

## SEASONAL VARIABILITY OF AEROSOL COMPOSITION IN SWITZERLAND: A MODELLING STUDY

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**Abstract:** In this study, we applied the MM5/CAMx model system over Switzerland for winter and summer periods in 2006. The focus is on the formation and transport of aerosols and the contribution of various sources to the aerosol formation both in winter and summer seasons. Our model system uses three nested domains with 27 km (Europe), 9 km (central Europe) and 3 km (Switzerland) resolutions. The concentrations of aerosol components are calculated for particle sizes smaller than 2.5  $\mu\text{m}$ . The model's capability to reproduce the aerosol concentrations is investigated by comparing the model results with the measurements performed during the same periods. In general, the modelled concentrations of inorganic aerosols agree quite well with the AMS measurements, whereas organic aerosols are underestimated. The chemical composition of aerosols in summer differs from that in winter. Both measurements and model predictions indicate that organic aerosols and particulate nitrate are the major components of the winter aerosol composition in Switzerland. In summer, organic aerosols dominate the aerosol composition and they are mostly secondary organic aerosols formed from the biogenic precursors. Recent measurements suggest that wood-burning emissions might contribute significantly to the aerosol concentrations, especially in winter. The lack of wood burning emissions in emission inventory could cause partly the underestimation of organic aerosols. The secondary organic aerosol (SOA) formation will be soon improved by using a new model version where oligomerization and SOA formation from isoprene and sesquiterpenes are implemented.

**Key words:** *aerosol modelling, CAMx, SOA, biogenic emissions*

### 1. INTRODUCTION

Quantitative measurements of aerosols in Switzerland indicate that organic aerosols are the major components of the aerosol composition both in summer and winter (Lanz, et al., 2007; 2008). Additional measurements using  $^{14}\text{C}$  as tracer show that biogenic emissions in Zurich contribute about 60 and 27% to organic carbon (OC) in summer and winter, respectively (Szidat, et al., 2006). It was also suggested that wood-burning emissions might contribute significantly to the aerosol concentrations, especially in winter. Understanding the partitioning behaviour of semi-volatile species between the gas and aerosol phases can help us to predict how changes in anthropogenic and biogenic activity will influence the formation of aerosols in the atmosphere. Modelling secondary organic aerosol (SOA) formation is among the most demanding aspects associated with atmospheric organic photo-oxidation. The current models often underestimate SOA concentrations (Cousin, et al., 2005; Volkamer, et al., 2006; Zhang, et al., 2004). Recent experimental evidence for oligomerization reactions in organic aerosols indicated the need to readdress the current assumptions in models about the partitioning of oxidation products in the gas and the particle phase (Dommen, et al., 2006; Kalberer, et al., 2004). A recent model study by Morris, et al., (2006) showed that including mechanisms such as polymerization, SOA formation from isoprene and sesquiterpenes, led to increased SOA yields. In Switzerland which has a very complex terrain, there are very few model studies on aerosols (Andreani-Aksoyo lu, et al., 2003; Andreani-Aksoyo lu, et al., 2008). This study uses the opportunity of having detailed aerosol measurements to validate the aerosol model and provides information about the seasonal variation of aerosol composition and distribution in Switzerland.

### 2. METHOD

In this study, the 3-dimensional photochemical model CAMx (Comprehensive Air Quality Model with Extensions, version 4.40) (Environ, 2006) was applied with 3 nested domains. The coordinate system was Lambert Conic Conformal. The resolutions of the three domains were 27, 9 and 3 km, respectively with 14 -layers in a terrain-following coordinate system. The model top was set at  $\sigma = 0.55$ , which corresponds to a geometric layer top at sea level of about 7000 m. The simulations started always at 0000 UTC on the first day and ended at 2400 UTC on the last day of the months January and June in 2006. There were detailed aerosol mass spectrometer (AMS) measurements available for Zurich in January 2006 and for Payerne in June 2006. We applied the meso-scale model MM5 (PSU/NCAR, 2004) as meteorological driver for CAMx. MM5 was initialized by assimilated data of the COSMO-7 forecast model of MeteoSwiss. The emission inventory was prepared by compiling European and Swiss anthropogenic emissions from various data sources, as described in Keller, et al., (2008). Emissions of PM<sub>2.5</sub> and PM<sub>10</sub> of 9 source categories were obtained from INFRAS and Meteotest for the reference year 2000. A factor of 1.5 was used for POA/EC emissions. Using land use and meteorological data, biogenic emissions were calculated by means of temperature and irradiance dependent algorithms (Andreani-Aksoyo lu and Keller, 1995). In the biogenic emission inventory, the most abundant species are monoterpenes, which are emitted mainly by Norway Spruce and fir trees. Initial and boundary conditions were obtained from the output of similar periods generated by the global model MOZART (Horowitz, et al., 2003). In this study, the CBM-IV mechanism with the extensions for aerosol modelling was used (Gery, et al., 1989). Calculations of aerosols with  $d < 2.5 \mu\text{m}$  were performed using the fine/coarse option of the aerosol module.

