

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

**N. Hock et al.**

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Reply to Referee 1

By Johannes Schneider and Ulrich Pöschl (on behalf of all co-authors)

First of all we thank Referee 1 for the thorough review, constructive criticism, and generally positive evaluation of our paper. The comments and suggestions are highly appreciated and will be taken into account upon revision of the manuscript. Answers to individual major comments (cited in italics) are given below.

### **Abstract**

*The abstract is a bit too long and lack of focus, I suggest rewriting.*

We will consider this and try to improve the abstract upon revision.

*Also, is the R2 of OM1 vs. PM1 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.*

Answer: The  $r^2$  of OM1 vs. PM1 was determined after averaging as shown in Fig 2d, since we added EC2.5 to the AMS data to obtain PM1. Using the time resolution of the AMS data (and then without EC2.5), we obtain an  $r^2$  of 0.89. This differs not significantly from the  $r^2$  value of 0.90 that we obtain after averaging. We will mention that in the revised version. We do not agree that the site was significantly impacted by urban emissions. Our data suggest that urban emissions were less important, although the measurement site is only about 60 km south-west off Munich, but the prevailing wind directions were westerly.

*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?*

Answer:

As pointed out in our manuscript, we consider the value of 30% as a “first-order estimate subject to high uncertainties” (p. 8635, l. 27). The determination of proteins by the applied methods can indeed be influenced by interferences with other sample components, As mentioned in our manuscript and detailed in the referenced literature (Franze, 2004; Franze et al., 2005; Fehrenbach, 2006). Therefore, we stated (p. 8623, l. 9) that "The reported values have to be considered as equivalent concentrations which approximate the actual protein content of the samples but may be influenced by related macromolecular substances - e.g., humic or humic-like substances, respectively". In this study, we have had no opportunity to check the measurement results with alternative methods. Accordingly, we pointed out that further analyses will be required

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to corroborate the findings. Nevertheless, we are confident that the presented results are realistic. Other recent studies using different techniques have indicated similarly high abundances of proteins and primary biological particles in air particulate matter (Jaenicke, 2005; Pöschl, 2005; Elbert et al., 2006; Fehrenbach, 2006; Despres et al., 2007; and references therein).

*Secondly, as the protein measurements were done to the filter samples, they actually represent PM<sub>2.5</sub>. 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 PM<sub>2.5</sub>. It is also a question what fraction of the detected protein in PM<sub>2.5</sub> is associated with PM<sub>1</sub>. 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 OM<sub>1</sub> of 8% if a large fraction of protein is possibly in particles in the size range of 1 - 2.5 micron?*

Answer:

We will clarify this aspect in the revised manuscript ("Fig 9: PAHs and proteins in PM<sub>2.5</sub>:..."). The relatively small differences between PM<sub>2.5</sub> and PM<sub>1</sub> (< 10%, estimated from the size distributions, Fig. 4), the close correlation between OM<sub>1</sub> and proteins measured in PM<sub>2.5</sub> (Fig. 9b), and the additional finding that the proteins are better correlated with OM<sub>1</sub> than with the difference between PM<sub>2.5</sub> and PM<sub>1</sub> indicate that a large fraction of the detected proteins reside in PM<sub>1</sub>. Nevertheless, we agree that the plot of the protein/OM<sub>1</sub> ratio may be misleading and will omit it in the revised manuscript.

*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*

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*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.*

Answer:

We will remove this statement, which is indeed only an assumption so far. Laboratory test experiments are planned but have not yet been performed.

*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.*

Answer:

The reason that the OOA/HOA analysis as developed and published by Qi Zhang et al. (EST 2005, ACP 2005) was not included in this work is that at the time of writing of this paper there was another paper pending publication where the HOA/OOA analysis of the HAZE data is used, namely Qi Zhang et al., "Ubiquity and Dominance of Oxygenated Species in Organic Aerosols in Anthropogenically - Influenced Northern Hemisphere Midlatitudes", GRL, 2007. Now this paper is published, and we can show the results from the HOA/OOA analysis and give reference to the Zhang et al.-paper.

