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EXTENDED ABSTRACT

Theoretical analysis of simplified $NO–NO_2–O_3$ chemistry for near-road NO_2 estimation

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Abstract

Simplified chemical schemes are commonly used in local and urban-scale dispersion models to estimate NO_2 concentrations. However, the impact of different approximations on these schemes and of key input parameters on predicted concentrations has been little explored. In this work, we present a sensitivity analysis comparing four commonly used formulations (one- vs two-reaction schemes; stationary vs time-dependent) and evaluating their sensitivity to emission and background conditions, under different pollution conditions (high, moderate, low). Results highlight that differences between formulations can be as large as 30–36% particularly under moderate and low pollution, and that substantial deviations from the NO_2 equilibrium value can occur within 50 m of the source, depending on the wind speed. These insights may help to understand sources of uncertainty around formulations and parameters for near-road applications.

Introduction

NO_2 near road arises due to emissions of NOx from on road sources and the subsequent $NO–NO_2–O_3$ rapid chemistry, superimposed on transport and dispersion. Atmospheric dispersion models usually include NOx chemistry in a sequential (modular) approach. In this process, the system of ODEs is applied locally and evolves independently after transport and dispersion. This makes models such as R-LINE (Valencia et al., 2018) or DAUMOD-GRS (Pineda Rojas and Venegas, 2013) computationally efficient. Despite the widespread use of simplified $NO–NO_2–O_3$ chemistry within these types of air quality models, formulations vary widely regarding assumptions and parameters used (Kimbrough et al., 2017), and little discussion has been given in the literature to the role of these differences or of the parameters involved on the simulated NO_2 concentration. Local sensitivity analysis under designed numerical experiments can help to understand these influences under a wide range of conditions (e.g., Pineda Rojas and Bikiel, 2019). This work presents a theoretical exercise aimed at analyzing how basic chemical assumptions and key input parameters influence the modeled NO_2 concentration in the near-road environment. Our objective is to assess whether and how the formulation, background concentrations, and emission characteristics (such as the NO_2/NOx fraction) affect the predicted NO_2 values under typical near-road urban conditions.

Methodology

The two reactions dominating chemistry formation of NO_2 at short time scales are:

$$\text{R1: } NO + O_3 \rightarrow NO_2\text{, with reaction constant } k$$

$$\text{R2: } NO_2 \rightarrow NO + O_3\text{, with reaction constant } J$$

Common assumptions are: only R1 dominates, R1 dominates and it is instantaneous and both reactions are in equilibrium which implicitly assumes a large residence time of the emitted pollutants. While these reactions are relatively fast, wind transport and atmospheric dispersion can be even faster depending on wind speed (WS), affecting the distance at which equilibrium is achieved. In this work, we study the sensitivity of NO_2 to different formulations and parameters within near-road distances, i.e., within the first 100 meters from the road.

The analysis is divided into three parts: (1) base case dynamics, (2) comparison of commonly used formulations under different pollution levels, and (3) sensitivity analysis to key parameters.

For the Base Case (BC) analysis, the non-stationary two-reaction scheme is numerically integrated, assuming the following initial concentrations: NO_2 = 20 ppb, NO = 80 ppb and O_3 = 30 ppb. The temporal evolution of the three species is illustrated. In order to understand the role of chemistry near the source, the variation of the NO_2 concentration is plotted as a function of distance from the source for different wind speeds (WS = 0.5, 1, 2, 4 and 6 m/s).

Second, the sensitivity of NO_2 concentration to the formulation assumptions (F1: instantaneous one-reaction, F2: non-stationary one-reaction, F3: photochemical steady state two-reaction, F4: non-stationary two-reaction) is assessed for three scenarios of pollution:

- High: NOx = 300 ppb, f-NO_2 = 0.2 and O_3 = 20 ppb
- Moderate: NOx = 100 ppb, f-NO_2 = 0.4 and O_3 = 30 ppb
- Low: NOx = 30 ppb, f-NO_2 = 0.6 and O_3 = 40 ppb

Third, we perform sensitivity tests by partitioning the initial concentrations into local and background contributions, to study the impact of key parameters/variables: fraction of NO_2 in NOx emission (f-NO_2: 0.1–0.3), and background NO_2 and O_3 concentrations (0–40 ppb). These tests are carried out for the non-stationary two-reaction scheme (F4), under BC conditions defined as local NOx = 100 ppb with f-NO_2 = 0.2, background O_3 = 30 ppb and background NO_2 = 0.

