

Secondary aerosols in Switzerland and northern Italy: Modeling and sensitivity studies for summer 2003

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[1] The formation and transport of secondary aerosols during a 4-day period in summer 2003 were studied using the 3-dimensional air quality model CAMx (Comprehensive Air quality Model with eXtensions) over an area covering regions north and south of the Swiss Alps with different air pollution characteristics. The modeled components were particulate sulfate, nitrate, ammonium, primary (POA) and secondary organic aerosols (SOA) and elemental carbon (EC) with a particle diameter smaller than 2.5 μm . Highest concentrations were predicted in northern Italy. The modeled sum of particle mass concentrations was in general lower than PM_{2.5} measurements most probably due to an underestimation of organic aerosols. Differences between the regions in the north and the south of the Alps are discussed with respect to the aerosol concentrations and to the sensitivity of aerosol formation. Sensitivity tests using reduced NH₃ and NO_x emissions suggest that in northern Switzerland secondary aerosol formation is unlikely to be limited by NH₃ but rather by HNO₃. On the other hand, aerosol formation around Milan seems to be similarly dependent on HNO₃ and NH₃ most of the time. However, there are times when limitation by NH₃ is stronger. The contribution of biogenic sources to SOA was predicted to be rather high, about 80% in the north, matching the measurements whereas it was lower in southern Switzerland (40%).

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1. Introduction

[2] Atmospheric aerosols are known to have adverse health effects. In addition, they play an important role in climate change by modifying the radiative balance of the atmosphere [IPCC, 2007]. The legal threshold for the yearly average for PM₁₀ (particles smaller than 10 μm in aerodynamic diameter d) is 20 $\mu\text{g}/\text{m}^3$ in Switzerland. As a short-term threshold, the concentration averaged over 24 h may exceed 50 $\mu\text{g}/\text{m}^3$ only once a year. PM₁₀ concentrations in Switzerland frequently exceed the threshold values, especially south of the Alps. The health relevant particles are considered to be those with smaller sizes ($d < 1 \mu\text{m}$ or $d < 2.5 \mu\text{m}$). However, at present there is no ambient air quality standard for PM₁ or PM_{2.5} in Switzerland. While the formation of gaseous pollutants such as ozone is well known, there is still a lack of knowledge about aerosol formation. Gehrig and Buchmann [2003] evaluated the long-term PM_{2.5} and PM₁₀ measurements at various Swiss sites. The chemical composition of atmospheric PM was

investigated by Hueglin *et al.* [2005] showing that organic matter, sulfate and nitrate are the main contributors to the annual PM_{2.5} mass concentration at rural, near-city and urban background sites. At kerbside sites, organic matter (30%) and elemental carbon (17%) are the two main contributors while inorganic aerosols all together contribute around 30% to the annual aerosol concentration. The authors also showed that nitrate levels were much lower in summer than in winter. Recently, Lanz *et al.* [2007] characterized submicron ambient aerosol in summer 2005 at an urban background site in Zurich using positive matrix factorization (PMF) for aerosol mass spectrometer (AMS) data. The authors concluded that only a small (<10%) fraction of organic PM originates from freshly emitted fossil fuel combustion while other primary sources contribute with similar or higher importance such as charbroiling (10–15%) and wood burning (10%) and food cooking (6%). A high fraction (60–69%) of the measured organic aerosol mass was shown to be oxygenated organic aerosol (OOA) which was interpreted mostly as secondary organic aerosol (SOA).

[3] Understanding the partitioning behavior 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

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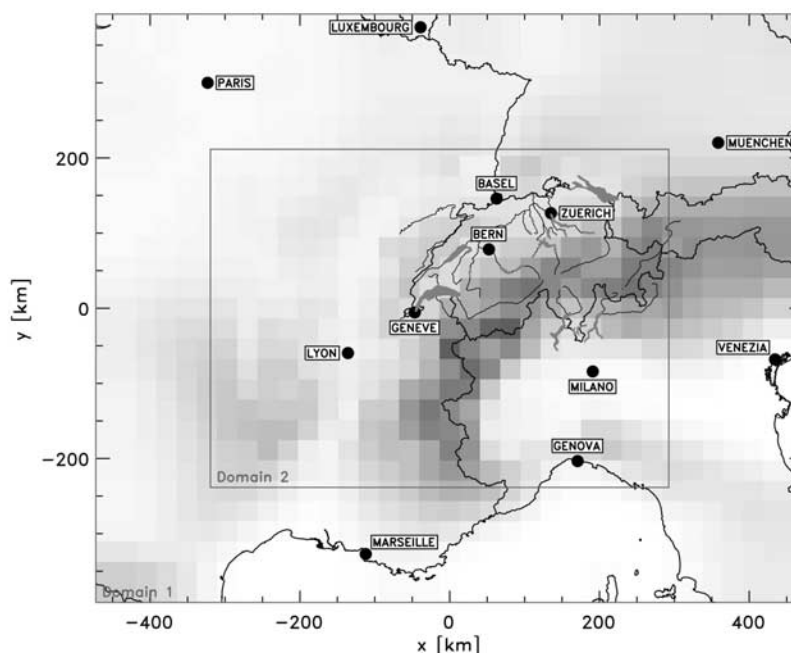


Figure 1. Coarse and fine domains over the topography.

atmosphere. With this understanding, appropriate control strategies can be developed.

[4] In recent years several air quality models have been upgraded to include aerosol dynamical processes such as coagulation, nucleation, evaporation, and condensation [Schell *et al.*, 2001; Hass *et al.*, 2003]. More recently, a transition from bulk to size-resolved treatment of aerosol microphysics and chemistry has been undertaken to better account for aerosol processes [Zhang *et al.*, 2004; Held *et al.*, 2004]. Modeling secondary organic aerosol (SOA) formation is among the most demanding aspects associated with atmospheric organic photo oxidation because the formation process depends on (a) the representation of the parent organic species that lead to condensable products after being oxidized, (b) the gas-phase chemistry where condensable species are formed, and (c) the representation of the gas/particle partitioning process of the condensable compounds. The temperature dependence of SOA formation is another key point of uncertainties affecting models. The current models often underestimate SOA concentrations [Zhang *et al.*, 2004; Cousin *et al.*, 2005]. 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 that are not treated yet in current models, such as polymerization, SOA formation from isoprene and sesquiterpenes, led to increased SOA yields.

