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**Development and
implementation of a
simplified EMEP
photochemistry scheme for
urban areas in EPISODE**

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Summary

The aim of the present project was to develop and implement, primarily in the EPISODE model and subsequently as part of the AirQUIS system, a simplified photochemistry scheme for urban areas.

The new scheme developed and implemented in EPISODE 3.0, is based on the EMEP oxidant mechanism, but contains only 45 compounds and about 70 reactions, as compared to 70 compounds and about 150 reactions in the standard EMEP mechanism. The new scheme contains a reduced number of compounds and reactions relevant for an urban atmosphere.

The motivation for the development for the new scheme was twofold: First it was needed to find a photochemistry scheme for urban areas containing as few compounds and equations as possible, so that it could be run with reasonable CPU time and use of memory on a standard Windows based PC, either as a standalone application or as part of the AirQUIS system. The second reason for the development was to modernise the photochemistry scheme, making it up-to-date with respect to equations and reaction coefficients, and with respect to the numerical solution of the resulting non-linear system of ordinary differential equations (stiff ODEs). In the implementation here, the stiff ODE system is solved using state-of-the-art numerical methods, based on fast Gauss-Seidel iterative techniques, with numerical error control and restart in case of detected numerical inaccuracies. All reaction rates and coefficients have been updated according to the latest IUPAC (2001) survey.

The new photochemistry scheme has successfully been run in a standalone version of EPISODE 3.0 for the city of Berlin, as part of the City Delta model intercomparison study. The calculations was performed for a total simulation period of about 6 months. It has also been tested and compared with a more extensive and complete EMEP photochemistry scheme. The latter study show that the scheme retains the essential aspects of photochemical reactions in an urban atmosphere with good accuracy.

The new simplified scheme has so far only been implemented in EPISODE 3.0. Further development is needed to be able to run the scheme as part of the AirQUIS system. This development is however only of administrative art. It involves developing some new menus in AirQUIS to be able to handle new parameters introduced by the photochemistry scheme, such as relative humidity, cloud cover, precipitation and dry and wet deposition velocities. It also involves development in AirQUIS to handle storage and retrieval of some or all of the 45 photochemical compounds.

Development and implementation of a simplified EMEP photochemistry scheme for urban areas in EPISODE

1 Introduction

The purpose of the present project was to develop and implement, primarily in the EPISODE model and subsequently as part of the AirQUIS system, a new simplified photochemistry model (scheme) for urban areas. With a simplified model we think of a model which is simpler, i.e. containing fewer compounds (components) and/or equations than the present classical EMEP scheme which already was part of the EPISODE model. The present EMEP scheme implemented in EPISODE 2.3 contained some 70 compounds and about 150 reactions. The idea was to try to see if it was possible to develop a new and simplified scheme containing maybe on the order of about half of the compounds and a similar reduction in the number of reaction equations.

The reason for the need in reduction of the number of compounds and/or reactions is for this to be fitted within the framework of the AirQUIS system. This AQMS system with its graphical user interface (GUI) and GIS based system is run on a PC platform. In order to keep both the size of the system to be solved to a reasonable size, and the CPU time to a reasonable level, it was necessary to try to reduce the number of compounds and/or reactions down to a minimum, while maintaining the essential and most important aspects of chemical reactions taking place in the urban atmosphere on reasonable space and time scales. One of the places where the new scheme may find application is in urban areas and cities in China.

In Chapter 2 we review existing and popular photochemistry schemes for the purpose of identifying a natural starting point for the development of the simplified scheme.

In Chapter 3 the new simplified scheme is developed and described.

In Chapter 4 the practical numerical implementation of the scheme is described. It was important to use the most up to date numerical solution techniques to solve the photochemistry equations.

In Chapter 5 some computational results using a simple box model comparing the new photochemical scheme with the more comprehensive and standard EMEP mechanism is given. Also some results running the new photochemistry solver as part of a nested version of EPISODE 3.0 for the city of Berlin (from the City Delta project) is presented.

Finally in Chapter 6, remaining future development needed in the AirQUIS system to include the new photochemistry scheme, but which is outside the scope

of the present project, is described. Some new parameters which will be needed in this context are identified.

In Appendix A, a condensed description of the new 45 compound EMEP photochemistry scheme is given, describing the compounds and equations involved together with a complete description of all reaction coefficients and equations.

2 Evaluation of available chemical schemes

A wide range of photochemical mechanisms and models are applied today, from extremely detailed and comprehensive codes including thousands of reactions like the Master Chemical Mechanism (MCM) (Jenkin et al., 1997) down to highly simplified, so-called "lumped", mechanisms. A lumped chemistry implies that the calculations are carried out only for a small group of selected compounds that are meant to be representative for the thousands of organic compounds actually involved. Normally, either a *structural* lumping or a *compound* lumping is used. Structural lumping, as used in CBM-IV, groups together compounds with similar functional groups, like alkanes, alkenes, aldehydes etc., while compound lumping denotes a lumping of certain pre-defined compounds. Although these two kinds of lumping may overlap considerably, main differences exist in the interpretation and application. Compound lumping may e.g. use a plain summation of compounds whereas structural lumping may use a summation weighted by the number of functional groups or the number of carbon atoms.

Obviously, for a 3D CTM like EPISODE, to be run on a PC platform, the mechanism and number of compounds has to be reduced to a minimum. A literature study was carried out and a number of available chemical schemes were identified. Table 1 gives an overview of chemistry codes easily accessible and applied in various models.

Table 1: Various photochemical schemes.

Scheme	No. of compounds	No. of reactions	Used by	Variations
EMEP	70	150	EMEP	
CBM-IV	32	81	UAM ROM LOTOS	CBM-IV-LOTOS CB4-TNO CBM-IV-99
SAPRC	~54	~158	CALGRID REM3	SAPRC-90, -93, -97, -99
RADM	55	156	RADM (EPA) EURAD	RADM2 RACM (69 spec.) ReLACS (37 spec.)
ADOM	47	114	ADOM	
UiB	51	111	Univ. of Bergen	

CBM-IV which is developed by the US Environmental Protection Agency (US EPA), as well as SAPRC and RADM are all American codes widely applied in photochemical models. As the compact CBM-IV mechanism uses a structural

lumping, it is not easily compatible with the EMEP mechanism, which uses a compound lumping.

A number of model intercomparison studies have been carried out and are reported in the literature, either including all processes in the model (Hass et al., 1997) or focusing on the chemistry only (Kuhn et al., 1998). Furthermore, several critical reviews have been carried out for models applied in the US (Dodge, 2000; Russell and Dennis, 2000). In the case studies reported by Kuhn et al. (1998), the ozone formation in the EMEP mechanism is among the fastest, i.e. giving the highest ozone production, whereas the CBM-IV is among the slowest. In the same study, when compared to the very detailed IVL mechanism which includes some 1800 reactions and 700 compounds, the EMEP mechanism gave very satisfactory results. A separate evaluation of the EMEP mechanism compared to the complex IVL mechanism revealed a close agreement between the prediction by these two codes, giving e.g., a difference in calculated formaldehyde of less than 10% (Anderson-Sköld and Simpson, 1999).

