Atmos. Chem. Phys. Discuss., 8, S1228–S1236, 2008
www.atmos-chem-phys-discuss.net/8/S1228/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Carbon monoxide observations from ground stations in France and Europe and long trends in the free troposphere" *by* A. Chevalier et al.

Anonymous Referee #2

Received and published: 2 April 2008

General Comments:

The paper discusses a very useful data set that combines surface and aircraft measurements of carbon monoxide. The data set deserves discussion in the literature, but the present manuscript has such significant shortcomings that it must be rejected. I recommend resubmission when these shortcomings are corrected. These shortcomings are specifically discussed below.

Specific Comments:

1) This paper intends to put the CO observations over Europe into the context of the

global CO distribution. Therefore, in the paragraph on pgs 3315-3316 the authors rightfully give a review of concentrations and trends of CO globally and in the mid-latitude northern hemisphere. However, that discussion needs some revision; specifically:

a) A reference is required for the sentence "CO measurements in ice cores have indicated that the CO concentration was about 50-90 ppb during the pre-industrial period."

b) The statement - "Measurements since 1995 showed a continuous global decrease of CO mixing ratios but at a significantly reduced rate." - needs revision. The NOAA/GMD analysis actually shows that from 1992 to 2007, the global CO has remained, on average, nearly constant with interannual variability of +/- 10% (see http://www.esrl.noaa.gov/gmd/Photo_Gallery/GMD_Figures/ccgg_figures/tn/co_tr_global.png.html).

c) The statement - "At present time, concentrations could reach around 1-10 ppm in urban areas and about 150 ppb in clean areas far away from local sources of pollution in mid-latitudes of the Northern Hemisphere." - needs revision. In the clean areas the annual average drops to about 125 ppbv, and in summer the average drops to approximately 100 ppbv.

2) Point 1b) above implies that the discussion of the possible causes for the decrease of atmospheric CO at the beginning of the 1990s that begins on pg. 3017 should be significantly revised. In particular, reduced anthropogenic emissions of CO in North America and Europe may be balanced by increased emissions in other, developing regions of the northern hemisphere.

3) The implicit, and in some places explicit, assumption upon which the authors base their analysis is that CO is stratified in the troposphere as a function of elevation above sea level, and that surface measurements at an elevated site can be directly compared with airborne measurements at the altitude corresponding to that elevation. This is highly problematic in many cases. It is a reasonable assumption for nighttime measurements at isolated mountain sites, but a very poor assumption at a surface site of significant elevation (e.g. 1500m) near emission sources compared to an aircraft

ACPD
8, S1228–S1236, 2008

above the boundary layer at the same altitude. During daytime even mountain-top sites are affected by emissions from much lower elevations due to mountain-valley flow regimes and other orographic effects (see e.g. the work done in the VOTALP study - http://www.boku.ac.at/imp/votalp/). The significance of such effects will have to be discussed for each site. This discussion will be particularly important to justify the paragraph:

"A particular attention can be paid to the three highest stations around 3000m (PDM, ZSP and JUN). Due to their high altitude, they are expected to be the most representative of the background conditions and large scale transport. They are indeed supposed to be little influenced by nearby emissions sources and their altitude is close to the level 700 hPa. That is why surface time series of JUN, ZSP and PDM can be compared to MOPITT 700 hPa retrieval, unlike the other stations that are too low to give sense to a comparison."

4) Further, with regard to the preceding quoted paragraph, the justification for a direct comparison between the three highest sites and the MOPITT 700 hPa retrieval must be thoroughly discussed. The MOPITT 700 hPa retrieval is not a direct measurement of CO at 700 hPa. Rather, it is an average over the 700 hPa averaging kernel (see e.g. the Emmons et al., 2004 reference in the present paper), which has a full-width at half-maximum from approximately 250 to 800 hPa.

5) The Frankfurt profiles in Figures 3 and 5 require much fuller discussion. When individual vertical profiles measured by aircraft are examined, above the boundary layer CO is generally nearly constant with altitude with occasional encounters with plumes of transported emissions. Within the boundary layer, the CO vertical profile is again nearly constant, but usually significantly elevated above the free troposphere concentration, depending upon the influence of nearby emission sources. The Frankfurt profiles do not show this behavior, and seem to imply that CO decreases monotonically with altitude. This misimpression arises from at least two sources. First, the MOZAIC profile is not strictly a vertical profile, but also includes significant influence from hor-

