Documentation Chemistry Module DALES V3.2

Kees van den Dries and Jordi Vilà-Guerau de Arellano

Meteorology and Air Quality Section
Wageningen University (The Netherlands)

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1 Introduction

DALES is equipped with the necessary tools to study the chemical transformations of atmospheric compounds within the boundary layer. This can be done by switching on the CHEMICAL MODULE.

In this documentation, we describe the two main parts of the module: the chemical solver TWOSTEP and the reaction rate calculation depending on thermodynamic conditions. Thereafter, we explain the input files and specific options of the chemistry module. We close it by showing the results of two numerical experiments which serve as an example of the DALES performance: (1) turbulent reacting flow under clear conditions (CABAUW case) and (2) turbulent reacting cases in cloudy boundary conditions (shallow cumulus ARM case).

2 Chemical solver

2.1 Description

The conservation equation for an atmospheric compound reads:

$$\frac{\partial \widetilde{\varphi}}{\partial t} = -\frac{\partial \widetilde{u_j}\widetilde{\varphi}}{\partial x_j} - \frac{\partial R_{u_j,\varphi}}{\partial x_j} + \mathcal{S}_{\varphi} \tag{1}$$

If the atmospheric compounds react, the source or sink term in Equation 1 needs to be included in the numerical calculation. For a generic compound φ_l, this reaction term reads:

$$\mathcal{S}_{\varphi_l} = \mathcal{P}(t, \varphi_m) - \mathcal{L}(t, \varphi_m)\varphi_l \qquad m = 1, ..., n. \tag{2}$$

The respective terms $\mathcal{P}(t, \varphi_m)$ and $\mathcal{L}(t, \varphi_m)$ are nonnegative and represent production and loss terms for the compound φ_l reacting on time t with the n species φ_m.

In DALES, we solve the term $\mathcal{S}_{\varphi_l}$ using the chemical solver TWOSTEP extensively described and tested by Verwer (1994) and Verwer and Simpson (1995). In short, this chemical solver is an implicit method with second-order accuracy based on the two-step backward differentation formula. Since in atmospheric chemistry we are dealing with chemical system characterized by a wide range of chemical time scales, *i.e. stiff system of ordinary differential equations*, the two-step solver is able to adjust the time step depending on the chemical reaction rate.

2.2 Algorithm: TWOSTEP

Here, we follow closely the description by Verwer and Simpson (1995). The two-step method is based on the variable-step, second-order backward differentiation (BDF) formulas. This formula reads (for sake of notation simplicity φ_l is written as y):

$$y^{n+1} = Y^n + \gamma\ \tau\ f(t_{n+1}, y^{n+1}) \tag{3}$$

where

$$\tau = t_{n+1} - t_n \tag{4}$$

$$\gamma = \frac{c+1}{c+2} \tag{5}$$

$$c = \frac{t_n - t_{n-1}}{t_{n+1} - t_n} \tag{6}$$

$$Y^n = \frac{(c+1)^2 y^n - y^{n-1}}{c^2 + 2c}. \tag{7}$$

It is selected a second-order formula in view of the modest accuracy requirement. The scheme can be extended to high-order BDF formulas. Expression 3 of y^{n+1} can be written as:

$$y^{n+1} = F(y^{n+1}) = \frac{Y^n + \gamma\ \tau\ \mathcal{P}(t_{n+1}, y^{n+1})}{I + \gamma\ \tau\ \mathcal{L}(t_{n+1}, y^{n+1})} \tag{8}$$

where I is the identity matrix.

The iteration number is prescribe beforehand and the final iterate is assigned to be the new approximation of y^{n+1} at the new time point t_{n+1}. Both variable and constant step-sizes can be used. In the selection of the variable step-size, it is used the local error indicator (E):

$$E^{n+1} = \frac{2}{c(c+1)} \left(c y^{n+1} - (1+c) y^n + y^{n-1} \right). \tag{9}$$

