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### SENSITIVITY OF MODELLED SECONDARY ORGANIC AEROSOLS (SOA) TO BIOGENIC VOC (BVOC) EMISSIONS IN SWITZERLAND

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#### Abstract

Biogenic VOC (BVOC) emissions play a significant role as precursors of secondary organic aerosol (SOA) both on a regional and global scale. The modelling of SOA requires knowledge of the factors that determine the emission rate of the most relevant biogenic species. Even though there are still considerable uncertainties, the data availability for isoprene or monoterpenes is relatively good. Very little data, however, is available for sesquiterpenes, mostly because they are challenging to measure. Smog chamber experiments using sesquiterpenes as precursors have shown high SOA yields. This is thought to be due to the high molar mass of oxidation products and their associated low volatility. The air quality model CAMx (Comprehensive Air quality Model with extensions, by ENVIRON) includes a sesquiterpenes pathway to SOA that would partly close the gap between observations and model predictions of organic aerosols. In this model exercise, the sensitivity of SOA formation in Switzerland in June 2006 to BVOC emissions is studied. We use CAMx version 5.10 with CB05 chemical mechanism and the coarse-fine aerosol option. MM5 version 3.7.4 is used as meteorological driver. We study the effect of different parameterisations of BVOC emissions that are based on earlier work of our group and new data reported by others. In this paper, we report the sensitivity of the model output to the emissions of isoprene, monoterpenes and sesquiterpenes for two different sites in Switzerland.

**Key words:** CAMx, SOA, BVOC, monoterpenes, sesquiterpenes, isoprene

#### INTRODUCTION

Several studies have shown that the biogenic production of volatile organic compounds is several orders of magnitude larger than the anthropogenic emission of these pollutants (Hallquist *et al.*, 2009). In summer, the oxidation of these biogenic volatile organic compounds (BVOCs) is suspected to contribute substantially to particulate matter in Switzerland (Szidat, 2009). The three most important classes of BVOC are isoprene (C<sub>5</sub>H<sub>8</sub>), monoterpenes (C<sub>10</sub>H<sub>16</sub> compounds containing two isoprene units) and sesquiterpenes (C<sub>15</sub>H<sub>24</sub> compounds containing three isoprene units). Together with NO<sub>x</sub> (mostly from anthropogenic sources), these compounds contribute to the formation of secondary pollutants such as ozone and secondary organic aerosol (SOA). Sesquiterpenes are believed to be very effective SOA precursors (Bonn and Moortgat, 2003), since they have a much lower volatility than lighter isoprenoids even before being oxidized, mostly due to the higher molar mass. However, there is still a debate on the volatility of the products of sesquiterpene ozonolysis. There are indications that they are more volatile than currently believed in the modelling community (Asa-Awuku *et al.*, 2009). In the chemical transport model CAMx, sesquiterpene oxidation products are currently treated as non-volatile, which means that once formed, they stay in the aerosol phase until removed from the system. The aim of this study is to evaluate the influence of BVOC emissions on SOA formation in Switzerland in June 2006 with a special focus on sesquiterpenes.

#### METHODOLOGY

This study was carried out with the offline-coupled MM5-CAMx modelling system. It was driven by our CAMxRunner Modelling framework that is presented as a poster at this conference. MM5 (Version 4.7.5) ran with the ETA boundary layer scheme (Janjić, 1994) using three nested domains. The other two domains were nudged towards COSMO-7, whereas the innermost domain (which is the domain of interest) ran freely. Since we focus on Switzerland, the innermost domain with a horizontal resolution of 3km x 3km covers only Switzerland. The nesting factor is 3, resulting in a resolution of 27km x 27km in the master domain. The lower right corner of the master domain is about 4° west of Cadiz and its upper right corner is about 2° west of Vilnius. The coordinate projection is Lambert Conformal, which is suitable for mid-latitudes. CAMx (Version 5.10, (ENVIRON, 2009)) used the same grid setup, except the usual buffer cells around all non-master domains. Version 5.10 of CAMx features a new chemical solver – the existing CMC (Chemistry Mechanism Compiler) solver was replaced by the EBI (Euler-Backward Iterative) solver. Other new features such as the ACM2 (Version 2 of the Asymmetric Convective Model) scheme for vertical transport were not used.