ACPD

8, S1228–S1236, 2008

izontal gradients. As the aircraft approaches or leaves the airport, the lower altitudes are sampled in the vicinity of the large urban sources near the airport, while the higher altitudes are sampled over more sparsely populated areas with much smaller emission sources. Second, the Frankfurt profiles are averaged over a wide range of boundary layer depths. Nighttime and winter profiles are likely to encounter very high CO levels confined to a shallow boundary layer, while mid-day profiles during warm weather are likely to encounter much lower CO levels distributed uniformly through a much deeper boundary layer. The monotonic decreases in CO with altitude in the averaged Frankfurt profiles in Figures 3 and 5 are probably accurate, but they present a misleading picture of the vertical distribution of CO without significant further discussion. Further, as suggested by Referee #1, the Frankfurt profile should be compared with the corresponding Paris profile.

6) As implied by points 3) and 5) above, the justification for the comparison between the surface sites, which are necessarily within the boundary layer, and the aircraft profiles, which average varying amounts of free troposphere data with highly polluted Frankfurt-area boundary layer data, needs a full discussion. The surface sites are presumably 24-hour average results, while the MOZAIC profiles are likely concentrated at particular times of day. The influence of this difference requires discussion.

7) On page 3324, the statement - "Since MOZAIC data are not influenced by surface and local effects above 1200 m. a.s.l. (Chevalier et al., 2007), the surface data can be considered as representative of free-tropospheric conditions."- is not correct. In fact, Chevalier et al., 2007 state that "The planetary boundary layer can reach altitudes of 2 to 3 km during the summer..." and "the photochemical production (of ozone) in the boundary layer remains detectable at high-altitude sites during sufficiently lasting pollution episodes...". If the boundary layer can grow to above 1200 m, and if ozone produced in the boundary layer can be transported to high-altitude sites, then MOZAIC data cannot necessarily be considered as representative of free-tropospheric conditions. Clearly further discussion is required.

ACPD

8, S1228–S1236, 2008

8) The authors state that "... the ozone profile is marked by a transition in ozone level and variability around 1200 m. Such a transition does not seem to exist for CO." may be technically correct, but is surely misleading. The ozone transition is certainly related to the boundary layer-free troposphere transition. Individual CO profiles also show strong transitions at the boundary layer-free troposphere transition. The lack of an apparent transition in the illustrated profiles must result from the highly-averaged nature of these profiles. This issue requires a full discussion.

9) Throughout the paper the discussion of the CO sink due to reaction with OH is misleading, and in some respects, certainly in error. Specifically:

a) With regard to the statement "...in winter, these CO emissions are not compensated by the OH sink" is not really accurate. More correctly, the OH concentration is lower, so steady-state, background CO in the northern hemisphere increases, but during all seasons, the background CO in the northern hemisphere approaches steady-state.

b) pg. 3326 - The statement - "This is an indication that the CO background concentration is mostly modulated by chemical destruction efficiency (linked to OH availability), since the destruction rate is proportional to the CO concentration" makes no sense, and is incorrect. Northern hemisphere, mid-latitude average OH varies by about a factor of 4, yet the seasonal variation in Figure 6 is less than 25%. Clearly the seasonal variation of CO concentrations must be affected by other factors. This is supported by the seasonal cycle of ethane; its OH lifetime is comparable to CO, but it has a much more pronounced (greater than a factor of 2) seasonal cycle.

c) The statement from pg. 3329 - "This result suggests that during the JJAS period, when the oxidizing capacity of the atmosphere is maximum, OH radicals are abundant enough to absorb any variations in CO input into the atmosphere. During the JFMA period, on the contrary, there are not enough OH in the atmosphere to balance enhanced emissions (heating in winter and non-methanic hydrocarbons in spring)" - seems to indicate a fundamental lack of understanding of OH in the troposphere. OH does have

ACPD

8, S1228–S1236, 2008

Interactive Comment

a strong seasonal variation, but this variation is certainly not driven by changing CO emissions (although variation in the magnitude of CO emissions to the troposphere does have a relatively small but significant effect on global average OH concentrations). During both winter and summer enough OH is produced in the troposphere to fully react with the emitted CO, but in winter the average OH concentration is lower leading to slower removal of CO. If the CO sources were constant, then the approximately steady-state concentrations of CO in winter would be higher. Really the interaction of the tropospheric chemical cycles that control the concentrations of CO, methane, hydrocarbons, and OH is too complex to be amenable to the simple interpretations that the authors attempt. Consequently the authors' conclusion - "The causes of the decrease in CO concentrations since the 1980s hence has to be searched in late winter - early spring" - is not justified.

