

# Diurnal variation of C<sub>2</sub>-C<sub>5</sub> organosulfates detected during PEGASOS field campaign

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Keywords: SOA, isoprene, methacrolein, glyoxal.

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Recent studies have shown that isoprene and monoterpene originating organosulfates are present in the field and laboratory secondary organic aerosol (SOA) samples. The formation of organosulfates is suggested to involve the interaction of oxidation products of biogenic volatile organic compounds (VOCs) and sulfur containing species from anthropogenic sources, and suggested to be marker compounds for processed SOA (Hallquist, *et al.*, 2009). Although the mass fraction of organosulfates in total sulfate mass is typically smaller than 15% (Stone *et al.*, 2012; Hawkins *et al.*, 2010; Lukács *et al.*, 2009), the mechanisms provide an important means to form low volatile SOA compounds from oxygenated VOCs that are typically too volatile to form SOA.

In the present study, a series of isoprene originating organosulfates were analysed in ambient fine particle samples (PM<sub>1</sub>) that were collected during a PEGASOS (Pan-European Gas-Aerosol-Climate Interaction Study) field campaign in June and July 2012. The campaign was carried out at the San Pietro Capofiume in the North Eastern part of the Po Valley, Northern Italy. The sampling site is approximately 40 km away from Bologna and impacted by both anthropogenic and natural emissions from surrounding cities and agricultural fields. The PM<sub>1</sub> samples were collected using a Digiel High-Volume sampler (Hagnau, Switzerland) twice a day (daytime, 9 a.m. to 9 p.m., and nighttime, 9 p.m. to 9 a.m.). The filter samples were extracted with methanol, evaporated to dryness under a gentle stream of nitrogen at 10°C, and reconstituted in 200 µL of methanol/H<sub>2</sub>O solution (50/50, v/v). The extracts were analysed by Ultra Performance Liquid Chromatography coupled to Electrospray Ionisation Quadrupole Time-Of-Flight Mass Spectrometry (UPLC/(-)ESI-QTOFMS (Iinuma *et al.*, 2009).

A series of isoprene originating organosulfates were detected in the samples. These are *m/z* 153 (hydroxyacetone organosulfate, C<sub>3</sub>H<sub>5</sub>O<sub>5</sub>S<sup>-</sup>), 155 (glyoxal organosulfate, C<sub>2</sub>H<sub>3</sub>O<sub>6</sub>S<sup>-</sup>), 169 (methylglyoxal organosulfate, C<sub>3</sub>H<sub>5</sub>O<sub>6</sub>S<sup>-</sup>), 183 (methacrolein organosulfate, C<sub>4</sub>H<sub>7</sub>O<sub>6</sub>S<sup>-</sup>), 199 (methacrolein organosulfate, C<sub>4</sub>H<sub>7</sub>O<sub>7</sub>S<sup>-</sup>) and 215 (methyltetrol organosulfate, C<sub>5</sub>H<sub>11</sub>O<sub>7</sub>S<sup>-</sup>). Figure 1 shows a time series of these compounds. Owing to lack of authentic standard compounds, only the signal intensities are compared in this study. In general, the intensities of these signals were higher in the daytime samples than in the nighttime samples, indicating that the formation of these compounds involves the photochemical oxidation.

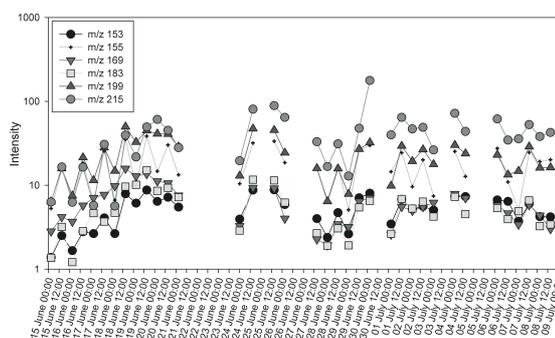


Figure 1. Time series of isoprene originating organosulfates detected in this study.

Table 1 summarises the correlation coefficients determined for the detected organosulfates. Although statistically significant correlations were obtained between all the compounds, the *m/z* 215 compound showed somewhat weaker correlations than the others, which may be related to the formation mechanisms of the *m/z* 215 compound.

Table 1. Correlation coefficients between detected organosulfate compounds

	<i>m/z</i> 153	<i>m/z</i> 155	<i>m/z</i> 169	<i>m/z</i> 183	<i>m/z</i> 199	<i>m/z</i> 215
<i>m/z</i> 153	1.00					
<i>m/z</i> 155	0.78	1.00				
<i>m/z</i> 169	0.64	0.55	1.00			
<i>m/z</i> 183	0.83	0.70	0.83	1.00		
<i>m/z</i> 199	0.86	0.82	0.84	0.91	1.00	
<i>m/z</i> 215	0.72	0.64	0.24	0.48	0.57	1.00

This work was supported by EU FP7 IP PEGASOS (FP7-ENV-2010/265148).

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