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Discussions

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

Anonymous Referee #2

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General Comments

The paper presents peroxide data from the FREETEX 2003 experiment on Jungfraujoch. This data can provide an insight into the rates of photochemical processing as well as the physical processes such as dry and wet deposition. The authors illustrate the importance of the data, largely through detailed discussion of individual case studies. However, there are number of points that give me some concern. These are mostly related to discussions which tend to make generalisations, which at times are misleading, even inaccurate and illogical. I have detailed these below. I believe that the authors must address these before the manuscript is acceptable for publication.

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Specific Comments

Major

Section 3.2 Effect of local and synoptic scale meteorology

I struggle to follow many of the arguments presented in section 3.2. This is not helped by the size of Figure 4 which makes it difficult to read the values of parameters and to see exactly how changes in one parameter are related to those of another.

Was the vector averaged local wind direction really constant (312 degrees) throughout the whole campaign ? What was the standard deviation on the vector averaged local wind direction ? Given that the ‘synoptic wind direction’ was south westerly for 8 days (28 February to 2 March, 5 to 6 and 10 to 12 March) out of a 14 day campaign (27 February to 12 March), I would suggest that it was not “in general from the west/north-west (consistent with the observed wind direction)”.

The CO during the 28 February to 2 March and 10 to 12 March south westerly periods was mostly around the campaign average of 140 ppb. Between the 5 and 6 March it is true that the CO does increase to 190 ppbv, but a doubling only occurs because the CO had fallen to around 100 ppb earlier in that same south westerly period. It was not double the average value as Forrer et al observed. I therefore question the statements “During south-westerly flow, primary photochemical pollutants e.g. CO and NOx, were often enhanced” and “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.” This leads me to further question the statement “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).” As I see it much of this south westerly air flow did not contain high concentrations of pollutants. Further the trajectories, as presented, do not provide clear evidence for the air masses during these periods having passed over these regions.

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Even though 3 of the 4 cases of hydroperoxide maxima occurred in south-westerly air-masses, which were supposedly associated with polluted air, the authors state that high hydroperoxide concentrations were only present when NOx concentrations were low. Thus the authors do point out that the south westerly air was at times not heavily polluted. It therefore confuses me why the authors try to link these south westerly episodes with polluted air, when they subsequently argue that the hydroperoxide maxima occurred mostly in photochemically aged air from the south west (i.e. NOx/NOy ratios $<$ 0.3). But this just confuses me further as the NOx/NOy ratios appear to be rarely below 0.3, with the exception of the case on the 11 March. This is backed up by the following discussion in section 3.3 where the criteria of NOx/NOy $<$ 0.3 and CO $<$ 200 ppbv are used to define free tropospheric air and leads to the conclusion that only 4% of the air sampled was free tropospheric. Given that the CO maximum was 190 ppb, then the NOx/NOy ratio must have been less then 0.3 most of the time. Similarly the toluene/benzene ratio of less than 0.5 only appears to hold for the case on the 11 March.

Obviously the south westerly air flow can bring very different air masses. The case on 6 March is an example of this with rapidly changing concentrations. The increase in the CO to 190 ppbv and the associated NOx spike appear to occur after the fall in the peroxide concentrations. It is difficult to read the detail of Figure 4, but the peroxide maxima on the 6th looks like it is associated with lower CO, possibly a small increase in NOx, the NOy data appears to be missing for much of the duration of the maxima, but increases afterwards with the CO increase. The NOx/NOy ratio indicates fresh pollution after the peroxide maximum, but it is difficult to say what it would have been during much of the maxima. There is also a gap in the toluene/benzene ratio data, but the point prior to the gap is also high. May be the air with fresher pollution led to the observed decrease in peroxide concentrations, but what led to the maxima in the first place ?

