1 NO_2 chemistry scheme in OSPM and other Danish models

Note prepared by Ruwim Berkowicz, Matthias Ketzel, Per Løfstrøm and Helge Rørdam Olesen. National Environmental Research Institute, Aarhus University. March 2011.

URL:
http://www.dmu.dk/en/air/models/background/no2chemistry/ (introduction)
http://www2.dmu.dk/AtmosphericEnvironment/Docs/NO2scheme.pdf (document)

1.1 Introduction

The present note briefly explains the scheme for NO_2 chemistry applied in the Danish local scale models OSPM, OML-Multi, OML-Highway and UBM. It will be referred to as the OSPM scheme. Furthermore, the note illustrates the results of the scheme and the consequences of certain simplifications (assuming photochemical equilibrium, respectively using the 'ozone limited approximation').

The note has been written to supplement the description of the OSPM scheme which is given in the Fairmode Guidance document on modelling of NO_2 by Denby et al. (2010). Here we refer to a set of basic equations for NO_X chemistry given in that document. For convenient reference, the equations and the accompanying explanation are reproduced here in the following section (Section 1.2). The actual explanation of the OSPM scheme follows in Section 1.3.

1.2 The basic equations

This section recapitulates the equations for the chemical reactions for NO_X chemistry. It is taken from the document by Denby et al. (2010).

First, the main features involved are explained. Next, the actual equations are presented.

Some atmospheric compounds have such slow chemical reaction rates that they can essentially be treated as inert tracers when applying air quality modelling on the urban scale. However, this is not the case for Nitrogen dioxide (NO_2) since it is a species that is rapidly formed from Nitrogen oxide (NO) through its reaction with ozone (O_3). Indeed, if this is the only important reaction, as it is at night time under most urban conditions, then NO will be transformed to NO_2 until all the NO is converted to NO_2 or until all the ozone is used up (*ozone limited approximation*). Given typical concentrations in the urban atmosphere this reaction takes place on a time scale of just a few minutes but this is dependent on concentrations and also on temperature. The rate of this reaction is important for modelling since the time it takes for exhaust emissions of NO (and NO_2) to reach a traffic monitoring station is only a few seconds whilst the time it takes for emissions to reach an urban background station is a few tens of minutes – 1 hour. As a result the proportional con-

centration of NO_2, compared to NO, near to traffic sources is generally lower than at urban background stations.

In addition to the conversion of NO to NO_2 the other major daytime reaction that affects NO_2 is the destruction of NO_2 by photolysis, i.e. sunlight breaks the NO_2 molecule into an NO molecule and a ground state oxygen molecule. This reaction rate may also be quite fast (10 – 30 minutes) in sunny environments. As a result a balance can be reached within an hour such that the production of NO_2 is balanced by its destruction. This is called the photostationary state or the *photochemical steady state*.

On longer time scales, and dependent on the amount of hydrocarbons emitted in the atmosphere, there may also be a chemical production of NO_2 that results from the reaction of peroxyl radicals (the result of the photolysis of hydrocarbons) and NO (equation (1-4) in the following). This reaction takes place with a time scale of hours and can have an important impact on both NO_2 and eventually ozone concentrations in the urban environment.

The eventual fate of NO_2 is determined by a number of reactions but the most important of these is the conversion of NO_2 to Nitric acid (HNO_3) (Equation (1-5)) which occurs at the rate of several hours to a day. Nitric acid is readily removed from the atmosphere through deposition processes. As a result of this time scale, NO_2 has an atmospheric lifetime of just a day or two, and as such is not transported over large distances.

1.2.1 Important chemical reactions for NO_2 in the urban environment

The creation of NO_2 by the oxidation of NO with O_3 (Equation 1-1) is a very fast reaction that takes only a few minutes under typical urban atmospheric conditions. The production of NO_2 is balanced by its decay in the presence of sunlight (1-2), where $h\nu$ is the energy from a photon with a wavelength λ < 420 nm, and the subsequent creation of ozone (1-3) with the generated ground state oxygen molecule (O). This last reaction requires some other molecule (M) for the reaction to occur.

$$O_3 + NO \rightarrow NO_2 + O_2 \qquad (1\text{-}1)$$

$$NO_2 + h\nu \rightarrow NO + O \qquad (1\text{-}2)$$

$$O + O_2 + M \rightarrow O_3 + M \qquad (1\text{-}3)$$

In urban environments the emission of hydrocarbons, mostly in the form of volatile organic compounds, and the subsequent production of peroxy radicals RO_2 (including hydrogen peroxide HO_2), generated by the oxidation of these hydrocarbons, will also affect the oxidation of NO to NO_2. Here R represents any configuration of a range of hydrocarbons after the removal of a hydrogen atom H. The NO will react with the peroxy radicals in the following way.

