Atmos. Chem. Phys. Discuss., 6, S3527–S3541, 2006
www.atmos-chem-phys-discuss.net/6/S3527/2006/

Atmospheric
Chemistry
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Discussions

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

S. J. Walker et al.

Received and published: 4 October 2006

We respond to the reviewer’s specific major comments:

1) Section 3.2 Effect of local and synoptic scale meteorology

1a) 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?

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> The standard deviation of the vector-averaged wind direction was 312+/-68°. We agree that there were significant changes in the wind direction and have altered the text accordingly so that it now reads:

“The mean vector-averaged local wind direction (+/- 1 sigma) throughout the campaign was north-westerly (312+/-68°) with no consistent change in the local wind direction during the hydroperoxide maxima. Thus, the local wind direction appears to offer little information on the magnitude of the hydroperoxide concentration.”

1b) Given that the ‘synoptic wind direction’ was south westerly for 8 days (28 Feb to 2 Mar, 5 to 6 and 10 to 12 Mar) out of a 14 day campaign (27 Feb to 12 Mar), I would suggest that it was not “in general from the west/northwest (consistent with the observed wind direction)”.

> We agree that this sentence is misleading, and we need to clarify that the south-westerly trajectories were only for short periods during some of the days listed. We have calculated that ˜55% of the back-trajectories during the campaign were of west/north-westerly origin. We have altered the text accordingly and this paragraph will be modified to read as follows:

“The “synoptic wind direction” (diagnosed from the last day of transport described by the trajectory) was from the west/north-west for ˜55% of the campaign (consistent with the observed wind direction) except in periods during the 28 February to 2 March, 5 to 6 and 10 to 12 March when air-masses with a south-westerly character were sampled (see Fig. 3 for examples of these trajectories).”

2a) 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."

> We agree that south-westerly air-masses sometimes gave rise to low concentrations of primary photochemical pollutants. We acknowledge that the CO concentrations were not double their average value. We have modified the text to read as follows:

"During south-westerly flow, primary photochemical pollutants e.g. CO and NOx, were sometimes enhanced, as illustrated in Whalley et al. (2004) for this campaign and previously seen in past campaigns at this site (Forrer et al., 2000; Carpenter et al., 2000)."

"Similar conditions to those described by Forrer et al. (2000) occurred on 6 March when high concentrations of CO (>190 ppbv) and intense NOx (˜4 ppbv) were observed."

2b) 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.

> To clarify this statement, we have modified the text (see below). The light blue (12:00) and green (18:00) trajectories for 6th March (Figure 3, bottom left panel) clearly show an ascending air-mass from the south-west.

"The sources of these polluted south-westerly air-masses could be the industrialized region of the Valais Valley (southern Switzerland) or the Po Valley (northern Italy), consistent with Seibert et al. (1998) and Forrer et al. (2000)."

2c) 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).

$>$ We have addressed this concern in 2a.

2d) 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.

$>$ To clarify, the NOx/NOy ratio only drops below 0.3 during five short periods (each $<$3 hours) before, and for a longer period during, 11/03 (07:00) to 12/03 (18:00). This is why such a small % of the campaign was classified as free tropospheric. We have further addressed the issue of the criteria used to classify free tropospheric air in our response to the first anonymous reviewer (see points 2 and 3 in our previous response). The toluene/benzene ratio drops below 0.5 for much of the campaign, including during three of the four hydroperoxide maxima (01/03, 09/03 and 11/03). Using the criteria of Chin et al., [1994], we can only assign the last hydroperoxide maxima (11/03) as a photochemically-aged south-westerly air-mass. The text will be altered to reflect this as follows:

“High hydroperoxide concentrations were only present when NOx concentrations were low. The south-westerly air-mass sampled during 11 March was also photochemically aged based on the distinction of Chin et al. (1994), who used a NOx/NOy ratio of $<$0.3 to evaluate when an air-mass could be described as photochemically aged.”

2e) 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.

$>$ Increase in CO and relative humidity, and the trajectories indicate that the air-mass changes from a descending to an ascending south-westerly at the time of the decrease in hydroperoxides (˜12:30 GMT) on 6 March. We agree that the associated NOx spike occurred slightly later than this (˜15:00). We agree that it is difficult to identify what caused the reduction in hydroperoxides, and the text has been altered to explain this:

“Using these classifications, the high NOx levels during 6 March, which in combination with wet and dry deposition in the humid ascending air-mass was likely to have 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).”

2f) 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?

$>$ The reviewer makes a good point here and we agree that it is difficult to decide upon what caused the increase in hydroperoxides in the first place on 6 March. The text has been modified to refer the reader to Section 3.4 where these high concentrations of hydroperoxides are discussed and Section 3.4 has been altered as indicated:

(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 (from their initial high values described in Section 3.4), 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).”

