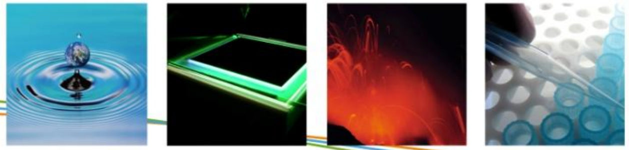


06/07/2010

Non-linear chemical reaction terms for ozone chemistry in CFD-based Air Quality modelling

Bart De Maerschalck, Stijn Janssen, Clemens Mensink

Outline

- Motivation
- CFD-model: Envi-met
- Chemical reaction terms and reaction coefficients
- Examples:
  - Street canyon
  - Street canyon with vegetation
  - Highway with vegetation barrier

Motivation

- Traffic: direct emissions of NO and NO_2
- After emission: *fast* chemical reaction with ozone: formation of secondary NO_2:

$$\mathrm{NO} + \mathrm{O_3} \quad \longrightarrow \quad \mathrm{NO_2} + \mathrm{O_2}$$

- At the same time:

$$\mathrm{NO_2} + h\nu \longrightarrow \mathrm{NO} + \mathrm{O}$$

$$\mathrm{O} + \mathrm{O_2} \longrightarrow \mathrm{O_3}$$

- If a chemical equilibrium is reached:

$$\frac{[\mathrm{NO}][\mathrm{O_3}]}{[\mathrm{NO_2}]} = \frac{j_{NO_2}}{k_{NO}}$$

vito
vision on technology

Motivation

- Equilibrium is dynamically reached during transport
- In complex urban environments (e.g. Streetcanyon) due to continuous mixing with fresh NO, NO_2 and O_3, equilibrium stat not reached within the domain of interest
- Secondary NO_2 has a signifacant contribution
- For regulatory purposes: NO_2 concentration is required

- -> implementation of chemical transformation process in CFD-based air quality and micro-climate model (Envi-met)

CFD-model: Envi-met

- Envi-met: Micro climate + Air quality
  - Prof. M . Bruse, University of Mainz, Germany (www.envi-met.com)
- CFD based
  - Reynolds Averaged Navier Stokes
  - K-ε Turbulence model
  - Structured mesh, resolution 0.5 – 10m
- Soil model
  - Water content
  - Temperature
- Radiative flux model
  - Sw / Lw
  - Clouds / shadows
- Vegetation model:
  - Aerodynamic resistance, source-term in turbulence model.
  - Absorption of gases through the stomata, size dependent deposition on the leaf surface of PM

Gas Dispersion: Eulerian approach

Advection — Turbulent mixing — emissions — Local sink terms

$$\frac{\partial C_i}{\partial t} + \boldsymbol{u} \cdot \nabla C_i + \nabla \cdot (\boldsymbol{K_i} \cdot \nabla C_i) = E_i - S_i + R_i$$

Non-linear reaction terms:
Couples dispersion equations of NO, NO2 and O3

Chemical reaction terms

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

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

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

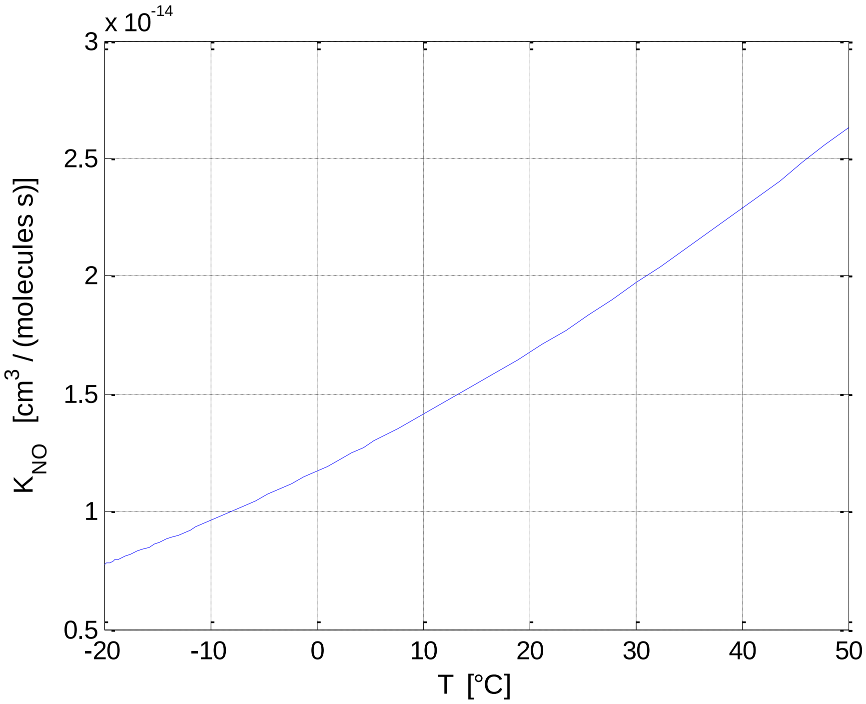
- K_{NO} - bimolecular reaction rate coefficient (temperature)
- j_{NO_2} – Phototlysis coefficient (UV)
- [ ] – concentrations in ppb (-> convert to proper units)

