

Second International Conference Buildings  
and the Environment, June 1997, Paris

## A NEW REACTIVE MODEL FOR INDOOR AIR QUALITY ANALYSIS

P. BLONDEAU<sup>(\*)</sup>, M. SPERANDIO<sup>(\*)</sup>, F. ALLARD<sup>(\*)</sup> and F. HAGHIGHAT<sup>(\*\*)</sup>

(\*) L.E.P.T.A.B - Université de La Rochelle, Ave. Marillac, F-17042 La  
Rochelle Cedex 01

(\*\*) C.B.S. Concordia University, 1455 De Maisonneuve Blvd., Montréal  
H3G1M8, Canada

### ABSTRACT

Indoor Air Quality analysis needs at first an accurate prediction of indoor pollutant concentration levels. However, most of pollutant concentration prediction models consider the pollutants as passive elements. Our study introduces the more common gas-phase chemical reactions occurring in indoor spaces.

We developed a model taking into account more than 20 different reactions influencing the concentration level prediction of NO<sub>x</sub> compounds, ozone, carbon monoxide and sulphur dioxide from the knowledge acquired in the field of tropospheric chemistry. As the model was designed to assess the dynamic variations of indoor solar actinic irradiance, it particularly can deal with the photochemical dissociation reaction of NO<sub>2</sub>.

A case study using real outdoor pollution and climatic data enables us to show the large influence of these homogeneous processes on the indoor pollutant concentration prediction, and demonstrates the necessity of taking them into account in the frame of an healthy air quality analysis.

### 1- INTRODUCTION

During the last 20 years, considerable progress has been made in developing mathematical models for predicting pollutant concentrations in ambient air. By comparison, most indoor air quality simulation tools have remained relatively primitive, ignoring or representing by rough models both homogeneous (molecules and particles interactions inside the gas phase) and heterogeneous (interactions of gaseous molecules with solid or liquids) processes within which pollutant species are involved.

Regardless of homogeneous chemistry, NAZAROFF and CASS [1] were the first who tried to transfer the knowledge developed in the field of tropospheric chemistry to indoor environments. They used a 57 reactions kinetic mechanism to predict the dispersion of nitrogen oxides and their decomposition into nitric and nitrous acids. WESCHLER and al [2] and AXLEY and al [3] then proceeded to theoretical analysis of this mechanism and experiments in order to define simplified model and to identify the main pathways to HNO<sub>3</sub> generation indoors. The works we present in this paper aim to demonstrate how gas-phase chemical reactions may influence the indoor concentration predictions of the

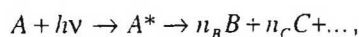
more commonly found outdoor inorganic pollutants. As a result, after describing the basis of homogeneous atmospheric chemistry, we present the selected chemical mechanism, the simulation hypothesis and the way dynamic variations of the indoor actinic irradiance and outdoor concentrations of non pollutant species are estimated from meteorological and pollutant concentrations data. The need of taking into account homogeneous chemistry in IAQ simulation tools is finally assessed by relating the contaminant indoor concentration differences with and without reactive model to their corresponding safety threshold limit values.

## 2- METHODOLOGY

### 2.1- Fundamentals of the gas-phase chemical reactions

In the field of outdoor air pollution analysis, the detailed mechanism of gas-phase atmospheric chemistry is used to be divided into two broad categories which are photochemical and thermal reactions.

Photochemical reactions are initiated by the absorption of a photon by an atom, molecule, free radical or ion leading to its activation. Of all the photolytically activated reactions possible, photolytic dissociation is then the most common one; it consists in the fragmentation of the original species into its component constituents. If  $A$  and  $A^*$  respectively represent the reactive element in its electronic ground and excited states, the whole process can thus be summarised by the following unimolecular reaction [4]:



For low concentrations of  $A$ , the resulting molecular concentration rate of change of both reactive species and reaction products are given by the following equations:

$$\frac{d[A]}{dt} = -k_1[A] = -\frac{1}{n_B} \frac{d[B]}{dt} = -\frac{1}{n_C} \frac{d[C]}{dt} = \dots \quad (\text{eq. 1})$$

