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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Chemical composition of free tropospheric aerosol for PM1 and coarsemode at the high alpine site Jungfraujoch" *by* J. Cozic et al.

J. Cozic et al.

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General comment: We thank the referees for their helpful comments and we believe that they helped in improving the quality of the paper. On the attached sheets we describe how we will accommodate the referees' comments in the revised version.

Scientific comments:

Anonymous Referee #1

Referee 2.1 Jungfraujoch Station First paragraph comments

Answer: No cloud cover has been measured continuously from 2003 to 2007. Only for individual field campaigns a PVM was installed. The cloud cover was thus obtained for

February-March 2004, August-September 2004 and February-March 2005. For these campaigns the cloud covers were 42%, 23% and 40%, respectively, thus showing a slightly lower cloud cover in the summer campaign than for the winter periods. The effect of riming processes along with other sink processes is outside the scope of this study. Such work was performed at the Jungfraujoch by Poulida et al. (1998) and it is not intended to repeat it here.

Referee Second paragraph comments

Answer: No seasonal shift in the wind direction can be observed. In the last 9 years the wind was at 65% North and 35 % south but no significant variation over the year could be observed. Higher concentrations in the boundary layer could also be a reason for the enhanced concentration at the Jungfraujoch after vertical transport. However, our experience is that vertical transport itself is typically more important. First evidence on the importance of vertical transport for the Jungfraujoch aerosol was already published in 1991 (Baltensperger et al., 1991), followed by many other studies. Lugauer et al., (1998, 2000) published detailed analyses on the influence of aerosol transport at the Jungfraujoch. It was shown that the vertical aerosol transport by thermally driven convection, acting between spring and late summer, was found to be the dominant transport process. Nyeki et al. (2000) also showed how the PBL evolves in summer around the Jungfraujoch. More information will be added to the revised manuscript to corroborate this dominance of the influence of the PBL on the seasonal cycles at JFJ. The seasonal variation of SO2 and sulfate will be discussed further below.

Referee 2.2 Inlet comments

Answer: We have done the calculations for the sampling efficiency showing that the vast majority of aerosol particles and cloud droplets are sampled for wind speeds up to 20 m/s (Weingartner et al., 1999). Above this limit we do not trust these simplified calculations anymore, due to the complexity of various additional effects (turbulence, etc). In addition, Henning et al. (2002) showed by differentiating size distributions measured

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downstream of different inlets (total - interstitial) and comparison to cloud microphysical measurements (FSSP) that the total inlet has a very high sampling efficiency for cloud droplets. Concerning the percentage of wind speeds above 20 m/s: over the last 9 years it was very low, with only 2.6% indicating that this did not really affect the sampling.

Referee 2.5 Chemical composition of aerosol filter samples comments

Answer: Detection limits for each species were given by Henning et al. (2003) and will be added to the paper. Frequency of measurements: Additional information concerning the frequency of measurement will be added to Table 1.

Referee 3.1.1 Determination of the mass absorption efficiency comments

Answer: Our regression was identical to the reduced major axis regression. This will be mentioned in the updated version.

Referee 3.2 Long-term chemical composition 1st paragraph comment

Answer: The sampling frequency will be moved to Table 1.

Referee interesting references for discussing long-term measurements of aerosol ionic composition.

Answer: We were aware of these papers but did not include them in the previous version because we decided to give only a selection here, i.e., an overview paper (Putaud et al., 2004) and two exemplary papers showing either only averages or just one component (Malm et al., 2002, and Malm et al., 2004), but not to summarize all papers presenting only one component or those that are not easily comparable to the results presented in this paper. In the updated version an extended selection of the papers will be added. An explicit reasoning on all papers pointed by the reviewer is given below.

Fischer et al., 2007: This paper presents results from a site at 1500 m and on a season

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averaging time. It presents a clear seasonal cycle for every component with minima in winter and maxima in summer. The concentrations of this site are quite comparable to the ones at the Jungfraujoch. This will be mentioned in the revised version.

Husain et al., 2004: This paper presents long-term measurements of sulfate at Whiteface Mountain. In the previous version of the manuscript the paper of Malm et al., 2002 was mentioned as an overview of sulfate trends in the US. In the updated version the paper of Husain et al., 2004 will be added as a mountain site with a seasonal cycle comparable to the Jungfraujoch.

