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## ATMOSPHERIC TRANSPORT MODEL APPLIED TO UNDERSTAND THE EFFECT OF BIOGENIC EMISSIONS TO SECONDARY ATMOSPHERIC AEROSOL IN HEIMIBOREAL ZONE

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**Abstract:** Biogenic VOC-s are known as precursors of primary aerosol in the atmosphere, however, their exact roles are not well known yet. This study is aimed to (1) clarify the possible contribution of boreal and hemi-boreal forest VOC emissions to the aerosol formation and (2) testing the performance of regional atmospheric modelling tools in respect of dispersion of biogenic emissions. The SILAM model with built-in isoprene and monoterpene emission module (CAMx based on Guenther scheme) was run for May – August 2006 in Baltic Sea region. Currently these VOC-s are included into the CB4 chemistry module only as ozone precursors. In this study they are advected as passive tracers. Modelled VOC-tracer concentrations were compared with sub-half-micrometre aerosol concentrations, simultaneously measured in Preila (western coast of Lithuania), Tahkuse (south-western Estonia), Hyytiälä (southern Finland) and Värriö (northern Finland), over 7000 hourly values in total. Linear correlation coefficients between measured and modelled concentrations were found 0.45 for both Preila and Tahkuse, 0.56 for Hyytiälä and 0.72 for Värriö. Bilinear regression result, based on summary monoterpenes and sulphate (AQME II model run, FMD), is even better correlated with aerosol: 0.60 for Preila, 0.58 for Tahkuse, 0.83 for Hyytiälä and 0.76 for Värriö. Thus, biogenic VOC-s and sulphates are likely two major contributors to the sub-half-micron aerosol in the Nordic-Baltic region and their importance is growing from south to north. According to the regression lines, about 5 – 20% of emitted biogenic VOC-s are converted into aerosol – this is in fair agreement with results of earlier studies based on backward trajectories of air mass. Contribution of sulphate ion is roughly by order of magnitude larger – evidently, the sulphates constitute typically most of sub-half-micron aerosol mass. Selection of “clean” air mass directions, based on adjoint modelling with SILAM, improves the correlations of measured aerosol modelled concentrations with biogenic VOC slightly. This study demonstrates that a state-of-art advection-diffusion model with proper emission database is capable to predict the accumulation mode aerosol concentrations in the atmosphere. More research in aerosol dynamics is needed to refine the results.

**Key words:** isoprene, monoterpenes, sub-micron aerosol, SILAM, advection-diffusion model.

## INTRODUCTION

The biogenic VOC-s are known as precursors of primary aerosol in the atmosphere. However, their exact roles are not well known yet. It was proven by Tunved *et al.* (2006), applying backward tracing of air mass trajectories, that concentrations of aerosol in the boreal forest zone of North Europe are highly correlated with time spent by air mass over the forested areas. Moreover, quantitative estimation of emissions through the trajectories gave that 7 – 8% of VOC-s are likely converted into aerosol particles smaller than 0.45  $\mu\text{m}$ , in both Hyytiälä and Värriö monitoring stations, in southern and northern Finland respectively.

This study is aimed to (1) clarify the possible contribution of hemi-boreal forest VOC emissions to the aerosol formation and (2) testing the performance of a air quality modelling system SILAM in respect to dispersion of biogenic emissions. In other words, the procedure described by Tunved *et al.* (2006) is updated with numerical advection-diffusion modelling instead of backward trajectories approach and the research area is extended to south to include the hemi-boreal forest in Baltic countries and Russia besides the Scandinavian boreal forest. The possible impact of sea salt, anthropogenic and natural sulphur emissions to the atmospheric aerosol is investigated through correlative relations.