SOA formation in CAMx 5.10 is based on a partitioning scheme called SOAP (Strader *et al.*, 1999). It uses seven pairs of condensable gasses and corresponding aerosol phase species. Anthropogenic SOA is formed from toluenes and xylenes alone, while biogenic precursors are isoprene, monoterpenes and sesquiterpenes. Both anthropogenic and biogenic SOA undergoes slow oligomerisation (Kalberer *et al.*, 2004) – the product species SOPA (anthropogenic) and SOPB (biogenic) no longer partition to the Gasphase. Sesquiterpene products also no longer partition back to the Gasphase, once they are formed.

Biogenic emissions were generated using two different approaches: emCAMx is based on several older studies (Andreani-Aksoyoglu and Keller, 1995), whereas the new simplified model SimBioEmCAMx uses basal emission data from (Steinbrecher *et al.*, 2009). Both emission models share the same anthropogenic emission, their landuse data and meteorological input.

SimBioEmCAMx is based on the approach by (Guenther, 1997) where the emission rates of the different compounds are calculated as:

$$\begin{aligned}
 E_{\text{Isoprene}} &= e_{0\_isop\_photo\_i} * bmd_i * \gamma \\
 E_{\text{Monoterpene}} &= e_{0\_mt\_photo\_i} * bmd_i * \gamma + e_{0\_mt\_pool} * bmd_i * \exp(\beta * (T - T_0)) \\
 E_{\text{Sesquiterpene}} &= e_{0\_sq\_pool\_i} * bmd_i * \exp(\beta * (T - T_0))
 \end{aligned}$$

$e_{i0}$  are the basal emission rates of the given compound for tree  $i$  as given by (Steinbrecher *et al.*, 2009) in [ $\mu\text{g Compound}/(\text{h} * \text{g leaf dry weight})$ ] at  $30^\circ\text{C}$  and  $\text{PAR}=1000\mu\text{mol m}^{-2} \text{s}^{-1}$ . The factor  $b_{\text{md}}$  is the biomass density of tree  $i$  [ $\text{g leaf dry weight} / \text{m}^2$ ]. The environmental correction factor  $\gamma$  includes both a term for temperature as well as for PAR (photosynthetically active radiation) (Guenther, 1997).  $\beta$  controls the response to the temperature, we use a value of  $0.09 \text{ K}^{-1}$ .  $T$  is the leaf temperature in  $^\circ\text{C}$  and  $T_0$  is the reference Temperature  $30^\circ\text{C}$ .

The unit of the result is  $\mu\text{g Compound}/(\text{h} * \text{m}^2)$  – the emitted species mass per hour and square meter of projected tree area. We distinguish between species whose emission is controlled by VOC production (such as isoprene and monoterpenes) and species whose emission is controlled by evaporation from storage pools (such as sesquiterpenes). emCAMx contains a radiation transfer model, which accounts for light scattering in the canopy and temperature changes resulting from shading. SimBioEmCAMx does not account for these effects.

Table 2 contains the emission scenarios that were used. Scenario *SQT10\_5.10* is based on the assumption that sesquiterpene emissions are about 10% of the molar monoterpene emissions. This assumption was used by other modellers, e. g. (Lane *et al.*, 2008), but often, these assumptions (like in the paper cited) are based on the US vegetation. *Sem207* uses the parameters given in (Steinbrecher *et al.*, 2009) “as is”. This resulted in much lower emissions than with the original emCAMx, which includes canopy-correction which, in turn, reduces the emission rates. We further investigated this using the potential maximal values for the basal emission rates (Steinbrecher, 2010). We conducted the run *Sem208* which we see as an “upper limit” run, where sesquiterpenes of *Sem207* are larger by a factor of 10 and monoterpene emissions larger by a factor of 1.5. In the case of sesquiterpenes, such high values, according to Steinbrecher, are only realistic under stressful conditions (very high ozone, high temperatures or draught).

