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SENSITIVITY OF OZONE AND SECONDARY AEROSOL FORMATION TO EMISSIONS IN SWITZERLAND

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Abstract: We modelled the air quality in Switzerland for summer and winter periods in 2006 using the MM5/CAMx model system. The aerosol module in CAMx version 4.5 has 7 secondary organic aerosol (SOA) classes, including pathways from anthropogenic and biogenic precursors; oligomerization of particles is taken into account as well. Gaseous and particulate pollutant concentrations were compared with detailed gas and aerosol measurements. Several sensitivity studies were performed with modified NO_x, VOC, NH_3 and isoprene emissions. The effects of reduced NO_x and VOC emissions on ozone in summer were different in the north and in the south of Switzerland, indicating that the formation of ozone has different sensitivities to its precursors. Comparison with our earlier studies suggested that ozone sensitivity has changed since 1993: it has become more NO_x-limited. Isoprene emissions were predicted to affect ozone levels especially in the southern part of Switzerland where isoprene is mostly emitted. Inorganic aerosol formation is predicted to be more sensitive to NO_x emissions than NH_3 in the modelled region. Both model results and measurements suggest that organic aerosols dominate the aerosol composition in summer. In winter, particulate nitrate becomes important too. Predicted secondary organic aerosols (SOA) mainly come from biogenic precursors such as monoterpenes and sesquiterpenes. In winter, the primary organic aerosol (POA) fraction was found to be higher than SOA at Zurich in both model predictions (56%) and measurements (59%). In summer, however, POA was overestimated and SOA underestimated indicating the possible volatility of POA that was not taken into account yet in the CAMx model.

Key words: ozone, secondary aerosols, biogenic VOCs, oligomerization, NOx, VOC, NH₃ sensitivity.

INTRODUCTION
PM10 concentrations in Switzerland frequently exceed the legal threshold values (20 µg m^{-3} yearly, 50 µg m^{-3} daily average). Several long-term PM measurements, as well as data obtained from field campaigns, show that the organic portion is most abundant (Lanz *et al.*, 2009). Organic aerosol (OA) is composed of both primary organic aerosol (POA) and oxidized organic material such as secondary organic aerosol (SOA). These particles affect climate forcing and human health, but their sources and evolution remain poorly characterized. New studies indicate that OA and its precursor gases evolve by becoming increasingly oxidized, less volatile, and more hygroscopic, leading to the formation of oxygenated organic aerosol (OOA (mostly interpreted as SOA)) (Jimenez *et al.*, 2009). Analysis of submicron aerosols in Switzerland revealed that only a small fraction of organic aerosols originates from freshly emitted fossil fuel combustion and a high fraction is OOA (Lanz *et al.*, 2007). Modelling organic aerosols is among the most demanding aspects of air quality simulations because the formation processes and evolution are poorly understood. In spite of the recent improvements in air quality models organic aerosols can be underestimated by several orders of magnitude (Hodzic *et al.*, 2009). The recently-developed volatility basis-set approach improved the agreement between organic aerosol model results and AMS (aerosol mass spectrometer) measurements (Robinson *et al.*, 2007; Tsimpidi *et al.*, 2010).

Several PM measurements during January 2006 in Switzerland (Lanz *et al.*, 2008) found exceptionally high aerosol concentrations. Additional measurements within the frame of the European EMEP programme were performed at Payerne in June 2006. These detailed aerosol measurements provide a good opportunity to test the models under different meteorological conditions over the complex terrain of Switzerland. Accordingly, the MM5/CAMx model system was used to simulate the air quality in Switzerland in winter (January) and summer (June) 2006. The study focussed on the importance of biogenic emissions for secondary organic aerosol formation and on the sensitivity of ozone formation to its precursor emissions. These parameters were compared with those obtained in our earlier studies to show the effect of the large emission reductions in the last couple of decades.

