Development of a Simplified Photochemistry Scheme for Urban Areas

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Abstract

A simplified photochemistry scheme for urban areas has been developed and implemented into the local scale Eulerian model EPISODE. The chemical scheme 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 EMEP mechanism. The stiff ODE system is solved using fast Gauss-Seidel iterative techniques with numerical error control. The simplified scheme has been compared with the EMEP scheme, and the comparison shows that the scheme retains the essential aspects of photochemical reactions in an urban atmosphere with very good accuracy. The photochemistry scheme has successfully been run for the city of Berlin, as part of the City Delta model intercomparison study.

Chemistry

The EMEP chemistry (Simpson, 1993) is designed for calculating photochemical reactions on a regional European scale, covering clean, background conditions as well as polluted semi-urban areas. For the local-scale model EPISODE (Slørdal et al., 2003), 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:

I) $RO_2 + RO_2$ reactions were omitted

It is well known that RO_2 in the main ozone formation reaction:

$$RO_2 + NO \rightarrow RO + NO_2 \quad (1)$$

competes with the self-reaction(s)

$$RO_2 + HO_2 \rightarrow RO_2H + O_2 \quad (2)$$
$$RO_2 + RO_2 \rightarrow ... \quad (3)$$

where R stands for an organic fraction, and RO_2 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 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 $CH_3O_2 + HO_2$ and the $HO_2 + HO_2$ reactions, were omitted in the simplified scheme.

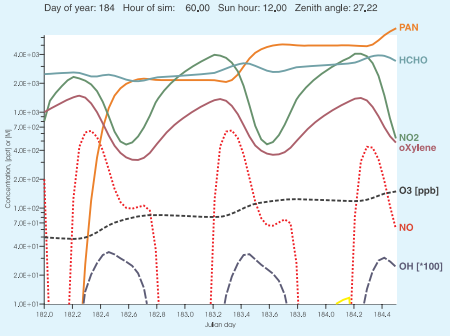

Figure 1. 60 h of calculations with the condensed 45 compounds mechanism in a box model with chemistry and emissions only.

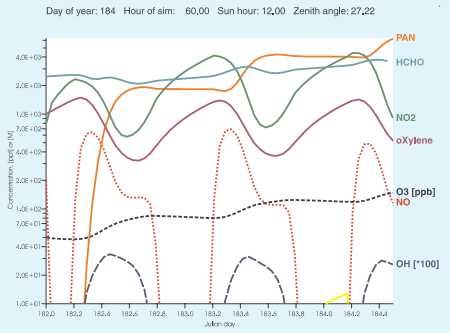

Figure 2. Same as Figure 1 but using the standard EMEP chemistry.

II) Simplified isoprene mechanism

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

$$C_5H_8 + OH \rightarrow C_5H_8R \quad (4)$$
$$C_5H_8R + NO \rightarrow MVK + HCHO + HO_2 + NO_2 \quad (5)$$
$$MVK + OH \rightarrow MVKO_2 \quad (6)$$
$$MVKO_2 + NO \rightarrow CH_3COCHO + HCHO + HO_2 + NO_2 \quad (7)$$

where MVK stands for methyl vinyl ketone.

With these two types of simplifications, a condensed 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.

Test Applications

Test calculations were carried out to compare the condensed mechanism with the standard EMEP mechanism by using a box version of the chemistry. An example of these test calculations is given in Figure 1 and Figure 2. The figures show the result of 60 h integration which is much longer than a characteristic residence time inside an EPISODE model domain. Furthermore, the calculations were carried out for rural conditions with lower NO_X concentrations (NO_X ~ 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 small. The condensed mechanism gives slightly lower concentrations of NO and NO_2, while the ozone concentration is almost identical in the calculations.

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 (http://rea.ei.jrc.it/netshare/thunis/citydelta/). 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 using EPISODE with the EMEP45 chemistry.

The EPISODE model was run at a spatial resolution of 10 km in a 300 x 300 km² region, and 6 vertical layers were used up to a height of 2000 m. The simulation period was the 6 months between April and September.

The correlation coefficient and the bias in mean O_3 and over the six month period is shown for one of the monitoring sites in the Berlin area in figure 3. The EPISODE model, number 16, has one of the lowest biases of all the models for O_3 and a correlation coefficient > 0,6.

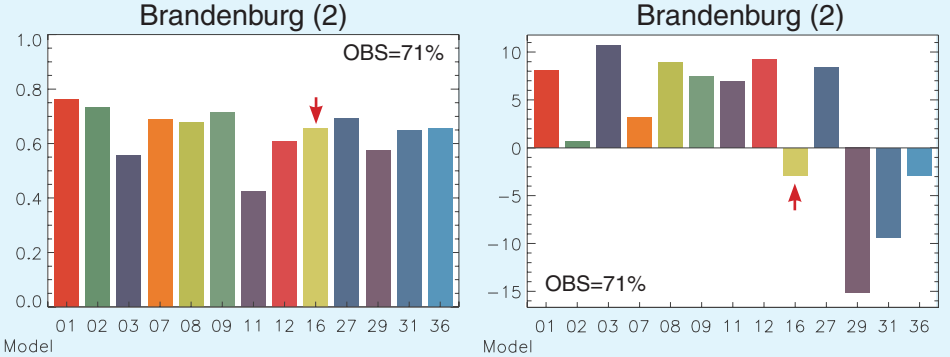

Figure 3. Linear correlation (left panel) and bias (right panel) for the results from 13 different models (numbered) vs. the observed ozone concentrations at Brandenburg within the City Delta project for the Berlin area. The EPISODE model with the EMEP45-chemistry is model #16 (light green, red arrow).

References

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