



# Inverse modeling of pollution episodes over the Paris area using a photochemical box model

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## Abstract

We develop an urban photochemical simplified model. This model works as a full 3D model but the concentration of simulated species are averages within large atmospheric boxes of the urban boundary layer. This model has the advantage of being computer-time costless. It is particularly suited for the Paris area. The originality of the application of the model presented here is that it is used in inverse mode. That is, we use the model to diagnose the upstream concentrations of ozone that make the model simulation fit some observed concentrations in the urban area. The inverse modeling requires the development of the *adjoint* of the model.

Among the simplifications performed on the model, a reduced chemical mechanism is developed by a new methodology that could be called "optimal lumping", which consists in fitting stoichiometric coefficients and emission weights to a more realistic chemical mechanism in a variational way also requiring the adjoint of the chemical code.

We demonstrate that this upstream ozone concentration is a very sensitive parameter. There are two main causes of the urban ozone episodes in the Paris area. The first one is the local production of pollutants, mostly by traffic, and the other one is due to advection of high rural concentration of ozone. Each case is observed about half of the time during urban episodes.

## 1 Introduction

Paris is not a very polluted city. However, pollution peaks, albeit unrequent, reach levels comparable to those of the most polluted cities in the world. This paper is designed to present an air quality numerical model that accompanies the series of local measurements made by the AIRPARIF survey network, for diagnostics and prediction of pollution episodes.

Our aim is to develop a numerical tool that is easy to use and fast to run in order to test hypothesis about the origins of pollution on the scale of the city and eventually make predictions on a daily basis. This constraint lead us to consider a very simplified model based on a small ensemble of boxes covering Paris and its suburban areas. Several previous models of this kind have been developed so far and have shown satisfactory results (see for instance [1]). The novel aspect of the present study is due to the development of the *adjoint* of the model [2], providing to the user a diagnostic power that cannot be reached

by the direct modeling approach. This diagnostic capacity is made possible by the use of the model in inverse mode. That is, given the actual concentration of one or several pollutants, one may ask the model what the causes are, under certain circumstances. This article presents such an application.

We diagnose the relative part of regional transport of ozone versus local production over the Paris area during the last few summers. The main question we address is whether the major peaks observed over the city are due to large-scale transport of already high ozone concentration produced upstream or whether they result from local emissions of NO<sub>x</sub> and VOCs combined with solar radiation. The study is made under the national PRIMEQUAL air quality research program financed by the Ministère de l'Environnement.

Section 2 presents briefly the model. Section 3 reports the inverse modeling application of the model: the retrieval of the upstream ozone boundary fluxes. Section 4 contains a summary and a short discussion.

## 2 The model

### 2.1 Geometry

The model, called CHIMERE, is an extremely simplified reactive transport model. Its geometry covers the Ile-de-France area with 5 horizontal geographical entities and 2 layers. The model contains therefore 10 boxes within which the average concentration of 68 reactive chemical species is simulated.

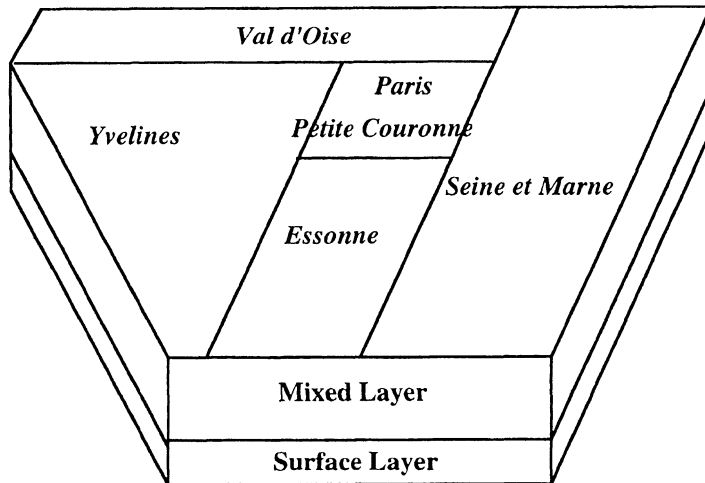


Figure 1: Schematic picture of the model geometry

A schematic picture of the model geometry is represented in Fig. 1. Each geographical region represents a district of the Ile-de-France. The central region is the urban area, called PPC (Paris and the Petite Couronne). The surface layer (the bottom layer) is 50m high, while the top of mixed layer (upper layer) varies with time according to meteorological conditions and represents the top of the urban boundary layer.

