Scaling the turbulent transport of chemical compounds in the surface layer under neutral and stratified conditions

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SUMMARY

A model of the vertical transport of chemically reactive species is presented which is applicable to all possible stability conditions in the atmospheric surface-layer. The non-dimensional formulation adopted allows any chemical scheme to be included. An equation hierarchy is presented for a fully second-order closure description of the process. The model describes comprehensively the turbulence/chemistry process by calculating the mean concentrations, the turbulent fluxes and concentration covariances of the chemical species. It explicitly takes into account the chemical transformation in first- and second-order variable equations. The model is applied to the NO–NO$_2$–O$_3$ cycle and to the so-called “night-time” chemical scheme of nitrogen oxides. An analysis of the flux budget indicates that the relative importance of the chemistry term in the flux equation varies with distance from the surface. For atmospheric neutral conditions, it is suggested that the chemistry term in the flux equation can be used to make an a priori evaluation of the possible effect of chemistry upon the flux of a chemical species. The model also shows that under stable conditions, despite the greatly reduced activity of turbulence, differences can occur between the turbulent transport of an inert tracer and that of a chemically reactive species. Under any stratification and for typical surface-layer fluxes of nitrogen oxides, the intensity of segregation is very low and can in general be neglected in model calculations.

KEYWORDS: Atmospheric chemistry Boundary layer Nitrogen oxides Turbulence

1. INTRODUCTION

A pioneering study by Lenschow (1982) showed that, in the equation for mean conservation of a reacting chemical compound, terms for chemical production and depletion will cause the solution of the equation to be different from that for conservation of an inert tracer. The differences may be listed as follows:

(i) in conditions of steady state, horizontal homogeneity and neutral stratification, the turbulent flux of the reacting chemical compound diverges with height and, as a consequence, the mean concentration deviates from the logarithmic profile that is typical for inert trace gases;

(ii) whilst the relationship between flux and gradient is a function of stability in both regimes, for reacting chemical species the flux–gradient relationship depends also on the time-scale for chemical process relative to that for turbulent transport and on the ratios of the local fluxes of the various chemical species;

(iii) the inability of turbulence to mix the chemical species adequately leads to segregation of the species and therefore to a reduction in the chemical activity.

These differences are most likely to be found when the time-scale of the chemical transformation is comparable to that of the turbulent transport.

Fitzjarrald and Lenschow (1983) extended the work of Lenschow (1982) by solving the conservation equation for chemically reactive species in an atmospheric surface-layer with neutral stability. They also considered the effect of chemistry upon the fluxes and suggested that the flux–gradient relationship is dependent not only on the atmospheric stability but also on the chemistry of the species. Other studies and other different approaches to the description of the process followed (e.g. Thompson and Lenschow 1984; Lenschow and Delany 1986; Brost et al. 1988; Kramm 1989; Gao et al. 1991; Hamba 1993; Vilà-Guerau

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de Arellano et al. 1993; Gao and Wesely 1994). Almost all these authors focused on the chemical scheme NO–NO2–O3. This cycle plays a key role in boundary-layer chemistry since the nitrogen oxides are precursors to acids and also govern the budget of tropospheric ozone (O3). Moreover, having a time-scale comparable to that of turbulence, this scheme is likely to differ from that for an inert tracer in the ways listed under (i), (ii) and (iii) above.