These results give a general confidence in the EMEP chemical mechanism. Additionally, there are other good reasons to apply a mechanism that is easily compatible with the standard EMEP code, as for example the ongoing model development cooperation between EMEP-MSC/W and NILU. Thus, it was concluded that a simplified version of the EMEP chemical routine would be preferable in the following work.

3 Development of a simplified 45 compound EMEP scheme

The EMEP chemistry is designed for calculating photochemical reactions on a regional European scale, covering all kinds of environments from clean, background conditions to polluted semi-urban areas and time scales of several days. For EPISODE, the requirements are less strict – the model will only be applied for more polluted regions and the residence time of the atmospheric compounds will normally be limited to less than a day. Given these conditions, the chemistry implemented in EPISODE could be simplified while still being compatible with the EMEP model.

Two main types of simplifications were done:

1) *RO₂ + RO₂ reactions were omitted*

It is well established that RO₂ in the main ozone formation reaction:



competes with the self-reaction(s)

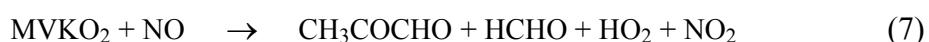


R stands for an organic fraction, and RO₂ denotes a peroxy radical. In low-NO_x environments (NO < 50 pptv), the rates of reaction (2) and (3) will be similar or faster than reaction (1), whereas at NO_x-levels typical of moderately (or more)

polluted areas, reactions (2) and (3) will be negligible compared with reaction (1). Thus, all reactions of type (2) and (3), except for the $\text{CH}_3\text{O}_2 + \text{HO}_2$ and the $\text{HO}_2 + \text{HO}_2$ reactions, were omitted in the simplified EMEP scheme.

2) Simple isoprene mechanism

The isoprene mechanism presently included in the EMEP chemistry (Simpson, 1995) is fairly extensive and was significantly simplified in the EPISODE mechanism. Reactions (4) – (7) below show the reduced 4-reactions isoprene scheme used:



where MVK stands for methyl vinyl ketone.

With these two types of simplifications, a condensed EMEP mechanism with the number of compounds reduced from 70 to 45 and the number of reactions reduced from about 150 to about 70 was obtained.

Dry deposition is included in the simplified scheme but wet-scavenging is presently not. Furthermore, all reaction rate constants were revised and updated according to the most recent edition published by IUPAC (IUPAC, 2001). For reactions not available in IUPAC the reaction rates as given by Simpson (1993) are used. A complete description of the simplified scheme is given in Appendix A.

4 Numerical implementation of the simplified scheme

The atmospheric photochemistry equations defined by the condensed mechanism described in Chapter 3 (and Appendix A) forms a stiff non-linear system of ordinary differential equations (stiff ODE):

$$\frac{dy}{dt} = f(t, y) = P(t, y) - L(t, y) \cdot y, \quad k = 1, \dots, m. \quad (8)$$

where y is the solution vector containing m compounds ($m = 45$), and P and L describe the photochemistry production and loss terms respectively. Here $P(t, y)$ is a vector of size m and $L(t, y)$ a diagonal matrix of size $m \times m$.

To integrate this system of equations, a new numerical solver has been implemented in EPISODE. The solver is based on work described in Verwer and Simpson (1995).

First the system of non-linear equations (8) is approximated by a variable-step, second order Backward Differentiation Formula (BDF):

$$y^{n+1} = Y^n + \gamma \cdot \tau \cdot f(t_{n+1}, y^{n+1}) \quad (9)$$

where $\tau = t_{n+1} - t_n$ is the time step between the solution values y^n and y^{n+1} , and where $\gamma = (c+1)/(c+2)$, $c = (t_n - t_{n-1})/(t_{n+1} - t_n)$ and $Y^n = ((c+1)^2 y^n - y^{n-1})/(c^2 + 2c)$.

By exploiting the chemical kinetics form of the differential equation (8), the non-linear system of equations (9) can be written in component form:

$$y_k^{n+1} = \frac{Y_k^n + \gamma \cdot \tau \cdot P_k(t_{n+1}, y^{n+1})}{1 + \gamma \cdot \tau \cdot L_k(t_{n+1}, y^{n+1})} = F_k(y^{n+1}), \quad k = 1, 2, \dots, m. \quad (10)$$

where P_k is the k 'th element of the vector P , and L_k is the k 'th element on the diagonal of the matrix L . A Gauss-Seidel iterative method is then employed in order to solve (10) numerically for y^{n+1} , given the values y^n and y^{n-1} at the two previous time steps t_n and t_{n-1} .

As initial iterate we use the following extrapolation formula:

$$y^{(0)} = y^n + \frac{1}{c}(y^n - y^{n-1}) \quad (11)$$

which is the same as described in Verwer and Simpson (1995).

One iteration of the Gauss-Seidel method proceeds as follows: First we calculate $y_1^{n+1} = F_1(y^{(0)})$ from (10) using the initial iterate (11). Then we immediately replace the first element $y_1^{(0)}$ in the initial iterate with y_1^{n+1} , before calculating $y_2^{n+1} = F_2(y^{(0)})$ using this modified initial iterate. Then we replace $y_2^{(0)}$ with y_2^{n+1} before calculating $y_3^{n+1} = F_3(y^{(0)})$. We repeat this procedure until all components of the solution vector y_k^{n+1} , $k = 1, \dots, m$, have been calculated. The whole procedure represents one iteration of the Gauss-Seidel method.

A certain number of iterations of this Gauss-Seidel method is then used in order to give an approximate solution to (10). As shown in Verwer and Simpson (1995), the Gauss-Seidel iterative method, on the type of photochemistry scheme employed here, converges rapidly, so only a small number of iterations is usually required. In their paper they found that only two iterations were most often enough. Consequently, we have also implemented the method using only two iterations per time step. This can however easily be changed later if need be.

In order to retain accuracy of the solution of the stiff ODE, a local error indicator vector is used:

$$E^{n+1} = \frac{2}{c(c+1)}(cy^{n+1} - (1+c)y^n + y^{n-1}) \quad (12)$$

Based on this local error indicator vector, we calculate the weighted error norm:

$$\|E^{n+1}\|_w = \max \left(\frac{|E_k^{n+1}|}{W_k^n} \right), \quad W_k^n = \text{atol}_k + \text{rtol}_k \cdot |y_k^n| \quad (13)$$

where atol_k and rtol_k for $k = 1, \dots, m$, are the component-wise defined absolute and relative error tolerances. If $\|E^{n+1}\|_w \leq 1.0$, the integration step is accepted. Otherwise it is rejected.

In our implementation the relative error tolerances are currently set equal to 0,1 (10% relative error) for all compounds. The absolute error tolerances are set in a range between $2,5 \cdot 10^8$ molec/cm³ to $1,0 \cdot 10^{15}$ molec/cm³ depending on compound.

For practical purposes though, we have in the actual implementation omitted the first three compounds (OP, OD, and OH) when calculating the weighted error norm (13). The reason for this is that it is rather meaningless to operate with error control on these three components, since these are very fast compounds. Because of this we also use the following approximation, instead of (10), for these three components:

$$y_k^{n+1} = \frac{P_k(t_{n+1}, y^{n+1})}{L_k(t_{n+1}, y^{n+1})}, \quad k = 1, \dots, m \quad (14)$$

since they converge very rapidly to the steady state value given by (14).

