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A PHOTOCHEMICAL MODELLING STUDY OF OZONE AND FORMALDEHYDE GENERATION AND BUDGET IN THE PO BASIN

L. Liu¹, S. Andreani-Aksoyoglu², J. Keller², G. O. Braathen³, M. Schultz⁴, A. S.H. Prévôt², I. S. A. Isaksen¹ - ¹University of Oslo, Oslo, Norway, ²Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen, Switzerland, ³Norwegian Institute for Air Research, Kjeller, Norway, ⁴Forschungszentrum Jülich GmbH, Germany

TRANSFORMATION OF AROMATICS BY OH RADICALS AND CONSECUTIVE STEPS: RATES AND PATHWAYS

C. Zetzsch - University of Bayreuth, Atmospheric Chemistry Research Laboratory, 95440 Bayreuth, Germany

OZONE PRODUCTION FROM GRENOBLE CITY DURING THE AUGUST 2003 HEAT WAVE: MODELLING AND ANALYSIS

Eric Chaxel, Jean-Pierre Chollet - Laboratoire des Ecoulements Géophysiques et Industriels, Université J. Fourier, INPG, CNRS, BP 53, 38041 GRENOBLE CEDEX 9, France

INTERCOMPARISON BETWEEN NATIONAL AND REGIONAL SCALE PHOTOCHEMICAL POLLUTION SIMULATIONS OVER NORTHERN ITALY

A. Balanzino¹, C.Pertot², G.Pirovano³, M.Causa⁴, E.Ferrero¹, S.Alessandrini³, M.P.Costa³ - ¹Dipartimento di Scienze e Tecnologie Avanzate (DISTA), Universita' del Piemonte Orientale, "A.Avogadro", Via Bellini 25/G, 15100 – Alessandria, ²CESI, Via Rubattino 54, 20134 – Milano, ³CESI RICERCA, Via Rubattino 54, 20134 – Milano, ⁴Dipartimento di Chimica, Universita' di Napoli "Federico II", Via Cintia, 80126 – Napoli

A PHOTOCHEMICAL MODELLING STUDY OF OZONE AND FORMALDEHYDE GENERATION AND BUDGET IN THE PO BASIN

L. Liu¹, S. Andreani-Aksoyoglu², J. Keller², G. O. Braathen³, M. Schultz⁴, A. S.H. Prévôt², I. S. A. Isaksen¹ ¹University of Oslo, Oslo, Norway ²Laboratory of Atmospheric Chemistry, Paul Scherrer Institut, Villigen, Switzerland ³Norwegian Institute for Air Research, Kjeller, Norway ⁴Forschungszentrum Jülich GmbH, Germany

Abstract

A photochemical dispersion model, CAMx (Comprehensive Air quality Model with eXtensions) was used to simulate a high ozone episode observed in the Po basin (northern Italy) in autumn 2003. The study focused on formaldehyde and ozone, and a budget analysis was set up for three different areas (urban, downwind, suburban) around the Milan metropolitan region. In addition, a sensitivity study was carried out based on 11 different VOC emission scenarios. The results of the budget study show that the strongest O_3 production rate occurs in the downwind area of the city of Milan. More than 80% of the HCHO concentration in the Po basin is secondary photochemically produced from other VOCs. Although the paraffinic (PAR) emissions are fairly large, the largest reduction of O_3 levels can be obtained by reduced xylene (XYL) emissions. 20% reduction of total anthropogenic VOC emissions leads to 15.5% (20.3 ppbv) reduction of O_3 peak levels in the Po basin.

1. Introduction

Formaldehyde (HCHO), the smallest and most abundant aldehyde, is a principal atmospheric intermediate in the oxidation of hydrocarbons. By photolysis and the reaction with OH, it serves as a source for carbon monoxide and importantly for the hydroperoxyl radical (HO₂), leading to ozone production in the presence of NO_x (nitrogen oxides). Formaldehyde is directly emitted from biomass burning and fossil fuel combustion, and secondarily produced by oxidation from both biogenic and anthropogenic hydrocarbons.

The Po Basin in northern Italy is a densely industrialized and populated area. Because of the large emissions and fair weather conditions in summer, high ozone episodes are frequently observed in this region. (Prévôt et al. 1997; Dommen et al., 2002; Baertsch-Ritter, 2003, 2004). For better understanding of the role of formaldehyde, two field campaigns were carried out in 2002 and 2003 in the vicinity of Milan as part of the EU project FORMAT (Formaldehyde as a Tracer of Oxidation in the Troposphere).

In this study, we used the Eulerian photochemical dispersion model CAMx (ENVIRON, 2004) to simulate the high ozone episode in autumn 2003 observed in the FORMAT campaign. The study focused on the formaldehyde and ozone production in the Po Basin. A detailed budget analysis of HCHO and ozone was carried out for three different areas, representing urban, downwind, and suburban areas. In addition, 11 different VOC emission scenarios were designed for a sensitivity study of the HCHO and ozone production in the Po Basin.



Figure 1: Model domains and surface measurements sites during the FORMAT campaign. Three areas chosen in Po basin for budget study were also indicated.

2. The FORMAT 2003 Campaign and meteorological conditions

The FORMAT 2003 campaign was carried out in Lombardy (northern Italy) from 12 September to 5 October. The fair weather period lasted until 22 September, when a low-pressure system took over in this region. From 23 September on, the weather conditions were unstable, both temperature and radiation were variable and the temperature during this period hardly exceeded 20°C. The two different weather periods can be distinguished: the fair weather period during the first 10 days and the unstable weather period later on.

The summer vacation ends at the end of August, so the emissions in September represent typical emission conditions. Two surface sites (Alzate and Bresso, see Figure 1) were set up as downwind sites. They are identical to the stations in the previous FORMAT campaign in 2002 (Hak et al., 2005; Liu et al., 2007). During the campaign period, the target component HCHO was measured at surface sites. Additional measurements of species such as O₃, CO, NO, CO₂, NO₂, SO₂, HONO, VOC were used for better understanding of emissions and the photochemical evolution over this region.