## METHODS

The SILAM model with Eulerian core (Sofiev *et al.*, 2006, 2008) was applied for modelling the atmospheric advection and dispersion. The emissions of isoprene ( $\text{C}_5\text{H}_8$ ) and monoterpenes ( $\text{C}_{10}\text{H}_{16}$ ) were based CAMx emission model and European land use database (Poupkou *et al.*, 2010). In present stage the SILAM model includes chemical reactions with VOC-s in CB4 scheme for ozone production only. The SILAM runs made in this study do not include chemical reactions of biogenic VOC-s and following transformation to aerosol phase, thus VOC-s are advected as passive tracers. Also, the sea salt concentrations in the air were calculated, using built-in emission scheme of SILAM. Concentrations of sulphur dioxide and sulphates originate from AQME II (Air Quality Model Evaluation International Initiative) project results by Finnish Meteorological Institute, these are based on SILAM runs as well. The AQME II model domain includes entire Europe with nearly 28 km resolution, the biogenic VOC run was made for northern Europe within 53 – 71 degrees N and 6 – 36 degrees E, thus all Nordic and Baltic countries and north-western Russia, with nearly 22 km resolution (Figure 1). Additionally, inverse (adjoint) runs of SILAM were made to trace back the air masses from measurement sites – brief description of techniques see (Kaasik *et al.*, 2010). Based on these runs, time intervals of air masses from “clean” directions (i.e. relatively large fraction of forest and less human activities) were subjectively selected (see Figure 1).

The aerosol measurements originate from campaign carried out at Preila, Lithuania (55°22'23"N, 21°2'2"E) during May 25 – August 13, 2006 (Kikas *et al.*, 2012) and routine measurements from the same time interval at Tahkuse (58°18'52"N, 24°33'19"E), Hyytiälä (61°50'49"N, 24°17'42"E) and Värriö (67°45'17"N, 29°36'35"E) monitoring stations located in western Estonia, southern and northern Finland respectively. The measurement device was electric aerosol spectrometer EAS (Tammets, 2002) in Preila and Tahkuse and single-particle optical analyser DMPS in Hyytiälä and Värriö. Hourly mean mass concentrations were applied in statistical procedures. In analogy with (Tunved *et al.*, 2006) sub-half-micron aerosol was extracted from measured size distributions. Due to device-specific size fractions the exact size ranges were 3 – 420 nm in Preila, 10 – 420 nm at Tahkuse, 3 – 450 nm in Hyytiälä and Värriö. Measurement data sets do not include chemical composition of aerosol, thus only statistical relations between total aerosol mass and modelled precursor concentrations can be derived.

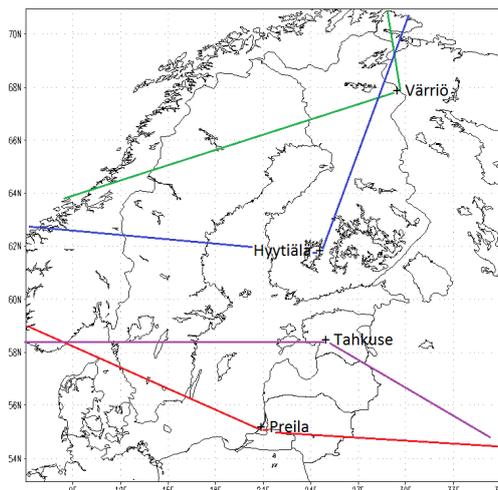


Figure 1. Modelling domain for biogenic VOC runs and locations of aerosol measurement stations. Green, blue, violet and red lines indicate respectively for Värriö, Hyytiälä, Tahkuse and Preila the selected relatively clean northern, western and (in case of Tahkuse and Preila) Eastern sectors. Southernmost directions are excluded from selection for all stations.

## RESULTS

Hourly measured aerosol concentrations against the modelled accumulated concentrations of biogenic VOC-s for all four stations are plotted in Figure 1. Evidently, the fit is improving from south to north and is better for selected directions than for the general data set, except of the northernmost station of Värriö.