(Section 3.4:) “The high levels of hydroperoxides in this event were therefore thought to be due to a combination of photochemically aged air with an abundance of HOx, low NOx, and little surface deposition, but ultimately it is difficult to decide upon what caused these hydroperoxide maxima.”

2g) I expect that the conclusion drawn at the end of this section is correct - i.e. that much of 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 clearly and at this point they haven’t even discussed the photolysis rates.

$>$ We accept that photolysis rates must be discussed before this conclusion, to better quantify whether photolysis rates or flow regimes controlled the concentration of hydroperoxides at Jungfraujoch. We have plotted H2O2 and CH3OOH concentrations against the photolysis rate coefficient, j(O1D) for 10:00 to 14:00 each day during the campaign and found the R2 to be ˜0. We have therefore added a sentence to describe this, which reads as follows:

“As described earlier, the relationship between hydroperoxides and primary pollutants (notably NOx) is complicated. Hydroperoxide concentrations were sensitive to the NOx concentration within these air-masses. High hydroperoxide concentrations were only present when NOx concentrations were low. The correlation coefficient between H2O2 or CH3OOH concentrations and the photolysis rate coefficient, j(O1D) for 10:00 to 14:00 each day during the campaign gave a R2 of ˜0 which indicates that the concentrations of hydroperoxide are not determined by their photochemical production.”

2h) 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? (> see 1b) Are the south westerly air masses polluted? (> see 2a) Are the hydroperoxide maxima associated with polluted conditions or not? (> see 2d) Are these south westerly air masses photochemically aged? (> see 2d) If so, why do they not fall in to the free tropospheric air mass classification? (> see 2d)

> We agree that this section was previously unclear and we feel the above alterations and additions (2a to 2g) have addressed the reviewer’s comments on this section.

3) Section 3.3 Sampling of boundary layer and free tropospheric air.

3a) 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 difficulty of choosing criteria to classify free tropospheric air was addressed in our response to the first anonymous reviewer (see points 2 and 3 in our previous response). Night-time data was removed using this filter. We also tried to remove periods of cloud by screening out periods where the relative humidity was above 90% rather than using radiation data. Using this filter, 18% of the data remained rather than just 4% using the criteria of Carpenter et al., [2000]. This will be added into the final manuscript so the text 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 25 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. If for these criteria, relative humidity above 90% is used to screen out cloudy days rather than global radiation, then 18% of the data satisfies the 'free tropospheric' definition."

3b) 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 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.

$>$ We have addressed the concerns regarding the classification of free tropospheric air in 2d and 3a. Air satisfying 'free tropospheric' criteria was only sampled for short periods during some of the hydroperoxide maxima (6, 9 and 10 March). We agree that other factors could have existed to increase hydroperoxides in addition to the reduction in dry deposition. The text will be altered to better address these concerns, to read as follows:

"The periods that satisfied free tropospheric criteria occurred for a short time on the

4, 6, 7, 9 and 10 March and for longer periods towards the end of the campaign (11 to 12 March). Some of these examples occurred during elevated hydroperoxide levels (i.e. 9, 10 and 11 to 12 March), which could be due to the reduction in deposition as a hydroperoxide sink. However, other factors must be affecting hydroperoxide concentrations in the air classified as 'free tropospheric' during the 11 to 12 March as there are short periods when the concentrations reduce to <LoD."

4) Section 3.4 Impact of high and low NOx on hydroperoxides

4a) "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 southwesterly, ascended air-mass (from 750-850 hPa, ˜2 km)." if anything concludes the opposite. The discussion that follows in the paper illustrates my point.

> We agree that these phrases are conflicting. The text will be altered accordingly to better communicate these details, this paragraph will be modified to read as follows:

"It was shown earlier that enhanced hydroperoxide concentrations were measured in south-westerly air, when NOx levels and depositional sinks were reduced."

4b) "In the early morning of 6 March (Example A, Table 2), high levels of hydroperoxides (1.0 and 0.4 ppbv H2O2 and CH3OOH respectively) occurred in drier, south-westerly air that had remained at relatively constant altitude (600-700 hPa), with relatively low CO (˜110 ppbv) and NOx levels (˜0.3 ppbv), compared to the rest of the campaign. However, a spike in NOx of over 1 ppbv, at 07:00 caused a brief, partial reduction in hydroperoxides, due to suppression of HO2 by elevated NOx. This air-mass displayed a moderate NOx to NOy ratio (˜0.6), together with a relatively large increase in longerlived alkanes compared to small increases in short-lived alkenes (see Whalley et al., 2004). 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?

> We agree that we should also refer to the trajectory for 06:00 (the dark blue trajectory), as well as the one for midnight as the high hydroperoxide levels were measured throughout this period of level air and has been added (see below). We acknowledge that the caption in the bottom left panel of Figure 3 is misleading and it will be altered accordingly (see below).