METHODS
We used the CAMx (Comprehensive Air Quality Model with extensions) air quality model, version 4.51 (Environ, 2006) to simulate air quality in January and June 2006. The meso-scale model MM5, version 3.7.4 (PSU/NCAR, 2004) was used to generate the meteorological fields for CAMx. Three nested model domains were used in a Lambert Conic Conformal projection to cover a large part of Europe, central Europe and Switzerland with horizontal resolutions of 27 km x 27 km, 9 km x 9 km and 3 km x 3 km, respectively. The MM5 simulations, which used 31 terrain-following σ–levels up to 100 hPa, were initialized by COSMO7 analyses data. The planetary boundary layer (PBL) height was calculated by the Eta PBL option, using the Mellor-Yamada scheme. The CAMx simulations used a subset of 14 of the MM5 σ-layers, of which the lowest had a thickness of about 40 m at a surface pressure of 950 hPa. The model top was set at σ=0.55 which corresponds to a geometric top layer at sea level of about 7000 m. The initial and boundary concentrations for the first domain were adapted from the output of global model MOZART (Horowitz *et al.*, 2003). The photolysis rates were calculated using the TUV photolysis pre-processor (Madronich, 2002). Dry deposition of gases was based on the resistance model of (Wesely, 1989). The CB05 gas-phase mechanism was used (Yarwood *et al.*, 2005). The aerosol species with particle size smaller than 2.5 µm included sulphate, nitrate, ammonium, POA, SOA and elemental carbon. Partitioning of condensable organic gases to secondary organic aerosols was calculated using a semi-volatile equilibrium scheme called SOAP (Strader, 1999). It was assumed that the SOA oligomerized to a non-volatile form with a lifetime of about 1 day (Kalberer *et al.*, 2004). Oligomerization slowly forms organic aerosol oligomers called SOPA (anthropogenic) and SOPB (biogenic). Aqueous sulphate and nitrate formation in cloud water were calculated using the RADM aqueous chemistry algorithm (Chang *et al.*, 1987). Partitioning of inorganic aerosol constituents between the gas and aerosol phases was modelled with ISORROPIA (Nenes *et al.*, 1998).

To harmonize emission data from different sources and reference years, emissions were converted to a common reference year, 2005. The annual emissions and time functions for Europe were provided by the Freie Universität Berlin (FUB) (Builtjes *et al.*, 2002). Emissions in Switzerland were calculated separately. Annual road traffic emission data with a spatial resolution of 250 m and also the spatial distributions of total annual NMVOC emissions from industries and households were both provided by INFRAS (Heldstab and Wuethrich, 2006). Annual NO_x, PM2.5 and PM10 emissions from residential activities, heating, industry, off-road traffic, rail transport and agriculture/forestry on a 200 m resolution as well as ammonia emissions from manure, waste treatment and road traffic were taken from Meteotest. Biogenic emissions were calculated for the CAMx domains using the land use and meteorological data. For each European country the deciduous and coniferous forest fractions were split into different tree species according to (Simpson *et al.*, 1999). Inside Switzerland, the global data were replaced by data of the "Arealstatistik" (100 m resolution) issued by the Federal Office of Statistics (BFS, 1999) and by forest data (1 km resolution) taken from the "Landesforstinventar" (Mahrer and Vollenweider, 1983). About 24% of the Swiss area is covered by forests of which 71% are coniferous. Norway Spruce (picea abies) and fir (abies alba) are the most abundant species (49% and 15% of the trees, respectively). Monoterpenes are the most important biogenic VOC species in Switzerland emitted mainly by the Norway spruce and fir trees. Isoprene, on the other hand, is emitted mostly by oak trees, which cover only 2% of the Swiss forests (mainly in the south). The method for the estimation of biogenic emissions is given in Andreani-Aksoyoğlu and Keller (1995) which has been updated using recent literature data. The emission rates of sesquiterpenes were assumed to be about 10% of those of monoterpenes as estimated by Steinbrecher *et al.* (2009).

RESULTS AND DISCUSSION

Meteorology
The meteorological conditions in January 2006 were analysed and classified using time series of measurements at various meteorological stations in Switzerland together with MM5 results (Andreani-Aksoyoğlu *et al.*, 2009). The temperatures were above zero, wind speed was moderate and there was no precipitation during the first week. The next period was characterized by low wind speed and an extended fog layer over the Swiss Plateau, as well as lower temperatures. Then a warm front arrived causing precipitation, higher wind speed and a rapid temperature increase. Mixed conditions prevailed for the rest of the month. The meteorological model could reproduce wind fields reasonably well for most of the days. Comparison of the vertical profiles of potential temperature predicted by MM5 with those from soundings at Payerne, however, showed that the temperature inversions during the low-wind periods could not be reproduced. The June 2006 summer period was divided into 3 parts. Measurements and model predictions for meteorological parameters and pollutant concentrations matched reasonably well in the first period, which was mostly dry with increasing temperatures and moderate to strong winds. Later, when the wind speed was lower, wind speeds and night temperatures were overestimated. There was some precipitation in the third period.