3. Modelling system and setup

The CAMx is an Eulerian photochemical dispersion model that allows for an integrated assessment of gaseous and particulate air pollution over many scales ranging from urban to regional (ENVIRON 2004). The model incorporates two-way grid nesting in this study. The CBM-IV mechanism, used in this study, includes isoprene chemistry based on Carter (1996), a total of 96 reactions and 37 gas species are included. The meteorological inputs for the CAMx model were prepared with the meso-scale model MM5 (PSU/NCAR, 2004). In this study, the most recent version 3.7.2 is used. There are 25 vertical layers up to 100 hPa. The MM5 is initialized by data calculated by aLMo (alpine model), a forecast model run by MeteoSwiss with a resolution of about 7 kilometers. The 4-dimensional data assimilation (FDDA) option within MM5 was applied with aLMo data in order to obtain better meteorological fields.

In this study, the anthropogenic emissions are taken from various European data sources. On the European level, the annual emissions were provided by the Free University of Berlin (FUB). Emissions of Lombardy region were taken from CITY_DELTA project. Biogenic emissions such as monoterpenes and isoprene, were calculated using land use data, surface temperature and solar irradiance (Andreani-Aksoyoglu et al. 1995; Keller et al., 1995).

Two nested model domains in CAMx were defined in this study (Figure 1). The coarse domain has a horizontal resolution of 27 km x 27 km, the resolution of the fine domain is 9 km x 9 km. There are 10 vertical layers. Both initial and boundary conditions for CAMx were extracted from the global model MOZART (Horowitz, 2003). In this study, the CAMx model simulation was performed for the period from 12 to 21 September 2003. Eleven scenarios were designed to investigate the variation of the HCHO and ozone concentrations and their budgets (Table 1). We also defined three areas for the budget analysis (Figure 1). Area 1 covers the Milan city and its surroundings, Area 2 contains regions north of Milan city. Area 3 is a suburban area east of the city. The calculation of the budget was done for the base case and for all emission scenarios to obtain detailed information on HCHO and O_3 production for different VOCs emission scenarios.

4. Base case

During the campaign period, both HCHO and CO concentrations were measured in the late night and early morning in the city centre of Milan. When the photochemistry is not yet active, the measured concentration ratios might be regarded as emission ratios (Dommen et al., 2003). A ratio of 0.0029 between HCHO and CO was found from the measurements, the HCHO emissions in the base case were calculated from the measured emission ratio. In this study, the wind data measured at the surface stations during the campaign period show somewhat lower wind speeds than the model simulation. During daytime (8:00 to 17:00 LT), the average measured wind speed was 0.79 m/s, whereas the simulated wind speed was 1.3 m/s. We reduced the wind speed by a factor of 0.67) and used them for the base case and for further sensitivity studies.

The model performance has been compared with the measurements obtained from the FORMAT 2003 campaign that was carried out in the Po basin, and also compared with the measurements from the Lombardy region. The modelled and measured O_x ($O_x = O_3 + NO_2$) from the Lombardy region were compared to evaluate the model simulation. Overall the model seems to predict the O_x concentrations fairly well in this region. The comparison shows that the model is able to reproduce the high ozone levels and most of the variability. The model can also simulate HCHO and NO₂ reasonably well, although both these compounds are often influenced by local emissions.

5. Sensitivity study for different VOC emission scenarios

The sensitivity study of ozone and HCHO is carried out based on 11 different VOC emissions scenarios, the results are indicated in Table 1.

during the daytime $(12:00 - 18:00 \text{ L1})$, and for HCHO were calculated for whole day $(0:00-24:00 \text{ L1})$.					
Scenarios	Change in peak	Change in peak O ₃	Change in HCHO	Change in daytime O ₃	
(Emission change)	НСНО		chemistry	chemistry	
S1 (CITY-DELAT	+ 51.9 %	+ 3.2 %	-41.2 %	+ 1.3 %	
HCHO emissions)					
S2 (no HCHO)	- 16.7 %	- 1.2 %	+18.2 %	-0.68 %	
S3 (no isoprene)	- 0.1 %	- 0.2 %	0.0 %	-0.07 %	
S4 (-20% PAR)	- 1.7 %	- 2.7 %	-2.03 %	-2.77 %	
S5 (-20% OLE)	- 5.0 %	- 1.5 %	-2.70 %	-1.69 %	
S6 (-20% ETH)	- 4.7 %	- 1.5 %	-6.76 %	-1.83 %	
S7 (-20% TOL)	- 0.7 %	- 1.7 %	-0.68 %	-0.10 %	
S8 (-20% XYL)	- 5.0 %	- 5.1 %	-5.41 %	-5.30 %	
S9 (-20% ALD2)	- 1.0 %	- 0.4 %	-1.35 %	-0.53 %	
S10 (-20% MEOH)	- 0.1 %	- 0.4 %	-0.68 %	-0.07 %	
S11 (-20% all VOCs)	- 22.7 %	- 15.5 %	-16.2 %	-17.5 %	

Table 1: The differences of simulated daily peak concentrations and chemical production rates of O_3 and HCHO in Po basin between base case and different emissions scenarios. The values are calculated for O_3 during the daytime (12:00 – 18:00 LT), and for HCHO were calculated for whole day (0:00-24:00 LT).

In scenario 1, the simulated peak HCHO levels are 51.9% higher than in the base case indicating that there are fairly large uncertainties in the existing emission inventories. On the average, the afternoon peaks of the O_3 concentration are 3.2% higher than in the base case. Although the HCHO levels increased, the budget results indicate a 41.2% reduction of the net O_3 production compared to the base case. In Scenario 2, without HCHO primary emissions, 16.7% HCHO and 1.2% O_3 concentration reductions compared to the base case were found. The budget results show 18.2% increased net chemical HCHO production and a minor (0.68%) reduction of O_3 production. Without isoprene emissions (Scenario 3) only minor influences on peak O_3 (0.2%) and peak HCHO (0.1%) are found. Because of the short lifetime of isoprene and HCHO, the influence of isoprene might still be important at locations close to sources.

