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Atmospheric Chemistry and Physics Discussions

Interactive comment on “Polar organic compounds in rural $PM_{2.5}$ aerosols from K-puszta, Hungary, during a 2003 summer field campaign: sources and diurnal variations” *by* A. C. Ion et al.

A. C. Ion et al.

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We would like to thank this reviewer for the time and effort spent in evaluating our paper. The comments have been helpful and have improved the paper.

Reviewer: Additional remarks: Cavalho et al (2003) (already cited in the reference list) showed a clear size dependency for mannitol and malic acid. Whereas malic acid was observed mainly on particles smaller than 1 micrometer, mannitol had a significant amount even in the coarse fraction $>$ 2.5 micrometer (about 50% in the size range 2.1-4.2 micrometer at the German site). The work discussed here deals only with PM2.5, although 2.5-10 micrometer particles were also sampled. Particle swelling due to a

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higher humidity in night-time may shift the cut point towards smaller particles and may also contribute to lower night-time concentrations of mannitol in PM2.5. Another recent study (Yu et al., 2005) found some differences in day and nighttime samples (PM2.1 of rural aerosol) for e.g. malic acid and succinic acid. The concentration profiles were strongly influenced by the global meteorological situation.

Response: The results on the mannitol size distributions reported by Carvalho et al. (2003) were already discussed in the original manuscript. The data on malic acid size distributions by these authors have been included in the revised manuscript (section 3.1): “Similar results were obtained for arabitol, mannitol, and malic acid for size-fractionated aerosols collected at a rural (meadow) site in Melpitz, Germany; in contrast, arabitol and mannitol were found to be mainly associated with the fine size mode for aerosols collected at a boreal forest site, Hyytiälä, Finland (Carvalho et al., 2003).”

We agree that particle swelling due to a higher humidity during night-time may shift the cut point towards smaller particles and may also contribute to lower night-time concentrations of mannitol (and arabitol) in PM2.5. This explanation has been added in the revised manuscript (section 3.2): “Furthermore, hygroscopic particle growth due to a higher relative humidity during night-time (Table 1) may shift some of the smaller particles that contain mannitol and arabitol to the coarse size fraction during night.”

With regard to the recent study by (Yu et al., 2005), we noted that malic acid could only be detected in 9 (out of 42 collected) day-time samples and in 2 (out of 10 collected) night-time samples and that the meteorological conditions were very different from those of our study, so that a comparison with these data is not very relevant.

Reviewer: Section 2.1: I missed some data on the meteorological situation (global transport, rain, humidity and temperature).

Response: Data on the meteorological situation have now been given in the revised manuscript. A new section has been added to Experimental section:

“2.2 Meteorological data and ozone Standard meteorological data (i.e., temperature, wind speed and direction, relative humidity (RH), and amount of precipitation) and ozone concentrations were measured by the Hungarian Meteorological Service with 1-hour time resolution. Mean values of the day-time and night-time averaged and maximum data for the period 4 June through 1 July, during which separate day and night samples were collected, are given in Table 1. For precipitation, total data for day-time and night-time of that period are reported. Overall, the campaign can be characterized by stable meteorological conditions. The weather was especially warm and dry. Notable rainfall was only observed during the nights of 9, 15, 16, 28, and 29 June and 3 July (more than 80 mm in each case).”

Reviewer: How was the WSOC determined?

Response: see our response to the comments made by reviewer #1.

Reviewer: Section 2.2, page 1869 line 5: Calibration curves were build using a standard mixture. What concentration range was covered by the calibration, was the response linear, what was the limit of determination/quantification?

Response: For this, we refer to a previous study that is explicitly mentioned in the revised version, i.e., Pashynska et al. (2002). Briefly, the concentration ranges always covered the concentrations determined, and the responses were linear. The limits of determination/quantification were not determined since sensitivity was not a critical issue.

Reviewer: Section 2.2, page 1869 line 14: Does the excellent precision of about 10% include the extraction and derivatisation step?

Response: Yes, the precision of about 10% was achieved including extraction and derivatization; again, we refer to our previous method development study by Pashynska et al. (2002). The main reason why this high precision is achieved is that two internal recovery standards (methyl xylanopyranoside and D3 malic acid) are added to the samples which are structurally related to the analytes and automatically correct for all analyte losses during sample workup, including the derivatization step. The principles of this methodology have been thoroughly discussed in our old paper: M. Claeys, S. P. Markey and W. Maenhaut: Variance analysis of error in selected ion monitoring assays using various internal standards. A practical study case, Biomed. Mass Spectrom., 4, 122 128 (1977).

Reviewer: Section 3.1, page 1870 line 4-8: The recovery rates $>$65 to 72% were determined by spiking blank filters, and “are expected to be higher for real samples due to carrier effects” - are there any data on spiked loaded filters?

Response: For this, we refer to previous work by Zdráhal et al. (2002) who reported data on spiked loaded filters, i.e., for the polar compound, 1,2,3-trihydroxyhexane, which was used as recovery standard for levoglucosan (no internal recovery standard was used in the latter work so that precise recovery data were required for the determination of the concentrations). While the recovery rate for spiked blank filters was 65%, the recovery rate for spiked loaded filters was 73%. In the present work, we do not require precise recovery rate data because the two internal recovery standards (methyl xylanopyranoside and D3 malic acid), added to the samples and structurally related to the analytes, automatically correct for all analyte losses during sample workup.

Reviewer: Table 2: N=63 for all samples, but day-time and night-time samples are 27+28=55?

Response: At the end of the campaign, eight 24-hour samples were collected which makes the total 55+8=63.

Reviewer: Additional literature data which should be worked in: Yu et al., Environ. Sci. Technol., 39, 707-715, 2005.

Response: This reference has been cited where appropriate in the revised version, but, as already pointed out above, not in regard with diel differences of malic acid because of the limited data.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 1863, 2005.