Modeling the Macroscopic Effect as NOx Sink of a Photocatalytic Surface under Real Outdoor Conditions

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Abstract

In the last decade, photocatalytic materials are being researched as a possible solution to reduce nitrogen oxides (NOx) concentrations in urban areas. Photocatalytic TiO_2 materials are activated in the presence of sunlight and act as a sink for the NOx concentration in urban air. Even if the behavior of the photocatalytic materials has been studied extensively in controlled conditions in laboratory, the efficiency in real urban areas is still matter of debate. Within the framework of the LIFE MINOx-STREET European Project, the photocatalytic effect under outdoor conditions is studied. The methodology chosen to analyze the effects of NO deposition in the real atmosphere is to combine field scale measurements and CFD (Computational Fluid Dynamics) modeling. A CFD model is then used to simulate the pollutants dispersion and NO deposition of the "photocatalytic island" experiment (German et al., *this conference*). Besides the influence of different atmospheric parameters are analyzed on NO depletion caused by photocatalytic materials.

1. Introduction

The high levels of emitted-traffic pollutants, mainly nitrogen oxides (NOx), are one of the most important concerns in several cities. Despite of the fact that limits have been imposed, those levels are still exceeded by many cities. In order to minimize the NOx contribution to urban atmosphere, photocatalytic materials are in use with the objective to reduce NOx levels.

The aim of the European Project LIFE MINOx-STREET is to investigate the efficiency of the photocatalytic materials in an urban area. For this reason, NO surface deposition is analyzed under laboratory tests. However it is necessary to know the behavior of these materials in environmental conditions. For that, the photocatalytic efficiency is evaluated in outdoor conditions with a combination of experimental measurements and modeling. This scenario is located in the city of Madrid (Spain) but far from the direct influence of traffic emission sources, so that the measured concentrations represent urban background concentration.

The main purpose of this work is to simulate pollutants dispersion and NO deposition of “Photocatalytic Island” experiment (German et al., this conference). In order to achieve this aim, CFD simulations results are evaluated by means of a comparison against experimental data. In addition, the influence of deposition velocity values, wind speed and coating material temperature on the photocatalytic efficiency is analyzed using CFD simulations.

2. CFD model

The CFD model used for this study is based on the Reynolds-averaged Navier-Stokes equations (RANS) with a k-Ɛ turbulent model. Using this kind of model, flows, dispersion of reactive pollutants and deposition effect can be simulated.

Nitrogen oxide (NO) and dioxide nitrogen (NO_2) are the primary emitted pollutants in an urban atmosphere due to traffic emissions. Study the photocatalytic effect on air pollution of a real city requires to asses NO

and NO_2 concentration. When NO and NO_2 are present in sunlight, ozone formation occurs as a result of the photolyisis of NO_2. This chemical mechanism is called photochemical steady state (3-reaction system) (Eq. 1).

$$\begin{gathered} NO_2 + h\nu \xrightarrow{J_{NO_2}} NO + O_3 \\ O + O_2 + \mathrm{M} \rightarrow O_3 + \mathrm{M} \\ O_3 + \mathrm{NO} \xrightarrow{k} NO_2 + O_2 \end{gathered} \quad (1)$$

Where M represents a molecule that absorbs excess energy and thereby stabilizes O_3 molecules formed (Seinfeld and Pandis, 1998). The photolysis rate J_{NO_2} and reaction rate constant k are dependent on zenith angle and temperature respectively.