### 3. RESULTS AND DISCUSSION

#### Winter Episode

The measured wind speed, precipitation, temperature as well as the measured and modelled CO mixing ratio in Zurich are shown in Figure 1. This period can be divided into five sections based on the meteorological conditions: In the first period between 1-6 January (I), temperatures were above zero and the wind speed was moderate. This period was followed by a colder and foggy episode (II) where the temperatures were below zero and wind speed was low. It lasted until 17 January when some precipitation occurred, temperatures rose above zero and wind speed became stronger (III). The fourth period (IV), had mixed conditions with variable wind speed—mostly low to moderate— and temperatures. The wind speed was high again during the last period at the beginning of February (V). The CO concentrations can be used as a proxy to investigate the performance of the meteorological model. The agreement between model and measurements is better during the first, third and fifth periods when the wind speed was moderate or high. On the other hand, the model underestimates the CO concentrations under low-wind conditions (periods II and IV). A similar behaviour was observed for the inorganic and organic aerosols (Fig. 2). In addition to the insufficient performance of the meteorological model during the second and fourth periods, there might be also other reasons causing underestimation such as lack of wood burning emissions, and/or oligomerization of SOA, which has not been treated yet in the model version used. EC predictions on the other hand, seem to match measurements during low-wind period, and overestimated in the high-wind period. This behaviour suggests that EC emissions are likely to be overestimated. Both measurements and model results suggest that the main components of the winter aerosols in Zurich are particulate nitrate and organic aerosols (Fig. 3). According to model predictions (not shown), primary organic aerosols (POA) dominate the organic aerosol composition (87%). Secondary organic aerosols (SOA) on the other hand, were predicted to be mainly biogenic. The fraction of modelled elemental carbon (EC) is higher than the measured one, indicating overestimated emissions, as mentioned before.

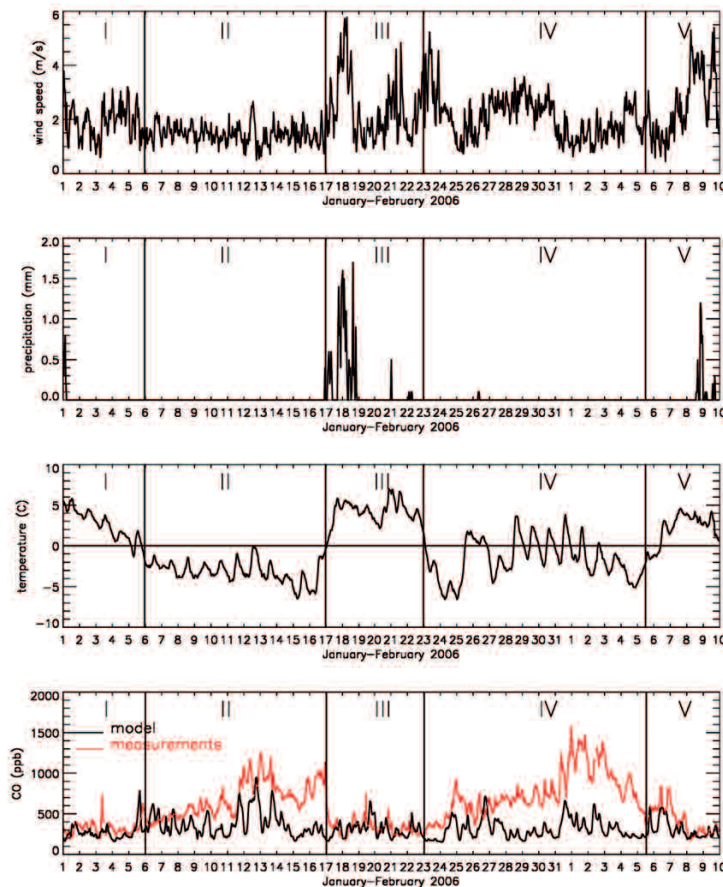


Figure 1. Measured wind speed ( $\text{ms}^{-1}$ ), precipitation (mm) and temperature (C) as well as the comparison of measured and modelled CO concentrations (ppb) in Zurich (NABEL station) during January 2006.

