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Atmospheric Chemistry and Physics Discussions



# *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 #1

We would like to thank Reviewer #1 for the helpful comments on our manuscript. We would respond to all points raised by reviewer #1 as follows:

1) Reviewer #1 raised a point concerning the weakness of the exclusive use of NOy/CO filter in the paper to classify undisturbed and disturbed free tropospheric conditions. Reviewer #1 especially raised a point regarding the influence of cloud processing in upslope motion and to what extend boundary layer air is mixed up into the air at the summit due to thermal up-slope winds.

Concerning the major comment of reviewer #1 for the weakness of the paper using only the NOy/CO filter for undisturbed FT conditions we did additional work using parameter 33 of the Alpine Weather Statistics (AWS) (Schuepp 1979; Wanner et al. 1998), Sunny day index (SND) and Radiation day index (RAD) following the work by Henne et al (2005a) to identify fair weather conditions that favour thermal convection. The SND and RAD criteria used data that were taken from the surface station network of MeteoSwiss. Stations on both sides of the Alps covering the whole Swiss plateau in the west-east direction and the Ticino area south of the Alps were selected (Henne et al., 2005). If the total sunshine duration per day was larger than 9 h for at least 50% of the stations in the north and 50% of the stations in the south, a day was categorized as being a "sun day" (SND). If the total amount of incoming solar radiation per day to the earth's surface was larger than 19 MJ m-2 at more than 50% of the stations in the north and south, a day was categorized as being a "radiation day" (RAD). Atmospheric conditions on days selected by RAD and SND index can be seen as necessary conditions to create thermally induced up-slope flow. However, undisturbed FT conditions might still be present at high altitudes, if mixing and up-slope transport was limited to lower altitudes. A region of 444 km in diameter over the central Alps is considered according to Schüepp's weather classification in AWS. Each day is attributed to a specific synoptic weather type based on a number of meteorological parameters including the surface pressure and the 500 hPa heights. There are 40 weather types in AWS which can be sorted out into three large categories (Convective, Advective and Mixed). The Convective category has three sub-classes, anticyclonic (A), indifferent (I) and cyclonic (C), while Advective category has four sub-classes, West (W), North (N), East (E), and South (S).

What we actually did was to see what is the distribution of AWS, SND and RAD indices for the undisturbed FT days selected in our paper following the NOy/CO criterion ($<$1st quartile). The findings were the following:

a) concerning the AWS 33% of the selected undisturbed FT days were Anticyclonic



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35% were Indifferent 26% were Advective days (N,W,S,E) 4% were Mixed 2% only Cyclonic days

b) concerning the SND criterion 22% of the selected undisturbed FT days were classified as Sunny days

c) concerning the RAD criterion 27% of the selected undisturbed FT days were classified as Radiation days

We found out that only 13% of the selected undisturbed FT days (17 days) were fulfilling the criteria of a sunny day, radiation day and anticyclonic or indifferent day which can be potentially affected by thermal convection. Out of these 17 days, the 14 days were during the warm period from May to September which is the period that thermal convection can affect JFJ. These 14 days account for 19% of the selected days within the period from May to September.

Hence the NOy/CO filter worked quite well in excluding days which can have a high potential for thermal convection from ABL. This has been also clearly indicated in Figure 7 of Zellweger et al. (2003) where undisturbed FT days were accompanied by the lowest NOy/CO ratio values during all seasons. Furthermore the NOy/CO filter works well for thermally induced transport, because the vertical gradient of NOy is usually much more pronounced compared to CO in a continental location.

Other upslope transport processes which can influence the JFJ site include Foehn (both north and south), and synoptical lifting. These processes are often associated with precipitation, which potentially scavenges some NOy species (HNO3, particulate nitrate). This scavenging will lower the NOy/CO ratio, and it could then be misinterpreted as free tropospheric air masses. However, due to its location in a continental area, the pronounced vertical gradients of NOy species favour higher NOy/CO ratios even during periods with potential precipitation scavenging. For example, south Foehn events during spring and autumn were always associated with high(est) NOy/CO ratios (see Figure 7 of Zellweger et al., 2003), despite precipitation loss of NOy. We agree with referee #1 that the use of NOy/CO may be problematic in more remote areas, but for JFJ this simple filter gives useful information. Furthermore out of the selected undisturbed FT days following the NOy/CO criterion ($<$1st quartile) only 5% can be potentially affected by Foehn and only 2% by cyclonic synoptic systems which are weather conditions that favour precipitation. This implies the limited influence of precipitation on EN calculation for the selected undisturbed FT days Finally, cloud processing itself is not a problem for the NOy/CO ratio. It will maybe reduce the HNO3, but not the total nitrate content unless there is precipitation as discussed in the previous paragraph. Particulate nitrate (at least volatile forms such as NO3NH4 or HNO3 absorbed on droplets) will also be measured as NOy with the setup at JFJ. Therefore cloud processing alone should not influence the NOy/CO ratio, as long as it is not accompanied by precipitation.