The main drawback of the majority of these studies is that none of the descriptions of the process of turbulent transport of chemical compounds included all these characteristics. In some studies, the chemical transformation was considered only with regard to the mean concentration (Fitzjarrald and Lenschow 1983; Thompson and Lenschow 1984; Lenschow and Delany 1986; Kramm 1989; Vilà-Guerau de Arellano et al. 1993). In others, the influence of chemistry on the turbulent fluxes was taken into account but the analysis was limited to neutrally stable atmospheres (Fitzjarrald and Lenschow 1983; Brost et al. 1988; Gao et al. 1991; Vilà-Guerau de Arellano and Duynkerke 1992; Gao and Wesely 1994). Hamba (1993), who studied the process in the convective boundary-layer, neglected important contributions that chemistry makes to the fluxes of the chemical species (Verver 1994). The extension to different stratifications was made by Vilà-Guerau de Arellano et al. 1995). They analysed different stratifications by applying Monin–Obukhov similarity theory to chemical compounds. The study, however, analysed only the NO–NO2–O3 chemical system. Furthermore, the corrected flux–gradient relationships and concentration covariances were not used to determine the mean concentration and the flux profiles.

A characteristic of all previous calculations of the mean concentration of chemically reactive compounds in the boundary layer is that the concentration covariances, which appear in the equation for the mean concentration after Reynolds averaging, are assumed to be small compared to the mean concentration and so are neglected. The concentration covariance between NO and O3 was estimated by Vilà-Guerau de Arellano and Duynkerke (1993) who determined its order of magnitude as a function of the flux value and of the ratio between the time-scale of turbulence and that of chemistry.

Many campaigns have been organized to collect measurements of the deposition and emission of chemical species (Wesely et al. 1982; Delany et al. 1986; Wesely et al. 1989; Duyzer and Fowler 1994). However, because of the complex chemistry of the boundary layer and the difficulty of collecting high-frequency measurements of specific chemical species, there has not yet been any marked increase in our understanding of the process. Consequently numerical modelling is very important.

In the present paper, we investigate the turbulent transport of chemical species in the atmospheric surface-layer using a one-dimensional model to calculate the mean variables. The model explicitly takes into account the effect of chemistry on mean concentration, on the concentration flux and on covariances. It can be used for any stratification (stable, neutral or unstable) of the surface-layer. We present a non-dimensional formulation for the mean and the second-moment equations. It provides information about the parameters governing the turbulent transport of chemically reactive species in the surface-layer. The formulation allows any chemical scheme to be included. The model is applied to two chemical systems: the NO–NO2–O3 cycle and the so-called ‘night-time’ cycle of nitrogen oxides.

2. GOVERNING EQUATIONS FOR CHEMICALLY REACTIVE SPECIES

The Reynolds-averaged conservation equation for concentration $C_i$ (from now on expressed in parts in 10$^9$ by volume (p.p.b.)) reads (Lenschow 1982)
\[
\frac{\partial \overline{C_i}}{\partial t} + \frac{\partial \overline{U_j C_i}}{\partial x_j} + \frac{\partial \overline{u_j c_i}}{\partial x_j} = \overline{Q_i} + \overline{S_i}.
\]  (1)

From now on we will indicate the turbulent fluctuation of a variable \((c = C - \overline{C})\) in lower case and the average with overbars.

From left to right one can distinguish the following terms: the rate of change with time, advection, turbulent-flux divergence, sources and sinks due to chemical transformation, and emissions and depositions.

The majority of chemical species in the atmosphere undergo first- and second-order chemical reactions. The generic form of the chemical term that appears in the equation for conservation of the mean concentration can be expressed as

\[
\overline{Q_i} = \text{[sign]} \sum_l j_i \overline{C_i} + \text{[sign]} \sum_{m,n} k_{mn} \overline{(C_m \overline{C_n} + c_m c_n)}.
\]  (2)

The [sign] of the first term on the right-hand side of (2) accounts for the production of chemical species \(C_i\) (positive sign and \(l, m\) or \(n \neq i\)) or depletion (negative sign and \(l, m\) or \(n = i\)). The index \(l\) is the total number of species undergoing first-order chemical reactions at a reaction rate \(j_i\), whereas \(n\) and \(m\) are the total numbers of species undergoing a second-order reaction at a rate \(k_{mn}\).