Scenarios 4-10 allow a comparison of the influence of emissions of the VOCs in the CBM-IV categories. The similar influences on HCHO peak concentrations are found for OLE, ETH and XYL, around 5% reduction when the emissions are reduced by 20%. Among all the scenarios, the highest reduction of the O_3 levels is caused by reduced XYL emissions. OLE, ETH and TOL have similar influence on O_3 levels. PAR is emitted in large amounts but has a low reactivity, and its impact is relatively higher on ozone concentrations than on formaldehyde, probably because ozone is also more long-lived. The two aromatic hydrocarbon groups TOL and XYL have comparable emission strength, and there is 5.4% reduction of HCHO chemical production due to XYL emission reductions compared to only 0.68% reduction of HCHO chemical production by the change of the TOL emissions. The results show that the strongest reduction of O_3 concentrations is caused by XYL emission reduction, whereas the largest influences on O_3 chemical production by reducing ALD2 since the emissions are not large. MEOH does not show so much influence on HCHO production and concentration because of the low emission strength and rather low reactivity. The last scenario (11) included a 20% reduction of O_3 peak levels in this region.

6. Conclusions

The Eulerian photochemical dispersion model CAMx was used to simulate the ozone episode over the Milan metropolitan region in September 2003. This work is aimed at studying the influences of different VOC emissions on ozone and HCHO production in this region. The modified HCHO emissions improved the model results, which indicated the uncertainties in the emission inventory. By comparing with the local wind measurements, the wind speeds were reduced by a factor of 0.67 for the model simulation. Improved emission estimates and higher model resolution are needed for investigating the role of biogenic emissions in the Po basin. A budget study was set up for three areas: Urban (Area 2), downwind of urban (Area 1), and suburban regions (Area 3) of Milan city. A few conclusions can be drawn from the budget analysis: The photochemical O₃ production is the strongest in Area 1, about 4 ppbv/hour on average during daytime, 3 ppbv/hour in Area 2, and 2.5 ppbv/hour in Area 3. Area 1 acts as an O₃ source for downwind regions during day and night. With the strong emissions from the city of Milan, about 50% of O₃ is lost by titration in Area 2 during nighttime. Area 3 receives a small impact from the Milan emissions, and this area serves as an O₃

source for its downwind regions despite the low O_3 production rates. Of all the HCHO in the Po basin, the primary HCHO emissions contribute about 10-20%, whereas more than 80% of HCHO is secondarily produced. The largest HCHO production rates are found in Area 2. However the highest HCHO concentration accumulation was found in Area 1. The sensitivity shows that the model produces much higher HCHO peak levels (51.9%) and somewhat increased O_3 peaks (3.2%) compared to the base case when the primary HCHO emission inventory from the CITY-DELTA project was used. Without isoprene emissions, the peak levels of O_3 and HCHO are scarcely changed. The sensitivity runs with a 20% reduction of anthropogenic VOC emission categories show that XYL has the largest influence on the averaged afternoon peak ozone, and the largest reductions on HCHO chemical production are caused by reduced OLE, XYL or ETH, emissions. Although the PAR emissions are fairly large, a 20% reduction of total anthropogenic VOC emissions leads to a 15.5% reduction of the O_3 levels in the Po basin. This agrees with previous studies which show that the O_3 production is highly VOC sensitive in this region.

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TRANSFORMATION OF AROMATICS BY OH RADICALS AND CONSECUTIVE STEPS: RATES AND PATHWAYS

C. Zetzsch

University of Bayreuth, Atmospheric Chemistry Research Laboratory, 95440 Bayreuth, Germany

ABSTRACT

The present study employs two complementary methods, the smog chamber and the flash-photolysis/resonance fluorescence technique. Benzene, toluene and p-xylene have been investigated in a smog chamber in N_2 with added traces of oxygen to reveal the scavenging of the OH-adducts by O_2 . Data on the aromatics benzene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline have been obtained as a function of temperature in the absence and presence of the three tropospheric scavengers oxygen, NO and NO₂. The initial and consecutive steps

Aromatic + OH ⇔ Aromatic-OH	(1, -1)
Aromatic + OH \rightarrow Radical	(2)
Aromatic-OH + O ₂ , NO ₂ , NO \rightarrow Products	(3a, 3b, 3c)

and their mechanisms will be discussed in view of the existing literature.

1. INTRODUCTION

The atmospheric transformation of aromatics during daylight is mostly initiated by OH radicals. Rate constants for the reactions of OH radicals with aromatics have been studied by various absolute and relative techniques, and these compounds are known to contribute a large portion to photochemical ozone production in cities and the surrounding recreation areas. Addition of OH is a major pathway, and the rates of the consecutive steps with the tropospheric scavengers O_2 , NO and NO₂ have been investigated.

Emissions of aromatics still account for 20-30% of the non-methane hydrocarbons in urban air, and their atmospheric chemistry has extensively been reviewed (Calvert et al., 2002). Their high ozone and particulate creation potential is not yet fully understood and justifies further work on their degradation mechanism (Jenkin et al., 2003, Bloss et al. 2004). This paper summarises our work on the OH-initiated degradation of aromatics and the consecutive steps in the presence of O_2 and other atmospheric scavengers.

