

## ***Interactive comment on “Rural continental aerosol properties and processes observed during the Hohenpeissenberg Aerosol Characterization Experiment (HAZE2002)” by N. Hock et al.***

### **Anonymous Referee #1**

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This manuscript examines aerosol properties and processes at a rural location in Southern Germany. Results from a suite of aerosol and gas phase measurements are reported. Main points discussed include PM<sub>1</sub> composition, OM to OC ratio, gas-particle partitioning of NH<sub>4</sub>NO<sub>3</sub>, HOA and OOA, organic aerosol processing, and nucleation. These results are new, interesting, and fit to the scope of ACP. Listed below are four major comments followed by the detailed comments that I have on this manuscript:

1) The abstract is a bit too long and lack of focus, I suggest rewriting. Also, is the R<sub>2</sub> of OM<sub>1</sub> vs. PM<sub>1</sub> determined after averaging over long time periods (as shown in Fig 2d)?

If so, it is more appropriate to report the R2 using the recorded AMS data. It may also be helpful to make it clear that this study was done at a rural site impacted significantly by urban-emissions.

2) How valid is the estimate of 30% biomaterial in PM2.5? Colorimetric methods tend to suffer from matrix effect. Was such effect evaluated for protein quantification in this paper? Secondly, as the protein measurements were done to the filter samples, they actually represent PM2.5. It is important to clearly state this point in the text as well as in the figure caption of Fig 9 that the protein data were for PM2.5. It is also a question what fraction of the detected protein in PM2.5 is associated with PM1. Primary biogenic aerosols tend to be more enriched in larger particles, meaning that the submicron aerosols seen by the AMS may contain only a small fraction of the detected protein. This possibility needs to be discussed in this paper (e.g. page 8635). I suggest the discussions on the paragraph in page 8635 - 8634 to be revised. What's the use of this ratio of proteins to OM1 of 8% if a large fraction of protein is possibly in particles in the size range of 1 - 2.5 micron? Most importantly, the second last sentence of the paragraph (line 7-9, page 8636) is vague and just not supported by this analysis. What's the basis of stating "primary biogenic particles are likely to be detected as OOA by the AMS"? If this statement is based on mass spectral pattern, it will be useful to show a spectrum of primary biogenic particles and compare it to the ambient OOA mass spectra reported in the literatures.

3) The section on HOA and OOA needs revisions. First of all there is a typo on the title, replace "line" with "like". Second, m/z 44 and 57 are only the rough representations of OOA and HOA. At rural locations, a major fraction of m/z 57 can be oxygenated, unlike in cities where m/z 57 detected is mostly C4H9+. Third, is there a reason that the OOA and HOA analysis results are not presented in this paper although section 3.4.1 takes the title of oxygenated organic aerosols and hydrocarbon like organic aerosols? Presenting the OOA and HOA analysis results could improve the discussions. Finally, the claim that "A highly oxidized aerosol can be an indicator  $\checkmark$  for aerosols formed

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from oxidized biogenic precursors” needs references.

4) The section 3.5 on new particle formation needs major revision. I do not think the data supports the claim of new particle formation or nucleation. It is more appropriate to say those were particle growth events. There is just not enough data in this paper to discuss the mechanism of new particle formation, neither is there enough evidence to suggest that ternary H<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O-NH<sub>3</sub> mechanism was responsible. Also, was N<sub>3</sub>-14 determined by taking the differences between the two CPC measurements? If so, say it in the text. How were the SMPS data of different size ranges merged? When were they both available? Fig. 12 and 13 do not show SMPS data below 8 nm. Fig 1 suggests the occurrence of quite a few particle growth events. What's the reason that the May 18 and 21 events were discussed when SMPS data for particles smaller than 8 nm don't seem available? The authors could focus on discussing the growth mechanism of particles and include relevant analyses like those done by Zhang et al., 2005 and Allan et al., 2006.

Specific comments:

The size of Fig 1 can be increased to make it more readable. I also suggest the dates in all the figures be shown in regular formats as done for fig 12 and 13.

Line 10, page 8633, it is appropriate to cite Zhang et al. 2005a and Alfarra et al. 2004 at here.

Line 15, page 8633, replace “be” with “by”

Line 17-19, page 8633, revise this sentence. Clarify the meaning of “high oxidized aerosol can be an indicator for processed, aged aerosol”. What kind of indicator? Are there references for the statement “(highly oxidized aerosol can be indicator) for aerosol formed from oxidized biogenic precursors”?

Line 8-10, page 8634, is this sentence meant to point out the fact that the sizes of m/z 18 and 44 are equal in the HAZE mass spectra shown in Figure 8? This is not

surprising as the  $m/z$  18 signal is set to be the same size as  $m/z$  44 in organic aerosol mass spectra by default (Allan et al., 2004)

Discussions in Page 8634, are there any measure of the photochemical age of the air mass from Po Valley detected during this study? It can be useful to repeat at here that BT analysis indicate air mass traveled from Po Valley 18 -48 hours ago.

Last sentences, page 8634, need to provide support for the statement that the site is strongly influences by local biogenic emissions.

How important was biomass burning during this study? Were there measurements of tracers/markers for biomass burning? The average mass spectra (Fig. 8) show hints of enhanced  $m/z$  60, which could indicate the presence of biomass burning OA. Has this possibility investigated?

Line 25, page 8635, it will be helpful to give references for the statement of “the relative abundance of proteins in biomass is typically on the order of  $\sim 10\%$ ”.

Line 13, page 8636, using the phrase “highly time resolved” is inappropriate. Those filter samples had time resolution on the order of hours.

Line 21, page 8636, it will be helpful to point out the VOC precursors of sabinic and ketolimonic acids.

Line 5, page 8637, what’s the concentration of nitrogen oxides?

Line 7, page 8638, revert the order of “small” and “diameter”.

References:

Allan, J.D., A.E. Delia, H. Coe, K.N. Bower, M.R. Alfarra, J.L. Jimenez, A.M. Middlebrook, F. Drewnick, T.B. Onasch, M.R. Canagaratna, J.T. Jayne, and D.R. Worsnop, A generalised method for the extraction of chemically resolved mass spectra from Aerodyne aerosol mass spectrometer data, *Journal of Aerosol Science*, 35 (7), 909-922, doi: 10.1016/j.jaerosci.2004.02.007, 2004

Zhang, Q., C.O. Stanier, M.R. Canagaratna, J.T. Jayne, D.R. Worsnop, S.N. Pandis, and J.L. Jimenez, Insights into the chemistry of new particle formation and growth events in Pittsburgh based on Aerosol Mass Spectrometry, *Environmental Science & Technology*, 38 (18), 4797-4809, 2004.

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