The turbulent flux of concentration \(\overline{u_j c_i}\) in (1) and \(\overline{c_m c_n}\) in (2), i.e. the concentration covariance, represent the influence of the turbulent character of the flow on the concentration \(C_i\). In the case of second-order chemically reactive species, the closure problem already present in the turbulent fluxes extends to \(Q_i\) which includes the concentration covariances resulting from Reynolds averaging of the nonlinear chemical term.

The flux and the concentration covariances can be calculated by means of the equation that governs their evolution (second-order closure approach). If one assumes that the mean flow is in the \(x\) direction \((\overline{V} = \overline{W} = 0)\) and that it changes only in the vertical direction \(z\), the second-moment equation for the turbulent flux is (e.g. Vilà-Guerau de Arellano et al. 1995)

\[
\frac{\partial \overline{w c_i}}{\partial t} = -\overline{w^2} \frac{\partial \overline{C_i}}{\partial z} - \frac{1}{P_0} \left( \frac{\partial P}{\partial z} \right) \frac{\partial \overline{w^2 c_i}}{\partial z} + \beta \frac{\partial \overline{c_i}}{\partial z} + \overline{R_{w c_i}},
\]  (3)

where \(w\) represents the velocity fluctuation in the \(z\) direction. The terms in (3) can be interpreted physically (from left to right) as the change with time of the vertical flux, the flux production resulting from the vertical gradient of mean concentration \(\overline{G}\), the pressure gradient term \(\overline{P}\), the turbulent vertical transport of the flux, the flux produced by buoyancy \(\overline{B}\) and the chemical term. As indicated in previous studies and in (3), if the species considered are chemically active, the chemical transformation represents a process of production (or even destruction) for the flux (Fitzjarrald and Lenschow 1983). The general form of the chemical term of the flux equation (3) may be written as

\[
\overline{R_{w c_i}} = \text{[sign]} \sum_l j_i \overline{w c_i} + \text{[sign]} \sum_{m,n} k_{mn} \overline{(w c_m c_n + \overline{w c_m} + \overline{w c_m c_n})},
\]  (4)

where the first term on the right-hand side represents flux production (positive sign) or flux depletion (negative sign) resulting from first-order chemical reactions and the second term represents production or depletion resulting from second-order chemical reactions.

The conservation of the second-moment \(\overline{c_i c_k}\) depends upon the mean-concentration gradient of the species \(C_k\) and \(C_i\), the covariance transported by molecular diffusion, the
covariance transported by vertical-velocity fluctuations, dissipation by molecular diffusion
and a chemistry term (Vilà-Guérard de Arellano and Dunsterke 1993). As in the case of
the fluxes, the chemistry acts on the budget of the concentration covariance in the form of
a term for production or destruction which depends on the chemical scheme considered.
The generic form of the chemical term in the covariance equation is

$$
\bar{R}_{i,j,k} = [\text{sign}] \sum_{l,h} j_{ln} \bar{c}_l \bar{c}_h
$$

$$
+ [\text{sign}] \sum_{m,n} k_{mn} \{ \overline{C_m (c_n c_n' + \bar{c}_n c_n') + \overline{c_m} (\bar{c}_n c_m' + \bar{c}_n \bar{c}_m') + \bar{c}_n c_m' + c_m \bar{c}_n' \},
$$

where the first term on the right-hand side represents production (positive sign) or depletion
(negative sign) as a result of first-order chemical reactions, and the second term production
or depletion as a result of second-order chemical reactions.

An important general aspect that should be considered in dealing with turbulent
variables of chemically reactive species is that any conservation equation of second or
higher order moments in which concentration fluctuations appear has to contain a chemical
term.

Equations (1) and (3) and the equation for concentration covariance constitute the
basic set for determining the evolution of the mean concentration of a chemical species
in a second-order closure model. In order to solve the fluxes and the covariance, one
has to parametrize the pressure-gradient term of (3) and the dissipation term in the co-
variance equation. Moreover, the flux and the covariance equations have to be com-
plemented by the governing equations of the other second-order moments (velocity variance,
temperature-concentration covariance, concentration variances) in order to obtain a closed
set of equations.