## 2.2 Physical processes

The physics of the model includes horizontal transport of species across the boundaries of the boxes, including transport of 3 “regional” species across the upwind boundaries: Methane, carbon monoxide and ozone. Rural methane concentration is taken as 1.8 ppm, rural CO concentration is taken as 100 ppb and rural ozone is varying with time. The inverse modeling application presented here precisely consists in determining the rural concentrations knowing the urban ones.

Vertical mixing is also parametrized as a function of meteorological conditions. It includes mixing between the two layers, in the form of a turbulent diffusion whose diffusivity coefficient depends only on the vertical virtual potential temperature gradient. Mixing of air between the mixed layer and the free troposphere only occurs during the morning rise of the boundary layer through the entrainment process. The height of the mixed layer is derived from local METEO-FRANCE radiosoundings, using the vertical profiles of virtual temperature and mixing ratio. These soundings are taken twice daily, approximately at midnight and noon. We therefore have only two values per day of the mixing height. The hourly values of the mixing height are then obtained by an interpolation between these values. The interpolation coefficients (4 per day, 2 for the rise and 2 for the collapse) are also taken as variable in the inverse modeling process. Most of the meteorological data are given for the two layers by ECMWF meteorological analysis. Cloudiness is obtained from direct measurements made by METEO-FRANCE.

## 2.3 Emissions

The emission inventory used has been established by the CITEPA (Centre Interprofessionnel Technique d’Etudes sur la Pollution Atmosphérique) company. It is based on the CORINAIR [3] methodology locally adapted to the Île-de-France area. The values given by this inventory are sectorwise annual mass emissions of NO<sub>x</sub>, CO, SO<sub>2</sub>, CH<sub>4</sub> and NMVOC (Non Methane Volatil Organic Compounds). We therefore need other informations about time variations and sectorwise NMVOC profiles. The former are given by a blend of industrial informations, time variations given by the european program EUROTRAC/GENEMIS [4], and a published work by Sallès et al. [5] giving typical diurnal profiles of traffic emissions.

NMVOC speciation is also achieved by blending 3 sources of informations: the speciation provided by GENEMIS [4] data, the PORG [6] speciation for the United Kingdom and the NAPAP [7] speciation (used for combustion activity sectors). The total mass of NMVOCs is splitted into the 32 NAPAP [7] hydrocarbon classes, to which is added the isoprene for biogenic emissions in suburban areas.

The NMVOC speciation is then adapted to the 11 model-emitted NMVOCs: ethane, *n*-butane, ethene, propene, isoprene, *o*-xylene, formaldehyde, acetaldehyde, methanol, ethanol and methyl-ethyl-ketone. The aggregation procedure from the 33 NAPAP NMVOC classes follows the work of Middleton et al. [8].

## 2.4 Chemical Mechanism

The chemical mechanism, MELCHIOR, has been developed at the Service d'Aéronomie [9], starting from a previous mechanism proposed by Hov et al. [10]. It contains a classical inorganic part and the oxydation cycles of 11 primary NMVOCs. It includes explicit peroxy radical recombinations as well as formation of nitrates and pernitrates. The 11 NMVOCs are each assumed to be representative of a class of NMVOCs of similar chemical structure, a strategy also used in other air quality models [11] and RADM [12].

