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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.

**Anonymous Referee #1**

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The paper describes the seasonal variability of ozone production efficiency for free tropospheric conditions above the Jungfraujoch at 3580 m asl, based on a multi-year data set of in-situ O3, NOx, NOy and CO measurements. While numerous studies indicate net ozone production in the polluted continental boundary layer, experimentally derived information on the ozone tendency in the free troposphere is rather limited. This is due to the fact that measurements in the free troposphere generally ask for airborne platforms. Alternatively, in situ measurements on high mountainous sites can be used, as long as suitable data filters are applied to differentiate free tropospheric air from air masses influenced by recent transport from the boundary layer. This is a non-trivial task, since mountainous sites are often influenced by thermal winds, resulting in up-sloping transport from lower altitudes during daylight hours and down-sloping winds during the night. Thus, in most studies describing measurements on mountains (see e.g. the studies on MLOPEX), free tropospheric conditions are discussed in connection with down-sloping air during the night, while daylight measurements are generally found to be affected by up-ward transport from lower layers. The present paper uses the NOy/CO as a filter to differentiate between undisturbed and disturbed free tropospheric airmasses during the day, relying on results from a previous study at the same site (Zellweger et al., 2003). Personally I consider the almost exclusive use of this filter as a particular weakness of the paper. Although I agree with the authors that this ratio can to some degree be interpreted as a parameter to assess the aging process occurring in an air parcel, there are other important processes that influence this ratio and that should be taken into account. In particular, cloud processing of airmasses during up-slope conditions will strongly modify this ratio towards lower values (retention of HNO3), which in this paper would be assigned to photochemical processing, indicating free tropospheric airmasses. Cloud processing will not only affect the NOy/CO ratio, but would also tend to increase the O3/NOz ratio, thus indicating higher O3 production efficiency in these airmasses. Since at least some of the conclusions drawn in this paper - i.e. higher ozone production efficiency in free tropospheric air - is based on the applicability of the NOy/CO ratio to differentiate between undisturbed and disturbed free tropospheric air, a more in-depth discussion of the effects of up-sloping air and associated cloud processing should be performed before the paper is published in ACP.

Specific comments:

Page 9323, Observed and steady state calculations of EN: Since this study only uses daytime observations, to what extend is boundary layer air mixed into the air at the summit due to thermal up-sloping wind? Have you estimated the boundary layer contribution based e.g. on ozone or relative humidity sounding? In the same paragraph it is stated that only 617 days out of 2557 were used for the analysis, mainly based on a



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filter setting a lower limit for the correlation between $O_3$ and $NO_z$ to $r > 0.5$. Does that mean that on roughly 75% of the days no statistical significant correlation between $O_3$ and $NO_z$ was observed, implying no photochemical $O_3$ formation?

Page 9324, Equation 2: I think equation is not necessarily a lower limit for the ozone production efficiency. Restriction to $CH_4$/CO chemistry also implies that $HNO_3$ formation is the sole sink of $NO_x$. Addition of higher hydrocarbons will also result in the formation of PAN and alkyl nitrates, which establish additional sinks for $NO_x$. An underestimation of $NO_x$ sinks in equation 2 would lead to an overestimation of EN. Maybe that is part of the reason why the theoretical value for EN in Figure 5 tends to be higher than observations.

Page 9328, last paragraph and discussion on the following pages: As pointed out in the introduction I have a strong feeling that the ratio of $NO_y$/CO alone is not sufficient to distinguish between disturbed and undisturbed FT conditions. Thermal winds will most probably always add some boundary layer air to the airmasses measured at the summit, at least during daylight hours. Additionally, cloud processing in convection or upsloping airflow, will affect both the $NO_y$/CO and the $O_3/NO_z$ ratio. Therefore, additional filters are needed to estimate the amount of boundary layer air mixed into the probed airmasses and to detect cloud processing of air parcels.

Minor comments:

Page 9320, Site description and characteristics: The authors mention the Aletsch glacier; to what extend is the ice of the glacier a local source of $NO_x$?

Figure 1: Is the calculation of the regression based on a major reduced axis fit, taking into account uncertainties in both variables?

Figure 2: Does the figure include all data or only daytime measurements?

Figure 3: Although $NO_x$ and CO show no trends, there seems to be an increasing $NO_y$ concentration in later years, leading to a decrease in $NO_x/NO_y$ ratios? Is this



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significant and what could be the cause of this decrease in NOx/NOy?

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Interactive comment on Atmos. Chem. Phys. Discuss., 6, 9315, 2006.