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3-DIMENSIONAL MODELING OF GASEOUS AND PARTICULATE POLLUTANTS IN SWITZERLAND

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ABSTRACT

An exceptionally hot and dry period in August 2003 was simulated using the 3-dimensional CAMx air quality model. The formation and transport of ozone and secondary aerosols were evaluated. Simulations suggest that the speed reduction of vehicles from 120 km h^{-1} to 80 km h^{-1} on the highways in Switzerland would have a small effect (1 %) on peak ozone concentrations. However, it should be noted that the NO_x and primary particle concentrations would decrease leading to an additional improvement of the air quality. The secondary aerosols such as particulate nitrate, sulfate, ammonium and secondary organic aerosols (SOA) smaller than 2.5 μm were calculated for the same period. The modelled secondary aerosol mass concentrations in Switzerland, averaged over the entire period vary between 5 - 8 μg m^{-3} depending on location. In southern Switzerland higher concentrations were predicted. The contribution of biogenic sources to SOA is quite high (around 70%) in the north whereas it is relatively lower in southern Switzerland (40%). These results agree well with findings from measurements. Importance of initial and boundary conditions were also discussed. Model results suggest that enough ammonia exists to neutralize sulphate and then to produce ammonium nitrate in the northern part of the domain. Sensitivity test using reduced NH_3 and NO_x emissions suggest that secondary aerosol formation is unlikely to be limited by NH_3 in northern Switzerland but rather by HNO_3. On the other hand, aerosol formation in the region of Milan was predicted to be limited by NH_3.

Key Words : Air Quality Modeling, Aerosols, Ozone, SOA, CAMx, MM5

1. INTRODUCTION

The exceptionally hot and dry summer in 2003 led to ozone levels exceeding the ambient air quality standards in many parts of Europe (Buwal, 2003). The long heat wave during the first half of August caused severe health problems especially in western Europe. As an emergency action to reduce ozone levels in southern Switzerland, the speed limit on some highways in Canton Ticino and in Canton Graubünden was reduced from 120 km h^{-1} to 80 km h^{-1} during one week. However, it was not possible to assess the effectiveness of the speed limit reduction due to the cold front arrived in the south towards the end of that period. In the first part of this modeling study, we investigated the effectiveness of speed reduction to reduce ozone levels.

In the second part of the study, we modelled secondary aerosols. Although formation of gaseous pollutants such as ozone is well known, there is still a lack of knowledge about aerosol formation, especially about the formation of secondary organic aerosols (SOA). But also little is known about the concentrations of inorganic aerosols in Switzerland. Gehrig and Buchmann (2003) evaluated the long-term PM2.5 and PM10 (particles smaller than 2.5 and 10 μm in diameter, respectively) measurements at various sites in Switzerland. The chemical composition of atmospheric PM on the other hand, was investigated by Hueglin et al. (2005). The legal threshold for yearly average is 20 μg m^{-3} for PM10 in Switzerland. As a short-term threshold, the concentration averaged over 24 hours may exceed 50 μg m^{-3} only once a year. PM10 concentrations in Switzerland frequently exceed the limit values especially in the south of the Alps. Although the health relevant particles are probably those with smaller sizes (< 1 μm or < 2.5 μm), at present there is no ambient air quality standard for PM1 or PM2.5 in Switzerland. Understanding the partitioning behavior of semi-volatile species between the gas and aerosol phases can help us predict how changes in anthropogenic and biogenic activity will influence formation of aerosols in the atmosphere. With this understanding, appropriate control strategies could be developed. However, applications of aerosol models are partly limited due to lack of speciated aerosol measurements with high time and space resolution. Most of the aerosol model applications have been performed in the United States and Canada (Held et al. 2004; Yin et al. 2004). There are very few applications in Europe (Bessagnet et al. 2004; Cousin et al. 2005). Aerosols have been introduced as air quality indicators through PM10 and in the near future PM2.5 will be introduced. In view of the forthcoming European legislation on particles, air quality simulations including aerosol processes are urgently needed. Although some 3-dimensional modeling studies were conducted for ozone in Switzerland (Andreani-Aksoyoglu et al. 2001; Kuebler et al. 2002) there is hardly any model study on PM yet (Andreani-Aksoyoglu et al. 2003). In this study, the secondary aerosols such as particulate nitrate, sulfate, ammonium and secondary organic aerosols (SOA) were calculated for the particle size smaller than 2.5 μm, for the same period as described in the first part.

