CFD Modeling of Reactive Pollutants in an Urban Street Canyon using Different Chemical Mechanisms

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Introduction

- At microscale the atmosphere and urban distributions interaction generates a complex flow and heterogeneous dispersion of pollutants within the canopy.
- An accurate understanding of Urban Air Quality requires considering a coupled behavior between dispersion of reactive pollutants and atmospheric dynamics.
- Urban Air Pollution → Traffic emissions
  - Nitrogen Oxide (NO)
  - Nitrogen dioxide (NO₂)
  - Volatile Organic Compounds (VOCs)
Limitations

- In a real and complex geometry, the required computational time is large.
- Implementing chemical reactions in a CFD model increase the CPU time considerably due to the coupling of pollutant transport equations.

Objectives

To simulate the pollutants dispersion considering chemistry:

- To reproduce reactive pollutant distribution using the simplest chemical mechanism minimizing CPU time.
- Analyze the conditions in which the implementation of a complex chemical mechanism is necessary.
Structure

To model in 2D and 3D idealized urban geometries:

- The chemical and dynamic coupling under different chemical approaches:
  - (a) Passive tracer (non-reactive)
  - (b) NOx-O$_3$ photostationary state (PSS)
  - (c) Complex chemical mechanism (CCM)

- Evaluation of the influence of atmospheric parameters (wind speed and ozone concentration)

Quantify the variation on NO and NO$_2$ concentration with the use of chemical mechanism
Chemical Mechanisms

Passive Tracer  Considering NO and NO$_2$ non-reactive

Photostationary State

\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}_3 \\
\text{O} + \text{O}_2 + M & \rightarrow \text{O}_3 + M \\
\text{O}_3 + \text{NO} & \rightarrow \text{NO}_2 + \text{O}_2
\end{align*}
\]

Complex Chemical Mechanism  23 chemical species
25 chemical reactions

Due to the limitation of CPU time, CCM has been reduced based on Regional Atmospheric Chemistry Mechanism (RACM) using CHEMATA program software (Kirchner, 2005)
Ozone

- \( O_3 = 10 \text{ ppb} \)
- \( O_3 = 40 \text{ ppb} \)

Geometry

- 2D
- 3D

Wind Speed

- \( u(z = 2H) = 2 \text{ m s}^{-1} \)
- \( u(z = 2H) = 4 \text{ m s}^{-1} \)

- Passive tracer (non-reactive)
- NOx-\( O_3 \) photostationary state (PSS)
- Complex chemical mechanism (CCM)

Different ratios of VOCs-to-NOx emission:
- \( \text{VOCs/NOx}=1/5 \)
- \( \text{VOCs/NOx}=1/2 \)
CFD Model description

- Reynolds-averaged Navier-Stokes (RANS) equations with a k-ε turbulence model
- Transport equations of chemical species

\[
\frac{\partial C_i}{\partial t} + U_i \frac{\partial C_i}{\partial x_j} = D \frac{\partial^2 C_i}{\partial x_j \partial x_j} + \frac{\partial}{\partial x_j} \left( K_c \frac{\partial C_i}{\partial x_j} \right) + \left[ \Delta C_i \right]_{\text{Chem}} + S_{C_i}
\]

- Computational domains
  - 2D-geometry: Street-Canyon
    - 24x40x64 m
  - 3D-geometry: Staggered Array of cubes:
    - 64x64x64 m
    - \( \lambda_p = 0.25 \)
Simulation Set up

- Boundary conditions for momentum equations
  - Simulating an infinite number of streets
    - y-direction → zero gradient boundary conditions
  - x-direction → Periodic Conditions:
    \[ \frac{\partial P}{\partial x} = \rho \frac{u_T^2}{4H} \]

Flow field:

2D-Geometry

3D-Geometry

\( u_T \): Reference velocity
H: Buildings height

\( u_T = 0.45 \, \text{m s}^{-1} \)
\( u_T = 0.225 \, \text{m s}^{-1} \)
Simulation Set up

