

## H13-65

## DIRECT IMPLEMENTATION OF NON-LINEAR CHEMICAL REACTION TERMS FOR OZONE CHEMISTRY IN CFD-BASED AIR QUALITY MODELLING

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**Abstract:** In this paper we present the implementation of a chemistry model that transforms the NO<sub>x</sub> composition dynamically during transportation for a CFD-based air quality model. For that, the scalar advection equations for NO, NO<sub>2</sub> and O<sub>3</sub> are coupled by non-linear reaction terms and solved simultaneously. The model is implemented and tested in the Envi-met local air quality and micro climate model (Bruse 2007; De Maerschalcck, Janssen *et al.* 2009).

**Key words:** Key CFD-based air quality modelling, Ozone chemistry.

## INTRODUCTION

The last decade Computational Fluid Dynamics (CFD) has gained interest as a practical tool for local air quality modelling in complex environment like street canyons, urbanized areas industrial plants. CFD-based air quality models are capable of solving complex three-dimensional flows around obstacles like buildings, trees and vehicles. After solving the wind and turbulence field, the dispersion of pollutants in the atmosphere can be simulated either in a Lagrangian approach, tracking individual particles after release, or a Eulerian approach, that is solving a 3D scalar advection equation. Until now, most CFD-based air quality models solve for an inert gas, similar to wind tunnel modelling. However, it is well understood that nitrogen oxides are reacting fast with ozone while a European air quality directive is specific for NO<sub>2</sub>. Regarding traffic emissions about 80% of NO<sub>x</sub> emission is NO, but depending on the ozone background concentrations and meteorological conditions this will react and for secondary NO<sub>2</sub> which can have a significant effect on the local air quality.

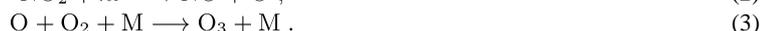
## OZONE CHEMISTRY IN THE TROPOSPHERE

Nitrogen oxides are ubiquitous urban air pollutants mainly emitted by traffic, power plants and industry. Nitric oxide is on mass basis the most important nitrogen compound emitted into the atmosphere. Nitric oxide is formed from atmospheric nitrogen (N) at high temperatures as in combustion processes. More than 90 percent of the emitted oxide consists of nitrogen oxide (NO), while the remaining party is emitted as nitrogen dioxide (NO<sub>2</sub>) (Berkowicz 1998). Once emitted from the tail pipe, nitrogen oxide will react with ozone:



Under typical tropospheric boundary layer conditions, this reaction takes place within a time span of a couple of seconds up to minutes, depending on the background concentrations NO, NO<sub>2</sub> and O<sub>3</sub> and meteorological conditions.

NO<sub>2</sub> is the first reaction product of the atmospheric oxidation process of the emitted NO. However, the freshly formed nitrogen oxide will absorb solar ultraviolet radiation ( $200\text{nm} < \lambda < 420\text{nm}$ ) and forms again NO and O<sub>3</sub>:



Reaction (3) happens quasi immediately. Therefore, in general reactions (2) and (3) are considered as one and O<sub>2</sub> in the atmosphere is accepted as being constant.

The reaction of NO with O<sub>3</sub> and the photolysis of NO<sub>2</sub> form a cycle which occurs rapidly over the timescales of seconds up to minutes. Under most tropospheric conditions, NO and NO<sub>2</sub> will coexist as a mixture, called NO<sub>x</sub>. If a steady state is reached, the following equilibrium holds:

$$\frac{[\text{NO}][\text{O}_3]}{[\text{NO}_2]} = \frac{j_{\text{NO}_2}}{k_{\text{NO}}}, \quad (4)$$

where the parentheses indicate the number concentration of the compound in molecules/cm<sup>3</sup>.  $k_{\text{NO}}$  is the second order or bimolecular reaction rate coefficient in (1) and is dependent on the ambient temperature (Seinfeld and Pandis 2006):

$$k_{\text{NO}} = A_0 \exp\left(-\frac{E}{R T}\right), \quad (5)$$

with

$$A_0 = 2.2 \times 10^{-12} \frac{\text{cm}^3}{\text{molecule s}}, \quad (6)$$

$$\frac{E}{R} = 1430 \text{ K}. \quad (7)$$

Figure plots the reaction rate as a function of the temperature.