The dynamic schemes (F2 and F4) are solved using the exact analytical solution for $NO_2(t)$, obtained from the quadratic formulation of the coupled system. All scenarios consider the following values for the reaction constants:

$$k = 3.5\times10^{-4}\ \mathrm{ppb}^{-1}\cdot\mathrm{s}^{-1}$$

$$J = 5\times10^{-3}\ \mathrm{s}^{-1}$$

Results

Figure 1 illustrates NO_2 concentration as a function of distance for different WS values. Marked differences are observed between the two WS selected extremes: equilibrium is reached within 50 m for WS = 0.5 m/s, while it takes nearly 700 m for WS = 6 m/s. At 50m from the source (representative of an urban traffic site), a 6 m/s wind leads to an NO_2 of 25 ppb, quite far from its equilibrium value (~40 ppb).

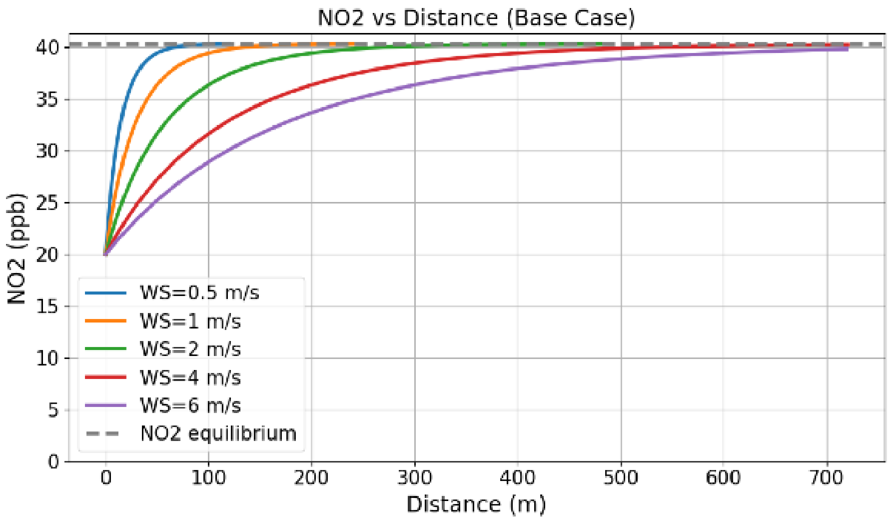


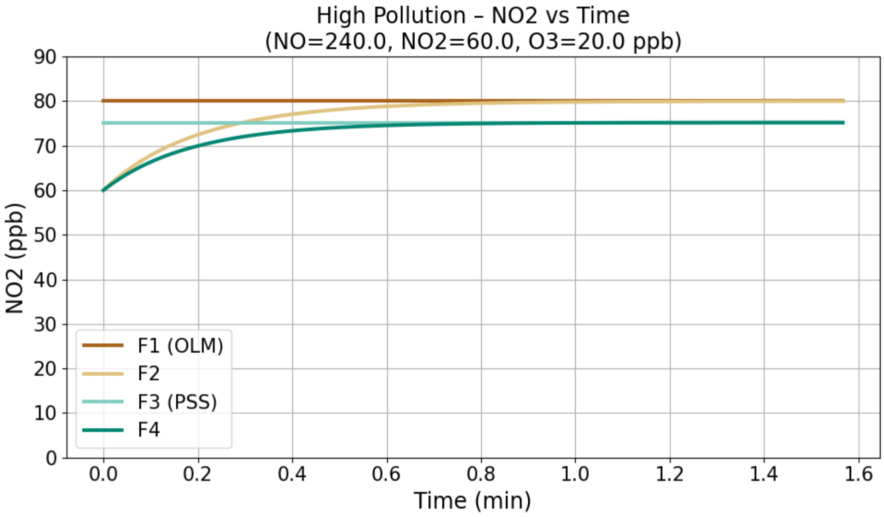
Figure 1: NO_2 concentration vs distance for different WS values (colored curves). The NO_2 concentration at equilibrium is indicated in grey dashed line.