Considering the weighted error norm

$$||E^{n+1}||_w = max(|E_k^{n+1}/W_k^n) \tag{10}$$

and

$$W_k^n = atol_k + rtol_k |y^n|, \tag{11}$$

where $atol_k$ and $rtol_k$ are the componentwise defined absolute and relative error tolerance to be specified. If $||E^{n+1}||_w \leq 1.0$, then the integration step is accepted and otherwise rejected. The new step-size τ_{new} is estimated by the common formula

$$\tau_{new} = max \left(0.5, min \left((2.0, \frac{0.8}{\sqrt{||E^{n+1}||_w}} \right) \right) \tau_{old}. \tag{12}$$

The step-size is further constrained by a prescribed minimal and maximal value. If two successive rejections occur we simply restart the process. Hence, we then define τ such that the weighted error norm is equal to one, *i.e*

$$\tau = min \left(\frac{W_k^0}{|f_k(t_0, y^0)|} \right). \tag{13}$$

Figure 2.2 shows the subroutines included in the chemistry module. At the subroutine TWOSTEP the expressions and variables have been named differently and adapted from the paper. Below we write down the main expressions.

Expression (7) reads:

$$ysum = a1y1 + a2 * yold, \tag{14}$$

where

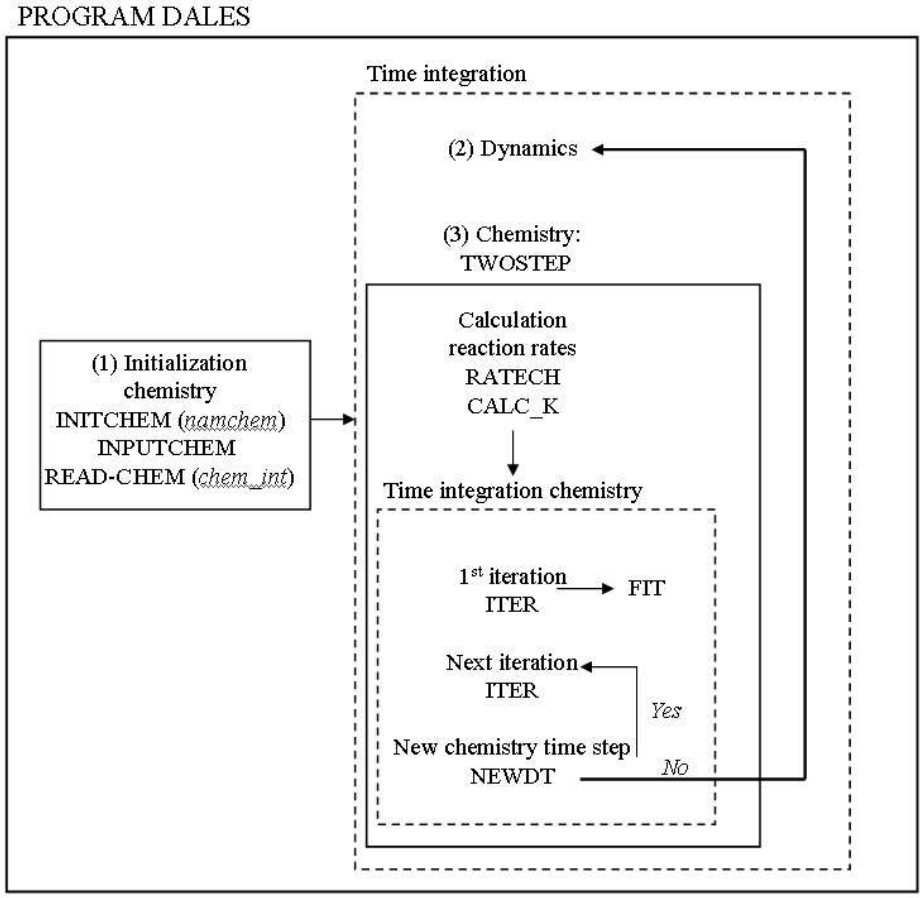

Figure 1: Flow chart of the chemistry module. The subroutines to initialize the module are INITCHEM, INPUTCHEM and READCHEM (reads the chemical mechanism specified at the file chem.inp). The chemical solver TWOSTEP is done after all the dynamics have been done. It includes: (a) calculation of the reaction rate RATECH and CALCK, and (b) the iteration procedure ITER and the calculation of the new time step NEWDT.