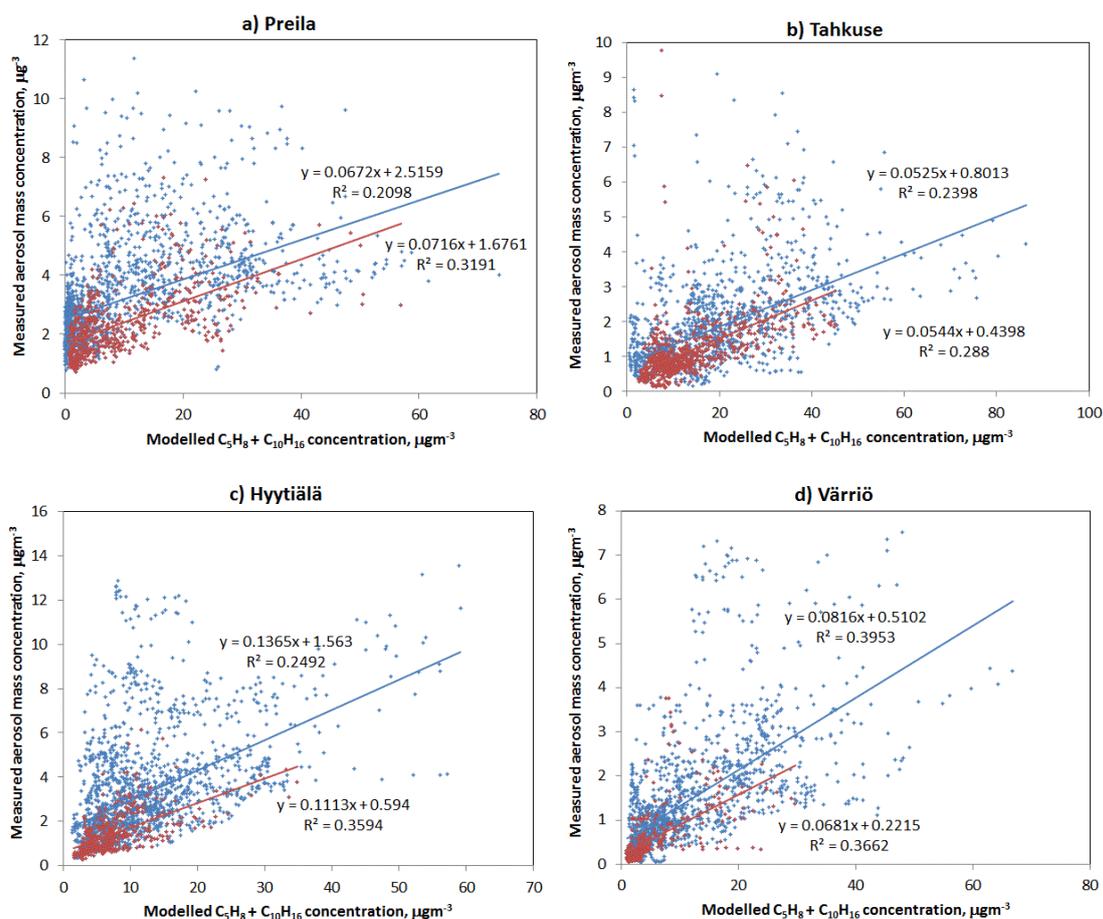


Figure 2. Measured sub-half-micrometer aerosol concentrations *versus* modelled biogenic VOC concentrations (hourly data points and linear fit) for Preila (a), Tahkuse (b), Hyytiälä (c) and Värriö (d). Complete data set is given in blue and directionally selected (“clean” directions) in red.

In Figure 3 are given time series of measured aerosol concentrations compared to modelled concentrations of biogenic VOCs and sulphate. It is evident that some peaks of aerosol coincide with peaks of VOC and some with SO<sub>4</sub>, a few of them with both. Thus, bilinear regression of aerosol against VOC and sulphate might give better fit than each of these precursors separately. The results of bilinear fits are given in Table 1. Adding the modelled sea salt and sulphur dioxide into the regression gave only very limited improvement of fit and is not listed there. Modelled sulphate concentrations separately fit remarkably to measured aerosol: determination coefficient R<sup>2</sup> is 0.21 for Preila, 0.18 for Tahkuse, 0.47 for Hyytiälä and 0.11 for Värriö. However, these coefficients are lower than for VOC, except for Hyytiälä. Let us point out that the linear correlation coefficient is nearly equal to R in this range – thus, correlations in Figure 1 range from 0.45 to 0.72 and in Table 1 from 0.58 to 0.83.

