

Determination of selected organic species in PM_{2.5} aerosol from a summer field campaign at K-puszt, Hungary

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In an earlier study (Ion et al., 2005), we reported on a number of polar organic compounds, including photo-oxidation products of isoprene, levoglucosan, malic acid and sugar alcohols, which were measured by gas chromatography/mass spectrometry (GC/MS) for PM_{2.5} aerosol collected during a 2003 summer field campaign at the forested site of K-puszt, Hungary. In 2006 a follow-up summer field campaign was conducted, whereby a total of 68 high-volume PM_{2.5} samples (again typically separate day-time and night-time samples) were collected. Whereas it was very hot and dry during the entire 2003 campaign, the 2006 campaign was characterized by two distinct periods, with the first half of the campaign unusually cold and the second half warm; besides, the air masses often originated over the North Sea and/or the Atlantic Ocean during the cold period, whereas during the warm period they had a continental character and were more stagnant (Maenhaut et al., 2008).

The samples from the 2006 campaign were analysed for organic and elemental carbon (OC and EC) with a thermal-optical method, using a NIOSH-like protocol (Birch and Cary, 1996). Water-soluble organic carbon (WSOC) was determined as described by Viana et al. (2006). Methanesulphonate, oxalate, malonate and succinate were measured by ion chromatography (IC) (Maenhaut et al., 2011). Fifteen organic acids (e.g., 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), *cis*-pinonic, *cis*-pinic, terebic, terpenylic) and 5 nitrooxy organosulphates (OSs) were determined by liquid chromatography/MS (LC/MS), as described by Gómez-González et al. (2012). All concentration data for the actual samples were corrected for field blanks.

Whereas the polar organic compounds accounted for 1.2% of the OC during both day-time and night-time in the 2003 campaign, the 4 IC organic compounds accounted for 2.5% of the OC during both day-time and night-time of the cold period of the 2006 campaign; during the warm period their contribution was somewhat larger (i.e., 3.1%). For the 20 LC/MS compounds, the contribution to the OC was 1.5% during both day-time and night-time of the cold period and 2.0% during the warm period. Of the LC/MS compounds, MBTCA and *cis*-pinonic, *cis*-pinic and terpenylic acid were the major contributors to the OC.

For a number of LC/MS compounds strong day/night differences were noted, especially during the warm period, with concentrations that were up to a factor of 10 higher during the night-time than during the day-time. This was the case for *cis*-pinic, terpenylic, homo-

terpenylic, and especially caric acid (see Figure 1); this is explained by transfer from the vapour to the particulate phase for these compounds during the cool night. A strong day/night difference was also seen for the OSs (not shown); enhanced night-time levels for these OSs were also observed at sites in Brasschaat and Hamme in Belgium (Gómez-González et al., 2012; Kahnt et al., 2013).

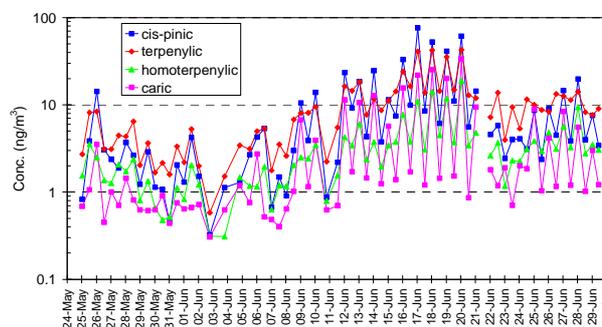


Figure 1. Concentration of 4 monoterpene marker compounds in the individual samples.

As a consequence of the pronounced day/night differences for *cis*-pinic, terpenylic, homoterpenylic, and caric acid, these compounds were highly correlated with each other (all $R > 0.8$). Many more good ($R > 0.7$) and high ($R > 0.8$) correlations were observed; for example, among the three IC diacids and between OC and WSOC, the three IC diacids, terebic, terpenylic, ketolimonic, homoterpenylic, MBTCA, diaterpenylic acid, and (2R,3R)-2-hydroxyterpenylic, suggesting that the three IC diacids were like the terpene-derived compounds also mainly from biogenic origin.

Birch, M.E. and Cary, R.A. (1996) *Aerosol Sci. Technol.* **25**, 221-241.

Gómez-González, Y., Wang, W., Vermeylen, R., Chi, X., Neiryneck, J., Janssens, I.A., Maenhaut, W. and Claeys, M. (2012) *Atmos. Chem. Phys.* **12**, 125-138.

Ion, A.C., Vermeylen, R., Kourtchev, I., Cafmeyer, J., Chi, X., Gelencsér, A., Maenhaut, W. and Claeys, M. (2005) *Atmos. Chem. Phys.* **5**, 1805-1814.

Kahnt, A., et al. (2013) *Atmos. Environ.* **81**, 561-568.

Maenhaut, W., Raes, N., Chi, X., Cafmeyer, J. and Wang, W. (2008) *X-Ray Spectrom.* **37**, 193-197.

Maenhaut, W., Wang, W. and Chi, X. (2011) *Boreal Env. Res.* **16**, 273-287.

Viana, M., Chi, X., Maenhaut, W., Querol, X., Alastuey, A., Mikuška, P. and Večeřa Z. (2006) *Atmos. Environ.* **40**, 2180-2193.