Atmos. Chem. Phys. Discuss., 7, S4431–S4436, 2007
www.atmos-chem-phys-discuss.net/7/S4431/2007/

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.

Anonymous Referee #1

Received and published: 29 August 2007

Reviewer Comments MS-NR: acpd-2007-0298 Title: Chemical composition of free tropospheric aerosol for PM1 and coarse mode at the high alpine site Jungfraujoch Author(s): J. Cozic, and CLACE members

Overall Comments The paper presents data from a long term aerosol measurement campaign at Jungfraujoch. The paper does not represent a significant advancement to the field of aerosol research, but it does present data from a very interesting location. There are relatively few mountain sites where such measurements are made routinely. As currently written this paper does not increase our understanding of aerosol chemistry and processing, it only broadens the record of aerosol measurements in the lower

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

free troposphere. These measurements are labor intensive and of high quality. They deserve to be presented alongside a more comprehensive analysis. Specific suggestions to improve the analysis are provided by section.

2.1 Jungfraujoch Station First paragraph: How does cloud cover vary seasonally? How does cloud cover vary interannually, i.e. how representative is the Baltensperger et al. (1997) study to the years covered by this particular measurement campaign? How does cloud cover in the winter (freezing fog) change aerosol concentrations? Freezing fog / riming may reduce aerosol lifetimes and thus measured concentrations. Have there been any studies which have documented the deposition of aerosols in rime ice at this station?

Second paragraph: Is there a seasonal shift in the prevailing winds at this site? The authors loosely attribute the strong seasonal cycle in aerosol parameters only to local scale meteorology which causes injections from the planetary boundary layer to reach the site during warm summer afternoons. It would be appropriate to be more thorough here. Are there any local estimates of boundary layer heights for this region? Local sounding data? Other factors play into the seasonal cycle of the aerosol components, most notably changes in photochemistry (SO2 oxidation) and changes in emissions (NH3 and biogenic emissions are highly temperature dependent). If this information is included in other references, please highlight that here.

2.2 Inlet

How does the inlet cut-off size vary with wind speed? What percentage of the time are wind speeds above 20 m/s?

2.5 Chemical composition of aerosol filter samples

Specific detection limits for each species should be listed. They can vary substantially by component due to impurities in the filters.

Table 1: Add a column to include the frequency of each type of measurement, eg.

Every six days for chemical composition measurements.

3.1.1 Determination of the mass absorption efficiency

2nd paragraph: Why was reduced major axis regression not used for the data? How does the use of this type of regression change the results? See the following reference:

Ayers, G.P. (2001), Comment on regression analysis of air quality data, Atmospheric Environment, 35, 13 pp. 2423-2425.

3.2 Long-term chemical composition

1st paragraph: Information on sampling should be moved forward to methods section. Here are some other references of interest discussing long-term measurements of aerosol ionic composition. The first reference should be an especially useful comparison paper, since it discusses aerosol composition measurements at the highest site in eastern North America. The second two papers refer to long-term measurements at Whiteface Mountain in NY. Composition at this site has been well documented and many other papers are available.

Fischer, E.V., L. D. Ziemba, R. W. Talbot, J. E. Dibb, R. J. Griffin, L. Husain, and A. N. Grant (2007), Aerosol major ion record at Mount Washington, J. Geophys. Res., 112, D02303, doi:10.1029/2006JD007253.

Husain, L., P. P. Parekh, V. A. Dutkiewicz, A. R. Khan, K. Yang, and K. Swami (2004), Long-term trends in atmospheric concentrations of sulfate, total sulfur, and trace elements in the northeastern United States, J. Geophys. Res., 109, D18305, doi:10.1029/2004JD004877.

Schwab, J. J., and K. L. Demerjian (2004), Aerosol chemical composition in New York state from integrated filter samples: Urban/rural and seasonal contrasts, J. Geophys. Res., 109, D16S05, doi:10.1029/ 2003JD004078.