Reaction rate coefficient

$$k_{NO} = A_0 \exp\left(-\frac{E}{R}\frac{1}{T}\right)$$

$$A_0 = 2.2 \times 10^{-12} \frac{cm^3}{molecule\ s}$$

$$\frac{E}{R} = 1430\ K$$



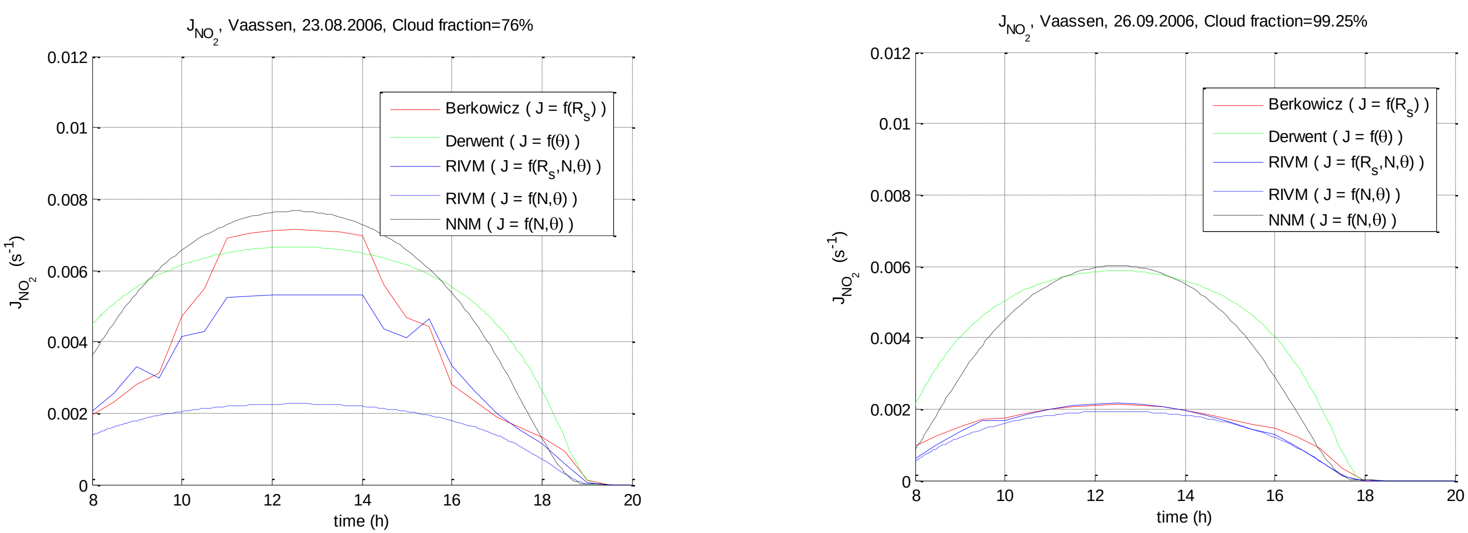
Photolysis coefficient

» Theoretically: integration over arctic flux: $j_{NO_2} = \int_{295nm}^{400nm} \sigma_{NO_2}(\lambda, T)\phi_{NO_2}(\lambda_1, T)I(\lambda)\,\mathrm{d}\lambda$

» Practically: empirical formula based on solar radiation[1]:

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

» R_s computed in Envi-met by radiative scheme



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

[1] R. Berkowicz and O. Hertel. Technical Report DMU LUFT – A131, National Environmental Research Institute, Roskilde, Denmark, 1989.

Are k_{NO} and j_{NO_2} computed properly?

- If a chemical equilibrium is reached:

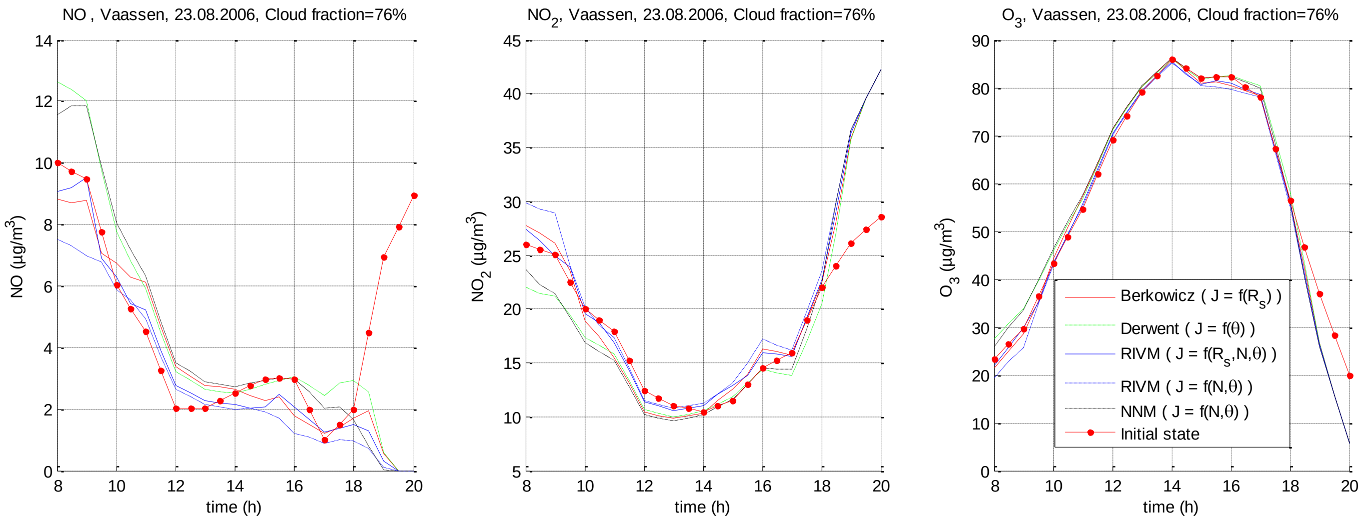
$$[\mathrm{NO_2}] = [\mathrm{NO_2}]_0 + \frac{1}{2}\left([\mathrm{O_3}]_0 + [\mathrm{NO}]_0 + \frac{j_{NO_2}}{k_{NO}}\right) - \frac{1}{2}\sqrt{D}$$

$$[\mathrm{NO}] = -\frac{1}{2}\left([\mathrm{O_3}]_0 - [\mathrm{NO}]_0 + \frac{j_{NO_2}}{k_{NO}}\right) + \frac{1}{2}\sqrt{D}$$