Schwab et al., 2004: This paper presents results from sites below 600 m that are not comparable to JFJ. It will therefore not be included.

Malmet al., 2004: This paper is already mentioned in the manuscript as an example of the annual averages.

Referee 2nd paragraph comments

Answer: As explained previously Lugauer et al. (1998, 2000) published an analysis on the influence of aerosol transport at the Jungfraujoch. They showed that the vertical aerosol transport by thermally driven convection, mainly acting between late spring and late summer, was found to be the dominant transport process. For the winter period this process is less important and the Jungfraujoch is mainly located in the undisturbed free troposphere. As a consequence, the concentrations in the PBL are enhanced in winter, mainly due to this reduced vertical transport.

Later, Gehrig and Buchmann, (2003) presented an overview of seasonal variation of aerosol concentrations in Switzerland. They also showed that in Switzerland the concentrations in PM are higher in winter than in summer due to less efficient vertical dilution. This seasonal variation of this vertical transport results in the observed lower concentrations in winter at the Jungfraujoch.

Referee comments on seasonal cycle effects.

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Answer: The authors agree on the fact that photochemistry is enhanced in summer. However, in Switzerland the concentrations of SO2 are higher in winter than in summer (Fisseha et al., 2006; Hueglin et al., 2005). In combination with enhanced photochemistry in summer, the resulting sulfate is quite constant over the year (Hueglin et al., 2005). Thus the higher concentrations at the Jungfraujoch in summer are mainly due to vertical transport. This will be mentioned in the revised version.

Referee: Please provide specific numbers in the text.

Answer: The data will be included in the EMEP data base (http://www.nilu.no/projects/ccc/create/database.htm) (this will be mentioned also in the revised version) and will be available shortly; therefore we decided not to present this additional information here.

Referee comment on how the aerosol composition varies with upwind source region.

Answer: Trajectories were studied for Saharan dust episodes by Collaud Coen et al. (2004). For all other periods this is planned for a future study, using sophisticated models to understand the trends.

Referee: 3rd Paragraph comments

Answer: Long-term trends analyses were performed by two different methods. First the trends were calculated by the seasonal Mann-Kendall test associated with the Sen's slope estimator applied to each month of the year, so that the trend for each months (or season if desired) can be estimated. The yearly trends are meaningful only if the monthly trends are homogeneous in sign and amplitude. The seasonal Mann-Kendall test is a non-parametric test, which allows missing values as well as ties in values or in time, so that difference in sampling rate causes no difficulties for this test. Secondly, the long-term trends were also calculated by a least mean square fit on the monthly means, taken into account a constant term, a slope and the seasonality. For this test, no particular treatments were applied to the missing values. We did not estimate the

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trends with monthly means weighted by the number of data taken during the month, but the absence of statistical significance in both the unweighted least-mean square fit and in the Mann-Kendall test indicates that no statistical significant trends exist for the main chemical compounds. All these methods have been extensively described and referenced in Collaud Coen et al. (2007).

Referee: 3.3 Aerosol neutralization comments

Answer: This analysis was done and showed no influence of the wind direction. Concerning the influence of the season, the graph will be colored for the different months in the revised version. It shows that the high scatter for the low concentrations corresponds to the winter period where Jungfraujoch is in the free troposphere.

Referee: More work should be done to understand why the campaigns were so dramatically different (March 2004 versus Feb-March 2005).

Answer: We made a footprint analysis for the two periods (this will be included in the revised manuscript). This analysis shows how much time the trajectories spent close to the surface (below 1000 m above ground level). We find that for 2004 there was a larger contribution from the South especially also from Spain and Algeria, while for 2005 there was a relatively larger contribution from the North. This could be an indication for enhanced fine mode mineral dust in 2004, which would explain this high unexplained fraction; however, we do not have the possibility to investigate this further.

Referee comment on rigorous methods to determine aerosol acidity.

Answer: The authors agree and this will be mentioned in the revised version.

Referee 3.4 Chemical mass balance for PM1 and the coarse mode Last paragraph comments.

Answer: See above.

Anonymous Referee #2

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Referee: Abstract: p. 12146, line 14.

