**Atmospheric
Chemistry
and Physics**
Discussions

Interactive comment on "Classification of clouds sampled at the puy de Dôme (France) from 10 yr monitoring: mean features of their physico-chemical properties" *by* L. Deguillaume et al.

L. Deguillaume et al.

L.Deguillaume@opgc.univ-bpclermont.fr

General comments

The authors present the results of 10 years of measurements of chemical concentrations (including inorganic and some organic species) and supporting physical quantities made at puy de Dôme. The data are valuable and should be published.

We would like to thank the reviewer for the pertinent remarks. We hope that our re-

vised manuscript will satisfy the comments and corrections that were highlighted by the reviewer. In the revised manuscript, all the corrections are indicated by the red colour.

Detailed comments

1. Between the abstract and conclusions, the paper reads like a good scientific publication. However, the conclusions and the abstract are devoid of the many results discussed in the paper. Instead there is some speculative discussion and opinion. I don't understand what the authors intend here, but the abstract and conclusions need to be made consistent with the rest of the paper.

We agree with your general comment about the abstract and the conclusion. Consequently, we modify these two parts of the paper to be more consistent with the rest of the paper.

2. Abstract – line 12 – I can't find a discussion of "standard chemical scenarios" anywhere in the text. What do you mean by this, and how do you justify such a term in the abstract without any discussion elsewhere in the paper?

We modified this sentence in order to clarify this point. The new sentence is: "This dataset provides concentration ranges of main inorganic and organic compounds for modeling purposes on multiphase cloud chemistry".

3. Page 4, line 17 – why only "degradation" and not production?

Yes, we agree with this comment. We replaced "degradation" by "transformation".

4. Page 5, line 5 and lines 15-16 – "natural background site" implies a site that measures air free of local and regional anthropogenic influences. You demonstrate that is not the case for pdD. The same reasoning applies to the reference to of using these measurements as a benchmark for "natural free tropospheric conditions". How do you derive such conditions from your dataset?

The use of the term "free tropospheric conditions" is not adapted to the puy de Dôme

description. We apologize for this error. For this reason, we modify the text to avoid any confusion. In the text, we explained that the puy de Dôme station is impacted by the regional atmospheric background during the day and that it is more representative of larger synoptic-scale air masses during night-time.

The term "natural background site" is also replaced. We describe the puy de Dôme moutain as "a high altitude site that can generally be classified as rural". Therefore, this site can be impacted by regional anthropogenic influences.

5. Page 6, lines 8-13 – how is the liquid or ice transferred from the impaction plate?

The water was transferred with a sterile pipette directly into a glass vial just after the collection if the sample is liquid. If the sample is frozen, the water is transferred into a glass vial after a short melting period at room temperature. This is now indicated in the text for more clarity.

6. Page 6, lines 20-24 – how were the LWC and the TOC calibrated?

The instruments that measure the LWC and the TOC are calibrated. This is now indicated in the manuscript.

- The Gerber PVM-100 probe that allows measuring the LWC is calibrated. A spinning optical disk scatters the direct laser beam into the receiver optics and is used for calibration (see for more details: Hovenac, E. A., Dan Hirleman, E.: Use of Rotating Pinholes and Reticles for Calibration of Cloud Droplet Instrumentation. J. Atmos. Oceanic Technol., 8, 166–171, 1991.).

- Potassium hydrogen phthalate and sodium carbonate aqueous solutions were used in order to calibrate the instrument for the total carbon content (TC) and the inorganic carbon content (IC). The concentration ranges were between 2 and 30 mgC L-1. After that, TOC quantification was obtained by the difference between measured TC and IC.

7. Page 9, lines 19-22 – How are these criteria used to "further" classify cloud events, when they are derived from the PCA analysis already used to classify the events? Also,

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I don't understand the context of the mention of the 57 samples. Presumably the values in Table 1 are from the 138, and so what is the purpose of the discussion of the other 57?