The new time step, τ_{new} , is estimated by the formula:

$$\tau_{\text{new}} = \max \left(0.5, \min \left(2.0, \frac{0.8}{\sqrt{\|E^{n+1}\|_w}} \right) \right) \cdot \tau_{\text{old}} \quad (15)$$

where τ_{old} is the previous time step. The time step is further constrained by a prescribed minimum and maximum value. Currently the minimum time step is set equal to 0,1 seconds and the maximum time step is set equal to two times the time step used in the EPISODE model.

If two successive rejections occur the process is restarted. The missing starting value after a restart, or at the beginning of the simulation period, is calculated by the implicit Euler method:

$$y_k^{n+1} = \frac{y_k^n + \tau \cdot P_k(t_{n+1}, y^{n+1})}{1 + \tau \cdot L_k(t_{n+1}, y^{n+1})}, \quad k = 1, 2, \dots, m. \quad (16)$$

which is treated with the Gauss-Seidel iterative method in the same way as the second order BDF equation, using two iterations per time step.

As initial iterate $y^{(0)}$ in (16) we use directly the initial value y^0 instead of the extrapolation formula (11). In this case, however, the initial time step is computed by replacing E^{n+1} in (13) with $\tau \cdot f(t_0, y^0)$. Hence we define τ such that the weighted error norm is equal to one, i.e.,

$$\tau = \min \left(\frac{W_k^0}{|f_k(t_0, y^0)|} \right), \quad k = 1, 2, \dots, m. \quad (17)$$

The second order BDF scheme is then applied with the same time step, and after that the variable time step mechanism (15) is again activated. Normally (17) leads to a rather small initial guess for the time step which will be accepted, and then the time step will subsequently be increased according to (15).

For practical purposes though, we have in the actual implementation omitted the first three compounds (OP, OD, and OH) when calculating the time step using (17). The reason for this is that it is rather meaningless to operate with the sort of error control which are implicit in (17) for these three components since they are very fast. For these three components we always use the steady state approximation given by (14), instead of (16).

The above described photochemistry operator (EMEP45) is then used alternately with the transport (advection and diffusion) operator in the EPISODE model for every time step Δt in the model as follows:

$$\text{TRANSPORT}(\Delta t) \Rightarrow \text{EMEP45}(2\Delta t) \Rightarrow \text{TRANSPORT}(\Delta t)$$

where TRANSPORT is the total transport operator which includes all the horizontal and vertical advection and diffusion operators. Each transport operator works over a time span of Δt seconds, while the photochemistry operator works over a time span of $2\Delta t$ seconds. Each time EMEP45 is started it is considered as a restart in the algorithm, and thus the implicit Euler method is invoked with an initial internal time step for photochemistry calculated by (17).

5 Some computational results

A number of test calculations were carried out to compare the condensed mechanism with the standard EMEP mechanism. This was done by a separate software designed particularly for this purpose, using only a box version of the chemistry part (including emissions), separated from the rest of the EPISODE model.

An example of these test calculations is given in Figure 1 and Figure 2. These figures show the result of 60h integration which is much longer than a characteristic residence time inside an EPISODE model domain. Furthermore, these calculations were carried out for rural conditions with substantially lower NO_x concentrations ($\text{NO}_x \sim 4$ ppbv) than would normally be the case for EPISODE calculations. Even for these conditions, the difference between the standard EMEP and the reduced mechanism is fairly small. The condensed

mechanism gives slightly less concentrations of NO and NO₂, while the ozone concentration is almost identical in the calculations. For a situation more representative for an EPISODE application, i.e., more urban air mass and shorter time scale, these differences would be significantly smaller.

Ideally, a large number of systematic comparison calculations should be carried out by the box model approach. This has not been done. However, both the theoretical consideration and the test runs performed, give confidence that the simplification of the chemistry is not inducing major faults in the results.

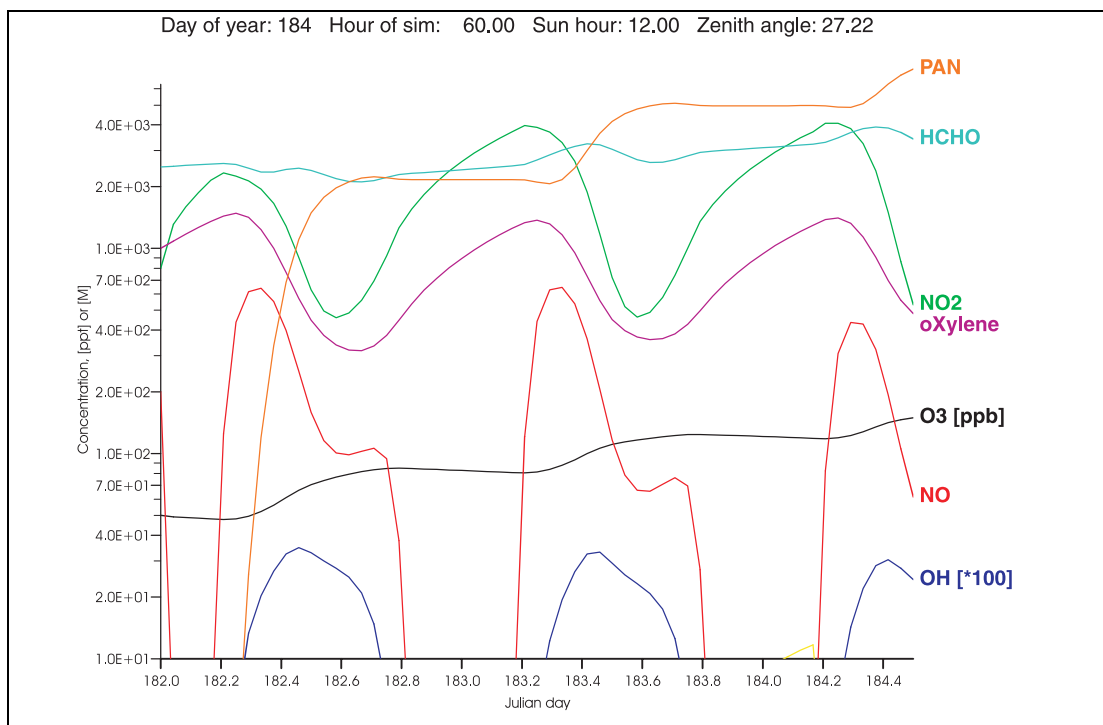


Figure 1: 60h of calculations with the condensed 45 compounds mechanism in a box model with chemistry and emissions only.