Table 2: Emission scenarios discussed

Scenario	BVOC model	Features
SQT10_5.10	emCAMx	Sesquiterpenes are prescribed as 10% of molar monoterpene Emissions
Sem207	SimBioEmCAMx	Basal emission rates taken from (Steinbrecher <i>et al.</i> , 2009)
Sem208	SimBioEmCAMx	“Upper limit values” for basal emission rates according to Steinbrecher (Pers. Comm.)

We will report results for the two Nabel measurement network (Bruggisser *et al.*, 2007) stations “Payerne” ( $6.94^\circ\text{E}$ ,  $46.81^\circ\text{N}$ , 489 m asl.) in the Swiss plateau and “Lugano” ( $8.96^\circ\text{E}$ ,  $46.01^\circ\text{N}$ , 281 m asl.) South of the Alps. Payerne represents a rural station, while the station of Lugano is urban.

## RESULTS AND DISCUSSION

### Emissions

Table 3 shows the total emissions in both the innermost domain that covers Switzerland and the outermost domain that surrounds a large part of Europe. None of these scenarios shows a predominance of isoprene that is predicted by other studies, including (Simpson *et al.*, 1999).

Table 3: Calculated BVOC Emissions for Switzerland (Innermost domain) and Europe (Outermost domain) for June 2006

Scenario		Switzerland	Europe
SQT10_5.10	Isoprene:	1.7 Gg	37.8 Gg
	Monoterpenes:	28.3 Gg	743.9 Gg
	Sesquiterpenes:	4.2 Gg	111.6 Gg
Sem207	Isoprene:	8.8 Gg	223.1 Gg
	Monoterpenes:	7.2 Gg	249.4 Gg
	Sesquiterpenes:	0.6 Gg	17.9 Gg
Sem208	Isoprene:	8.8 Gg	223.1 Gg
	Monoterpenes:	10.9 Gg	374.1 Gg
	Sesquiterpenes:	5.8 Gg	179.2 Gg

### SOA Formation

The three scenarios discussed differ strongly with respect to Total Biogenic Secondary Organic Aerosol for both locations (Figure 2). *Sem208* (the “Upper Limit” run) is dominated by its high contribution of sesquiterpenes which grows with temperature. In the second half of the month, temperatures increased at both stations, we attribute the dominance of *sem208* in the second half of the month in both cases to this fact.

The shape of the diurnal profiles for both locations are not in agreement with other studies (Sheehan and Bowman, 2001), however, aerosol mass spectrometer measurements (AMS) carried out at Payerne and subsequent factor analysis (PMF, (Lanz *et al.*, 2009)) shows a similar diurnal cycle with smaller amplitude (Figure 3).