The PCA analysis was performed on 138 samples of cloud water using the most discriminating variables between different groups : pH and Na^+, Cl^-, NO_3^-, NH_4^+ and SO_4^{2-} concentrations. Only 138 samples over the whole data set present values for at least 5 of the 6 selected variables. If more than one of the variables among these 6 variables are not given, the samples is not considered in the statistical analysis (* see below for more details). Based on this analysis, mean, maximum and mininum values for these 6 variables are then calculated for the 4 categories (see Table 1). These values are then used as "criteria" to classify the cloud samples that have been not considered in the statistical analysis. Back-trajectories are also considered for the classification of the remaining cloud samples.

We are aware that this was not clearly explained in the manuscript. Therefore, we modify the text as following: " For each cluster, mean, maximal and minimal values of the variables used for the statistical analysis were calculated; these values are used as criteria to classify cloud events that have not been considered in the PCA analysis. These criteria are summarized in Table 1".

* A very important problem in applications of PCA, such as multivariate statistical process control applications, is the estimation of scores when the observation vector has missing data. Simca's approach to score calculations for such incomplete observations are based on methods described in :

Nelson, P.R.C., Taylor, P.A., MacGregor, J.F.: Missing data methods in PCA and PLS: Score calculations with incomplete observation, Chemometrics and Intelligent Laboratory Systems, 35, 45-65, 1996. These methods perform reasonable well with moderate amounts of missing data (up to 20% of the measurements). In our study, only 1 missing value at most is permitted that should minimize errors.

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8. Page 13, lines 5-6 – add N2O5 to the bracketed trace gases. Also "concentration" on line 6 should be concentrations.

Yes, N2O5 is also important and should be mentioned. These two corrections are considered in the new manuscript. The reference from Leaitch et al. (1988) was also added to illustrate the contribution of gaseous N2O5 to HNO3 in cloud.

Leaitch, W. R., Bottenheim, J. W., and Strapp, J. W.: Possible contribution of N2O5 scavenging to HNO3 observed in winter stratiform cloud, Journal of Geophysical Research, 93, 12569-12584, 10.1029/JD093iD10p12569.

9. Page 13, lines 8-9 – I assume that you mean something to the effect that "The relatively high correlations suggest that the contributions to the ammonium, nitrate and sulfate ion concentrations are larger from nucleation scavenging than from gas scavenging." Perhaps, but what about the relative contributions seen in the dry aerosol at pdD over the years; e.g. does it show that much more NH4NO3 in polluted air during the daytime? Nitrate is frequently and in many places evident in higher concentrations in cloud water samples relative to sulphate than in dry aerosol samples. That argues for a predominantly gas-phase source (HNO3 in the daytime; N2O5 in the night-time), and HNO3 can also be correlated to sulphate.

In the previous publication from Sellegri et al. (2003), the behavior of several key atmospheric compounds (mainly inorganic species: sulfate, nitrate, ammonium, etc.) was followed at the puy de Dôme using complementary sampling inlets, in the interstitial, residual and liquid phases of the multiphase cloud system.

By this way, they provided a quantification of phase partitioning of several inorganic and organic species. For sulfate, they showed that half was transferred to the liquid phase by nucleation scavenging and that half originated from the gaseous SO2 dissolution. HNO3/NO3- also mainly lied in the liquid phase in equilibrium with the prediction of Henry's law; about 50% of the liquid phase NO3- evaporates back to the gas phase, indicating that at least this fraction of the liquid NO3- originates from dissolved gaseous

HNO3. The contribution of dissolved HNO3 to the concentration of the droplets should be higher than these 50%, as a clear NO3- enrichment of the residual aerosol phase is observed relative to SO42- and NH4+, compared to the interstitial aerosols. They concluded that in-cloud gas-to-particle transfer of HNO3 possibly plays a key role in aerosol acidification. For ammonium, a large fraction (around 70%) lies in the interstitial gaseous phase and only half of liquid NH4+ originates from the gas phase. This leads to a clear deviation from Henry's law equilibrium and to the subsaturation of the liquid phase, presumably due to mass transfer limitation. Particulate ammonium does not compensate for dissolved NH3 to reach equilibrium. Gaseous NH3, which seems to be in higher concentrations than in other high altitude sites, therefore plays a key role in neutralizing cloud droplets at puy de Dôme.