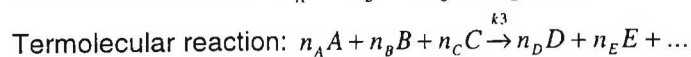
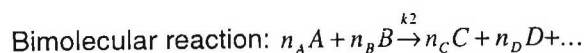
where the first order rate constant  $k_1$  (s) depends on the integral of the actinic irradiance  $I(\lambda)$  (photons.m<sup>-3</sup>.s<sup>-1</sup>) which corresponds to the radiant intensity per unit wavelength, the absorption cross section  $\sigma_A(\lambda, T)$  of molecule  $A$  at wavelength  $\lambda$  (m) and temperature  $T$  (K), and the probability of dissociation (quantum yield)  $\Phi(\lambda, T)$  of the molecule upon the absorption of a photon:

$$k_1 = \int_{\lambda_1}^{\lambda_2} \sigma_A(\lambda, T) \Phi_A(\lambda, T) I(\lambda) d\lambda \quad (\text{eq. 2})$$

SEINFELD [4] indicates that in the lower atmosphere, the wavelength range of interest is approximately [280 nm, 730 nm]. As FINLAYSON-PITTS and PITTS do [5], he also proposes some values or mathematical functions for the

absorption cross sections and quantum yields of the more important reactive species.

The bimolecular and termolecular thermal reactions result from the collision of two or three atoms, molecules or ions which, under favourable thermodynamic conditions, combines and produces new chemical species:



In both cases, the molecular rates of production and removal of the involved elements can be expressed as a function of a rate constant (respectively  $k_2$  in units  $\text{m}^3 \cdot \text{molecule}^{-1} \cdot \text{s}^{-1}$  and  $k_3$  in units  $\text{m}^6 \cdot \text{molecule}^{-2} \cdot \text{s}^{-1}$  for the bimolecular and termolecular reactions), the stoichiometric coefficients of the reaction and the reactive element concentrations:

$$\frac{1}{n_A} \frac{d[A]}{dt} = \frac{1}{n_B} \frac{d[B]}{dt} = -k_2 [A][B] = \frac{-1}{n_C} \frac{d[C]}{dt} = \frac{-1}{n_D} \frac{d[D]}{dt} = \dots \quad (\text{eq. 3})$$

$$\frac{1}{n_A} \frac{d[A]}{dt} = \frac{1}{n_B} \frac{d[B]}{dt} = \frac{1}{n_C} \frac{d[C]}{dt} = -k_3 [A][B][C] = \frac{-1}{n_D} \frac{d[D]}{dt} = \frac{-1}{n_E} \frac{d[E]}{dt} = \dots \quad (\text{eq. 4})$$

Once again, many authors and organisations indicate rate constant values or temperature dependence laws for the reactions involved in the most important atmospheric pollutant transformations [4,6].

## 2.2- Formulation for the IAQ analysis

In the field of indoor air quality analysis, numerical tools seek to predict the dynamic change of zone average air pollutant concentrations by considering all kinds of transports. As a result, if the rate expressions presented above in the conventional kinetic format are converted into mass generation or removal rate expressions, the contributions of ventilation (or infiltration), internal sources (or sinks) and homogeneous chemistry to the concentration change of each element  $p$  of a well mixed single zone, can be represented by the following mass conservation equation:

$$\rho V \frac{dC_p}{dt} = \dot{m}(C_{o,p} - C_p) + S_p + \sum_{i=1}^{n_p} \left( K_{ip} \prod_{j=1}^{n_i} C_j \right) \quad (\text{eq. 5})$$

with:  $\rho$  : Density of air ( $\text{kg} \cdot \text{m}^{-3}$ )  
 $V$  : Room volume ( $\text{m}^3$ )  
 $C_p$  : Mass concentration of element  $p$  ( $\text{kg}_p \cdot \text{kg}_{\text{air}}^{-1}$ )  
 $t$  : time (s)  
 $\dot{m}$  : Ventilation or infiltration air flow rate ( $\text{kg} \cdot \text{s}^{-1}$ )  
 $C_{o,p}$  : Outdoor concentration of  $p$  ( $\text{kg}_p \cdot \text{kg}_{\text{air}}^{-1}$ )

