

Review of " Characterizing tropospheric ozone and CO around Frankfurt over the 1994-2012 period based on MOZAIC-IAGOS aircraft measurements" by H. Petetin et al.

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Summary:

This paper presents an interesting analysis of the very extensive data set of vertical profiles of ozone and CO over the Frankfurt region collected by the MOZAIC-IAGOS program. The authors address: 1) Climatological vertical profiles of the mean O₃ and CO concentrations, 2) Seasonal variations, 3) Annual and seasonal O₃ trends, 4) Annual and seasonal CO trends, and 5) Changes in the O₃ seasonal cycle. The paper has been improved from the previous draft, but significant problems still remain that must be corrected before the paper is suitable for publication.

Although the data set considered is the densest record of vertical ozone and CO profiles in existence, the findings presented in this work are, on the whole, not new. In my opinion, the paper would be ready for publication when the first set of major issues and the minor and significant issues listed below have been addressed. However, I encourage the authors to address the second set of major issues, also listed below, which would make the paper more useful.

Major issues to be addressed before the paper is suitable for publication:

- 1) p. 8, beginning on line 18. The authors write "The highest vertical gradients are found close to the surface all along the year (dry deposition and titration by NO) and at ...". In many continental locations over urban areas, high ozone concentrations are found near the surface, decreasing above the PBL, before increasing through the mid- to upper troposphere (sometimes described as a "C" shaped profile). Evidently the vertical profile over Frankfurt is different; this contrast should be discussed. One issue that should be included in that discussion is the influence of nighttime titration of ozone. If the data are limited to daytime only profiles, is a "C" shaped profile seen?
- 2) p. 13, line 14 - The comparison with satellite data should be made more quantitative.
- 3) Section 3.3.1 - The discussion of ozone trends should be greatly simplified and reduced in length. Previous studies (*Logan et al.*, 2012; *Parrish et al.*, 2012) have quantified the long-term changes of ozone in the lower to mid-troposphere in the central European region. The lack of significant trends and the marginally significant trends found for ozone in Section 3.3.1 and Table 1 are completely consistent with previous work, and hence do not add any new information. For example, the only significant trend for the mean ozone in Table 1 is in the winter. The European winter shape factors given in Table 2 of *Parrish et al.* (2012) give an average trend of $0.61 \pm 0.25 \text{ \%O}_3,2000 \text{ yr}^{-1}$, which is statistically consistent with all of the O₃ trends found in this work. All of the derived ozone trends should be removed from Table 1 (perhaps included in the Supplement) and only a very short discussion of the ozone trends included.

In this regard, picking a specific sub-period for analysis (here the 2000-2012 period) is statistically a very dangerous process, since relatively large trends can result from interannual variability over short periods (see for example, *Barnes et al.*, 2016). The discussion of the trends over the sub-period should be eliminated.

- 4) Section 3.3.2 – In contrast to ozone, less is known about the trends of carbon monoxide through the depth of the troposphere, and statistically significant trends are derived in this work, so discussion of these trends is useful. It may also be useful to include the relative CO trends, now given in Table 1, with the absolute CO trends, now given in Table S1, in a single table in the body of the paper.
- 5) Section 3.4.1 has been much improved but there are still problems that must be corrected. I do not believe that fitting of the seasonal cycle is correct. The problem is that the data are collected over the entire month, but the monthly average data are plotted at the start of the month (See Figure S7). Consequently, the derived date of maximum ozone is approximately one half month early. For example, the peak in the MT near the middle of the data record is approximately June 4. *Parrish et al.* (2013) found seasonal peaks of approximately June 20 at alpine peaks in Europe near 2003, which should be comparable to the MT data discussed here. The error identified above accounts for the difference in these findings. Fitting of the seasonal cycle must be corrected. I recommend the approach of Figure 1 of *Parrish et al.* (2013) where the monthly average data are plotted at the center of the month between 0 and 12, and t in Equation (1) of this paper in months, with values ranging between 0.5 and 11.5.