Note that a higher-order closure problem is still present in the flux and in the covari-
ance equations in the form of third-order moments.

3. Dimensionless Surface-Layer Formulation

In a study of the surface layer, we may assume that the mean concentration is in
a steady state (Nieuwstadt and Dunsterke 1996). This reduces the mean-concentration
equation to an ordinary differential equation that depends only on the vertical coordinate \( z \).
For the atmospheric surface-layer, the third-order terms in the flux and covariance equations
are one order of magnitude smaller than the other terms in the equation (Wyngaard and
coté 1971) and consequently can be neglected.

The non-dimensional form of the mean, flux and covariance equations provides us
with the dimensionless numbers which govern the behaviour of chemical species in the
atmospheric surface-layer. Because there are chemical terms in the equations, one must
introduce new scaling numbers which are not included in the similarity theory. Following
Vilà-Guérard de Arellano et al. (1995), in the case of chemically reactive compounds these
numbers are the Damköhler numbers (e.g. Georgopoulos and Seinfeld 1986) and the ratio
of local fluxes of the species (defined below).

On the basis of these assumptions and scaling variables, (1) now reads

$$
\xi \frac{\partial}{\partial \xi} \left( \frac{\xi}{\Phi_{C_i}} \frac{\partial \bar{C}_i}{\partial \xi} \right) + \bar{Q}_i = 0,
$$

where \( \xi \) is defined as \( \xi = (z + z_0)/L \), \( z_0 \) being a reference height and \( L \) the Monin–
Obukhov length; \( \bar{C}_i \) is the concentration made non-dimensional by the concentration at
the surface, $\Phi_{C_i}$ is the flux–gradient relationship of the species $C_i$, and $\bar{Q}_i$ is the chemical term. In (6), no sources or sinks are considered other than the chemical transformation. The turbulent flux in (6) has been parametrized according to the similarity theory

$$\Phi_{C_i} = -\frac{\kappa u_* z}{w_{C_i}} \frac{\partial \bar{C}_i}{\partial z},$$

(7)

where $\kappa$ is the von Kármán constant (equal to 0.4) and $u_*$ the friction velocity. The flux–gradient relationship in (7) is often chosen equal to that of heat ($\Phi_h$), i.e. a passive tracer (Fitzjarrald and Lenschow 1983; Thompson and Lenschow 1984; Lenschow and Delany 1986; Kramm 1989; Vilã-Guerau de Arellano et al. 1993). Analytical expressions of $\Phi_h$ under different stability conditions are available from micrometeorological turbulence measurements made in the surface layer (Högström 1988). Nevertheless, as anticipated by Fitzjarrald and Lenschow (1983) for neutral atmospheric conditions, and as determined by Vilã-Guerau de Arellano et al. (1995) for other stability regimes, the presence of chemical terms in the flux equation can cause the flux–gradient relationship of a chemical species to deviate from that of an inert gas. This means that there is a need for a corrected flux–gradient relationship that accounts for the chemical activity of the species $C_i$.

The non-dimensional form of the chemistry term $\bar{Q}_i$ in (6) can be written as

$$\bar{Q}_i = \frac{1}{\kappa z} \left\{ [\text{sign}] \sum_l \varphi_l D_l + [\text{sign}] \sum_{n,m} \varphi_m D_m (1 + I_s) \right\},$$

(8)

where, as in (2), the first and second terms on the right-hand side account for first- and second-order chemical reactions respectively. In (8), $D_l$ and $D_m$ are the Damköhler numbers mentioned above. They are defined as

$$D_l = \frac{\kappa z}{u_*} j_l; \quad D_m = \frac{\kappa z k_{mn}}{u_* C_n}.$$  

(9)