[5] Applications of aerosol models are partly limited due to the lack of speciated aerosol measurements at high temporal and spatial resolution. Most of the aerosol model applications have been performed in the United States and Canada [Held *et al.*, 2004; Yin *et al.*, 2004]. In Europe, there are relatively few applications [Bessagnet *et al.*, 2004;

Cousin *et al.*, 2005]. In Switzerland which has a very complex terrain, some 3-dimensional modeling studies were conducted for ozone [Kuebler *et al.*, 2002; Andreani-Aksoyoglu *et al.*, 2001]. However, there is hardly any model study on aerosols yet [Andreani-Aksoyoglu *et al.*, 2003]. For the region south of the Alps around Milan, most of the studies have concentrated on ozone or trace gases like VOCs, NO₂, and formaldehyde [Nefel *et al.*, 2002; Martilli *et al.*, 2002; Steinbacher *et al.*, 2005; Liu *et al.*, 2007; Ordonez *et al.*, 2006]. It was found that this region is one of the most polluted areas in Europe due to the high emissions but also due to the meteorological features of the Po valley that might be rather called the Po basin because of its topography and the related meteorology. Important for the study here were the findings concerning the strongly VOC sensitive ozone production of the Milan ozone plume for a large range of meteorological conditions [Baertsch-Ritter *et al.*, 2004]. In the last years, studies on particulate matter are also getting into the focus because of the very high concentrations in this area [Baltensperger *et al.*, 2002; Andreani-Aksoyoglu *et al.*, 2004; Putaud *et al.*, 2002; Lonati *et al.*, 2007]. This study provides an insight into spatial differences of aerosol formation and composition in the north and the south of the Alps. In view of the forthcoming European legislation on particles, air quality simulations including aerosol processes would be helpful.

2. Model Description

2.1. Model Setup

[6] In this study, the 3-dimensional photochemical model CAMx (Comprehensive Air Quality Model with Extensions, version 4.11 s) was used with 2 nested domains [Environ, 2003]. The coarse domain is 945 km × 783 km with a resolution of 27 km × 27 km (Figure 1). The fine domain contains 68 and 50 grid cells in the east-west and

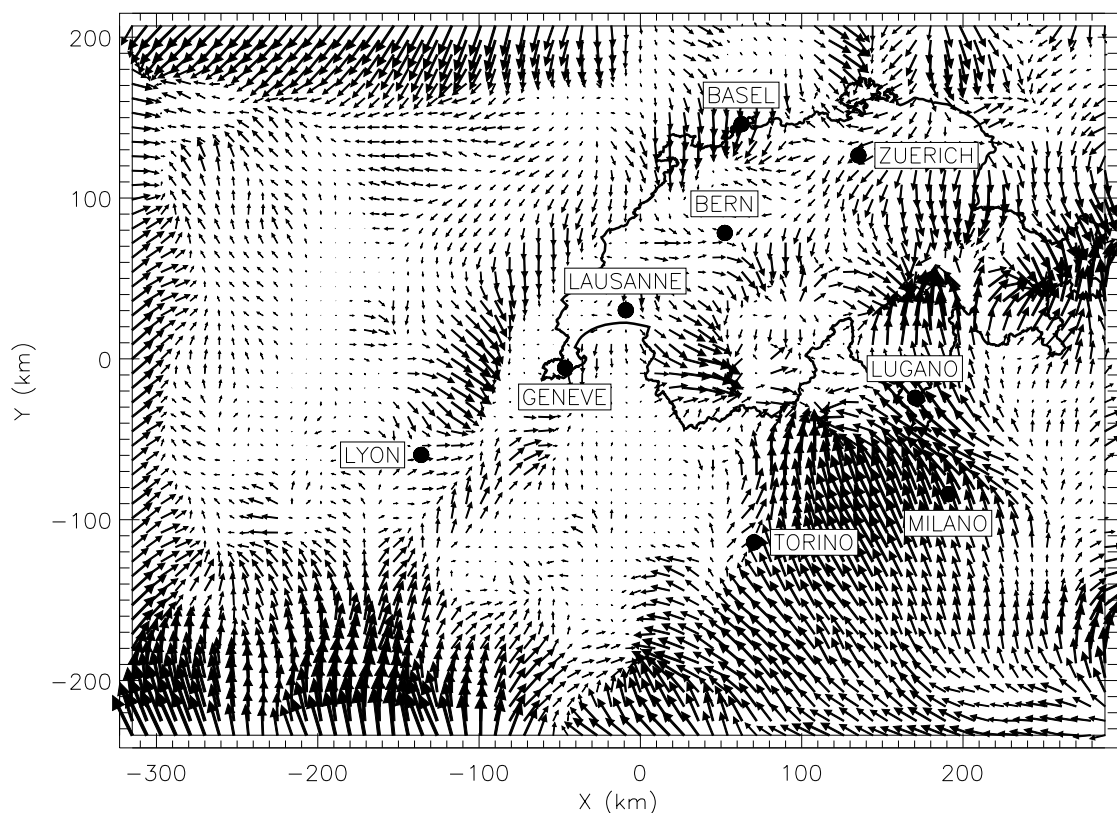


Figure 2. Wind fields over the fine domain on 5 August 2003, 1500 UTC. Maximum speed is 8 m/s.

north-south direction, respectively, with a resolution of $9 \text{ km} \times 9 \text{ km}$, covering all Switzerland and parts of the surrounding countries including the greater Milan area. There are 10 σ -layers in a terrain-following coordinate system, the first being about 40 m above ground. The coordinate system used in this study is the Lambert Conic Conformal system. The model top corresponds to about 550 hPa. Simulations started on 4 August 2003 at 0000 UTC and ended on 7 August at 2400 UTC. Meteorological data such as 3-dimensional wind fields, temperature, pressure, water vapor, vertical diffusivity, clouds and rainfall were calculated by the MM5 meteorological model [PSU/NCAR, 2004]. MM5 was initialized by assimilated data of the Alpine Model (aLMO) of MeteoSwiss. The four-dimensional meteorological data assimilation was conducted using surface measurements, balloon soundings and aLMO upper level data. Weather conditions during the 4–6 August period were characterized by a low-pressure gradient over Central Europe. A persistent anticyclone was located over the North Sea, and weak cyclonic regions over the Alps. On 7 August the pressure field flattened. The MM5 output is similar to the aLMO analysis at locations far from surface stations. Southern Switzerland, around Lugano was under the influence of southerly winds bringing polluted air from the Po Basin as often observed in this area [Nefel *et al.*, 2002; Thielmann *et al.*, 2002]. The wind speed on 5 August was stronger than on the other days (Figure 2). The wind direction north of the Alps, on the other hand, changed from west to north during the studied period.