- $S_p$ : Internal production or removal of  $p$  ( $\text{kg.s}^{-1}$ )  
 $K_{ip}$ : Composite term containing the rate constant of reaction  $i$  (unit depends on the nature of reaction  $i$ )  
 $n_p$ : Number of reactions involving  $p$   
 $n_i$ : Number of reactive species involved in reaction  $i$

As one can note, the gathering of all the mass conservation equations leads to a set of differential equations within which bimolecular and termolecular kinetics introduce non-linearities and impose that all the reactive element concentrations (pollutants and non pollutants) be calculated. As some of these species can have very short lifetimes, the system can moreover be very stiff. In our program, we have chosen to solve it by the BULIRSH-STOER algorithm using the BADER and DEUFLHARD semi-implicit discretization scheme [7] in order to avoid too long calculation times and convergence problems.

### 3- SIMULATION CONDITIONS

#### 3.1- Chemical mechanism

As a first application of the code, we focused our attention on the prediction of nitrogen monoxide (NO), nitrogen dioxide (NO<sub>2</sub>), ozone (O<sub>3</sub>), sulphur dioxide (SO<sub>2</sub>) and carbon monoxide (CO) indoor concentrations which are frequently used to characterise the outdoor pollution level.

By rejecting all thermal reactions which can not take place under temperature and pressure conditions of the lower troposphere and all photochemical reactions presenting nil absorption cross sections or quantum yields in the wavelength band [280 nm, 350 nm] (the solar radiation cutting threshold of the window is assumed to be 350 nm), we then selected 22 reactions in ATKINSON and al's [6] atmospheric kinetic mechanism (table 1).

$\text{O}_3 + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$\text{N}_2\text{O}_5 + \text{SO}_2 \rightarrow \text{N}_2\text{O}_4 + \text{SO}_3$	$\text{NO}_3 + \text{NO}_2 \rightarrow \text{NO} + \text{NO}_2 + \text{O}_2$
$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$	$\text{O}_3 + \text{SO}_2 \rightarrow \text{O}_2 + \text{SO}_3$	$\text{NO}_3 + \text{NO}_2(+\text{M}) \rightarrow \text{N}_2\text{O}_5(+\text{M})$
$\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$	$\text{NO}_2 + \text{SO}_2 \rightarrow \text{NO} + \text{SO}_3$	$\text{N}_2\text{O}_5(+\text{M}) \rightarrow \text{NO}_2 + \text{NO}_3(+\text{M})$
$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$\text{NO}_3 + \text{SO}_2 \rightarrow \text{NO}_2 + \text{SO}_3$	$\text{O} + \text{NO}(+\text{M}) \rightarrow \text{NO}_2(+\text{M})$
$\text{O}_3 + \text{NO}_2 \rightarrow \text{NO}_3 + \text{O}_2$	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$	$\text{O} + \text{NO}_2(+\text{M}) \rightarrow \text{NO}_3(+\text{M})$
$\text{O} + \text{NO}_3 \rightarrow \text{O}_2 + \text{NO}_2$	$\text{NO}_2 + h\nu \rightarrow \text{NO} + \text{O}$	$\text{O} + \text{SO}_2(+\text{M}) \rightarrow \text{SO}_3(+\text{M})$
$\text{O} + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2$	$\text{O} + \text{O}_2(+\text{M}) \rightarrow \text{O}_3(+\text{M})$	$\text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2$
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$		

*Table 1: Selected indoor homogeneous reactions*

Table 1 shows that a dynamic prediction of the 5 pollutant indoor concentrations requires the knowledge of the oxygen atom (O), oxygen molecule (O<sub>2</sub>), nitrate radical (NO<sub>3</sub>), dinitrogen pentoxide (N<sub>2</sub>O<sub>5</sub>) and sulphur trioxide (SO<sub>3</sub>) concentrations in air. As the O<sub>2</sub> concentration can be considered as constant, we have thus to deal with 9 different species.