$$RO_2 + NO \rightarrow NO_2 + RO \qquad (1\text{-}4)$$

The rates of these reactions will vary dependent on the concentrations of the peroxy radicals but in urban areas the reaction rates are typically of an hour or more. As a result they can make a significant contribution to the NO_2 concentrations, and eventually O_3 concentrations through equations (1-2) and (1-3)

Though there are a number of alternative reactions, the eventual loss of NO_2 will go through reactions such as

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (1\text{-}5)$$

This last reaction has a rate of between a few hours and a number of days, dependent on the availability of OH. This is one of the reactions that are responsible for the short lifetime of NO_2 in the atmosphere (~ one day).

As a consequence of equations (1-1) – (1-5) the rate at which NO_2 will change its concentration is given by its production (equations (1-1) and (1-4)) minus its loss (equations (1-2) and (1-5)):

$$\frac{d[NO_2]}{dt} = k_1[NO][O_3] + k_4[NO][RO_2] - J[NO_2] - k_5[NO_2][OH] \qquad (1\text{-}6)$$

where k_i is the reaction rate for Equations i and J is the photolysis rate coefficient for Equation (1-2). J depends on the amount of sunlight and this often represented by the height of the sun in the sky, or its inclination.

1.2.2 Photochemical steady state solution

Some local and urban scale models make use of the steady state solution to equations (1-1) – (1-3). The steady state solution is quite convenient because it allows the modelling of O_x ($O_x = NO_2 + O_3$) and NO_x ($NO_x = NO_2 + NO$) concentrations as non-reactive tracers, since these are conserved in Equations (1-1) – (1-3). After transport and diffusion of the O_x and NO_x concentrations, NO_2 concentrations can be calculated using the steady state solution to be presented as equation (1-9). This makes the method attractive since Gaussian type models, that only work on non-reactive species, can transport and diffuse O_x and NO_x and then calculate NO_2 from their resulting values

The basic photochemical steady state solution for NO_2 is obtained by ignoring the contribution of the peroxyl radicals (RO_2) and the hydroxyl radical (OH) to the production and loss of NO_2 and by setting the rate of change of NO_2 in Equation (1-6) to be zero, i.e. no change in NO_2. Under this condition we find a relationship between the compounds of NO_2, NO and O_3 that is given by the following:

$$[NO_2] = \frac{k_1}{J}[NO][O_3] \qquad (1\text{-}7)$$

Equation (1-7) tells us the relative concentrations but does not provide us with a solution for NO_2. To find a solution we make use of the fact that NO_x ($[NO_x] = [NO] + [NO_2]$) and O_x ($[O_x] = [NO_2] + [O_3]$) concentra-

tions are conserved in Equations (1-1) – (1-3) and these can be treated as non-reactive tracers. As a result we can write a steady state solution for NO_2 as:

$$f_{NO2}{}^2 - f_{NO2}(1 + f_{Ox} + J') + f_{Ox} = 0 \qquad (1\text{-}8)$$

where

$$f_{NO2} = \frac{[NO_2]}{[NO_x]}, \quad f_{Ox} = \frac{[O_x]}{[NO_x]} \text{ and } \quad J' = \frac{J}{k_1[NO_x]}$$

This has a solution of the form

$$f_{NO2} = \frac{(1 + f_{Ox} + J') - \sqrt{(1 + f_{Ox} + J')^2 - 4f_{Ox}}}{2} \qquad (1\text{-}9)$$

This equation describes the *photochemical steady state*, which can be further simplified to the *ozone limited approximation* in the case when destruction of NO_2 by sunlight is ignored.

1.3 The OSPM scheme

The previous section recapitulated the equations for NO_X chemical reactions and a basic steady state solution. The present section explains the steady state solution applied in the OSPM model, which takes turbulent mixing into account.

In order to include the effect of turbulent mixing, which occurs on similar time scales to the chemical reactions, Hertel and Berkowicz (1989) introduced a mixing (exchange) rate into Equations (1-1) – (1-3). This was applied in street canyon model OSPM (Berkowicz, 1998).

