Atmos. Chem. Phys. Discuss., 6, S3515–S3520, 2006
www.atmos-chem-phys-discuss.net/6/S3515/2006/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Processes controlling the concentration of hydroperoxides at Jungfraujoch Observatory, Switzerland" *by* S. J. Walker et al.

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Received and published: 4 October 2006

We respond to the reviewer's specific comments:

1) Section 3.2, page 7184, last paragraph: The authors imply that the high NOx levels during 6 March are associated with thermally induced daily upslope motions. I am not convinced how the authors come to this conclusion. Thermal convection is not strong during the cold part of the year at Jungfraujoch. Personally I doubt that thermal convection is the controlling transport process for this event at that time of the year. The air mass originates from the boundary layer of Po Valley but the process to reach the free troposphere alternatively can be a South Foehn event or dynamical uplift from a frontal passage. I suggest that the authors should look what is really the controlling

transport process for this case study.

> We agree with the reviewer's comments and have altered the text accordingly. This paragraph has been modified to read as follows:

"Using these classifications, the high NOx levels during 6 March, which in combination with wet and dry deposition in the humid ascending air-mass caused hydroperoxide concentrations to reduce, can therefore be classed as fresh emissions (NOx/ NOy ˜0.8) within a south-westerly, ascended air-mass (from 750-850 hPa, ˜2 km). The toluene to benzene ratio increased from a background level (the campaign median of ˜0.5) to values above 1.5, which was also indicative of fresh emissions at this site (Li et al., 2006a). The sources of these south-westerly air-masses appeared to be the industrialised region of the Valais Valley (southern Switzerland) or the Po Valley (northern Italy), consistent with Seibert et al. (1998) and Forrer et al. (2000). The latter found that the highest CO (double the average value) and NOx (>1 to <10 ppbv) concentrations were associated with winds that transported anthropogenic pollution to this site from these industrialized regions of Switzerland and Italy. Similar conditions to those described by Forrer et al. (2000) occurred on 6 March when a doubling of CO (>190 ppbv) and intense NOx (˜4 ppbv) was observed, due to upslope motion possibly associated with dynamical uplift from a frontal passage. Their paper described upslope motion associated with this south-westerly flow, as a process of transporting polluted air from lower altitudes to the site. The importance of these processes at this site was highlighted by Carpenter et al. (2000) who observed diurnal CO and H2O cycles indicative of daily upslope motion, and developed further by Zellweger et al. (2003)."

2) Section 3.3, page 7185, lines 22-26: The authors claim that only 4% of the data can be classified as free tropospheric following the selection criteria based on Carpenter et al [2000]. This is surprisingly a very low number for a late winter period at Jungfraujoch. Looking at Fig. 4 I noticed that the first criterion of CO<200 ppbv is satisfied for almost the whole campaign (except the last day of the campaign). Then the effective screening of the data is mainly based on the criterion of NOx/NOy<0.3. From Fig. 4 I see that the

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NOx/NOy ratio varies around 0.5 and hence this is actually the reason that sorted free tropospheric days are only 4%. However mind that the selection rule NOx/NOy$<$0.3 is arbitrary and cannot be considered as a golden rule throughout the year as there is a distinct seasonal variation of the ratio. For example a climatological mean value of a few years at Jungfraujoch for the ratio NOx/NOy in February is around 0.48, in March around 0.35 and in April around 0.33. Mind also that the Carpenter et al. [2000] paper refers to a period from mid-March to mid-April. Zellweger et al. (2003) suggested that an alternative parameter to assess the aging process that has occurred in an air parcel is the NOy/CO ratio, which accounts for both deposition and dilution effects. Zellweger et al. (2003) showed from NOy and CO measurements at JFJ from April 1997 to March 1999 that undisturbed FT conditions are always accompanied by the lowest NOy/CO ratios. I suggest that the authors have a look on the NOy/CO ratio values throughout the campaign in order to distinguish between disturbed and undisturbed free tropospheric conditions.

$>$ The reviewer makes a good point as identifying the air-mass origin through tracer concentrations is difficult due to the lack of a definitive classification. We have looked at other ratios such as the NOy/CO ratio as suggested by the reviewer, but have failed to find an objective parameter. Within the text we have discussed the difficulty associated with this, so that the modified text will read as follows:

"Identifying the air-mass origin through tracer concentrations is difficult due to the lack of a definitive classification. Various other subjective criteria, such as the NOy/CO ratio, have been utilised to define free tropospheric air. Based on various subjective criteria at Jungfraujoch, free tropospheric periods have previously made up 40% during March to August 1997 and 1998 (Zellweger et al., 2003) and 57% during 1993 to 1997 by Li et al., (2006)1 of the measurement period."

3) Section 3.3, page 7186, line 20-21: The authors state that most of the air observed during the campaign has a significant influence of the boundary layer. Did they reach this conclusion by simply looking the selection rules (see the previous paragraph of my

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comments) or did they cross-check the origin of the air-masses with back-trajectories for all days throughout the campaign? The authors should give more firm evidence for such a statement.