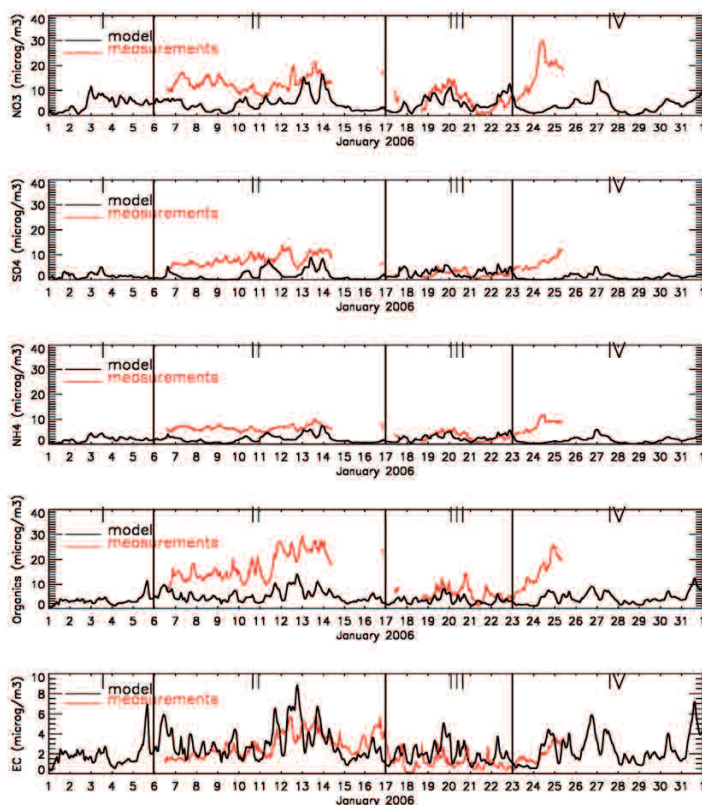


Figure 2. Comparison of modelled (PM2.5) and measured (PM1) (AMS) inorganic and organic aerosols as well as EC ( $\mu\text{g m}^{-3}$ ) in Zurich during January 2006.

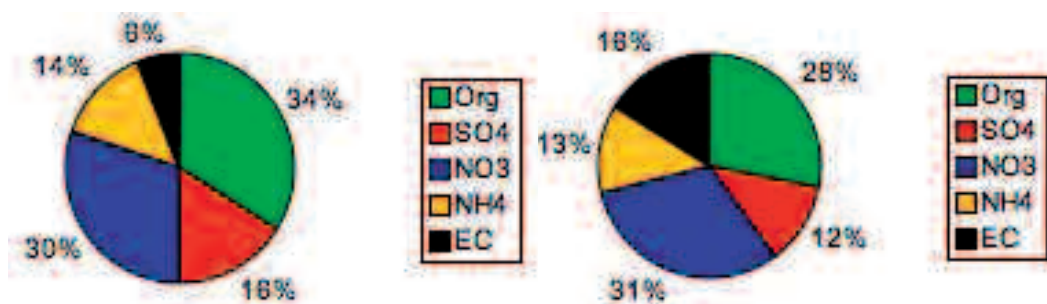


Figure 3. Fractional composition of winter aerosols in Zurich from measurements (PM1) (left) and model simulations (PM2.5) (right).

### Summer Episode

The meteorological parameters suggest that there was a low wind episode between 12 and 17 June. The performance of MM5 was reasonably good except that period with low wind speed. The model underestimates both inorganic and organic aerosol concentrations between 12 and 17 June at Payerne which is a rural site (Fig. 4). Inorganic aerosols, especially particulate nitrate, were overestimated during the first week, most probably due to too high boundary concentrations. Model predictions of inorganic aerosols between 7-12 June agree well with AMS measurements. On the other hand, the results look different for the organic aerosols. The AMS data match model results during the first week, but later they increase and become about 3 times higher than the modelled quantities during 12-17 June. In addition to the problems of meteorological model for the low-wind period, some other causes might lead to underestimation. The SOA formation from other sources (sesquiterpenes) and oligomerization are likely to be some of the reasons. Both model predictions and measurements suggest that the organic aerosols are the dominant fraction of aerosols in summer (Fig. 5). As shown in the figure, organic aerosol fraction is underestimated while particulate nitrate is overestimated. SOA dominates the organic fraction of aerosols by 60% and it is mainly biogenic (not shown). This is in agreement with  $^{14}\text{C}$  measurements carried out in northern Switzerland (Szidat, et al., 2006).