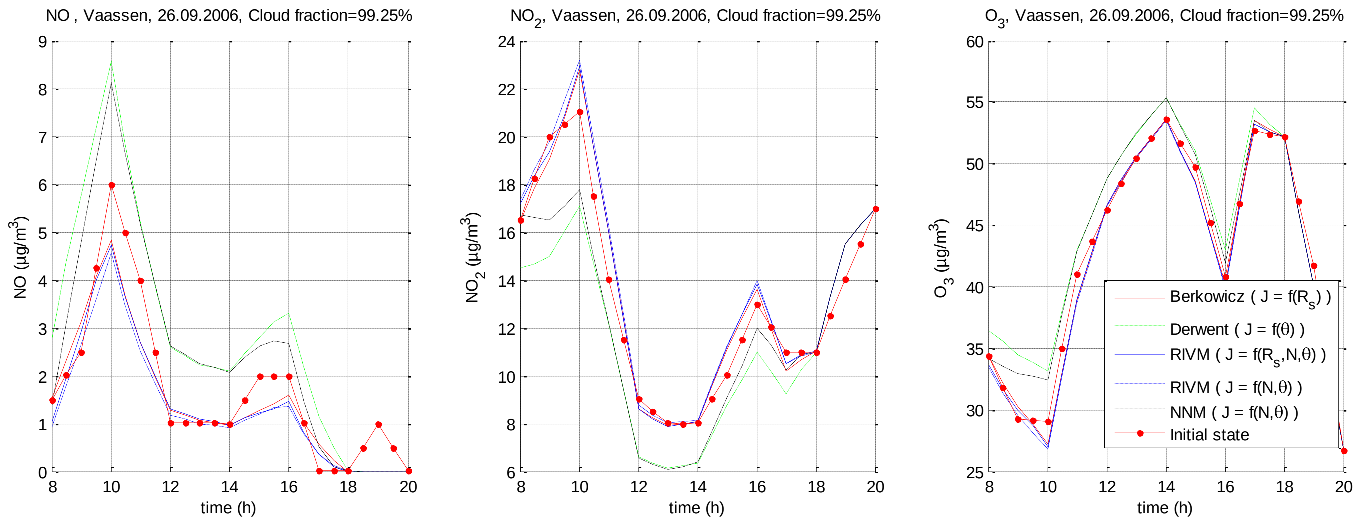
$$[\mathrm{O_3}] = -\frac{1}{2}\left([\mathrm{NO}]_0 - [\mathrm{O_3}]_0 + \frac{j_{NO_2}}{k_{NO}}\right) + \frac{1}{2}\sqrt{D}$$

$$D = \left([\mathrm{NO}]_0 - [\mathrm{O_3}]_0 + \frac{j_{NO_2}}{k_{NO}}\right)^2 + 4\frac{j_{NO_2}}{k_{NO}}\left([\mathrm{NO_2}]_0 + [\mathrm{O_3}]_0\right)$$

- Assuming the measured background concentrations are in equilibrium, and the coefficients are correctly calculated in Envi-met, the background cencentrations should be conserved: $[\ ] = [\ ]_0$



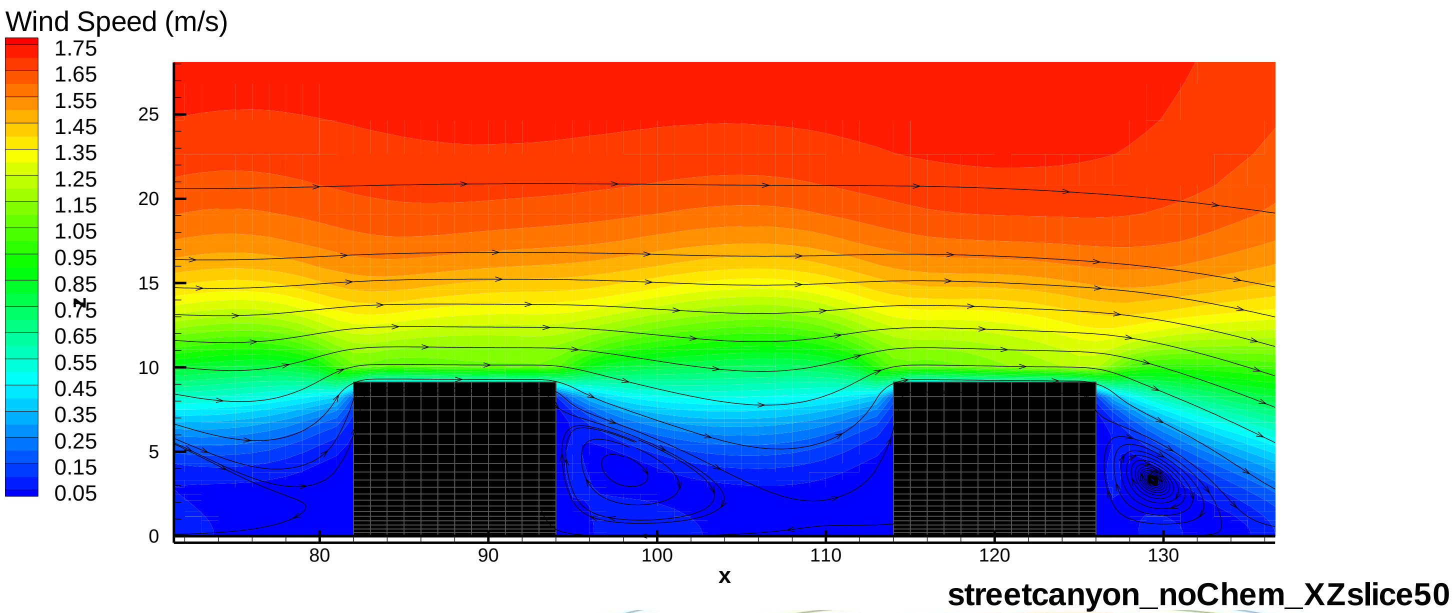
Measured rural background concentrations and computed equilibrium for NO (left), NO2 (middle), and O3 (right). (Vaassen, The Netherlands, 23/08/2006, 76% cloudiness)