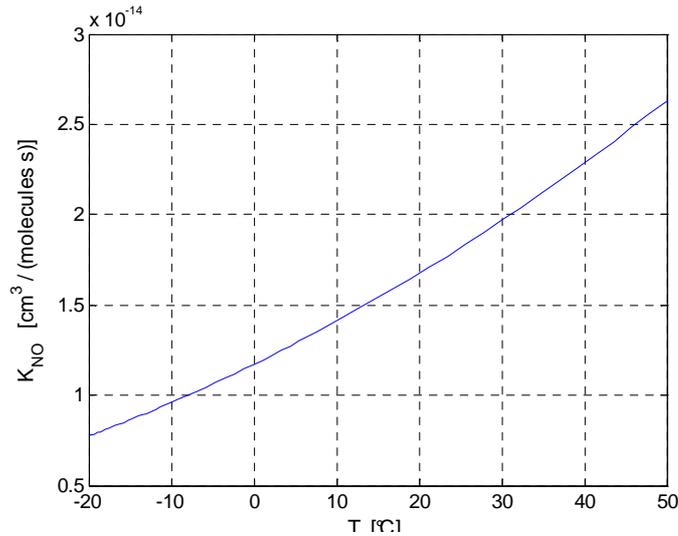


Figure 1 : Bimolecular reaction rate coefficient as function of the temperature

$j_{NO_2}$  is the photolysis coefficient of equation (2) and is dependent on the solar ultraviolet radiation. The computation is rather complicated. Theoretically one should integrate over the product of the  $NO_2$  specific absorption cross section with the quantum yield for photolysis and the spectral actinic flux within the limits of the ultraviolet spectrum (Seinfeld and Pandis 2006). However, for a fast estimate different parameterizations are available based on solar angle, solar radiation and cloud coverage (Berkowicz and Hertel 1989; de Leeuw 1995; van Ham and Pulles 1998).

For the implementation in the Envi-met model, the following empirical formulation based on the solar radiation is used:

$$j_{NO_2} = 0.8 \times 10^{-3} \exp(-10/R_s) + 7.4 \times 10^{-6} R_s, \quad (8)$$

with  $R_s$  the solar radiation measured in  $[W/m^2]$ . In ENVI-met in every cell the solar radiation is calculated based on the positions of the sun, cloud cover, local shadows and reflections. Figure 6 shows the estimated values during two different days at a location in the Netherlands based on different parameterization schemes. The red line is the one according to (8) where  $R_s$  is dynamically computed by the Envi-met model.

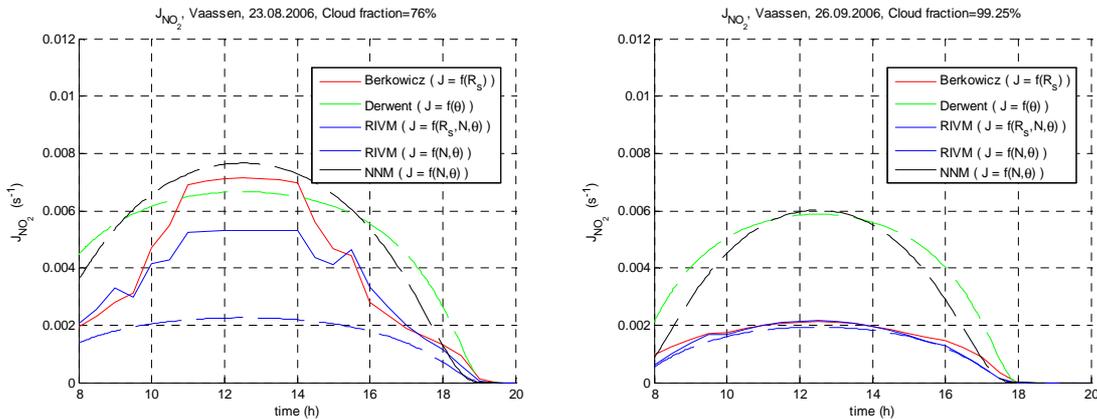


Figure 6: Computed photolysis coefficient during the day for Vaassen, The Netherlands (Left: 23/08/2006, mean cloud coverage 76%; Right: 26/09/2006, 99%)