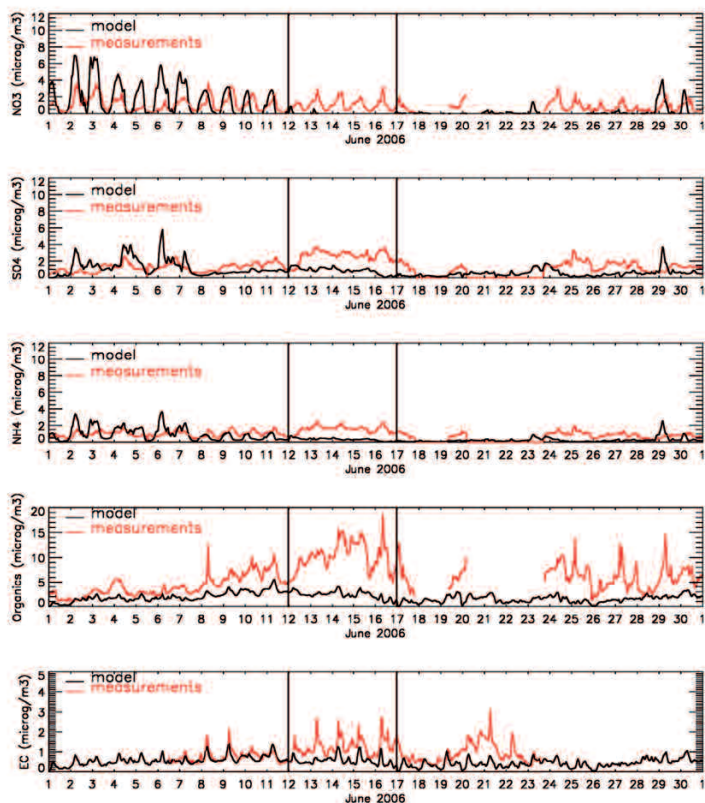


Figure 4. Comparison of modelled (PM<sub>2.5</sub>) and measured (PM<sub>1</sub>) inorganic and organic aerosols as well as EC ( $\mu\text{g m}^{-3}$ ) in Payerne during June 2006.

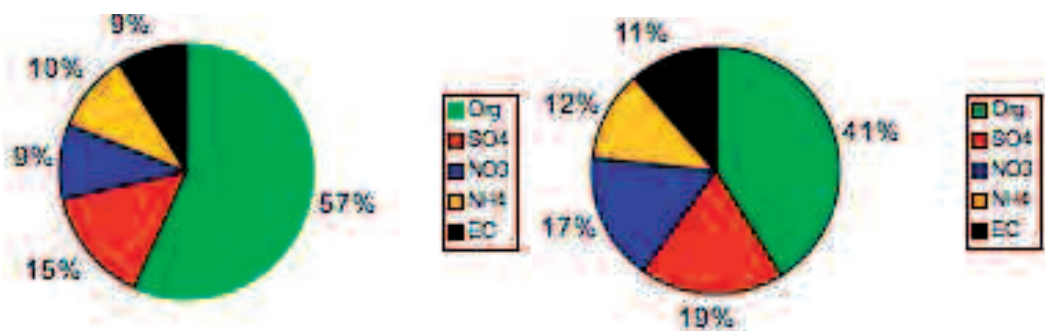


Figure 5. Fractional composition of summer aerosols in Payerne from measurements (PM<sub>1</sub>) (left) and model simulations (PM<sub>2.5</sub>) (right).

#### 4. CONCLUSIONS

In this study, we applied MM5/CAMx model system to Switzerland in winter and summer 2006 to investigate the aerosol components. The results suggest that the meteorological model MM5 can predict the meteorological parameters reasonably well during the studied periods except during low-wind situations. Both measurements and model simulations show that the main components of winter aerosols are particulate nitrate and organic aerosols. The fraction of POA is higher than SOA in Zurich. In summer, organic aerosols dominate the aerosol composition and they are mainly secondary. The comparison of model results with the data from the aerosol mass spectrometer (AMS) measured at Payerne during June 2006 shows an underestimation of organic aerosols. The model results suggest that secondary organic aerosols formed from the biogenic precursors (monoterpenes) can be more important than the SOA produced from the anthropogenic precursors both in winter and summer, although the absolute concentrations are much higher in summer. We are going to continue this work by implementing wood-burning and sesquiterpene emissions, and using a new SOA module including the polymerization mechanism for SOA.



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