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# Transboundary Photo-oxidants in Europe

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# Preface and Acknowledgements

This report was prepared for presentation at the twenty-fourth session of the Steering Body to EMEP (Co-operative Programme for Monitoring and Evaluation of the Long Range Transmission of Air Pollutants in Europe). It provides an overview of modelling activities during 1999-2000, including summaries of ongoing work on ozone stomatal flux modelling, biogenic VOC simulations, sea-salt and NaCl modelling, and comparison of the models with VOC and CO from the EMEP measurement network. An updated 5-year average set of source-receptor calculations from the Lagrangian model is presented. A summary of the state of the ozone network is given, along with kriged maps of measured ozone spanning 1989-1998.

We present also an appendix with a country-by-country summary of emission reporting, measurement status (ozone and VOCs), and results of the source-receptor modelling.

The Research Institute for Computer Architecture and Software Technology (FIRST) of the German National Research Centre for Information Technology (GMD), Berlin, is thanked for continued support with the Eulerian models. The cooperations with the Finnish Meteorological Institute, Melica (Gothenburg), Norwegian Institute for Air Research (NILU), Stockholm Environment Institute at York, England (SEIY), University of Bradford, England, and the University of Oslo, Norway, are also gratefully acknowledged. Egil Støren and Vigdis Vestreng are thanked for the emission figures for the Appendix, as is Leonor Tarrasón for useful discussions.

Work on the analysis of VOC measurements and on the deposition module has been partly supported by the Nordic Council of Ministers. Work on the deposition module was also financed by the UK Department of the Environment, Transport and the Regions (DETR).

The calculations presented in this report depend strongly on the meteorological data obtained from the Numerical Weather Prediction Model of the Norwegian Meteorological Institute. The calculations presented here have been made possible by access to the CRAY T3E computer at the Norwegian University of Science and Technology (NTNU) in Trondheim, Norway.



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# Chapter 1

## Introduction

### 1.1 Overview

This summary report for photochemical oxidants covers a number of topics related to the Lagrangian and Eulerian photo-oxidant models and their evaluation. We present in this report an overview of the last year's activities, giving main results and referring where possible to more detailed EMEP Notes or other publications. The main chapters cover a new deposition methodology to evaluate the stomatal flux of ozone, comparison runs for several isoprene chemistries, an evaluation of sea-salt and NaCl particles over Europe, source-receptor calculations, and evaluation of the models for VOC species and CO. A summary of the state of the ozone network is given, along with kriged maps of measured ozone spanning 1989-1998. Appendix A of this report presents a country-by-country summary of emission reporting, number of measurement stations (ozone and VOCs), and some results of the country-to-country modelling.

The Eulerian model is currently being extensively re-coded to "unify" the acidification, aerosol and ozone models, and indeed to develop a modular system at DNMI, so that pollutants and chemical schemes can be changed in an efficient and flexible manner. This work is briefly summarised in chapter 8.

The current summary report is thus very much an interim report, presenting ongoing work rather than finished products or significant new results. However, it will be seen that the Eulerian model is developing to cope with a number of new challenges, each of these requiring substantial investigations of basic science and technical possibilities.

A complete description of the EMEP oxidant models, and much of the data presented in this report, including the new source-receptor calculations, can be obtained as ASCII files from the EMEP web-site, <a href="http://www.emep.int">http://www.emep.int</a>
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## 1.2 Other publications

This photo-oxidant summary report accompanies EMEP Report 1/00 (EMEP MSC-W, 2000), which deals with the activities of MSC-W and CCC on acidification. A number of other reports and papers of relevance to oxidants and involving EMEP staff have become available in 1999/2000:

### Peer-reviewed

- Emberson, L., Ashmore, M.R., Cambridge, H.M., Simpson, D. and Tuovinen, J.P., 2000, Modelling stomatal ozone flux across Europe, *Environ. Poll.*, 109, No. 3, 403–414.
- Fowler, D., Cape, J.N., Coyle, M., Smith, R.I., Hjellbrekke, A.G., Simpson, D., Derwent, R.G., and Johnson, C.E., 1999, Modelling photochemical oxidant formation, transport, deposition and exposure of terrestrial ecosystems, *Environ. Poll.*, 100, 43–55.
- Jonson, J.E., Tarrasón, L. and Sundet, J., 1999, Calculation of ozone and other pollutants for the summer 1996, *Environ. Manag. Health*, 10, 245–257.
- Jonson, J.E., Kylling, A., Berntsen, T.K., Isaksen, I.S.A., Zerefos, C.S. and Kourtidis, K., 2000, Chemical effects of UV fluctuations inferred from total ozone and tropospheric aerosol variations, *J. Geophys. Res.*, 105, 14,561–14,574.
- Simpson, D. and Eliassen, A., 1999, Tackling multi-pollutant multi-effect problems – an iterative approach, *The Science of the Total Environment*, 234, 43–58.

