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Interactive comment on "Ozone production and trace gas correlations during the June 2000 MINATROC intensive measurement campaign at Mt. Cimone" *by* H. Fischer et al.

H. Fischer et al.

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We would like to thank the referee for his/her thorough review of our manuscript. We carefully checked his/her comments and made the following changes:

1 Isolation of airmasses that are truly free tropospheric: We agree with the referee that a subdivision into two regimes (daytime/nighttime) is not sufficient to differentiate between free tropopsheric and boundary layer influenced airmasses probed at the side. Nevertheless an isolation of truly free tropospheric airmasses is very difficult, due to the limited information on altitude profiles of the measured trace gases. Also, back-trajectory calculations are not very helpful, since they generally do not include sub-grid processes like orographic flows or convection. Nevertheless we tried to address this question by identifying nights with lowest mixing ratios for NOx, NOy, CO, HCHO

and number concentrations of cloud condensation nuclei (page 7). As stated in the manuscript, these airmasses are most probably truly free tropopsheric in nature.

2 Net ozone tendency In the revised version of the manuscript we changed the paragraph on pages 13/14 to discuss the NOP values derived at Mt. Cimone in more detail:

Figure 3 shows the mean daytime (06:00 to 20:00 GMT) net ozone production (NOP) rate (+- 1s-standard deviation), which gives an estimate of the on-site ozone tendency in a present-time frame. As such it describes the potential for ozone production in these airmasses in a Lagrangian experiment. The NOP evaluated for the period between June 14 (DOY 166) and June 28 (DOY 180) varies between approximately zero (June 23, DOY 175) and 0.2 to 0.3 ppbv/hr, indicating that 2 to 3 ppbv of ozone can be expected to be formed in these airmasses in the course of one day. Figure 2 shows that the average ozone concentration increases from a minimum value around noon (ca. 54 ppbv) to a late afternoon maximum of the order of 60 ppbv, which is of the same order of magnitude as the estimated net ozone production. Note, that a direct comparison is difficult due to the experimental set-up. While the NOP describes the photochemical ozone production in an Lagrangian frame, the observed increase of ozone at the site itself is due to local chemistry and advection of airmasses with different ozone content (Eulerian frame). Figure 3 also shows the average daily NO concentration, which is approximately 40 pptv. The NOP measured at the site is comparable to the daily average net ozone production rates deduced for the Jungfraujoch during the FREETEX?98 campaign in March/April 1998, that varied from around 0.1 ppbv/hr for relatively clean days to more than 1 ppbv/hr during the more polluted days at average daily NO mixing ratios of 27.3 and 260.5 pptv, respectively (Zanis et al., 2000b). Contrary to the positive NOP derived for these two mountainous sites in continental Europe, Cantrell et al. (1996) deduced a negative NOP (-0.15 ppbv/hr) for a mean NO concentration of 19 pptv at Mauna Loa during MLOPEX II in summer 1992, a remote site in the central North Pacific. The compensation point, where the production and destruction of ozone are in balance, is related to the NO concentrations in the range of 5 ? 50 pptv depend-

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ing on the conditions in the probed airmass, which explains the difference between net ozone destruction at Mauna Loa compared to net ozone production at the continental European site cited above.

3 We expanded the abstract and the summary by including the referee?s suggestion that the low trace gas levels are characteristic for continental background conditions.

4 Table 4: The data in Table 4 for downslope conditions stem from Table 2 (Intensive 4) of Atlas and Ridley, 1996. A similar compilation for upslope conditions is not available, therefore average noontime concentrations as cited in Table 1 of Cantrell et al., 1996 were used. In the revised manuscript we have clarified this in a footnote to Table 4.

5 Difference between upslope and downslope at mountainous sites: See comment under point 1.

6 Water vapour correction: The water vapour correction was applied to the ROx data to account for a dependency of the chain length of the radical amplifier on the ambient water concentration. It is true that this correction has not been made for most of the previous measurements. Nevertheless since details of the chain length and the water vapour concentrations are not available a correction of these reported data is not possible.

7 Fit procedure: In the original manuscript we used a linear regression, since this method was applied in most of the previous observations in the literature (with the exception of Parrish et al., 1998), but we agree with the referee that a reduced major axis fit accounting for errors in both the x and y variable is more appropriate. Therefore, we now cite the results of a bivariate fit in the captions of figure 4 to 8. Nevertheless, we use both fit procedures in the discussion of figure 4 and 5 for a comparison with literature data in section 3.4:

Figure 4 shows O3-CO scatter plots for the measurements at Mt. Cimone. Positive correlations between these species are observed during day and night with slopes of

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the order of 0.5, based on a reduced major axis fit accounting for errors in both the x and the y-variable, These values are slightly higher than observations at other sites in North America (Chin et al., 1994), the Atlantic coast of Canada (Parrish et al., 1993) and the central Atlantic ocean (Fischer et al., 1998; Parrish et al., 1998) during summer. Note that the majority of these results (Parrish et al., 1993; Chin et al., 1994; Fischer et al., 1994) are based on single sided linear regressions accounting only for errors in O3. A similar procedure would yield slopes of the order of 0.25 for the MINATROC data set, a value in much better agreement with these literature values.

and

Figure 5 shows the correlation among these species obtained at Mt. Cimone. The slope is about 16 (based on a reduced major axis fit) which is somewhat higher than observations in the eastern United States that showed values of DO3/DNOz between 8 and 12 (e.g. (Trainer et al., 1993; Poulida et al., 1994; Kleinmann et al, 1994)). Lower values of 4 - 6 DO3/DNOz were observed in the city plume of Freiburg at Schauinsland (Volz-Thomas et al., 1993).

Interactive comment on Atmos. Chem. Phys. Discuss., 2, 1509, 2002.