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Modelling photochemistry in alpine valleys

G. Brulfert, C. Chemel, E. Chaxel, and J. P. Chollet

Laboratory of Geophysical and industrial Fluid Flows, University J. Fourier, INP Grenoble, CNRS, BP53, 38041 Grenoble cedex, France

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Correspondence to: G. Brulfert (guillaume.brulfert@hmg.inpg.fr)

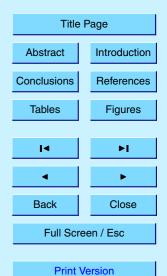
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Abstract

Road traffic is a serious problem in the Chamonix Valley, France: traffic, noise and above all air pollution worry the inhabitants. The big fire in the Mont-Blanc tunnel made it possible, in the framework of the POVA project (POllution in Alpine Valleys), to undertake measurement campaigns with and without heavy-vehicle traffic through the valley, towards Italy (before and after the tunnel re-opening). Modelling in POVA should make it possible to explain the processes leading to episodes of atmospheric pollution, both in summer and in winter.

Atmospheric prediction model ARPS 4.5.2 (Advanced Regional Prediction System), developed at the CAPS (Center for Analysis and Prediction of Storms) of the University of Oklahoma, enables to resolve the dynamics above a complex terrain.

This model is coupled to the TAPOM 1.5.2 atmospheric chemistry (Transport and Air POllution Model) code developed at the Air and Soil Pollution Laboratory of the Ecole Polytechnique Fédérale de Lausanne.

The numerical codes MM5 and CHIMERE are used to compute large scale boundary forcing.

Using 300-m grid cells to calculate the dynamics and the reactive chemistry makes possible to accurately represent the dynamics in the valley (slope and valley winds) and to process chemistry at fine scale.

Validation of campaign days allows to study chemistry indicators in the valley. NO_y according to O_3 reduction demonstrates a VOC controlled regime, different from the NO_x controlled regime expected and observed in the nearby city of Grenoble.

1. Introduction

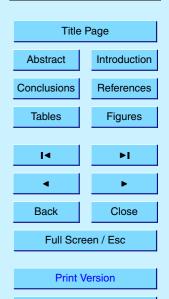
Alpine valleys are sensitive to air pollution due to emission sources (traffic, industries, individual heating), morphology (narrow valley surrounded by high ridge), and local meteorology (temperature inversions and slope winds). Such situations are rarely inves-

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tigated with specific research programs taking into account detailed gas atmospheric chemistry.

Several studies of the influence of atmospheric dynamics over complex terrain on air quality took place with field campaigns in the Alpine area over the last two decades. The program TRANSALP included an intensive sampling campaign with high density network for ozone measurements on a 300×300 km² area (Löffler-Mang et al., 1998). The POLLUMET program (Lehning et al., 1996) focused on processes controlling oxidant concentrations in the Swiss Plateau. These two programs mostly dwelt with meso scale processes, and did not take into account in detail atmospheric dynamics in narrow valleys. In the same way, one of the objectives of the MAP program (http: //www.map.ethz.ch/) was devoted to the study of the evolution of the planetary boundary layer in complex terrain at the meso scale, but no measurements were conducted in parallel on any aspect of atmospheric chemistry. The programs VOTALP I (Wotawa and Kromp-Kolb, 2000) and VOTALP II (http://www.boku.ac.at/imp/votalp/votalpII.pdf) were essentially devoted to the study of ozone production and vertical transport over the Alps. The modelling in this program (Grell et al., 2000), coupling a non hydrostatic model with a photochemistry model at a resolution of 1x1 km for the inner domain, showed, among other, the influence of the valley wind in the advection of chemical species from the foreland to the inner valley. The authors conclude that the evaluation of the pollutant budget in the valley requires a finer grid as well as a detailed emission inventory. Couach et al. (2003) present a modelling study coupling atmospheric dynamic and photochemistry (at a 2×2 km scale) in the case of the Grenoble (France) area, which is a large glacial valley in the French Alps. This study is connected to a 3-day field campaign conducted in summer 1999, including a large array of ground and 3-D measurements dedicated to ozone and its precursors. Again, this study showed the large influence of the valley wind on the distribution of ozone concentrations. The modelled ozone concentrations were in reasonable agreement with 3-D measurements. Finally, the Air Espace Mont Blanc study (Espace Mont Blanc, 2003) was conducted by the Air Quality networks in France, Italy, and Switzerland. The field

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study was based on a 1 year monitoring (June 2000–May 2001) at stations around the "Massif du Mont Blanc", for regulated species (SO₂, NO₃, O₃, PM₁₀ and PM_{2.5}).