2. METHODOLOGY

The reactions of benzene, naphthalene, toluene, m- and p-xylene, hexamethylbenzene, phenol, m-cresol and aniline with OH radicals have been studied by pulsed flash-photolysis/resonance fluorescence (FP/RF, see Perry et al., 1977, Wahner and Zetzsch, 1983, Witte et al., 1986, Zetzsch et al., 1997) at various temperatures from 298 to 420 K. Furthermore, the consecutive reactions of the adducts, resulting from the OH radicals and the aromatics, with the tropospheric scavenger molecules O_2 , NO and NO₂ have been studied by FP/RF measurements of OH profiles in the presence of the aromatics and the scavengers (see Knispel et al., 1990, Zetzsch et al., 1990). The FP/RF apparatus and the methodology of determining and evaluating the rate constants from the time profiles of OH have been described in detail recently (Koch et al., 2006). Biexponential time profiles of OH occur in the presence of the aromatics in the temperature range of adduct instability (i.e. by observing the decays of OH at temperatures where the thermal back-decomposition to OH is faster than 3s⁻¹, typically between 300 and 340 K) and with added O₂ or NO and triexponential time profiles occur in the presence of NO₂ (Knispel et al., 1990, Zetzsch et al., 1990, Koch et al., 2006). A global fit of the rate constants of the reaction mechanism (considering for a small diffusion loss of OH and the adduct from the observation zone) to sets of time profiles at fixed temperatures allows us to obtain precise values for the rate constants. A reliable extrapolation to room temperature can then be performed by the Arrhenius equation.

In addition, the reactions of benzene, toluene and p-xylene have been studied by the smog chamber technique at 298 K in almost pure nitrogen with added traces of O_2 ranging from 30 to 1000 ppm and at atmospheric conditions (21% of O_2), see Koch et al. (2006). The OH level is fairly constant in these measurements, and the rate constants of their reaction with the aromatics depend on O_2 since the

unimolecular decay of the adduct $(k_{.1})$ competes with the scavenging by O_2 . The apparent rate constant, k_{app} , then increases from the abstraction channel (k_2) to the sum of abstraction and addition (k_1+k_2) according to the equation $k_{app} = k_2 + k_1/(1+k_{.1}/k_{3a}[O_2])$.

3. RESULTS AND DISCUSSION

The FP/RF results from this study are summarised in table 1. The large OH-reactivity of hexamethylbenzene is in agreement with a previous study by Berndt and Böge (2001b) and it makes clear that this cannot be abstraction from the methyl groups, as follows from an observation of 3-hexene-2,5-dione from p-xylene hexamethyl-2,4-cyclohexadienone as a product of this ipso addition by Berndt and Böge. This fact and biexponential decays demonstrate clearly the existence of an ipso-adduct. The slightly higher necessary temperatures for observation of biexponential decays (> 350 K in our experiments) show that the adduct is even more stable than the OH-adducts of the other aromatics, where biexponential decays were observed at room temperature (or 320 K for aniline, phenol and m-cresol). The large OH-reactivity of aniline is in accord with the activating properties of the NH₂ substituent, and it appears that the joint action of 6 methyl groups in hexamethylbenzene cause a similar, activating effect.

The reactions of the OH-adducts of the aromatics hexamethylbenzene, phenol and m-cresol are two orders of magnitude larger than the other ones, this may again be the contribution of an ipso-adduct to the reaction. It should be noted, that there exists another reaction channel of a reversible addition of O_2 to the OH-adduct, and the equilibrium constant and the corresponding reactions have been first observed and determined by Bohn and Zetzsch (1999) for benzene-OH and Bohn (2000) for toluene-OH and finally been confirmed by Johnson et al. (2002) and Grebenkin and Krasnoperov (2004) for benzene in the gas phase. In a subsequent study, Johnson et al. (2005) observed the OH-adducts of various methylated aromatics from their UV absorption spectra. The irreversible reaction of O_2 (k_{3a}) with the OH-adduct of benzene ($1.6 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ in our FP/RF study) has been confirmed by Bohn and Zetzsch, 1999, ($2 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ by UV-absorption, to be corrected for an inhomogeneous radical distribution in the absorption cell). The irreversible reaction of O_2 (k_{3a}) with the OH-adduct of toluene ($5.6 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ in our FP/RF study) has been confirmed by Bohn and Zetzsch, 1999, ($2 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ by UV-absorption, to be corrected for an inhomogeneous radical distribution in the absorption cell). The irreversible reaction of O_2 (k_{3a}) with the OH-adduct of toluene ($5.6 \times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ in our FP/RF study) has been confirmed by Bohn (2000), determining (6.0 ± 0.5) $\times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ by cw-UV-laser longpath-absorption (6.0 ± 0.5) $\times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ in our FP/RF study) has been confirmed by Bohn (2000), determining (6.0 ± 0.5) $\times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ in our FP/RF study) has been confirmed by Bohn (2000), determining (6.0 ± 0.5) $\times 10^{-16} \text{ cm}^3 \text{s}^{-1}$ by cw-UV-laser longpath-absorption.

Table 1. : Rate constants for the reactions with the aromatics benzene (B), naphthalene (N), toluene (T), m-xylene (m-X), p-xylene (p-X), hexamethylbenzene (H), aniline (A), phenol (P) and m-cresol (m-C) at 298 K, except for k_{3a} , where the values are determined around 330 K.

