CHEMICAL REACTIONS AT STREET SCALE USING A LAGRANGIAN PARTICLE DISPERSION MODEL (LPDM)

Hadassah KAPLAN[1], Christophe OLRY [2], Jacques MOUSSAFIR[2], Olivier OLDRINI[3], Frédéric MAHE[4] and Armand ALBERGEL[2]

[1]IIBR, P.O.B 19, 74100 Ness-Ziona, Israel
[2]ARIA Technologies, 8 rue de la Ferme 92100 Boulogne-Billancourt, France
[3]MOKILI, 53 rue Dareau, 75014 PARIS - France
[4]AIRPARIF Surveillance de la qualité de l'air en Île-de-France 7 rue Crillon 75004 PARIS

Abstract: In the context of the FEDER AIRCITY project, Paris city is modeled with a 3m resolution in purpose of computing pollutant concentration relevant for human exposition. This project involves AIRPARIF (Ile-de-France air quality monitoring network), for emission and immission data, CEA (French atomic and alternative energy agency) for HPC availability, IGN (National Geographic Institute) for city 3D data. For pollutant dispersion modeling, PMSS software was selected including a parallelized fast 3D wind field and turbulence code and a parallelized stochastic LPDM. A key point in urban air quality is NO_2 concentration, so the NO/NO_2 transformation at the street scale is a key issue.
In this paper, a preliminary independent study will focus on fundamental questions.
After theoretical consideration, a practical case is carried on over the Paris Opera district. The results are compared with standard continuous measurements at 2 air quality stations of the AIRPARIF monitoring network.
Key-words: LPDM, urban pollution, street pollution, NO-NO$_2$ reaction

INTRODUCTION

In urban environment, especially near busy traffic axis, population is exposed to high level hazardous material concentrations, exceeding currently air quality standards. Such concentrations cannot be resolved by large scale models like CHIMERE or WRFchem which are limited by horizontal mesh size of order 1×1 km. On the other hand, street level models (domains of order 1×1km) which are capable to resolve concentrations down to 3m, require information about pollutant transported to the area from upwind regions which can react with the local emitted pollutants. Such concentrations which are considered as "background", can be calculated by larger scale models, simple models (Berkowicz (2000) [2]), or can be measured above roof level. In this paper, we use a Lagrangian diffusion model (LPDM) to calculate concentrations at street level. Lagrangian diffusion models are widely used to describe transport and diffusion of pollutant in complex flows (see for example inside urban canopy, Kaplan and Dinar (1996) [4]). They are flexible regarding sources configurations and therefore are suitable to describe pollutant emitted by traffic inside the urban canopy. In order to describe NO_2 formation from the emitted NO, Lagrangian model was extended to include chemical reaction of NO with the background ozone transported to the area (see also Middleton (2008) [6]). However in order to describe an interaction with background species, huge number of particles is required what makes the method inefficient. An alternative method was suggested by Alessandrini et al (2008) [1]. They introduce the "deficit" concept which is the difference between the constant background and the actual ozone concentration.Each of the released particles carries a "deficit" mass which is updated due to the reaction. In this paper we extend the reaction scheme suggested by Alessandrini to include photo-dissociation of NO_2. We include also the traffic induced turbulence in the LPDM model. This induced turbulence effects the pollutant dispersion near the source and therefore influence the reaction rate. The model is applied to the Opera district of Paris and results are compared with monitoring stations measurement.

MODEL FORMULATION

The model describes emission of NO_x from traffic into a constant background of ozone BO_3 . Transport and diffusion are calculated using stochastic lagrangian particle model. The reactant, NO, O_3 and the product NO_2 are treated in a similar way to that described by Alessandrini and Ferrero (2008) [1]. Each particle released from the source carries an initial mass of NO, NO_2 and a "deficit" from the background,defO_3, mass which is set to zero at t=0. At each time step concentrations are calculated, and the particles masses are changed due to the chemical reaction and the photo-dissosiation of NO_2. The rate of change of the particles' masses due to the chemical reaction is given by:

$$\frac{dm_{NO}}{dt} = -\frac{dm_{defos}}{dt} = -\frac{dm_{NO_2}}{dt} = -k\left(B_{O3}\, m_{NO} - \langle C_{NO} \rangle\, m_{defos}\right) + J m_{NO_2} \qquad (1)$$

