

Comprehensive chemical characterisation of biogenic volatile organic compounds and secondary organic aerosols at the research station Melpitz

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A significant amount of non-methane volatile organic compounds (VOCs) enters the atmosphere from various sources. Although highly uncertain, their emissions are estimated to be in the order of 1300 TgC yr^{-1} , and approximately 90% is considered to originate from biogenic sources (Goldstein and Galbally, 2007). Once they are in the atmosphere, they are removed by either physical processes (wet or dry deposition) or chemical processes (oxidation). During the oxidation processes, the VOCs are transformed into less volatile compounds that eventually form secondary organic aerosols (SOAs).

Isoprene and monoterpene originating organic compounds are typically the most abundant SOA constituents detected in ambient organic aerosols (Hallquist *et al.*, 2009). Laboratory studies on the oxidation of biogenic VOCs have improved our knowledge about the structures of SOA marker compounds and their source processes in recent years. In spite of this, there still is a large uncertainty in the contribution of biogenic SOA to ambient OA. Here, we present the results from the detailed chemical characterisation of biogenic VOCs and SOA compounds sampled at the research station Melpitz during July 2013. The VOCs were collected on a Tenax TA cartridge every four hours. The VOC samples were analysed by a thermal desorption GC/MS. The SOA samples were collected using a PM_{10} Digitel Hi-Vol sampler for 24 hours. The PM samples were analysed by Ultra Performance Liquid Chromatography coupled to Electrospray Ionisation Ion Mobility Spectrometry Time of Flight Mass Spectrometry (UPLC/ESI-IMS-TOFMS).

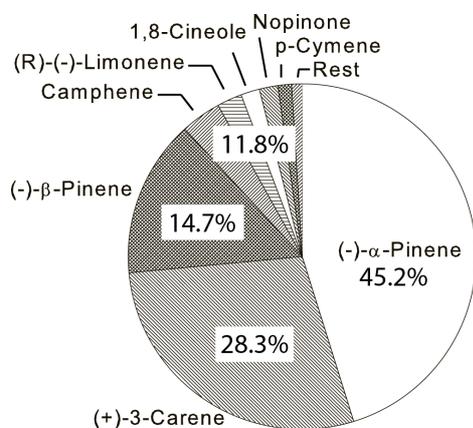


Figure 1. Average biogenic VOC composition during July 2013.

The most dominant monoterpene was α -pinene followed by 3-carene, β -pinene and camphene (Figure 1). These four VOCs account for about 90% of the monoterpenoids at the Melpitz site with a significant contribution of 3-carene. Although no tree type data is available about the surrounding forest at the Melpitz site, a type of Scots pine (*Pinus sylvestris*) that emits predominantly 3-carene (Yassaa *et al.*, 2012) is likely a responsible species for this. The total monoterpene mixing ratio during the campaign ranged from a few pptv to several ppbv. The nighttime mixing ratios of monoterpenes were significantly higher than those of daytime, most likely due to the development of a shallow nocturnal boundary layer at the site.

The UPLC-MS analysis of the PM_{10} samples showed a number of biogenic SOA marker compounds (Figure 2). Among those, an intensive peak of caric acid from 3-carene oxidation was observed in the samples. Its estimated concentration ranged from 13 ngm^{-3} to 209 ngm^{-3} , indicating that 3-carene as one of the most important SOA precursor VOCs at the Melpitz site. Another major SOA marker compound detected at the site was 3-methyl-1,2,3-butanetricarboxylic acid (MBTCA, Szmigielski *et al.*, 2007). This compound is suggested to be a later generation oxidation product of α -pinene and β -pinene, and a marker compound for processed SOA.

This study shows that the simultaneous determination of SOA compounds and their precursor VOCs is an essential step towards better understanding of SOA source processes.

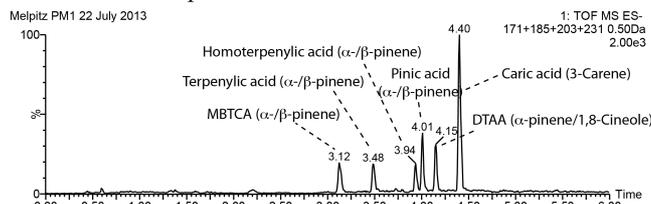


Figure 2. An example of extracted ion chromatogram from the analysis of a PM_{10} sample.

Goldstein, A.H., Galbally, I.E., (2007). Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* **41**, 1514-1521.

Hallquist, M., et al. (2009) *Atmos. Chem. and Phys.* **9**(14), 5155-5236.

Szmigielski, R., et al. (2007) *Geophys. Res. Lett.* **34**(24), L24811 doi:DOI: 10.1029/2007GL031338.

Yassaa, N., et al. (2012) *Atmos. Chem. and Phys.* **12**(15), 7215-7229, doi:Doi 10.5194/Acp-12-7215-2012.