2. MODELLING METHOD

A period between 4 and 7 August 2003 was simulated using the 3-dimensional CAMx (Version 4.11s) air quality model with 2 nested domains (Environ, 2004). The size of the coarse domain was 35 grid cells in the east-west direction and 29 grid cells in the north-south direction with a resolution of 27 km x 27 km. The fine domain contained 68 and 50 grid cells in the east-west and north-south direction, respectively, with a resolution of 9 km x 9 km. There were 10 σ-layers in a terrain-following Lambert Conic Conformal coordinate system, the first being about 30 m above ground. The fine domain covered Switzerland and some part of the surrounding countries including the greater Milan area. Meteorological data such as 3-dimensional wind fields, temperature, pressure, water vapour, vertical diffusivity, and clouds/rainfall were calculated by the MM5 meteorological model (PSU/NCAR, 2004). MM5 was initialized by data of the Alpine Model (aLMo) of MeteoSwiss. The four dimensional data assimilation was conducted using surface measurements,

balloon soundings and aLMo upper level data. The emission inventory was prepared by compiling European and Swiss anthropogenic emissions from various data sources. Using land use and meteorological data, biogenic emissions were calculated by means of temperature and irradiance dependent algorithms. Initial and boundary conditions were obtained from the European model REM-3/CALGRID output. Calculations of aerosols smaller than 2.5 μm were performed with the fine/coarse option of the aerosol module. Primary particle emissions were not considered due to the lack of a particle emission inventory. The sensitivity of aerosol formation to ammonia and nitric acid was studied by performing two simulations where NH_3 and NO_x emissions were reduced by 50 %, respectively.

3. RESULTS AND DISCUSSION

3.1 Ozone

The highest ozone mixing ratios in the lowest layer were predicted generally in the afternoon around 15:00 UTC. As seen in Figure 1, highest levels were predicted around Lugano, in southern Switzerland under the influence of southerly winds with polluted Po Basin air (see Figure 2 for the wind fields). The comparison of the model predictions and measurements is given in detail elsewhere (Keller et al. 2004).

One of the short-term measures to reduce ozone levels discussed during that hot period in 2003 was to decrease the speed limit on the highways. We investigated the effect of such emission reductions on ozone in a scenario case. In this scenario, the maximum speed limit on the Swiss highways was reduced from 120 to 80 km h^{-1} and corresponding emission rates were used in the model simulations. The decrease in NO_x emissions due to this kind of speed reduction is about 4% of the total Swiss NO_x emissions. On the other hand, VOC emissions are not significantly affected. The effect of speed reduction on ozone is small, less than 1% in the afternoon (Figure 3). The main reason for this low number is the fact that the homemade fraction of ozone due to Swiss emissions is around 25%. It should be noted that the NO_x concentrations and the primary particle concentrations would also decrease in such a scenario. This leads to a relief in addition to the small ozone reduction during these summer smog conditions. The effect on primary aerosols cannot be evaluated in this study due to the lack of primary particle emissions. We conclude that the local and short-term emission reductions are not large enough to reduce ozone levels effectively. Long-term emission developments in Switzerland as well as in the surrounding countries are more important.

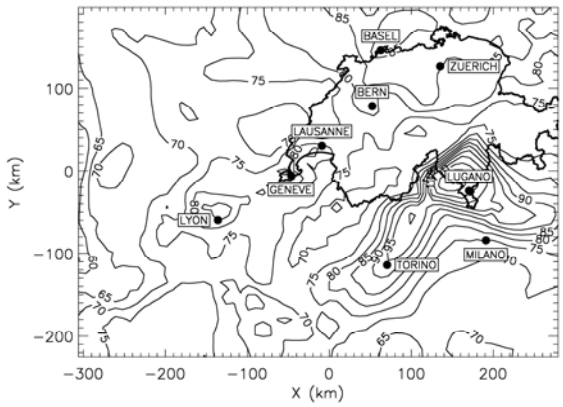

Figure 1. Modelled O_3 mixing ratios (ppb) in the fine domain on 5 August 2003, at 14:00-15:00 UTC.