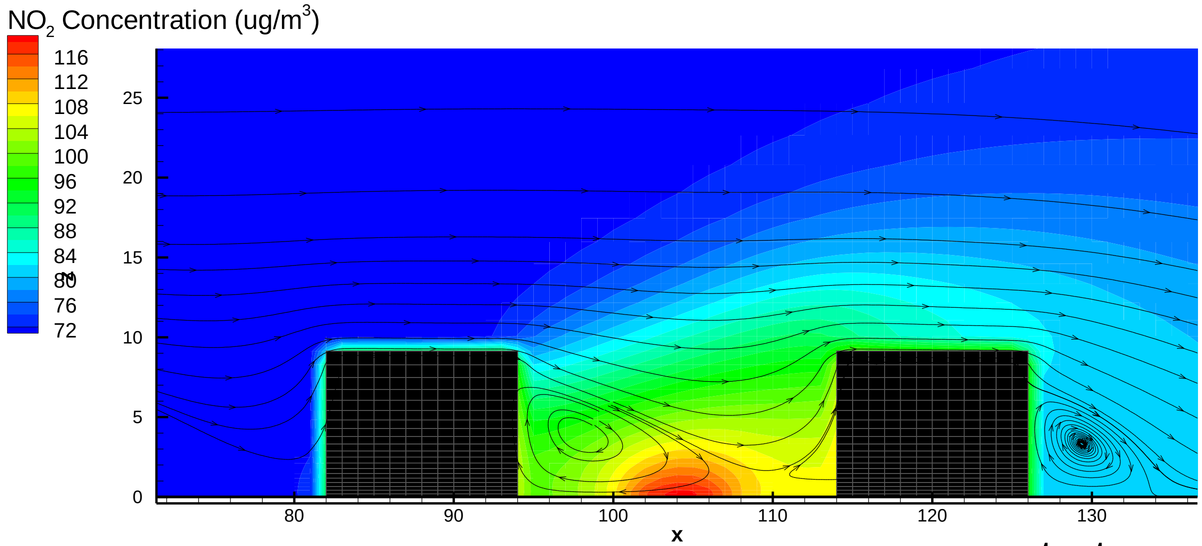
Measured rural background concentrations and computed equilibrium for NO (left), NO2 (middle), and O3 (right). (Vaassen, The Netherlands, 26/09/2006, 99% cloudiness)