In this equation k is the reaction rate, J is the photo-dissociation constant. The concentrations are in ppm and the masses in molar volume. By summation over all particles in the grid cell divided by the cell volume V_{cell}, we obtain the ensemble averaged (<>) reaction rate equation:

$$\frac{d<C_{NO}>}{dt} = -\frac{d<C_{NO_2}>}{dt} = -k < C_{NO} > (B_{O_2} - < C_{defos} >) + J < C_{NO_2} > = -k < C_{NO} >< C_{O_2} > + J < C_{NO_2} > \quad (2)$$

The reaction described by equation (2) does not include the segregation terms contributed by the concentration fluctuations. More details about the segregation term can be found in Kaplan (2011) ([5]). The sensitivity test with and without the segregation terms shows that the influence on the results is negligible in our street case study. However, in case of reacting plumes from point sources the segregation term is important and should be included in the calculations.

In addition to the NO_X gases, the moving vehicle induced an additional turbulence to the background turbulence which effects the cloud dispersion near the source. This induced turbulence is modeled as an injected turbulence kinetic energy (TKE). The emission rate of the turbulent kinetic energy Q_{TKE} should be modeled or measured. In our study, we assign to each of the released particle, an initial amount of TKE. At each time step the TKE is calculated at each grid cell by summation over the contributions of all particles in the cell. The additional turbulence velocity σ_v is:

$$\sigma_v = \sqrt{\frac{2}{3} TKE} \quad (3)$$

MODEL APPLICATION AND EVALUATION

The model is applied to the Paris Opera district for 24 hours at 25.2.2011. Results are compared with two monitoring station operated by AIRPARIF, at Haussmann street (H) and at the opera (O). The vehicle emission parameters were supplied by AIRPARIF. These parameters include hourly average of NO_X release rate per unit length [µg/(sec·m)], source height and source width. An example of the data is presented in figure 1.

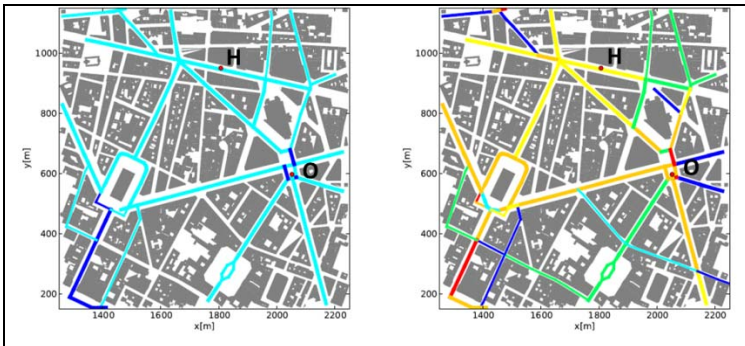

Figure 1: Emission rate of NO_x in the Opera district at 25.2.2011 Left at 3 am right at 3 pm *level in [µg/s.m] azur- 10-100;blue:100-200;green:200-300;yellow:300-400;orange:400-900;red: >900*

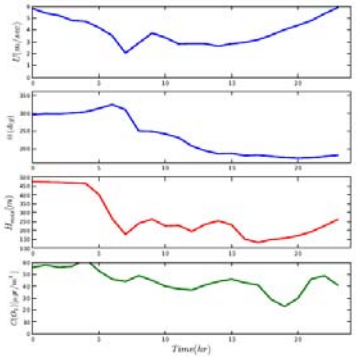

Figure 2: Meteorological parameter in the Opera district at 25.2.2011 *From top to bottom: wind velocity wind direction at 53m,mixing layer height, ozone concentration measured on the 3rd floor of Eifel tour*

A 3D city data was supplied by IGN (National Geographic Institute). The meteorological parameters were calculated using WRF model by AIRPARIF. The calculated parameters are presented in fig 2. The 3D meteorological field were interpolated into the urban canopy using the building data and using the constraint of mass consistency as described in Rockle (1990) [7].