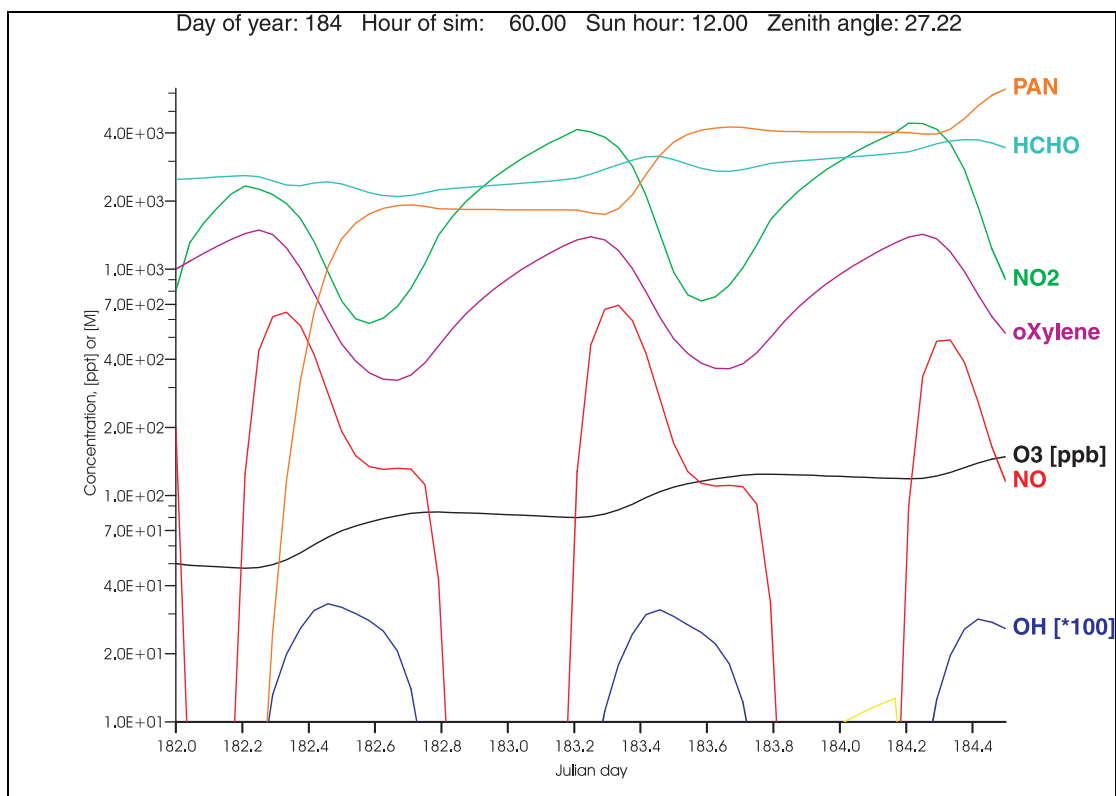


Figure 2: Same as Figure 1 but using the standard EMEP chemistry.

The simplified chemistry scheme has also been applied in a real case simulation for the city of Berlin as part of the City Delta study. City Delta is an activity organized by the EU-CAFÉ programme with the aim of studying the long term model response to urban-scale emission-reduction scenarios. As part of this programme the emission inventory, at a resolution of 1 km, and meteorology, at a resolution of 10 km, was made available to the participants for several cities in Europe for the year 1999. One of these cities, Berlin, was modelled at NILU using EPISODE and provided the test bed for many of the improvements presented in this report.

In total 13 different models were applied to the Berlin data for validation and intercomparison, all using boundary conditions provided by EMEP. The gaseous phase compounds of interest to this study were O₃ and NO₂. The EPISODE model was run at a spatial resolution of 10 km in a 300 x 300 km region and 6 vertical layers were used up to a height of 2000 m. The simulation period was the 6 months between April – September. Some results of the simulations are shown below.

In Figure 4 the mean observed and EPISODE simulated concentrations over the 6 month period at 9 different stations for O₃ and NO₂ are shown. Mean values for O₃ agree very well with those observed, but for NO₂ some stations are not well represented. However, in the intercomparison between models this was shown to be generally the case.

In Figure 5 the bias in mean O₃ and the correlation coefficient over the six month period is also shown. All 13 models from the intercomparison study are presented.

The EPISODE model, number 16, has one of the lowest biases of all the models for O_3 and a correlation coefficient $> 0,6$ for almost all stations. In general EPISODE performed very well in these simulations for most diagnostic tests.



Figure 3: Road map of the Berlin simulation region showing the positions of stations used in the validation study.

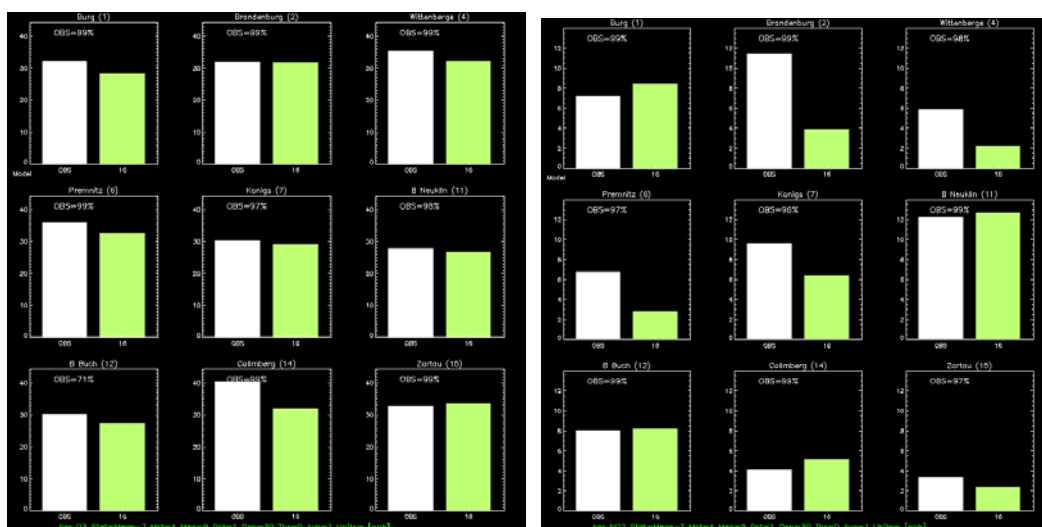


Figure 4: Comparison of observed (white) and simulated (light green) mean O_3 (left) and NO_2 (right). Concentrations are in ppb.

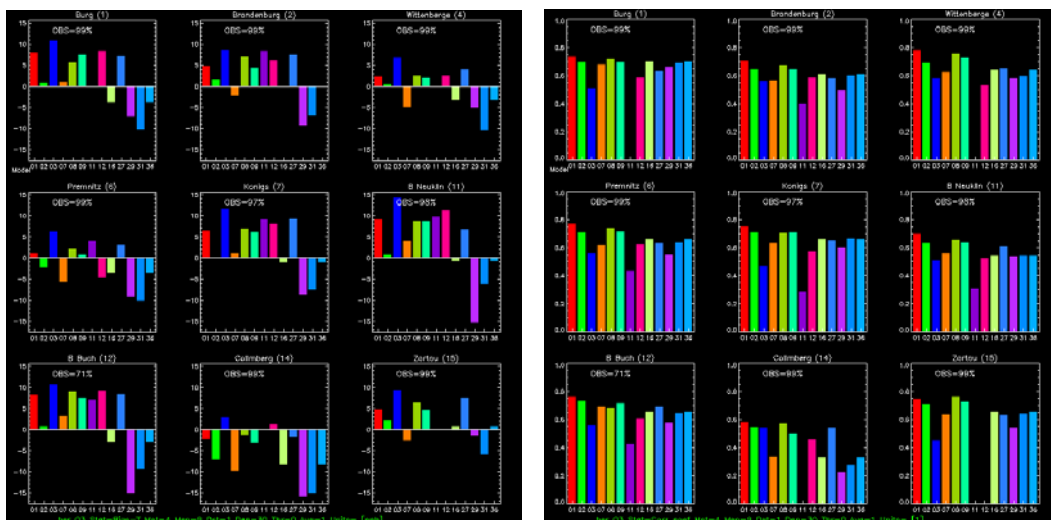


Figure 5: Intercomparison of the models in the study showing the mean bias for O_3 (left) and the correlation coefficient for O_3 (right). Concentrations are in ppb. EPISODE is model 16 (light green) in the intercomparison study.