Example 1: street canyon

- Low windspeed 1.5 m/s
- High background: 24µg/m³ NO, 72µg/m³ NO_2, 71µg/m³ O_3

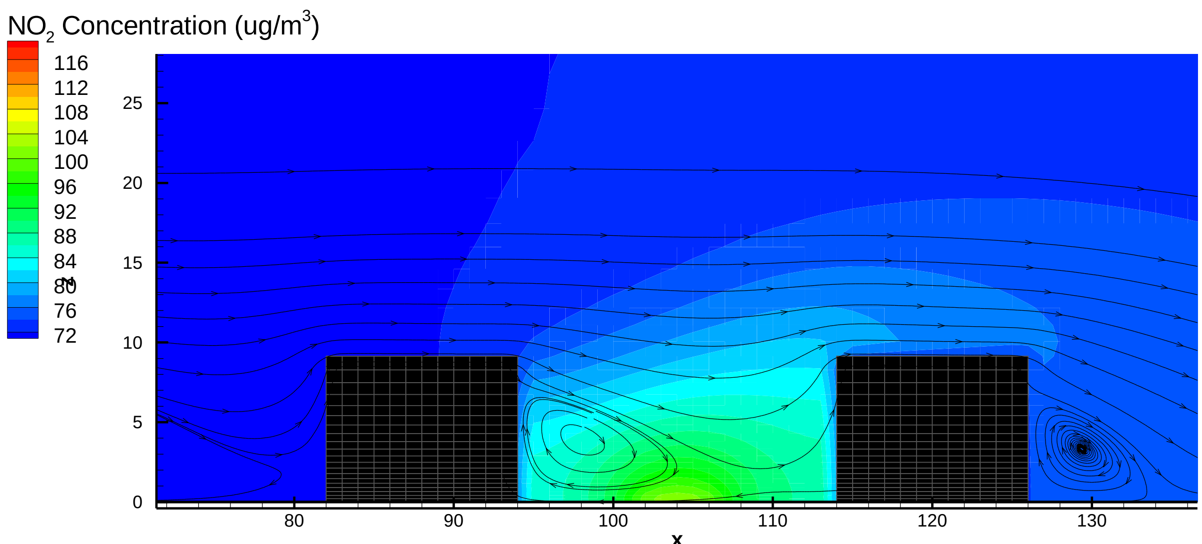


Chemistry included
No clouds



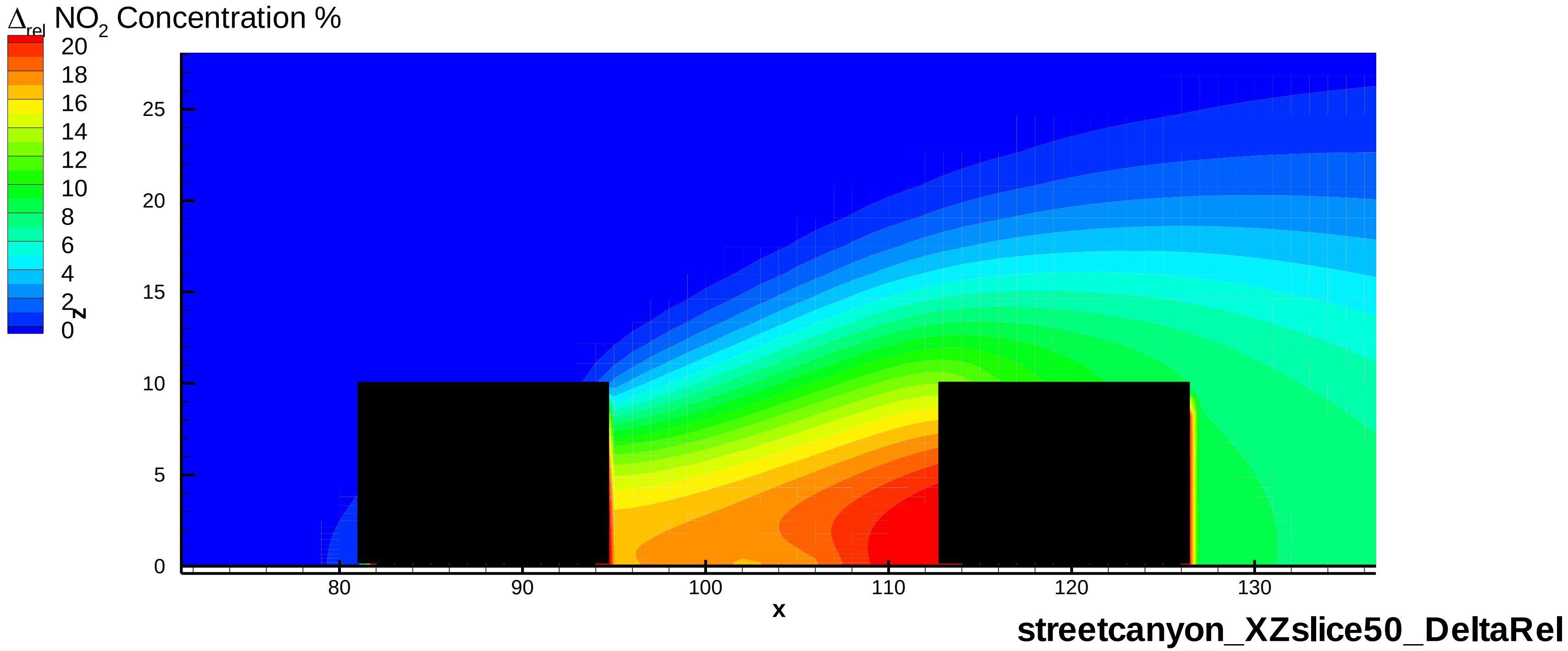
streetcanyon_XZslice50

No chemistry



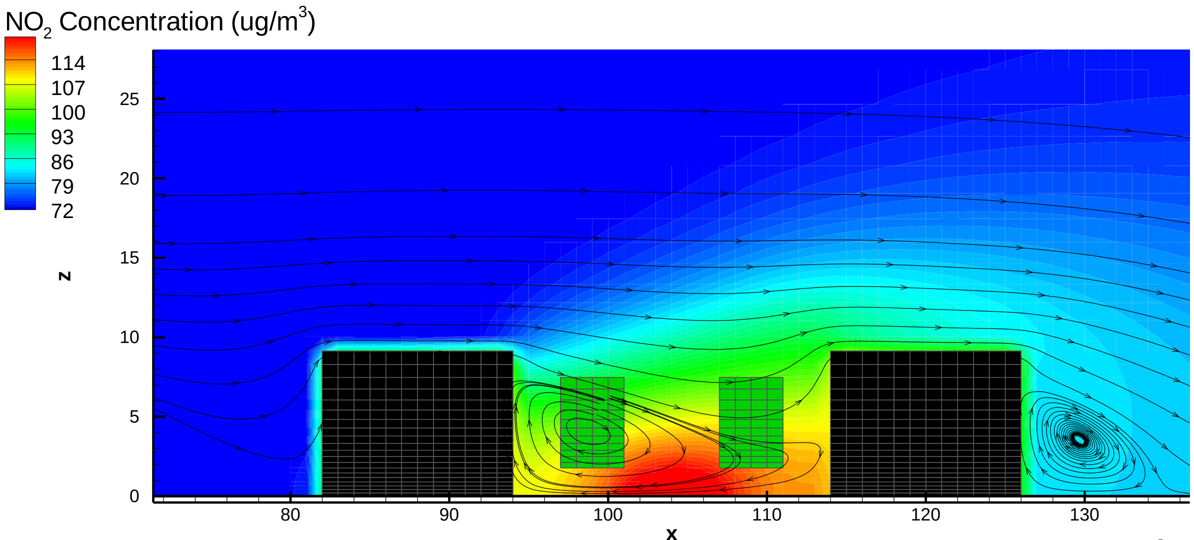
streetcanyon_noChem_XZslice50

Secondary NO_2 production (%)



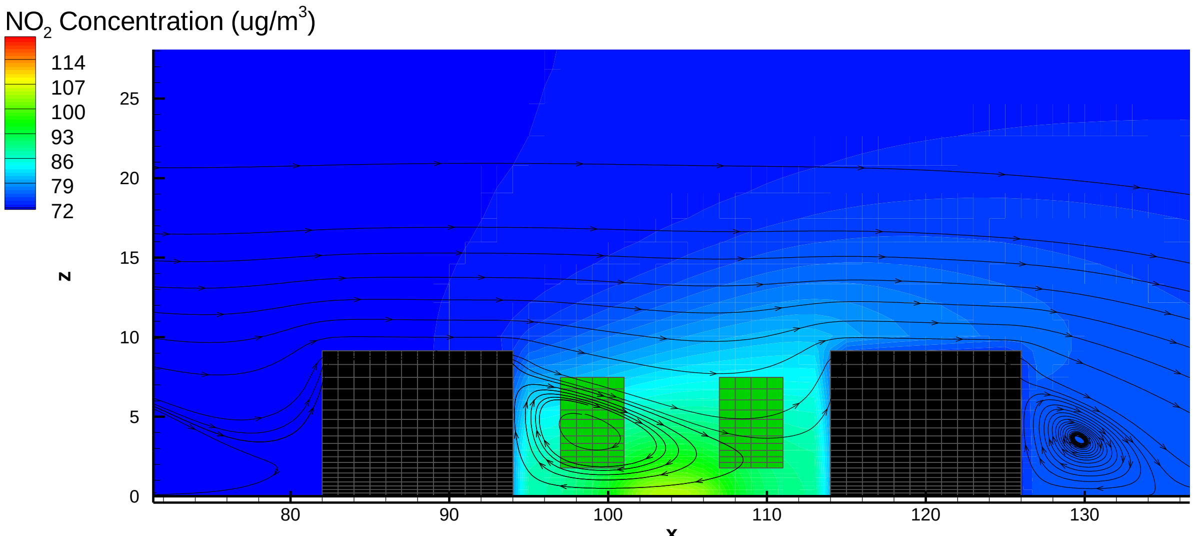
Example 2: Street canyon with vegetation