The mechanism includes a total set of 195 reactions with 32 photolytic ones. The photolysis rates are calculated using the radiative model developed by Isaksen et al. [13] and improved by Johnson et al. [14]. The total ozone column is fixed to 300 DU, with the assumption of no aerosols. Cloudiness is taken into account by multiplying the photolysis rates by the factor

$$\Phi(\mu) = 1 - 0.75\mu^{4.3}$$

where  $\mu$  is the cloud fraction. This parametrization was proposed by van Loon [15].

## 3 Inverse modeling of upstream ozone concentrations

Figure 2 compares the concentration (in  $\mu\text{g}/\text{m}^3$ ) of ozone from a simulation of the model with the observed average concentrations measured by 7 stations of the AIRPARIF network in the urban box of the model, during the first 15 days of the month of July 1994 which was a particularly polluted month. In this simulation, the upstream ozone was kept fixed to value of 60 ppb. Around the 4-9 of this month, the weather was rather windy and cloudy, and the model overestimates daily concentrations. We attribute this overestimation to the too high value of upstream ozone. Indeed, 60 ppb is a typical value of moderate regional pollution episodes, but the typical rural concentration during windy and cloudy days at this period of the year is rather 30-40 ppb. Note also that the peak observed on July 3 is largely overestimated. This figure clearly shows the need of an upstream ozone estimation that varies with time.

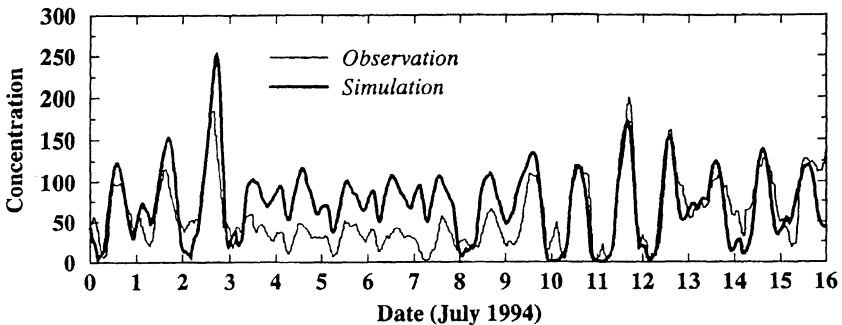


Figure 2: Concentration of ozone, in the urban model box, in  $\mu\text{g}/\text{m}^3$ , observed from AIRPARIF and simulated by the model using noncalibrated upstream ozone, during the period 1-15 July 1994.

### 3.1 The simplified chemistry and the “optimal lumping” method

Our aim is to calculate for 4 summer seasons (summer=july+august), 1992 to 1995, a daily value of upstream ozone, which requires a lot of computer time if the chemical mechanism is left as is. Therefore we designed a simplified chemical mechanism involving only 21 species and 50 reactions. All peroxy radical recombinations but the HO<sub>2</sub>-radical ones are removed, as well as the oxydation cycles of all NMVOCs but the propene and the *o*-xylene. In fact, all NMVOC emissions (but the propene ones) are lumped into the *o*-xylene one. This procedure requires an adjustment of the emissions themselves which must be increased by a certain factor, depending on the geographical area. Also, the products of the oxydation of the *o*-xylene must include formaldehyde which is produced by other NMVOCs, with a stoichiometric coefficient. Actually, the two stoichiometric coefficients of the carbonyls produced by the NO→NO<sub>2</sub> transformation by the peroxy radical formed by *o*-xylene+OH are adjusted. These carbonyl compounds are the formaldehyde and the methyl glyoxal. Since we have 5 geographical regions and 2 stoichiometric constants to adjust, we are facing a problem with 7 variables to be adjusted.

A reference simulation is performed with the complete-chemistry model, for the month of july 1994, and the 7 coefficients (grouped into the vector  $X$ ) are adjusted using a variational approach, that we could call “optimal lumping”. We try to find the minimum of the cost function:

$$J(X) = \sum_{Boxes} \sum_S \int_{Simulation} (C_c(t) - C_s(t))^2 dt$$

where the integral is over the whole simulation period,  $S$  is an ensemble of species simulated both by the simplified and the complete chemical mechanisms,  $C_c$  is the concentration simulated by the complete chemistry and  $C_s$  the concentration simulated by the simplified chemistry. In this way, the unknown parameters of the simplified chemical mechanism are optimally *fitted* to the complete mechanism.