10) Bottom of pg. 3324 - discussion of the seasonal variation in biomass burning emissions of CO needs to be included. Also, the at the end of the first paragraph on pg. 3325, the interannual variations are very likely primarily due to variations in biomass burning, not "to varying synoptic conditions (temperature, solar exposure) from year to year at the different places", as suggested by the authors.

11) On pg. 3325 - the paragraph discussing Figure 5 is not at all clear; it must be clarified.

12) On pg. 3325 - the paragraph discussing Figure 6 is misleading. The surface measurements do show a gradient between JUN and ZSP, but the MOPITT data show little spatial gradient as is evident in Figure 5.

13) The discussion of Figure 8 is not persuasive. The analysis presented in Figure 9 is much more informative. Figure 8 should be eliminated. (The years of the month should be included in the date on Figure 8 if it were to be included.)

14) The last paragraph of Section 3, pg 3327 is very confusing; it needs to be considerably clarified.

ACPD

8, S1228–S1236, 2008

15) The trends analysis in Section 4 should be greatly improved and made much more quantitative; specifically:

a) The generally accepted statistical test is 95% confidence limits; the authors should follow this convention, or justify their use of 90% confidence limits.

b) The derived trends seem to all be zero within even the authors' 90% confidence limits; a clearer discussion of the statistical significance is required.

c) The difference in the trends between JFMA and JJSA discussed in the first paragraph on page 3328 has even less statistical significance. The difference in these trends is 1.21 ppbv/yr and propagation of the confidence limits (addition in quadrature) of the two seasonal trends suggests a 90% confidence limit of 2.02 ppbv/yr.

d) The analysis associated with Table 3 should definitely be eliminated; none of the differences in the trends from running decades are significant.

e) The authors correctly note that at PDM "No confidence interval can be reasonably discussed here due to the small number of data points used for the trend calculation." However, a confidence limit is included in Figure 10; it should be removed.

f) The comparison of the measurement techniques at PDM should be discussed before the trend at that site is discussed. Given the systematic differences in the techniques, the PDM "trend" must be treated with skepticism.

g) Figure 12 indicates a positive trend over a significant fraction of the time period of the upper panel of Figure 10. This certainly reduces the confidence in the derived negative trends, and should be more fully discussed.

h) In my judgment there is some evidence for a negative trend from these data sets, but it is far from definitive. Other workers have discussed trends in CO concentrations in various regions of the globe. The authors must quantitatively compare their trends with those derived in other work to the fullest extent possible to provide more confidence in their results.

ACPD

8, S1228–S1236, 2008

i) The significance of the PDM trend is discussed relative to the interannual variability observed at ZSP. I think that this is a fruitful approach, but needs to be done in a much more quantitative manner.

16) Section 4.2 has very significant problems. It should be completely rewritten, or perhaps better, eliminated. Specifically:

a) The second paragraph discussing Figure 13 is not useful and very confusing; this discussion should be eliminated. The text seems to indicate that Figure 13 compares yearly total number of fire pixels with yearly average CO concentration at three sites, while the figure caption indicates that the fire pixels are just for the JFMA season. If the latter is correct, then winter-early spring time wildfires in Europe, North America and Asia, are not expected to contribute significantly to the CO budget, so the finding is trivial. If the former is correct, and the authors are arguing that the analysis of Novelli et al. (2001) is incorrect, then a much more significant analysis is required. In either case, this paragraph and Figure 13 should be eliminated.

b) Pg. 3330, lines 18-20 cite the work of Meszaros et al., 2004 as showing "that the total incremental change in CO concentrations by the European sources is twice as important as the inward advection (transport from other continents)." This cited work is seriously flawed: it is not true that European sources are twice as important as inward advection. This is quite evident from Figure 6 of the present paper. In the winter air advecting into and out of Europe has CO concentrations of about 160 ppbv and 190 ppbv, respectively; in summer the corresponding concentrations are about 100 ppbv and 130 ppbv, respectively. Clearly the European contribution is only about 20 to 30 % of the CO advected into Europe. Much of the discussion in Section 4.2 is implicitly based upon the Meszaros et al. conclusion, and thus must be extensively revised if it is to be included.

c) The last paragraph of Section 4.2 is unsupported speculation and should be removed. There is also no need to include Figure 1 in this paper. It should be removed.

ACPD

8, S1228–S1236, 2008

17) The Conclusions and Abstract must be extensively revised when the issues listed above are addressed.

18) In many places the writing has significant repetition and is overly wordy. Once the paper has been revised as needed, the discussion should be carefully edited for clarity, conciseness and (as also noted by Referee #1) the English usage improved.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3313, 2008.