The EPISODE computations were performed on a 2 GHz Pentium 4 based PC running Windows XP. The calculations took about 6 CPU hours for one month of simulation.

6 Future development

This report presents the status of the photochemistry module in EPISODE at the present stage. A continuous development of the model will necessarily take place and make the documentation gradually obsolete. The model could be developed in all aspects, and a few of these possibilities are mentioned below.

6.1 3D meteorological fields as input

Whereas the previous applications of EPISODE (and the former EMEP chemistry) have been limited to the PBL, an extension of the EPISODE model domain in the horizontal and vertical make it necessary to include vertical variations in the meteorological data used in the photochemistry. For an altitude up to, say, 1500 m, these vertical differences will normally have a negligible effect. When applied for higher altitudes, the vertical variations in temperature (T), pressure (P) and relative humidity (RH) may become important and should be included. The 3-body reactions which are pressure dependent and the strongly temperature dependent PAN stability are important to take into account in this respect. The vertical variation in relative humidity is of importance for the formation of OH radicals through the $O(^1D) + H_2O$ reaction. The photochemistry presently included is designed for taking into account variations in P, T and RH and it's thus only a question of including these 3D fields in EPISODE.

6.2 Aerosol formation

There is presently a very limited parameterization of aerosols in the chemistry. An improved aerosol module will probably be required in the future. It should also be noted that the present formation rate of aerosols is set to a constant rate without any dependence on relative humidity, which is clearly inaccurate. An increased aerosol formation rate for high values of RH should be included.

6.3 Wet scavenging

While wet scavenging processes probably has a minor influence on the ozone formation it is an essential process to include if aerosol calculations are to be included. Wet scavenging processes could e.g., be adopted from the Unified EMEP model.

6.4 Implementation in AirQUIS

The aim of the present project was to implement a new simplified photochemistry scheme within the scope of the EPISODE model. The EPISODE model is the central air pollution dispersion model used in NILUs AirQUIS system (Air Quality and Information System). However, in order to use the new simplified photochemistry scheme as part of AirQUIS, parts of the AirQUIS system must also be modified. This development falls outside the scope of the present project, but we describe here some of the issues involved.

The development which is needed within the AirQUIS system involves making some new menus with new parameters needed by the 45 compound simplified EMEP photochemistry scheme. These new parameters are:

- Relative humidity (% or 0-1)
- Cloud cover (octal or 0-1)
- Precipitation (mm/h)
- Dry deposition velocities for some of the 45 compounds (cm/s) (the rest is 0)
- Wet deposition scavenging ratios for some of the 45 compounds (the rest is 0)
- Possibly a land/sea indicator (0/1)

The relative humidity, cloud cover and precipitation parameters can be given either as a spatial and/or temporal constants, or be based on gridded fields of values updated e.g. every hour. The dry deposition velocities and the wet deposition scavenging ratios can be given as constant values for some of the 45 different compounds, the rest being simply set to 0. The land/sea indicator can be given either as a constant, for example 1, if the city or area is inland from the coast, or as a gridded field of values if the city or area lies at the coast.

It is also necessary to be able to handle the 45 different compounds simultaneously in different parts of the AirQUIS system, like in menus or when storing, retrieving and presenting concentration values.

It must also be ensured that enough RAM memory is available on the PC where the AirQUIS system is to be run, since running the photochemistry model with 45 compounds uses a lot more memory than a single compound model run, especially if the number of grid cells is large.

Finally one must also bear in mind that the photochemistry calculations uses molec/cm³ as the basic unit of concentration. In AirQUIS, µg/m³ is the basic unit of concentration. Routines for converting between these two units should therefore also be included, either in the EPISODE model or in AirQUIS.

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Appendix A
Description of the simplified 45 compound EMEP
scheme

A.1 Compounds

The simplified EMEP photochemistry scheme contains the following 45 compounds:

Table A1: Compounds used in the simplified scheme.

Nr.	Primary name	Secondary name/description	Molecular weight
1	OP	O(3P)	16
2	OD	O(1D)	16
3	OH		17
4	O3	Ozone	48
5	HO2		33
6	H2O2		34
7	NO	Nitrogen oxide	30
8	NO2	Nitrogen dioxide	46
9	NO3	Nitrate (gaseous)	62
10	N2O5		108
11	HNO3		63
12	SO2	Sulphur dioxide	64
13	Sulphate	SO4	96
14	H2		2
15	CH4	Methane	16
16	CH3O2		47
17	HCHO	Formaldehyde	30
18	CH3OH		32
19	CH3O2H		48
20	CO	Carbon monoxide	28
21	C2H6	Ethane	30
22	C2H5O2		61
23	CH3CHO		44
24	CH3COO2		59
25	PAN	CH3COO2NO2	121
26	C2H5OH		46
27	n-C4H10	n-butane	58
28	secC4H9O2		89
29	CH3COC2H5	MEK (methyl ethyl ketone)	72
30	CH3COCHO2CH3		103
31	CH3COCOCH3		86
32	C2H4	Ethene	28
33	CH2O2CH2OH		77
34	C3H6	Propene	42
35	CH3CHO2CH2OH		91
36	o-Xylene	C8H10	106
37	oXylOHO2	C6H3H(O2)CH3(OH)CH3	155
38	Memaldial	CH3COCHCHCHO	98
39	CH3COCHO	Methylglyoxal	72
40	MemalO2	CH3COCH(OH)CH(O2)CHO	147
41	HCOCHO	Glyoxal	58
42	Isoprene	C5H8	68
43	IsopO2	OHC5H8O2	117
44	MVKetone	CH3C(O)CHCH2	70
45	MVKO2	HOCH2CH(O)C(CH3)O	103

A.2 Reaction equations and coefficients

Generally, in all equations, the atmospheric molecular density M is set equal to $2,55 \cdot 10^{19}$ molec/cm³. The O₂ part is calculated as 20,95% of M . The air temperature in Kelvin is denoted by T .

The water vapour concentration H₂O in the atmosphere in molec/cm³ is calculated based on the relative humidity RH in % and air temperature T in Kelvin as follows:

$$H_2O = RH \cdot ESAT / (1,38 \cdot 10^{-17} \cdot T)$$

where

$$ESAT = 6,1078 \cdot e^{-XZ}$$

$$XZ = (597.3 - 0.57 \cdot (T - 273.16)) \cdot 18 / 1.986 \cdot (1/T - 1/273.16)$$

All reaction rates are based on the latest IUPAC recommendations, (<http://www.iupac-kinetic.ch.cam.ac.uk/>) partly published by Atkinson et al. (2000), if no other reference is given. In the equations all rates k have unit molec/(cm³ · s).