Results from the sensitivity to formulations show that under the high pollution scenario (**Figure 2.a**), NO_2 reaches equilibrium at 0.6 min for the two non-stationary formulations (F2 and F4), while moderate and low pollution scenarios present larger values and greater differences between T_{eq} = 2 min (for the 1-reaction scheme) and 5 min (for the 2-reaction formulation). Differences in the NO_2 equilibrium values of the two formulations are relatively small (7%) in the high pollution scenario and larger (30-36%), comparable in magnitude to the overall chemistry contribution in the low/moderate pollution conditions (**Figure 2.b**).

The sensitivity to key parameters shows that, while both f-NO_2 and $[NO_2]_0$ influence the initial NO_2 concentration ($[NO_2]_0 = [NO_2]_b$ + f-NO_2 x $[NOx]_s$), the differences between sensitivity curves (for example, those corresponding to the extreme cases of f-NO_2) slightly decrease with time, indicating a larger relative impact of potential errors in this parameter within short distances (or times) where the chemical formation of NO_2 is relatively low (not shown). On the other hand, a value of $[O_3]_b = 40$ ppb increases NO_2 from 40 ppb to 67 ppb (67%) at the equilibrium which occurs at 1.5 min. In all three cases, considerable differences are observed over short distances (< 100 m) between WS = 1 m/s and 4 m/s. At 50 m, less than half of the difference between the initial ($[NO_2]_0$) and the equilibrium ($[NO_2]_{eq}$) values is obtained for WS = 4 m/s.

The slope of NO_2 versus NOx increases with the NO_2/NOx emission fraction but not with background NO_2, highlighting the dominant role of emissions but also the sensitivity of NO_2 to NOx (not shown).

(a)



(b)

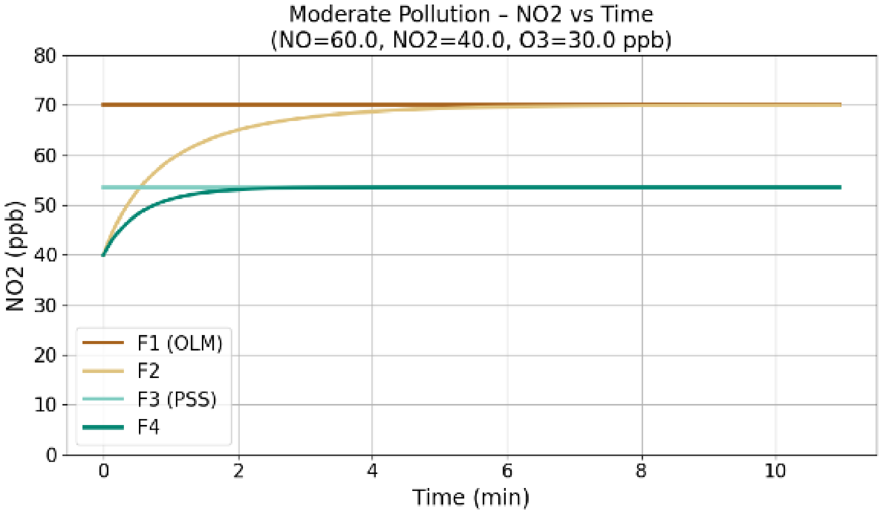


Figure 2: Temporal evolution of NO_2 concentration for different formulations, under high (a) and moderate (b) pollution scenario conditions.

Conclusions

This work presents a sensitivity analysis of NO_2 estimated using a commonly used NO–NO_2–O_3 scheme to key parameters and assumptions under typical urban and near-road conditions. Under high pollution, the impact of formulation assumptions is small, but under moderate or low pollution the difference between one- and two-reaction schemes can be comparable to the total chemical contribution due to higher available O_3 and lower initial NO_2. All tested parameters (background NO_2 and O_3, fraction of NO_2 in NOx emissions) have considerable impact under moderate pollution: $[NO_2]_b$ and f-NO_2 affect initial NO_2, while $[O_3]_b$ drives chemistry. $[O_3]_b$ influence dominates at low NOx, whereas f-NO_2 is more relevant at high NOx. In the immediate vicinity of high traffic environments, NO_2 can remain close to its initial value (far from equilibrium) depending on wind speed, indicating a limited role of chemistry except at very low WS. This may explain the good performance of empiricalNO_2-NOx relationships at near-road sites. Future studies including transport and dispersion, and comparison with observations, may help support the selection of formulations for such microenvironments by considering multiple factors.

References

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