Taking into account that the reaction (1-3) is very fast, the set of the chemical reactions is simplified to

$NO + O_3 \longrightarrow NO_2$

$NO_2 + hv \longrightarrow NO + O_3$

This leads to the following rate equations, including the additional exchange terms:

$$\frac{d[NO]}{dt} = -k_1[NO][O_3] + J[NO_2] + \frac{[NO]_v}{\tau} + \frac{[NO]_b - [NO]}{\tau}$$

$$\frac{d[NO_2]}{dt} = k_1[NO][O_3] - J[NO_2] + \frac{[NO_2]_v}{\tau} + \frac{[NO_2]_b - [NO_2]}{\tau}$$

$$\frac{d[O_3]}{dt} = -k_1[NO][O_3] + J[NO_2] + \frac{[O_3]_b - [O_3]}{\tau}$$

All terms with the index b refer to background concentrations, while index v refers to contributions due to direct emissions. The terms without index refer to the actual (total) concentrations in the street. Note that $[NO_x]_v = [NO]_v + [NO_2]_v$ and $[NO_2]_v = f_d[NO_x]_v$. f_d is the fraction of NO_x which is directly emitted as NO_2. The exchange terms are governed by the time scale τ.

Assuming a steady-state condition (all time derivatives set to zero) leads to the following analytical solution to the above set of equations. This equation represents the 'OSPM method':

$$[NO_2] = 0.5\left(B - \left(B^2 - 4\left([NO_x] \cdot [NO_2]_o + [NO_2]_n \cdot D\right)\right)^{1/2}\right) \qquad (1\text{-}10)$$

where

$[NO_2]_n = [NO_2]_v + [NO_2]_b$

$[NO_2]_o = [NO_2]_n + [O_3]_b$

$B = [NO_x] + [NO_2]_o + R + D$

The photochemical equilibrium coefficient is given by $R = J/k_1$, while $D = (k_1 \tau)^{-1}$ is the exchange rate coefficient.

Although the method was originally developed for street canyon applications and will be referred to as the OSPM method, it is now used for all Danish local scale models i.e. OSPM (Berkowicz, 2000a), OML-Multi (Olesen et al, 2009), OML-Highway (Berkowicz et al., 2007) and UBM (Berkowicz, 2000b). The only difference between the different models is the procedure used for calculation of the time scale τ.

In the case of application for street canyons (OSPM), the time scale τ refers to pollutants residence time in the street. For the urban scale (OML and UBM), τ is the transport time ($\tau = x/u$). In the case of multiple sources (OML-Multi, OML-Highway and UBM) τ is calculated as a NO_x weighted average over all the sources.

For the special case when τ is very large (D=0), the above formula converges to the photochemical equilibrium formula (1-9), while the ozone limited approximation is obtained when the photolysis process is also neglected (R=0).

Application of the OSPM method is illustrated in Figure 1.1 for two years for the street Jagtvej in Copenhagen. Additionally, the results obtained using the photochemical equilibrium and ozone limited approximations are shown. Only the NO_2 conversion formulas are tested here, so no dispersion modelling is involved. The NO_x values shown here refer to the measured concentrations in the street, while the NO_2 values are measured (black symbols), respectively modelled according to Equation (1-10) (red symbols). The difference in behaviour observed between the two years is mainly due to the much larger fraction of directly emitted NO_2 in the year 2006 compared to 1997. This fraction is computed hourly based on traffic composition, and the yearly average is indicated in the figures by the slope of the dashed lines. A summary of the annual average values is presented in Table 1.1. The OSPM method results are in a

reasonable agreement with the observed NO_2/NO_x relationships. The photochemical equilibrium and especially the ozone limited approximations result generally in too high values.

Table 1.1. Annual average values derived from the hourly data presented in the figure.

Year	NO_X measured (ppb)	NO_2 measured (ppb)	NO_2 modelled (ppb)	NO_2 photoch. equilibrium (ppb)	NO_2 ozone limited (ppb)	f_d (%)
1997	70.7	22.7	24.9	30.4	33.1	5.1
2006	59.9	27.6	27.4	33.8	37.0	14.7

