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Atmospheric Chemistry and Physics Discussions

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Interactive Comment

Interactive comment on "Seasonal variability of measured Ozone production efficiencies in the lower free troposphere of Central Europe" *by* P. Zanis et al.

P. Zanis et al.

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Reply to Reviewer #2

We would like to thank Reviewer #2 for the helpful comments on our manuscript. We would like respond to all points raised by reviewer #2 as follows:

1) Reviewer #2 suggested that the text should mention O3 loss processes.

We added the following paragraph:

The relative importance of ozone production and loss processes in the troposphere is highly sensitive to competition between reaction of peroxy radicals with NO, and cross- or self-reactions of the peroxy radicals, and hence the local NOx and peroxy radical concentrations. Predominantly, in the low-NOx regime (“clean” atmosphere) the tendency is to have net ozone destruction, whereas when adequate NOx is present (typically NOx>50 pptv) the tendency is to have net ozone production (Crutzen, 1988; Penkett, 1988). In low NOx conditions, ozone is destroyed by photolysis by near-ultraviolet light and by reaction with HO2 and OH. Based on measurements of peroxy radicals and other relevant chemical species and photochemical parameters at JFJ, positive net ozone production rates were calculated in the vast majority of the days during FREETEX ’98 (from mid-March to mid-April) ranging from around 0.1 ppbv h-1 on relatively clean days to more than 1 ppbv h-1 on relatively polluted days (Zanis et al., 2000a). Positive net ozone production rates were also calculated from observations during FREETEX ’96 (mid-April to mid-May) and FREETEX ’01 (mid-February to mid-March) (Zanis et al., 2003).

We added a comment for this point in pages 3 (starting at line 22 and ending at line 2 of page 4) and page 13 (starting at line 22 and ending at line 15 of page 14) of the revised manuscript.

2) Reviewer #2 raised a question for the time window selected between 8 AM and 8 PM to perform the regression calculation of EN.

The actual reason for the selection of this time window was to increase the number of points used in order to carry out the regression analysis while keeping daytime data. The reviewer is right mentioning that this selection includes a few hours of darkness in winter. We have been aware of that and we have done daily EN calculations for the time window between 9 AM and 5 PM but the results were similar with the 8 AM to 8 PM time window.

3) Reviewer #2 raised a question whether the selection criteria deduce EN values biased towards those conditions that give better than average regression fits eliminating days with low photochemical activity and days with net ozone loss which in turn may have a seasonal effect.

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The reviewer is right but this is in a sense unavoidable because the longer photochemical lifetime of ozone during the cold season implies that photochemistry can be more easily masked by transport processes. Taking all the days without selection rules we cannot calculate a reasonable monthly EN value because we even have a large number of days (429) with negative correlation between O3 and NOz ($r<-0.5$) which can be partly related to downward transport from upper troposphere or even lower stratosphere. The selection criteria are used in order to decouple photochemistry from transport and in turn to carry out a reasonable EN estimation. In that sense there is a bias towards the photochemical control. The fact that 75% of the days do not meet the criterion of $r>0.5$ does not imply no ozone production for these days but that transport masks photochemistry. For example it is not coincidence that during winter we have less days meeting the criterion of $r>0.5$ when ozone chemical lifetime is longer.

We added a comment for this point in page 13 (starting at line 22 and ending at line 15 of page 14) of the revised manuscript.

4) Reviewer #2 suggested adding a comment for Figure 8 that the seasonal cycle in O3 is due to two factors, the seasonal dependence of EN and the seasonal dependence of NOz.

We followed the suggestion of the reviewer and we added a comment on that in page 27 (lines 7-8).

5) Reviewer #2 questioned the order of magnitude increase of EN from winter to summer attributed to Liu et al. (1987).

The reviewer is absolutely right that this statement was based on Figure 3 of Liu et al. paper where it is actually shown the DeltaO3/ NOx and not EN. In fact summer and winter EN values are similar. We modified the text accordingly.

We added a comment for this point in page 7 (lines 3-4) of the revised manuscript.

6) Reviewer #2 raised a question whether Equation 1 is also valid for low NOx condi-

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tions.

Reviewer #1 is right that Equation 1 is also valid for low NOx conditions. This has been clearly shown in Figure 6 of the paper by Zanis et al. (2000b) where Equation 1 has been validated with respect to chemical box model calculations. A comment was added in the text specifying that Equation 1 is valid from low to mid NOx conditions (page 14, line 16).

7) Reviewer #2 asked to validate the indirect temperature dependence of EN given by equation 2 due to the temperature dependence of the ratio NO/NO2.

We evaluated that the percentage change of EN through the temperature dependence of the ratio NO/NO2 is 2-3 % for 20% increase in temperature. We added a comment specifying this effect in page 15 (lines 20-23).

8) Reviewer #2 raised a question about the effect of PAN on EN taking into account that equation 2 does include this effect.

The question that Reviewer #2 raised is very reasonable since PAN and PNA formation which are not considered in Equation 2 can reduce the EN value. The higher PAN or PNA formation means lower EN and vice-versa. The question is when PAN is an active or a passive tracer at JFJ. In summer PAN can have an influence in EN calculation whereas PNA has minimal effect. In winter/early spring PAN has a minimal effect on En and PNA a significant effect. We added a comment for this point in pages 6 (lines 2-12) and 21 (lines 14-15) of the revised manuscript.

9) Reviewer #2 raised a question why we plotted in Figure 5 EN with respect to NOy/CO and not with respect to NOx in order to make a connection with the literature.

The reviewer is right that EN is better to be plotted against NOx in order to make a direct connection with the rest of the literature. When doing that we saw the EN versus NOx relationship in our data. However our intention was to show the EN versus NOy/CO plot because we used the NOy/CO as a filter to disaggregate between aged and fresh polluted air masses and hence we wanted to display the consistency of using this chemical filter. We decided to keep this figure as it is in the paper in order to give emphasis on the NOy/CO filter.

10) Reviewer #2 raised a question for the discussion of dilution in page 9328, lines 23-28.

If we follow an air mass from the source to the receptor then a correlation between O3 and NOz could be explained either by photochemistry or by dilution of the air mass. However if the reason for the O3 versus NOz correlation would have been dilution we should not expect a change of EN for different NOx levels. Hence photochemistry is the most probable reason for the O3 versus NOx correlation.

11) Reviewer #2 questioned the use of Figure 7a.

We show Fig. 7a for the following two reasons: a) To use all the available data to distinguish between two large classes and see the effect of this classification. b) To show that with a stricter criterion we go towards to what we would expect from disaggregating the data with the NOy/CO filter thus indicating the consistency of our filtering methodology.

We added a comment for this point in page 24 (starting at line 24 and ending at line 3 of page 25) of the revised manuscript.

12) Reviewer #2 questioned the meaning of the phrase “discernable selection rule” in page 9333, line 2.

We rephrased accordingly as follows: " ... is not a distinct selection rule." This means that this selection rule for the respective cold months does not help to distinguish between undisturbed and disturbed FT conditions.

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