These previous studies underlined the limitations of the models in handling detailed atmospheric dynamics in complex terrain when using only 1x1km resolution, while these processes are the dominant factors controlling the concentrations fields.

Following the accident under the Mont Blanc tunnel (Fig. 1) on 24 March 1999, international traffic between France and Italy was stopped through the Chamonix valley (France). The heavy-duty traffic (about 2130 trucks per day) has been diverted to the Maurienne Valley, with up to 4250 trucks per day. The POVA (POllution in Alpine Valleys) program was launched in 2000.

The general topics of the program are the comparative studies of air quality and the modelling of atmospheric emissions and transport in these two French alpine valleys before and after the reopening of the tunnel to heavy duty traffic to identify the sources and characterize the dispersion of pollutants (Jaffrezo et al., to be submitted, 2005¹). The program includes several field campaigns, associated with 3-D modelling in order to study impact of traffic and local development scenarios.

Firstly the area of interest and numerical models in use are presented together with methods to prescribe boundary conditions. Main features of the emission inventory are given. After a validation from comparison with field experiments for dynamic and chemistry, computations of photochemical indicators during a summer IPO concludes to a VOC sensitive regime.

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¹Jaffrezo, J. L., Albinet, A., Aymoz, G., Besombes, J. L., Chapuis, D., Jambert, C., Jouve, B., Leoz-Garziandia, E., Marchand, N., Masclet, P., Perros, P. E., and Villard, H.: The program POVA "Pollution des Vallées Alpines": general presentation and some highlights, Atmos. Chem. Phys. Discuss., to be submitted, 2005.

2. The area of interest

The Chamonix valley is 23 km long, closed in its lower end by a narrow defile (the Cluse pass) and at the upper side by the Col des Montets (1464 m a.s.l.) leading to Switzerland (Fig. 1). The general orientation of the valley is globally NE-SW. With North latitude of 45.92° and East longitude of 6.87°, the centre of the area is at approximately 200 km from Lyon (France), 80 km from Genève (Switzerland) and 100 km from Torino (Italy). The valley is rather narrow (1 to 2 km on average on the bottom part) and 5 km from ridge to ridge, with the valley floor at 1000 m a.s.l. on average, surrounded by mountains culminating with the Mont Blanc peak (4810 m a.s.l.). Vegetation is relatively dense with many grassland and forest areas (Fig. 2).

There are no industries or waste incinerators in the valley, and the main anthropogenic sources of emissions are vehicle traffic, residential heating (mostly with fuel and wood burning), and some agricultural activities. The resident population is about 12 000 but tourism brings in many people (on average 100 000 person/day in summer, and about 5 millions overnight stays per year), mainly for short term visits. There is only one main road supporting all of the traffic in and out of the valley, but secondary roads spread over all of the valley floor and on the lower slopes. During the closing of the Mont-Blanc tunnel leading to Italy, the traffic at the entrance of the valley (14 400 vehicles/day on average) was mostly composed of cars (91% of the total, including 50% diesel powered), with a low contribution of local trucks (5%) and of buses for tourism (1%). Natural sources of emissions are limited to the forested areas, with mainly coniferous species (95% of spruce, larch and fir).

3. Model for simulation

Because of the orography, slopes winds are observed. Their thickness is around 50 to 200 m and depends on local orography effects. Horizontal resolution must be under 1 km to describe correctly meteorological and chemistry processes. A terrain following

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coordinate is appropriate to the vertical resolution. Non-hydrostatic models have to be used at meso-scale. The influence of regional meteorology and ozone concentration is important, overlapping models give boundary conditions.

To sum up, the modelling system for the valley itself is made of the meso-scale atmosphere model ARPS 4.5.2 and the troposphere chemistry model TAPOM 1.5.2.

3.1. Model for atmosphere dynamics

Large eddy simulation was used to study meso-scale flow fields in both valleys. The numerical simulations presented here have been conducted with the Advanced Regional Prediction System (ARPS), version 4.5.2 (Xue et al. 2000, 2001). Lateral boundaries conditions were externally-forced from the output of larger-scale simulations performed with the Fifth-Generation Penn State/ NCAR Mesoscale Model (MM5) version 3 (Grell et al., 1995). MM5 is a non-hydrostatic code which allows meteorological calculation at various scales with a two-way nesting technique. In the present study three different domains were used with MM5 (Table 1). For the Chamonix valley modelling with ARPS, two grid nesting levels were used as shown in Table 1. A geographical description of domains is available in Fig. 3.