The optimisation process necessitates a nonlinear minimization algorithm. We used the quasi-newton algorithm. This is an iterative algorithm requiring at each step the knowledge of the cost function and its gradient with respect to the parameters  $X$ . The gradient is calculated using the adjoint of the model, following the mathematical formulation of Talagrand and Courtier [2].

Figure 3 compares the simulation of two species by the two mechanisms, after adjustment, over the same period as in Figure 2. The two species are the ozone and the PAN. The PAN is not included in the list of species over which the minimization is performed, but the ozone is. We see that in both cases the concentrations obtained by the simplified mechanism are satisfactorily reproducing that of the complete mechanism. We verified that this good agreement is also verified on another time period independant of that over which the variational adjustment has been made.

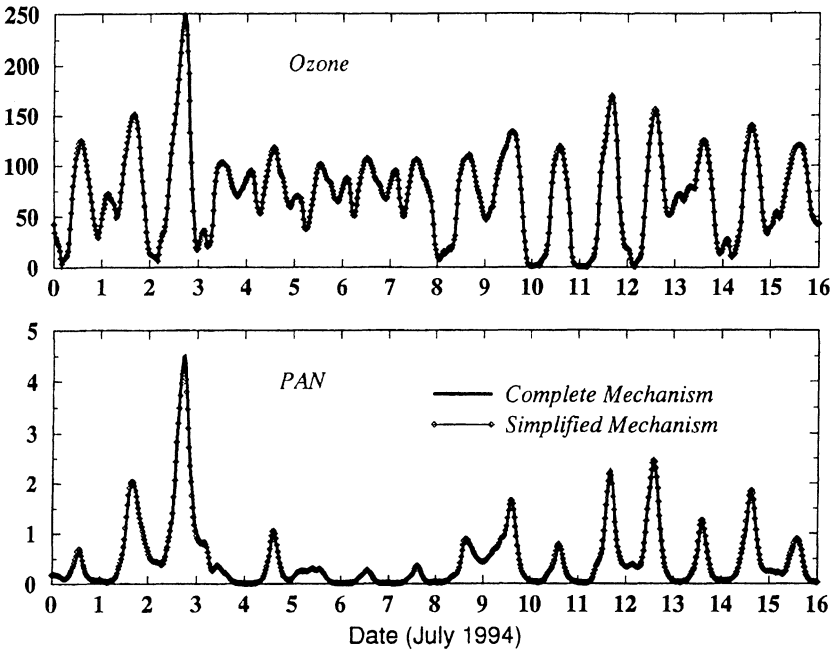


Figure 3: Simulation of ozone (top), in  $\mu\text{g}/\text{m}^3$ , and PAN (bottom), in ppb, in the urban box by the complete MELCHIOR mechanism and the simplified mechanism (1-15 July 1994).

### 3.2 Inverse modeling of the upstream ozone

We now try to recover the values of the upstream ozone that the model needs to simulate the observed concentrations of  $\text{NO}$ ,  $\text{NO}_2$  and  $\text{O}_3$  within the urban PPC box of the model in the surface layer. For each day, one value of upstream ozone is sought, as well as also 4 parameters of the interpolation of the mixing height. This makes a variable vector  $Y$  of dimension 5 per day, i.e.  $248 \times 5 = 1240$  components on total. Now the retrieval of these values is performed over the 4 summers, using the simplified chemical mechanism. The procedure used is also variational and using the adjoint of the model. However, the cost function is now:

$$\begin{aligned}
 J(Y) = & \int_{\text{Simulation}} ([O_3]_s(t) - [O_3]_o(t))^2 dt \\
 & + \int_{\text{Simulation}} ([NO_2]_s(t) - [NO_2]_o(t))^2 dt \\
 & + \int_{\text{Simulation}} ([NO]_s(t) - [NO]_o(t))^2 dt
 \end{aligned}$$

where indices  $s$  denote the simulated concentrations and indices  $o$  the observed concentrations (in the urban box of the model). Using the same quasi-newton algorithm, we find the minimum of the above cost function, and a value of the upstream ozone is found for each simulated day. Once the unknowns are estimated, the model is run using the complete chemical mechanism.