- Traffic Emissions
  - Located at the bottom
  - NOx fixed emissions:
    \[
    S_{NO} = 112 \, \mu g \, m^{-1} \, s^{-1} \\
    S_{NO_2} = 17 \, \mu g \, m^{-1} \, s^{-1}
    \]
  - VOCs emissions: Complex Chemical Mechanism
    - VOCs-to-NOx emissions:
      \[
      \begin{align*}
      \text{VOCs/NOx} &= 1/5 \quad \text{(CCM5)} \\
      \text{VOCs/NOx} &= 1/2 \quad \text{(CCM2)}
      \end{align*}
      \]
Simulation Set up

- **Top Conditions**
  - Constant concentration at the top
    - NO: 16 ppb
    - NO2: 35 ppb
  - Important role within the canyon
  - VOCs concentration at the top change with emission ratio
  - \([O_3]\) is computed using photostationary equilibrium and is dependent on zenith angle (\(\theta\))

\[
\begin{align*}
\theta &= 45° \\
\theta &= 78°
\end{align*}
\]

\[
\begin{align*}
J_{NO_2} &= A \exp(B/cos(\theta)) \\
[O_3] &= \frac{J_{NO_2} [NO_2]}{k [NO]}
\end{align*}
\]

- \(\theta = 45°\): \(O_3 = 40\) ppb
- \(\theta = 78°\): \(O_3 = 10\) ppb
Evaluation of Atmospheric Parameters

Study scenarios

Ozone

- $O_3 = 10$ ppb
- $O_3 = 40$ ppb

(Low $O_3$) (High $O_3$)

Wind Speed

- $u(z = 2H) = 2 \, m \, s^{-1}$ (Ut0225)
- $u(z = 2H) = 4 \, m \, s^{-1}$ (Ut045)

Geometry

- 2D
- 3D

Passive tracer (non-reactive) ($P$)

NOx-$O_3$ photostationary state ($PSS$)

Complex chemical mechanism (CCM)

- VOCs/NOx=1/5 (CCM5)
- VOCs/NOx=1/2 (CCM2)

VOCs-to-NOx emission
Evaluation of Atmospheric Parameters

- In order to compare the scenarios, the concentration is normalized:
  \[ C_{\text{norm}} = \frac{C u_\tau W}{Q} \]  
  \[ (\text{Street Canyon}) \]
  \[ C_{\text{norm}} = \frac{C u_\tau A^2_{Em}}{Q} \]  
  \[ (\text{Staggered Array of cubes}) \]
  W: Street width
  L: Street length
  Q: Source emission rate  \( (\mu g \, m^{-1} \, s^{-1}) \)

- The difference with respect to Passive tracer is quantify using:
  \[ \delta C \, (\%) = \frac{C_{\text{norm}} - C_{\text{norm}}(P)}{C_{\text{norm}}(P)} \times 100 \]
Wind Speed

\[ \delta [\text{NO}] \]

- \( \delta C (\text{Ut045}) > \delta C (\text{Ut0225}) \)
- Bigger differences with higher VOCs emissions

\[ \delta C (%) = \frac{C_{\text{norm}} - C_{\text{norm}}(P)}{C_{\text{norm}}(P)} \times 100 \]
More ventilation implies less differences between chemical mechanisms.

\[ \delta C (\%) = \frac{C_{\text{norm}} - C_{\text{norm}}(P)}{C_{\text{norm}}(P)} \times 100 \]
Wind Speed

$\delta [\text{NO}_2]$

- $\delta C (\text{Ut045}) > \delta C (\text{Ut0225})$
- Differences between all chemical systems

\[
\Delta C (\%) = \frac{C_{\text{norm}} - C_{\text{norm}(P)}}{C_{\text{norm}(P)}} \times 100
\]
Wind Speed

$\delta \left[ \text{NO}_2 \right]$

From difference to NO2 in a 2D geometry, the difference between chemical mechanism doesn't exist.

$$\delta C (\%) = \frac{C_{\text{norm}} - C_{\text{norm}}(P)}{C_{\text{norm}}(P)} \times 100$$

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Wind Speed
Vertical profiles

- Horizontal spatial averaged of $[NO]_N$ and $[NO_2]_N$

$\delta C (Ut045) > \delta C (Ut0225)$

- Lower velocity implies more differences between chemical systems

$(solid\ line): Ut045$  
$(dashed\ line): Ut0225$
Now, we analyze the influence of Ozone established at the top of the domain.