### Other

- Dye, C., Hayman, G.D., Possanzini, M., Nielsen, C., Oehme, M., 2000. CATOME Final Report, 2000. Contract No: ENV4-CT97-0416.
- Emberson, L., Simpson, D., Tuovinen, J.P., Ashmore, M.R. and Cambridge, H.M., 2000, Towards a model of ozone deposition and stomatal uptake over Europe, EMEP MSC-W Note 6/2000.
- Friedrich, R. and Reis, S., editor, 2000, *Tropospheric Ozone Abatement. Developing efficient strategies for the reduction of ozone precursor emissions in Europe*, Springer, Berlin, (contains "Regional modeling of tropospheric ozone", pp. 83-98, by D. Simpson and J.E. Jonson, and "Optimising regional ozone reduction strategies", pp. 99-120, by S. Reis, D. Simpson and R. Friedrich).
- Jonson, J.E., Tarrasón, L. and Bartnicki, J. 2000, Effects of international shipping on European pollution levels, EMEP MSC-W Note 5/2000.
- Monks, P., Lindskog, A., Scheel, H.E., Scuepbach, E., Solberg, S., Zanis, P., Apituley, A., Beekmann, M., Bonasoni, P., Coyle, M., DeMeur, D., Girgziene, R., Haszpra, L., Klasinc, L., Roemer, M., Simmonds, P., 1999. Observations and origin of a spring ozone maximum. In: Lindskog, A., Beekmann, M., Builtjes, P., Monks, P., Roemer, M., Schuepbach, E., Solberg, S. (eds.). TOR-2 Annual report 1998, pp. 17–59, EUROTRAC-2, ISS, GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, München, Germany. (Also printed by: Monks, P.S., 2000, A review of the observations and origins of the spring ozone maximum. *Atmos. Environ.*, 34 (21), 3545–3565.)
- Solberg, S., 1999. Photochemical processes in the troposphere as studied by model calculations. A contribution to TOR2. In: Lindskog, A., Beekmann, M., Builtjes, P., Monks, P., Roemer, M., Schuepbach, E., Solberg, S. (eds.). TOR-2 Annual report 1998, pp. 149–152, EUROTRAC-2, ISS, GSF-Forschungszentrum für Umwelt und Gesundheit GmbH, München, Germany.

## 1.3 Definitions, statistics used

The basic units used throughout this report are ppb (1 ppb = 1 part per billion by volume) or ppm (1 ppm = 1000 ppb). At 20°C and 1013 mb pressure, 1 ppb ozone is equivalent to  $2.00 \mu\text{g m}^{-3}$ .

A number of statistics have been used to describe the distribution of ozone within each grid square:

**Mean of Daily Max. Ozone** - First we evaluate the maximum modelled concentration for each day, then we take the 6-monthly mean of these values, over the 6-month period 1 April - 30 September.

**AOT40** - the accumulated amount of ozone over the threshold value of 40 ppb, i.e..

$AOT40 = \int \max(O_3 - 40ppb, 0.0) dt$  where the *max* function ensures that only ozone values exceeding 40 ppb are included. The integral is taken over time, namely – the growing season as defined at the Bern and Kuopio critical level workshops (Fuhrer and Achermann, 1994, Kärenlampi and Skärby, 1996). For crops and natural vegetation AOT40 is taken over 3 months (May-July), which we denote **AOT40<sub>c</sub>**. For forests a six month period is used (April-September), denoted **AOT40<sub>f</sub>**. In both cases only daylight hours are included.

**AOT60** - the accumulated amount of ozone over the threshold value of 60 ppb, i.e.

$AOT60 = \int \max(O_3 - 60ppb, 0.0) dt$  - in this case, the integral is taken over 6 months, and only daytime ozone included.

As the Lagrangian model does not work with hourly averages, but rather gives values of calculated ozone at 0, 6, 12 and 18 GMT each day, some approximations are necessary to compare with true 1-hour and AOT-type guidelines. We generally assume that each output value of the model corresponds to an hourly value. The daytime-average required for AOT values is simply obtained from the 12 and 18 GMT values, assuming each value is representative of a 6-hour average. This procedure introduces only moderate errors for AOT40 (see Malik et al., 1996), but is obviously less accurate for AOT60.

The AOT40 levels reflect interest in long-term ozone exposure which is considered important for vegetation - critical levels of 3 000 ppb.h have been suggested for crops and natural vegetation, and 10 000 ppb.h for forests (Kärenlampi and Skärby, 1996).

The AOT60 measure reflects the revised WHO guidelines which sets 120  $\mu gm^{-3}$  (60 ppb) as an 8-hour moving average. The UN-ECE workshop on 'health effects of ozone and nitrogen oxides in an integrated assessment of air pollution' (UN-ECE, 1997) agreed that a simple statistic such as AOT60 could be used as a preliminary indication of ozone levels above the recommended WHO guideline for integrated assessment modelling purposes. The justification for this is that AOT60 is a statistic which incorporates both the amount of ozone above 60 ppb and the frequency of exceedance, both of which are known to be important. However, it is clear that this statistic cannot be directly coupled to health impact assessments. (In any case, the EMEP models are not designed for calculating ozone exposure inside urban areas, which would be required for any meaningful health-risk assessment.)

It should be noted though that AOT values are very sensitive to systematic biases in both modelled and observed data (especially when ozone concentrations lie just below or above the threshold limits). Simpson et al. (1998) showed that a 10% uncertainty in measured hourly ozone can lead to differences of typically 100% and 200% (for one site 1000%) in AOT40 and AOT60 respectively. In an analysis of 8 sites for 1994-1996, Tuovinen (2000) found that  $x\%$  uncertainties in the mean concentration lead to uncertainties of 2-10 times  $x\%$  in AOT40. Problems are greatest for those areas where ambient ozone levels lie often below, but close to the thresholds, so that even small uncertainties in ozone concentration may lead to this threshold being crossed or not.

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## Chapter 2

# Ozone deposition and stomatal flux modelling

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### 2.1 Introduction

A new ozone deposition model has been developed for use within the EMEP photochemical model, intended to calculate ozone uptake into different vegetation classes as well as ozone loss from the planetary boundary layer.

