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

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Summary:

This paper presents an interesting analysis of the extensive data set of vertical profiles of ozone and CO over the Frankfurt region collected by the MOZAIC-IAGOS program. The analysis of the CO data is quite interesting and deserves publication when some problems are addressed. The analysis of the ozone data has serious problems. First, and very importantly, I think that the statistical significance of all the ozone analysis is not adequate, and even the analysis that is done is not carefully considered in the discussion and in reaching conclusions. One glaring example is the first sentence of Main Result #2 in Section 5 - Summary and conclusions:

> "On an annual basis over the 1994–2012 period, tropospheric ozone shows increasing upward trends with altitude, from +0.11±0.21 and +0.13±0.18 ppb yr^{-1} in the lower and mid-troposphere to +0.22±0.23 ppb yr^{-1} in the upper troposphere."

None of these trends are statistically significantly different from zero, and there are certainly no statistically significant differences between them. This would be even clearer if the trends were expressed on a relative basis (as suggested in the first major issue below.

Second, I think that there is an error in the sine function fitting to the ozone seasonal cycle. In order for this paper to be further considered for publication, a much more rigorous analysis of statistical uncertainties must be completed, and the discussion and conclusions extensively revised with that analysis fully and carefully considered. Fixing the error in the seasonal cycle analysis will be straight forward, but here again the statistical uncertainties must be carefully evaluated.

Major issues:

1) In my opinion, the discussion of ozone trends (Section 3.3.1) is completely inadequate. The problem that the authors face is that their data record, although the densest record of vertical ozone profiles in existence, is short (1994-2012, or 19 years) in terms of that required to precisely quantify long-term changes. This problem is well indicated by the first sentence of the section, which can be shortened to read: "Considering mean ozone concentrations over the whole 1994–2012 period, annual trends are not statistically significant at the 95% confidence level." The same statement is close to correct for the 5th and 95th percentiles. Further detailed discussion of insignificant or nearly insignificant trends is not useful.

   Discussion of 10-years moving trends of is also not useful, since they are all of marginal significance, highly covariant since successive trends differ in only one year's of data, and prone to biases. This is particularly true of this data set, since the year 2003, which had anomalously high ozone due to the European heat wave, occurs in the middle of the data record. During the early 10-year periods, this year comes at the end, which would tend to give positive trends. During the later 10-year periods, this year comes at the beginning, which would tend to give negative trends, or obscure what otherwise might have been a significant positive trend.

   I suggest the authors utilize the approach of Parrish et al. (2014). This reference shows that long-term changes are best analyzed by normalizing the data to a reference year, and expressing the changes as a percent of that reference. They suggest the year 2000 for this reference. This normalization then allows trends to be directly compared between studies at different locations or altitudes (as is the case in the present study). Importantly, this reference finds that all European sites have a common trend when expressed in this manner. If the authors follow the same process they can quickly and directly compare their derived long-term changes to those calculated from the parameters reported in Table 2 of Parrish et al. (2014). If their derived trends agree with those calculated within statistical uncertainty, then the discussion is ended, as the trends reported here support the conclusions in that reference, but provide no new information. I am confident that the authors will find such agreement. Quantifying changing trends is more quantitatively done on the basis of a statistically significant quadratic term (Logan et al., 2012; Parrish et al., 2012) rather than 10-year moving trends.

It is useful that the authors discuss trends in the 5th and 95th percentiles as well as means. However, these should be discussed in the context of whether there are any statistically significant differences between those percentiles and the means. As far as I can tell, there are no such differences.

Finally, all of the error analysis for the trends implicitly assumes that the there is no covariance between data from successive years. Recent work (e.g., Lin et al., 2014) shows that such covariance can be important. Thus, the present data set must be examined for such covariance; if it is significant, then the confidence limits on derived trends must be widened accordingly. (I realize that most ozone trends analysis in the literature has not considered such covariance, but it is now apparently important.)