[7] The emission inventory was prepared by compiling European and Swiss anthropogenic emissions from various

data sources similarly as Keller *et al.* [2008]. The annual emissions and time functions for Europe were provided by the Freie Universitaet Berlin (FUB). For the grid cells located in Switzerland, emissions were replaced by the Swiss data. Factors for each SNAP (Selected Nomenclature for Air Pollution) category to convert VOCs to CBM-IV species were provided by TNO in the Netherlands. For Switzerland, the seasonal dependence of residential and industrial emissions, the weekly variation of industry, and the diurnal patterns of residential, industrial and road traffic emissions were provided by INFRAS (<http://www.infras.ch>). The spatial resolution is 250 m and the reference year is 2000. Ammonia emissions from manure, waste treatment and road traffic were provided by Meteotest (<http://www.meteotest.ch>) for the year 2000 on a 1 km grid. These emissions have strong seasonal (lowest in winter and highest in spring and summer) and diurnal variation (lowest at night and highest at noon). NH_3 emissions at noon are about three times higher than at night, during the studied period. Emissions of primary $\text{PM}_{2.5}$ and PM_{10} of 9 source categories were obtained from INFRAS and Meteotest. The spatial resolution is 200 m and the reference year is 2000. Using land use and meteorological data, biogenic emissions were calculated by means of temperature and irradiance dependent algorithms [Andreani-Aksoyoglu and Keller, 1995]. In the biogenic emission inventory, the most abundant species are monoterpenes, which are emitted mainly by Norway Spruce and fir trees. Less abundant is isoprene, emitted by oak trees and pasture, mainly in the southern part of Switzerland.

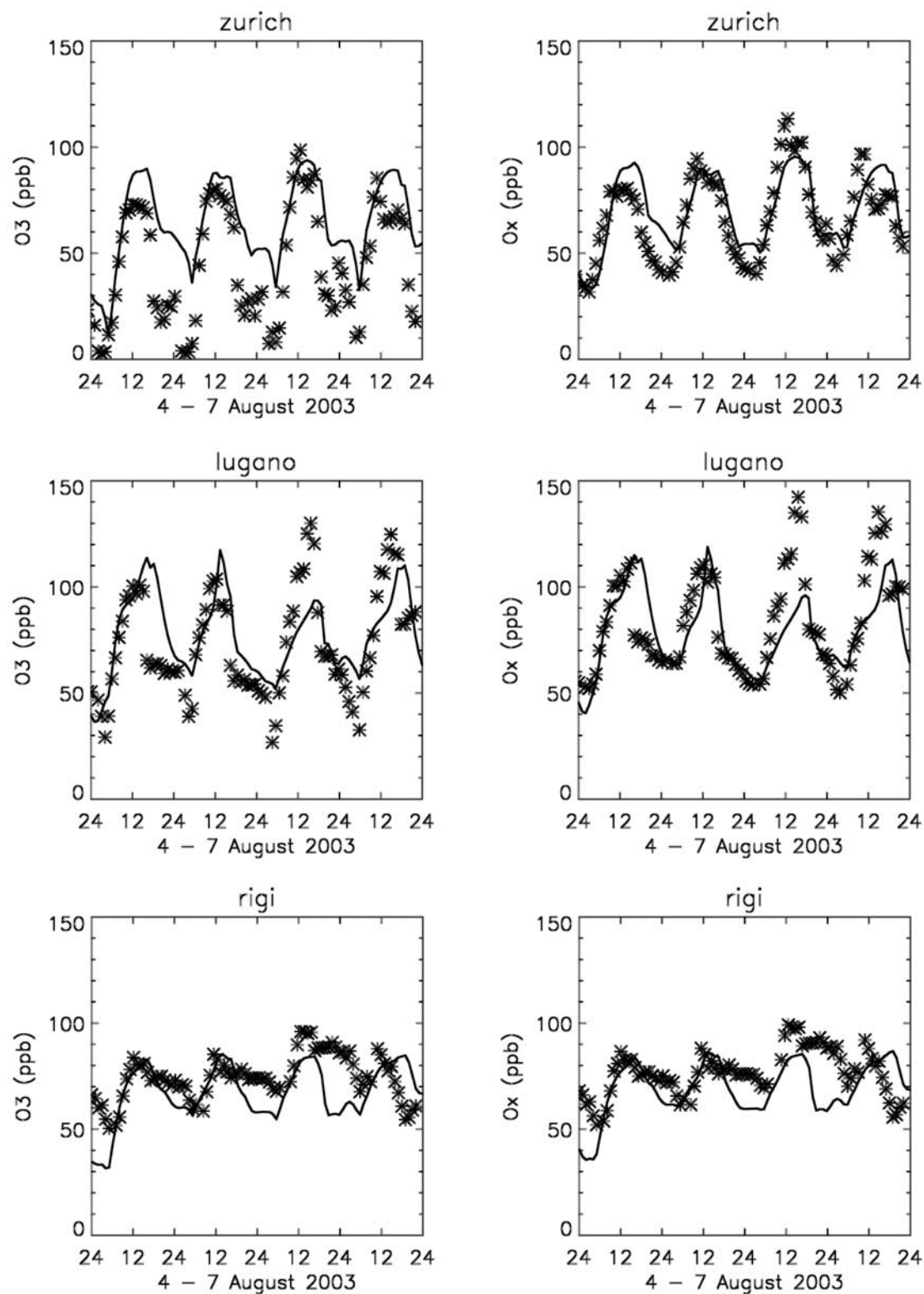


Figure 3. Comparison of measured (asterisks) O_3 and O_x ($O_3 + NO_2$) (ppb) with model results (solid line) at Zurich (urban, north), Lugano (urban, south) and Rigi (mountainous).