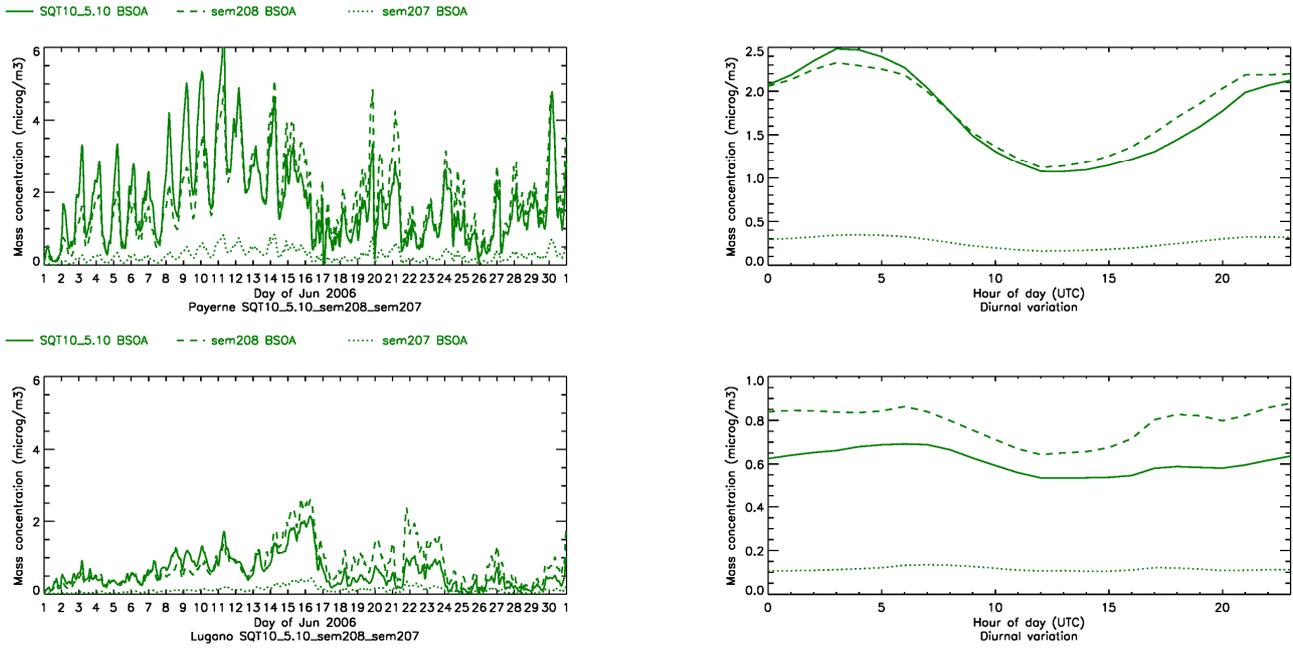


Figure 2: Results for Total BSOA

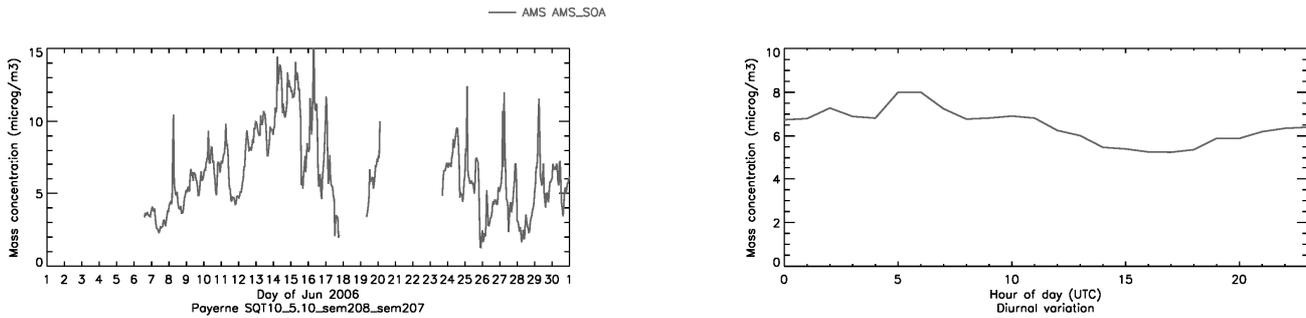


Figure 3: Results from FA-AMS data (Payerne only)

Modelled particulate sulfate shows a similar diurnal pattern at Payerne as measured and modelled SOA with a peak between 3 and 5 UTC and a weaker peak at 16 UTC. However, Measured particulate sulfate shows different behaviour with a broad peak around 10UTC (noon).

The diurnal pattern of the sesquiterpene SOA is similar to the other compounds (Figure 4) even though one might expect a peak around 10UTC due to strong production and the absence of partitioning back to the gasphase. The reason for this may be the strong influence of the boundary layer height: even though production of sesquiterpenes is strongest around noon, the increased boundary layer height dilutes the pollutants strongly.

The Monoterpene time series (Figure 5) show that the predicted emissions of emCAMx (SQT10\_5.10) are much higher than those by SimBioEmCAMx.

Time series of isoprene are not shown here, since the absolute concentrations of isoprene SOA was always smaller than  $0.15 \mu\text{g}/\text{m}^3$ .

In Payerne, all three scenarios show a clear dominance of sesquiterpene SOA in average BVOC (Figure 6). The contribution of monoterpene SOA is large when using the existing emission model emCAMx, or when increasing monoterpene emission rates as in Sem208. The relative contribution of isoprene is high when using the original basal emissions (Sem207) – but in this case, the total SOA produced is very low compared to the other two scenarios.