3.2. Model for atmosphere chemistry

ARPS is coupled off-line with the TAPOM 1.5.2 code of atmospheric chemistry (Transport and Air POllution Model) developed at the LPAS of the EPFLausanne (Clappier, 1998; Gong and Cho, 1993). 300-m grid cells to calculate dynamics and reactive chemistry make possible to accurately represent dynamics in the valley (slope winds) (Anquetin et al., 1999) and to process chemistry at fine scale.

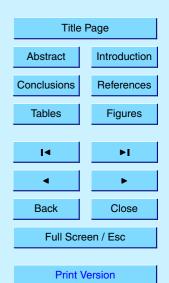
TAPOM is a three dimensional eulerian model with terrain following mesh using the finite volume discretisation. It includes modules for transport, gaseous and aerosols chemistry, dry deposition and solar radiation. It takes into account the extinction of solar radiation by gases and aerosols in the gaseous chemistry calculation.

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TAPOM uses the Regional Atmospheric Chemistry Modelling (RACM) scheme (Stockwell et al., 1997). RACM is a completely revised version of RADM2. The mechanism includes 17 stable inorganic species, four inorganic intermediates, 32 stable organic species (four of these are primarily of biogenic origin) and 24 organic intermediates, in 237 reactions. In RACM, the VOCs are aggregated into 16 anthropogenic and three biogenic model species. The grouping of chemical organic species into the RACM model species is based on the magnitudes of the emissions rates, similarities in functional groups and the compound's reactivity toward OH (Middleton et al., 1990). RACM was compared with other photochemical mechanisms and it gives very good results for O₃ with regards to the percentage of deviation of individual mechanisms from average values (Jimenez et al., 2003).

For the boundary conditions, CHIMERE, a regional ozone prediction model, from the Institut Pierre Simon Laplace, gives concentrations of chemical species at five altitude levels (Schmidt, 2001) using its recent multi-scale nested version. Then, CHIMERE is used at a space resolution of 27 km and 6 km to give chemical species initialisation and boundaries. Chemical concentrations calculated on a large scale domain are used at the boundaries of a smaller one. Then, we can have a very good description of the temporal variation of the background concentrations of ozone and of other secondary species.

The whole methodology of modelling system to obtain photochemical simulations is described Fig. 4.

4. Emission inventory

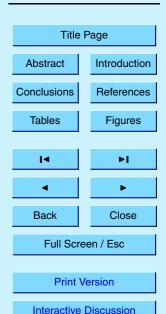
The emission inventory is based on the CORINAIR methodology and SNAPS's codes, with a $100 \times 100 \, \text{m}$ grid and includes information (land use, population, traffic, industries...) gathered from administrations and field investigations. The area covers $695 \, \text{km}^2$. The emission inventory is space and time-resolved and includes the emissions of NO_x , CO, CH_4 , SO_2 and non methane volatile organic compounds (NMVOC).

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As expected, the result which includes both biogenic and anthropogenic sources, shows very large emissions of pollutants due mainly to the presence of road transport and plants (Table 2).

These emissions are lumped into 19 classes of VOC as required by the Regional Atmospheric Chemistry Mechanism (RACM) (Stockwell et al., 1997).

Emission classes are given in the Table 3. The emission inventory takes into account roads and access ramps to the tunnel adjusting emissions to the slope of the road. A specific feature of emission is the significant contribution of heavy vehicles (>32 tons).

5. Validation

A first step in modelling Chamonix valley was to do computations in a simplified case of no forcing by synoptic wind and open boundary conditions (Brulfert et al., 2003). Then, atmospheric circulations develop by themselves from thermal processes only. Such a configuration enhances features specific to the valley and mimic the worst conditions for pollution because of a lack of mean transport. This idealized case is not so far from the situation frequently observed in Chamonix with dynamics inside the valley decoupled from synoptic meteorology. Thus dynamic is restricted to convection and slope wind from sun heating (solar radiation was chosen to correspond to June).

The simulations presented here are not realized in this simplified case but take a full account of the real meteorology of the week of computation during the summer POVA IPO (5 July 2003 to 11 July 2003).

5.1. High-resolution meteorological simulation: comparison with surface and wind profiler data

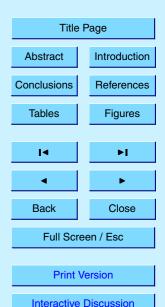
The redistribution of pollutants and therefore the ozone production is very dependent on meteorological conditions. The observed meteorological situation during the 7 days of intensive period of observation (IPO) is summarized in Table 4. A north westerly

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wind with sun prevailed. In this complex mountainous area, wind balance and slope winds are important for the transport of chemical species.