Ozone
The predicted concentrations of ozone in June 2006 were higher in the south than in the north. The time series indicate good agreement between modelled and measured peak ozone concentrations during the first period, which had moderate and strong winds. In the low-wind period however, peak ozone levels were underestimated. In an earlier study, we found that 50% reductions in NO_x and VOC emissions in 1993 resulted in a NO_x-limited regime in most of the region except downwind of Zurich and around Lake Geneva where ozone formation was predicted to benefit substantially from VOC reductions as seen in Figure 1 (Andreani-Aksoyoğlu *et al.*, 2001). There have been substantial emission reductions both in Switzerland and the surrounding countries since then, so we performed similar sensitivity tests to see if there has been any change in ozone sensitivity to its precursor emissions during the last 13 years. The results of the simulations with emission reductions in June 2006 suggest that ozone sensitivity changed substantially - especially in the north around Zurich. The calculations for 1993 suggested a VOC-limited regime downwind of Zurich and also around Lake Geneva. Ozone formation in those areas seems not to be sensitive to VOC emissions in 2006, however, due to substantial emission reductions since the 1990s.
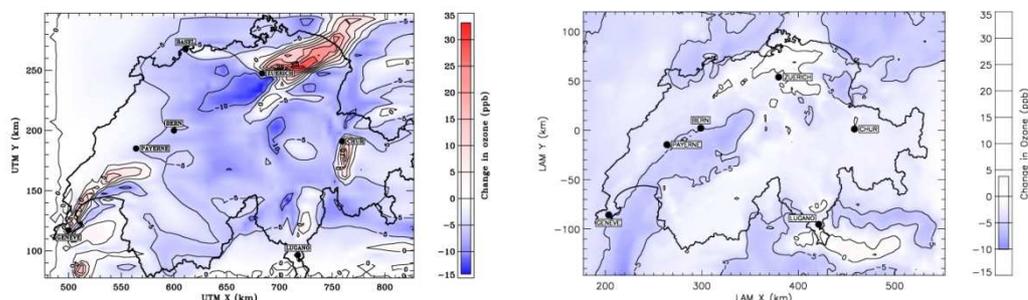
Figure 1: Difference in peak ozone concentrations (ppb) between two simulations with 50% NO_x and VOC emissions. Blue colour indicates NO_x-sensitive, red colour VOC-sensitive regimes. July 1993 (left) adapted from (Andreani-Aksoyoğlu *et al.*, 2001), June 2006 (right).

The time series of changes in ozone concentrations due to 30% reduction of NO_x and VOC emissions in June 2006 are shown in Figure 2 for three different locations. Payerne is a rural site in the Swiss Plateau. Ozone concentrations are affected only by NO_x reductions at this site. The reductions in VOC emissions do not affect ozone levels significantly at Zurich. Ozone concentrations increase at night when NO_x emissions are reduced indicating less titration with NO, which is typical for urban

areas. This effect disappears on weekends (3-4, 10-11, 17-18, 24-25 June 2006), reflecting the different NO_x/VOC ratios then. Lugano is an urban site in the south of the Alps. At this location, ozone concentrations are affected by changes in both VOC and NO_x emissions and the sensitivity to these emissions varies with the meteorological conditions.