- $\delta C$ (High $O_3$) > $\delta C$ (Low $O_3$)
- Differences between all chemical systems with high $O_3$

$\delta C (%) = \frac{C_{norm} - C_{norm}(P)}{C_{norm}(P)} \times 100$
Ozone

$\delta [NO_2]$

- $\delta C$ (High $O_3$) > $\delta C$ (Low $O_3$)
- Differences between all chemical systems with high $O_3$

$\delta C \, (\%) = \frac{C_{norm} - C_{norm}(P)}{C_{norm}(P)} \times 100$

High $O_3$

Low $O_3$

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Horizontal spatial average of $[NO]_N$ and $[NO_2]_N$

- The same vertical profile: PSS and CCM5
- High $O_3$: Importance of NOx/VOCs emission ($[NO_2]_N$)
- Low $O_3$: the difference between chemical mechanism is insignificant
The average of $\delta C$ below the canopy

$$\delta C = \frac{C_{norm} - C_{norm}(PS)}{C_{norm}(PS)}$$
Conclusions

✓ The biggest change in [NO] and [NO₂] is obtained between chemical mechanisms and tracer (non-reactive)

✓ In the case of high [O₃], the errors induced by the use of PSS are lager when the VOCs-to-NOx emission ratio increases → Lower [NO]  
Higher [NO₂]

✓ With lower [O₃] at the top of the domain, [NO] and [NO₂] can be simulated by a simple or complex chemical mechanisms due to the differences between mechanisms are negligible.

✓ The influence of a complex chemical mechanism is slightly smaller in 3D than 2D geometry since major ventilation is produced within the street.
Thank you for your attention
Aditional Slides
Simulation Set up

Top Conditions

- Constant concentration at the top

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>NO</td>
<td>16 ppb</td>
</tr>
<tr>
<td>NO2</td>
<td>35 ppb</td>
</tr>
<tr>
<td>CO</td>
<td>200 ppb</td>
</tr>
<tr>
<td>SO2</td>
<td>2 ppb</td>
</tr>
</tbody>
</table>

Important role within the canyon

Ozone concentration is computed using photostationary equilibrium and is dependent on zenith angle ($\theta$)

\[
\theta = 45^\circ \\
\theta = 78^\circ
\]

\[
J_{NO_2} = A \exp\left(\frac{B}{\cos(\theta)}\right)
\]

\[
[O_3] = \frac{J_{NO_2}[NO_2]}{k[NO]}
\]

(A and B are constant)

\[
O_3 = 39.8 \text{ ppb}
\]

\[
O_3 = 10.2 \text{ ppb}
\]

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Simulation Set up

الف. Top Conditions

- **VOCs concentration** at the top change with emission ratio

<table>
<thead>
<tr>
<th>Emission scenarios</th>
<th>VOCs-to-NOx=1/5</th>
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<td>VOCs</td>
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- Volumetric proportion within VOCs group are:

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<td>HCHO</td>
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Simulation Set up

- Traffic Emissions

  - NOx fixed emissions:
    \[ S_{NO} = 112 \, \mu g \, m^{-1} s^{-1} \]
    \[ S_{NO_2} = 17 \, \mu g \, m^{-1} s^{-1} \]

  - VOCs emissions

    Complex Chemical Mechanism

  - Some VOCs are joined in specific chemical groups

  - VOCs-to-NOx emissions:
    \[ \text{VOCs/NOx} = 1/5 \quad \text{(in ppb)} \]
    \[ \text{VOCs/NOx} = 1/2 \quad \text{(in ppb)} \]

- Volumetric proportion within VOCs group are:

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Validation

❖ CFD Model
  ▪ Validated previously with tunnel measurements in:
    o Papers

❖ Complex Chemical Mechanism
  ▪ Validated previously with results of box model
  ▪ Experimental measurements