To validate the simulated meteorological fields, we compare the model results to surface observations (Fig. 5). We note that the observed and modelled variables are in good agreement.

Temperature at sites 'Les Houches', 'Chamonix' and 'Argentière' shows good amplitudes for the minimum and maximum, respectively at 01:00 and 13:00 TU. A slight discrepancy at minimal value may be attributed to the difficulties in accurately modelling cooling of lower layer and humidity content of soil canopy at night.

Wind force at site 'Clos de l'ours' corresponds to measurement with maximum at 13:00 TU, nocturnal cycle is present. The computed wind velocity at the station 'Bois du Bouchet' is more important than the real velocity because of a local effect with this station: trees are very close and slow down wind at ground level especially when flowing down valley.

Shifts in wind direction occur at the right times at sites 'Bois du Bouchet', 'Argentière' and 'Clos de l'ours' at 08:00 and 20:00 TU.

Profiler data are in good agreement with values from the model (Fig. 6a and b): wind reversal starts and stops at the same time. The altitude of the synoptic wind is well represented. Model results taken into account come from the first layer above the topography. ARPS works with a terrain following coordinate.

The boundary layer thickness is well simulated all along the day as it may be observed from wind profiler vertical profiles. Discrepancies are observed on 9 July, but it is a stormy day with instable weather. More details on dynamics process will be described in a separate paper devoted to dynamics.

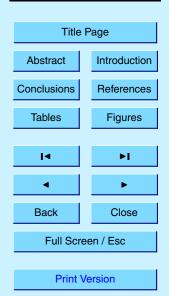
Finally, we can say that the simulated meteorological fields are very realistic: temperature does not show any bias. The evolution of the thickness of the inversion layer is well simulated. Wind direction and forces are well reproduced with wind reversal observed at the same times in the model and from measurements. Therefore, meteorological fields may be viewed as realistic enough to drive transport and mixing of

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chemical species.

5.2. High-resolution chemistry simulation: comparison with surface data

Concentrations of pollutants in the valley (such as O_3 or NO_2) are rather low at least when compared with large cities: values peak at 75 ppb for O_3 and 40 ppb for NO_2 compared to 100 ppb for O_3 and 50 ppb for NO_2 in nearby city of Lyon or Grenoble. To validate the simulated chemical fields, model results and surface observations are compared during the summer 2003 IPO. Model results taken into account come from the first layer above the topography. TAPOM works with a terrain following coordinate.

Ozone from the observation and from the model is in good agreement in both urban and rural stations (Fig. 7). Both spatial and temporal variability of the simulated ozone concentrations correspond reasonably well to the measured values. Figure 9 shows the correlations between the measured and simulated ozone concentrations for all the IPO days except for the stormy day (9 July 2003). Values of correlation coefficients are significantly high with $0.73 < R^2 < 0.76$.

These results can be compared to the same correlations in Grenoble during a high ozone episode with R^2 =0.64 for urban station and R^2 =0.42 for suburban stations (Couach, 2004).

Background stations ('Col des Montets' and 'Plan de l'aiguille') are directly under regional influence. The amplitude of the variation of ozone concentrations are low, it does not make sense to give correlation coefficient. The relative mean error on ozone concentration all along the IPO (with the stormy day) is 14% at the site 'Plan de l'aiguille' and 6% for the site 'Col des Montets' (respectively 12 and 3% without the first day spin up).

It is possible to observe a more important effect of local sources in the south part of the valley: amplitude of ozone concentration is more important for 'Chamonix centre', 'Clos de l'ours', 'Bossons' and 'Bois du Bouchet'. There is a titration of ozone by NO emissions. In the north part of the valley, amplitude of concentration is less important, with values of background at site 'Argentière' and 'Col des Montets'. Road traffic is less

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important there.

The influence of regional ozone in the valley is preponderant. If we correlate daily maximum of ozone concentration at every site with the concentration of background stations at the same hour, high values of coefficients of correlation are obtained (R^2 =0.87 for 'Col des Montets' station and R^2 =0.79 for 'Plan de l'aiguille' station) as shown with Fig. 10.

Ratio of regional O_3 concentration over urban stations daily maximum (at the hour of the maximum) gives important information about regional influence of O_3 . High values (\approx 1) are associated with regional preponderance and lows values with local influence. Here, we have important values (ratio>0.96 when compared with the two background stations).

NO₂ concentration at sites 'Bossons', 'Clos de l'Ours' and 'Argentières' leads to the same conclusion as for ozone (Fig. 8): only the south part of the valley is really affected by traffic emissions. Concentrations of NO₂ decrease when going to the north of the valley. Dilution of pollutants by wind transport is weak: important concentrations are observed only close to the sources. NO₂ correlations are satisfactory but an improvement of the emission inventory for city and secondary traffic should improve results.