"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 and dark blue line, bottom left panel, in Fig. 3)."

"Level south-westerly (from 00:00) changing to ascending south-westerly (from 12:00)"

4c) 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

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.... air coming from the north.” As I said above, I am not convinced that Case D has significantly lower peroxide concentrations than Case C.

> We have corrected the mistake (i.e. referring to Case B) so that this sentence reads as follows (see below). We use ‘intense’ to mean high in hydroperoxides. The peak values of H2O2 during 9 March (Case D) are lower in concentration than 1 March, 6 March (Case A) and 11 to 12 March (Case C). We agree that increased water vapour concentrations are also a factor. We have altered the text to better reflect this:

“Again a lack of NOx and dry deposition allowed hydroperoxides to accumulate, but these peaks are lower in concentration than for the other examples (1, 6 and 11 to 12 March) that arrived in south-westerly air, which lends support to the findings that more HOx was available in south-westerly air-masses, which have been subjected to more intense sunlight, water vapour concentrations and so have enhanced radical concentrations.”

“Air coming from the south-west with moderate levels of NOx displays higher hydroperoxide concentration than air which is more significantly polluted air, or air coming from the north.”

5) 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.

$>$ We confirm that there is a break in the data. We agree that the section below is taking the interpretation too far and so it has been shortened in the final manuscript to the following:

“It appears that H2O2 concentrations during this event reduced faster than CH3OOH due to its much higher solubility (the ratio of Henry’s Law coefficients, HH2O2/HCH3OOH˜260) but because of the data gap during this hydroperoxide reduction, the role of uptake into water droplets and dilution by changing air-masses is unclear.”

6) Section 3.6 Agreement with a previous photochemical box model

“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 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.) 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.

$>$ The reviewer makes an important point here and we agree that the classification used for free tropospheric air is simplistic, although no better approaches appear to exist. As we have stated in our previous response to the first anonymous reviewer (see point 5 in this previous response), the Ayers et al. [1992] paper was wrongly referenced as free tropospheric measurements (the paper reports measurements from the marine boundary layer). We agree that the lack of an anti-correlation between O3 and H2O2 does not imply that the air has been wrongly classified as ‘free tropospheric’. In addition to the changes for point 5 in the previous response, the text will be altered as follows to address this concern:

“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 other factors such as the difference in lifetime between the two species, or the possibility that NOx could be mixed out of the boundary layer (e.g. via convection or frontal systems) so that when free tropospheric air is sampled at JFJ, it may contain sufficient NO in it for O3 production to occur.”

7) Minor corrections

7a) Many of the chemicals names are not defined.

$>$ The text has been altered to ensure all chemical names are defined.

7b) 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).

> The text has been altered as follows: “According to Lee et al. (2000), substantial suppression of hydroperoxide production occurs at NO concentrations exceeding 100 pptv. It is calculated that NO concentrations below 3 to 20 pptv are needed for hydroperoxide production to dominate over the reaction between HO2 and NO (Reeves and Penkett, 2003; Crutzen and Zimmermann, 1991; Finlayson-Pitts and Pitts, 1986).”

7c) 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.

> The text has been altered as below. The initial products of CH3OOH photolysis is OH and CH3O (which can go on to form CH2O): “Other important H2O2 and CH3OOH sinks are their reaction with OH radicals and photolysis at ultraviolet wavelengths.”

7d) Page 7181 line 15: What are the units of the flow rate 27 / min-1 ?

> The text has been altered to read “2.7 l min-1”.

7e) Page 7184 line 3: Figure 3 is referred to after Figures 4 and 5. > The text has been altered accordingly and the figures are numbered in the order they are referred to in the final submission.

7f) 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.

> The reviewer is correct: there is a large data gap in NOy during this event on 6 March. However, there is a ˜4 hour (09:40 to 13:30) period at the end of the hydroperoxide

maxima where NOy was measured, and the mean NOx/NOy ratio was calculated to be ˜0.6 which is what is referred to here and in Table 2.

7g) Table 2: Both start and end times should be given. When referring to trajectory colour, there should be a pointer to Figure 3.

> Table 2 has been edited accordingly: “Air-mass altitude origin (Figure 3 panel and trajectory colour)” “Time: 00:00 to 13:30 6 March; 13:30 to 23:50 6 March; 07:00 11 March to 18:00 12 March; 14:00 9 March to 15:20 10 March”

7h) 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)?

> The captions given in Figure 3 give a general description to the main direction and altitude origin for the day’s trajectories, the captions have been made more specific to account for this (also see point 4b above): “Descending north-westerly (from 00:00) changing to ascending north-westerly (from 12:00)”

7i) Figure 4 - Rather small to see the detail necessary for the discussion.

> Figure 4 will be enlarged in the final manuscript submission.

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