Figure 4 shows, for the same period as in Figures 2-3, the adjusted simulation of the urban ozone concentration. The improvement is clear with respect to noncalibrated ozone fluxes. Figure 5 shows the daily ozone peaks simulated by the adjusted model as a function of the observed peaks, for the 248 simulated days. Note the quite good correspondance between the peaks.

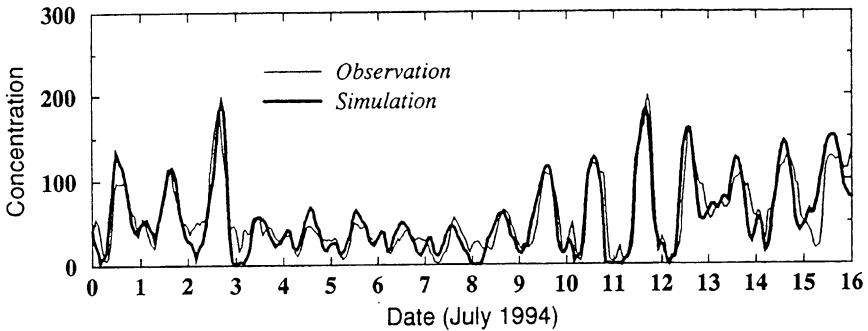


Figure 4: Same as in Figure 2 but for the simulation with adjusted upstream ozone.

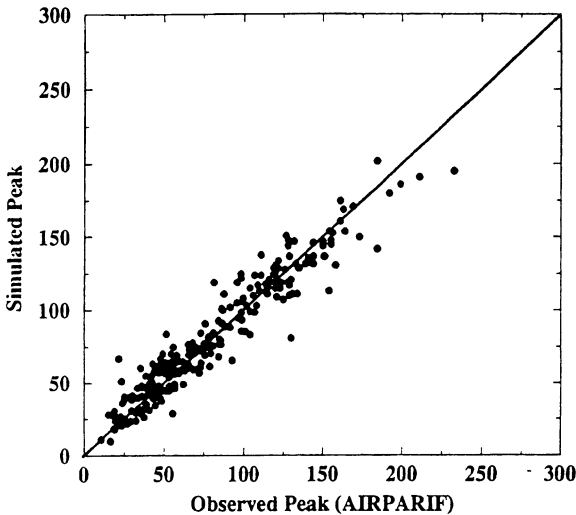


Figure 5: Simulated daily peaks (after adjustment) vs. observed ones.

### 3.3 Validation of the upstream concentrations

The validation of the above inverse modeling exercise is somewhat difficult, due to the lack of rural measurements around the Ile-de-France. However, as a first approximation, we can estimate that these concentrations can be compared to the mean boundary-layer concentrations that are obtained from the MOZAIC measurements. MOZAIC is a european project on ozone and water vapor measurements taken from commercial aircrafts. We have calculated

these average values (from 0 to 1000m) from flights taking off from, or landing at, the Paris Charles de Gaulle airport. However only 43 flights were available for the period concerned by our study, and we removed, for the comparison, the days when the airport was potentially located downwind of the city, i.e. when wind was coming from the South-West direction.

Figure 6 shows the comparison of the MOZAIC concentrations and those estimated by the inverse model. We note a quite good correlation between them. This result tends to show that if there are some model errors that are compensated by the variational adjustment, they should be relatively minor as far as ozone only is concerned.