Nitric acid levels are low but well simulated (Fig. 8). CO concentration (Fig. 8) measured and simulated are more than 15 times inferior to the air quality norm (8591 ppb, on 8 h).

6. Photochemical indicators to distinguish ozone production regime

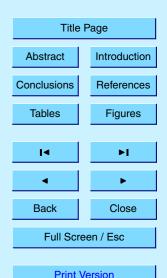
Narrow valleys in mountainous environment are very specific areas when it comes to air quality. Emission sources are generally concentrated close to the valley floor, and very often include industries and transport infrastructures. For developing ozone abatement strategies in a specific area, it is important to know whether the ozone production is limited by VOC or NO_x . In order to understand the impact of the emissions sources on ozone production regime, three simulations are performed. All of them are based

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on meteorology and emission inventory of 7 July 2003. Run B is the simulation of 7 July. Run N corresponds to an arbitrary reduction in NO_x emissions of 50%. Run V is obtained with an arbitrary reduction in VOC emissions of 50%. The three runs are described in Table 5.

7 July 2003, is representative of a summer sunny day with mean pollution level. Photochemical indicators are considered in order to distinguishing NO_x limited and VOC limited ozone formation.

The indicator under consideration is NO_y ($NO_y = NO_x + HNO_3 + PAN$) (Milford et al., 1994). The rationale for NO_y as an indicator is based in part on the impact of stagnant meteorology on NO_x -VOC sensitivity. Stagnant meteorology and associated high NO_x , VOC, and NO_y cause an increase in the photochemical life times of NO_x and VOC, with the result that an aging urban plume remains in the VOC-sensitive regime for a longer period of time. With more vigorous meteorological dispersion and lower NO_x , VOC and NO_y an aging urban plume would rapidly become NO_x sensitive (Milford et al., 1994).

Figure 11 illustrates the NO_x -VOC sensitivity for the simulations (runs N and V) in the bottom of the valley. Only meshes of the terrain with an altitude less than 1500 m above sea level are considered in order to include all the anthropogenic sources. Although a significant part of the domain area is rural-type, effects of non rural emission predominate.

The Fig. 11 shows the change in ozone concentrations associated with either reduced VOC (run V) or reduced NO_x (run N) relative to the domain. The positive values represent locations where, by decreasing the emission, a reduction in ozone is obtained while negative values result from locations where reduced emissions cause more ozone.

According to the results, the ozone production is VOC limited: only a diminution of VOC leads to a reduction of ozone concentration (run V). This conclusion differs from what was observed in the nearby city of Grenoble (100 km from the valley in a Y shape convergence of three deep valleys) where a NO_x controlled regime was observed (Couach, 2004).

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7. Conclusions

A system of models has been built to model dispersion and evolution of pollutants in a narrow valley. This system is based on several atmosphere dynamics and gas chemistry numerical codes selected for their ability to deal with processes developing at different length and time scales. TAPOM and ARPS codes are used for fine space resolution when CHIMERE and MM5 are used at larger scales.

Three-dimensional photochemical simulations have been performed for a 7 day period with this system of models, during the POVA intensive period of observation in the topographically complex and narrow Chamonix valley. Results from the numerical simulation are in good agreement with observations. Wind direction and forces are well reproduced with wind reversal observed at the same times in the model and from measurements. The evolution of the mixed layer thickness induced by thermal convection is well represented with growth in the morning and decay at night. These features of atmosphere dynamics are of major importance for transport and dilution of pollutants.

Computed concentrations are in good agreement with measured values, for both primary and secondary pollutants. Correlation between maximum of ozone and background values (0.8) suggests the regional origin of the pollutant. Dilution of pollutants by wind transport (e.g. NO_2) is weak: important concentrations are observed only close to the sources.

For a later purpose of suggesting reduction strategy, the general trend of chemical process has to be characterized. Well chosen indicators based on some species concentrations allow to determine a prevailing mechanism. The NO_y indicator shows that the region of the maximum ozone is VOC saturated.

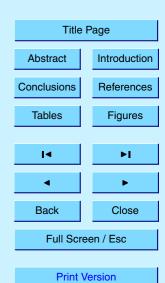
With the transfer of traffic from Chamonix to Maurienne valley because of the accident of Mont-Blanc tunnel, program POVA investigates also Maurienne. As for Chamonix valley, primary and secondary pollution is considered with measurements and numerical simulations based on the very same system of models. Ozone production regime and indicators obtained in the two valleys will be compared.