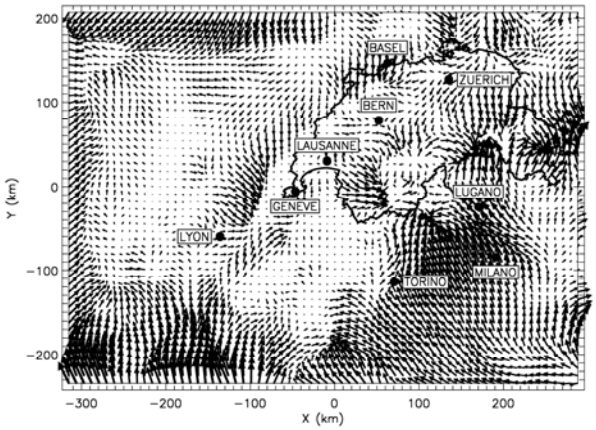

Figure 2. Modelled wind fields in the fine domain on 5 August 2003, at 14:00-15:00 UTC.

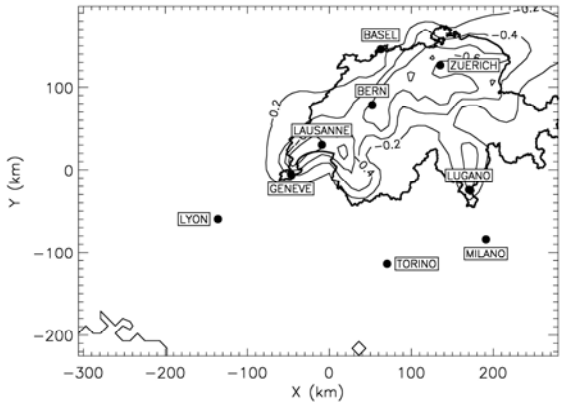

Figure 3. Predicted change in O_3 mixing ratios (%) due to speed limit reduction in the fine domain on 7 August 2003, at 13:00-14:00 UTC.

3.2. Secondary Aerosols

As seen in Figure 4, the highest afternoon secondary aerosol mass concentrations were predicted in the south. The modelled secondary PM2.5 concentrations averaged over the entire period vary between 5-8 μg m^{-3} in Switzerland. The diurnal variations of predicted individual particulate species show a good correlation between ammonium (blue) and nitrate (red) concentrations at locations in the north such as Zurich and Taenikon (east of Zurich), whereas sulfate (green) levels remain almost constant, around 2-3 μg m^{-3} (Figure 5). These results suggest that in northern Switzerland, enough ammonia exists to neutralize sulfate and then to produce ammonium nitrate. On the other hand, at the southern site Lugano, nitrate levels are very low and the correlation between sulfate (green) and ammonium (blue) indicate the deficiency of ammonia to produce ammonium nitrate in the south. Around Milan, aerosol concentrations are higher than in Switzerland. The average secondary PM2.5 during the period studied is about 15 μg m^{-3}. Especially sulfate concentrations are higher than those in the north.

Calculations suggest that the contribution of biogenic SOA to total SOA is quite high, about 70% in the north on average over the entire period (see Figures 6 and 7). These results are in a good agreement with measurements including particulate ^{14}C analysis in Zurich (Szidat et al. 2004). The high biogenic contribution is due to the high monoterpene emissions from Norway Spruce trees. On the other hand, biogenic contribution to SOA is relatively lower in the south, for example 40% in Lugano and about 23 % around the polluted area of Milan. Unfortunately there is no speciated aerosol measurements during the period we studied. We compared therefore our results with ambient aerosols measured in summer 2002 in Zurich (Szidat et al. 2004). Measurements cover 4 periods between 16 August and 8 September 2002 (Table 1). Model predictions in general, are in the same range as the measurements. The high biogenic contribution is also in a good agreement with measurements.

Initial and boundary conditions (IC and BC, respectively) used in the model simulations may have significant effects on the results. In order to check for these effects, three more simulations using different IC and BC values were carried out in addition to the base case. As seen in Table 2, in the first case, very low values (1.10^{-9} μg m^{-3}) were used for particles in IC and BC files and they were constant in time and space. In the second case, annual means of long-term measurements given by Hueglin et al. (2005) were used. In the third case REM3/CALGRID output was used, but as constant in time and space. The last case (set 4) is the base case where IC and BC were taken from REM3/CALGRID output and the data is variable in time and space. Results of these tests are shown in Figure 8 for Lugano (south) and Zurich (north). It is clearly seen that use of constant values from measurements (set 2, red) and models (set 3, green) lead to overestimation. On the other hand, results of simulations using space and time invariant, but very low particle concentrations (set 1, blue) are closer to the base case where IC and BC were taken from the REM3/CALGRID output and variable in time and space. These results indicate the importance of IC, BC definition in model simulations.