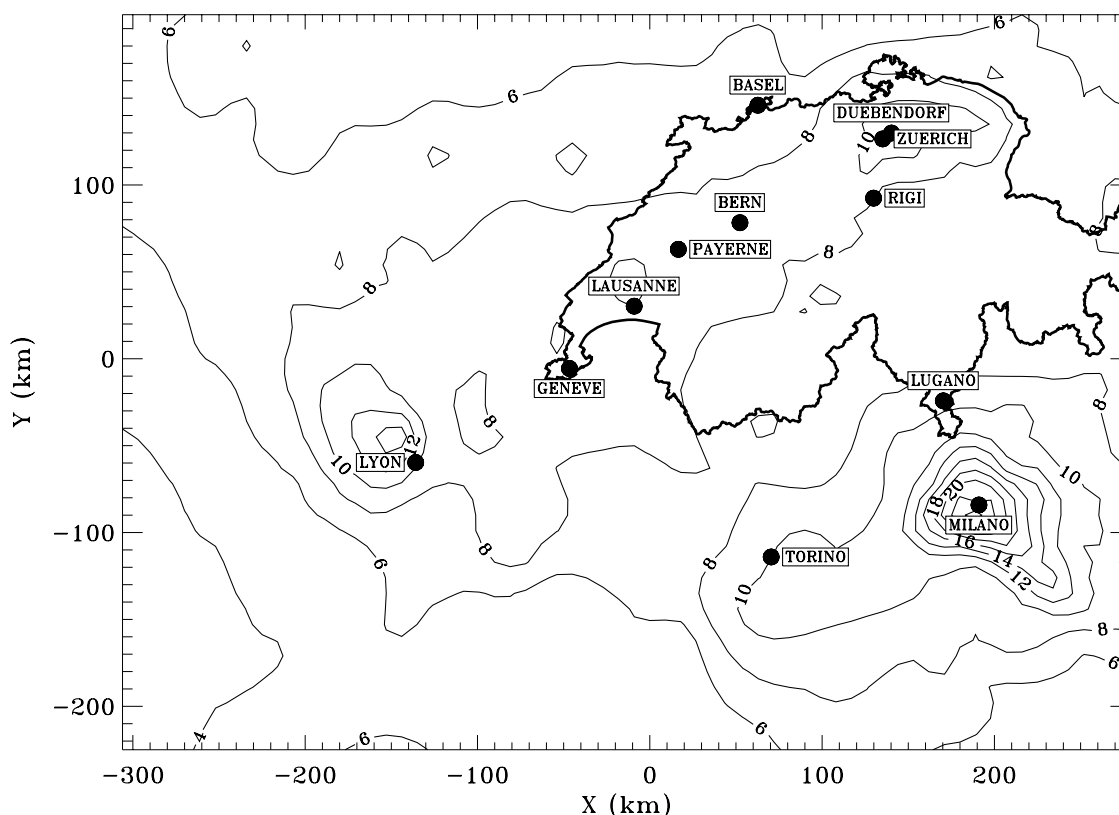


Figure 4. Modeled daily average aerosol ($d < 2.5 \mu\text{m}$) mass concentrations ($\mu\text{g}/\text{m}^3$) on 7 August 2003.

[8] Initial and boundary conditions were obtained from the regional European model REM-3/CALGRID. Calculations of aerosols with $d < 2.5 \mu\text{m}$ were performed with the fine/coarse option of the aerosol module. The sensitivity of aerosol formation to ammonia and nitric acid was studied by performing various simulations with reduced emissions of NH_3 and NO_x .

2.2. Gas Phase Chemistry

[9] The CBM-IV [Gery *et al.*, 1989] mechanism with the extensions for aerosol modeling in CAMx (mechanism 4) was used for the simulations of this study. It includes condensable organic gas species and a second olefin species to account for the biogenic olefins (representing terpenes). The gas-phase photochemistry forms aerosol precursors via the OH initiated oxidation of SO_2 to sulfate, production of nitric acid, and formation of condensable organic gases. Photolysis rates are derived for each grid cell assuming clear sky conditions as a function of five parameters: solar zenith angle, altitude, total ozone column, surface albedo and atmospheric turbidity. CAMx treats then the impacts of cloud cover (if any) on photolysis rates using the cloud file produced by the MM5 meteorological model. Dry deposition of gases is based on the resistance model of Wesely [1989].

2.3. Aerosol Chemistry

[10] The aerosol precursors are supplied to the aerosol chemistry module, which performs the following processes: aqueous sulfate and nitrate formation in cloud water using the RADM aqueous chemistry algorithm [Chang *et al.*, 1987], partitioning of inorganic aerosol constituents (sul-

fate, nitrate, ammonium, sodium, and chloride) between the gas and particle phases using the ISORROPIA thermodynamic module [Nenes *et al.*, 1998], partitioning of condensable organic gases (CG1-CG4) to secondary organic aerosols (SOA1-SOA4) to form a condensed organic solution phase using a semi-volatile equilibrium scheme called SOAP [Strader *et al.*, 1998]. Recent experiments show that primary emissions evaporate substantially upon dilution to ambient conditions and photo-oxidation of those vapors produces SOA far exceeding that from traditional precursors [Robinson *et al.*, 2007]. This would lead to underestimation of SOA concentrations by current models while the POA contribution is overestimated.

[11] Dry deposition of particles occurs via diffusion, impaction and/or gravitational settling. The resistance approach used in UAM-AERO has been adopted in CAMx [Kumar *et al.*, 1996]. The wet scavenging model implemented in CAMx calculates the following processes: wet scavenging of gases within and below precipitating clouds, of gases dissolved in cloud water, of in-cloud aerosols, and wet scavenging of dry particles below precipitating clouds.

3. Results and Discussion

3.1. Gas Phase

[12] Since secondary aerosols are formed from their gaseous precursors, it is important that gaseous species are modeled correctly. The measured concentrations of some gaseous species such as ozone and O_x ($\text{O}_3 + \text{NO}_2$), from the national monitoring network (NABEL) are shown in Figure 3 together with the model results for the stations in Rigi