2) I think that the treatment of the carbon monoxide trends also requires reconsideration. The authors correctly conclude in Section 3.23.2 that their data show statistically significant negative trends. However, the interpretation of those trends requires further thought. Specific problems include:

- Careful thought must be given to whether absolute concentration trends (as the authors choose) or relative concentration trends (i.e. % change/year) should be discussed. As Figure 2 clearly demonstrates, CO is much lower in the MT and UT than in the LT. If the total emissions of CO to the atmosphere were changed by 10%, then one would simplistically expect a 10% change in the LT, MT and UT. In that case, analysis of relative concentration trends would give the same trend in the 3 layers, but analysis of the absolute concentration trends would give much larger trends in the LT, simply because the CO concentrations are larger there. This problem becomes exacerbated when one considers that CO has a background that is independent of anthropogenic emissions; this background arises from secondary CO produced from oxidation of naturally emitted methane and biogenic VOCs. Thus, changes in anthropogenic emissions do not give proportional changes in CO concentrations. I suggest that the authors reformulate the CO trends analysis as relative concentration trends, and carefully consider the influence of the background concentration of secondary CO in discussing the significance and causes of these trends. Specific issues in this regard are discussed in the following bullets.
- p. 23855, beginning on line 18 - The authors state: "This decrease of mean CO concentrations is actually associated to a decrease in occurrence of high CO episodes". This statement is supported by a statistically significant difference between the trends of

the mean and the 95th percentile only in the LT, not in the MT or UT. This should be clarified.

- p. 23855, beginning on line 18 - The authors state: "Interestingly, trends highly depend on altitude, with decreasing negative values while one moves away from the surface." At best, the difference is statistically significant for the absolute concentration trends only between the LT and UT. When relative concentration trends are considered, even that difference likely will become statistically insignificant.
- Discussion beginning on p. 23856, line 8 - This largely deals with statistically insignificant trends. Such discussion is not useful and should be eliminated, or put on a more solid statistical basis.
- The comparison of the MOZAIC-IAGOS LT data with those from German WMO stations is useful. Perhaps it should come early in the discussion of the CO data.
- The authors may wish to discuss the trends of the 5th percentile of CO.

3) Equation (2) and its discussion are incorrect. For example if $\psi = 0$, then $\psi_{month} = 365/4 = 91.25$. Thus the equation gives the phase in days, not months. If the 365 is replaced by 12, then the units are in months. However, then if $\psi = 0$, $\psi_{month} = 3$, which corresponds to the maximum at the end of March. Thus, ψ_{month} = to 0 and 5.5 (not 1 and 6.5) correspond to an ozone peak on 1 January and the 15 June, respectively. This misinterpretation has led to an error of 1 month in the date of ozone ordinate in Figure 6. It is clear from the left panel of Figure 3 and the discussion in Section 3.2 that the seasonal peak of the sine function fit to the seasonal cycle should have a maximum in mid-June to early July, not one month earlier as Figure 6 indicates.

4) It is critical to clearly explain the description of the error calculation (p. 23858, lines 13-15). In particular, how is the "number of points" calculated? Very importantly, it is not the number of points shown in Figure 6, since the points co-vary to a high degree as each of the points has 90% of the same data as the previous or following point. The "number of points" must be properly calculated as the number of independent points, i.e. the degrees of freedom. There are really only about 2 independent pieces of information in each curve in Figure 6. I suspect that the authors may be underestimating the errors, and that the apparent shift of phase and change of amplitude of the seasonal cycle in Figure 6 are not statistically significant. If this suspicion is correct, then all of the discussion in Section 4 will require major modification. Perhaps an approach similar to that given for the seasonal amplitude as discussed in "Significant Issue" #9 below will provide a useful approach. Also the error shown in the figure does not indicate the precision of the date of the seasonal maximum; this is a critical piece of information.

5) In Section 4.2, I suggest that the longest possible time periods, not just 1995 to 2012, be utilized for the sonde and surface measurements. This is because the longer the time period, the more precise the trend determinations. I realize that the authors wish to investigate the same time period in all of these data sets, but the primary obstacle they face is lack of precision in the determinations. If they were to ever find trends in the different data sets that were statistically significantly different, then they would return to the issue of differing time periods, but that is not likely to be a problem.