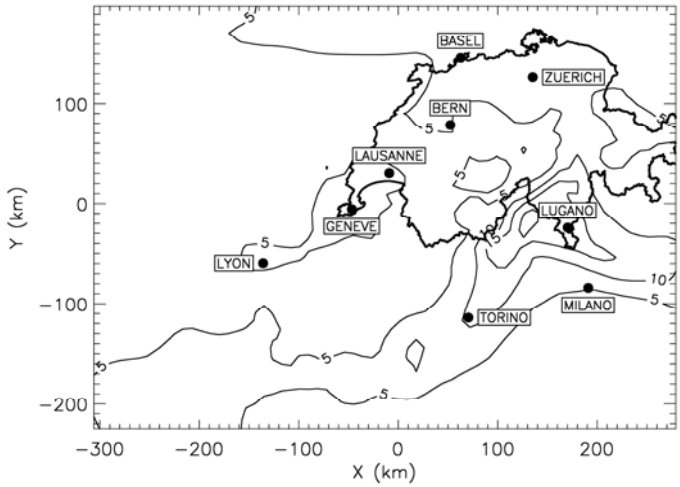

Figure 4. Modelled secondary PM2.5 aerosol mass concentrations (μg m^{-3}) on 5 August, 2003, 14:00-15:00 UTC.

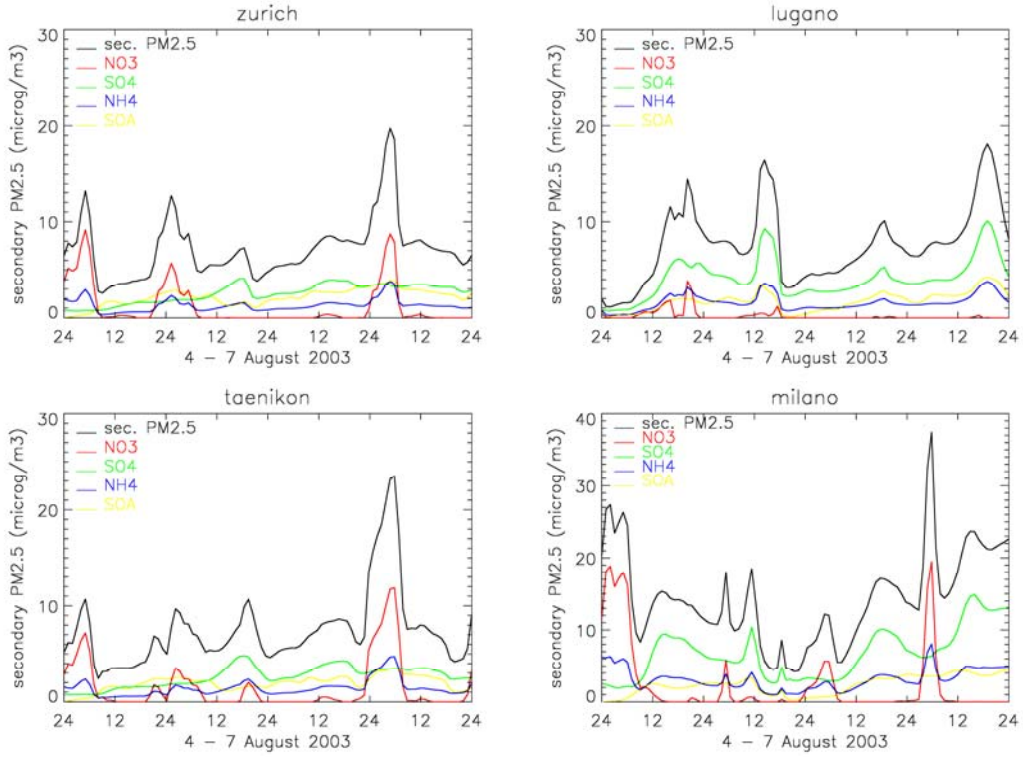

Figure 5. Diurnal variation of modelled particulate nitrate, sulfate, ammonium, secondary organic aerosols and the total secondary PM2.5 particles (μg m^{-3}) in Zurich (urban, north), Lugano (urban, south), Taenikon (suburban), Milan (urban, Italy).