$$a1 = \frac{(c+1)^2}{c^2+2c} \qquad a2 = \frac{-1}{c^2+2c} \qquad c = \frac{1}{ratio} \qquad ratio = \frac{t_{n+1}-t_n}{t_n - t_{n-1}}. \tag{15}$$

The equivalent expression (9) in the subroutine ITER is:

$$ynew = max(0, \frac{ysum + gdtYP}{1 + gdtYL}). \tag{16}$$

The local error indicator (expressions 10 and 11) is

$$ytol = atol + rtol * abs(y) \tag{17}$$

and

$$errtel = max(errtel, abs(\frac{c\ ynew - (1+c)\ y + yold)}{ytol}). \tag{18}$$

Finally, the new time step defined in 12 at the subroutine NEWDT reads:

$$dt = max(0.5, min(2., \frac{0.8}{\sqrt{errlte + eps}} dt). \tag{19}$$

3 Reaction rate calculation

3.1 Description

A simple chemical mechanism can serve us as an introduction of the specific form of $\mathcal{P}(t, \varphi_k)$ and $\mathcal{L}(t, \varphi_k)$. Atmospheric chemistry mechanism are composed by first- and second-order reactions. Third-order reactions normally involve water vapor or an air molecule, *i.e.* nitrogen or oxygen. Due to the much larger concentration of these compounds than the reactant concentration, third-order reaction rates are normally expressed as a pseudo second-order reaction, *i.e* $k_{2nd} = k_{3rd}[M]$ where $[M]$ is a molecule of H_2O or air. Therefore, a generic atmospheric chemical mechanism composed by a first- and a second-order reaction reads:

$$a \xrightarrow{j} b \ + \ c \tag{20}$$

$$b \ + \ c \xrightarrow{k} a, \tag{21}$$

where a, b and c are atmospheric compound concentrations, j and k are the first- and second-order reaction rate. For reactant a the $\mathcal{L}$ and $\mathcal{P}$ are respectively:

$$\mathcal{L} \ = \ -j \tag{22}$$

$$\mathcal{P} \ = \ kbc. \tag{23}$$

The photodissociation rate j depends on the ultraviolet actinic flux and specific photodissociation properties of the compound. Therefore, in DALES j is a function on the diurnal variability (latitude, day of the year) and the presence of clouds. j-values are updated every time step. The cloud influence on the actinic flux is implemented using a function that depends on the cloud optical depth (Eq. 28) (Vilà-Guerau de Arellano et al., 2005). The reaction rate k depends on the absolute temperature, on the water vapor content (only for certain specific reactions) and the pressure. Depending on the reaction, several reaction rate expressions can be specified at DALES. Moreover, The generally very low concentrations of chemical species in the atmosphere allows us to neglect the heating contribution of the reactions on the liquid water potential temperature $\widetilde{\theta}_l$, or on the water content $\widetilde{q}_t$ and $\widetilde{q}_r$.

For the chemical solver, it is essential that the concentration of the species is nonnegative. Therefore, the entire numerical discretization for the reactants, spatial and temporal integration of advection and diffusion and temporal integration of the chemistry, has to satisfy the following three numerical properties: it has to be conservative, monotone and positive defined. Of the advection schemes that are implemented in DALES, the kappa scheme is best suited to enforce monotonicy and po sitivity.

The chemistry module is designed to be very flexible in order to allow study of different chemical mechanisms. Required input parameters include the number of reactant and inert scalars, and of chemical species, their initial vertical profiles and surface fluxes, and a list of chemical reactions, together with the reaction rate functions. More information on the chemistry module can be found at Vilà-Guerau de Arellano et al. (2005) and Vilà-Guerau de Arellano et al. (2009).

3.2 Algorithm: First-order reaction rate

In addition to the diurnal variability dependence on the latitude and day of the year, j-values are strongly perturbed by the presence of clouds. Because clouds alter the different proportions

of direct and diffuse ultraviolet radiation, the actinic flux (and therefore the photolysis rates) has different values below, in, and above the clouds (Madronich, 1987). We have implemented this effect by calculating at every time step a factor below and above the clouds and by applying this factor to the clear sky value of the photolysis rate j_{clear} following Chang et al. (1987):

$$j_{clouds} = F\ j_{clear} \tag{24}$$

Above the cloud, the factor (F) is defined as:

$$F = 1 + \alpha\ (1 - t_r)\ cos(\chi_o). \tag{25}$$

While, below the cloud, F is defined as:

$$F = 1.6\ t_r\ cos(\chi_o). \tag{26}$$

Here, t_r is the energy transmission coefficient for normally incident light, χ_o is the solar zenith angle, and α is a reaction dependent coefficient (for nitrogen dioxide and ozone α=1.2 and 0.7 respectively).