The model parameters

The reaction rate k and the photo dissociation constant were obtained by the expression suggested by Smith (1996) [8]:

$$k = 43.6\, e^{-\frac{1370}{T}} \quad [1/(\text{sec}\cdot\text{ppm})] \quad (4)$$

$$J = 0.0145\, e^{-\frac{0.4}{\cos(\theta)}} \quad [1/(\text{sec})] \qquad (5)$$

T is the air temperature and θ is the zenith angle which depends on the date and the hour of the day. There is uncertainty in three parameters of the model:

1. **The background ozone concentration:** There are many ozone measurements in Paris but the upwind concentration to take into account as an inlet value remains an open question. An sensitivity study was done and some results are given below.
2. **The NO/NOx ratio at the source:** The value we use in our calculations is 0.75. This is based on the value reported in AIRPARIF report (2011) [3].
3. **The induced turbulence emission rate $\dot{Q}_{TKE}$:** Since we do not have any information about the traffic induced turbulence, a simple model is derived to estimate the rate of emission of the TKE: Denote by N the number of vehicles per second and by V their average velocity. The induced turbulence kinetic energy emitted by a single vehicle is proportional to $(\alpha \cdot V^2)$ where α is a constant of order 0.1. Since V is of the order of 10m/sec the emission rate of the turbulence kinetic energy, $\dot{Q}_{TKE}$ is proportional to N. The emitted amount of NO_x by a single vehicle is about 0.2g/s . Therefor N =$\dot{Q}_{NOx}$/0.2 where $\dot{Q}_{NOx}$ is the emission rate of NO_x. It follows that

$$\dot{Q}_{TKE} = 5\, K\, \dot{Q}_{NOx}$$

where K is constant and on our calculations we use an arbitrary value of 0.5.

Concentration evaluation

Before evaluating the NO_2 concentration, we check the inert species NO_x. The predicted NO_x concentration (in ppm) does not depend on the reaction and therefore on the background ozone concentration. It does depend on the NO/NOx ratio, on the induced turbulence model and the calculated flow field. The NO_x concentration is presented in figure 3 for the two monitoring stations Haussmann and Opera. The simulated values are for NO/NOx ratio of 0.75. By change the NO/NOx ratio from 0.75 to 0.9 the predicted NOx concentration increase by 6%. Deviation of more than factor 2 from the measured data is observed only in the Opera station in the early morning. In most hour of the day the predicted values are similar to the measured values.

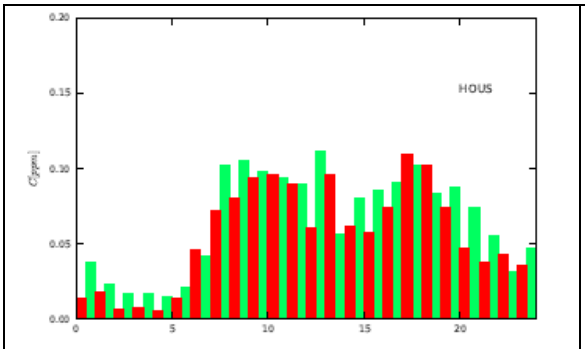

Figure 3a : Predicted versus measured NOx concentration [ppm] at Haussmann station

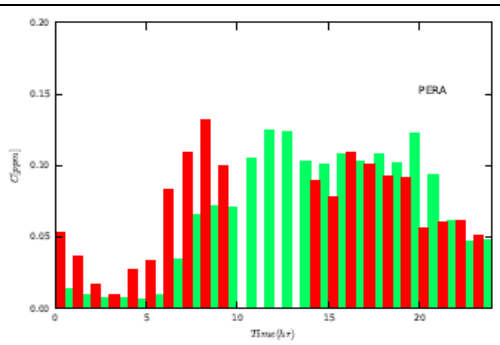

Figure 3b : Predicted versus measured NOx concentration [ppm] at Opera station

The calculated NO_2 concentration underestimates the observed one by an average factor of about 0.6. This underestimation can be explained by underestimation of the background ozone concentration. As mentioned before, the measurements at the Eifel tour are above the mixing layer height and therefore do not represent the background. We repeat the calculations with constant background of ozone of 75μgr/m3. Although there is quite good agreement with the measurements, the simulated concentration are biased toward underestimation of the measured one during all hours of the day.