Chemistry included



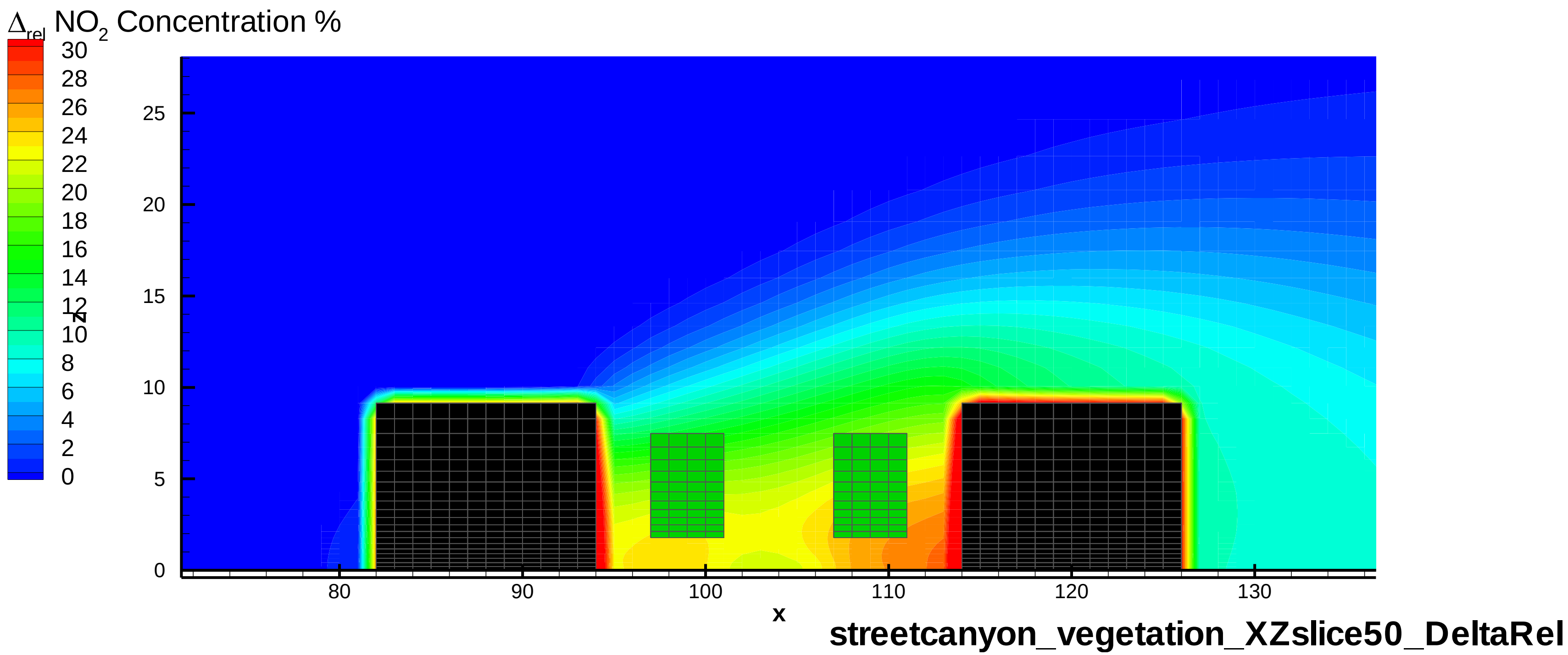
streetcanyon_vegetation_XZslice50

No chemistry



streetcanyon_vegetation_noChem_XZslice50

Secondary NO_2 production (%)