*Finally, the claim that “A highly oxidized aerosol can be an indicator for processed, aged aerosol, but also for aerosol formed from oxidized biogenic precursors.” needs references.*

Answer:

The data obtained at the free tropospheric site (Jungfraujoch, Panel c) of Fig. 8) show that aged, processed aerosol is highly oxidized, while measurements at smog cham-

bers (e.g., Bahreini et al., EST 2005) show that SOA produced by oxidation of biogenic precursor is oxidized, too. These studies will be referenced accordingly. Furthermore, it is not unexpected that SOA produced by oxidation of biogenic precursor is oxidized: Upon reaction of monoterpenes with OH or ozone, partial oxidation of the hydrocarbon is initiated. This frequently proceeds via ring opening reactions (Atkinson, 1997), thus producing two functional groups. Reactions occur quite rapidly, often the lifetime is less than an hour (Atkinson, 1997). Partially oxidized products still are generally very reactive versus OH radicals and ozone (in case of remaining double bonds). Thus, after biogenic emission reactive monoterpenes are expected to be oxidized and partly decomposed due to rapid photochemistry within hours. The resulting products are oxygenated hydrocarbons that end up in the aerosol phase, and thus, aerosol formed from such precursors will produce mass spectra showing typical OOA signatures.

*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>3-14</sub> 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.*

Answer:

Here we do not agree with the referee. We think that our findings do very well support the conclusion that new particle formation events were observed: We used the particle

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number concentration between 3 nm and 14 nm ( $N_{3-14}$ ) to identify nucleation events. This quantity was obtained by subtracting the number concentrations measured by two CN counters with different cut-offs (this was stated on page 8621, line 16-18). This is a very common quantity that is widely used to identify nucleation (see review article by Kulmala et al., *J. Aerosol Sci.*, 2004). We selected these two nucleation events because the  $N_{3-14}$  values were highest during these events (see figure 1). The SMPS data were recorded using the "long DMA" (size range 7-300 nm) between May 16 and May 23 and using the "nano-DMA" (3-65 nm) between May 24 and May 31. Of course it was unfortunate that the "nano-DMA" was used only in the second half of the campaign where the particle formation events were less pronounced. However, we think that  $N_{3-14}$  is well suited to identify nucleation events.

Regarding the conclusion that ternary nucleation is the most likely explanation to explain the observations, we repeat the argumentation that we already used in the reply to referee 2:

Our measurement results are in good agreement with the detailed particle formation study of Birmili et al (ACP, 2003). At the same location they found similar H<sub>2</sub>SO<sub>4</sub> concentrations and similar particle formation rates (about  $1 \text{ cm}^{-3}\text{s}^{-1}$ ), and they obtained fair agreement with ternary nucleation rate calculations but no indications for the involvement of oxidized organic compounds in new particle formation. Ammonia was unfortunately not measured but certainly present in the gas phase, because of high agricultural activity in the surrounding rural area.

As outlined in our manuscript, the observed nucleation events can be explained by ternary nucleation. We cannot rule out that organic species were involved, but, as stated by Kulmala et al., *J. Aerosol Sci.*, (2004): "Organic vapours could, in principle, participate in nucleation, but nucleation mechanisms that involve organics have not yet been identified". On the other hand, our results do indicate that organics have played an important role in the growth of newly formed particles, because the increase of particulate organics during the observed particle growth phases was similar to that of

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inorganics (sulfate and nitrate; Fig. 13). These aspects will be further clarified in the revised manuscript. Moreover, we will include a comparison with other observations of nucleation/growth events as reported by Zhang et al., EST, 2005 (Pittsburgh data) and Allan et al., ACP, 2006 (Quest, Finland), pointing out the differences in atmospheric conditions. Note, however, that neither of these studies included gas-phase H<sub>2</sub>SO<sub>4</sub> measurements.

Specific comments:

We will consider these comments upon revision of our manuscript.

### References (in addition to those included in the original discussion paper)

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