The intermediate values between cloud top and cloud base are calculating by interpolating at the different cloud layers. Based on measurements of $\mathrm{j_{NO_2}}$ (Früh et al., 2000), the linear interpolation assumption likely overestimates the photolysis rate in the middle to lower regions of the cloud while underestimates the photolysis rate near cloud top.

The energy transmission coefficient t_r depends on the cloud optical depth and a scattering phase function asymmetry factor (f) equal to 0.86 for the typical cloud particle size ranges under study (Joseph et al., 1976). The expression reads:

$$t_r = \frac{5\ -\ e^{-\tau}}{[4\ +\ 3\tau(1-f)]}. \tag{27}$$

The cloud optical depth (τ) is calculated according to the expression given by Stephens (1984)

$$\tau = \frac{3}{2}\frac{W}{\rho_l}\ r_e^{-1}, \tag{28}$$

where W is the vertically integrated liquid water ($kg\ m^{-2}$), ρ_l is the water density ($kg\ m^{-3}$) and r_e is the effective radius. Here, we have used a constant value of $r_e = 10\ \mu m$. For clouds characterized by values of $\tau < 5$ and for regions between clouds, we have assumed the photolysis rate of clear sky conditions. Regions between clouds may actually have enhanced photolysis rates due to cloud scattering. Here, we are simply investigating the importance of cloud scattering in the cloud column. Our control simulation includes the modification of photolysis rates due to cloud scattering, while a sensitivity simulation excludes this effect on the chemistry.

3.3 Algorithm: Second-order reaction rate

In DALES, the rate reactions are calculated according to various dependences and functions. The coefficient of these functions are specified in the input file chem.inp. Below, we give the functions included at DALES:

- 1: constant
- 2: the reaction is dependent on temperature according to:

$$k_i = A\ e^{\frac{B}{T}}, \tag{29}$$

  where T is the temperature and A and B are constants.

- 3: the reaction is dependent on temperature according to:

$$k_i = A \left(\frac{T}{B}\right)^C e^{\frac{D}{T}}, \tag{30}$$

where T is the temperature and A, B, C, D are constants.

- 4: the reaction is dependent on temperature according to (notice that by including the air molecule in k_1 this reaction becomes a pseudo **2nd-order reaction** rate):

$$k_i = \left(\frac{k_1 k_2}{k_1 + k_2}\right) G \tag{31}$$

where k_1 and k_2 are defined as:

$$k_1 = A \left(\frac{T}{300}\right)^B e^{\frac{C}{T}}[M] \qquad k_2 = D \left(\frac{T}{300}\right)^E e^{\frac{F}{T}}, \tag{32}$$

where T is the temperature, $[M]$ is the air density, and A, B, C, D, E and F are constants. G is a factor.

Notice that k_1 and k_2 are the equivalent constants of k_0 and k_{inf} in Atkinson et al. (2004).

- 5: the reaction is dependent on temperature according to (notice that by including the air density in k_1 this reaction becomes a pseudo **1st-order reaction rate**):

$$k_i = \left(\frac{k_1 k_2}{k_1 + k_2}\right) G \tag{33}$$

where k_1 and k_2 are defined as:

$$k_1 = A \left(\frac{T}{300}\right)^B e^{\frac{C}{T}}[M] \qquad k_2 = D \left(\frac{T}{300}\right)^E e^{\frac{F}{T}}, \tag{34}$$

where T is the temperature, $[M]$ is the air density, and A, B, C, D, E and F are constants. G is a factor.

Notice that k_1 and k_2 are the equivalent constants of k_0 and k_{inf} in **??**.