We added discussion for this point in pages 10 (starting at line 9) and 11 of the revised manuscript.

2) Reviewer #1 raised a few specific comments in page 9323 of the paper regarding the influence of thermal convection on the EN calculation, if we have estimated boundary layer contribution based on ozone or relative humidity soundings, and if the days with ρ$<$0.5 (75% of the days) are days with no photochemical ozone formation.

A large systematic effect of thermal convection from ABL is not expected in the selected undisturbed FT days as we pointed out already in point 1 of our reply. Furthermore typical thermal upslope conditions at JFJ during summer are accompanied by transport of ozone from ABL up to JFJ with lower concentrations than the typical free tropospheric ozone values (unless of export from ABL to FT of high ozone during summer smog episodes). This implies that thermal upslope wind masks local ozone photochemical production in FT. As has been shown by Schuepbach et al. (2001) this can reduce the afternoon ozone values at JFJ by at least 6-8 % in July and August. For these reasons the use of O3 is not a suitable tracer of ABL. Henne et al. (2005) quantified the amount of ABL air in the lee of the Alps to be about 25% at 3500 m MSL for fair weather days



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during the warm season which can be seen as an upper limit for JFJ, being located in the center of the Alps.

The concept of EN works only as long as no air mass change takes place (or is assumed). The fact that 75% of the days do not meet the criterion of ρ$>$0.5 does not imply missing ozone production for these days but that transport masks photochemistry. For example it is not coincidence that during winter we have less days meeting the criterion of ρ$>$0.5 when ozone chemical lifetime is longer. Furthermore there are a significant number of days (429) with negative correlation between O3 and NOz (ρ$<$-0.5) which can be partly related to downward transport from upper troposphere or even lower stratosphere.

We added a comment for this point in pages 8 (lines 2-4), page 13 (starting at line 22 and ending at line 15 of page 14) of the revised manuscript.

3) Reviewer #1 pointed that Equation 2 in page 9324 is not necessarily a lower limit for the ozone production efficiency.

What Reviewer #1 pointed is absolutely true 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.

4) The specific point raised by Reviewer #1 in Page 9328 is discussed in point 1 of our reply where the use of additional filters is considered to assess the influence of thermal upslope winds.

We added discussion for this point in pages 10 (starting at line 9) and 11 of the revised manuscript.

5) Reviewer #1 raised a question in page 9320 of the paper as to what extend the ice of the glacier is a local source of NOx.

Even though there are publications that show evidence for NOx production by heterogeneous reactions in Antarctica and they claim for Antarctic condition a large influence on ozone in PBL in Antarctica, there is no firm evidence from experimental work for a substantial local source for NOx from the Aletsch glacier.

5) Reviewer #1 raised a question in Figure 1 for the calculation of the regression coefficients.

We have calculated the regression coefficients with both methods, simple linear regression (O3=5.9 NOz + 57.5, R2=87%) and with the organic correlation method that takes into account the uncertainties in both axes (O3=6.3 NOz + 57.0, R2=87%).

We added a comment for this point in page 13 (lines 7-10) of the revised manuscript.

5) Reviewer #1 raised a question whether Figure 2 includes all data or only daytime measurements. The monthly medians in Figure 2 were calculated from all data but even if we use the daytime data from 08:00 to 20:00 we get the similar result. We added a comment for this point in page 16 (lines 5-7) of the revised manuscript.

6) Reviewer #1 raised a question in Figure 3 for the cause of NOx/NOy decrease in later years as a consequence of an increasing trend in NOy and no trend in CO and NOx.

This is an interesting point for which we can only speculate. Indeed looking at the monthly average NOx/NOy ratios from 1998 to 2004 there is a slight decreasing trend associated with a positive trend in total NOy and a slightly positive trend in NOx. This actually results from the relatively higher NOy values from 2002 to 2004. However when looking at the most recent data up to 2006 the NOy monthly values become slightly lower after 2004. Hence the positive trend in NOy it does seem to continue after 2004, and longer time series are needed for a trend analyis.

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