Answer: The sentence will be reworded "while calcium and nitrate were the only two measured components contributing to the coarse mode".

Referee: p. 12147. line 3.

Answer: This will be changed.

Referee: p. 12147, line 6-7.

Answer: This will be changed.

Referee: p. 12147, line 15.

Answer: This part just summarizes the different ways of producing SO2. No distinction is done in these measurements between SO2 from anthropogenic emissions and SO2 derived from DMS. However, the Jungfraujoch site is quite far from the sea and thus not strongly influenced by SO2 from DMS emissions. Therefore sulfate at the Jungfraujoch is assumed to be mainly anthropogenic.

Referee: p. 12148, line 23.

Answer: This will be changed.

Referee: p. 12149, line 12.

Answer: The reference of the WMO/GAW Aerosol Measurement procedures guidelines and recommendations (September 2003) (WMO TD No. 1178) will be added.

Referee: p. 12149, line 25.

Answer: The contribution of dust or HULIS was estimated for the relevant wavelength (630 nm) and showed that both do not significantly influence the BC measurements. The only occasion for which dust may influence the BC measurements is during intensive Saharan dust episodes. This will be added in the revised manuscript.

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Referee: p. 12150, line 9 and 10.

Answer: Absorption coefficients have been measured by a MAAP (given in units of inverse meters) and have also been intercompared with other absorption instruments such as the PSAP and the Aethalometer (Cozic et al., 2006). The mass absorption efficiency is defined as the absorption coefficient normalized by the BC mass concentration and is given in units of m2/g. It is determined by the slope in Figure 1. We agree that BC and EC are not identical, and the relationship needs to be determined for each specific site. This is exactly why we determined this mass absorption efficiency. This is perfectly in line with the recommendation of the Scientific Advisor Group for Aerosol, stating that BC concentration from absorption measurements should only be given if a site specific mass absorption efficiency has been determined by simultaneous absorption and EC measurements (GAW, 2003, p17).

Referee: p. 12151, paragraph 1.

Answer: In addition to the CH4 calibration the instrument was as well calibrated for the prevailing ambient pressure. The sampling and gas analysis flows were also calibrated on site and sucrose calibrations were performed in the lab.

Referee: p. 12151, line 27.

Answer: This will be changed.

Referee: p. 12152, line 1.

Answer: This will be changed.

Referee: p. 12152, line 2.

Answer: This will be changed.

Referee: p. 12152, line 8.

Answer: No organics are measured behind this inlet.

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Referee: p. 12152, line 11.

Answer: This will be changed.

Referee: p. 12152, line 12.

Answer: This was indeed unclear, because more specific information was only given further below. The information that gaseous nitric acid is expected to be lost to the stainless steel inlet line and is thus not sampled on the Nylon filter will be moved to this section for clarification.

Referee: p. 12152, line 19.

Answer: It means less than 0.1 particles per "pied cube" for particles below 0.1 um. It is the norm ISO 14644-1where this clean room is ISO-1. This is a standard nomenclature and will not be included into the manuscript.

Referee: p. 12152, line 26.

Answer: Yes, and it will be changed.

Referee: p. 12152, line 29.

Answer: This will be changed as well.

Referee: p. 12153, line 4.

Answer: This will be changed.

Referee: p. 12153, line 14.

Answer: This will be changed.

Referee: p. 12154, line 2.

Answer: This will be changed.

Referee: p. 12154.

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Answer: The AMS size and flow calibration was performed at the JFJ at the start of the experiments and the response of the instrument was regularly calibrated using ammonium nitrate aerosol in situ at the site. Hence, the data are shown as mass concentrations at ambient temperature and pressure, and the size calibration was correct for the pressure at the JFJ.

Referee: p. 12155, line 5.

Answer: We agree.

Referee: p. 12156, line 16.

Answer: This was tested and we found that both dust and HULIS did not contribute much to the absorption measurements at this wavelength (630nm). Dust only influences the absorption during strong mineral dust episodes. This will be mentioned; see also our answer to the comment by referee 1.

Referee: p. 12156, line 19.

Answer: This will be changed.

Referee: p. 12156, line 21.

Answer: This will be changed.

Referee: p. 12157, line 6.

Answer: A reference will be included in the revised manuscript.

Referee: p. 12157, line 10.