The 3-body and unimolecular reaction rates are denoted by k = RC3B (k₀, k_∞, F_c). They are calculated as a function of the low-pressure limit (k₀), the high-pressure limit (k_∞), and the broadening factor (F_c) using the following expression:

$$RC3B = (k_0 k_\infty / (k_0 + k_\infty)) \cdot F_c^{1/(1 + \log_{10}(k_0 / k_\infty)^2)}$$

The groups of reaction coefficient numbers used is given in Table A2. In addition 16 different photo-dissociation coefficients are used.

Table A2: Groups of reaction coefficient numbers used in the simplified scheme.

Coefficient nr.	Coefficient type	Unit
1-39	Inorganic chemistry	molec/cm ³ ·s
40-59	Aerosol formation	"
60-159	Organic chemistry	"
160-179	Dry deposition	"
200-219	Emission	"

Below all equations in the simplified EMEP photochemistry scheme are given. First the gaseous phase reactions are described. Each reaction equation is given together with its associated reaction rate. This is then followed by a description of the photolytic reactions.

Gaseous phase reactions

Inorganic chemistry

1) OP + O₂ -> O₃
 $k = 5.67E-34 \cdot (T/300.)^{**(-2.8)} \cdot M$

2) OD + M -> OP
 Assumes 21% O₂ and 79% N₂:
 $k = 0.21 \cdot 3.2E-11 \cdot \text{EXP}(+67./T) + 0.79 \cdot 1.8E-11 \cdot \text{EXP}(+107./T)$

3) OP + NO -> NO₂
 $k = RC3B(1.0E-31 \cdot (T/300.)^{**(-1.6)} \cdot M, 3.0E-11 \cdot (T/300.)^{**0.3}, 0.85)$

4) H₂O + OD -> 2 · OH
 $k = 2.2E-10$

5) O₃ + NO -> NO₂
 $k = 1.4E-12 \cdot \text{EXP}(-1310./T)$

6) $O_3 + NO_2 \rightarrow NO_3$
 $k = 1.4E-13 * EXP(-2470./T)$

7) $O_3 + OH \rightarrow HO_2$
 $k = 1.7E-12 * EXP(-940./T)$

8) $O_3 + HO_2 \rightarrow OH$
 $k = 2.03E-16 * EXP(693./T) * (T/300)**4.57$

9) $NO + NO_3 \rightarrow 2. * NO_2$
 $k = 1.8E-11 * EXP(+110./T)$

10) $NO + HO_2 \rightarrow NO_2 + OH$
 $k = 3.6E-12 * EXP(+270./T)$

11) $NO_2 + NO_3 \rightarrow NO + NO_2$
 $k = 4.5E-14 * EXP(-1260./T) ! DeMore, 1992$

12) $NO_2 + NO_3 \rightarrow N_2O_5$
 $k = RC3B(3.6E-30 * (T/300.)**(-4.1) * M, 1.9E-12 * (T/300.)**(0.2), 0.35)$

13) $NO_2 + OH \rightarrow HNO_3$
 $k = RC3B(3.3E-30 * (T/300.)**(-3.0) * M, 4.1E-11, 0.4)$

17) $N_2O_5 \rightarrow NO_2 + NO_3$
 $k = RC3B(1.0E-3 * (T/300.)**(-3.5) * EXP(-11000./T) * M, 9.7E14 * (T/300.)**(0.1) * EXP(-11080./T), 0.35)$

20) $OH + H_2 \rightarrow HO_2$
 $k = 7.7E-12 * EXP(-2100./T)$

21) $OH + HO_2 \rightarrow$
 $k = 4.8E-11 * EXP(+250./T)$

22) $OH + H_2O_2 \rightarrow HO_2$
 $k = 2.9E-12 * EXP(-160./T)$

24) $HO_2 + HO_2 \rightarrow H_2O_2$
 $k = (2.2E-13 * EXP(+600./T) + 1.5E-33 * EXP(+980./T) * M) * (1. + 1.4E-21 * EXP(+2200./T) * H_2O)$

25) $OH + HNO_3 \rightarrow NO_3$
 $k = 2.4E-14 * EXP(+460./T) + 6.5E-34 * EXP(+1335./T) * M / (1. + 6.5E-34 * EXP(+1335./T) * M / (2.7E-17 * EXP(+2199./T)))$

26) $SO_2 + OH \rightarrow HO_2 + Sulphate$
 $k = RC3B(4.0E-31 * (T/300.)**(-3.3) * M, 2.E-12, 0.45)$

27) $SO_2 + CH_3O_2 \rightarrow Sulphate + HCHO + HO_2$
 $k = 4.0E-17 ! EMEP$

Aerosol formation

40) $H_2O_2 \rightarrow$
 $k = 5.0E-6 * M / 2.55E19 ! EMEP$

41) $CH_3O_2H \rightarrow$
 $k = 5.0E-6 * M / 2.55E19 ! EMEP$

42) $N_2O_5 \rightarrow$
 $k = 5.0E-6 * M / 2.55E19 ! EMEP$

43) $HNO_3 \rightarrow$
 $k = 5.0E-6 * M / 2.55E19 ! EMEP$

45) $Sulphate \rightarrow$
 $k = 5.0E-6 * M / 2.55E19 ! EMEP$

Organic chemistry: Methane chemistry

60) $CH_4 + OH \rightarrow CH_3O_2$
 $k = 1.85E-12 * EXP(-1690./T)$

61) $CH_3O_2 + NO \rightarrow HCHO + HO_2 + NO_2$
 $k = 2.8E-12 * EXP(+285./T)$

64) $\text{CH}_3\text{OH} + \text{OH} \rightarrow \text{HCHO} + \text{HO}_2$
 $k = 1.4\text{E-}13 + 3.1\text{E-}12 \cdot \exp(-360./T)$

66) $\text{CH}_3\text{O}_2 + \text{HO}_2 \rightarrow \text{CH}_3\text{O}_2\text{H}$
 $k = 3.8\text{E-}13 \cdot \exp(+780./T)$

67) $\text{CH}_3\text{O}_2\text{H} + \text{OH} \rightarrow \text{HCHO} + \text{OH}$
 $k = 1.0\text{E-}12 \cdot \exp(+190./T)$! EMEP

68) $\text{CH}_3\text{O}_2\text{H} + \text{OH} \rightarrow \text{CH}_3\text{O}_2$
 $k = 1.9\text{E-}12 \cdot \exp(+190./T)$! EMEP

69) $\text{HCHO} + \text{OH} \rightarrow \text{CO} + \text{HO}_2$
 $k = 8.2\text{E-}12 \cdot \exp(+40./T)$

70) $\text{HCHO} + \text{NO}_3 \rightarrow \text{CO} + \text{HO}_2 + \text{HNO}_3$
 $k = 5.8\text{E-}16$

71) $\text{CO} + \text{OH} \rightarrow \text{HO}_2$
 $k = 1.3\text{E-}13 \cdot (1. + 0.6 \cdot (M/2.55\text{E}19)) \cdot (300./T)$

Organic chemistry: Ethane chemistry

80) $\text{C}_2\text{H}_6 + \text{OH} \rightarrow \text{C}_2\text{H}_5\text{O}_2$
 $k = 6.9\text{E-}12 \cdot \exp(-1000./T)$

82) $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2 + \text{NO}_2$
 $k = 2.5\text{E-}12 \cdot \exp(+380./T)$