This model differs from other deposition schemes through the use of a detailed stomatal conductance model that is used to evaluate the stomatal component of total ozone deposition. The stomatal component constitutes a significant proportion of total ozone deposition especially during the summer daylight periods when vegetation is most physiologically active. The calculation of this stomatal component of ozone flux is of special significance since it is widely recognised as an important determinant of ozone impacts to vegetation, and as such is more easily applicable to impacts studies than the AOT40 concept of level-I. The use of such flux-based approaches has been identified as an option for the future establishment of Level II ozone critical levels (Fuhrer and Achermann, 1999). The development of such methods should enable future assessments of the actual damage caused by ozone to vegetation and subsequently provide the techniques to perform associated economic assessments of impacts such as losses of crop yields forest productivity.

This latest version of this model is described in detail in EMEP Note 6/2000 (Emberson et al., 2000a), and builds upon earlier work reported in for example Emberson et al. (1996, 2000b) and Brown et al. (1996). The model has been parameterised for all surfaces i.e. vegetated and non-vegetated so that it can be applied across Europe. This model is still under development, but with one major exception (soil water treatment, see below), the methodology is essentially ready for use. Indeed, comparisons with available measurements have reassuring results although some matters remain to be understood (Emberson et al., 2000a, Tuovinen et al., 1999). One major task remains which is not methodological - that of establishing good databases to define the spatial and temporal variation of leaf area index, but for the comparison performed so far we have used default or local vegetation parameters.

### 2.2 Methodology

The basic calculation of deposition velocity uses a standard 3-resistance approach:

$$V_g(z_{ref}) = \frac{1}{R_a(z_{ref}, z_0) + R_b + R_c} \quad (2.1)$$

where,

$R_a(z_{ref}, z_0)$  ( $s\ m^{-1}$ ) is the aerodynamic resistance between  $z_{ref}$  and the top of the vegetation canopy (formally,  $d + z_0$ .)

$R_b$  ( $s\ m^{-1}$ ) is the quasi-laminar layer resistance to ozone,

$R_c$  ( s m<sup>-1</sup>) is the surface (canopy) resistance to ozone.

Since we are interested in estimating the deposition flux to several different land-use types within each grid square, we need to evaluate all the resistance terms of eqn. (2.1) for each land-use type, similar to the an approach implemented in the EMEP acid deposition models (Seland et al., 1995, Jakobsen et al., 1997).

Further details of the  $R_a$  and  $R_b$  terms will not be given here (see Emberson et al., 2000a). The formula used for  $R_c$  is:

$$R_c = \frac{1}{\frac{LAI}{R_{sto}} + \frac{SAI}{R_{ext}} + \frac{1}{R_{inc} + R_{gs}}} \quad (2.2)$$

where,

$LAI$  is the leaf-area index (m<sup>2</sup>, one sided),

$SAI$  is a surface area index (m<sup>2</sup>,  $0.5 \leq SAI \leq LAI$ ),

$R_{sto}$  is the stomatal resistance

$R_{ext}$  is the external leaf-resistance (cuticle+surface)

$R_{inc}$  is the in-canopy resistance, modelled as  $14 SAI \cdot h / u_*$

$R_{gs}$  is the ground surface resistance (soil or other ground cover, e.g. moss)

Derivation of the land-cover specific stomatal resistance component of ozone flux is calculated as described previously in Emberson et al. (2000b):

$$1/R_{sto} = g_{max} \cdot g_{age} \cdot \max(g_{min}, g_{light} \cdot g_{temp} \cdot g_{VPD} \cdot g_{SWP})$$

Where  $g_{max}$  is the maximum stomatal conductance in units of mmol O<sub>3</sub> m<sup>-2</sup> s<sup>-1</sup> expressed on a projected leaf/needle area basis;  $g_{age}$  is the relative  $g$  determined by leaf/needle age. For the needle bearing vegetation groups  $g_{age}$  is calculated as a function of the seasonal variation in the proportion of current to older needles and associated variability in needle conductance.  $g_{min}$  is the minimum daytime stomatal conductance observed under field conditions.  $g_{light}$  is the relative  $g$  determined by irradiance which is calculated for the canopy using the canopy radiative transfer model described by Norman (1982).  $g_{temp}$  is the relative  $g$  determined by temperature;  $g_{VPD}$  is the relative  $g$  determined by the leaf-to-air vapour pressure deficit (VPD) and  $g_{SWP}$  is the relative  $g$  determined by the soil water potential (SWP), (related to soil moisture deficit, SMD). Relative  $g$  factors are expressed on a scale of 0-1 and used to modify  $g_{max}$ .

## 2.3 Some results

Emberson et al. (2000a) and Tuovinen et al. (1999) have presented an extensive range of results and evaluations for this deposition module. Here we present just a few examples of these results to illustrate the variation in deposition velocities obtained with the new methods. As in the above reports, these preliminary calculations assume  $g_{SWP} = 1$  and cloud-free conditions, so the calculations are for comparison with observations under similar conditions.

Figures 2.1-2.2 shows the diurnal variation (monthly-average) in deposition velocity (here calculated for a height of 3 m above the vegetation) calculated for a deciduous forest and for semi-natural vegetation (moorlands, heathlands) in Switzerland. These results are shown for 4 equally-spaced months throughout the year, centered around the month with greatest  $V_g$  values. These plots also show the percentage of the ozone flux which is stomatal, illustrating the large variation in this important pathway's importance.

