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Atmospheric Chemistry and Physics Discussions

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

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Reply to Referee 2

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

First of all we thank Referee 2 for the thorough review, constructive criticism, and 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 comments (cited in italics) are given below.

OM/OC-ratio

In order to investigate the OM/OC ratio during this study, the authors compare the OM

measured by AMS on submicron aerosol to the OC determined on PM2.5 samples. The authors should clarify in detail which are the assumptions required to make significant the comparison of different fraction of the suspended particulate matter; they should also estimate the relative error for the OM/OC ratio reported.

Answer:

Indeed, a comparison of submicron aerosol and PM2.5 measurements has to be done and interpreted cautiously. Accordingly, we have clearly specified the involved size ranges throughout our manuscript, and we will clarify this aspect further upon revision. On the other hand, the relations appear to be fairly straightforward in this study, because the mass size distributions (3 examples are displayed in Figure 3) measured with an optical particle counter (300 nm to 9 μm) indicated that only a small fraction of PM2.5 mass resides in the size range of 1-2.5 μm (<= 10 %). We clarify this aspect in the revised manuscript, and we will add a discussion of the relative error for the reported OM/OC ratios.

Source of organics

As concern the source of oxidized organic aerosol, the conclusions are not consistent with the results and discussion section. Paragraph 3.4.1 points out that highly oxidized organic aerosol might be an indicator of aged aerosol or biogenic emissions. In the same paragraph the authors claim that the aerosol in the Hohenpeissenberg area was dominated by local biogenic emissions (page 8634), as shown by the AMS fragmentation pattern. In the conclusion paragraph the oxidized organics are then attributed to photochemically aged aerosol.

Answer:

Photochemical transformation of biogenic aerosol precursors like terpenes usually proceeds very fast (on a timescale of a few hours). What we intended to say is that the measurement site was not influenced by fresh anthropogenic emissions but mainly by

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local biogenic emissions which were processed in the atmosphere and ended up in the aerosol phase. We will make this point clearer.

Nucleation:

The assessment of ternary nucleation seems weak. Is this the only possible explanation? What evidence rules out organics in new particle formation? Is the measured value nucleation or growth?

Answer:

Our measurement results are in good agreement with the detailed particle formation study of Birmili et al. (2003). At the same location they found similar H2SO4 concentrations and similar particle formation rates (about 1 cm-3s-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. In our study the particle formation rate was inferred from the number concentration of fine particles between 3 and 14 nm (difference of two CN counters with different cut-offs), which is the same approach as taken by Birmili et al. (2003). During the observed particle formation events, the increase of ultrafine particle number concentration (3-14 nm) was following an increase of gas-phase H2SO4 concentration with the typical time lag needed for nucleated particles to grow into the size range > 3 nm (about 1 - 2 hours, see Figures 12 and 13). 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.

The authors should consider the findings of other groups, especially in more urban influenced areas (see McMurry on St. Louis, Pandis on Pittsburgh, Russell on Boston, or even O'Dowd on Ireland).

Answer:

A detailed comparison with urban studies from the North-Eastern US reporting very high sulfate concentrations and binary H2SO4/H2O nucleation (e.g. Pittsburgh, Zhang et al., EST, 2004) would go beyond the scope of our paper, which is focused on rural aerosol properties and processes in central Europe. The nucleation events observed by O'Dowd et al. in Ireland (Nature, 2002) were attributed to iodine species emitted from the sea, which are not likely to play an important role at Hohenpeissenberg. Nevertheless, we will add references upon revision of our manuscript and point out the differences in the atmospheric conditions triggering the nucleation events.

Citation of previous work

The paper shares a major weakness of several similar papers that it cites primarily AMS literature and fails to acknowledge earlier findings on OM/OC, preferential scavenging, organic aging and sources. Since these are presented as major new findings of this work, the failure to cite the precedents is a serious flaw that reflects poorly on otherwise interesting work, and poorly on a journal that would publish it without proper referencing.

Answer:

The observed OM/OC ratios are one of many measurement results reported in our paper, and we had not intended to present them as "major new findings". Since our study was not focused and we are not specialized on the investigation of OM/OC ratios, we have indeed not given a comprehensive literature overview on this aspect. In the re-

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vised manuscript we will include several additional references (Bae et al., Atmospheric Environment, 2006; El-Zanan et al., Chemosphere, 2005; Yu et al., Atmospheric Environment, 2005; Gelencser, 2004; Seinfeld and Pandis, 1998) and we would be happy to include more, if the referee could name other specific references that should be cited.

The other points raised by referee 2 will be taken into account upon revision of our manuscript.

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

Bae, M.-S., K. L. Demerjian, and J. J. Schwab, Seasonal estimation of organic mass to organic carbon in PM2.5 at rural and urban locations in New York state, Atmospheric Environment, 40, 7467 - 7479, 2006.

El-Zanan, H. S., D. H. Lowenthal, B. Zielinska, J. C. Chow, and N. Kumar, Determination of the organic aerosol mass to organic carbon ratio in IMPROVE samples, Chemosphere, 60, 485-496, 2005.

Gelencser, A., Carbonaceous Aerosol, Springer, Dordrecht, 2004

O'Dowd, C. D., J. L. Jimenez, R. Bahreini, R. C. Flagan, J. H. Seinfeld, K. Hämeri, L. Pirjola, M. Kulmala, S. G. Jennings, and T. Hoffmann, Marine aerosol formation from biogenic iodine emissions, Nature, 417, 632 - 636, 2002.

Yu, L. E., M. L. Shulman, R. Kopperud, and L. M. Hildemann, Fine organic aerosols collected in a humid, rural location (Great Smoky Mountains, Tennessee, USA): Chemical and temporal characteristics, Atmospheric Environment, 39, 6037 - 6050, 2005.

Interactive comment on Atmos. Chem. Phys. Discuss., 7, 8617, 2007.