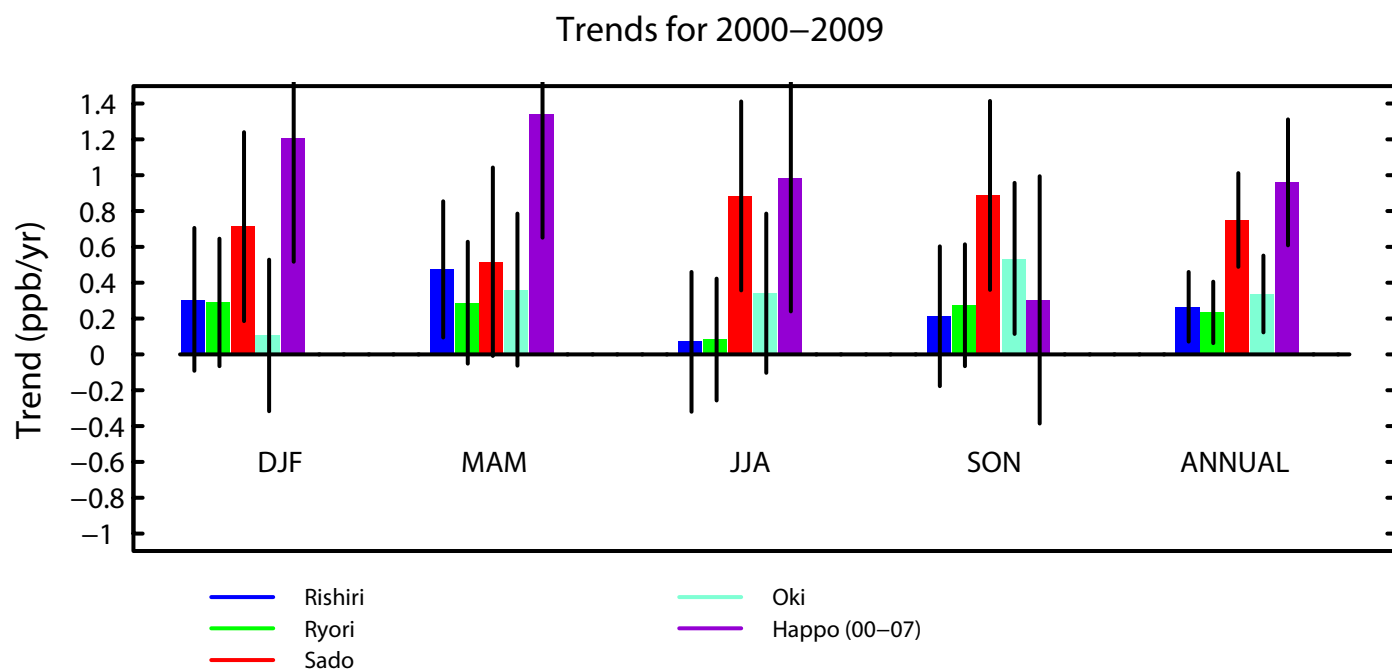


Figure 4. Seasonal and annual linear trends in ozone ( $\text{ppb year}^{-1}$ ) for 2000–2009 for Japanese sites, except for Happo for which the trends are for 2000–2007. Two standard errors are given.