Reaction	В	Ν	Т	m-X	p-X	Н	А	Р	m-C
Total react. $(k_1 + k_2)/10^{-12} \text{ cm}^3 \text{s}^{-1}$	1.1	27	6.4	21	16	200	100	25	56
Abstraction $(k_2/10^{-13} \text{ cm}^3 \text{s}^{-1})$	< 0.3	<2	5.7	20	24	?	?	55	51
Adduct + $O_2 (k_{3a}/10^{-16} \text{ cm}^3 \text{s}^{-1})$	1.6	<1	5.6	1.8	8.8	1800	6	300	600
Adduct + NO ₂ ($k_{3b}/10^{-11} \text{ cm}^3 \text{s}^{-1}$)	2.8	?	3.6	-	3.5	?	5	3	4
Adduct + NO $(k_{3c}/10^{-13} \text{ cm}^3 \text{s}^{-1})$	< 0.3	<1	< 0.3	< 0.3	<1	?	< 0.1	< 0.7	< 0.3

Assuming that HO₂ radicals are the main product from reaction (3a), - this is true for observations in the aqueous phase as well, see Pan et al, 1993, the recycling of OH by the reaction HO₂ + NO \rightarrow NO₂ + OH has been used in additional FP/RF measurements with O₂ and traces of NO (Koch et al., 1997, Zetzsch et al., 1997). These experiments gave quite complex time profiles of OH but confirmed the data for reaction (3a) in table 2 for benzene, toluene, m-xylene and naphthalene and enabled us to determine values at much lower temperatures, obtaining a value of $2x10^{-16} \text{ cm}^3 \text{s}^{-1}$ for benzene at 273 K, $5x10^{-16} \text{ cm}^3 \text{s}^{-1}$ for toluene at 258 K, and $20x10^{-16} \text{ cm}^3 \text{s}^{-1}$ for m-xylene at 286 K.

A study of the reactions of the OH-adduct with NO (k_{3c}) requires extreme care to purify the NO from NO₂ traces, and this is the reason why an earlier study by Zellner et al. (1985) failed to observe the low reactivity of NO, where our data in table 1 demonstrate the excellent capabilities and finally limitations of the technique.

The large reactivity of the OH-adducts with O_2 predominates under all tropospheric conditions, as shown in table 2, using the data from our FP/RF study, and confirmed by several other authors. This finding had

the consequence that further product studied have been performed either in the absence of NO_2 or over a much wider range of NO_2 levels (Berndt and Böge, 2001a, 2003, 2006, Bethel et al., 200, Volkamer et al., 2002, Klotz et al., 2002). It appears that larger yields of phenolic products are generally found in the absence of NO_2 and that these are the most relevant products from the OH-initiated transformation of aromatics troposphere. Cleary, further product studies on the transformation of phenols are needed.

Table 2. Level of NO₂ in air (21 vol-% O₂), where 50% of the OH-adducts are scavenged by NO₂. Note, that the level of OH would be extremely low in the air at ppm-levels of NO₂, because of the reaction OH + NO₂ \rightarrow HNO₃

Aromatic	[NO ₂] _{1/2} (ppm)		
	FP/RF	Chamber reference	
Benzene	1.3	~2 Volkamer et al. (2002)	
Toluene	3.3	reasonable agreement ^{a)}	
p-Xylene	5.1	4.3 Bethel et al. (2000)	
Phenol	330	29Berndt and Böge (2003)	

a) see Discussion by Atkinson and Aschmann (1994)

4. CONCLUSIONS

Of the three potential consecutive steps the reaction with O_2 is found to predominate under all tropospheric conditions. A major part of the reaction with O_2 is extremely fast and reversible but even the slower, irreversible path (determined in the present study) is much more important than any reaction with NO_x . NO is found to be more than three orders less reactive than NO_2 , and it requires ppm levels of NO_2 to compete with O_2 . Previous smog chamber studies overlooked this problem of a limited environmental relevance at ppm-levels of NO_2 , where ring opening products are largely exaggerated and photochemistry of carbonyl compounds perturbs the observations. More recent studies confirm increased yields of phenolic ring retaining products and reinvestigate the fate of NO_x , recycling of OH radicals from the OH-adduct and from HO₂ and the particle formation, where the yields of secondary aerosol have been underestimated in the past. In spite of the big progress there are still more than enough open questions on aromatics.

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Ozone production from Grenoble city during the august 2003 heat wave : modelling and analysis

Eric Chaxel, Jean-Pierre Chollet Laboratoire des Ecoulements Géophysiques et Industriels, Université J. Fourier, INPG, CNRS BP 53, 38041 GRENOBLE CEDEX 9, France jean-pierre.chollet@ujf-grenoble.fr

ABSTRACT

The heat wave from 1 to 16 august 2003 is considered in the city of Grenoble (French Alps). The modelling system (PREVALP) is based on several models operating on nested domains : MM5 for dynamics, CHIMERE for chemistry (18 km and 6km grid size) and METPHOMOD for both dynamics and chemistry (6 km and 2 km grid size). The analysis of the results shows that during the heat wave, the mixing layer is thicker, up to 3500 m agl, hence inducing transport of ozone to high altitude. Two regimes were diagnosed : (1) a freely developing convective layer, (2) a layer trapped under south wind which makes ozone precursors accumulate in the city. Local ozone production is estimated to be 40% of the plume maximum in case (2) and only 30% in case (1).

1. INTRODUCTION

The heat wave from 1 to 16 august 2003 is of special interest because of high mortality rate, even if it is not yet clear how affected by air quality. Anyway, ozone concentrations were abnormally high for two weeks although wind conditions have changed. Moreover these concentrations did not evolve exactly like mean values observed in Europe or in Paris (Vautard et al., 2005). The particular location of Grenoble which is surrounded by mountains may be suspected to play a major role in air quality and a main concern is about the part of the ozone due to local traffic and industry in order to assess efficiency of reduction policies.

The city of Grenoble (400 000 inhabitants) is located in the Alps at the crossing between 3 valleys (figure 1), at an altitude of 214km with surrounding summits reaching 2000 to 3000 meters. Depending on weather conditions, atmosphere dynamics local to the valley may be significantly decoupled from synoptic winds. GRENOPHOT field campaign in 1999 (Couach et al., 2003, 2004) gave insights to these processes through on site measurements and the development of numerical modelling.



Fig.1 left : Grenoble area (north at the top of the picture) ; right : computational domains (red line : dx = 6 km grid, white line : dx = 2 km grid)

As suggested in figure 1, the orography is complex. Slope and valley winds develop especially in summer with patterns much more intricate than in nearby Chamonix and Maurienne valleys (Chaxel et al., 2005) especially in the southern part of the region.