As an illustration of the possible effect of SMD on the calculations, we present some new results made with the 1998 meteorological data-set prepared and evaluated by Sandnes-Lenschow and Tsyro (2000). Figure 2.3 shows the calculated deposition velocity for a location in Portugal, both with and without modelling of SMD. In this case the SMD was modelled using the modified Thornthwaite methodology of Mintz and Walker (1993). As well as clearly showing the possible importance of SMD modelling for such locations, this figure is also interesting in showing that even without SMD effects, ozone deposition velocities are substantially reduced from around 12 noon onwards. This is caused by the significant vapour-pressure deficits also associated with hot climates, so that stomatal-closure occurs anyhow from mid-day onwards. This behaviour contrasts strongly with that found further north (not shown), where deposition velocities peak around noon and have a symmetrical distribution.

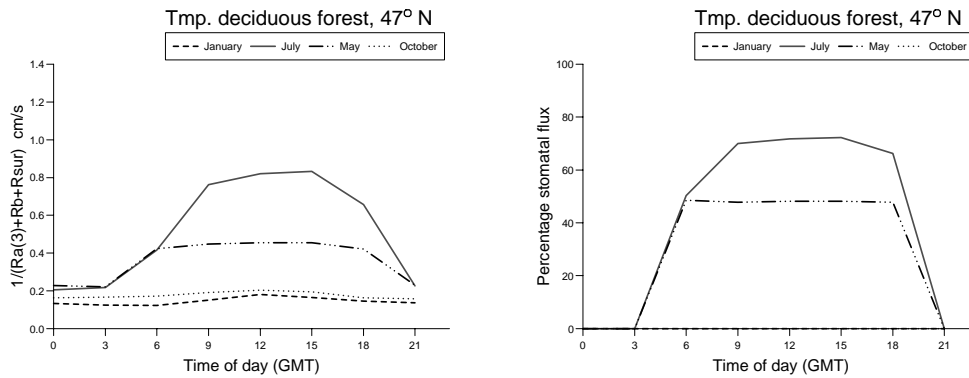


Figure 2.1: Diurnal variation in mean deposition velocity (left) and the percentage of stomatal contribution (right), calculated as monthly averages for 1997. Calculations for deciduous forest for a location in Switzerland, assuming  $g_{SWP} = 1$  and cloud-free conditions.

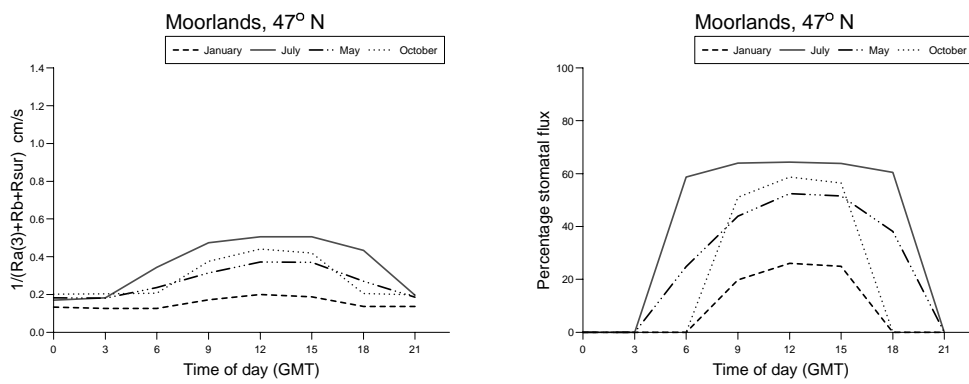


Figure 2.2: As Fig. 2.1 but for semi-natural vegetation (moorlands/heathlands).

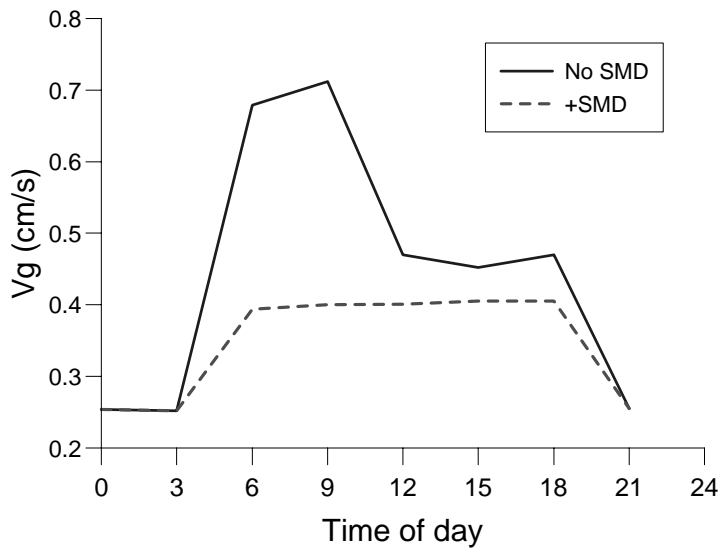


Figure 2.3: Diurnal variation of deposition velocity for a site in Portugal, for July 1998. Calculations with and without preliminary SMD effect

## 2.4 Ongoing and Future work

The main work which is taking place or planned and which should significantly improve the usage of the deposition module for European applications includes:

- Inclusion of soil-moisture methodology. As noted above, one major question which still remains is how to deal with soil moisture. In southern parts of Europe especially (but also sometimes in northern Europe), the effects of dry weather and drought can have dramatic consequences on vegetation and stomatal uptake, the latter being severely restricted to prevent water-loss. This stomatal closure will frequently protect the plant from high ozone concentrations which are often associated with the dry sunny weather. A significant exception here is irrigated crops, where the irrigation designed to improve plant growth may encourage uptake of elevated ozone concentrations and hence cause unforeseen damage. Although clearly important, the prediction of soil moisture deficits (SMDs) poses special challenges for a number of reasons. Such predictions are very sensitive to the assumed soil characteristics, to the accuracy of the rainfall data from the NWP model, and to the accuracy of any scheme to predict evapotranspiration. Although it is straightforward to build a set of model equations to describe SMD, it is very difficult to evaluate these predictions against the real world. A lot of work has been done on this part of the model, but at the present stage the choice of scheme is still open, and the options range from a very simple parameterisation (seasonal, climatological factors) to monthly or daily modelling of SMD.
- Improved land-use data-bases. The current databases of the Stockholm Environmental Institute which have been used in say Emberson et al. (2000b) have very great detail in the number of vegetation categories and their spatial resolution. However, in common with other similar data-bases the information concerns areal coverage rather than biomass. The main improvement which could be made would then be to include some description of LAI variations as well as areal coverage of vegetation. Possibilities range from rather simple approaches (e.g. LAI as a function of latitude) to detailed satellite-derived databases.

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## Chapter 3

# Chemical descriptions of isoprene chemistry: influence on ozone

Yvonne Andersson-Sköld and David Simpson

### 3.1 Introduction

Isoprene ( $C_5H_8$ ) is emitted in large quantities by vegetation (Guenther et al., 1995, Simpson et al., 1995, 1999). Emissions are greatest on those days with high temperatures when ozone formation is most likely, and since this hydrocarbon is very reactive with OH it is expected to contribute to photochemical ozone formation in many regions of Europe.

Isoprene is also by far the most reactive hydrocarbon species in the EMEP oxidant models, and so it is important to evaluate the treatment of this species at regular intervals. For the Lagrangian model the isoprene mechanism (EMEP-PS) is an adapted version of that suggested by Paulson and Seinfeld (1992), see Simpson et al. (1993), Simpson (1995). The EMEP version of this mechanism has 19 species and is therefore rather complex in comparison to the chemistry of other VOC species. To a certain extent this complexity is justified by the importance of isoprene. On the other hand the uncertainties in the emissions of this species are so large that a detailed mechanism may be unwarranted. The Eulerian model (Jonson et al., 1998) uses a much simpler mechanism, based upon Lloyd et al. (1983). This scheme as applied in EMEP (EMEP-L83) has only 4 reactions, and neglects reaction between isoprene and  $NO_3$  and  $O_3$ . This chapter reports on work undertaken to compare the current isoprene chemistries with recently developed isoprene mechanisms, with a view to exploring a new isoprene mechanism for use in both EMEP models.

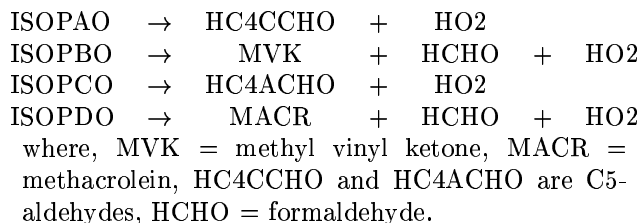
Numerous studies on the chemistry of isoprene and its reaction products have allowed detailed representation of this species in explicit reaction schemes. Among the available oxidation schemes, the most detailed and updated is probably that of the Master Chemical Mechanism (MCM) (Jenkin et al., 1997, Pilling et al., 1999). This isoprene oxidation scheme consists of more than 325 reactions before oxidation products such as glyoxal and methyl glyoxal are formed.

In oxidant models such as those of EMEP MSC-W, the total number of chemical and photochemical reactions are around 120 for all anthropogenically species considered in the model. In all such chemical-transport models, there is a strong need for simplified oxidation schemes for all species, including isoprene and other BVOC.

In the present EMEP oxidant scheme (Simpson et al., 1993, Simpson, 1995), the methodology to reduce the chemical scheme is to replace groups of compounds by representatives, e.g. most heavy alkanes are represented by n-butane, and only the major reaction pathways of n-butane are followed. To reduce the MCM isoprene oxidation mechanism to a mechanism of similar size and behaviour as the EMEP scheme, the most relevant would be to use the same methodology as normally applied in the EMEP model, replacing as many species as possible by representatives already present in the EMEP scheme.

In the MCM isoprene oxidation scheme of Jenkin et al. (1997), the first reaction step gives peroxy radicals which mainly reacts to form oxy radicals, nitrates and peroxides.

The major reaction path gives a peroxy radical, ISOPBO<sub>2</sub>, from which the alkoxy radical, ISOPBO, produces formaldehyde and methylvinylketone (MVK), 50%. The two major reaction paths, ISOPBO<sub>2</sub> and ISOPDO<sub>2</sub>, give oxy radicals which form formaldehyde and MVK or methacrolein (75%). The remaining paths of oxy radicals form C5-aldehydes which in their next reaction cycle forms MVK or methacrolein as the major products.



Methylvinylketone (MVK) and methacrolein have similar absorption spectras (e.g., p60. Le Bras, 1997), they are both unsaturated (alkene substituted) oxygenates, and their reactivities are fairly similar, (methacrolein is somewhat more reactive than MVK).