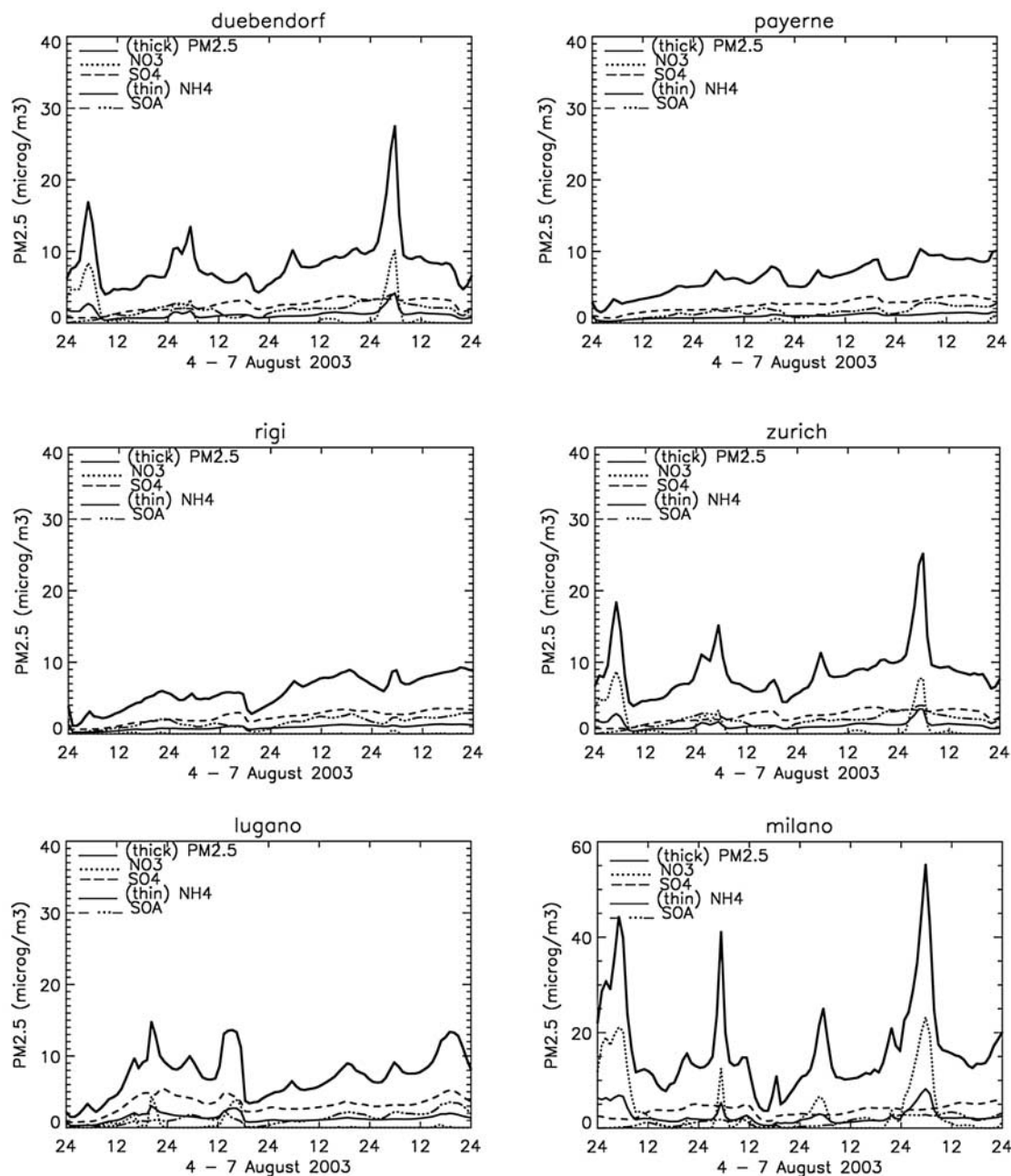


Figure 5. Diurnal variation of modeled particulate ($d < 2.5 \mu\text{m}$) nitrate, sulfate, ammonium, secondary organic aerosols and the total PM_{2.5} (sum of inorganic and organic aerosols, and EC) ($\mu\text{g}/\text{m}^3$) at Duebendorf (suburban, north), Payerne (rural), Rigi (mountainous), Zurich (urban, north), Lugano (urban, south), Milan (urban, Italy).

(mountainous), Zurich (urban, north), and Lugano (urban, south). Comparison of O_x concentrations provides a better evaluation of the model than ozone by eliminating the local NO titration effects at night. The model results of gaseous species are in reasonable agreement with measurements in northern Switzerland (within 20%) whereas ozone levels in Lugano were underestimated during the last two days. As ozone is an important precursor of OH, this might lead to an underestimation of the secondary particulate components.

3.2. Aerosol Phase

3.2.1. Base Case

[13] The modeled daily average PM_{2.5} concentrations in Switzerland were around $10 \mu\text{g}/\text{m}^3$. As seen in Figure 4, the highest aerosol mass concentrations were predicted in the polluted area of Milan, which has high emissions of primary particles and of gaseous precursors for secondary aerosols. The fraction of primary to secondary particles in Milan is the highest (0.47) in the smallest model domain. The relatively higher aerosol levels in the southern part of

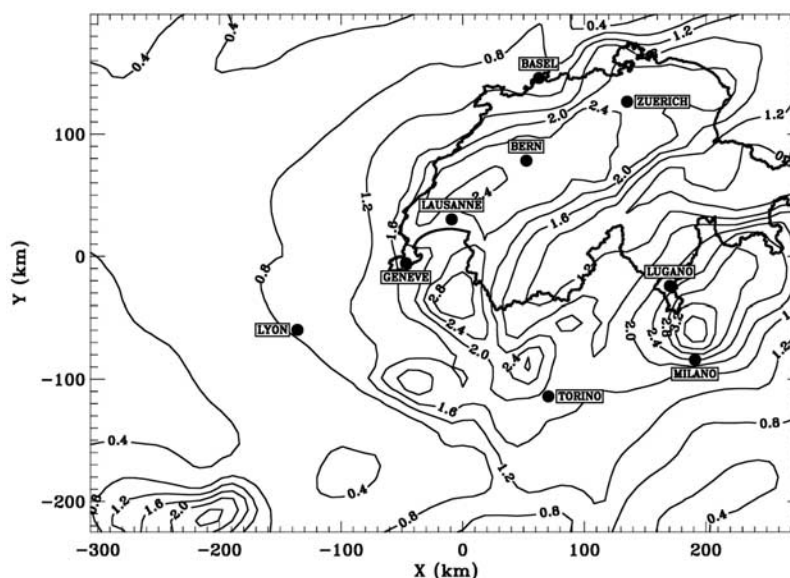


Figure 6. Modeled concentrations ($\mu\text{g}/\text{m}^3$) of total SOA ($d < 2.5 \mu\text{m}$) on 7 August 2003, 1500 UTC.

Switzerland are probably due to the vicinity of the Milan area and the thermal winds toward the Alps advecting also high ozone concentrations [Prévôt *et al.*, 1997]. The ratios of the traffic related primary particles (POA and EC) to secondary particles in Lugano are lower (0.18) than in Zurich (0.33) in spite of the underestimation of ozone in Lugano. The diurnal variations of the predicted individual particulate components in Figure 5 show a high correlation between ammonium and nitrate concentrations at locations in the north such as Zurich and Duebendorf. Sulfate levels, however, remain almost constant at around $3 \mu\text{g}/\text{m}^3$. These results suggest that in northern Switzerland, enough ammonia exists to neutralize sulfate and to produce ammonium nitrate. In contrast to the northern sites, nitrate levels are very low at the southern site Lugano, and sulfate and ammonium are highly correlated. Around Milan, aerosol concentrations, in particular the sulfate concentrations are higher than in Switzerland (see Figure 5). The predicted daily average PM_{2.5} during the studied period is about $20 \mu\text{g}/\text{m}^3$. At night and in the morning, the correlation between nitrate and ammonium both in Zurich and Milan indicates the formation of ammonium nitrate. The sulfate and ammonium peaks seen at the southern sites in the afternoon show ammonium sulfate production. The ratios of inorganic to organic aerosol fractions are higher (about 2.5) in the southern part of the Alps (Lugano, Milan) than in the north (about 1.5 in Zurich and Duebendorf).

[14] The model simulations suggest that the contribution of biogenic SOA (formed from the precursors emitted by trees) to total SOA is rather high, about 80% in the north (see Figures 6 and 7). ^{14}C measurements of different carbonaceous particle fractions from ambient aerosols showed that the water soluble organic compounds (WSOC) comprised 76–96% biogenic carbon at Zurich in summer 2002 [Szidat *et al.*, 2004a]. Furthermore, an extended ^{14}C model approach revealed for OC that $\sim 14\%$ of the biogenic fraction originated from biomass burning emissions for that campaign [Szidat *et al.*, 2006]. Applying this biomass

burning contribution to WSOC suggests that 65–82% of this fraction originates from biogenic SOA. This serves as an upper estimate, as biomass burning may be more important for WSOC than for total OC and, moreover, water-soluble primary biogenic particles are neglected. This high biogenic fraction agrees well with the model prediction of about 80% biogenic contribution to SOA in Zurich. The biogenic contribution in northern Switzerland comes from the Norway Spruce forests due to their abundance and high monoterpene emissions [Andreani-Aksoyoglu and Keller, 1995]. On the other hand, it is substantially lower in southern Switzerland (about 40%) and in the polluted area in northern Italy (15–25%). The modeled biogenic contribution to SOA in northern Italy agrees well with our previous study [Andreani-Aksoyoglu *et al.*, 2004].