2. METHODOLOGY

The modelling system (PREVALP) is based on several models operating on nested domains. It may be viewed as an extension of PREVAIR system (Vautard et al. 2001) to regions in mountainous area.. It is based on dynamics and chemistry models operated on nested domains in order to take full account of interactions between synoptic weather and local atmosphere dynamics. Non hydrostatic models are used because of scales under interest, topography and convective effects,. Chemical reactions are handled through photochemistry reactions. It is somewhat similar to the modelling system developed for nearby Chamonix and Maurienne valley (POVA) (Brulfert et al, 2005), except for the solver used at smaller scales. The METPHOMOD (Perego, 1993) model was selected for the finer grids as being already used by Couach et al.

(2003, 2004) on the very same site. The cartesian grid well fits the local orography which combines slopes with cliffs. METPHOMOD runs simultaneously the dynamics and the chemistry, the latter with the 72 species RACM chemical scheme.

The dynamics is computed at 18 km grid and 6 km grid with MM5 (Grell et al. 1995) and the chemistry is computed with CHIMERE (Vautard et al. 2001) with the same grids (18 km and 6 km) and a 44 species chemical scheme. METPHOMOD allows to compute at the same time atmosphere dynamics and chemistry at 6 and 2 km grids. Emission inventory is based on EMEP data at 50 km and data specific to the site by CITEPA at 6 km and 1 km. Emissions are desegregated with time according to season, day and hour of the day. Biogenic emissions are fully considered as most of mountains around Grenoble are covered with forest.

PREVALP was run on GRENOPHOT data (ground data and wind profilers) in order to check the results (Couach et al. 2003,2004). The methodology was also tested against ESCOMPTE data (23 to 27 june 2001) in Marseille site where orography combines to sea breeze (Chaxel, 2006)

3. RESULTS AND DISCUSSION

Calculation has been operated during the whole summer 2003 in order to check the capability to deal with a wide range of summer conditions. Computed meteorology has been validated against data from ground stations : wind force and direction with special attention paid to wind reversals. Significant discrepancies in the humidity may be attributed to difficulties in modelling vegetation in abnormally dry conditions. Nevertheless, associated errors in temperature do not exceed 2 degrees. Ozone is given in fig. 2. with peak values up to 200 μ g/m³ which are correctly given by the model.



Fig 2 : ozone concentration from 1 to 15 august 2003 at Le Versoud ; black line : model, grey line : measures,

A local production of ozone is calculated as $PO_3^{loc} = O_3 - O_3^R$, where O_3^R is the concentration of regional ozone calculated at the boundaries of the METPOMOD domain. As shown in figure 4, this local production strongly depends on the day, On 5 august 2003, the CBL is trapped under south wind, the local production is high and located in the southern part of the Grenoble area. The competing north valley wind and south synoptic wind induce a front resulting into an ascending circulation which carries ozone up to high altitude (see also figure 3). On 6 august 2003, convective layer develops freely with wind blowing from north. In figure 5, free and trapped CBL regimes are identified during the heat wave episode. Local production is 40% of the plume maximum in the trapped CBL case and only 30% in the free CBL case. The difference is at its most at night with 15% to 20% of local O3 at night versus 5 to 10% at sunny hours



Fig. 3 : O3 (ppbV) and wind on 5 august 2003 at 17:00, south to north from left to right

The vertical mixing is much more important in the heat wave episode than during the 1999 GRENOPHOT campaign with mixing layer up to 3500 m agl,.



Fig. 4 production of local ozone *pO3* in ppbV on 5 august 2003 at 15:00 (left) and 6 august 2003 at 15:00 (right), grey scale ranges from 0 to 45



Fig. 5: Ozone from production local to the south part of Grenoble area, integrated from 1500 to 2500m in altitude (red arrow for trapped CBL regime , blue arrow for free CBL regime)

4. CONCLUSIONS

PREVALP numerical model was checked to appropriately simulate air quality in Grenoble for period ranging from days to months. Atmospheric trends from large to local scales are well reproduced at least in the limit of the 2 km grid resolution.

The heat wave developed general trends over whole Europe but local bias are characteristics of mountainous regions. Focus is put on Grenoble but conclusions can be extended to cities featuring similar orography. Nevertheless, the exact way each location develops a particular dynamics depends on details in terrain and valley orientations versus synoptic wind and the PREVALP model should be run in each case in order to get quantitative estimations.

As being oriented towards both process analysis and forecast, the model chain was designed to be possibly run on small computer (typically bipro PC computer) with rather short computing time (typically 3 hours to simulate a day with a 2 km grid). Atmospheric Dynamics and chemistry solvers need not to be significantly improved, at least as long as restricted to gaseous photochemistry. Improvements in emission modelling are needed with more exhaustive inventory. Because of deciduous and pine forests in mountains surrounding town, biogenic emissions have to be evaluated with better accuracy especially with season dependence. Influence of atypical events like heat wave on vegetation and therefore biogenic emissions are to be considered. Although O3 is less sensitive to emissions than primary pollutants (CO, NO..), estimation of traffic emissions needs to be continuously improve. Comparisons with measurements and forecasts are sensitive to the distribution of emissions with time (season, day of the week, hour) with a need of adjusting functions in use to the real traffic on the day of interest. Efficient and fast calculations make also possible to easily change emissions and assess result sensitivity to emission hypothesis.

Beyond the 2003 case under consideration here, scenarios were computed in the frame of Grenoble PPA (Atmosphere protection Plan) to assess air quality in 2010 with various traffic scenarios. The numerical tools under use make possible to refine the grid and run on faster and more parallel computers in order to take a better account of town canopy (e.g. 200 meters grid). This could aim at give better distribution in space for the purpose of air quality scenarios.

Moreover heat wave may be viewed as typical of what is being expected in future due to global warming especially with temperatures remaining high at night. Therefore, summer 2003 may be used to generate meteorological episodes to test air quality scenarios for future.