- 6: the reaction is dependent on temperature according to (it is a 1st order reaction):

$$k = (k_1 + k_2) k_3 \tag{35}$$

where

$$k_1 = A\, e^{\frac{B}{T}} \qquad k_2 = C\, e^{\frac{D}{T}} \qquad k_3 = E\, e^{\frac{F}{T}}[H_2O] \tag{36}$$

where T is the temperature, $[H_2O]$ is water vapor molecule and A, B, C, D, E and F are constants. G is factor.

- 7: this reaction rate is similar to 3, but for third-order reactions. It reads:

$$k_i = A \left(\frac{T}{D}\right)^C e^{\frac{B}{T}}, \tag{37}$$

where T is the temperature and A, B, C, D are constants.

It has to be mentioned that the code is flexible to introduce new functions to calculate the reaction rate.

The values of the constants and factors are taken from Atkinson et al. (2004) and therefore specified in the following units $s{-}1$ (first-order) and $cm^3 molec^{-1} s{-}1$ (second-order). Since the reactant calculations are carried out in mixing ration units (ppb) at every time step the reaction rate are calculated depending on the pressure level, absolute temperature and specific moisture content. The conversion factor from $molecule/cm^3$ to ppb is based on the ideal gas law reads:

$$k(\frac{1}{ppbs}) = \frac{P(mb)}{T(K)} \frac{N_{Avo}}{R_d} k(\frac{cm^3}{molec\ s}) \frac{1(m^3)}{1\ 10^6(cm^3)}\ 1\ 10^{-9}(ppb) \tag{38}$$

where R_d is the gas constant for dry air 8.314 10^{-2} in $\frac{mb\ m^3}{K\ mol}$ and N_{Avo} is the Avogadro number equal 6.023 10^{23} (mol^{-1}).

4 Input files

In order to use the CHEMISTRY option the following files are needed:

- *chem.inp* The chemical mechanism is specified including the number of species, reactants and the dependences of the reaction rate (see figure 4).

```
# FORMAT OF inputchem
# EVERY ITEM SHOULD BE SEPERATED BY AT LEAST ONE SPACE
# EXCEPT FOR THE COEFFICIENTS IN THE REACTIONS
# PUT NONACTIVE CHEMICAL COMPONENTS WITH COEFFICIENTS IN ()
# and no empty lines are allowed

# The first real line should specify the chemical components
# (the line above it should start with a @) followed by the atol and rtol
# values for each species
#
@  1       2       3       4       5       6       7       8       9       10      11      12      13
  O3      NO      NO2     HNO3    RH      R       HO      HO2     H2O2    CO      CO2     H2O     INERT
  1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5    1e-5
  1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2    1e-2
#
#-------------------------------------------------------------------------------------------------------------
# kr2nd  |Name |Rad |func1|  A    |   B   |   C   |   D   |  E   |   F  |  G   | chemical reaction
#        |     |Dep |     |       |       |       |       |      |      |      | with inactive species
#        |5char|int |int  | real  | real  | real  | real  | real | real | real |          in ( )
#-------------------------------------------------------------------------------------------------------------
# all reactions must have a name
2.396E-13 R_CO   0    1     1.0      1.0     1.0     1.0      1.0    1.0    1.0   HO + CO    -> HO2 + CO2
7.197E-11 R_RH   0    1     1.0      1.0     1.0     1.0      1.0    1.0    1.0   RH + HO    -> HO2 + R
#HxOy
1.0       R_23   0    2    4.8e-11   250     1.0     1.0      1.0    1.0    1.0   HO + HO2   -> H2O + (O2)
1.0       R_25   0    2    1.7e-12   -940    1.0     1.0      1.0    1.0    1.0   HO + O3    -> HO2 + (O2)
1.0       R_26a  0    6    2.2e-13   600   1.9e-33  980    1.4e-21 2200    1.0   2HO2       -> H2O2 + (O2)
1.0       R_28   0    3    2.03e-16  300     4.57   693      1.0    1.0    1.0   HO2 + O3   -> HO + (2O2)
#NOx
1.0       R_43   0    4    3.3e-30   -3.0    0.0    4.1e-11  0.0    0.0    0.4   HO + NO2   -> HNO3
1.0       R_45   0    2    3.6e-12   270     1.0     1.0      1.0    1.0    1.0   HO2 + NO   -> NO2 + HO
#Atkinson
1.0       R_54A  0    2    1.4e-12  -1310    1.0     1.0      1.0    1.0    1.0   NO + O3    -> NO2
#The 2 following reactions are radiation dependent
#exp(-.575)=.562705     Kdiurnal = Kconstant / .562705 if same diurnal funtions as R_NO2
#func1 = 0 => constant K   func = 1 => diurnal K
5.0667e-6 R_O3   1    1      1.0      1.0     1.0     1.0      1.0    1.0    1.0   O3         -> 2HO + (O2)
0.0167    R_NO2  1    1      1.0      1.0     1.0     1.0      1.0    1.0    1.0   NO2 + (O2) -> NO + O3
$ end of chemical reactions specified by $ as first character on line
#
#   function = 0 => Meaning K colum kn2rd in PPB*sec no temp dependence
#   function = 1 => Meaning K colum kn2rd in cm3/molecule*sec no temp dependence
#   function = 2 => K = K (cm3/molecule*sec)
#            MEANING of A..G          K = A * exp (B/T)
#   function = 3 => K = K (cm3/molecule*s)
#            MEANING of A..G          K = A * (T/B)^C * exp (D/T)
#   function = 4 => K = K'* K"/(K'+ K")* G (cm3/molecule*sec)
#            MEANING of A..G          K'= A * (T/300)^B * exp(C/T)[M]      K" = D * (T/300)^E * exp(F/T)    Fc = G
#   function = 5 => K = K'* K"/(K'+ K")* G (/sec)
#            MEANING of A..G          K'= A * (T/300)^B * exp(C/T)[M]      K" = D * (T/300)^E * exp(F/T)    Fc = G
#   function = 6 => K =  (K'+ K")*K'" (cm3/molecule*s)
#            MEANING of A..G          K'= A * exp (B/T) K"= C * exp(D/T)  K" = 1 + E * exp(F/T)[H2O]
#   function = 7 => K = K (cm6/molecule2*s)for above R63Ab reaction K = A * (T/1)^O * exp(O/T)=A*1*1 = A
```