In the CFD model, the chemical term is defined as formation and depletion of a compound in the chemical reactions and it is introduced in the transport equation for each chemical specie (for example Eq. 2 is the equation for NO). More details can be found in Sanchez et al. (2015).

$$\frac{\partial[NO]}{\partial t} + U_j \frac{\partial[NO]}{\partial x_j} = D \frac{\partial^2[NO]}{\partial x_j \partial x_j} + \frac{\partial}{\partial x_j}\left(K_c \frac{\partial[NO]}{\partial x_j}\right) + J_{NO_2}[NO_2] - k_1[O_3][NO] + S_{NO} \quad (2)$$

The deposition effect over the photocatalytic surface is modeled as a function of atmospheric concentration close to the surface and a deposition velocity (V_d) depending on the photocatalytic material. It is introduced in the transport equation as a sink term close to the photocatalytic material (Eq. 3).

$$Deposition\ Flux\ = -[NO] \cdot V_d \quad (3)$$

3. Case description

In Fig. 1 the experimental system and computational domain used are shown. The simulation domain size is 40mx40mx20m and a polyhedral mesh with a grid resolution of 0.5 m besides of prism layers close to ground at 0.08, 0.2 and 0.4 m is used.

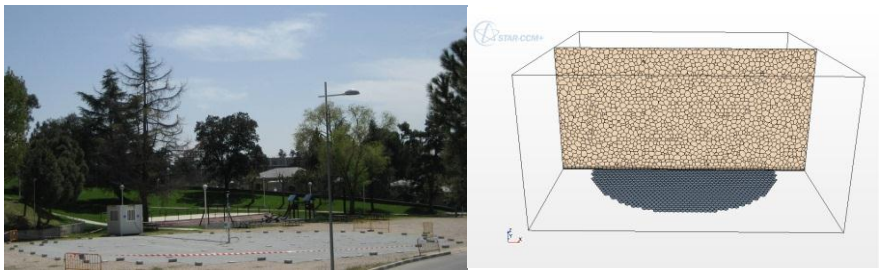


Fig. 1. Experimental system and simulation domain

The experimental system consists of a photocatalytic coating which is implemented in a circular surface of 30 m in diameter over a flat terrain. An analyzer is located out of the photocatalytic coating representing the background NOx (reference level), as well as a tower of measurements placed in the middle of the "photocatalytic island" (German et al., this conference). Within the tower, NO and NO_2 concentrations are obtained in air samples at 3 heights (Table 1).

Table 1. Heights of the concentrations measurements

	Measurements levels (m)	
NO and NO2 concentrations	N1	0.16
	N2	0.85
	N3	2.7

Measured background NOx concentrations are implemented in the CFD model as input values of concentration. While, the experimental concentrations taken in the tower are averaged over 10 min to be compared with the simulated NO concentration results.

The experimental scenarios to be compared with CFD model are selected at 1200UTC, 1230UTC, 1300UTC, 1330UTC and 1400UTC on 29th October 2014.

At the inlet boundary, wind speed and turbulent kinetic energy and its dissipation rate are defined as

$$U_{in} = \frac{u_*}{\kappa} \ln\left(\frac{z}{z_0}\right) \quad (4)$$

$$k_{in} = \frac{{u_*}^2}{{C_\mu}^{1/2}} \quad (5)$$

$$\varepsilon_{in} = \frac{{C_\mu}^{3/4} {k_{in}}^{3/2}}{\kappa\, z} \quad (6)$$

Where z_0 and u_* are atmospheric roughness length (0.001m) and friction velocity. Measured wind speed is around 1 m s^{-1} at 3.42 m for all scenarios. Therefore in order to reproduce experimental conditions, the implemented friction velocity is 0.05 m s^{-1}.

The photocatalytic coating is heated by solar radiation. This heating causes that the coating temperature is 10 degrees higher than air temperature. This temperature difference is fixed in all simulated scenarios with T_{air} and $T_{coating}$ equal to 294 and 304 K, respectively.

Inlet NO and NO2 concentrations are implemented corresponding to measured values at reference level. The initial concentration of O3 is computed considering photostationary equilibrium, $\mathrm{O_3} = \mathrm{J_{NO_2}NO_2/k\,NO}$. Chemical constants k and $\mathrm{J_{NO_2}}$ are dependent on temperature and zenith angle, respectively.

Table 2. Inlet concentrations and the zenith angle (ZA) for each scenario.