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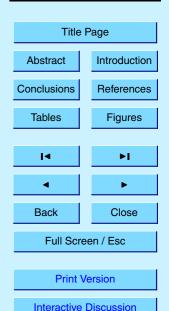
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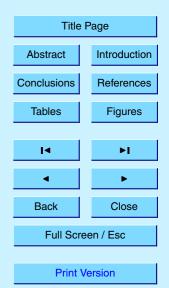
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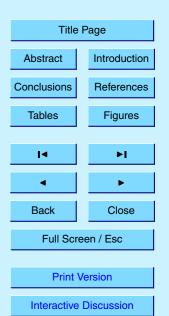


Table 1. Hierarchy of computational domains.

		Typical extend	Grid nodes nx E-W×ny N-S	Grid size Δx=Δy (km)	Code in use for simulation
Domain 1	France	1500 km	45×51	27	MM5
Domain 2	Southeastern France	650 km	69×63	9	MM5
Domain 3	Savoie mountains	350 km	96×96	3	MM5
Domain 4	Haute-Savoie Dept.	50 km	67×71	1	ARPS
Domain 5	Chamonix valley	25 km	93×103	0.3	ARPS

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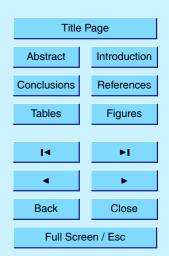
Table 2. Emissions inventory in the area of interest (t.year⁻¹).

	СО	NMVOC	NO _x	SO2	PM
Yearly emissions (t.year ⁻¹)	827	535	551	194	79
Biogenic sources (% of the year)	0%	51%	2%	0%	0%
Commercial and residential plants (% of the year)	30%	3%	10%	61%	91%
Road transport (% of the year)	70%	19%	88%	39%	9%
Domestic solvent (% of the year)	0%	15%	0%	0%	0%
Gasoline distribution (% of the year)	0%	12%	0%	0%	0%

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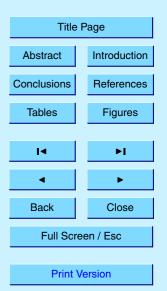
Table 3. Classes of the emission inventory.

Traffic sources	Anthropogenic sources	Biogenic sources
Heavy vehicles	Commercial boiler	Forest
Utilitarian vehicles on motorway	Residential boiler	Grassland
Utilitarian vehicles on road	Domestic solvent	
Cars	Gas station	
Cars in city		
Aerial traffic		

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Table 4. IOP meteorology.

-	05/07/03	06/07/03	07/07/03	08/07/03	09/07/03	10/07/03	11/07/03
Description of the situation		禁	禁		2	No.	
Tmin (°C)	4	5	6.5	7	8.5	8	8
Tmax (°C)	22	24	25	26	26	28	27
Isotherm 0°C	3700 m	3850 m	3700 m	4200 m	4000 m	4100 m	4000 m
Wind description at 4500 m a.s.l.	NW 2.5 m/s	NW 4 m/s	W 4 m/s	(<1m/s) Not significant	(<1m/s) Not significant	N to NW 5.5 m/s	NW 7 m/s

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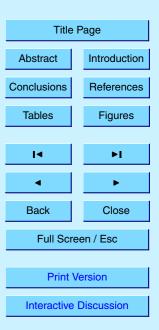
Table 5. Runs to determine ozone production regime.

	Date	Duration	Emissions
Run B	7 July 2003	24 h	All
Run N	7 July 2003	24 h	Run B -50% NO _x
Run V	7 July 2003	24 h	Run B – 50% VOC

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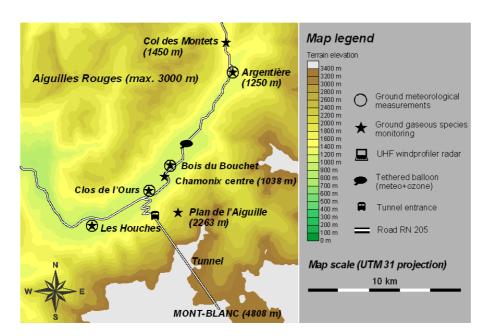
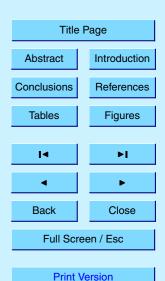


Fig. 1. Topography of Chamonix valley: main measurement sites (centre of the valley: Latitude 45.92° N, longitude 6.87° E). Road is the white line.