### CHEMICAL EQUILIBRIUM

Assume that  $[NO]_0$ ,  $[NO_2]_0$  and  $[O_3]_0$  are the initial number concentrations put in a reactor of constant volume at constant temperature and radiation. After a short time a steady state will be reached for which the photostationary state relation (4) holds. From the conservation of nitrogen and the stoichiometric reaction of  $O_3$  with  $NO$  follows (Seinfeld and Pandis 2006):

$$[NO] + [NO_2] = [NO]_0 + [NO_2]_0, \quad (9)$$

$$[O_3]_0 - [O_3] = [NO]_0 - [NO]. \quad (10)$$

One can solve now the chemical equilibrium in the reactor and get:

$$[\text{NO}_2] = [\text{NO}_2]_0 + \frac{1}{2} \left( [\text{O}_3]_0 + [\text{NO}]_0 + \frac{j_{\text{NO}_2}}{k_{\text{NO}}} \right) - \frac{1}{2} \sqrt{D}, \quad (11)$$

$$[\text{NO}] = -\frac{1}{2} \left( [\text{O}_3]_0 - [\text{NO}]_0 + \frac{j_{\text{NO}_2}}{k_{\text{NO}}} \right) + \frac{1}{2} \sqrt{D}, \quad (12)$$

$$[\text{O}_3] = -\frac{1}{2} \left( [\text{NO}]_0 - [\text{O}_3]_0 + \frac{j_{\text{NO}_2}}{k_{\text{NO}}} \right) + \frac{1}{2} \sqrt{D}, \quad (13)$$

with:

$$D = \left( [\text{NO}]_0 - [\text{O}_3]_0 + \frac{j_{\text{NO}_2}}{k_{\text{NO}}} \right)^2 + 4 \frac{j_{\text{NO}_2}}{k_{\text{NO}}} ([\text{NO}_2]_0 + [\text{O}_3]_0) \quad (14)$$

One can assume that for a rural background concentration, NO, NO<sub>2</sub> and O<sub>3</sub> are in equilibrium. We now can verify that the parameterization in (8) together with the modelled solar radiation holds by using the computed photolysis coefficients to estimate the equilibrium state according to (11) to (14). The initial numbers are taken from nearby rural measurement stations. Theoretically, if the measured background concentration is in equilibrium and the photolysis coefficient is estimated well, the computed equilibrium should not differ from the local measurements.

The measured background concentrations are compared to the modelled equilibrium state for two days at the location of Vaassen, the Netherlands (Janssen, De Maerschalck *et al.* 2008). The measured background concentration is the mean from three Dutch rural background concentrations. Again the red line is based on the parameterisation in (8). The red line with the bullets is the measured mean background concentration.