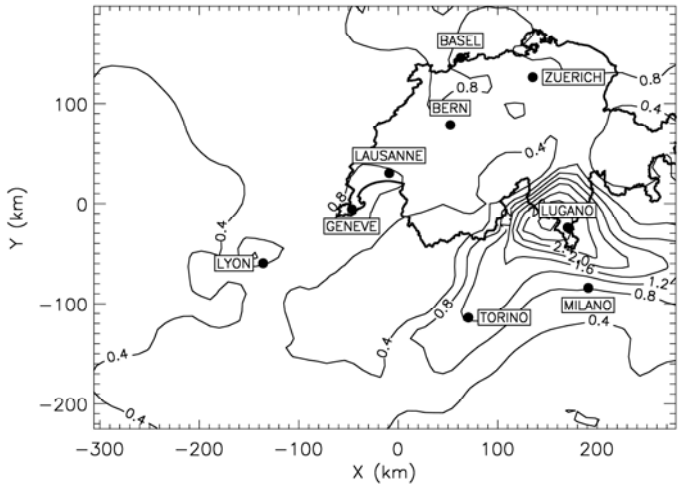

Figure 6. Modelled anthropogenic SOA (PM2.5) concentrations (μg m^{-3}) on 5 August, 2003, 14:00-15:00 UTC.

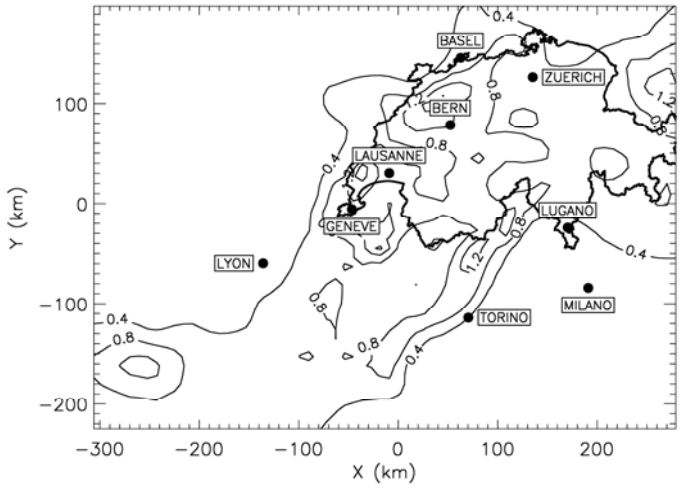

Figure 7. Modelled biogenic SOA (PM2.5) concentrations (μg m^{-3}) on 5 August, 2003, 14:00-15:00 UTC.

Sensitivity tests using reduced NH_3 and NO_x emissions suggest that secondary aerosol formation is unlikely to be limited by NH_3 in northern Switzerland as seen in Figure 9, but rather by HNO_3 (therefore by NO_x emissions). The blue color in the figure indicate the HNO_3 sensitive areas over the Swiss Plateau, especially around Zurich. On the other hand, aerosol formation in the southern part of Switzerland and northern Italy was predicted to be limited by NH_3. However, such sensitivity analyses strongly depend on NH_3 emissions which have high uncertainties.

Table 1. Comparison of model results with measurements in Zurich (Szidat et al., 2004).

species	measurements 16 Aug. - 8 Sept. 2002	model predictions 4 – 7 Aug. 2003
SO_4 (μg m^{-3})	1.6 – 4.8	1.1 – 3.3
NO_3 (μg m^{-3})	0.5 – 2.0	0.1 – 2.3
NH_4 (μg m^{-3})	0.7 – 2.3	1.1 – 1.7
SOA (μg m^{-3})	1.0 – 3.1	1.3 – 2.9
Biogenic SOA (%)	65 - 82	60 - 67

Table 2 . Model runs with various IC (initial conditions) and BC (boundary conditions)

Run	IC, BC	Variability in time and space
Set 1	low default values given in CAMx	constant
Set 2	NO_3, SO_4, NH_4, EC from Hüglin et al. (2005)	constant
Set 3	NO_3, SO_4, NH_4, EC from REM3/CALGRID output	constant
Set 4 (base case)	NO_3, SO_4, NH_4, EC from REM3/CALGRID output	variable