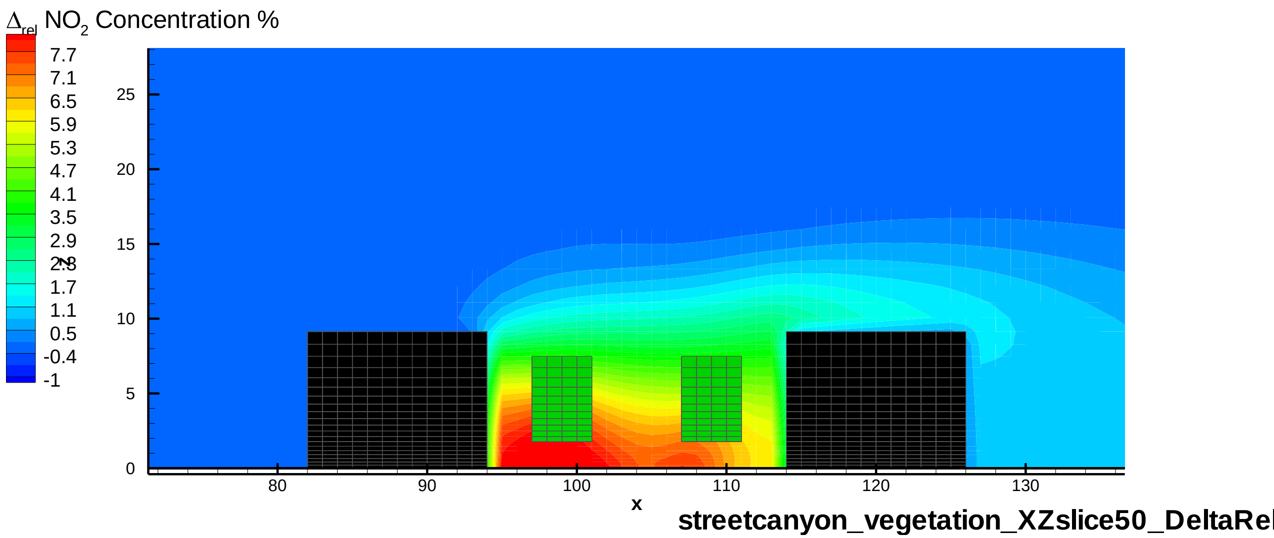


vito vision on technology

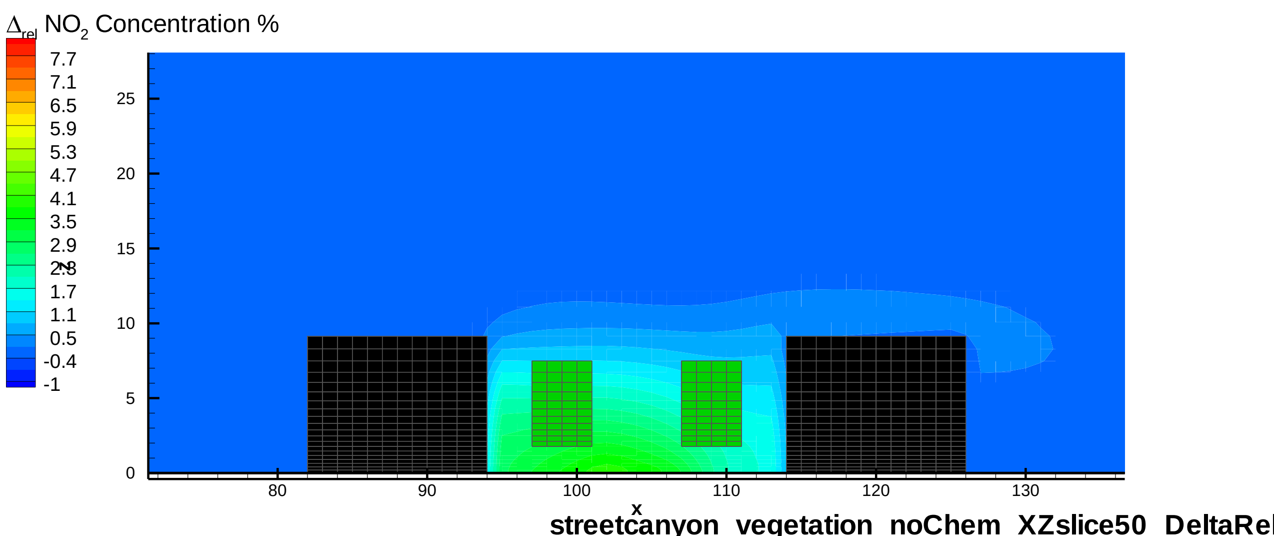
06/07/2010

The effect of the vegetation in the street

Chemistry included

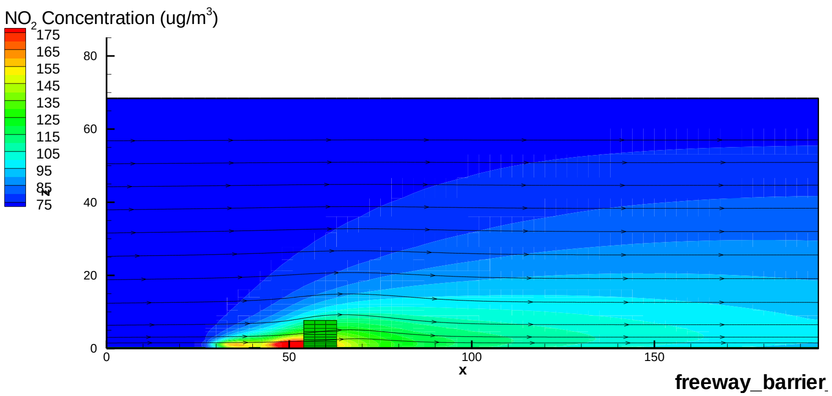


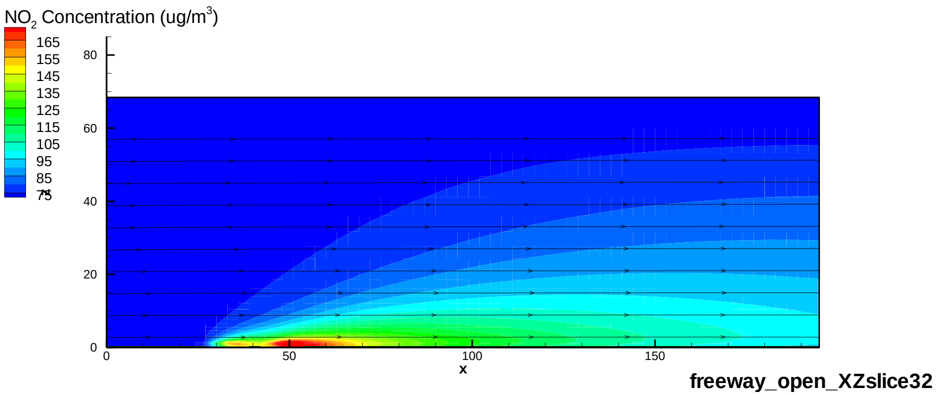
No chemistry



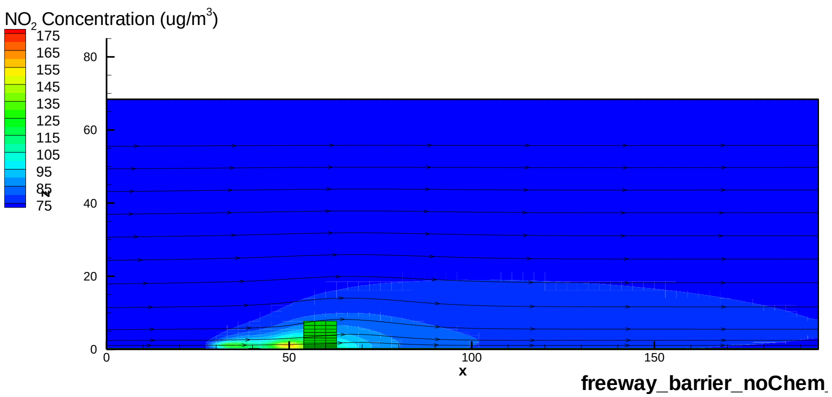
Example 3: highway with vegetation barrier

