Atmos. Chem. Phys. Discuss., 6, S2700–S2703, 2006
www.atmos-chem-phys-discuss.net/6/S2700/2006/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 25 August 2006

General Comments: This paper focuses on the investigation of the processes controlling the concentration of hydroperoxides (mainly hydrogen peroxide and methyl hydroperoxide) which have been measured in the framework of the Free Tropospheric Experiment during February/March 2003 at the Jungfraujoch Observatory (3,580 m asl) in the Swiss Alps. To my knowledge these hydroperoxide measurements are the first that have been published so far for the high Alpine station of Jungfraujoch, an important GAW station for the Free Troposphere. It is obvious that hydroperoxide measurements are important in order to understand and quantify the gas-phase free radical chemistry, which in turn is essential for the photochemical control of tropospheric ozone. I think the paper deserves publication but I have a few points that the authors should consider

carefully before the final acceptance of the manuscript.

Specific Comments: 1) In Section 3.2, in 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.

2) In Section 3.3, in 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 Jungfrauch. Looking at Fig. 4 I noticed that the first criterion of CO$<$200 ppbv is satisfied for almost the whole campaign (except the last day of the campaign). Then the effective screening of the data is mainly based on the criterion of NOx/NOy$<$0.3. From Fig. 4 I see that the NOx/NOy ratio varies around 0.5 and hence this is actually the reason that sorted free tropospheric days are only 4%. However mind that the selection rule NOx/NOy$<$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

ACPD
6, S2700–S2703, 2006

EGU

a look on the NOy/CO ratio values throughout the campaign in order to distinguish between disturbed and undisturbed free tropospheric conditions.

3) In Section 3.3, in 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 comments) or did they cross-checked 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.

4) In Section 3.6, page 7189, lines 24-26: The authors state that the mean observed H2O2 observations of 206ś261 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.

5) In 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.

ACPD
6, S2700–S2703, 2006

EGU

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

ACPD

6, S2700–S2703, 2006

Interactive Comment

EGU