Isoprene is an important biogenic precursor for ozone formation. As noted earlier, isoprene emissions in Switzerland are relatively low. Since uncertainties in biogenic VOC emissions are high, we investigated the sensitivity of ozone to isoprene emissions in our model domain. Increasing isoprene emissions substantially (20x) leads to an increase in ozone concentrations of only about 5 ppb in the Swiss Plateau because of very low isoprene emissions in that region. However, it causes an increase of up to 20 ppb in the south where more isoprene is emitted by oak forests. The effect on ozone is higher on warmer days.
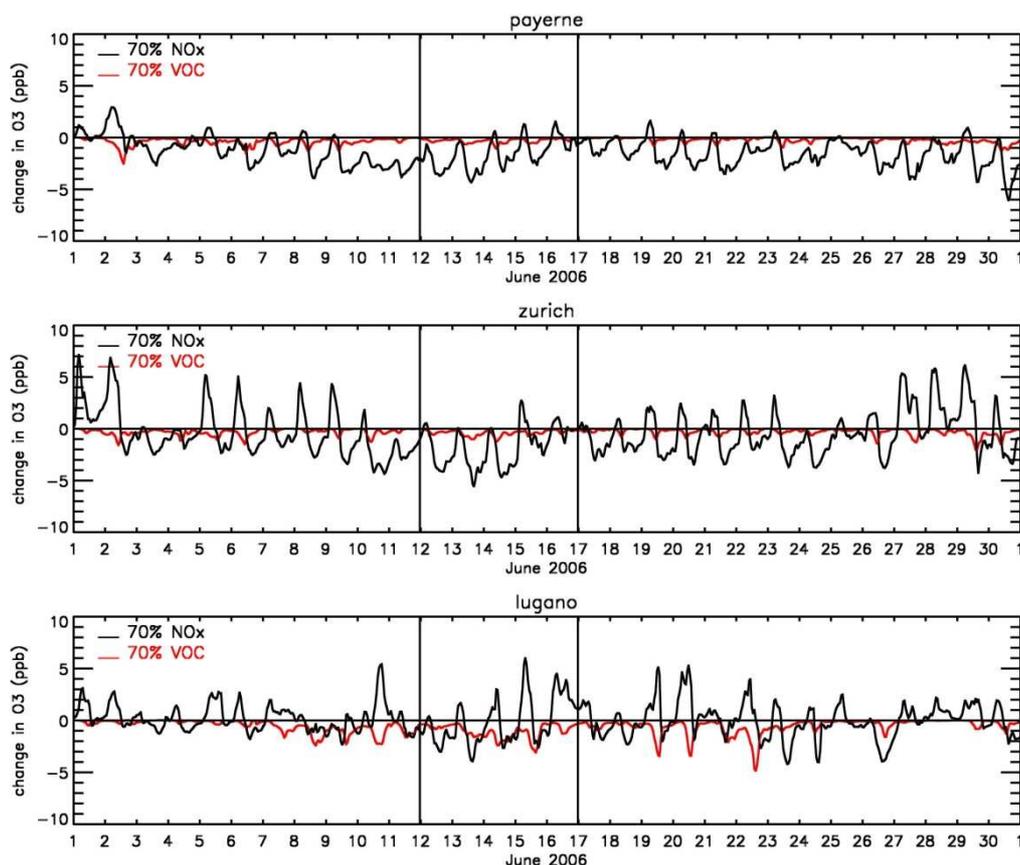
Figure 2: Change in ozone concentrations (ppb) due to 30% reductions in NO_x and VOC emissions in June 2006 in Payerne (rural), Zurich (urban background, north) and Lugano (urban, south).

Aerosols

Modelled PM2.5 refers to the sum of primary aerosol (elemental carbon (EC) and primary organic aerosol (POA)) and secondary inorganic (particulate nitrate, sulphate, ammonium), as well as secondary organic aerosol (SOA). The model predictions for PM2.5 were compared with the available aerosol mass spectrometer (AMS) measurements in both winter and summer episodes. Model results and measurements were similar during the high-wind periods whereas model results were lower than measurements during the low-wind periods. Both measurements and model results suggest that the main aerosol components in winter are particulate ammonium nitrate and organic aerosols. On the other hand, organic aerosol dominates the particle composition in summer. The absolute concentrations of measurements and model predictions are similar in high-wind periods, but they differ by about a factor of two in low-wind periods.

