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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Aircraft measurements of nitrogen oxides, ozone, and carbon monoxide during MINOS 2001: distributions and correlation analyses" *by* J. Heland et al.

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General Comments: The paper attempts an analysis of an interesting data set. However, major revisions are required before the paper is suitable for publication. Specifically:

1) The authors must present a much more comprehensive discussion of their correlation analyses. Two principles must be kept in mind in this discussion: a) First, it is straightforward to present the correlations between measured concentrations of various species as the authors do in Figs. 4 - 7. However, these correlations do not provide any direct information regarding the cause of the correlation. The cause must be clearly established from other information. In some cases the authors draw conclusions based

on correlations, but the conclusions are not supported by clearly demonstrated cause and effect. Some conclusions are likely erroneous. Specific examples are discussed below. b) Second, the linear relationships on the linear-linear plots that are described by the correlations are fundamentally "mixing curves". That is, they represent mixing of two parent air masses with differing concentrations of the respective species. The lines of data points represent air samples with differing fractions of the parent air masses mixed together. The cause of a correlation can only be unambiguously assigned if it can be shown that one parent air mass is related to the other parent air mass by the cause cited. For example, one parent air mass could be "background air" and the other parent air mass that same background air with added anthropogenic emissions. However, mixing curves are often seen between parent air masses that have very different histories. In those cases, slopes of correlations give little if any information regarding the differences between the air masses. Assigning simple interpretations to such slopes without additional supporting evidence likely leads to erroneous conclusions. In this regard, it is important to consider not only the slopes of the linear regressions, but also their intercepts. Specific examples are also discussed below.

2) The slope derived from a linear regression to data with a relatively low correlation coefficient is strongly dependent upon the correlation method (deviation from linear relationship assigned to one variable only versus allowing deviations in both variables) and the relative weighting of the data. The authors must clearly define the method they chose and explain the validity of their choice.

3) In the discussion of the $\Delta[O_3]/\Delta[NOy]$ in section 3.2.1 the authors cite several references that have used the correlation slope $\Delta[O_3]/\Delta[NOz]$ as an upper limit to the ozone production efficiency. There is a very good reason for the "upper limit" qualification. Greater removal of NOz than O_3 from an air mass will increase the $\Delta[O_3]/\Delta[NOz]$ slope to a value higher than the actual ozone production efficiency. Chin et al. ,1994 (cited by the authors) discuss this and demonstrate its strong influence in boundary layer air masses. It is expected to have a much stronger influence in polluted air masses that

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are exported from the boundary layer to the free troposphere. Several studies (e.g. Stohl et al., J. Geophys. Res., 107 (D11), 4131, doi: 10.1029/2001JD000519, 2002) have shown that there is very efficient removal of NOy species during transport from the boundary layer. As a result $\Delta[O_3]/\Delta[NOz]$ simply does not provide any reliable information regarding ozone production efficiency without a careful evaluation of the extent of removal of the NOz species. In this regard the relationships between $\Delta[CO]/\Delta[NOy]$ and between $\Delta[O_3]/\Delta[NOz]$ and $\Delta[O_3]/\Delta[CO]$ may be useful.

4) The reliable measurement of NOy or NOz, especially from aircraft, is very difficult. For example Bradshaw et al. (J. Geophys. Res., 103 (D15), 19,129-19,148, 2001) discuss some of the difficulties encountered with these measurements in the NASA GTE program. In this paper the authors must give enough information regarding the NOy measurements and NOz determinations so that they can then give defensible confidence limits for the slopes derived from these measurements. For example in Table 3, the relatively small confidence limits given for the derived slopes are likely not consistent with the experimental uncertainties of the measurements that lead to those slopes. Also when the authors compare their results with those from the literature, they must acknowledge that many of the literature results are biased by these experimental problems.