84) $\text{CH}_3\text{CHO} + \text{OH} \rightarrow \text{CH}_3\text{COO}_2$
 $k = 4.4\text{E-}12 \cdot \exp(+365./T)$

86) $\text{CH}_3\text{COO}_2 + \text{NO}_2 \rightarrow \text{PAN}$
 $k = \text{RC3B}(2.7\text{E-}28 \cdot (T/300.)^{**(-7.1)} \cdot M, 1.2\text{E-}11 \cdot (T/300.)^{**(-0.9)}, 0.3)$

87) $\text{PAN} \rightarrow \text{CH}_3\text{COO}_2 + \text{NO}_2$
 $k = \text{RC3B}(5.5\text{E-}3 \cdot \exp(-12064./T) \cdot M, 3.9\text{E}16 \cdot \exp(-13628./T), 0.3)$! LACTOZ, 1992

89) $\text{CH}_3\text{COO}_2 + \text{NO} \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$
 $k = 7.8\text{E-}12 \cdot \exp(+300./T)$

93) $\text{C}_2\text{H}_5\text{OH} + \text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{HO}_2$
 $k = 4.1\text{E-}12 \cdot \exp(-70./T)$

Organic chemistry: N-butane chemistry

100) $\text{nC}_4\text{H}_{10} + \text{OH} \rightarrow \text{secC}_4\text{H}_9\text{O}_2$
 $k = 9.1\text{E-}12 \cdot \exp(-405./T)$

101) $\text{secC}_4\text{H}_9\text{O}_2 + \text{NO} \rightarrow 0.65 \cdot \text{CH}_3\text{COC}_2\text{H}_5 + 0.35 \cdot \text{CH}_3\text{CHO} + 0.35 \cdot \text{C}_2\text{H}_5\text{O}_2 + 0.65 \cdot \text{HO}_2 + \text{NO}_2$
 $k = 4.2\text{E-}12 \cdot \exp(180./T)$! EMEP, 2002

103) $\text{CH}_3\text{COC}_2\text{H}_5 + \text{OH} \rightarrow \text{CH}_3\text{COCHO}_2\text{CH}_3$
 $k = 1.3\text{E-}12 \cdot \exp(-25./T)$

104) $\text{CH}_3\text{COCHO}_2\text{CH}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{CH}_3\text{COO}_2 + \text{CH}_3\text{CHO}$
 $k = 5.0\text{E-}12$! Lesclaux, 1992

Organic chemistry: Ethene chemistry

110) $\text{C}_2\text{H}_4 + \text{OH} \rightarrow \text{CH}_2\text{O}_2\text{CH}_2\text{OH}$
 $k = \text{RC3B}(7.\text{E-}29 \cdot (T/300.)^{**(-3.1)} \cdot M, 9.\text{E-}12, 0.48)$

111) $\text{CH}_2\text{O}_2\text{CH}_2\text{OH} + \text{NO} \rightarrow 2 \cdot \text{HCHO} + \text{HO}_2 + \text{NO}_2$
 $k = 4.2\text{E-}12 \cdot \exp(180./T)$! EMEP, 2002

113) $\text{C}_2\text{H}_4 + \text{O}_3 \rightarrow \text{HCHO} + 0.42 \cdot \text{CO} + 0.12 \cdot \text{HO}_2 + 0.12 \cdot \text{H}_2$
 $k = 9.1\text{E-}15 \cdot \exp(-2580./T)$

Organic chemistry: Propene chemistry

120) C3H6 + OH -> CH3CHO2CH2OH
 $k = RC3B(8.0E-27*(T/300.)^{*(-3.5)*M}, 3.E-11, 0.5)$

121) CH3CHO2CH2OH + NO -> CH3CHO + HCHO + HO2 + NO2
 $k = 4.2E-12*EXP(180./T) ! EMEP, 2002$

123) C3H6 + O3 -> 0.50 CH3CHO + 0.50 HCHO + 0.07 CH4 + 0.40 CO + 0.31 CH3O2 + 0.28 HO2 + 0.15 OH + 0.07 H2
 $k = 5.5E-15*EXP(-1880./T)$

Organic chemistry: O-xylene chemistry

130) oXylene + OH -> oXylOH2
 $k = 1.4E-11 ! Atkinson, 1990$

131) oXylOH2 + NO -> Memaldial + CH3COCHO + HO2 + NO2
 $k = 4.0E-12 ! Lesclaux, 1992$

132) Memaldial + OH -> MemalO2
 $k = 5.6E-11 ! Bierbach, 1994$

133) MemalO2 + NO -> CH3COCHO + HCOCHO + HO2 + NO2
 $k = 9.0E-12 ! Lesclaux, 1992$

134) CH3COCHO + OH -> CH3COO2 + CO
 $k = 1.7E-11 ! EMEP$

135) HCOCHO + OH -> HO2 + 2. * CO
 $k = 1.2E-11 ! EMEP$

Organic chemistry: Isoprene chemistry

140) Isoprene + OH -> IsopO2
 $k = 2.7E-11*EXP(+390./T)$

141) IsopO2 + NO -> MVKetone + HCHO + HO2 + NO2
 $k = 4.2E-12*EXP(+180./T) ! Assumed equal to rate 121$

142) MVKetone + OH -> MVK2
 $k = 4.1E-12*EXP(+453./T) ! Paulson and Seinfeld, 1992$

143) MVK2 + NO -> CH3COCHO + HCHO + HO2 + NO2
 $k = 1.4E-12*EXP(-180./T) ! Paulson and Seinfeld, 1992$

The photolytic reactions

The zenith angle θ is calculated by the expressions:

$$\delta = 23,27 \cdot \cos((D - 172)/365)$$

$$\cos \theta = \cos(\varphi) \cdot \cos(\delta) \cdot \cos((H - 12)/24) + \sin(\varphi) \cdot \sin(\delta)$$

$$\theta = \arccos(\max(0,017, \cos \theta))$$

where

D = Day of the year

H = Local time

φ = Site latitude

The photolytic reaction rates are calculated according to the expressions:

$$\begin{aligned}
 j_i &= \text{CLF}_i \cdot A_i \cdot \exp(B_i / \cos(\theta)) && \text{for } \theta < 60^\circ \\
 j_i &= \text{CLF}_i \cdot A_i \cdot \exp(B_i \alpha(\theta)) && \text{for } 60^\circ \leq \theta < 89^\circ \\
 j_i &= \text{CLF}_i \cdot A_i \cdot \exp(B_i \alpha(\theta=89^\circ)) && \text{for } \theta \geq 89^\circ
 \end{aligned}$$

where θ is the zenith angle and α denotes the optical air mass for large zenith angles, i.e. when the sun is low, and CLF_i is the cloud correction factor for reaction number i calculated as follows:

$$\begin{aligned}
 \text{CLF}_i &= (1,0 - \text{CL}/0,2) + \text{CL1}_i \text{CL}/0,2 && \text{for } \text{CL} \leq 0,2 \\
 \text{CLF}_i &= \text{CL1}_i + (\text{CL} - 0,2) (\text{CL2}_i - \text{CL1}_i) / 0,6 && \text{for } \text{CL} > 0,2
 \end{aligned}$$

where the actual cloud cover $\text{CL} \in [0, 0,8]$. Tabulated values for A, B, CL1, CL2 and α are given in table A3 below.