The confidence limits on the results are given, and they indicate significant changes in both the magnitude and the phase of the ozone seasonal cycle. However, I am not yet convinced that the confidence limits are correct. I have examined the Press et al. (2007) reference that the authors cite for their determination of confidence limits. In that material, I do not see how the authors treated the very strong covariance of the individual data points in Figure 7; more information is required in the paper or in the Supplement. However, I suggest a second method be employed to calculate the confidence limits of the trends. The authors employ the excellent strategy of analyzing data from two separate, independent periods: 1995-2003 and 2004-2012. In effect, they obtain two determinations (with confidence limits) each of the magnitude and phase of the seasonal cycle, which represent averages over the separate periods. To determine if the magnitude or phase is significantly different between the two periods, let us represent the quantity (with confidence limit) for the earlier and later periods by $A \pm \sigma_A$ and $B \pm \sigma_B$, respectively. A and B are significantly different if their difference ($A - B$) is significantly different from zero. The confidence limit of the difference is approximated by $(\sigma_A^2 + \sigma_B^2)^{1/2}$. If the absolute value of $A - B$ is greater than the confidence limit of the difference, then the trend is significant. Examining the 95% confidence intervals in Figure 7 suggests to me that not all of trends will be significant when evaluated in this manner. This suggested approach differs from that used by the authors, but the results should be approximately the same. These issues should be discussed. Note that even if the phase shifts in the upper troposphere are not statistically significant, the discussion in Section 3.4.2 regarding the altitude dependence of the seasonal shift is still valid, since the confidence limits provide constraints on how large the seasonal shift could be, and that constraint will be lower than the statistically significant shift found in the lower troposphere.

Major issues to make the paper more useful:

- 1) Section 3.1.1 discusses the vertical profile of ozone. Previous work has also reported vertical profiles of ozone over nearby locations in Europe. It would be useful to quantitatively compare and contrast the profiles presented here with those measured at such locations (e.g.,

sondes from Hohenpeissenberg, Germany). If a comparison can be done with the sondes over the same period of time as the MOZAIC-IAGOS flights, then the accuracy of the sonde data could be evaluated. A comparison of the MOZAIC-IAGOS CV with the sonde CV would also be very informative.

- 2) Section 3.2.2 - I would expect the MT CO data above Frankfurt to compare well with surface CO concentrations at remote sites at the latitude of Frankfurt. A quantitative comparison with the zonal averages from Novelli and coworkers (*Novelli et al.*, 1998; 2003) should be included. I suspect that this comparison will be more informative than the comparisons of the LT data with a few German surface sites.

Significant issues:

- 1) p. 10, lines 15-16 - This sentence is confusing. As shown by the seasonal cycle of CO illustrated in Fig. 5, CO in the free troposphere does indeed change significantly from one season to the other; please clarify.
- 2) p. 10, line 19 and p. 13, line 15 - It is not clear to me that a maximum of primary CO emissions occurs in winter (at northern mid-latitudes), especially if biomass burning emissions are included. This issue should be discussed in more detail with references.
- 3) p. 12, beginning on line 14 - If the spring 1998 anomaly is indeed related to enhanced STE, then one might expect a stronger anomaly in the MT and UT, which are closer to the source of the STE, than in the LT; however that does not seem to be the case. This should be discussed further.
- 4) p. 12, lines 18-20 - Exactly what is being correlated must be clarified. Are these correlations of annual averages? What can be the cause of this correlation? Has anyone noted this before? More discussion is required.
- 5) p. 13, lines 22-25 - If I understand correctly, aircraft do not emit significant amounts of CO. A reference should be given if my understanding is incorrect; otherwise the discussion should be revised.
- 6) Throughout the discussion of trends, the authors should keep clearly in mind that the lack of a statistically significant trend derived from their data does NOT mean that there is no trend. Rather a trend may exist, but their data are too variable to extract that trend. For example, on p. 18, the sentence "Conversely, all trends in autumn are insignificant." is correct, but the previous phrase "...while the $P_5(\text{CO})$ is decreasing only in winter (in the MT and UT) and summer (only in the LT)" is not worded correctly. A similar problem exists in line 11 on p. 20; the present analysis does not establish a significant difference in the trends between winter and spring/summer.
- 7) p. 18, lines 22-24 - The wording of this introductory sentence is awkward. It should be clearly stated that if the trends in ozone are significantly different between seasons, then there is necessarily a change in the seasonal cycle.
- 8) Figure 7 has a trace of "Fit error" in each graph. This quantity is not defined, and not discussed in the manuscript. I suggest these traces be removed from the graphs, or at least defined and discussed in the paper.

- 9) p. 22, lines 18-20: This discussion of ozone anomalies is not clear. I cannot see any relevance to Figure 7. This discussion must be improved.

Minor issues:

- 1) p. 3, line 10 - The authors write "... the confidence in the results remains limited by the high uncertainties at stake in both models and ...". This is not proper English usage.
- 2) p. 3, lines 30-31 - The authors write "... limited representativeness of measurements in the boundary layer measurements...". Eliminate one of the "measurements".
- 3) The caption to Figure 5 should define the meaning of the shaded regions.
- 4) p. 11, lines 13-14 - The sentence should read: "In the MT and UT, maximum concentrations occur between May and August (highest concentrations in July).
- 5) p. 12, line 4 - Start new paragraph.
- 6) p. 12, line 9 - Remove "have".
- 7) p. 19, line 5 – The last time period should be (2004-2012) not (2003-2012).

References

Barnes et al., 2016

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