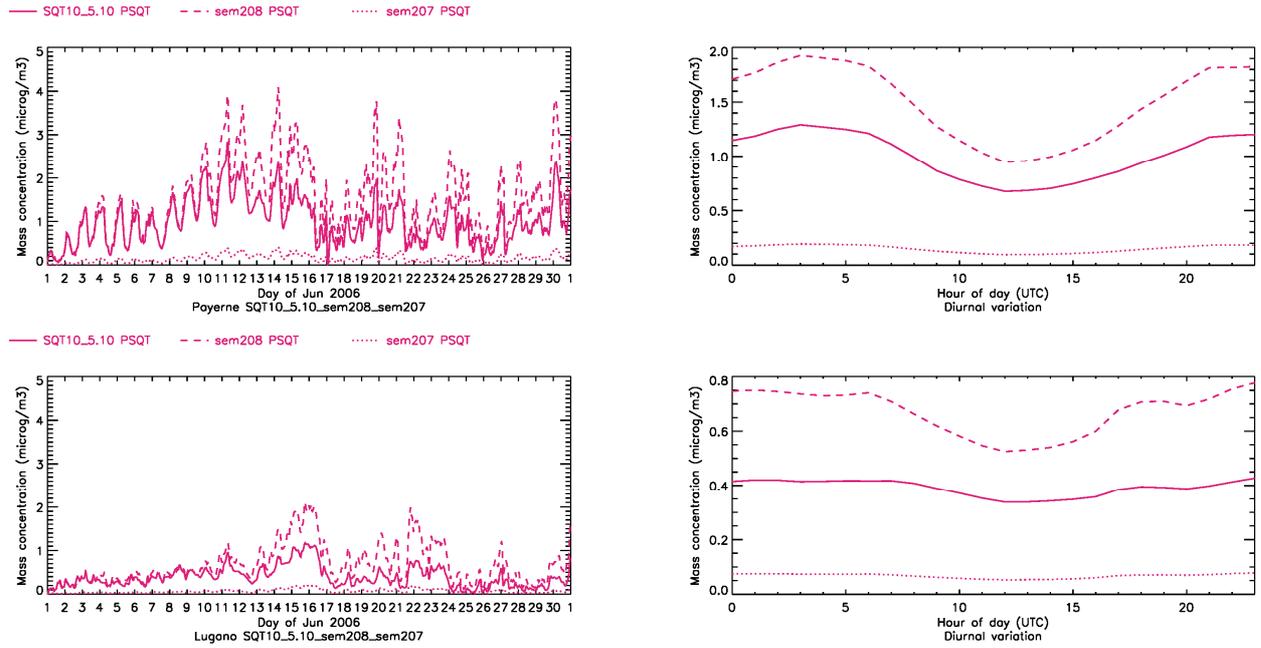


Figure 4: Results for SOA from sesquiterpenes

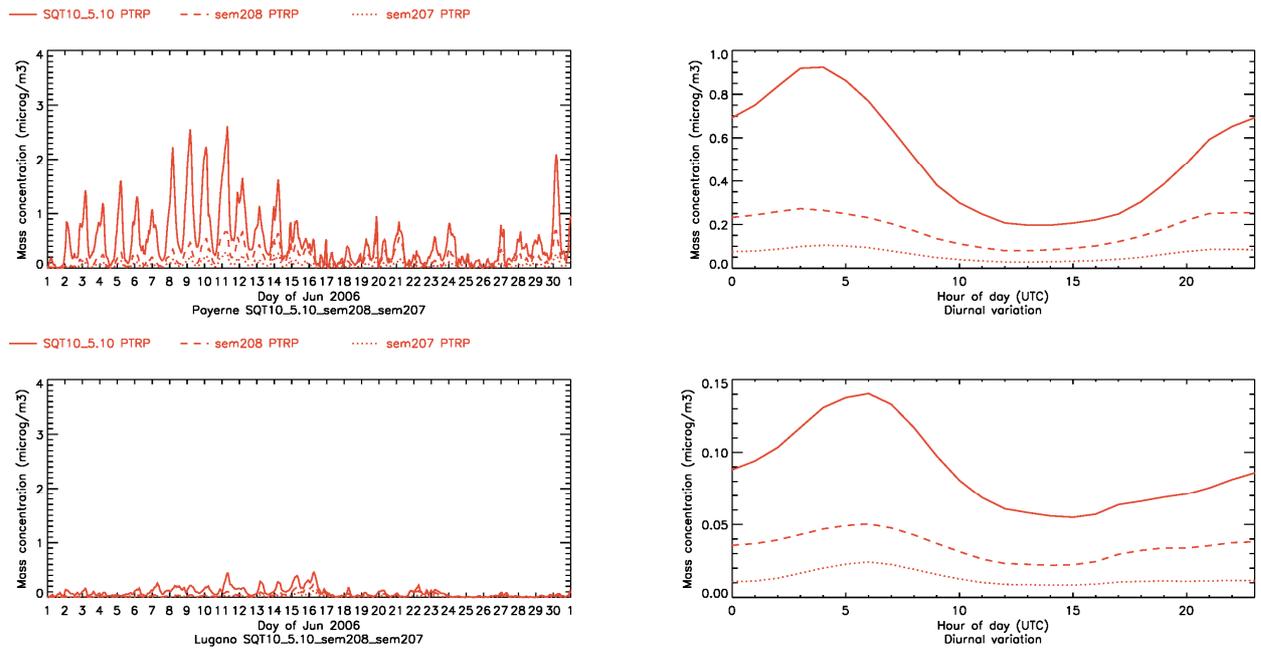


Figure 5: Results for SOA from Monoterpenes

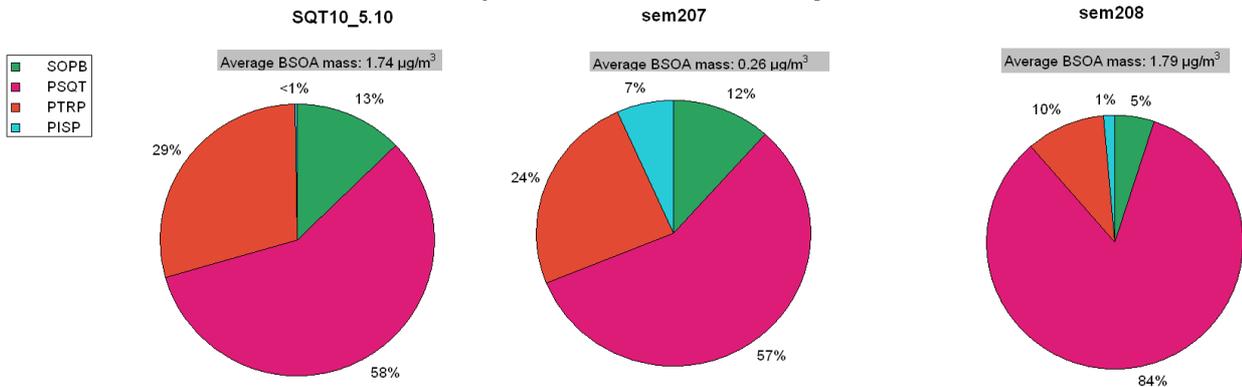


Figure 6: Average contributions of sesquiterpene SOA (PSQT), monoterpene SOA (PTRP), isoprene SOA (PISP) and oligomerised SOA (SOPB) to BSOA mass in Payerne, June 2006

## CONCLUSIONS AND OUTLOOK

We showed almost linear behaviour of SOA with respect to BVOC emissions in the relatively low concentration range studied. Isoprene emissions may play an important role globally, but our results suggest that in Switzerland they are not very important, mostly due to the predominant tree species.

From the comparison of the runs sem208 and SQT10\_5.10 we conclude that the assumption that sesquiterpenes are 10% of the Monoterpene emissions is exaggerated for Switzerland, since sem208 is really an extreme case.

The correct modelling of sesquiterpenes might be very complicated, because of the relevance of these compounds as stress signals (Mentel *et al.*, 2009). Especially the ozone concentration seems to have an influence on sesquiterpene emissions. This implies that online emissions models might be needed, where emissions are generated in each CTM time step.

New formation mechanisms as put forward by (Robinson *et al.*, 2007) might change this picture fundamentally.

Also the influence of land use data on biogenic emission data must be stressed, it is favourable to use the same data source at all resolutions (grid sizes) if possible.

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