5) In the discussion of $\Delta[O_3]/\Delta[CO]$ in section 3.2.1 the authors cite slopes of ~ 1 (considerably greater than generally observed in polluted air masses as indicated in the authors' Table 2) as an indication of photochemical ozone production. However, with regard to principle b) above, the authors offer no proof of this. In fact, in our own aircraft studies we have seen $\Delta[O_3]/\Delta[CO]$ slopes of ~ 1, but we have not been able to reproduce those slopes from simple photochemical production, even in box-models of photochemical processing of likely mixtures of anthropogenic emissions from industrial regions. One alternate explanation is that outflow of thunderstorms, where anthropogenic emissions are mixed with lightning produced NOx, allows greater O_3 production than from the anthropogenic emissions alone. A second alternate explana-

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tion is that the relatively steep slope results from a mixing curve between background air and an air mass that is itself a mixture of anthropogenic pollution (giving the high CO levels) and stratospheric influenced air (giving the high O_3 levels.) Such mixing of polluted air with stratospheric air is evidently relatively common in the free troposphere as cyclonic air streams mix. For example, see Cooper et al., (J. Geophys. Res., 106 (D6), 5437-5456, 2001; J. Geophys. Res., 107 (D7), 4056, doi: 10.1029/2001JD000901, 2002; J. Geophys. Res., 107 (D7), 4057, doi: 10.1029/2001JD000902, 2002). Even in the present paper, the authors discuss just such a juxtaposition of air masses below 3 km in Fig. 7.

6) In the discussion of Δ[CO]/Δ[NOy] in section 3.2.1 the authors attempt to reconcile their significant slopes of 40-50 with biomass slopes of $\sim$120 and a polluted region value of 12. This ratio cannot be interpreted without consideration of the differential removal of NOy with respect to CO.

7) In the discussion of Δ[NOx]/Δ[NOy] in section 3.2.1 the authors use correlation analysis, but treat the results as the ratio [NOx]/[NOy]. The slope is approximately equivalent to the average ratio if the intercept of the linear regression is negligible, but why do the authors use the relatively complicated and possibly more error-prone correlation analysis rather than working directly with [NOx]/[NOy] ratios? This choice must be discussed and justified by the authors, or they should analyze the ratios directly. (In the treatment of Δ[O_3]/Δ[NOy], Δ[O_3]/Δ[NOz], Δ[O_3]/Δ[CO] and Δ[CO]/Δ[NOy], there are significant intercepts that need to be treated through correlation analysis.)

8) In the discussion of Δ[NOx]/Δ[NOy] in section 3.2.1, the authors indicate that a ratio of 0.3 or less indicates photochemically aged air. This is a reasonable value only for the boundary layer in emission regions. In the free troposphere, values of 0.1 or less indicate aged air masses (see for example Jaeglé et al., Geophys. Res Lett., 25, 1705-1708, 1998.)

9) In Section 3.2.2 (a), the discussion of the stratospheric air sampling would be much

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clearer if the measured O_3 levels were included in Figure 6. These are much more sensitive to the presence of stratospheric influence than either of the slopes discussed. For example the correlation $\Delta[O_3]/\Delta[CO]$ is negative between, as well as within, the 2 time intervals of stratospheric air. This should be discussed. The lack of correlation between NOx and NOy should also be discussed.

10) In Section 3.2.2 (b), the discussion of the correlations is confusing and contradictory. It must be greatly strengthened or eliminated. Specific aspects that must be improved are: a) In the boundary layer, how can a slightly negative slope of $\Delta[O_3]/\Delta[NOy]$ help to unambiguously identify fresh emissions? The only discussion to this point in the paper identifies positive $\Delta[O_3]/\Delta[NOy]$ slope with anthropogenic emissions. Furthermore, the "good correlation of $\Delta[CO]/\Delta[NOy]$" cannot indicate common sources since the slope is negative, not positive in this case. b) In the discussion of the stratospheric influence below 3 km, it would again be very helpful to indicate the absolute O_3 levels. c) In the discussion of the layer between 6 and 7 km, the $\Delta[O_3]/\Delta[CO]$ slope is too high to be due to simple photochemical production from anthropogenic emissions. Here it would be very helpful to present the scatter plot of the O_3 versus CO measurements so that the reader can directly judge the correlation and its cause. The absolute levels of CO and NOy are likely much better tracers for anthropogenic pollution, if it is indeed present in this layer. d) In the discussion of the layer at approximately 11-12 km, the authors cite "relatively constant and low $\Delta[O_3]/\Delta[NOy]$ and $\Delta[O_3]/\Delta[CO]$ ratios indicating boundary layer air ...." Actually, the $\Delta[O_3]/\Delta[CO]$ ratio varies between 1 and 4, not at all constant and not low compared to boundary layer values (0.2 to 0.4) in their table 2. The $\Delta[O_3]/\Delta[NOy]$ values appear to be relatively constant at about 50, but that appears to be typical of most of the altitude profile on this flight, and much higher than the PBL values near 10 in their table 1.