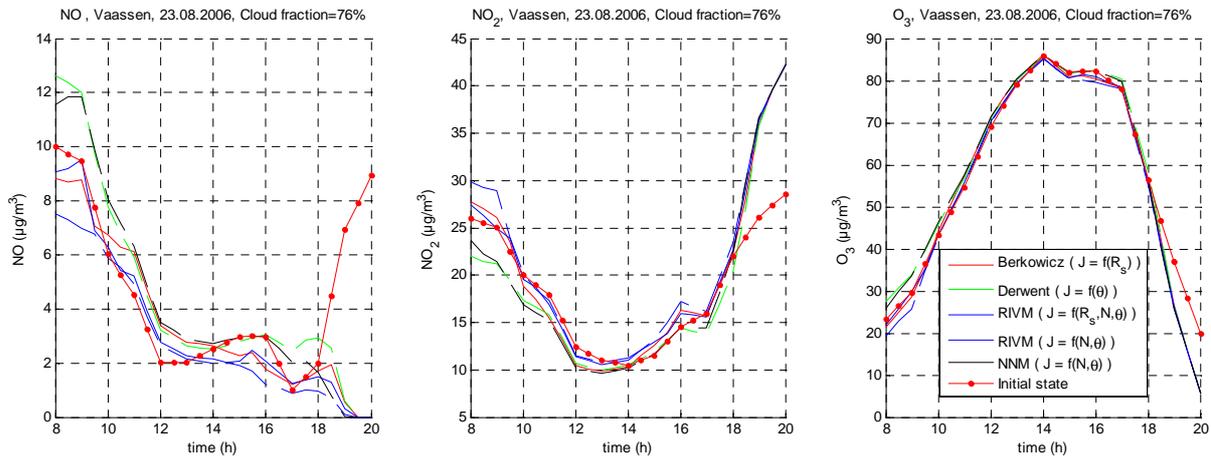


Figure 3: Measured rural background concentrations and computed equilibrium for NO (left), NO<sub>2</sub> (middle), and O<sub>3</sub> (right). (Vaassen, The Netherlands, 23/08/2006, 76% cloudiness)

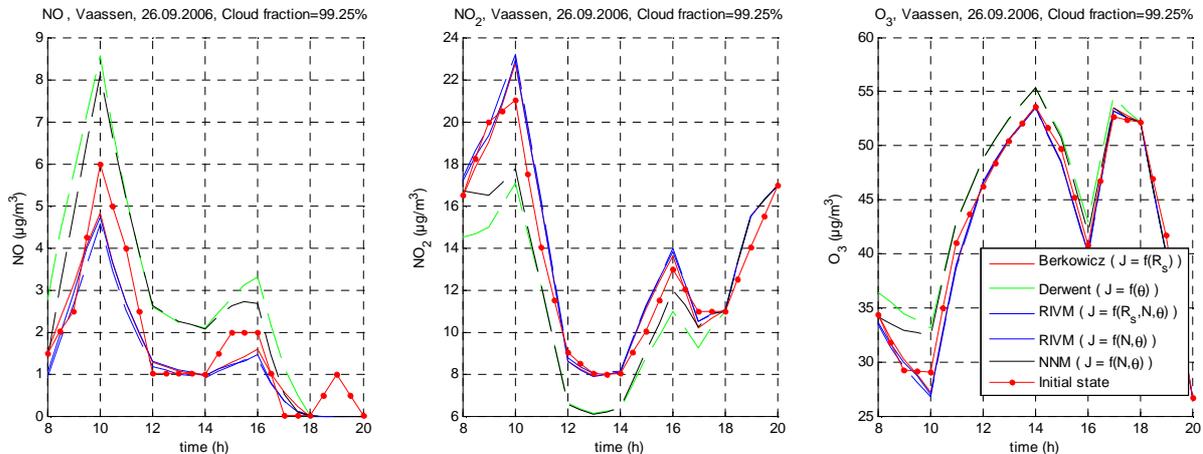


Figure 4: Measured rural background concentrations and computed equilibrium for NO (left), NO<sub>2</sub> (middle), and O<sub>3</sub> (right). (Vaassen, The Netherlands, 26/09/2006, 99% cloudiness)

### DYNAMIC CHEMICAL TRANSFORMATION PROCESSES IN CFD BASED AIR QUALITY MODELS

The dispersion of a certain gas  $i$  can be described by a scalar dispersion equation for the concentration  $C_i(x, y, z)$ :

$$\frac{\partial C_i}{\partial t} + \mathbf{u} \cdot \nabla C_i + \nabla \cdot (\mathbf{K}_i \cdot \nabla C_i) = E_i - S_i + R_i, \quad (15)$$

with  $E_i(x, y, z)$  the local emissions of compound  $i$  and  $S_i(x, y, z)$  the sum of all sink terms (deposition, interaction with vegetation, sedimentation, ...).  $R_i$  is the chemical reaction term and is in general dependent on the concentration of all compounds involved in the reaction. The advection velocity and the turbulent reaction terms are computed by the flow solver of the CFD model.