To reduce the MCM mechanism to a mechanism of similar size and behaviour as the EMEP scheme the optimal would be to find species already present in the EMEP scheme to be used as representatives for MVK and methacrolein. The most similar species in the EMEP model that could substitute the alkene part of MVK and methacrolein is propene. The remaining part (CH<sub>3</sub>O) has to be represented by an oxygenated species. For MVK the remaining part is a ketone which is similar to methylethylketone (CH<sub>3</sub>COC<sub>2</sub>H<sub>5</sub>, MEK). For methacrolein the remaining part is an aldehyde where the most similar species in the EMEP model is acetaldehyde (CH<sub>3</sub>CHO).

## 3.2 The study

Table 3.1 lists the schemes that have been used to investigate possible alternatives for the EMEP isoprene oxidation scheme. Most of the schemes given are different simplifications of the full MCM isoprene oxidation mechanism. The differences among these schemes are relatively low and can be regarded as tests to find which reactions or reactions products that are crucial to describe the ozone formation due to isoprene oxidation, for realistic conditions.

These schemes have been implemented into the chemical scheme in the IVL photochemical trajectory model (Andersson-Sköld, 1995). Simulations have been done to calculate the contribution to ozone from isoprene by the individual schemes under two different emission conditions. The calculated ozone concentrations have than been compared to the ozone concentrations obtained using the full MCM isoprene oxidation scheme under otherwise similar conditions.

One set of simulations have been done based upon the 'Plume-2' scenario as previously used for comparison studies (Poppe et al., 1996, Kuhn et al., 1998, Andersson-Sköld and Simpson, 1999). The scenario used here, which we call 'Plume-2bio', differs only from Plume-2 in the sense that here the heterogeneous reaction between water and dinitrogen pentoxide has now been included, assumed to occur with a rate of  $5 \times 10^{-6} \text{ s}^{-1}$  (Simpson et al., 1993), and that isoprene emissions are added. As a daily average this added isoprene emissions corresponds to 12.7% of the anthropogenic NMVOC emissions (by mass), corresponding to the average of the relation between anthropogenic emissions and isoprene emissions in western Europe (Simpson et al., 1995). Emissions only take place during daylight hours though, in which case the isoprene emissions, at 25% of the other NMVOC emissions, are responsible for a significant part of the VOC reactivity.

For this study, another situation has been set up to test more NO<sub>x</sub> rich conditions, by simply increasing the NO<sub>x</sub> emissions in the model 5 times. (This NO<sub>x</sub>-rich scenario was also used in Andersson-Sköld and Simpson (1999) and Andersson-Sköld and Holmberg (2000)).

## 3.3 Results and discussion

The simulated concentration of ozone using the full MCM isoprene oxidation scheme implemented into the IVL oxidation scheme are seen as a function of time in Figure 3.1 for the

Table 3.1: Chemical schemes investigated as candidates for possible simplified alternatives for isoprene.

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S1a)	EMEP-PS (Paulson and Seinfeld, 1992, Simpson et al., 1993)
S1b)	EMEP-L83 - scheme of Lloyd et al. (1983) as applied by Jonson et al. (1998)
Derived from MCM	
S2)	only the route forming ISOPBO2 in the MCM isoprene oxidation scheme
S3)	only the route forming ISOPDO2 in the MCM isoprene oxidation scheme
S4)	only formation of ISOPBO2 in the initial reaction, and the degradation products of ISOPBO2 are represented by only CH3COC2H5, C3H6, HCHO also the chemistries of ozone and the nitrate radical have been simplified to have these species as representative products
S5)	only formation of ISOPBO2 in the initial reaction, and the degradation products of ISOPBO2 are represented by CH3COC2H5, C3H6, HCHO. The ozone and nitrate radical chemistries have been kept as in the MCM oxidation scheme
S6)	as in 5) but the nitrate radical reaction with isoprene has been completely inactivated.
S7)	as in 4) but the representatives are CH3COC2H5, C3H6, HCHO, CH3CHO
S8)	only formation of ISOPDO2 in the initial reaction, and the degradation products of ISOPBO2 are represented by only methacroleine, CH3COC2H5, C3H6, HCHO and CH3CHO also the chemistries of ozone and the nitrate radical have been simplified to have these species as representative products
S9)	as S8) but the nitrate radical reaction with isoprene has been completely inactivated.
S10)	Simplified version of S8)
S11)	only formation of ISOPDO2 in the initial reaction, and the degradation products of ISOPBO2 are represented by only CH3COC2H5, C3H6, HCHO and CH3CHO also the chemistries of ozone and the nitrate radical have been simplified to have these species as representative products
S12)	simplified version of S11)
S13)	simplified version of S12)
Propene-based systems	
S14)	propene is used as representative for isoprene
S15)	the products in the isoprene reaction are the as the products of propene
Other	
S16)	Stockwell et al. (1997)

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Plume-2bio case. Ozone levels simulated with and without isoprene emissions in the European base case are given.

In Figure 3.2 the difference between the ozone concentrations simulated with and without isoprene are given for a number of chemical schemes. Table 3.2 summarises these  $\Delta$ ozone values for all schemes after 12, 48 and 96 hours. In the simulation referred to as the isoprene base case the full MCM scheme has been used to describe the oxidation of isoprene. From Figures 3.1-3.2 a contribution to ozone from isoprene to ozone under those conditions is seen but is not very high. Although the contribution to ozone is low it can be seen that the chemical description matters when assessing the changes. The best agreement between the isoprene base case and the more simplified schemes is found using the very simple schemes which are simplifications of the Route D in the MCM mechanism, schemes S12 and S13.