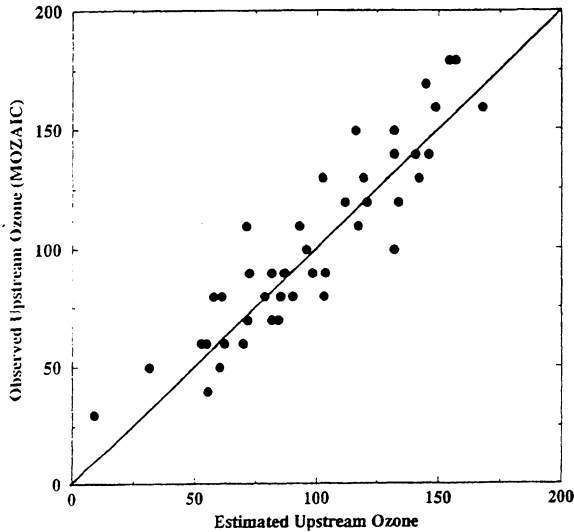


Figure 6: Upstream concentrations of ozone, in  $\mu\text{g}/\text{m}^3$ , deduced from the MOZAIC measurement, vs. the ones estimated by the inverse model.

### 3.4 Local ozone formation and regional transport

We now want to distinguish the two processes that lead to high ozone concentrations in the urban area of the Ile-de-France, namely the ozone production by the local pollutant emissions and the large-scale transport of ozone. Figure 7 shows the daily peaks of ozone in the surface layer of the urban model region against the upstream concentrations obtained by inverse modeling. Most of the time (about 75%), the urban concentrations are weaker than the upstream concentrations. However there are scattered urban peaks that are far larger (about 100-150  $\mu\text{g}/\text{m}^3$ ) than the upstream values. These days correspond to weak winds of variable direction, when oxydation of NMVOCs has time to take place and to dominate the ozone titration by NO. This figure shows that about half of the highest concentrations appear during days of local production, and about half during days of advection of high rural ozone concentrations.

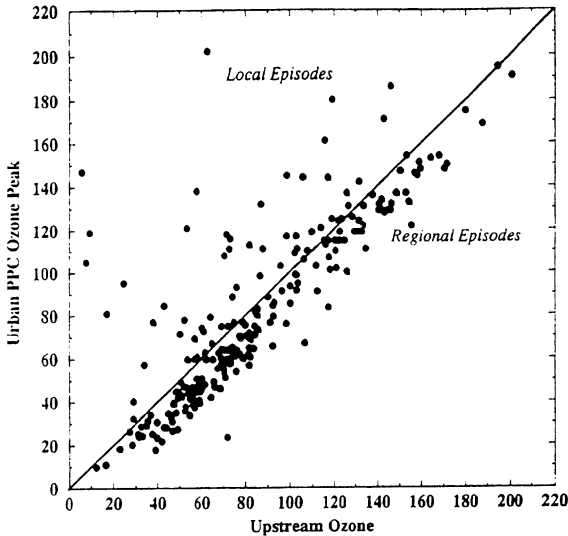


Figure 7: Urban ozone daily peaks against the upstream concentrations, in  $\mu\text{g}/\text{m}^3$ , as estimated from the inverse model.

It is noteworthy that our model does not elucidate the causes of high rural concentrations. This could be done only by means of backtrajectories and regional modeling of photochemistry. Therefore, it is possible that some of these high concentrations are due to a recirculation of the trajectories having, one or several days before, crossed the Ile-de-France area.

#### 4 Conclusion

We have developed an urban photochemical simplified model. This model works as a full 3D model but the concentration of simulated species are averages within large atmospheric boxes of the urban boundary layer. This model has the advantage of being computer-time costless. However it requires informations almost as complex as a full 3D model of an urban atmosphere.

The originality of the application of the model presented here is that it is used in inverse mode. That is, we use the model to diagnose the upstream concentration of ozone that make the model simulation fit some observed concentrations in the urban area.