To summarize, this study shows that the aerosol particle contributes to half of the chemical composition (sulfate, nitrate, ammonium) of the cloud droplets, the other part resulting from the dissolution of gaseous precursors. This was confirmed by numerical simulations by Leriche et al. (2007) that showed also an important contributions of the gas phase in the aqueous concentrations of nitrate, sulfate and ammonium. Moreover, the relative contributions of the gas phase in the aqueous concentration of nitrate is not much more important than the one for sulfate (gas phase dissolution of SO2 followed by its aqueous oxidation). We can therefore argue that nitrate, sulfate and ammonium are correlated because of the significant contribution of the particulate phase for all of these compounds but also because the gas phase contributions are similar for these 3 species.

References (already cited in the manuscript):

Leriche, M., Curier, R., Deguillaume, L., Caro, D., Sellegri, K., and Chaumerliac, N.: Numerical quantification of sources and phase partitioning of chemical species in cloud: application to wintertime anthropogenic air masses at the puy de Dôme station, Journal of Atmospheric Chemistry, 57, 281-297, 2007.

Sellegri, K., Laj, P., Marinoni, A., Dupuy, R., Legrand, M., and Preunkert, S.: Contribution of gaseous and particulate species to droplet solute composition at the puy de Dôme, France, Atmospheric Chemistry and Physics, 3, 1509-1522, 10.5194/acp-3-1509-2003, 2003.

10. Page 14, lines 1-3 – The statement "for most of the values reported elsewhere in the world" is incorrect. See Leaitch et al. (JGR, 1986 and JGR, 1988), and there are other more recent observations that also show increased nitrate in cloud water relative to sulphate.

We agree with your comment. The text was corrected to avoid any confusions and the following references have been added to illustrate the increase of nitrate in cloud water relative to sulphate:

Brüggemann, E., Gnauk, T., Mertes, S., Acker, K., Auel, R., Wieprecht, W., Möller, D., Collett Jr., J.L., Chang, H., Galgon, D., Chemnitzer, R., Rüd, C., Junek, R., Wiedensohler, A., and Herrmann, H.: Schmücke hillcap cloud and valley stations aerosol characterisation during FEBUKO (I): Particle size distribution, mass, and main components, Atmospheric Environment, 39(23-24), 4291-4303, 2005.

Hayden, K. L., Macdonald, A. M., Gong, W., Toom-Sauntry, D., Anlauf, K. G., Leithead, A., Li, S. M., Leaitch, W. R., and Noone, K.: Cloud processing of nitrate, Journal of Geophysical Research-Atmosphere, 113, D18201, 10.1029/2007JD009732, 2008.

Hill, K. A., Shepson, P. B., Galdavy, E. S., Anastasio, C., Kourtev, P. S., Konopka, A., and Stirm, B. H.: Processing of atmospheric nitrogen by clouds above forest environment, Journal of Geophysical Research, 112, D11301, 1029/2006JD008002, 2007.

Leaitch, W. R., Strapp, J. W., Wiebe, H. A., Anlauf, K. G., and Issac, G. A.: Chemical and microphysical studies of nonprecipitating summer clouds in Ontario, Canada, Journal of Geophysical Research, 91(D11), 11821-11831, 10.1029/JD091iD11p11821, 1986.

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Lee, A. K. Y., Hayden, K. L., Herckes, P., Leaitch, W. R., Liggio, J., Macdonald, A. M., and Abbatt, J. P. D.: Characterization of aerosol and cloud water at a mountain site during WACS 2010: secondary organic aerosol formation through oxidative cloud processing, Atmospheric Chemistry and Physics, 12, 7103-7116, 10.5194/acp-12-7103-2012, 2012.

Page 14, lines 10-14 – Also, see Leaitch et al. JGR 1986 for another discussion of calcium in cloud water samples.

In the publication from Leaitch et al. (1986), they highlighted that cloud water samples with the highest concentrations of Ca^{2+} and Mg^{2+} were generally those with the highest SO_4^{2-} and NO_3^- concentration. They suggested that the Ca^{2+} and/or Mg^{2+} may have been present as nitrate salt ($CaNO_3$, $MgNO_3$) or sulfate salt ($MgSO_4$, $CaSO_4$), associated with giant-sized particles. The presence of these salts was a possible explanation for the excess NO_3^- and SO_4^{2-} measured in their samples.

