



Diurnal variation of C2-C5 organosulfates and their precursor volatile organic compounds during PEGASOS field campaign in Po Valley, Italy

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Isoprene and monoterpene originating organosulfates are ubiquitously present in the ambient organic aerosols. These organosulfates form from the reactions of oxidation products of biogenic volatile organic compounds (VOCs) and acidic sulfate particles from anthropogenic sources, and they are marker compounds for processed SOA. These reactions provide important mechanisms to form low volatile SOA compounds from oxygenated VOCs that are otherwise too volatile to form SOA.

In the present study, a series of isoprene originating organosulfates were analysed in ambient fine particle samples (PM₁) that were collected during a PEGASOS (Pan-European Gas-Aerosol-Climate Interaction Study) field campaign in June and July 2012 that was carried out at the San Pietro Capofiume in the North Eastern part of the Po Valley, Northern Italy. The sampling site was located approximately 40 km away from Bologna and impacted by both anthropogenic and natural emissions from surrounding cities and agricultural fields. The PM₁ samples were collected twice a day (9 a.m. to 9 p.m. and 9 p.m. to 9 a.m.). The filter samples were analysed with UPLC-IMS-TOFMS (Ultra Performance Liquid Chromatography coupled to Ion Mobility Spectrometry and Time of Flight Mass Spectrometry). Additionally, VOC samples were collected with Tenax TA cartridges six times a day (1:00-5:00, 5:00-9:00, 9:00-13:00, 13:00-17:00, 17:00-21:00, 21:00-1:00) and subsequently analysed by TD-GC/MS (Thermal Desorption Gas Chromatography Mass Spectrometry).

The mixing ratios of isoprene methyl vinyl ketone (MVK) were the highest in late afternoon and whereas methacrolein (MACR) showed the opposite trend. The diurnal variation of isoprene is consistent with its emission that requires both temperature and light.

Isoprene originating organosulfates with m/z 153 (C₃H₅O₅S⁻), 155 (C₂H₃O₆S⁻), 169 (C₃H₅O₆S⁻), 183 (C₄H₇O₆S⁻), 199 (C₄H₇O₇S⁻) and 215 (C₅H₁₁O₇S⁻) were detected in the filter samples. These signals were more abundant in the daytime samples than in the nighttime samples, indicating that they are formed from photochemical oxidation.