In Figure 3.3 a selection of mechanisms have been tested under similar conditions but with  $5 \times \text{NO}_x$ . As can be seen the change in ozone is now much more significant, up to 30 pbb, and all schemes give similar results. Considering the small deviations that do exist, the internal order varies from the base case simulation. Here the best fit between simplifications and the full MCM isoprene oxidation mechanism is seen for the EMEP-Paulson and Seinfeld (1992) mechanism. Very good agreements are also found for the simplified route S12, and the more

Table 3.2: Calculated  $\Delta$ ozone values with 16 chemical schemes, after 12, 48 and 96 hours. For plume-2 scenario

Scheme	$\Delta$ ozone values (ppb)		
	12 h	48 h	96 h
MCM	-0.26	0.99	2.67
S1a (EMEP-PS)	0.24	3.20	5.78
S2	-0.15	1.66	3.93
S3	-0.36	0.33	1.64
S4	0.11	4.21	6.82
S5	0.08	2.19	3.89
S6	0.16	3.67	5.31
S7	0.02	4.08	6.85
S8	-0.16	2.39	4.02
S9	-0.08	2.28	3.78
S10	-0.13	2.42	4.78
S11	-0.09	2.30	4.46
S12	-0.07	0.70	2.05
S13	-0.07	0.71	2.05
S14	0.08	1.94	3.15
S15	0.36	4.08	6.86

complex complete routes B and D (Schemes S2 and S3).

The MCM chemical mechanism has been chosen as the reference isoprene oxidation scheme. It is the most explicit scheme, although there are however, other published schemes available (e.g. Stockwell et al., 1997, Paulson and Seinfeld, 1992). It is also interesting to compare the two EMEP mechanisms, EMEP-PS and EMEP-L83. In Figures 3.4-3.5 a comparison of the simulated ozone concentrations are given for the European base case and the corresponding 5xNOx scenarios respectively using these schemes.

Under the two emission conditions investigated here it is clear that the simpler schemes tested here give ozone contributions similar to those of the more complex schemes, and that deviations are small when isoprene contributes significantly to ozone formation.

The conclusion therefore would be that most of the schemes presented in Figure 3.3 can be used to estimate the ozone formation from isoprene under European conditions. If possible the full MCM isoprene mechanism is recommended, but for advanced meteorological models requiring condensed chemical schemes the smallest scheme, e.g. schemes S11 or S12, or EMEP-L83, could be alternatives. Further investigations are, however, required to consider different emissions conditions and also the formation of other compounds such as the carbonyls. As shown in chapter 4 there are significant differences in the performance of the EMEP Lagrangian and Eulerian models as compared to HCHO measurements, and a plausible explanation might be that the different isoprene chemistries are responsible for this.

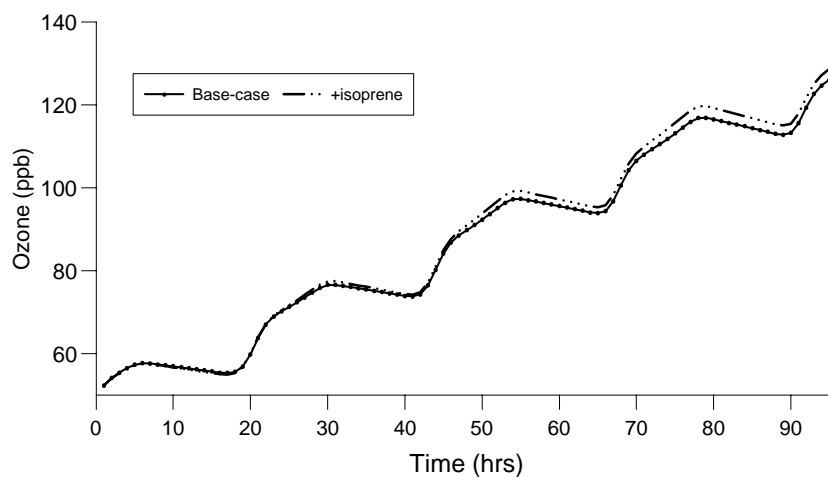


Figure 3.1: Simulated concentrations of ozone for the plume-2bio scenario, with and without isoprene emissions (see text). The base-case uses IVL-model chemistry, the +isoprene case uses chemistry from MCM2.

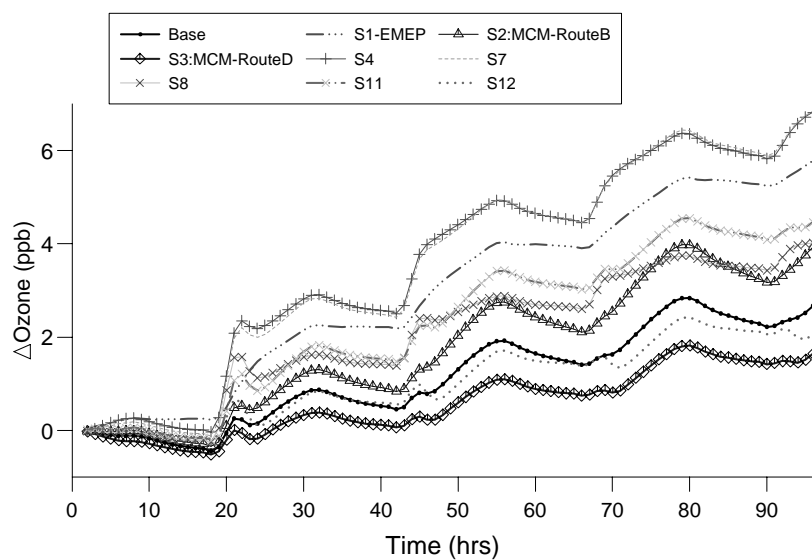


Figure 3.2: Simulated extra ozone concentrations with different isoprene mechanisms, plume-2bio