	1200UTC	**1230UTC**	**1300UTC**	**1330UTC**	**1400UTC**
ZA (rad)	0,94	0,95	0,97	1,01	1,06
NO (ppb)	15,04	23,74	22,29	15,10	9,52
NO2 (ppb)	24,49	32,25	32,19	28,57	23,60
O3 (ppb)	26,68	22,08	22,91	28,76	35,25

In order to model NO deposition over photocatalyitic coating, the NO surface deposition velocity is calculated from laboratory data following two different approaches:

(a) An estimation following a classical first-order kinetic. The result obtained is V_d(kin)=0.006m/s (Palacios et al., 2015).
(b) An approximation from the removed NO under testing conditions using a mass balance (V_d(Mass) =0.005m/s).

Both approaches provide similar values of V_d. Besides scenarios using a wide range of NO deposition velocities around the value estimated from mass balance method are also simulated.

4. Results

4.1. Comparison with experimental results

The CFD results for a friction velocity u_*=0.05 m s^{-1} are here evaluated against the experimental data. NO concentration is simulated, a) without deposition velocity, b) with V_d(Mass) and c) V_d(Kin).

Fig. 2 displays the NO concentration at 0.16 m for the 3 simulated cases and the experimental results at different hours. In all time scenarios the tendency of simulated NO concentration is in agreement with experimental results being closer to measurements in the cases using V_d(Mass) and V_d(Kin).

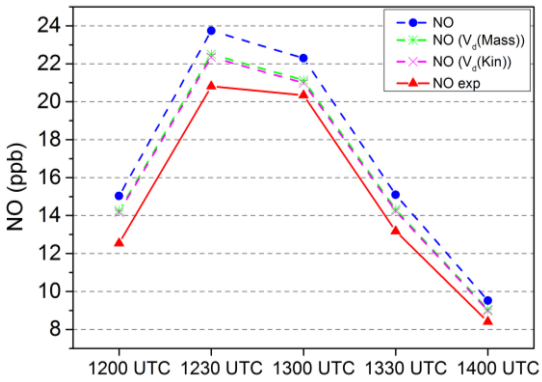
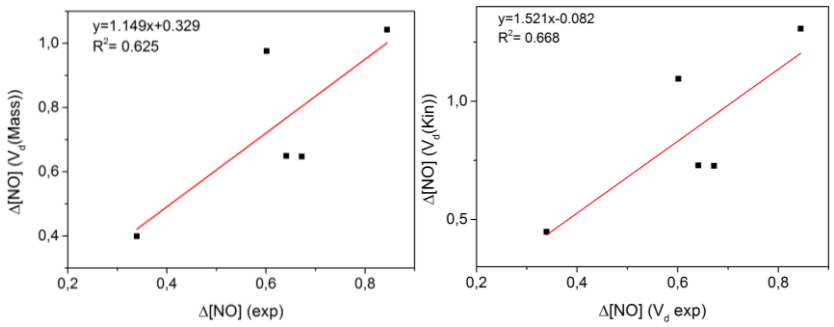


Fig 2. NO concentration obtained experimentally (NO exp) and using CFD model without deposition (NO) and with V_d(Mass) and V_d(Kin)

In order to study variations of NO concentration in height, the differences of NO concentration between the closest levels to ground, N_2 and N_1, are also compared ($\Delta[\mathrm{NO}] = [\mathrm{NO}](\mathrm{N}_2) - [\mathrm{NO}](\mathrm{N}_1)$, hereafter NO concentration gradient). In Fig. 3 the linear regression of simulated NO concentration gradient with V_d(Mass) and V_d(Kin) with respect to measure NO concentration gradient is shown. The resulting values of the CFD model

taking into account deposition velocity from laboratory tests are well correlated with outdoor experimental data.