The sensitivity of inorganic aerosol formation to NO_x and NH_3 emissions was tested by reducing each of these emissions by 50%. The results suggest that aerosol formation was more sensitive to NO_x emissions. The highest organic aerosol concentrations were measured in January 2006 during the low-wind period at Zurich (Figure 3, period II). In winter, both model predictions and data from factor analysis of AMS data (FA-AMS) suggest a higher fraction of OA is primary (POA) (model 56%, FA-AMS 59%). In summer, the secondary fraction is higher (model 69%, FA-AMS 94%). SOA/POA fractions were predicted well for the winter episode, but were lower compared to FA-AMS data in summer. This indicates the possible effect of POA volatility, which is not yet taken into account in the model. The model results suggest that SOA comes mainly from biogenic VOCs. The fractional compositions of modelled SOA for both episodes are shown in Figure 4. In general, SOA was formed from monoterpenes, sesquiterpenes and oligomerization of particles. In winter periods, the fraction of SOA from monoterpenes is higher; in summer sesquiterpenes lead to more SOA formation. In CAMx, SOA from sesquiterpenes is not allowed to partition back to the gas phase at higher temperatures, while monoterpene SOA does partition to the gas phase at higher temperatures, leading to lower fractions in the summer.
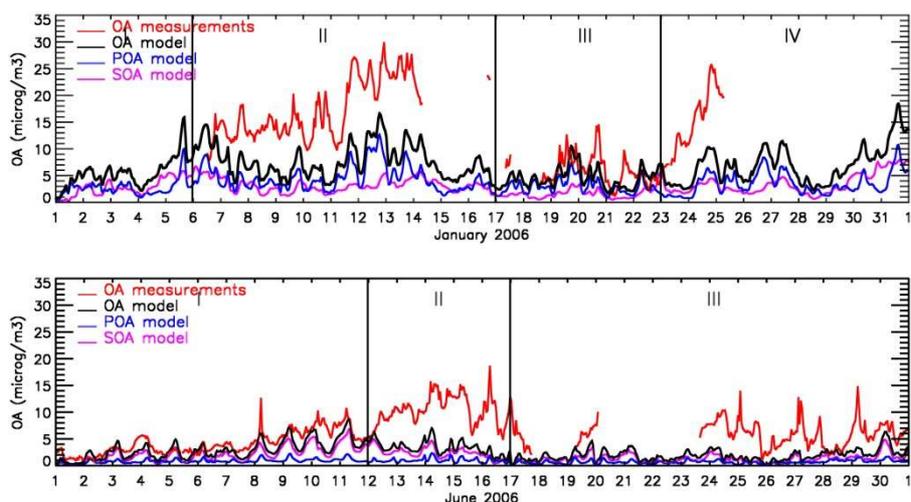
Figure 3: Comparison of modelled and measured organic aerosols as well as modelled POA and SOA in Zurich, January 2006 (top) and in Payerne, June 2006 (bottom).
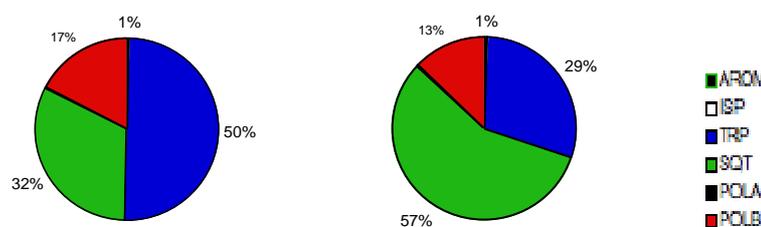
Figure 4: Fractional composition of modelled SOA in Zurich in January 2006 (left) and in Payerne in June 2006 (right). AROM: aromatic precursors, ISP: isoprene, TRP: monoterpenes, SQT: sesquiterpenes, POLA: polymerized anthropogenic SOA, POLB: polymerized biogenic SOA.

CONCLUSIONS

The air quality in Switzerland was modelled with the regional air quality model CAMx for summer and winter periods in 2006 under different meteorological conditions and several sensitivity tests were performed. Changes in isoprene emissions seem to affect ozone formation only in the southern part of Switzerland because of their very low emissions in the other regions. Comparison of model results with our earlier studies suggests that the sensitivity of ozone formation to precursor emissions might have changed since the 1990s. Ozone sensitivity in urban areas especially around Zurich seems to have shifted from a VOC-sensitive towards a more NO_x-sensitive regime due to large emission reductions in the last two decades.

Both measurements and model predictions suggested that the organic fraction of the aerosol phase was the most abundant; in winter particulate nitrate contributed significantly to the aerosol composition as well. Sensitivity tests with reduced NH_3 and NO_x emissions indicate that inorganic aerosol formation is mainly limited by NO_x emissions. In summer, organic aerosols, which were mainly SOA, dominated the aerosol composition. The contribution of the biogenic emissions to the SOA formation in the region was predicted to be very large and to stem mainly from monoterpenes and sesquiterpenes as well as oligomerization of SOA particles. Predicted POA and SOA fractions in Zurich in January 2006 were 56% and 44%, respectively, which agreed well with the FA-AMS data (59% and 41%, respectively). In summer, however, POA was higher and SOA lower compared to the FA-AMS data at the Payerne rural site, because the POA volatility is not taken into account in the CAMx model. Modelling of organic aerosols will be further investigated in the future using the volatility basis approach.

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