I expect that the conclusion drawn at the end of this section is correct - i.e. that much of

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the variability seen in the hydroperoxide concentrations observed can be attributed to changes in flow regime leading to changes in the levels of photo pollutants rather than local changes in photolysis rates - but I really don't think the authors have presented the case claerly and at this point they haven't even discussed the photolysis rates.

By the end of this section I haven't really got an understanding of the message that the authors are trying to make. Some statements seem to be inaccurate and the logic seems very confused and I am left with questions such as the following: Which is the predominant synoptic wind direction ? Are the south westerly air masses polluted ? Are the hydroperoxide maxima associated with polluted conditions or not ? Are these south westerly air masses photochemically aged ? If so, why do they not fall in to the free tropospheric air mass classification ?

Section 3.3 Sampling of boundary layer and free tropospheric air.

Is it sensible to screen out cloud by excluding periods when global radiation was below the campaign median ? That instantly removes 50% of the data, and potentially data in cloud free conditions or times when there was thin cloud possibly high above the site. How was night-time data dealt with ?

The authors write “The periods that satisfied free tropospheric criteria occurred for a short time on the 6 March and for longer periods towards the end of the campaign (9 to 12 March). Both examples corresponded to elevated hydroperoxide levels, most likely due to a removal of dry deposition as a hydroperoxide sink.” If the criteria for free tropospheric air were fulfilled for only 4% of the time, how come the periods that satisfied the criteria included “9 to 12 March” - 3-4 days ? I would suggest from Figure 4 that these criteria were not fulfilled for much of 9 or 10 March because the NOx/NOy ratio was $>$ 0.3. What is meant by “Both examples” ? the 6 and 9 to 12 March ? There were 3 elevated hydroperoxide levels over this period: on the 6th, the 9th and the 11th ? Which of these corresponded to free tropospheric air ? I think it is a bit too presumptious to put the elevated concentrations of hydroperoxide down to a reduced

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dry deposition sink. There are many other source and sink processes to consider. It looks to be as though there are times on the 11th when the free tropospheric conditions might be met and yet hydroperoxide is low.

Section 3.4 Impact of high and low NOx on hydroperoxides

“It was shown earlier that higher concentrations of photo-pollutants in south-westerly air can lead to enhanced hydroperoxide concentrations.” - based on the previous points above I challenge this statement. The main pollution event on the 6th occurred after the enhanced hydropeoxide concentrations. The statement in section 3.2 “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).” if anything concludes the opposite. The discussion that follows in the paper illustrates my point.

“In the early morning of 6 March(..), high levels of hydroperoxides (..) occurred in drier, south-westerly air that had remained at relatively constant altitude (600-700 hPa)Ě. These observations suggest slight photochemical aging and could be caused by some vertical mixing into the air-mass, by aged air from _650 hPa (_5 km), 5 days earlier (see black line, bottom left panel, in Fig. 3).” The black trajectory line applies to 00:00 GMT when air was said to have remained at constant altitude. “These observations” follow on from a description of a NOx spike at 07:00 GMT. Shouldn’t the blue trajectory line (08:00 GMT) be considered here. The caption in the bottom left panel in Figure 3 is “Ascending south westerly”. Is it ascending, descending or relatively constant ?

Of Case D the authors say, "...but these peaks are less intense than for the previous examples (A to C) that arrived in south-westerly air, which supports the findings that more HOx was available in south-westerly air-masses, which have been subjected to more intense sunlight and so have enhanced radical concentrations.”. Firstly, shouldn’t that be A and C since B was a case of suppressed hydroperoxides. Secondly, I am not convinced that case D is less intense than Case C, although I am not sure what “intense” means in this context. Thirdly, southerly flow may also bring air with more water vapour that could contribute to increased production of the hydroperoxides - as mentioned by the authors in the next paragraph.

“Air coming from the south-west with moderate levels of NOx exhibits significantly higher hydroperoxide concentration than .... air coming from the north.” As I said above, I am not convinced that Case D has significantly lower peroxide concentrations than Case C.