Because the selected kinetic mechanism includes the photochemical dissociation reaction of  $\text{NO}_2$ , indoor actinic irradiance had moreover to be assessed each time step in order to determine the transformation rate constant. In our program, it is estimated from PETERSON [8] outdoor ground level actinic irradiance and reflection coefficient numerical results by considering the sky as an isotropic diffuser, a constant 0.5 short wavelength absorption coefficient of the indoor walls and typical transmission characteristics for a single glass window.

### 3.2- Reference building

The reference building is a  $50 \text{ m}^3$  single zone office building whose  $2.5 \text{ m}^2$  window area is facing south. The HVAC system allows the airflow rate to vary from 0.5 ach to 3 ach.

Concerning the occupancy scheme and the resulting indoor emission rates, we consider two extreme cases: in the first one, no indoor pollution sources exists while in the second one, the room is occupied by 8 smokers between 8 and 12 am and 2 and 6 pm (the corresponding tobacco smoke CO and  $\text{NO}_2$  emission rates are given by COHAS [9]). In both cases, the indoor temperature is assumed to be  $25^\circ\text{C}$  all the day long.

### 3.3- Outdoor concentrations

Apart from the indoor emission rates, the modelling of indoor homogeneous chemistry requires the specification of all the species outdoor concentrations as boundary conditions. If, on the one hand, more and more data about ambient pollutant concentrations is now available, the non pollutant outdoor concentrations are rarely measured and may on the other hand be very difficult to specify. Fortunately, in our case, the reactions within which O,  $\text{NO}_3$ ,  $\text{N}_2\text{O}_5$  and  $\text{SO}_3$  are involved are so quick that it may be assumed they proceed instantaneously to steady state. Their concentration can therefore be related to the pollutants one and calculated at each timestep by the so-called pseudo steady state approximation.

## 4- RESULTS

The need of taking into account gas-phase chemical reactions into the IAQ simulation tools can easily be investigated by calculating the indoor contaminant concentrations with and without reactive model, that is to say by considering or not the last term of the conservation equation 5. These simulations have been carried out by considering a 24 day simulation period (15th July - 8th August 1994) and by using the real climatic data and contaminant average hourly outdoor concentrations (measured downtown La Rochelle by the Poitou-Charentes Regional Agency for Air Quality) as boundary conditions of the model.

The comparison of the two simulations results first demonstrated the low influence of homogeneous gas-phase chemistry on indoor CO and  $\text{SO}_2$  concentration levels: no significant differences could have been observed for

these species which, as indicated by the selected kinetic mechanism, are involved in very few reactions. On the other hand, we could notice great discrepancies between the predicted NO, NO<sub>2</sub> and O<sub>3</sub> concentrations with and without taking into account the homogeneous chemical processes.

As indoor as well as outdoor air quality is most of time assessed by comparing time weighted average concentrations with their corresponding safety threshold limit values, the observed differences have been related to these maximum allowable concentrations in order to define an IAQ misjudgement index when chemical kinetics contribution to the pollutants transport is neglected:

$$E_{\Delta t}^p = 100 \frac{C_{\Delta t,1}^p - C_{\Delta t,0}^p}{LRV_{\Delta t}^p} \quad (\text{eq. 6})$$

with:  $E_{\Delta t}^p$  : Indoor air quality misjudgement index regardless of pollutant  $p$  and exposure time  $\Delta t$  (%)

$C_{\Delta t,1}^p$  : Average concentration of pollutant  $p$  during period  $\Delta t$  with reactive model ( $\mu\text{g.m}^{-3}$ )

$C_{\Delta t,0}^p$  : Average concentration of pollutant  $p$  during period  $\Delta t$  without reactive model ( $\mu\text{g.m}^{-3}$ )

$LRV_{\Delta t}^p$  : Limited Risk concentration Value for a  $\Delta t$  exposure time to pollutant  $p$  ( $\mu\text{g.m}^{-3}$ )

As a result, figure 1 represents the hourly variations of  $E$  (averaged over the 24 day period) for the three reactive pollutants, the two occupancy schemes of the room and the minimum or maximum airflow rates while figure 2 represents the average daily values of the indices as a function of the airflow rate for a normal 8 hour workday. In both cases, the selected  $LRV$  values correspond to the World Health Organisation recommendations [10].