[15] There are only few aerosol measurements during the studied period. Figure 8 shows daily average measurements and model results of total ammonia ($\text{NH}_3 + \text{NH}_4$) and total nitrate ($\text{HNO}_3 + \text{NO}_3$) at the mountainous site Rigi on 4–7 August 2003. Model predictions for $\text{NH}_3 + \text{NH}_4$, which is dominated by NH_3 , are higher than the measurements (the modeled average over the whole period is $6.5 \mu\text{gN}/\text{m}^3$ whereas average of measurements is $3.5 \mu\text{gN}/\text{m}^3$). This might be because of the high uncertainty in NH_3 emissions as well as enhanced deposition of ammonia at the slopes of the mountain. On the other hand, the model seems to predict total nitrate concentrations reasonably well.

[16] In Table 1, the model results for the last two days are compared with all the available ambient aerosol measurements (August 2002 in Zurich [Fisseha *et al.*, 2006], August 1998 and 2002 at three sites of the NABEL network [Hueglin *et al.*, 2005]). Measurements for sulfate, nitrate and ammonium are available only for the years 1998 and 2002 (only for Zurich). The total measured concentrations of inorganic aerosols in earlier years are in general lower than the modeled values for 2003, except for Basel where measurements and the model results are almost the same. The measured PM_{2.5} concentrations were also higher in

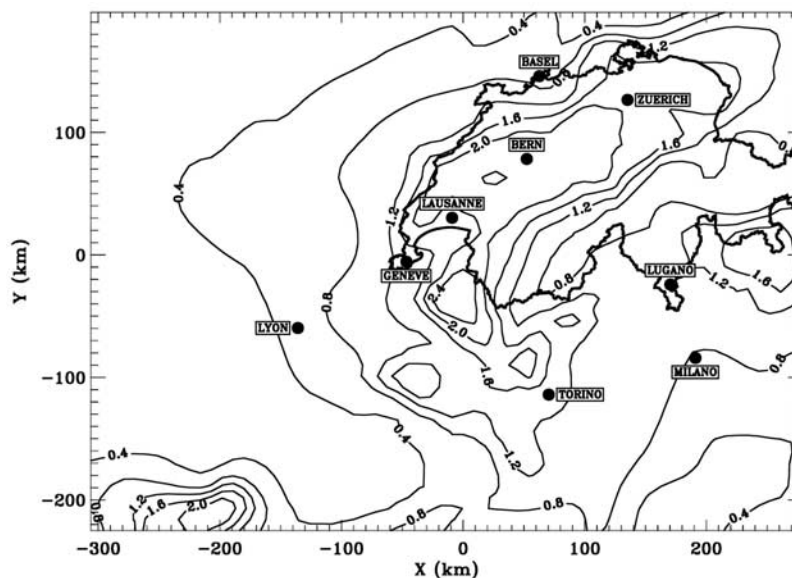


Figure 7. Modeled concentrations ($\mu\text{g}/\text{m}^3$) of biogenic SOA ($d < 2.5 \mu\text{m}$) on 7 August 2003, 1500 UTC.

August 2003 than in previous years at all four sites. Assuming that the relative increase in measured $\text{PM}_{2.5}$ was the same for the inorganic aerosol concentrations, the sum of sulfate, nitrate and ammonium for 2003 was estimated. These estimates of the measurements are close to the model predictions for inorganic aerosol concentrations, except for Basel. The $\text{PM}_{2.5}$ measurements include mineral dust, trace elements and an unknown fraction in addition to inorganic and organic aerosols and elemental carbon. The fraction of these additional species is about 20–25% of the total measured $\text{PM}_{2.5}$ mass and is thought to consist of water to a considerable extent [Hueglin *et al.*, 2005]. The modeled sum of the total particle mass concentrations is substantially lower than the measurements and varies between 8 and $11 \mu\text{g}/\text{m}^3$ in northern Switzerland. Besides the missing components, uncertainties in emissions

as well as the underestimation of organic aerosols might lead to lower values than measurements. The mechanisms recently shown [Kalberer *et al.*, 2004] to enhance SOA formation such as polymerization, SOA formation from isoprene and sesquiterpenes, are not yet implemented in the models and will be considered in future studies.

[17] The fractional composition of particles calculated by the model is compared with measurements for the same species in Figure 9. The measurements from August 1998 and 2002 show that the main components of summer aerosols are organic matter (56%) and sulfate (21–22%) in Zurich. Long-term measurements showed that nitrate has a high seasonal variability with much lower concentrations during summer than during winter [Hueglin *et al.*, 2005]. The model calculations indicate a similar composition, however, with lower (38%) organic aerosols (POA + SOA), and higher

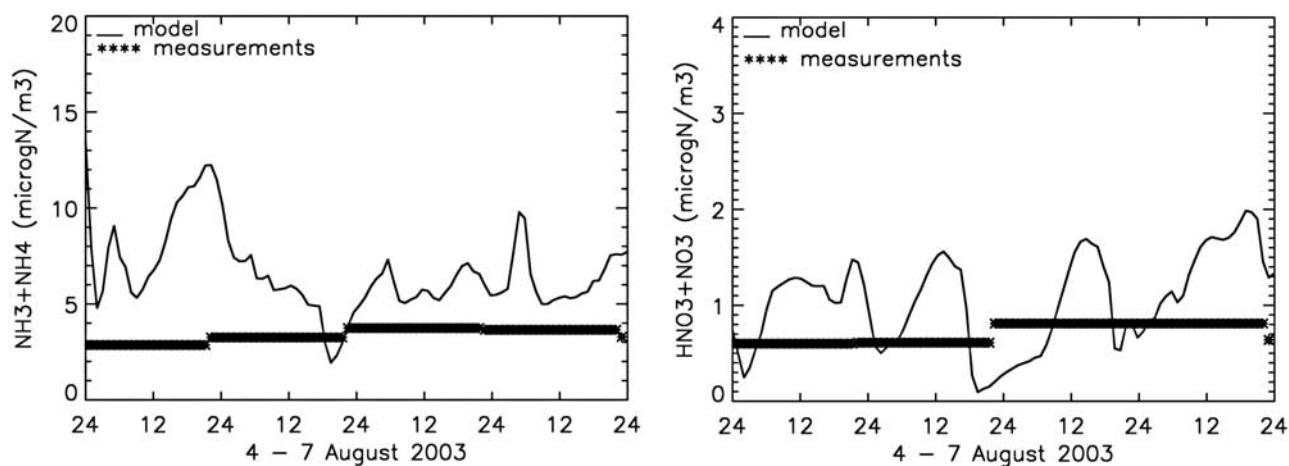


Figure 8. Comparison of measured (asterisks) $\text{NH}_3 + \text{NH}_4$ (left) and $\text{HNO}_3 + \text{NO}_3$ (right) concentrations with model results (solid line) at Rigi (mountainous site). Measurements are daily averages.