We demonstrate that this upstream ozone concentration is a very sensitive parameter. There are two main causes of the urban ozone episodes in the Paris area. The first one is the local production of pollutants, mostly by traffic, and the other one is due to advection of high rural concentration of ozone. Each case is observed about half of the time during urban episodes. This may have important consequences for an efficient air quality policy: If only local emissions are restricted, one can only expect to eliminate about half of the photochemical pollution episodes. A more efficient policy would certainly consist in a more global, nationwide reduction. It is nevertheless difficult to estimate to what extent the reduction should take place. Probably the extent is even at the european scale.



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## References

- [1] Jin, S. and K. Demerjian, 1993: A photochemical box model for urban air quality study. *Atmos. Environment*, 27B, 4, 371-387.
- [2] Talagrand, O. and Courtier, P. 1987. Variational assimilation of meteorological observations with the adjoint vorticity equation. I. Theory. *Quart. J. R. Met. Soc.*, 113, 1311-1328.
- [3] CORINAIR, 1994: CORINAIR France 1990. Estimation des émissions de polluants atmosphériques (SO<sub>2</sub>, NO<sub>x</sub>, COVNM, CH<sub>4</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NH<sub>3</sub>). Rapport final.
- [4] GENEMIS (Generation of European Emission Data for Episodes) project, 1994: EUROTRAC Annual report 1993, Part5, *EUROTRAC International Scientific Secretariat, Garmisch-Partenkirchen*.
- [5] Sallès J., J. Janischewski, A. Jaecker-Voirol and B. Martin, 1996: Mobile source emissions inventory model: application to the Paris area, *Atmos. Environ.*, 30, 1965-1975.
- [6] PORG (Photochemical Oxidants Review Group; chairman D. Fowler), 1993: Ozone in the United Kingdom, Third report of the United Kingdom Photochemical Oxidants Review Group, *Air quality Division, Department of Environment*.
- [7] Saeger, M., J. Langstaff, R. Walters, L. Modica, D. Zimmermann, D. Fratt, D. Dulleba, R. Tyan, J. Demmy, W. Tax, D. Sprague, D. Mudgett, S. Werner, 1989: The 1985 NAPAP emissions inventory (version 2): development of the annual data and modellers tapes, *EPA-600/7-89-012a*, November 1989.
- [8] Middleton P., W.R. Stockwell, and W.P. Carter, 1990: Aggregation and analysis of volatile organic compound emissions for regional modelling, *Atmos. Environ.*, 24, 1107-1133.
- [9] Lattuati, M., 1997: Impact des émissions européennes sur le bilan de l'ozone troposphérique à l'interface de l'Europe et de l'Atlantique Nord: apport de la modélisation lagrangienne et des mesures en altitude, thèse de doctorat, Université Paris 6.
- [10] Hov O., F. Stordal, and A. Eliassen, 1985: Photochemical oxidant control strategies in Europe: A 19 days case study using a lagrangian model with chemistry, *NILU TR5/95*.
- [11] Lurman F.W., A.C. Lloyd, and R. Atkinson, 1986: A chemical mechanism for use in long range transport / acid deposition computer modelling, *J. Geophys. Res* 91, 10905-10936.
- [12] Stockwell W.R., P. Middleton, and J.S. Chang, 1990: The second generation Regional Acid Deposition Model chemical mechanism for regional air quality modeling, *J. Geophys. Res* 95, 16343-16367.
- [13] Isaksen I.S.A., K.H. Mitbo, J. Sunde, and P.J. Crutzen, 1977: A simplified method to include molecular scattering and reflection in calculations of photon fluxes and photodissociation rates, *Geophysica Norvegica*, 31, 11-26.
- [14] Jonson J.E. and I.S.A. Isaksen, 1991: Tropospheric ozone chemistry: the impact of cloud chemistry, *J. Atm. Chem.* 16, 99-122.
- [15] van Loon, M., 1994: Numerical smog prediction I: The physical and chemical model. CWI report NM-R9411.



# **Section 14:**

# **Air Pollution Modelling**