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INTERCOMPARISON BETWEEN NATIONAL AND REGIONAL SCALE PHOTOCHEMICAL POLLUTION SIMULATIONS OVER NORTHERN ITALY

A. Balanzino¹, C.Pertot², G.Pirovano³, M.Causa⁴, E.Ferrero¹, S.Alessandrini³, M.P.Costa³

¹Dipartimento di Scienze e Tecnologie Avanzate (DISTA), Universita' del Piemonte Orientale "A.Avogadro", Via Bellini 25/G, 15100 – Alessandria <u>alessia.balanzino@mfn.unipmn.it</u>, <u>enrico.ferrero@mfn.unipmn.it</u>, 0131/360151 ²CESI, Via Rubattino 54, 20134 – Milano <u>pertot@cesi.it</u>, 0221251 ³CESI RICERCA, Via Rubattino 54, 20134 – Milano <u>gupirovano@cesiricerca.it</u>, <u>alessandrini@cesiricerca.it</u>, <u>m.costa@cesiricerca.it</u>, 0221251

⁴Dipartimento di Chimica, Universita' di Napoli "Federico II", Via Cintia, 80126 – Napoli <u>causa@unina.it</u>, +39 081674202

ABSTRACT

A photochemical pollution model system is used for simulating airborne dispersion and chemical reactions at two different scales. The first simulation is carried out on a mesoscale domain including the whole Italian peninsula, while the second one considers only a regional scale domain in the North-West of Italy, where urban and industrial areas are located. The model resolutions are 25 km and 5 km respectively. Simulations have been run from April to September 1999. Moreover the mesoscale scale simulation is used to provide the boundary conditions for the regional scale one. Emissions are derived from different inventories based on different territorial units. Both the simulations are performed using the RAMS meteorological model in order to provide meteorological input to the photochemical model CAMx. The results of the two simulations are compared together with measured ozone and nitrogen dioxide data and the effects due to the different scale and resolution are discussed.

1. INTRODUCTION

Ozone is considered one of the most significant pollutants with respect to the potential impacts to human health and natural ecosystem, both in terms of critical episodes and as long-term exposures. Consequently, in order to assess the comprehensive effects of photochemical pollution, not only ozone peak concentrations need to be examined, but also ozone exposures on "seasonal" scale need to be quantified. Modelling systems can represent suitable tools for this purpose (Carmichael et al., 1986). As a matter of fact, the Italian law designates the integrated use of representative stations, for monitoring activities, emission inventories and modelling systems, for simulating air pollutants transport, transformation and diffusion, as the best approach for air quality assessment. In this study an integrated modelling system has been developed in order to perform a simulation of the photochemical pollution. The proposed system is built around some main modules: the emission pre-processor, the prognostic non-hydrostatic meteorological model RAMS (Regional Atmospheric Modelling System, Pielke et al., 1992), the interface module RAMS-CAMx, which is distributed by Environ as free software (http://www.camx.com/down/support.php) and the Eulerian model CAMx (Comprehensive Air Quality Model with extensions, Environ, 2005). The modelling system has been applied over two different domains: a mesoscale domain (1400x1600 km²) including the whole Italian peninsula and a regional scale domain (250x250 km²) in Northwest Italy, covering main urban and industrial areas. In this paper, the results of the two simulations are compared together with measured ozone and nitrogen dioxide data with the aim of validating the simulation results. Also the effects due to the different scale and resolution are analysed and discussed.

2. METHODOLOGY

The proposed modelling system includes the meteorological model (RAMS), different interface modules (RAMS-CAMx), an emission processors and the photochemical model (CAMx). RAMS is most often used as a limited area model. It is constructed around the full set of the primitive dynamic equations. The model is driven by means of the nudging technique using the ECMWF (European Centrum for Medium Weather Forecast) analysis as boundary conditions. These fields are also used to give the initial conditions. The Mellor and Yamada scheme 2.5 (*Mellor and Yamada, 1982*) is used in RAMS to compute the vertical mixing coefficients. The RAMS simulation, for this summertime, is carried out using one grid. The interface modules are useful tools in order to translate hourly RAMS output meteorological fields to CAMx inputs. Different interface modules are available and should be run for each days of the simulation period. The first module provides height and pressure for each vertical grid level, horizontal wind components, temperatures, vertical diffusivities, water vapor, clouds and rain. Regarding the vertical diffusivity different options can be chosen. The second module provides topography and land use, and the last module provides the photolysis

rates. These 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.

The emissions processing system is designed to produce emission fields according to the model characteristics. The emissive data-set are derived from emission inventories, unfortunately it is impossible to take the simple datum so as it is, but it's necessary to elaborate it (Seinfeld, 1988). In fact an emission processor is needed to perform the following steps: the spatial disaggregation in order to allocate the territorial unit information onto grid cells; the temporal disaggregation in order to allocate the aggregate emissions to the temporal useful detail (usually hourly) and the hydrocarbon speciation in order to convert the total volatile organic compounds information in species-group required by the model. Starting from simple emission data inventory the processor performs the spatial splitting using "surrogate (or proxy) variables"; secondly the processor makes the temporal disaggregation using three modulation factors (monthly, daily and hourly) which indicate how yearly emissions, for different sectors, are issued on 12 months (12 splitting factors), on week days (7 splitting factors) and on 24 hours of a specific day (24 splitting factors); finally the hydrocarbon speciation is carried out: starting from the total volatile organic compounds emissions, defining a speciation profile (percent of single species volatile organic compounds on total volatile organic compounds) for each emissive splitting source and converting such information in species group required by the model (in our case the required species are 13). In this study, for the Italian regions, emission data are provided by the regional emission inventory (more detailed than national inventory); for European areas and for the portion of Mediterranean Sea emission data have been derived by the EMEP inventory that provides emission assessment over Europe on cells 50x50 km², referring to year 1999.

