

Interactive comment on « Seasonal variations in aerosol particle composition at the puy-de-Dôme research station » by E .J.Freney

Anonymous Referee #2

We are grateful for the valuable comments received from Anonymous Referee #2. **Reviewers comments (RC) are in bold.** The authors comment (AC) are in plain text. Please refer to the attached document “Supplementary figures” for the newly added figures.

This paper analyses the seasonal variation of aerosol chemical composition at an elevated site in central Europe. The focus of the analysis is on organic compounds, their ageing, and their relation to major inorganic compounds in different types of air masses and at different seasons. The analysis is scientifically sound and sufficiently original to be published in Atmospheric Chemistry and Physics. I have a few, mostly minor, suggestions for improvements

RC 2.1: The authors should mention in the text why they did not have any measurements from the spring season. Having springtime data would have completed the analysis in a nice way

AC: Measurements were carried out only during the periods mentioned in the paper: Autumn (September to October 2008), Winter (February to March 2009), and Summer (June 2010). Unfortunately there were no additional intensive sampling periods.

RC 2.2: Throughout the paper, statistical relations between different variable are described in a very loose way. It is incorrect to state that two variables correlate “to some extent” or “reasonably”. In some places of the text, it is written that a variable correlates with another one. Sure, even a non-existent correlation is a correlation.

AC: Additional text has been included.

Original text: Page 27151 Line 9: During the autumn, SV-OOA particles contributed 25 % to the total organic aerosol mass spectra, and correlates well with that of with reference mass spectra for SV-OOA ($r^2 = 0.81$) (Fig. 3) and to some extent with the time-series of BC ($r^2 = 0.33$)

Updated text: During the autumn, SV-OOA particles contributed 25 % to the total organic aerosol mass spectra, and correlates well with that of with reference mass spectra for SV-OOA ($r^2 = 0.81$) (Fig. 3), and with the time-series of BC ($r^2 = 0.12$).

Original text: Page 27148 Line 23: During the autumn, winter, and summer campaigns the NH_4 shows reasonable correlations with NO_3 ($r^2 = 0.67, 0.97, \text{ and } 0.32$, respectively) and SO_4 ($r^2 = 0.68, 0.85, \text{ and } 0.78$, respectively). The organic aerosol species are generally correlated with the inorganic species during the autumn (average r^2 with $\text{SO}_4, \text{NO}_3, \text{ and } \text{NH}_4 = 0.55$), and winter (average r^2 with $\text{SO}_4, \text{NO}_3, \text{ and } \text{NH}_4 = 0.62$), however during the summer these r^2 correlations decreased to approximately 0.15 for NH_4 and SO_4 and to <0.01 for NO_3 bearing particles because of the high contributions of organic aerosol particles to the submicron mass.

Updated text: During the autumn, winter, and summer campaigns the NH_4 shows correlations with NO_3 ($r^2 = 0.67, 0.97, \text{ and } 0.32$, respectively) and SO_4 ($r^2 = 0.68, 0.85, \text{ and } 0.78$, respectively). The organic aerosol species are correlated with the inorganic species during the autumn (average r^2 with $\text{SO}_4, \text{NO}_3, \text{ and } \text{NH}_4$ is 0.55), and winter (average r^2 with $\text{SO}_4, \text{NO}_3, \text{ and } \text{NH}_4$ is 0.62), however, during the summer these r^2 correlations decreased to approximately 0.15 for NH_4 and SO_4 and to <0.01 for

NO₃ bearing particles because of the high contributions of organic aerosol particles to the submicron mass.

RC 2.3: Finally, the authors have not reported whether observed correlations are statistically significant or not. The authors should check out the statistics and be more careful how they express the results of the statistical analysis.

AC: Additional text has been added discussing the significance of the different correlations.

Additional text:

Given the sample size for each experiment, any r^2 values greater than 0.1 are considered statistically relevant (The critical value for r^2 is 0.021, with a significance level of 0.001).

The strong correlations ($r^2 > 0.65$) among the inorganic species during the autumn, winter, and summer suggests that the inorganic species are mostly internally mixed. However, the lower correlation between organic and inorganic species suggests that some fraction of the organic species remain externally mixed.