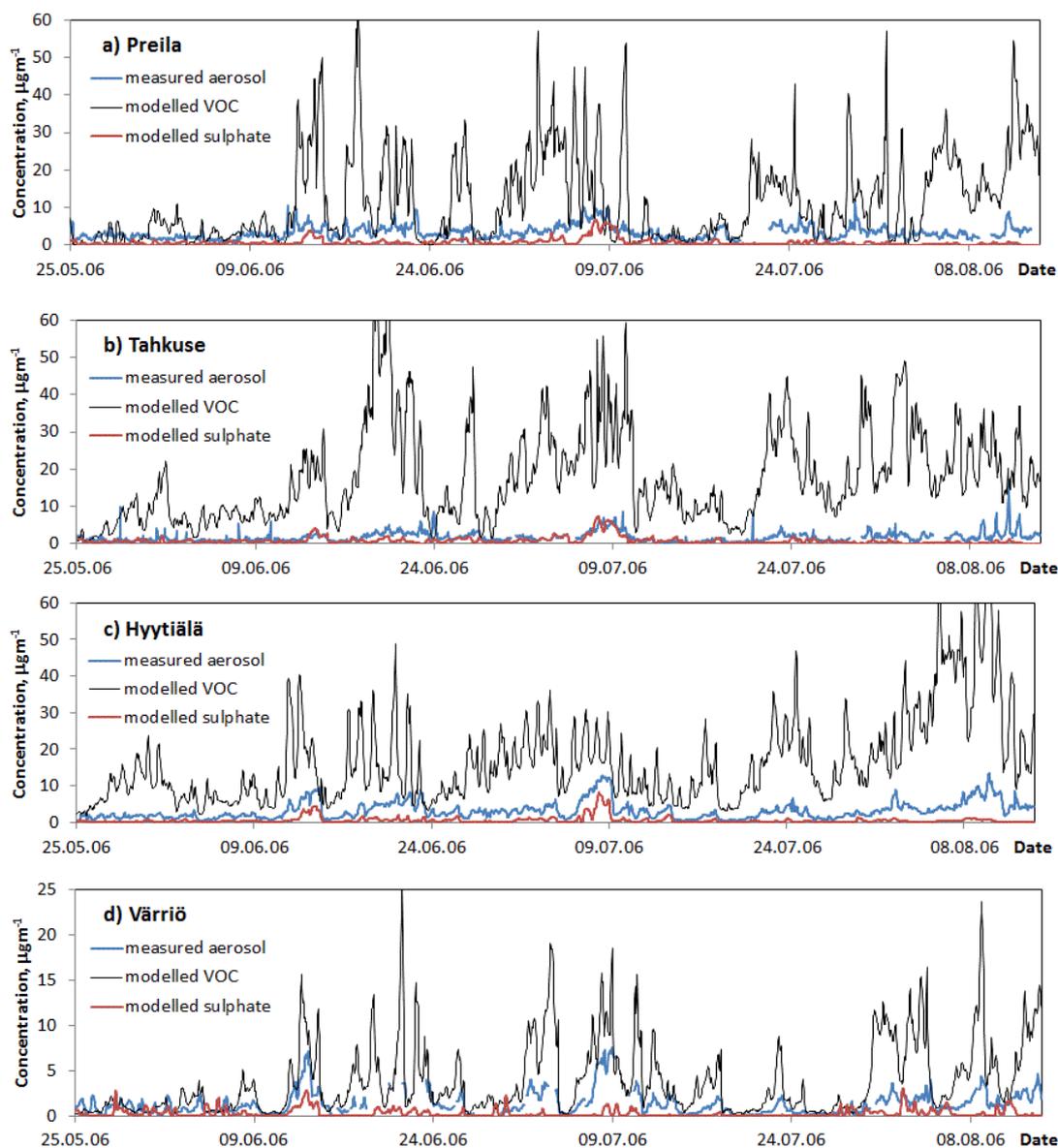


Figure 3. Time series plots for measured sub-half-micron aerosol, modelled biogenic VOC (sum of isoprene and monoterpenes) and modelled sulphate concentrations at Preila (a), Tahkuse (b), Hyytiälä (c) and Värriö (d) sites.