CAMx is an Eulerian photochemical dispersion model that simulates the emission, dispersion, chemical reaction and removal of pollutants in the troposphere by solving the pollutant continuity equation for each chemical species on system of nested three-dimensional grids.

The photochemical model CAMx implements an extended version of the CB-IV mechanism (*Whitten et al., 1980, Gery et al., 1989*) including aerosol and mercury chemistry and several additional inorganic reactions appropriate for regional modeling conditions. It includes 117 reactions and 67 species.

The regional scale domain (Figure 1a) covers an area of 250x250 km², including different North-West Italian regions, a portion of Mediterranean Sea, and some European areas. Therefore the domain is characterized by a main plain area (the Po valley), surrounded by elevated Alpine mountain and the sea.

The CAMx simulation area has been horizontally subdivided into 50x50 cells, with a space resolution of 5 km and the vertical domain extends up to 5490 [m agl], subdivided into 14 layers of growing thickness.

The mesoscale domain (Figure 1b) has an extension of $1400 \times 1600 \text{ km}^2$ spreading, with a grid step of 25 km, from 5°E to 20°E and from 35°N to 49 °N. Thirteen layers, up to 9000 m a.s.l, compose the vertical structure. The initial and boundary conditions for the mesoscale run have been provided by CHIMERE model (Vautard et al., 2005). Those for the regional run have been provided by the large-scale simulation (*M.P.Costa et al., 2006*).



Figure 1b

Both meteorological and photochemical models have been run for the whole summer 1999, from April to September supplying hourly concentrations fields. This period was selected because of the severe and critical ozone episodes generally occurring during the summer time. In fact the most high ozone concentrations, that exceed law limit, are detected on the hot months with intense solar radiation.

Photochemical simulations over the Italian domain have been performed by means of the same modelling system, but with different input data. More precisely, emissions covering Italian territory have been derived from the Italian official inventory, while initial and boundary conditions have been obtained by CHIMERE model (Vautard et al., 2005) runs. Finally, vertical diffusion coefficients have been reconstructed on the basis of the turbulent kinetic energy fields provided by RAMS.

3. RESULTS AND DISCUSSION

Ozone and nitrogen dioxide hourly time series from the air quality networks (Figure 1a) have been analyzed and, starting from obtained results, a reduced set of six representative monitoring stations has been selected to compare the results of the two simulations with measurements.

The comparison between observed and predicted ozone and nitrogen dioxide levels at two different monitoring sites is presented in the following Figures 2, 3. Regarding ozone, the daily maximum 8-hourly average concentration is shown, instead for nitrogen dioxide the mean daily concentration has been taken into account. The correlation coefficients are reported in table 1 for ozone and nitrogen dioxide and for both grid resolutions at rural, suburban and urban station.

The analysis demonstrates that ozone concentrations seem generally rather insensitive to the grid resolution in terms of statistical parameters (i.e. the correlation coefficient, table 1). Indeed, fine scale simulation has generally provided slightly higher correlation values than large scale one, with the exception of the urban stations of Torino Lingotto (st.3) and Limito (st.4) were fine scale model performances are clearly worse. Differently the comparison of the time series has put in evidence some relevant differences: a) fine scale simulation results are generally underestimated with respect to large scale concentrations; b) discrepancies increase moving from rural to urban stations.

Concerning the nitrogen dioxide, concentrations seems to be more sensitive than ozone to the grid spatial resolution, as they are more linked to emissions: the primary pollutant, directly emitted, is nitric oxide (NO), together with a small proportion of nitrogen dioxide (NO2). NO and NO2 are collectively known as nitrogen oxides (NOX) because they are rapidly inter-converted during the day. The differences between the two simulations can be observed as for correlation coefficient in table 1: the correlation improves using a grid spacing of 5 km. The nitrogen dioxide mean daily concentrations over six months differ in relation to the grid resolution, particularly near the urban areas (st.3, Torino Lingotto and st.4, Limito). As a matter of fact, the urban measured values are overestimated using the model with grid step 5 km, while the same values are underestimated using the model with larger grid spacing. Both simulations overestimate the observed values near the rural area south of Milan (st.2, Motta Visconti).



4. CONCLUSIONS

A photochemical pollution model system is used for simulating airborne dispersion and chemical reactions on two different scales, resolutions 25 km and 5 km respectively. The first simulation is carried out on a mesoscale domain including the whole Italian peninsula, while the second one considers only a regional scale domain in the North-West of Italy. The two simulations have been run for six months, from April to September 1999. The performed analysis suggests that varying horizontal grid resolution from 5 to 25 km can influence ozone concentrations, above all in the urban areas. Differences seem to be more related to the absolute values of the ozone concentrations than the temporal variability.

Generally nitrogen dioxide seems to be more sensitive to the grid resolution and model performance are generally better with the fine scale model that is able to better describe the emission pattern over the studied area. Anyway, fine scale model has also put in evidence some relevant overestimation, mainly in the urban areas, probably due to an underestimation of the vertical diffusivity. As a matter of fact the Mellor and Yamada 2.5 closure implemented in RAMS underestimate the turbulent kinetic energy, as shown by Trini Castelli et al., 2001 and Ferrero et al., 2003. This result probably explains also the ozone underestimation displayed at 5 km resolution.

So we can conclude that increasing model resolution allows to better depict the emission pattern and also to refine the description of the temporal evolution of both primary and secondary pollutants, even if fine scale model show a higher sensitivity to the reconstruction of the vertical turbulence. On the other hand, larger grid spacing reduces computational capabilities request that can be important in scenario studies. As a matter of fact, in a regulatory context, it's possible to optimise emissions abatement or decrement strategies by means of scenario studies performed using different spatial scales and it's possible to identify risky areas for the human health and to change the emissive panel. Therefore the spatial resolution can be selected taking into account different chemical species and performance indicators in order to set correctly the grid configuration.

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