Answer: Yes, the coating should be greater in summer than in winter due to more emissions and photochemistry. This is indeed expected to result in a higher mass absorption efficiency (which is normalized to the EC mass concentration), as seen in Figure 1. However, the concentration of BC is much higher in summer (due to enhanced vertical transport, see above), such that also the absorption coefficient has

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a strong maximum in summer (Collaud Coen et al., 2007).

Referee: p. 12157, line 15. Be

Answer: The main differences are due to the fact that: a) Lavanchy et al. used a 2-step thermal method which did not correct for potential pyrolysis, and b) the Aethalometer data were not corrected for scattering effects. This will be mentioned in the revised version.

Referee: p. 12157. line 25.

Answer: Filters sampled both TSP and PM1 as explained in section 2.5. Here, the sulfate of PM1 was compared to the AMS. This will be mentioned in the new version.

Referee: p. 12128.

Answer: The AMS and the Sunset Laboratory instrument are very different techniques, one is an offline method of slow thermal ramping to volatilize the OC while the other one uses rapid flash vaporization under vacuum. This should not prevent a comparison however. Comparing two very different methods is instructive as there is no operationally definition of OC available. The AMS heater temperature was set to 550°C and the fragmentation tables were set appropriately. Yes, the Sunset analyzer was sampling behind the TSP inlet and it was assumed that most of the OC is found in the submicrometer range. This comparison was supported by the sulfate data, where typically less than 20% of sulfate was in the coarse mode, even though there are sources for the coarse mode sulpsate (like gypsum from mineral dust).

Referee: p. 12159, line 2.

Answer: According to our answer above we believe that this error is within the uncertainty of the instrument.

Referee: p. 12159, line 8-9.

Answer: See above.

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Referee: p. 12159, line 9.

Answer: As explained in the text the same coefficient was used for winter and summer since no AMS comparison could be performed during summer. We agree that a measured value would be better, however we do not have this. Still we believe that the winter value is a better estimate than the use of any value stated somewhere for some other site in the literature. The conversion factor is mainly defined by the degree of oxidation of the organic carbon. The degree of oxidation is linked to the variability of the corresponding compound. As we have aged aerosol both in winter and summer at the Jungfraujoch, we believe that the uncertainty here is still within the combined uncertainty of the instruments (estimated to be 20%).

Referee: p. 12159, line 27.

Answer: More simultaneous SMPS data were available. The density estimated from the comparison of the SMPS mass and betameter mass was compared with the one estimated from the AMS composition in winter and was found to be 1.5 g cm-3.

Referee: p. 12160, line 9 to 15.

Answer: We never said that we expect this correlation.

Referee: p. 12160, line 24-25.

Answer: The paper by Sirois and Barrie, (1999) will be included into the manuscript to present long term measurements of the major inorganic component at a remote site. Concerning the other papers of Len Barrie most of the papers published in Arctic are not really comparable since they are focused on BC long term measurements, polychlorinated biphenyls, organochlorine pesticides, radionuclides, polycyclic aromatic hydrocarbons, heavy metal or on short campaigns.

Referee: p. 12161, line 17.

Answer: This paper will be included in the revised manuscript.

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Referee: p. 12161, line 21 to 23.

Answer: Here we refer to the fact that we have a limited data set rather than to the fact that a periodicity is masked.

Referee: p. 12162, line 9.

Answer: We agree that the aerosol is slightly acidic; however we would like to stress the point that by far the major fraction of sulfate is present as ammonium sulfate. In addition, we expect diffusion to be efficient since the particles are mostly liquid, based on HTDMA measurements (Weingartner et al., 2002 and Sjogren et al., 2007).

Referee: p. 12163, line 6.

Answer: It is justified as the particle size distribution of the accumulation mode is fairly constant as shown by Weingartner et al., 1999. This will be stated in the revised version.

Referee: p. 12163, line 25 to 27.

Answer: The referee appears to have misunderstanding this point. The two Saharan dust events have clearly a high non-determined fraction.

Referee: p. 12164, line 1.

Answer: This will be changed.

Referee: p. 12164, line 18.

Answer: we will change the sentence accordingly.

Referee: p. 12165, line 2-3.

Answer: New back-trajectories were made such that this text will change.

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