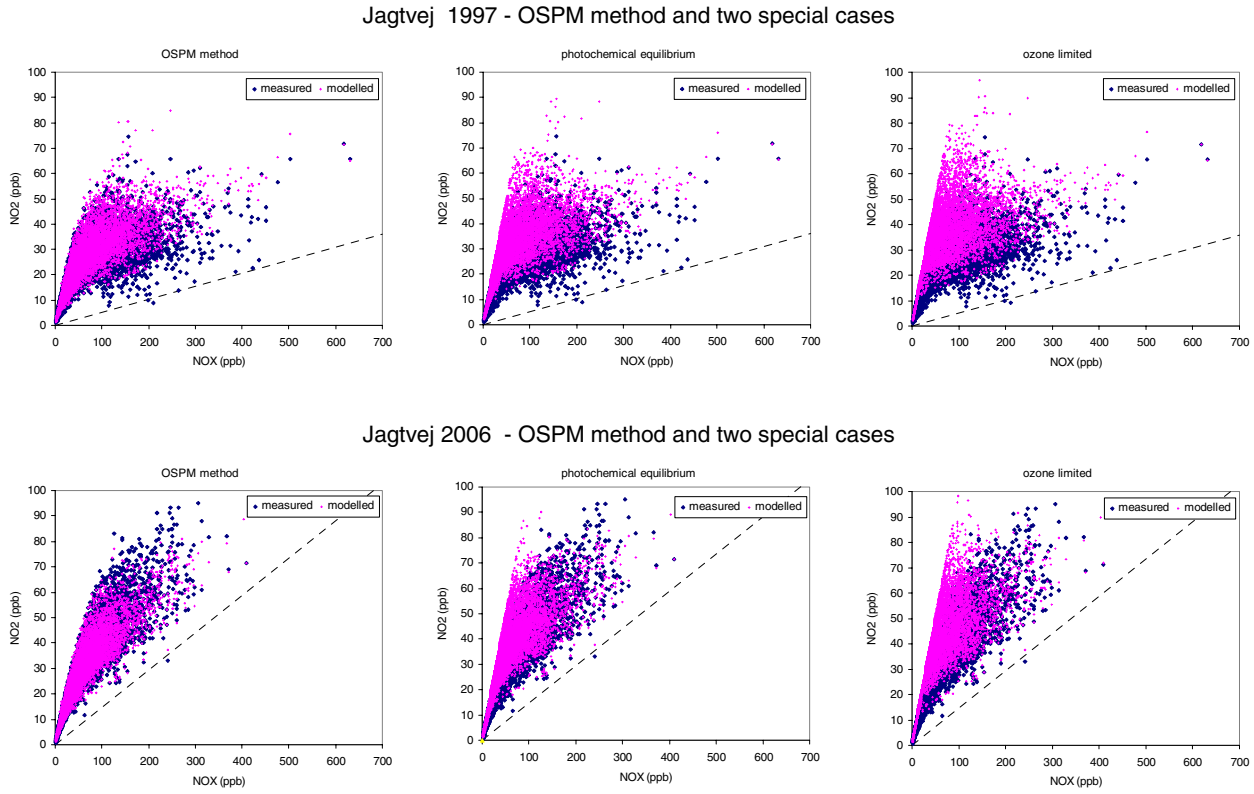

Figure 1.1. The upper row shows data for the busy street of Jagtvej in Copenhagen for 1997, while the lower shows 2006-data. Each data point in the figure represents a set of NO_X and NO_2 values for one hour. The black symbols indicate measured values, while the red represent NO_2 computed according to equation (1-10), the 'OSPM method'. Some of the black symbols are hidden behind red symbols.

The graphs in left column display results for the proper OSPM method, while the two subsequent columns show results for photochemical equilibrium and the ozone limited approximation, respectively. These can be derived as special cases of the OSPM method. The slope of the dashed lines indicates the fraction of directly emitted NO_2 from traffic for the two years.

1.4 References

Berkowicz, R. (1998). Street Scale Models, In J. Fenger, O. Hertel and F. Palmgren (eds.), Urban Air Pollution - European Aspects, Kluwer Academic Publishers, pp. 223-251.

Berkowicz, R. (2000a): OSPM – a Parameterised Street Pollution Model. Environmental Monitoring and Assessment 65: 323-331, 2000.

Berkowicz, R. (2000b). A Simple Model for Urban Background Pollution. Environmental Monitoring and Assessment. Vol. 65, pp 259-267.

Berkowicz R., Løfstrøm P., Ketzel M., Jensen S.S. and Hvidberg M. 2007. OML Highway – Phase 1: Specifications for a Danish Highway Air Pollution Model. NERI Technical Report no. 633.
http://www.dmu.dk/Pub/FR633.pdf

Denby, BR, Douros, I, Fragkou, L (2010, draft version 2.2): Modelling of Nitrogen Dioxide (NO_2) for air quality assessment and planning relevant to the European Air Quality Directive.
http://fairmode.ew.eea.europa.eu/fol404948/guidance-document/FAIRMODE_NO2_Guidance_document_v2_2.pdf (link valid February 2011; if it fails check http://fairmode.ew.eea.europa.eu/ for a newer version).

Hertel, O. and Berkowicz, R. (1989). Modelling NO_2 concentrations in a street canyon, DMU Luft A-131, 31p. NERI, P.O.Box 358, DK4000 Roskilde, Denmark.

Olesen, H.R., Berkowicz, R.B, Løfstrøm, P., 2007: OML: Review of model formulation. National Environmental Research Institute, Denmark. 130pp. NERI Technical Report No. 609, http://www.dmu.dk/Pub/FR609.pdf