Table 1. Comparison of Model Results With Measurements

Site	Date	SO ₄ ($\mu\text{g}/\text{m}^3$)	NO ₃ ($\mu\text{g}/\text{m}^3$)	NH ₄ ($\mu\text{g}/\text{m}^3$)	SO ₄ + NO ₃ + NH ₄ ($\mu\text{g}/\text{m}^3$)	Total ($\mu\text{g}/\text{m}^3$) (Inorganics, Organics, EC)	PM2.5 ($\mu\text{g}/\text{m}^3$)
Basel (suburban) Measurements	1–31.8.1998 ^a	3.20 ± 1.00	0.38 ± 0.20	1.34 ± 0.40	4.9		15.3
	1–31.8.2002 ^a						16.7
	6–7.8.2003 ^a				8.4 ^b		26.2
Model Bern (urban) Measurements	6–7.8.2003 ^a	3.0	0.01	1.12	4.1	8.1	
	1–31.8.1998 ^a	2.16 ± 0.90	0.25 ± 0.30	0.94 ± 0.40	3.3		19.2
	1–31.8.2002 ^a						20.3
	6–7.8.2003 ^a				4.4 ^b		25.3
Model Chaumont (urban) Measurements	6–7.8.2003 ^a	3.12	0.27	1.25	4.6	8.4	
	1–31.8.1998 ^a	2.30 ± 0.90	0.13 ± 0.10	1.07 ± 0.30	3.5		10.9
	1–31.8.2002 ^a						10.8
	6–7.8.2003 ^a				6.2 ^b		19.3
Model Zurich (urban) Measurements	6–7.8.2003	3.13	0.24	1.24	4.6	7.7	
	1–31.8.1998 ^a	2.64 ± 1.00	0.23 ± 0.30	1.12 ± 0.40	4.0		17.3
	1–31.8.2002 ^a						16.3
	8–30.8.2002 ^c	1.71 ± 1.32	0.83 ± 1.10	0.88 ^d	3.4		17.2
	6–7.8.2003 ^a				5.8–6.7 ^b		29.1 ^e
Model	6–7.8.2003	3.1	0.6	1.34	5.0	9.8	

^aNabel data [Hueglin *et al.*, 2005].^bEstimated using the change in PM2.5 from 1998 or 2002 to 2003.^cFisseha *et al.* [2006].^dEstimated assuming that the aerosol was fully neutralized with ammonia.^eEstimated from PM10, using PM2.5/PM10 ratio of 0.75 for Zurich given by Gehrig and Buchmann [2003].

(32%) sulfate. The fractions of other components are in a reasonable agreement with measurements. The concentrations of the traffic related primary particles (POA and EC) are lower than those of secondary particles, in accordance with various measurements carried out in Zurich [Szidat *et al.*, 2006; Lanz *et al.*, 2007]. The modeled fractional composition of particles in the south is different from the one in the north, with lower organic aerosols and higher sulfate (for example, 27% and 44% respectively, in Lugano).

3.2.2. Sensitivity to NH₃ and HNO₃

[18] The reaction of ammonium with sulfuric acid leads to the formation of ammonium sulfate. After all available sulfuric acid is neutralized, ammonia reacts with nitric acid leading to the formation of ammonium nitrate. The concentration of ammonia is therefore crucial for aerosol nitrate formation. At low ammonia levels, formation of ammonium nitrate is limited by the availability of ammonia. On the

other hand, in regions with high ammonia concentrations, ammonium nitrate formation may depend on the availability of nitric acid. In a sensitivity study for Los Angeles, Nguyen and Dabdub [2002] showed that the most effective control strategy for PM is the reduction of ammonia emissions.

[19] In order to investigate the sensitivity of aerosol formation to emissions in Switzerland, additional simulations were carried out with 50%, 70%, and 90% of the emissions of NH₃ and NO_x separately. In one case, both emissions were reduced by 30%. The sum of the secondary aerosol concentrations was calculated for each case. The relative changes in the diurnal variation of total secondary aerosol mass concentration due to various reductions of NH₃ and NO_x emissions reveal detailed information about the sensitivity of aerosol formation on emissions (Figure 10). The time of the largest relative changes differs among the sites. In Zurich, in the north of the Alps, a reduction in aerosol levels

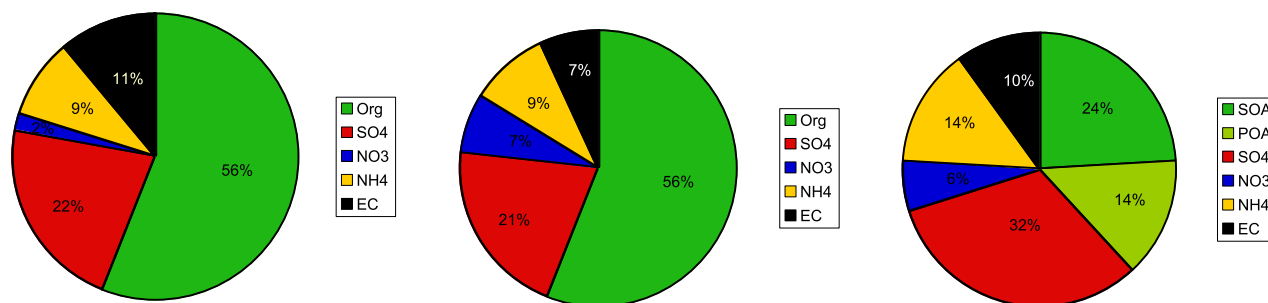


Figure 9. The fractional composition of the aerosols measured in August 1998 (left) [Hueglin *et al.*, 2005], in August 2002 (middle) [Szidat *et al.*, 2004b] and modeled (right) in Zurich. Model results refer to August 2003. The measured organic fraction contains both POA and SOA with an OM/OC ratio of 2.0.