RC2.4: Page 27143, line 13: Was the lower size limit of the SMPS really 50 nm? If yes, some reasoning for such a narrow size range measured by the SMPS should be given.

AC: The lower size limit measured by the SMPS is 10 nm using a long DMA, with the optimal size range between 20 and 800 nm. The text has been updated and corrected.

Original text: Page 27143, line 13: Particle size distributions between 50 and 300 nm were measured using a scanning mobility particle sizer (SMPS).

Updated text: Particle size distributions between 20 and 800 nm were measured using a scanning mobility particle sizer (SMPS).

RC2.5: It seems strange that the AMS description (section 2.3.1) is a subsection of the description of LIDAR and temperature measurements (section 2.3), not a subsection of its own in section 2.

AC: The LIDAR and temperature measurements have now been separated into two different sections.

Updated text: The heading of the ToF-AMS has been changed from 2.3.1 to 2.4. The heading of each of the other sections have been adjusted accordingly.

RC2.6: Page 27145: The authors mention that the procedure of calculating the AMS collection efficiency (CE) is similar to that in Middlebrook et al., (2011). Do they mean that their procedure is exactly the same, or have they adopted some kind of modification to that introduced by Middlebrook et al.

AC: Yes, our procedure of calculating the AMS collection efficiency was different. I added text in order to make this clear.

Original text: Page 27145 Line: 14. Middlebrook et al. (2011) illustrated, using a series of equations, how a composition dependent CE can be applied to particle mass concentrations. In this study, a similar composition dependent CE is applied to the data. When ammonium nitrate mass concentrations contribute less than 0.25 to the total aerosol particle mass a CE of 0.5 is used. As the

fraction of ammonium nitrate increases to a maximum of 0.78 (Pure NH_4NO_3) the applied CE approaches 1.

Updated text: Middlebrook et al, 2011, illustrated, using a series of equations, how a composition dependent CE can be applied to particle mass concentrations. Middlebrook et al., 2011 uses a constant CE of 0.45 for an ammonium nitrate mass fraction (ANMF) ≤ 0.4 and a linear CE increase up to 1 for ANMF > 0.4 . In this study, a similar composition dependent CE is applied to the data.

$$\text{CE}_{\text{DRY}} = \max(0.5, 0.264 + 0.943 \times \text{ANMF})$$

in which a constant CE of 0.5 is used for ANMF ≤ 0.25 and a linear CE increase up to 1 for ANMF > 0.25 . More details of this CE will be described in Nemitz et al., (2012). Since the majority of aerosol particles arriving at the pdD site are thought to be internally mixed, this composition dependent CE was applied to all species sampled by the AMS. In order to assess how accurate our chosen CE was at quantifying the mass of aerosol particles in the atmosphere, we compared the total volume of aerosol particles sampled by the AMS and BC with that sampled by a SMPS. The AMS volume was calculated by dividing the mass concentrations of organic and inorganic species by their respective densities (1.72 g m^{-3} for SO_4 , NH_4 , NO_3 , and 1.2 g m^{-3} for organics).

RC2.7: Page 27148, line 23: What is meant by neutralized air masses? That the collected particle-phase was roughly neutral? Please be more specific.

AC 5: Additional text is included.

Original text: The air masses were always neutralized

Updated text: During these measurements, ion balance is achieved for NH_4^+ , NO_3^- , and SO_4^{2-} , if NO_3^- is assumed to be from NH_4NO_3 , and SO_4^{2-} is assumed to be from $(\text{NH}_4)_2\text{SO}_4$. This is illustrated in Fig. S4 where the plot of the measured NH_4 vs predicted NH_4 falls along the 1:1 line. This shows that aerosol particles measured by the AMS are fully neutralised by ammonium and there are no acidic aerosol particles.

RC2.8: Page 27149: The last sentence of section 3.1 is vague and does not properly describe the results of the analysis presented later on. I suggest that the authors remove this sentence away altogether.

AC: We agree with the reviewer. This sentence has been removed.

Original text removed: “This might indicate different origins like biogenic precursors for secondary organic aerosols versus anthropogenic precursors for the inorganic components.”