(a) (b)

Fig 3. Linear regression of NO concentration gradient of simulation results and experimental measurements with (a) and (b)

The effect of varying the deposition velocity on NO concentration gradient is then analyzed simulating a range of deposition velocities around $V_d(\mathrm{Mass})$ (0.1V_d(Mass), 0.5V_d(Mass), V_d(Mass), 2 V_d(Mass) and 10V_d(Mass)) (Fig. 4). The experimental NO gradient falls between the curves obtained with 0.5V_d and 2V_d where V_d is the value computed from laboratory data. Therefore, modeling NO deposition with a surface deposition velocity within this range leads to simulations results close to experimental measurements.

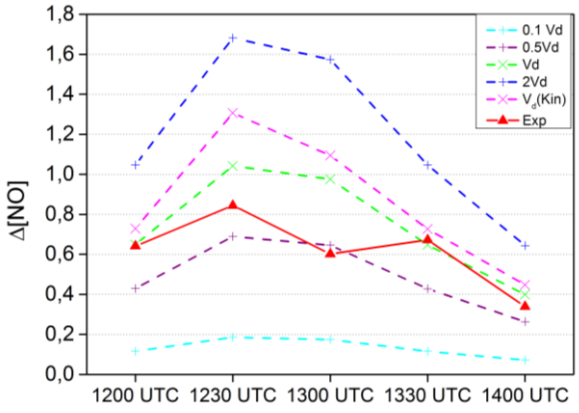
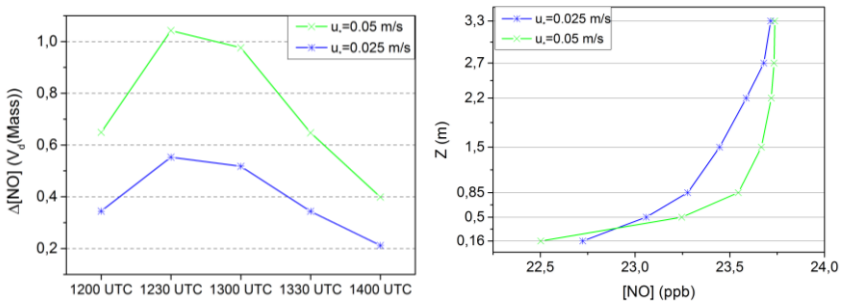


Fig 4. NO concentration gradient obtained experimentally and using CFD model

4.2. Variation with wind speed of the photocatalytic effect

In this section CFD simulations with different atmospheric parameters are carried out to assess their influence on NO depletion caused by photocatalytic materials.

All time scenarios are simulated keeping the same conditions of inlet concentration, temperature gradient and NO deposition velocity (V_d(Mass)), but halving the value of the friction velocity, u_*=0.025m s^{-1}, which implies reducing the wind speed by a factor 2.



(a) (b)

Fig 5. (a) NO concentration gradient and (b) vertical profile of NO concentration at 1200 UTC simulated with a V_d=0.005m s^{-1} for two wind speeds ($u_* = 0{,}05\ \mathrm{m\ s^{-1}}$ and $u_*' = 0{,}025\ \mathrm{m\ s^{-1}}$)

The decrease of velocity induces a higher influence of buoyant forces and this effect modifies NO concentration profiles (Fig. 5). In order to quantify this process, the bulk Richardson number (Ri_B) close to the ground is computed. Ri_B provides information about the ratio of buoyant and inertial forces and these values indicates the increase of buoyant effect and, consequently, vertical mixing. Ri_B is defined by, $Ri_B = gH\frac{(T_n - T_0)}{T_n\, U^2}$, where *n* and *0* are the values at 1.5m and at ground level respectively. For a lower wind speed, the NO concentration gradient between N_2 and N_1 levels is minor, in contrast, higher quantity of NO is deposited (Table 3). The Ri_B=-2.2 for u_*=0.025m s^{-1} indicating more atmospheric instability than for higher wind speed with Ri_B=-0.6. It implies more vertical mixing and as a consequence the vertical profile is modified. Hence the effect of deposition on NO vertical concentration can be observed into a higher height.