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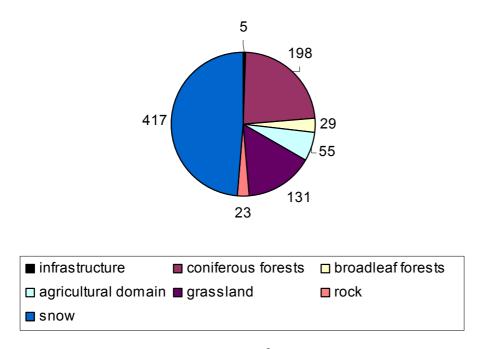


Fig. 2. Landuse of Chamonix valley in summer (km²).

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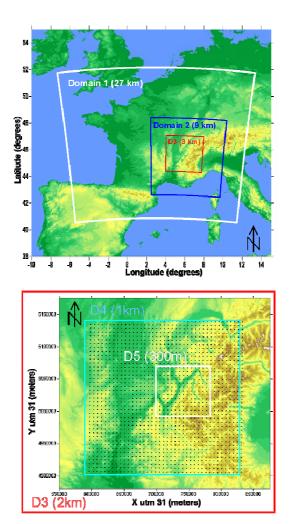
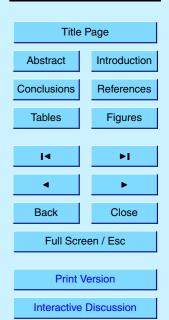


Fig. 3. Geographical description of MM5 (D1, D2, D3) domains over Europe and ARPS (D4,D5) domains over Haute-Savoie department.

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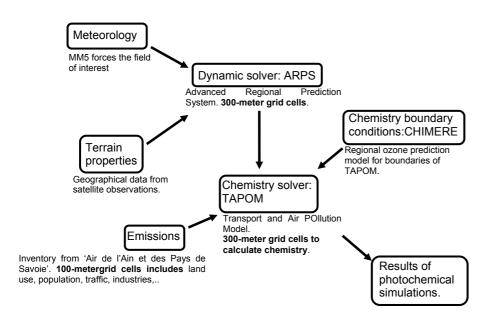
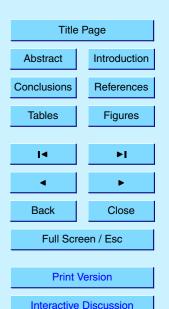


Fig. 4. Description of the modelling system for photochemical simulations.

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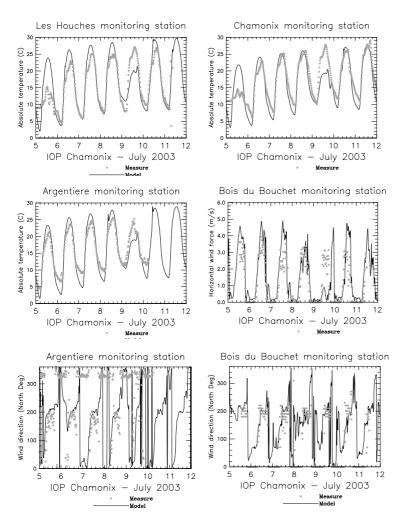


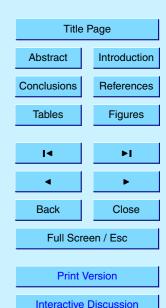
Fig. 5. Meteorological monitoring station compared to results from the simulation. Measure is represented by points, model by line.

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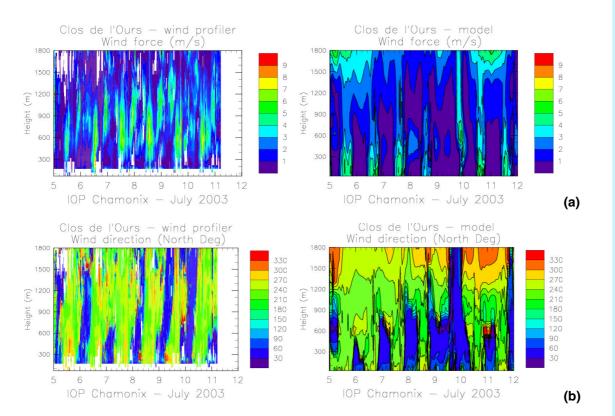
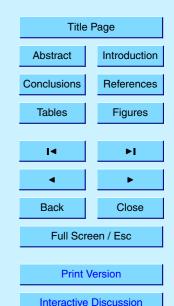


Fig. 6. (a) Wind force from the wind profiler (left) compared to results (right) from the computation. **(b)** Wind direction from the wind profiler (left) compared to results from the computation (right).