11) In Section 3.2.2 (c), the discussion is incomplete. Two figures with eight panels are presented, but there is little discussion of their significance. The layer at 9 to 10 km is discussed as "aged", but the NOx to NOy ratio is near 0.2, indicating that it is relatively

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fresh (see point 8 above.) Curiously, the authors discuss the intercept of the O_3 versus CO correlation. What is the atmospheric significance of such an intercept? (CO never approaches zero in the troposphere due to diffuse production of CO from methane.) This section must be greatly strengthened or eliminated.

12) Section 3.2.2 (d) is simply a restatement of the authors' conclusions (often unsupported or erroneous) from the preceding sections. This section must be thoughtfully re-evaluated with a clear picture of the limitations of the analysis upon which it is based.

13) In section 4 the authors give two rather far-reaching conclusions with which I strongly disagree: a) "The analysis of the mean vertical correlation profiles as measured during MINOS 2001 does therefore not reflect the special meteorological conditions and air mass origins over the Mediterranean in summer, but reveals a more general feature of the troposphere, which is also found in other regions in the northern hemisphere." This conclusion is evidently based upon the authors' finding that the quite large range of slopes from their correlations are broadly consistent with the large range of slopes from similar correlations previously reported in the literature. However, within these broad ranges there is a great deal of information regarding "special meteorological conditions and air mass origins" that the authors have simply not discussed in this paper. b) "The overall analysis of the time series and altitude profiles of the correlations during single flights in connection with back trajectory data revealed signatures from stratospheric air, Asian monsoon outflow, and European pollution". The authors do discuss one plume that they identify as Asian monsoon outflow and one as European pollution, but they do not even attempt to define the "signatures" of these broad sources. After all of the points above have been addressed by the authors, they must carefully reevaluate their conclusions.

Minor Specific Comments:

1) In Section 2, the authors briefly describe their ozone measurement as based on "UV-absorption". They then talk about "calibrating" it against an "ozone generator"

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which is in turn frequently "calibrated" against a standard device. Are not all of these different devices based upon Beer's Law? If so, the conversion between measured absorbance and concentration depends only on path length, absorption cross section, pressure and temperature. How then is a "calibration" of a Beer's Law instrument justified? If the field instrument were indeed operated in a manner inconsistent with Beer's Law, the authors must clearly document what adjustments were made and why. A clean, properly operating instrument based upon UV absorption must certainly be compared against other instruments, but should never be "calibrated". If comparisons fail, then the source of the failure must be found and corrected. Reliance upon an ad hoc "calibration" is not scientifically justified.

2) In Section 3.2, the months or season of the SIL campaign are not given. They should be indicated to show that it is indeed a summer time study. The POLINAT-2 campaign was conducted in the early autumn. The authors should discuss this seasonal difference between the campaigns and justify the comparison of the data sets, particularly for ozone, which has a large seasonal cycle in the troposphere.

3) In Section 3.2, the authors describe the CO as "approximately 100 ppbv" above 6 km. Really, the levels appear to be close to 80 ppbv, which is a more representative value for background tropospheric CO levels in the summer.

Technical Corrections: 1) The sub-heading 3.1.1 is not needed.

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