Significant issues:

1) Paragraph labeled 2) on p. 23848 - I do not fully understand the description of the criteria for defining the tropopause. In Figure 1, the tropopause is indicated to be at about 8.8 km, which appears to be the altitude at which the PV rises to 2 pvu. Yet, the 1.8 km thick layer with a minimum PV exceeding 2 pvu is above 8.8 km. I assume that the tropopause is set to the bottom of that 1.8 km layer. If this is correct, the description should be clarified.

2) Since ozone concentration increases with altitude on average, it seems that truncating a vertical profile when the aircraft exceeded a 400 km distance from the airport would bias the average ozone low for the UT for that flight. Was such a potential bias considered and evaluated? A brief discussion of this issue should be included. One question is whether this bias varies with season, which could potentially distort the seasonal cycle derived for the UT.

3) p. 23852, beginning on line 22 - The authors note that "In comparison with ozone, the daily CO variability at the monthly scale is lower and similar in the three tropospheric sublayers (around 14–16 %)." It is worth mentioning that this is qualitatively expected given the differing lifetimes of these two species, as noted by Junge (1974). A brief discussion of this issue and a reference here would be useful.

4) p. 23852, beginning on line 28 - The authors note that "Such a seasonal pattern is rather consistent with maximum emissions and minimum photochemical activity usually occuring around winter combined with a maximum secondary formation in summer." Given the long (1 to 3 months) lifetime of CO, it is expected that its seasonal cycle is delayed with respect to that of the emissions and photochemical activity. This issue should be briefly discussed.

5) In Equation (1), the authors are defining the variable "a" as the peak-to-peak amplitude, while standard mathematical notation defines the magnitude of the sine function as the zero to peak amplitude. This issue should be mentioned.

6) p. 23858, lines 6-7 - I do not understand the significance of this note. It is true, but it is not clear to me that this information is ever used in the paper. Perhaps it should be removed.

7) The authors must clearly define their use of the term "baseline", and use it consistently through the paper. It is first used on pg. 23845 to indicate air "coming from the Atlantic Ocean". In the introduction to Section 3.3 it is equated to the 5th percentile of the data. In Section 4.1 it is defined as the average ozone over one or several years. During the HTAP program, "baseline" was carefully defined to be approximately the same as it is first used in this paper. I suggest that this use be maintained here, and that the other two usages of the term be replaced by different terms. Importantly, the air "coming from the Atlantic Ocean" may well contain ozone concentrations much higher than the 5th percentile.

8) Section 4.1.1 gives no information beyond what was already discussed in Section 3.2.1. I suggest it be removed.

9) p. 23859, line 5 - Do the errors given correctly represent 95% confidence limits? If so, then the difference in the two numbers is 3.3 ± 3.0 ppb, which is significant at two sigma.

10) Section 4.3 occupies 5 pages of text and does not seem particularly relevant to the main focus of the paper. I am not an expert in atmospheric transport, but I cannot find anything really new in this section. I suggest that this section be eliminated, or at least greatly shortened, limiting the discussion to only what is required to discuss the shift in the seasonal cycle and the long term trends, and perhaps to what is novel in this analysis.

Minor issues:

1) p. 23843, line 18 - The authors write "... several sinks are at stake in the troposphere...". The meaning is not clear; perhaps better is "... several sinks are active in the troposphere...". There are other similar issues throughout the paper. A native English speaker should edit the paper by for these small issues. However, overall I did find the writing generally clear and even elegant.

2) The primary reference for instrumental details (Nédélec et al., 2015) is not included in the list of references.

3) p. 23851, line 26 - The authors are evidently discussing the "Highest monthly **mean** mixing ratios"; this should be made explicitly clear.

References

Junge, C.E., (1974), Residence time and variability 0f tropospheric trace gases, *Tellus, 26*, 477-488.

Lin, M., L. W. Horowitz, S. J. Oltmans, A. M. Fiore, and S. Fan (2014), Tropospheric ozone trends at Mauna Loa Observatory tied to decadal climate variability, *Nature Geoscience*, *7*, 136–143, doi: 10.1038/ngeo2066.

Parrish, D.D., et al. (2014), Long-term changes in lower tropospheric baseline ozone concentrations: Comparing chemistry-climate models and observations at northern midlatitudes, *J. Geophys. Res. Atmos., 119*, 5719–5736, doi:10.1002/2013JD021435.