Figure 2: Example of the chemical mechanism included in the input file cheminp.

- *scalar.inp* The initial vertical profiles of the n chemical species are specified
- *namoptions* The CHEMISTRY module is switched on. The surface fluxes of the species are specified.

5 Examples

The semi-complex chemistry (Table 2) which reproduces the diurnal variability of ozone is based on Galmarini et al. (1997); Krol et al. (2000), and it has been updated for this exercise.

Table 2. Chemical reaction scheme used in the numerical experiments of clear (CABAUW) and cloudy (ARM) . The functions used in the calculation of the reaction rate are defined below.

Num	Reaction	Reaction rate function
Diurnal scheme		
R1	$O_3 \stackrel{H_2O}{\rightarrow} 2OH + O_2$	D
R2	$NO_2 \stackrel{O_2}{\rightarrow} NO + O_3$	D
R3	$NO + O_3 \rightarrow NO_2 + O_2$	2
R4	$OH + CO \stackrel{O_2}{\rightarrow} HO_2 + CO_2$	1
R5	$OH + RH \rightarrow HO_2 + R$	1
R6	$HO_2 + NO \rightarrow OH + NO_2$	2
R7	$HO_2 + O_3 \rightarrow OH + 2O_2$	3
R8	$2HO_2 \rightarrow H_2O_2 + O_2$	6
R9	$OH + NO_2 \rightarrow HNO_3$	4
R10	$OH + O_3 \rightarrow HO_2 + O_2$	2
R11	$OH + HO_2 \rightarrow H_2O + O_2$	2
Nocturnal chemistry		
R12	$NO + NO_3 \rightarrow 2NO_2$	2
R13	$NO_2 + O_3 \rightarrow NO_3 + NO_2$	2
R14	$NO_2 + NO_3 \rightarrow N_2O_5$	4
R15	$N_2O_5 \rightarrow NO_3 + NO_2$	5
R16	$N_2O_5 + H_2O \rightarrow 2HNO_3$	2
R17	$N_2O_5 + 2H_2O \rightarrow 2HNO_3 + H_2O$	7

5.1 Clear Boundary Layer: Cabauw 27^{th} July 2003

5.2 Cloudy Boundary Layer: ARM 21^{th} June 1997

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