> The reviewer raises an important point that we must cross-check the chemical tracers that indicate boundary layer influence with the BADC 5-day back trajectories. On examination of each 6-hourly trajectory release, only 28% entered the boundary layer (assumed to be <1 km, ˜900 hPa) during the previous 5 days. This implies that a much higher percentage of sampled air had been of free tropospheric origin than had originally been calculated (4%) based on chemical tracers alone, using the criteria of Carpenter et al., [2000]. This suggests that the chemistry and dynamics disagree, which reiterates the diagnostic problems in classifying free tropospheric air. The text will be altered to account for this, and will read as follows:

"Carpenter et al., [2000] used the criteria of CO <200 ppbv, NOx/NOy <0.3, and a coarse screening of cloudy days, by excluding periods when global radiation was below the campaign median, to diagnose being within the free troposphere. Data collected as part of this campaign fulfilled these criteria for only 4% data coverage, which was lower than previous research of Carpenter et al. (2000) at this site, where free tropospheric air amounted to 17% using the same criteria during FREETEX 1998. However, on examination of each 6-hourly trajectory release, only 28% entered the boundary layer (assumed to be <1 km, ˜900 hPa) during the previous 5 days. This implies that a much higher percentage of sampled air may have been of free tropospheric origin than was calculated based on chemical tracers alone (4%) using the criteria of Carpenter et al., [2000]. Identifying the air-mass origin through tracer concentrations and trajectories is difficult due to the lack of a definitive classification. Various other subjective criteria, such as the NOy/CO ratio, have been utilised to define free tropospheric air. Based on these various subjective criteria at Jungfraujoch, free tropospheric periods have previously made up 40% during March to August 1997 and 1998 by Zellweger et al., (2003) and 57% during 1993 to 1997 by Li et al., (2006)1 of the measurement period."

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4) Section 3.6, page 7189, lines 24-26: The authors state that the mean observed H2O2 observations of 206 +/- 261 pptv during this campaign are more consistent with the box model calculations of Zanis et al. (1999) that include a surface depositional sink. However, there are a number of cases (e.g. the case C of Table 2) with photochemically aged air-mass which is representative of less disturbed free tropospheric air that the H2O2 observation is closer to the upper estimate of modeled H2O2 (1700 pptv). Furthermore I guess it is difficult for a 0-dimension chemical box model to simulate concentrations of species with lifetime of a few days such as H2O2. Their concentration at Jungfraujoch is mainly controlled by transport as also supported by the authors. From my point of view although the comparison of the observed H2O2 with the box model calculations including depositional sink of hydroperoxides shows to the direction that the air masses reached Jungfraujoch had an impact from the boundary layer, it does not provide firm evidence for such a conclusion as it can be more complex issue. I would suggest that the authors elaborate a bit more this conclusion.

> The reviewer makes an excellent point here and we agree that some air-masses have been subject to significant deposition and some have not. An example of the latter, as proposed by the reviewer, is case C (see Table 2), where the concentration of H2O2 (<=1424 pptv) is closer to the upper estimate of the box model, detailed in Zanis et al. (1999).

The text will be altered accordingly, to better communicate these details. This paragraph will be modified to read as follows:

"Their work simulated H2O2 concentrations in the order of a magnitude from 1700 and 170 pptv without and including dry deposition respectively. The mean observed H2O2 observations of 206 +/- 261 pptv during this campaign are thus much more consistent with the calculations that include a surface depositional sink. However, there was some indication of air-masses that were representative of less disturbed free tropospheric air (e.g. case C, Table 2), where the H2O2 concentration (<=1424 pptv) was closer to the upper estimate of the box model, detailed in Zanis et al. (1999)."

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5) Section 3.6, page 7190, lines 13-15: The absence of anti-correlation between O3 and H2O2 can be due to the long lifetime of O3 during winter at the free troposphere so that photochemical processing can be easily masked by transport. Mind also that the paper of Ayers et al. (1992) refers to unpolluted marine boundary layer and not to free troposphere. In boundary layer with 4-5 times more H2O than in the free troposphere the contribution of local photochemistry can be more clearly identified.

> The reviewer made a useful suggestion that the lack of anti-correlation between O3 and H2O2 could also be attributable to the difference in lifetime between the two species. We acknowledge that Ayers et al., (1992) describes a non-comparable situation, of measurements in the marine boundary layer at Cape Grim. The text will be altered accordingly to better communicate these details. This paragraph will be modified to read as follows:

"During the campaign, the data selected using the criteria of Carpenter et al., [2000] for free tropospheric air, also did not display a significant anti-correlation between O3 and H2O2 (R2 ˜ 0.2). This is consistent with simultaneous production of both O3 and H2O2 but is in contrast to the previously observed anti-correlation between O3 and H2O2 for the remote marine boundary layer [e.g. Ayers et al., 1992]. Again this observational evidence lends further support to the case that the JFJ station mainly sampled boundary layer air during this campaign. However, the lack of anti-correlation between O3 and H2O2 could also be attributed to the difference in lifetime between the two species."

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 7177, 2006.

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Interactive Comment