Table A3: Photolytic reactions and coefficients used in the simplified scheme.

Nr.	Reaction path	A	B	CL1	CL2
1	O3 -> OD	2.00E-04	1.400	0.86	0.33
2	O3 -> OP	1.23E-03	0.600	0.92	0.41
3	NO2 -> OP + NO	1.45E-02	0.400	0.91	0.38
4	H2O2 -> 2OH	2.20E-05	0.750	0.88	0.35
5	HNO3 -> NO2 + OH	3.00E-06	1.250	0.87	0.33
6	HCHO -> CO + 2HO2	5.40E-05	0.790	0.88	0.34
7	HCHO -> CO + H2	6.65E-05	0.600	0.89	0.35
8	CH3CHO -> CH3O2 + HO2 + CO	1.35E-05	0.940	0.87	0.33
9	CH3COC2H5 -> CH3COO2 + C2H5O2	2.43E-05	0.877	0.92	0.41
10	Not used				
11	CH3COCHO -> CH3CHO + CO	9.72E-05	0.877	0.92	0.41
12	HCOCHO -> HCHO + CO	5.40E-04	0.790	0.92	0.41
13	NO3 -> NO	3.53E-02	0.081	0.92	0.42
14	NO3 -> NO2 + OP	8.94E-02	0.059	0.92	0.42
15	N2O5 -> NO2 + NO3	3.32E-05	0.567	0.88	0.35
16	CH3O2H -> HCHO + OH + HO2	2.27E-05	0.620	0.88	0.35

The optical air mass function used is given in Table A4.

Table A4: The optical air mass function used in the simplified scheme.

Zenith angle	Optical air mass
60	2.00
61	2.06
62	2.12
63	2.20
64	2.27
65	2.36
66	2.45
67	2.55
68	2.65
69	2.78
70	2.90
71	3.06
72	3.21
73	3.40
74	3.59
75	3.83
76	4.07
77	4.40
78	4.72
79	5.16
80	5.60
81	6.18
82	6.88
83	7.77
84	8.90
85	10.39
86	12.44
87	15.36
88	19.79
89	26.96

A.3 Dry deposition

Currently dry deposition is calculated for the following compounds:

- O₃
- H₂O₂
- NO₂
- HNO₃
- H₂
- CH₃O₂H
- SO₂
- Sulphate

Constant dry deposition velocities, at a measurement height defined as 1 m, were applied in the model for the various compounds.

These dry deposition velocities were adjusted for height and stability according to the scheme proposed by Simpson (1993). In this scheme surface layer similarity theory is used to determine the concentration of a compound at height z_1 (measurement height) based on the concentration at height z_2 (model layer height) when given the deposition velocity v_d at z_1 , the stability length scale L (Monin-Obukhov length) and the friction velocity u_* . The ratio of the concentrations $C(z_1)$ and $C(z_2)$ can be calculated by:

$$\frac{C(z_1)}{C(z_2)} = 1 + \frac{v_d(z_1)}{\kappa u_*} (\Psi(z_2/L) - \Psi(z_1/L))$$

where Ψ is the influence function for heat transfer. This formula allows the concentration at the measurement height z_1 to be calculated based on the modeled height z_2 , which is used for output of the model results. This formula also allows adjustment of the effective deposition velocity within the model $v_d(z_2)$ based on the concentration at the model height z_2 . This model related adjustment can simply be written as:

$$v_d(z_2) = v_d(z_1) \frac{C(z_1)}{C(z_2)}$$

When the surface layer is stable, $C(z_1)$ can be significantly less than $C(z_2)$ if the deposition velocity is not small ($> 0,5$ cm/s). Under these conditions the deposition velocity $v_d(z_2)$ is also significantly less than $v_d(z_1)$. During unstable conditions with strong mixing $C(z_1)$ is close to $C(z_2)$ and so to is $v_d(z_2)$ to $v_d(z_1)$.

A.4 Wet scavenging

Presently no wet scavenging or liquid phase chemistry is included.

A.5 Emissions

Emission for all the different compounds is currently based upon primary emission of the following four compounds:

- NO_x
- SO₂
- CO
- VOC (Volatile Organic Compounds)

Please note that the compounds NO_x and VOC are not part of the chemistry scheme as such (NO_x is represented by NO and NO₂ separately).

Table A6 gives the emission of other compounds as dependent upon emission of the four above mentioned compounds which is implemented in the current version of the chemistry solver. The emission is assumed to be 0 for all other compounds not given in Table A6.

Table A6: Emission of compounds based on emission Q of NO_x , SO_2 , CO and VOC . Unit: molec/s.

Nr.	Emission of is set equal to
200	NO	Q_{NO_x}
201	NO_2	0
202	SO_2	Q_{SO_2}
203	H_2	0
204	CH_4	0
205	HCHO	$0.019671 \cdot Q_{\text{VOC}}$
206	CH_3OH	$0.020900 \cdot Q_{\text{VOC}}$
207	CO	Q_{CO}
208	C_2H_6	$0.078682 \cdot Q_{\text{VOC}}$
209	CH_3CHO	$0.001788 \cdot Q_{\text{VOC}}$
210	$\text{C}_2\text{H}_5\text{OH}$	$0.206455 \cdot Q_{\text{VOC}}$
211	n- C_4H_{10}	$0.421927 \cdot Q_{\text{VOC}}$
212	$\text{CH}_3\text{COC}_2\text{H}_5$	$0.042510 \cdot Q_{\text{VOC}}$
213	C_2H_4	$0.088517 \cdot Q_{\text{VOC}}$
214	C_3H_6	$0.062009 \cdot Q_{\text{VOC}}$
215	o-Xylene	$0.157513 \cdot Q_{\text{VOC}}$
216	Isoprene	0

The values in Table A6 represents only one possible way of splitting the NO_x and VOC emissions. The actual split should be adapted to the actual situation in each case when using the photochemistry scheme. Note also that the split refer to the volumes, i.e. number of molecules, and not to weight. In AirQUIS the split may be refined even further and defined for e.g. each kind of source type etc.



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ABSTRACT A new simplified photochemistry scheme for urban areas has been developed and implemented in EPISODE 3.0. The scheme is based on the comprehensive EMEP mechanism, but contains only 45 compounds and about 70 reactions, the minimal number essential for a city or urban atmosphere. The new scheme can be run with reasonable CPU time and use of memory on a standard Windows based PC. All reaction coefficients are updated according to the latest IUPAC 2001 survey. The resulting non-linear system of ordinary differential equations (stiff ODEs) is solved using state-of-the-art numerical methods, based on fast Gauss-Seidel iterative techniques, with numerical error control and restart in case of detected numerical inaccuracies. The new scheme has successfully been run in a standalone version of EPISODE 3.0 for the city of Berlin, as part of the City Delta model intercomparison study. The calculations were performed for a total simulation period of 6 months. The new scheme has also been compared with the complete EMEP photochemistry scheme. The latter study show that the scheme retains the essential aspects of photochemical reactions in an urban atmosphere with good accuracy. The new scheme has so far only been implemented in EPISODE 3.0. Further development is needed in order to run the photochemistry scheme as part of the AirQUIS system.			
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