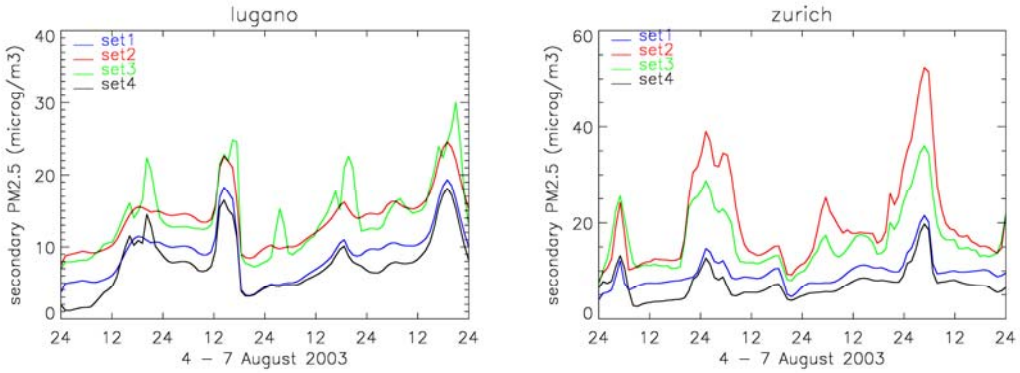

Figure 8. Sensitivity of modelled secondary aerosols to IC and BC. Description of various cases is given in Table 1. Set 4 (black) corresponds to base case.

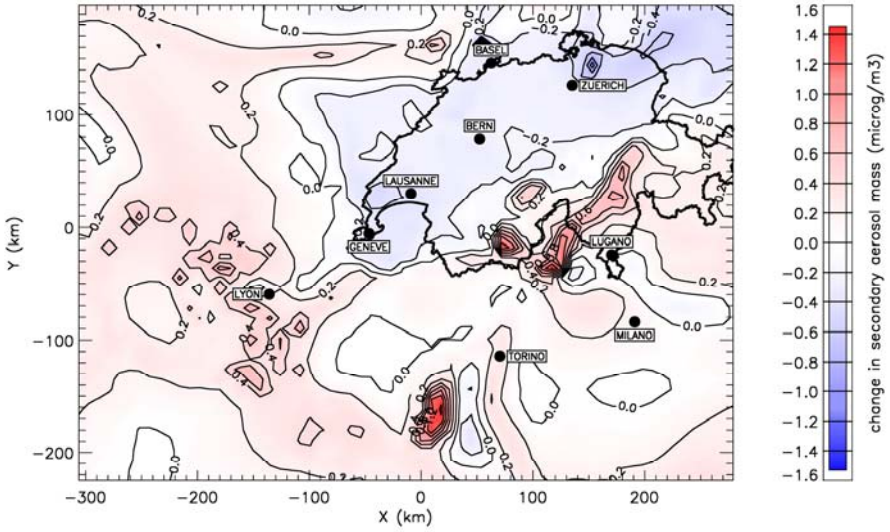

Figure 9.: Sensitivity of secondary aerosol formation to HNO_3 and NH_3 on 5 August 2003, 14:00-15:00 UTC. This figure shows the difference of two simulations with 50% reduction of NO_x and NH_3 emissions. Blue colour indicates HNO_3 sensitive and red indicates NH_3 sensitive areas.

4. CONCLUSION

The formation and transport of ozone and secondary aerosols were simulated by a three-dimensional air quality model during an exceptionally hot and dry period in August 2003. The influence of the traffic speed reductions from 120 km h^{-1} to 80 km h^{-1} was predicted to be low, about 1 %. Although the speed reduction in Switzerland for a short period of time is not enough to reduce ozone levels significantly, it should be noted that the NO_x and primary particle concentrations would decrease in such a traffic scenario. The predicted secondary PM2.5 mass concentrations are higher in southern Switzerland and model results are in a reasonable agreement with measurements. Sensitivity tests showed that initial and boundary conditions have a strong influence on the modelled particle concentrations. Results suggest that there is enough NH_3 in the northern part of Switzerland and therefore aerosol formation is rather limited by HNO_3. On the other hand, aerosol formation in southern Switzerland and northern Italy was predicted to be more sensitive to NH_3. The model results show a high contribution of biogenic sources (about 70%) to SOA formation in the northern part of Switzerland. This result is in agreement with the values obtained in another study using ^{14}C measurements for the source apportionment in Zurich. On the other hand, the biogenic contribution to SOA is relatively lower, about 40% in the south.

5. ACKNOWLEDGEMENTS

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