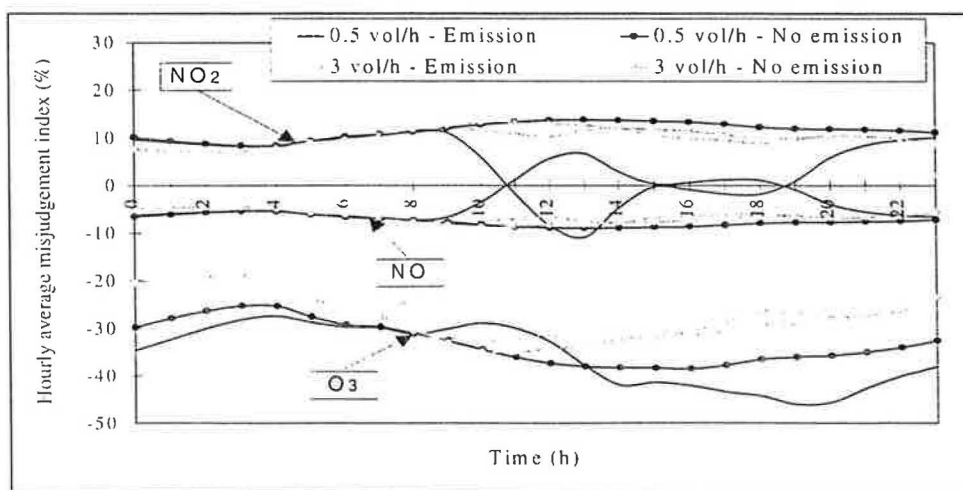


Figure 1: Average hourly misjudgement index as a function of time



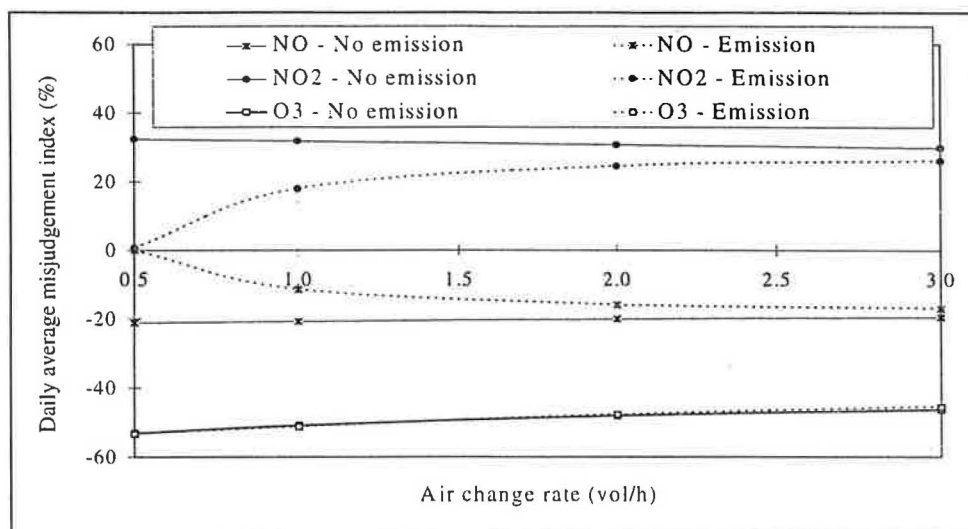


Figure 2: Average daily misjudgement index as a function of the airflow rate

Figure 1 shows that the absence of reactive term in the conservation equations of nitrogen oxides can either contribute to an overestimate ( $E < 0$ ) or an underestimate ( $E > 0$ ) of their hourly concentrations depending on the available amounts of chemically reactive species in the room. Nevertheless, we have to point out that the case considering a 0.5 ach airflow rate when smoking is allowed does not represent realistic conditions as indoor  $\text{NO}_2$  concentrations reach peaks corresponding to three times the LRV. In more realistic situations, i.e. in more common indoor concentration ranges, real NO and  $\text{NO}_2$  concentrations are respectively and systematically overestimated and underestimated by a quasi constant 10% of their LRV.