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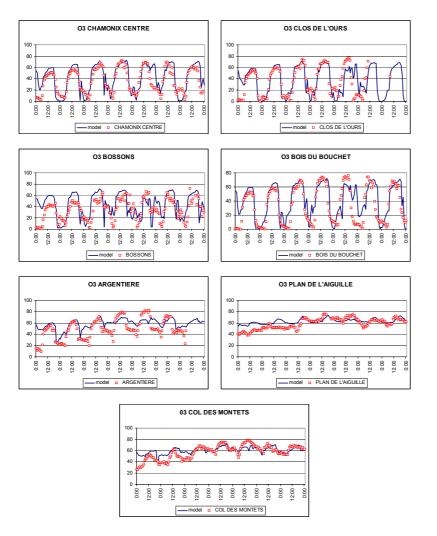
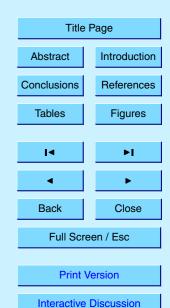


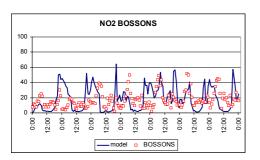
Fig. 7. O₃ monitoring station compared to the model (ppbV); from 5 July 2003 to 11 July 2003, TU, (IOP period). 1824

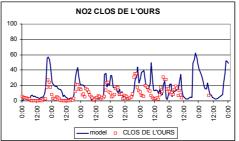
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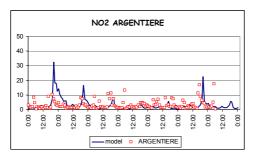
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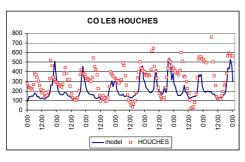
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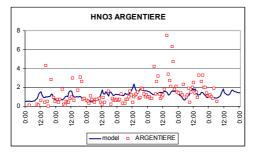


Fig. 8. CO, NO₂, HNO₃ monitoring station compared to the model (ppbV); from 5 July 2003 to 11 July 2003, TU, (IOP period).

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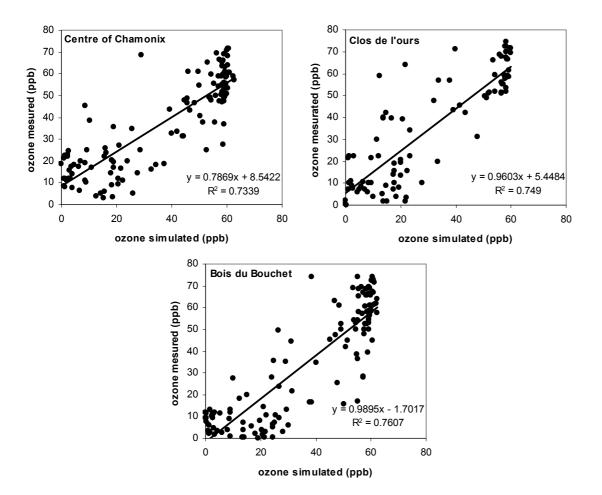
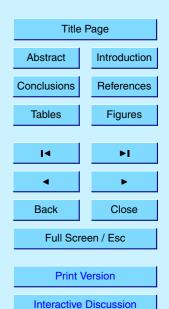


Fig. 9. Comparison between measured and simulated ozone in three sites for the IPO.

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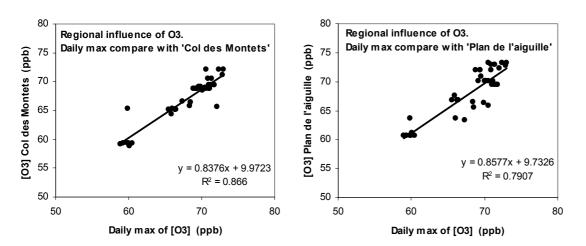
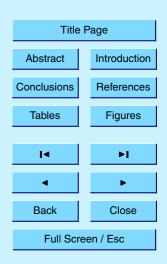


Fig. 10. Comparison between daily maximum of O_3 (6 sites) and concentration of O_3 at the same hour for background stations during the IPO.

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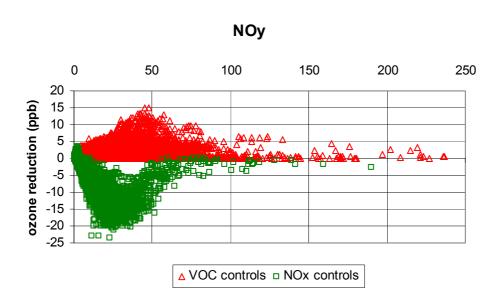


Fig. 11. NO_v according to ozone reduction with NO_x and VOC decrease.

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