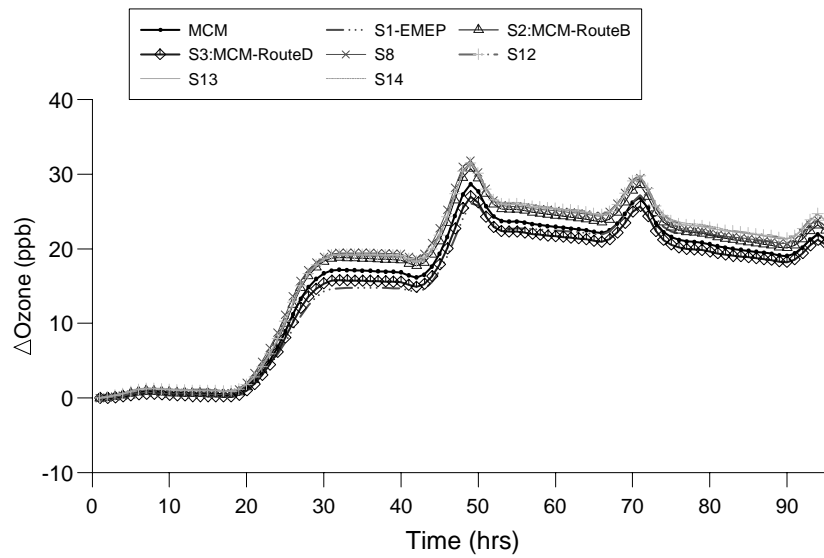


Figure 3.3: Simulated extra ozone concentrations with different mechanisms for isoprene, with  $5 \times \text{NO}_x$  emissions.

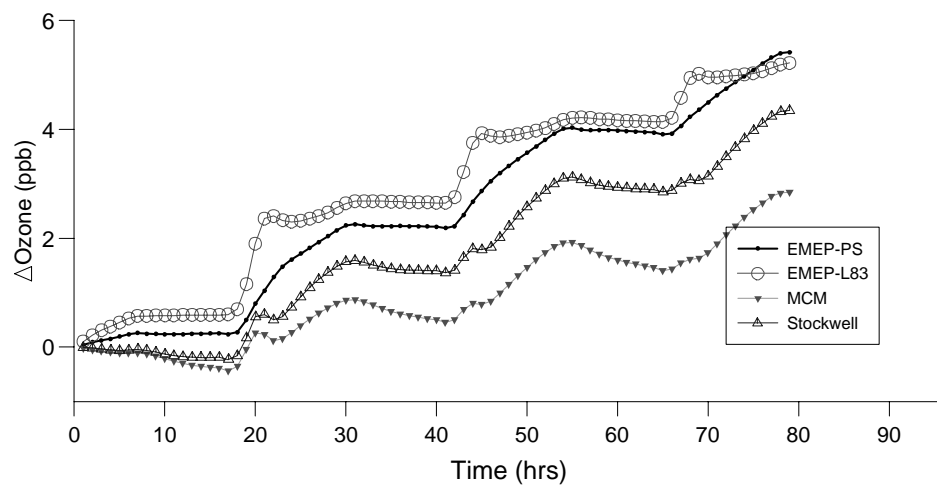


Figure 3.4: Comparison of EMEP-PS, MCM and Stockwell chemistries, Plume-2bio simulation



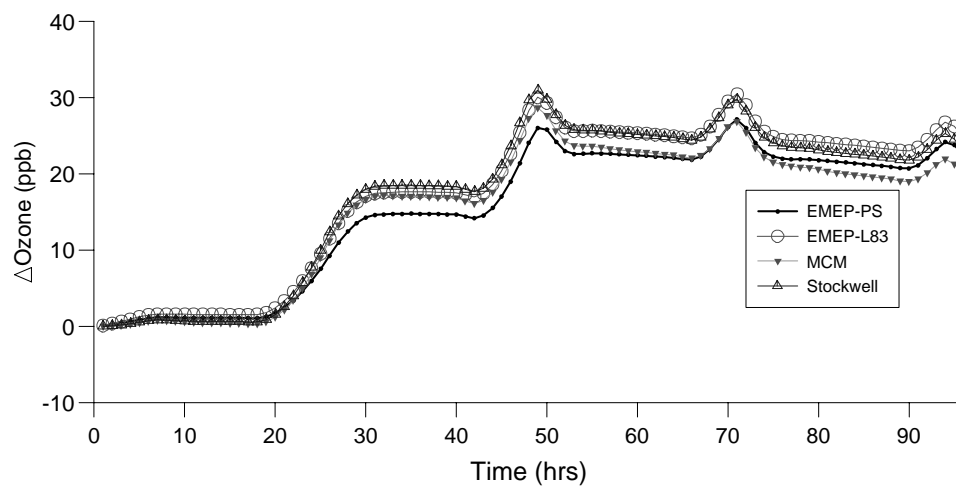


Figure 3.5: Simulated extra ozone concentrations with different isoprene mechanisms with  $5\times$ NO<sub>x</sub> emissions.

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