Table 1. Bilinear regression parameters. Independent variables are modelled total biogenic VOC (isoprene and monoterpenes) and sulphate concentrations, Dependent variable is measured sub-half-micron aerosol concentration.

Site	Intercept, $\mu\text{g}/\text{m}^3$	Slope for VOC	Slope for SO <sub>4</sub>	R <sup>2</sup>
Preila	2.125	0.057	0.703	0.36
Tahkuse	0.593	0.044	0.447	0.33
Hyytiälä	0.800	0.092	1.597	0.70
Värriö	0.337	0.236	0.659	0.58

## DISCUSSION

In general, the results, concerning the Hyytiälä and Värriö sites, are similar to those reported by Tunved *et al.* (2006): the expected biogenic VOC concentrations in the air are remarkably correlated with measured accumulation mode particle concentrations and about 10% of the total VOC mass seem to be converted into aerosol. However, the scatter of data points is much larger than nearly perfect fit ( $R^2=0.79$  for Värriö-Pallas and  $R^2=0.93$  for Hyytiälä) achieved in the mentioned work – that is valid even for the “clean” advection directions selected as nearly same. Of course, some difference can occur due to different data set, but also the exact scheme of bioVOC emission estimations may play a role: the CAMx scheme (Poupkou *et al.*, 2010) applied in this study differs from genuine Guenther scheme applied by Tunved *et al.* to monoterpenes only. Our study includes both monoterpene and isoprene emissions, as isoprene is considered more reliable in SILAM.

Data scatter is even larger for Tahkuse and Preila stations – that is an expected result, as much more different sources of aerosol precursors are present in more densely inhabited Baltic countries and in Russia nearby. Nevertheless, there is no doubt in correlative relation between biogenic VOC tracer and accumulation mode aerosol. Intercept of linear fit (Figure 2) is decreasing northward, being always smaller for directionally selected data in respect of complete set – thus, in expectedly cleaner air the unexplained background aerosol level is lower indeed. It is rather remarkable, that high concentrations of aerosol can occur with low concentration of VOC precursors, but low aerosol concentrations with high VOC-s almost never – a reasonable result, assuming that VOC-s cause the growth of nucleation particles in normal atmospheric conditions. Growth, of course, can occur due to other precursors as well, thus lack of VOC-s does not necessarily inhibit it.

According to Figure 3, some aerosol peaks are simultaneous with elevated concentrations of sulphate and obviously not related to VOC. Sulphate and biogenic VOC-s together explain in all stations the larger part of aerosol variability that each of them separately, as seen from Table 1. Whereas, according to slopes, the conversion ratio of VOC-s might be in order of 5 – 20%, the ratio for SO<sub>4</sub> is closer to 100% – that is natural, as sulphates always exist in solid or liquid phase. Some uncertainty, however, is related with exact size range of sulphate particles and mass of cations coupled with sulphate.

However, all the considerations above on biogenic VOC-s and sulphates as substances acting in aerosol formation remain indirect, as SILAM in present stage does not include the full aerosol chemistry and dynamics. Different airborne pollutants and natural admixtures, advected with the same air masses, and thus, highly correlated with either VOC or sulphate, can act in these processes. Nevertheless, state of science knowledge give strong evidence of both VOC-s and sulphates in chemical and physical processes leading to aerosol growth. This study appears one of supporting investigations for implementation of aerosol chemistry-dynamics module in SILAM that is in work yet.

## CONCLUSIONS

Existence of important correlations between emitted biogenic VOC-s emitted along air mass trajectories and climatically active sub-half-micrometre aerosol fraction in hemi-boreal zone of Europe is proven in addition to the boreal zone.

Suitability of SILAM model for studies on atmospheric VOC and aerosol relations is proven.

Important role of sulphates in aerosol formation processes in boreal and hemi-boreal zones, often independently of biogenic VOC-s is stressed.

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