For the photochemical reactions described above the dispersion equations for NO, NO<sub>2</sub> and O<sub>3</sub> have to be solved simultaneously. The partial differential equations are coupled with the following non-linear reaction terms:

$$R_{NO} = \left( \frac{d[NO]}{dt} \right)_R = -k_{NO} [NO][O_3] + j_{NO_2} [NO_2], \quad (16)$$

$$R_{NO_2} = \left( \frac{d[NO_2]}{dt} \right)_R = k_{NO} [NO][O_3] - j_{NO_2} [NO_2], \quad (17)$$

$$R_{O_3} = \left( \frac{d[O_3]}{dt} \right)_R = -k_{NO} [NO][O_3] + j_{NO_2} [NO_2]. \quad (18)$$

Notice that these reaction terms are given in number concentration while equation (15) is typically describing conservation of mass. In Envi-met all concentrations are mixing ratios measured in  $\mu g/kg_{air}$ , Therefore, equations (16) to (18) have to be converted to mass concentrations first.

Figure (Janssen, De Maerschack *et al.* 2008) illustrates the local effect of oxidation of traffic emitted NO on the local air quality. The continuous lines show the modelled NO and NO<sub>2</sub> concentrations downwind of a motor way. The green lines are for a motorway with a vegetation barrier, the red lines without a vegetation barrier. The position of the driving lanes and vegetation barrier are indicated by the red and green blocks. The green and red dots with error bars are the measured concentrations.

One can see that NO is decreasing faster than the NO<sub>2</sub> concentrations, both with and without a vegetation barrier. This is due to the fact the NO is reacting with ozone and forms secondary NO<sub>2</sub>. One can also notice that due to the vegetation the effect is even stronger. The vegetation slows down the local wind speed, so there is more time for the chemistry. At the same time, due to increased turbulence, more fresh ozone is mixed in which enhances the oxidation process as well.

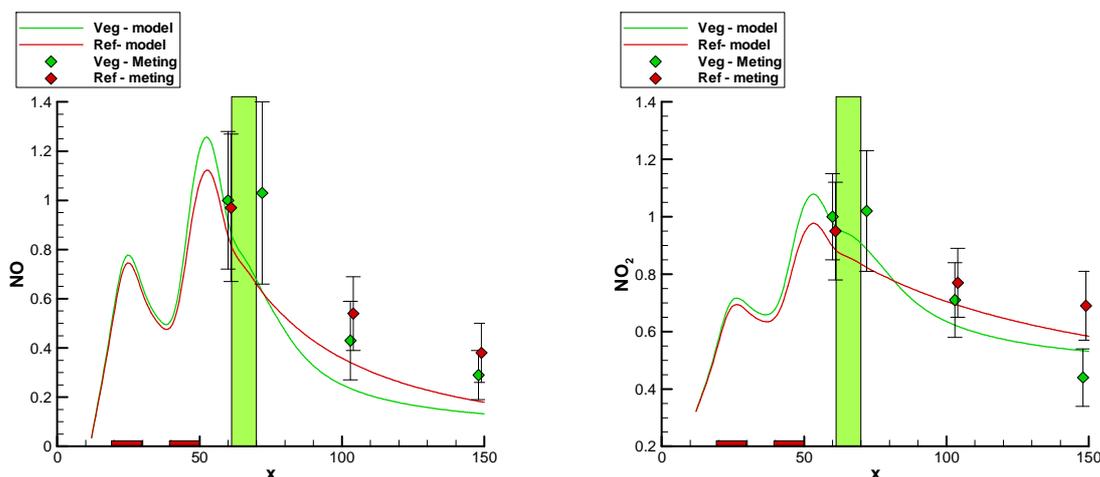


Figure 5: NO and NO<sub>2</sub> concentrations downwind of a highway with and without a vegetation barrier.

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