Perhaps also of interest: Malm, W. C., B. A. Schichtel, M. L. Pitchford, L. L.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

Ashbaugh, and R. A. Eldred (2004), Spatial and monthly trends in speciated fine particle concentration in the United States, J. Geophys. Res., 109, D03306, doi:10.1029/2003JD003739

2nd paragraph: How do aerosol concentrations and composition vary in the boundary layer air that is lofted to the Jungfraujoch site? Is(Are) there an appropriate reference(s) for lower elevations surrounding the site? How do the concentrations at Jungfraujoch compare with lower elevation sites? Is the seasonal cycle amplified at Jungfraujoch?

The authors must recognize that the seasonal cycle of the main ionic constituents (sulfate, nitrate, ammonium) is the product of changes in photochemistry and emissions. This paragraph implies that the seasonal cycle is only a product of meteorological conditions, which is likely incorrect. The sulfate seasonal cycle is a result of higher rates of summertime oxidation of sulfur dioxide to sulfate by photochemical intermediates such as the hydroxyl radical and aqueous-phase conversion by hydrogen peroxide and ozone. Ammonia emissions are highly temperature dependent, so emissions vary seasonally with a summer and springtime maximum corresponding to fertilizer applications. For general references on sulfate oxidation see: Kunen, S. M., A. L. Lazrus, G. L. Kok, and B. G. Heikes (1983), Aqueous oxidation of SO2 by hydrogen peroxide, J. Geophys. Res., 88, 3671-3674. and

Botha, C. F., J. Hahn, J. J. Pienaar, and R. Van Eldick (1994), Kinetics and mechanism of the oxidation of sulfur (IV) by ozone in aqueous solutions, Atmos. Environ., 20, 3207-3212.

Please provide specific numbers in the text. It is difficult to read values off Figure 6. For example, give the max TSP concentration for 2003. It would be best to provide a summary table along with Figure 6 that includes each species and the standard summary statistics (mean, median, max, std dev, det limit).

The authors should provide more information on how the aerosol composition varies with upwind source region. A more extensive analysis using HYSPLIT trajectories for each sample would be a fairly straightforward way to do this. This may provide some information on the interannual variability in the major constituents. Synoptic scale motions likely have a substantial impact on the aerosol composition at this site. If similar work has been done previously, the authors should cite it.

3rd Paragraph: How were trends calculated? Monthly? Seasonally? Annually? Or using Daily averages? Did sampling frequency of aerosol chemical composition change during the intensive campaigns, or were samples still taken only every 6 days? Were there any months missing any aerosol samples? Or were 5 samples available for every month? How was missing data handled if there were any?

3.3 Aerosol neutralization This section requires substantial further analysis. Figure 7 should be broken down in 2 ways: by season and by wind direction. Variations in aerosol neutralization may result from differences in the ratio of SO2 to NH3 emissions in various upwind sectors. Examining the relationship between the major anions (sulfate and nitrate) and the major cation (ammonium) in this way should provide information on factors impacting neutralization.

More work should be done to understand why the campaigns were so dramatically different (March 2004 versus Feb-March 2005). Were there substantially different flow regimes present during the two years? The authors should attempt to understand if there actually were any differences in the vertical air motion. Was there more subsidence in 2005? Does this correlate with large-scale weather patterns? If more subsidence was present, this should be reflected in the humidity measurements at the site.

The authors should also recognize that there are rigorous methods to determine aerosol acidity and state that these more rigorous methods were not used because additional necessary measurements were not made during the campaign. Methods to determine acidity are discussed here:

Keene, W. C., A. A. P. Pszenny, J. R. Maben, E. Stevenson, and A. Wall (2004), Closure evaluation of size-resolved aerosol pH in the New England coastal atmosphere during summer, J. Geophys. Res., 109, D23307, doi:10.1029/2004JD004801.

3.4 Chemical mass balance for PM1 and the coarse mode Last paragraph: The PM1 pie charts presented in Figure 11 are very different for the March 2004 and March 2005 campaigns. Again why? How did the meteorology differ during these two sampling campaigns? This is a big question, but certainly worth understanding.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 12145, 2007.