Table 3. NO deposition over photocatalytic coating in (ppb m^3 s^{-1})

	1200 UTC	1230 UTC	1300 UTC	1330 UTC	1400 UTC
$u_* = 0.05\ m/s$	24,59	38,77	36,42	24,71	15,61
$u_* = 0.025\ m/s$	27,14	42,79	39,87	27,28	17,23

4.3. Variation with temperature of the photocatalytic effect

The difference of coating and air temperatures has influence on vertical dispersion and thus on NO concentration gradient. For that reason, neutral cases with the same air and coating temperature are simulated and compared with non-neutral cases (T_{air}<$T_{coating}$).

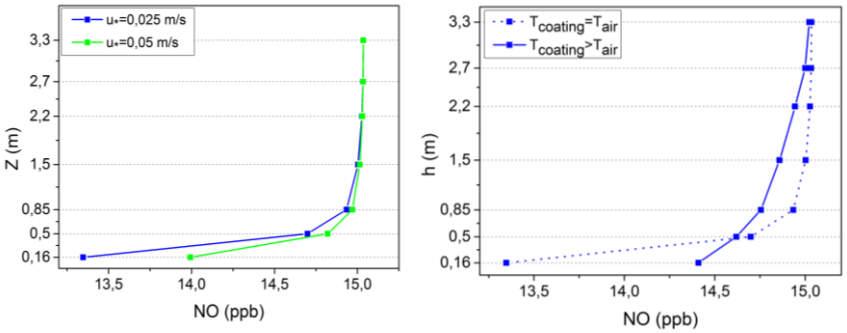


Fig 6. Vertical profile of NO concentration at 1200 UTC (a) for different wind with T_{air}=$T_{coating}$ (b) for T_{air}<$T_{coating}$ and T_{air}=$T_{coating}$ with same $u_* = 0{,}025\ m/s$

Firstly, the effect of wind speed on NO concentration for neutral case is analyzed (Fig 6a). NO concentration close to ground is slightly minor when the velocity is lower. In contrast, this behavior is different at first level for non-neutral cases, as explained in the previous section.

In Fig. 6b the vertical profiles for T_{air}=$T_{coating}$ and T_{air}<$T_{coating}$ with a fixed wind speed is shown. For a neutral case, NO concentration gradient between the closest levels to ground ($\Delta[\mathrm{NO}] = [\mathrm{NO}](\mathrm{N}_2) - [\mathrm{NO}](\mathrm{N}_1)$) is higher in comparison with non-neutral case. However, more vertical mixing caused by temperature differences induces lower NO concentration at higher height for non-neutral case. As a consequence, the effect of NO deposition is perceptible at higher heights.

5. Conclusions

This study is focused on evaluating dispersion pollutants including NO deposition effect over photocatalytic material in combination with experimental data in outdoor conditions. Simulated NO concentration are in good agreement with experimental measurements. The experimental NO concentration gradient is reproduced by CFD model when the deposition velocity implemented have a value similar to V_d calculated from laboratory data (between $0.5V_d$ and $2V_d$).

On the other hand, the influence of wind speed and the temperature difference of coating and air on deposition effect over photocatalytic coating are examined. The effect of wind speed variation on vertical profiles of NO concentration taking into account neutral and non-neutral cases is determined by the stability stratified environment. For different wind speed cases, the Bulk Richardson Numbers are Ri_B =-0.6 for u_*=0.05m s^{-1} and Ri_B =-2.2 for u_*=0.025m s^{-1} close to the ground increasing vertical mixing and modifying NO vertical profile. And therefore, the NO deposition effect is observed at higher height for non-neutral cases due to the vertical mixing induced by photocatalytic coating heating. Finally, note that, in general, the effect on NO concentration of the deposition over the photocatalytic coating is only observed at heights close to the ground and the difference with the unperturbed concentration is small (only a few ppb).

References

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