Contrary to nitrogen oxides, the most important reactions involving ozone contribute to its extinction. Neglecting these reactions thus always leads to an overestimate of  $\text{O}_3$  concentrations: the hourly  $E^{\text{O}_3}$  values vary from -20% to -45% depending on the air flow rate and the kind of emission.

If we except the unrealistic cases of high tobacco smoke emission and low ventilation airflow rates where near zero values of the daily indices  $E^{\text{NO}}$  and  $E^{\text{NO}_2}$  result from a balance between hourly overestimates and underestimates, figure 2 indicates that the risk assessment misjudgement may be more serious if indoor air quality is estimated by reference to the average daily pollutant concentrations. Even if the absolute value of the indices decreases when the ventilation airflow rate increases, the NO,  $\text{NO}_2$  and  $\text{O}_3$  concentration differences respectively remain close to 20%, 30% and 50% of their LRV.

## 5- CONCLUSION

In this paper, we have investigated the need of taking into account homogeneous chemistry processes in IAQ simulation tools by referring to the

way indoor air quality is currently assessed, i.e. by relating each hourly and daily average pollutant concentration to its corresponding safety threshold value. We showed by this mean that contrary to sulphur dioxide and carbon monoxide, nitrogen oxides and ozone cannot be considered as passive compounds: neglecting their chemical interactions may lead to significative prediction errors and invalidate indoor air quality analysis at the root (even if it does not affect the room total amount of pollutants prediction as NO, NO<sub>2</sub> and O<sub>3</sub> combine each other).

Finally note that these results only compose the starting point of a larger study including the identification of the most important reactions, an analysis of the influence of temperature and window area of the room on indoor pollutant concentrations and an accurate dynamic modelling of heterogeneous processes. More information on this topic is thus available in ref. [11].

## REFERENCES

- [1] NAZAROFF W.W., CASS G.R. Mathematical Modelling of Chemically Reactive Pollutants in Indoor Air. *Environmental Science and Technology*, 1986, Vol. 20, p. 924-934
- [2] WESCHLER C.J., BRAUER M., KOUTRAKIS P. Indoor ozone and nitrogen dioxide: A potential pathway to the generation of nitrate radicals, dinitrogen pentoxide, and nitric acid indoors. *Environmental Science and Technology*, 1992, Vol. 26, p. 179-184
- [3] AXLEY J.W., HARTZELL A.L., PEAHEY J.B. Transport of Reactive Gas-Phase Outdoor Air Pollutants Indoors. *Indoor Environment*, 1994, Vol. 3, p. 266-273
- [4] SEINFELD J.H. *Atmospheric Chemistry and Physics of Air Pollution*. New York : Editions Wiley and Sons, 1986. 738 p.
- [5] FINLAYSON-PITTS B.J., PITTS J.N. *Atmospheric Chemistry: Fundamentals and Experimental Techniques*. New York : Editions Wiley and Sons, 1986. 1098 p.
- [6] ATKINSON R. and al. Evaluated Kinetic and Photochemical Data for Atmospheric Chemistry. *Journal of Physical and Chemical Reference Data*, 1992, Vol. 21, N° 6, p. 1125-1568
- [7] PRESS W.H., TEUKOLSKY S.A., VETTERLING W.T., FLANNERY B.P. *Numerical Recipes in Fortran*. 2nd Edition. Cambridge (GB) : Cambridge University Press, 1992. 963 p.
- [8] PETERSON J.T. *Calculated Actinic Fluxes (290-700 nm) for Air Pollution Photochemistry Applications*. Washington DC (USA) : U.S. Environmental Protection Agency Rapport n° EPA-600/4-76-025, 1976
- [9] COHAS M. *Contribution à l'amélioration de la qualité de l'air intérieur des locaux d'habitation*. Thèse de doctorat: Université Pierre et Marie Curie - Paris VI, 1994. 210p.
- [10] W.H.O. *Indoor Air Quality: biological contaminants - Report on a WHO meeting*. Copenhagen (DK) : World Health Organization Regional Publications, European Series n° 31, 1988. 67 p.
- [11] BLONDEAU P. *Contribution à l'évaluation de la qualité globale des ambiances habitées - Rôle de la ventilation en période estivale*. PhD report: University of La Rochelle, 1996. 281 p.