

Interactive comment on “Cloud chemistry at the Puy de Dôme: variability and relationships with environmental factors” by A. Marinoni et al.

Anonymous Referee #2

Received and published: 1 April 2004

Review of Marinoni et al for Atmospheric Chemistry and Physics (ACP)

MS-NR: 2003-si05-67 Title: Cloud chemistry at the Puy de Dôme: variability and relationships with environmental factors Authors: A. Marinoni, P. Laj, K. Sellegri, and G. Mailhot

General Comments: The authors present an interesting paper on detailed cloud chemistry measurements at the Puy de Dome (PDD). There are few data available in the literature such as the ones presented here and the paper is a valuable addition to the literature. It is clearly written, well-referenced and, for the most part, has suitable figures and tables illustrating the main points.

I do, however, have some comments and criticisms that I would like to see the authors address before the paper is accepted into ACP. Most notably, much of the analysis

Full Screen / Esc

Print Version

Interactive Discussion

Discussion Paper

follows from table 3, yet this table includes averages of all the sample collections and some simple statistics on percentiles for each measured ion. However, the 78 samples were taken during only 16 cloud events. The authors state that there is little variation of cloud liquid water content or composition during each event, which leads me to believe that the 78 samples cannot be used as independent variables. Rather each event should be taken as independent and averages of samples within each run used. Not doing this will severely skew the statistics.

Secondly, the authors refer to the data set as a climatology, this is really stretching the point. The data are from 16 events between Feb and May spread between 2 years. How can this represent a climatology, especially as the SpE events (except for one) dominate the average?

Specific Comments: 853 The description of the site on page 853 is somewhat misleading. The authors state that the PDD is in the free troposphere during the winter months but clouds were often observed during this period. Does this mean that the cloud events were free tropospheric or is the general picture misleading? As the individual events are not really detailed it is difficult to establish in what conditions the samples were taken.

854 table 1 and 2: These tables hide several details. For example can the authors state the times, are all the samples day or night time samples. Which of the samples are supercooled, which are warm? Which periods are BG, ANT or SpE? Which are free tropospheric and can you identify sources of polluted especially during the SpEs?

line 17 How did you ensure that the clouds were non precipitating?

Line 24 Does the collector cut off vary in supercooled cloud conditions as ice builds on the collection plate?

855 line 2: So the collector dimensions are the same, not different

line 13-14 I agree with referee 1 a summary of aerosol collection, storage and sampling

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

is necessary here

857 table 3 is dominated by a few special events, the mean is not really a valid number, in nearly every case the mean is greater than the 75th percentile. It would be better to plot the median. Further no information on the differences of the various species between the different classifications BG, ANT and SpE.

It appears strange that many of the species have a sample size of 15, suggesting that they are all taken from the same 15 samples. Yet some of these species have minima that are below the detection limit.

Line 10: I fail to see how the authors can justify using a sample set of 78 samples and base their analyses on statistics based on the total number of samples and then make the statement that "no significant variation in solute concentration is observed amongst samples of the same event". The bias in the data set is then heavily skewed to only 3 events. The samples are therefore NOT independent. When trying to present overall statistically climatologies it is very important to ensure that there is no bias. I would prefer to see averaging the samples over each event, or as referee 1 suggests in each class (if the classes are listed in table 1 and 2 this will be easy to see) and presenting their median and range. It will then be possible to get a true flavour for the variability.

858 line 20-28 I get no feeling for how variable the composition is. How variable are the ratios of the different components in the cloud water?

859 line 3-4 The efficient oxidation of reduced nitrogen makes the nitrate a key substance? Do you mean oxidation of reduced nitrogen or oxidation of NO_x?

Line 13 needs rewriting, it does not scan correctly

Line 17 The authors must support the contention that there is significant ammonia in the lower free troposphere during winter. Can the events be due to upwelling air from the valley. How have the authors established whether the air is descending or uplifted?

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Not just climatologically but in the particular case studies they provide data for.

861 line 7: Figures 3 does not show the contribution CA makes to DOC as far as I can see.

Line 13: Facchini et al measured the monoacid fraction of the water soluble carbon, the authors measured the organic acid ions in cloud water, this may only be a subset of the Facchini measurements.

862 first few lines: The authors don't know the gas phase availability of the organic fraction. Suppose that the organic acids arise principally from within the particles that are heterogeneously nucleated, whereas significant nitric acid and sulphur dioxide are present in the gas phase of polluted air masses, which partition into the cloud water rapidly. This could potentially cause the inorganic ion concentrations to increase but not affect the organic ion content.

Line 17: table 5. Presumably table 5 uses all the data points as independent variables also. I wonder if the ratios are as robust if the different case studies are averaged and then compared, so if one case study runs through day and night then take the day and night time average and use these two numbers for each case.

864 line 18 Strictly the equation should include the density of water

line 24: I cannot see how (i) can explain a systematic difference, the differences due to such an effect are likely to be random aren't they?

865 lines 11-15 This is only the ionic fraction of the carboxylic acids. The authors cannot rule out further carboxylic acid in the aerosol that are dissolved but not ionic.

867 line 11: I really do question the use of the word climatology. Whilst I realise that such measurements are very time consuming to make and large data sets are therefore hard to come by. There are only 16 separate cloud runs taken between Feb and May. I do not see how this can be classed as a climatology.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)

Line 12: Were all these types classified in the free troposphere? There is no evidence for this presented. If this is a conclusion the authors have to demonstrate that the site is in the free troposphere during all these events.

Line 18 insert high before altitude sites

Line 23: this conclusion has not been shown anywhere in the paper.

868 line 8-9 I do not recall any analysis of air mass history in the data set presented. This statement needs to be supported in the paper.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 849, 2004.

[Full Screen / Esc](#)[Print Version](#)[Interactive Discussion](#)[Discussion Paper](#)