SENSITIVITY TO THE MODEL PARAMETERS

In order to check the influence of the different parameters of the model, we choose the measured data at 15:00. The basic case was calculated with induced turbulence constant of 0.5, NO/NOx ratio 0.75 and background ozone concentration as measured at the Eifel tour (44μgr/m3). The calculated concentrations are presented in table 1 together with the measured data. Sensitivity of the results to three parameters are studied:

	Calculated		Measured	
	Haussmann	Opera	Haussmann	Opera
NO2	50.8	71.7	75.	109
NO	103	146	91	100

Table 1: Calculated versus measured NO_2 & NO concentrations at 15:00 Model parameters: NO/NOx = 0.75; K=0.5; BO3 = 44[$\mu g/m^3$]

The NO/NOx ratio was changed to 0.9. The turbulence parameter was decreased by a factor of 2 (K=0.25). The Ozone background was doubled (BO3 = 88[$\mu g/m^3$]). Results are presented in table 2. In this table we can see that change of the NO/NOx ratio to 0.9 decreases the results to values. Change of the induced turbulence by a factor of 0.5 increases the NO_2 concentration by several percent as well as the NO concentration. Change of the ozone background concentration by a factor 2 increases the NO_2 concentration and decrease the NO concentration in a way that makes them closer to the measurements. However, in order to achieve better agreement with the measurements very high values of the background concentration are required which have no justification.

	NO/NOx=0.9		K=0.25		BO3=88[µg/m3]	
	Haussmann	Opera	Haussmann	Opera	Haussmann	Opera
NO2	30.1	41.7	65.1	80.1	63.7	90.3
NO	125	177.3	128.7	167.6	95.2	134.8

Table 2: Calculated versus measured NO_2 & NO concentrations at 15:00 with different model parameters

CONCLUSION

Diurnal pattern of NO, NO_2 concentrations in the urban canopy were calculated using a LPDM model including chemical reaction scheme and traffic induced turbulence. Results were compared with measurements at two monitoring stations in the Opera district of Paris. Sensitivity to the uncertain parameters of the model was studied. It is found that a value of NO/NOx ratio of 0.75 give the best agreement with the measurements. In absence of a reliable ozone background concentration measurements, a constant value of 75µ · gr/m3 was found to give the best agreement with measurements. The simulated concentrations are slightly biased toward underestimation of the measurements. This can be explained by a presence of a background NO_2 which is not included in the calculations. The urban-scale model can be used stand-alone if the background ozone concentration is available. It can be also coupled with meso-scale chemistry transport model. In this case it can be extended to include interaction with background radical pool (RP).

REFERENCES

[1] Alessandrini S. Ferrero E.: 2009,' A Hybrid Lagrangian-Eulerian Particle Model for Reacting Pollutant Dispersion in Non-Homogeneous Non- Isotropic Turbulence.' Physica A 388, 1375-1387.

[2] Berkowicz R.: 2000 'A simple model for urban background pollution', Environmental Monitoring and Assessment 65 259-267.

[3] Saglio J. F. : 2011,'Rapport d'activit & bilan de la qualit de l'air' P.77

[4] Kaplan H. Dinar N.: 1996 'A Lagrangian Dispersion Model For Calculating Concentration Distribution Within A Built-up Domain', Atmospheric. Environ. 42 (24), 4197-4207.

[5] Kaplan H. : 2011,'An Estimation of a Passive Scalar Variances Using A One -Particle Lagrangian Transport And Diffusion Model',submitted to physica A.

[6] Middleton D. R., Jones A. R., Redington A. L., Thomson D. J.,Sokhi S. R.,Luhana L., Fisher B. E. A.: 2008 'Lagrangian modelling of plume chemistry for decondary pollutants in large industrial plumes. Atmospheric. Environ. 42, 415-427.

[7] Rockle R. : 1990, ' Bestimmung der Str¨omungsverh¨altnisse im Bereich komplexer Bebauungsstrukturen' Ph. D. thesis Darmstadt, Germany.

[8] Smith J.D.B. Tomlin A.S. Berzins M. Pennington V. Pilling M.J.: 1996, 'Modelling the effects of Concentrated Emissions Sources on Tropospheric Ozone'. 19