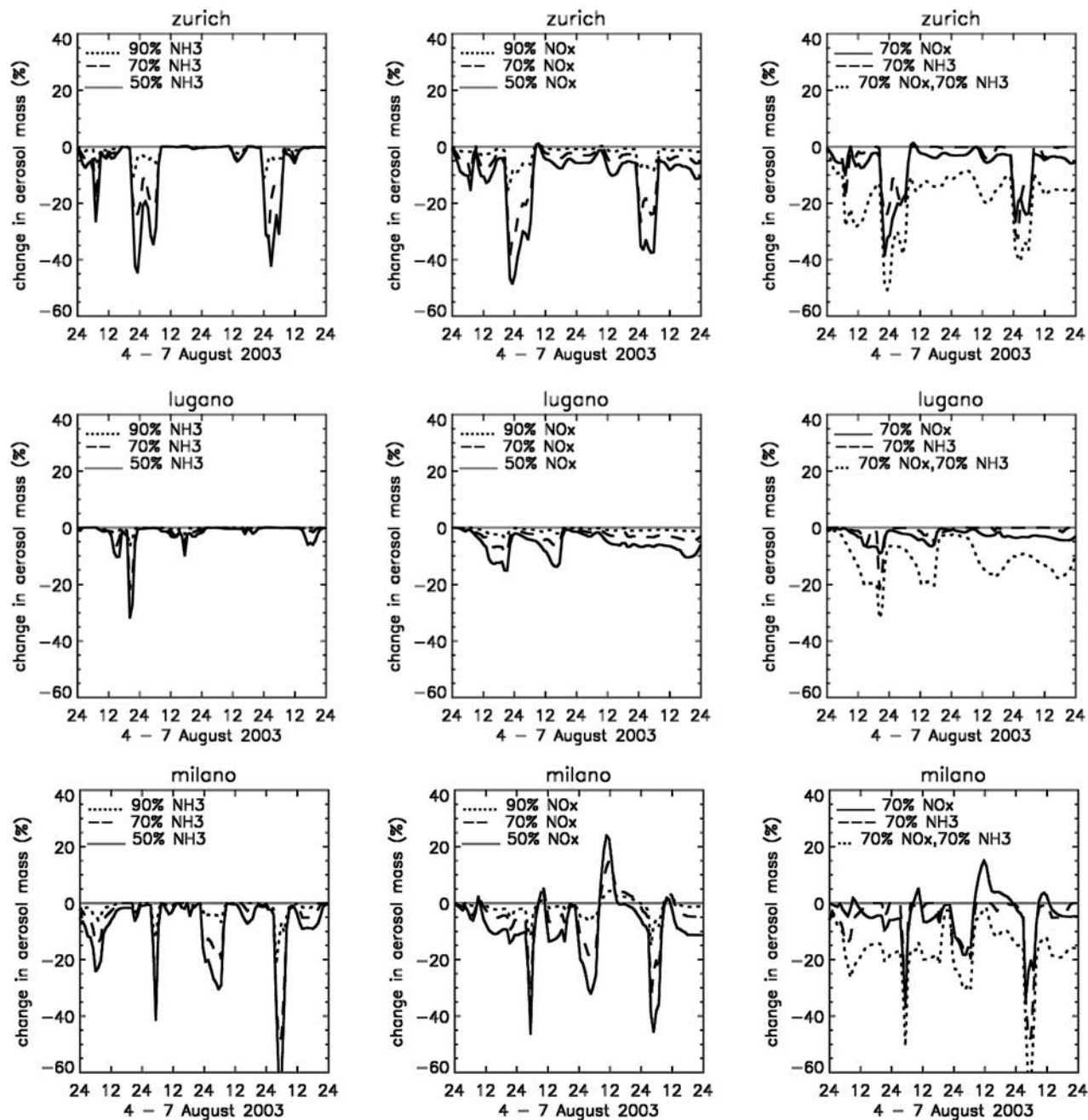


Figure 10. Diurnal variation of the change in secondary aerosol mass (%) relative to the base case for various NH_3 (left) and NO_x (middle) emissions, as well as comparison of the effect of a 30% reduction of the NO_x and NH_3 emissions on the secondary aerosol mass (right).

takes place mainly at night and during the morning hours and corresponds to the nitrate peak (see also Figure 5). In Lugano (south of the Alps), changes are relatively smaller. The reduction of NO_x emissions is predicted to be more effective to reduce secondary aerosol mass concentrations in Zurich than in Lugano.

[20] In Milan (northern Italy), the results differ from those in Switzerland. Both the nitrate peak in the morning and the sulfate peak in the afternoon decrease when ammonia emissions are reduced. The reduction of NO_x emissions leads to a decrease in nitrate in the morning. The aerosol

mass increases around noon due to increasing particulate sulfate concentrations. Evaluation of the model results shows that reducing NO_x emissions causes an increase in ozone concentrations as expected at urban areas with high emissions like Milan [Baertsch-Ritter *et al.*, 2003]. The increase in ozone levels which is highest on the third day (about 20%), and in OH radical concentrations is most probably the cause of increased particulate sulfate. Aerosol formation seems to be similarly dependent on HNO_3 and NH_3 most of the time. However, there are times when limitation by ammonia is stronger. The reduction of both

NO_x and NH_3 emissions seem to be the most effective way to decrease aerosol concentrations at all sites considered in Figure 10.

4. Summary and Conclusions

[21] The inorganic and organic aerosol mass concentrations over an area covering Switzerland and northern Italy were calculated during a short period in August 2003 by the CAMx air quality model. Comparisons with a few available measurement data suggest that the CAMx model is able to reproduce the secondary inorganic aerosol formation and distribution reasonably well while organic aerosols are underestimated. The most likely reasons for that are the SOA formation mechanism, which is based on partitioning theory and does not include other recently addressed processes such as polymerization as well as the uncertainties in emissions. However, the traffic-related primary particle concentrations were predicted to be lower than those of secondary particles in the urban area Zurich, as suggested by the measurements as well. In line with the $\text{PM}_{2.5}$ measurements, the modeled particle concentrations are higher in southern Switzerland and northern Italy. This is most probably due to the polluted Milan area with high emissions of precursors and the thermal winds advecting the pollutants toward the Alps as well as to higher solar radiation increasing photochemical activity. Sensitivity studies suggested that formation of inorganic aerosols in northern Switzerland is limited by nitric acid and therefore by NO_x emissions. Around Milan, aerosol formation seems to be similarly dependent on HNO_3 and NH_3 most of the time although there are times when limitation by ammonia is stronger.

[22] The model prediction of a high biogenic SOA fraction (about 80%) in northern Switzerland is supported by the ^{14}C data from Zurich [Szidat et al., 2004a]. This high fraction can be attributed to the large amount of monoterpene emissions from the Norway Spruce forests in the Swiss Plateau. In southern Switzerland where monoterpene emissions are lower, the biogenic contribution to SOA formation decreases to 40%. In northern Italy anthropogenic sources contribute much more to SOA formation, supporting our previous calculations [Andreani-Aksoyoglu et al., 2004].

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