For our dataset, the correlation coefficient R between Ca^{2+} (or Mg^{2+}) and NO_3^- and SO_4^{2-} can be determined for the continental and the polluted categories: (Continental air masses: $R(Ca^{2+}/NO_3^-) = 0.38$; $R(Mg^{2+}/NO_3^-) = 0.25$; $R(Ca^{2+}/SO_4^{2-}) = 0.03$; $R(Mg^{2+}/SO_4^{2-}) = 0.36$; polluted air masses: $R(Ca^{2+}/NO_3^-) = 0.47$; $R(Mg^{2+}/NO_3^-) = 0.78$; $R(Ca^{2+}/SO_4^{2-}) = 0.67$; $R(Mg^{2+}/SO_4^{2-}) = 0.54$)).

To our opinion, these compounds are not enough correlated for the continental air masses and seems to show some correlations for the polluted air masses. So, we cannot clearly conclude on the presence of these salts (nitrate salt ($CaNO_3$, $MgNO_3$) or sulfate salt ($MgSO_4$, $CaSO_4$)) in our samples. The possible sources of Ca^{2+} and Mg^{2+} should be discussed in another work where you need to combine both the chemical composition of the aqueous phase and the aerosol composition. However, we add in the new manuscript a sentence where we propose a potential source of nitrate salt ($CaNO_3$, $MgNO_3$) or sulfate salt ($MgSO_4$, $CaSO_4$) for the polluted air masses:

" For polluted air masses, it is possible that the Ca^{2+} and/or Mg^{2+} may have been

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present as nitrate salts (CaNO3, MgNO3) (R(Ca2+/NO3-) = 0.47; R(Mg2+/NO3-) = 0.78) or sulfate salts (CaSO4, MgSO4) (R(Ca2+/SO42-) = 0.67; R(Mg2+/SO42-) = 0.54) as suggested by Leaitch et al. (1986)."

11. Page 15, lines 12-14 – replace "On the opposite" with "In contrast, the polluted air masses exhibit much higher concentrations of nitrate in the cloud water and the cloud water samples in highly marine air are characterized by relatively high levels of chloride and sodium." (assuming that is what you mean).

We agree that this sentence was unclear. We replaced it by the sentence you wrote above.

12. Page 15, line 22 – in the context of air mass, what do you mean by origins?

We apologize for this error. We replace "origins" by "categories".

13. Page 15, lines 23-24 – how do you know they are acids and not salts?

In aqueous solutions, depending on their pKa, all the studied carboxylic acids can also be present as carboxylate anions (i.e., salts) where the carboxyl group is deprotonated. The analytical method (ion chromatography) allows to quantify the total concentration of the measured carboxylic acids (the acids + the anions). Regarding the pKa of the selected carboxylic acids and the pH of our cloud samples, these compounds are mainly present as carboxylate anions.

14. Page 16, lines 7-9 – A reference for this statement: Sorooshian, A., et al. (2006), Oxalic acid in clear and cloudy atmospheres: Analysis of data from International Consortium for Atmospheric Research on Transport and Transformation 2004, J. Geophys. Res., 111, D23S45, 10.1029/2005JD006880.

This reference has been added in the manuscript to illustrate our statement on the oxalic acid compound.

15. Page 18, lines 13-15 – Li S.-M., A. M. Macdonald, A. Leithead, W. R. Leaitch, W.

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Gong, K. G. Anlauf, D. Toom-Sauntry, K. Hayden, J. Bottenheim, D. Wang (2008), Investigation of carbonyls in cloudwater during ICARTT, J. Geophys. Res., 113, D17206, doi:10.1029/2007JD009364.

We forgot to refer to this interesting work on the quantification of carbonyls in cloud water by airborne measurements. This publication is now cited in the revised version of the manuscript.

16. Since you are characterizing bulk samples of cloud water, there should be some discussion of the potential differences of cloud water chemistry for different sizes of droplets within a cloud. For example, your continental and marine clouds may contain more sulfate in smaller droplets and more sodium in larger droplets, whereas nitrate may cover a broader range of droplet sizes if it comes from the gas phase. You reference work by Moore et al for example, which is one source you could draw on for this.

As the measurements were only bulk, we refrain from speculating on a size dependency of the chemical concentrations. This point would need further investigations and could be addressed in future work.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 22795, 2013.