Section 3.5 Wet deposition and cloud processing

The sharp decrease in the concentrations of the hydroperoxides on 1 March appear to coincide with a break in the data, so it is not entirely clear to me how the decrease rates were calculated.

The authors suggest in their conclusion to section 3.2 that much of the variability seen in the hydroperoxide concentrations observed can be attributed to changes in flow regime. The reduction in the peroxide concentrations on the 1st is likely to be due to exactly that. The air mass with lower peroxide concentrations may well have been subject to wet deposition or cloud processing, but the actual observed temporal change (i.e. the transition between one air mass and the next) should probably not be related to in-situ solubility rates of the peroxides.

Section 3.6 Agreement with a previous photochemical box model

“This is consistent with simultaneous production of both O_3 and H_2O_2 but is in contrast to the previously observed anti-correlation between O_3 and H_2O_2 for the free troposphere (e.g. Ayers et al., 1992). Again this observational evidence strongly supports the case that the JFJ station mainly observed boundary layer air during this campaign and did not strongly sample the free troposphere (even during periods where “free tropospheric” criteria were satisfied).” Many of the other studies of peroxides in the free troposphere (including Ayers et al., 1992) were in clean maritime environments where the NO concentrations were less than 20 pptv and when O3 production rates were low. On the other hand JFJ is in the middle of a continental region with large anthropogenic sources of NOx, which could lead to NOx being mixed out of the boundary layer (e.g. via convection or frontal systems) such that on the occasions when free tropospheric air arrives at JFJ it may contain sufficient NO in it for significant O3 production to occur. This would explain the difference from previous studies and does not mean that air meeting the "free tropospheric" criteria has been wrongly classified.

Minor

Many of the chemical names are not defined.

Page 7179 lines 18-24: "According to Lee et al. (2000), substantial suppression of hydroperoxide production occurs at NO concentrations exceeding 100 pptv. In contrast, it is calculated that NO concentrations below 3 to 20 pptv are needed for hydroperoxide production to dominate (Reeves and Penkett, 2003; Crutzen and Zimmermann, 1991; Finlayson-Pitts and Pitts, 1986)." I don't think these 2 statements are in contrast with each other. It may be that NO concentrations of 20 pptv or less are required for hydroperoxide production to dominate (- it should be specified what it dominates over) and it may also be true that above 100 pptv of NO the production of hydroperoxide that does exist is substantially suppressed. i.e. between 20 and 100 pptv there may still be significant hydroperoxide production, but that the self reaction of HO2 does not dominate over the reaction of HO2 with NO or perhaps over all other reactions of HO2. This would agree with the statements in section 3.6 referring to Zanis et al (1999) (page 7190 lines 8-10).

Page 7180 lines 1-3: "Other important H2O2 and CH3OOH sinks are the reaction with OH radicals and photolysis at ultraviolet wavelengths generating OH and in the case of CH3OOH, OH and CH3O." This sentence is trying to convey too much and thus is ambiguous or not completely accurate. E.g. the reaction of H2O2 with OH does not generate OH. CH3O should also be CH2O.

Page 7181 line 15: What are the units of the flow rate 27 / min-1 ?

Page 7184 line 3: Figure 3 is referred to after figures 4 and 5.

Page 7187 lines 11-12: “This air-mass displayed a moderate NOx to NOy ratio (0.6)” - It is hard to tell in Figure 4, but it looks to me as though the NOy data is missing at this time - 07:00.

Table 2: Both start and end times should be given. When referring to trajectory colour, there should be a pointer to Figure 3.

Figure 3 Plot: 9 March. Can these trajectories really be said to be descending ? It does not look like this for 12:00 (light blue) and 18:00 (green) GMT. Plot 6 March. Can these trajectories really be said to be ascending (black and dark blue) ?

Figure 4 - Rather small to see the detail necessary for the discussion.

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

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