

Polar organic compounds in PM_{2.5} aerosols from Brasschaat, Belgium, during a 2007 summer campaign: Sources and diel variations

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In recent secondary organic aerosol (SOA) research several novel tracers from the photooxidation of α - β -pinene have been structurally characterized that are also detected at significant concentrations in ambient fine aerosol and are thus useful for aerosol source characterization. These tracers include organosulfates and nitrooxy organosulfates (Surratt et al., 2007; 2008; Iinuma et al., 2007; Gómez-González et al., 2008), which have a mixed biogenic/anthropogenic origin since their formation requires sulfuric acid which is mainly from anthropogenic origin. In addition, a novel C₈-tricarboxylic acid, i.e., 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA), was elucidated and identified as a stable endproduct from the photooxidation of α - β -pinene in the presence of NO_x (Szmigielski et al., 2007). In the present study, the concentrations of known and novel α - β -pinene SOA tracers were determined in fine (PM_{2.5}; particulate matter with a diameter ≤ 2.5 μ m) aerosol samples from a mixed pine/oak forest in Belgium that is heavily impacted by pollution, their time series and diel variations were examined, and the effects of meteorological parameters (temperature) and trace gas concentrations (ozone, SO₂ and NO_x) were assessed.

Separate day and night PM_{2.5} aerosol samples were collected during a 2007 summer field campaign in the state forest "De Inslag", located in Brasschaat, Belgium, about 12 km to the northwest of the center of the city of Antwerp. The samples were collected on quartz fiber filters with a high-volume dichotomous sampler and extracted with methanol. Separation of the terpenoic acids was achieved using a T3 Atlantis (Waters) column and methanol as organic modifier. A second LC method using a Gold (Thermo Fisher) column and acetonitrile as organic modifier was developed to achieve separation for the isomeric α -pinene related nitrooxy organosulfates with molecular weight 295 (5 peaks). The LC/MS analyses were performed with an LXQ linear ion trap instrument (Thermo Fisher) in the negative ion electrospray ionization and full scan modes. For quantitation, use was made of two internal recovery standards (sebacic acid and octanesulfate) and calibration with reference standards. As to known α - β -pinene SOA tracers, *cis*-pinic (MW 186) and *cis*-pinonic acid (MW 184) were included, as well as the recently characterized MBTCA. Other targeted

terpenoic acids were the limonene SOA products ketolimononic and limonic acid, both with a MW of 186, and the Δ^3 -carene SOA tracers caric (MW 186) and caronic acid (MW 184).

MBTCA, *cis*-pinic and *cis*-pinonic acid showed average concentrations of 4.9, 0.9 and 2.8 ng m⁻³, and in total represented 0.23% of the organic carbon (OC). Of the targeted terpenoic acids, MBTCA exhibited the highest concentrations during the first days of the campaign that were characterized by high maximum temperatures (> 22°C), while *cis*-pinonic acid showed the lowest concentrations, a result consistent with the formation of MBTCA through further oxidation of *cis*-pinonic acid (Szmigielski et al., 2007). MBTCA and *cis*-pinonic acid (expressed as %C of OC) showed diel variations with maxima mostly during daytime, while *cis*-pinic acid mainly peaked at night.

The five α -pinene-related MW 295 nitrooxy organosulfates showed an average total concentration of 3.1 ng m⁻³, and represented 0.07% of the OC. They exhibited clear diel variations with maxima at night, consistent with observations first reported by Iinuma et al. (2007) and nighttime NO₃ radical chemistry as supported by Surratt et al. (2008). Interestingly, rather low concentrations of the MW 295 α -pinene SOA tracers were found during the first nights of the campaign (with maximum daytime temperatures > 22°C). These results hint that the latter α -pinene SOA tracers are formed during nights following days where α -pinene was not fully consumed by photooxidation, leaving a portion of the emitted α -pinene available for processing by nighttime NO₃ chemistry.

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