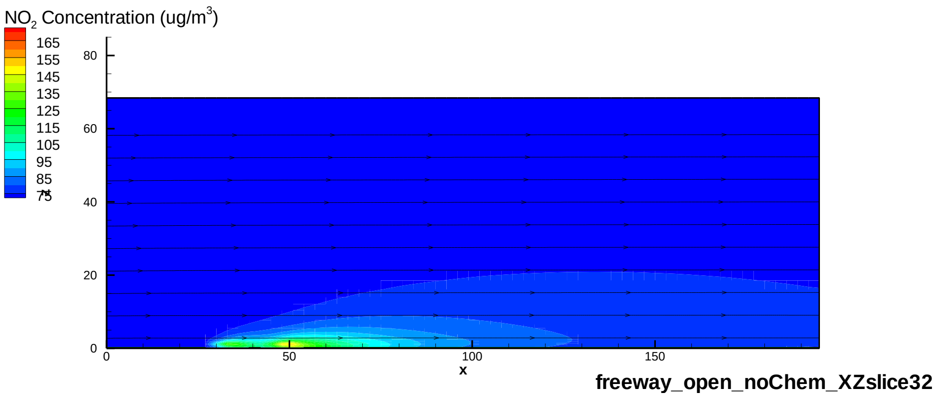
Chemistry included





No chemistry





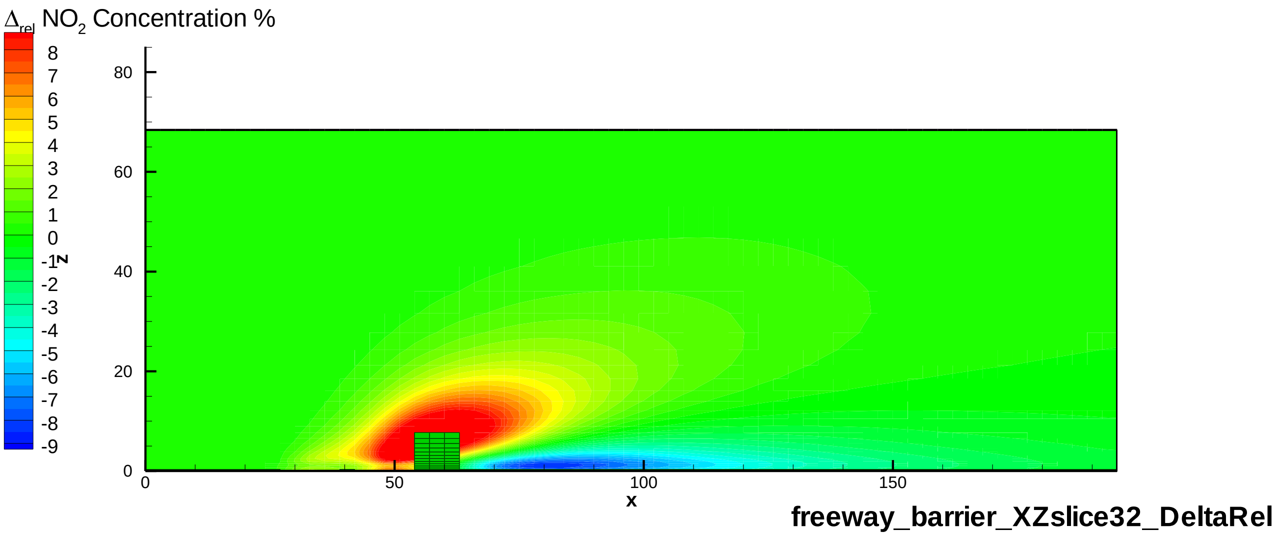
Vegetation Barrier

Open field

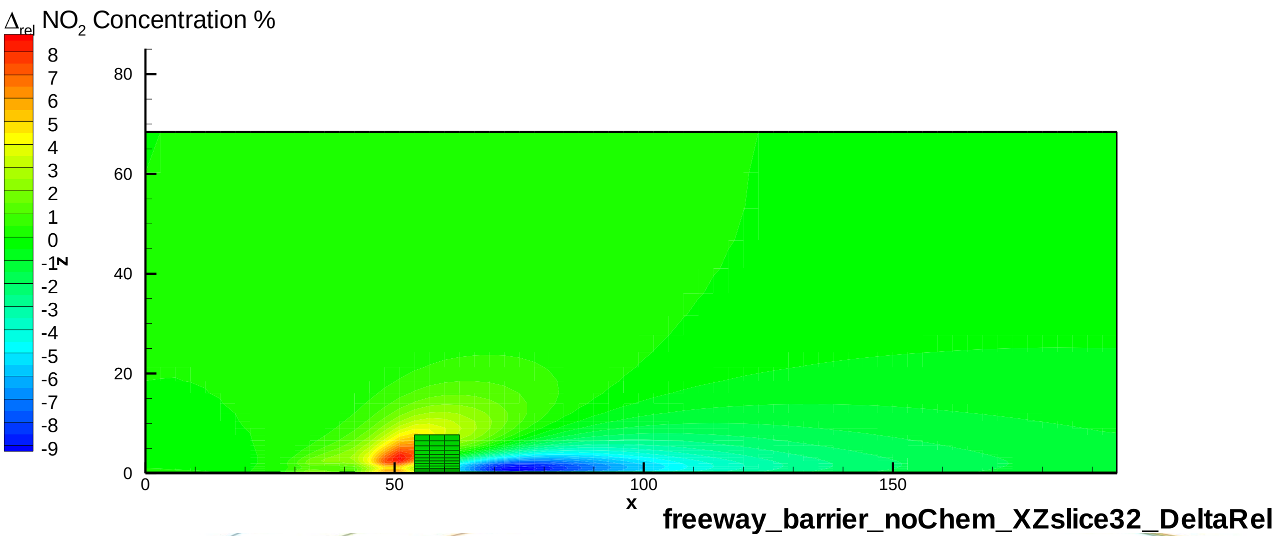
vito
vision on technology

Effect of the vegetation barrier

Chemistry included



No chemistry



Conclusions

- Dynamics chemistry model implemented in Envi-met
- Photolysis coefficients: empirical formulation based on modelled radiation
- Strong increase of NO_2 due to secondary NO_2 production even at small scales
- Different effects of the vegetation on NO_2 due to changes in secondary NO_2 production