The Damköhler numbers represent the ratio of the timescale of turbulence ($\tau_l = \kappa z / u_*$) to that of chemistry ($\tau_o = j^{-1}$ for first-order reactions and $\tau_o = (k_{mn} C_n)^{-1}$ for binary reactions). In (8) we have also defined the surface-concentration ratios

$$\varphi_l = \frac{C_l}{C_{l0}}, \quad \varphi_m = \frac{C_m}{C_{l0}}.$$  

(10)

The variable $I_s$ in (8) is defined as

$$I_s = \frac{c_m C_n}{C_m C_n}.$$  

(11)

and represents the intensity of segregation (Dankwerts 1952; Donaldson and Hilst 1972). $I_s$ accounts for the effect of turbulent mixing of the chemical species and is an important term in the presence of strong gradients of concentration (Sykes et al. 1992; Vilã-Guerau de Arellano and Duynkerke 1993; Galmarini et al. 1995). This term has been neglected in all previous studies of turbulent transport of chemical compounds through the surface layer (Thompson and Lenschow 1984; Lenschow and Delany 1986; Kramm 1989; Gao et al. 1991; Hamba 1993; Vilã-Guerau de Arellano et al. 1993; Gao and Wesely 1994).

When the mean equation is written in a non-dimensional form, the closure problem is present in the flux–gradient relationship $\Phi_{C_i}$ and in the intensity of segregation $I_s$. 
In order to determine the unknown second-moments, we use the second-order closure model proposed by Vilà-Guerau de Arellano et al. (1995). The model calculates the flux–gradient relationship of momentum $\Phi_m$, heat $\Phi_h$ and chemical species $\Phi_{C_i}$ as well as the concentration covariance $c_m c_n$ by solving the second-moment equations under conditions of steady state and horizontal homogeneity. In their model, the production and the depletion resulting from chemical reactions are included explicitly in all the equations that involve concentration as a turbulent variable. An appropriate parametrization of the pressure term and the presence of the buoyancy term (Vilà-Guerau de Arellano et al. 1995) in the flux equation allow us to study the turbulent transport of chemical species under both stable and unstable stratification, i.e. under stability conditions not considered by other second-order closure models of chemically reactive species (Brost et al. 1988; Gao et al. 1991; Gao and Wesely 1994).

As shown by Vilà-Guerau de Arellano et al. (1995), the chemical term in the non-dimensional equation of the flux (i.e. the non-dimensional form of (4)) reads

$$
\tilde{R}_{c_i} = \text{[sign]} \sum_l D_l \frac{c_{i_1}}{c_{i_2}} + \text{[sign]} \sum_{m,n} \left( D_m \frac{c_{m_n}}{c_{i_2}} + D_n \frac{c_{m_n}}{c_{i_1}} \right),
$$

(12)

where $c_{m_n}$ represents the concentration scale and is defined as

$$
c_{m_n} = \frac{\bar{w} c_m}{u^*},
$$

(13)

where $\bar{w} c_m$ is the local flux of the species $C_m$.

Comparing (8), the chemical term of the mean equation, with (12), we can see that the Damköhler numbers are present in both and define the relative value of the timescale of turbulence and the timescale of chemistry. Furthermore, the concentration ratio, present in the chemical term (8), is replaced in (12) by the ratio of the local fluxes.

The importance of the chemical terms within the mean-concentration equation and in the second-moment equations is linked to the conditions of chemical equilibrium. The term $\tilde{Q}_i$ in (6) is equal to zero when the production of species $C_i$ equals the chemical depletion. The chemical term (12) of the second-moment equation vanishes when there is a balance between the production terms and depletion terms. The difference between the two equilibrium conditions is that in the mean equation, equilibrium is attained as a result of the mean chemistry, whereas in the case of the second-moment equation it is also dependent upon the state of turbulence of the flow (Lenschow 1982) as indicated by the presence of the local fluxes. From now on we shall refer to the turbulence–chemistry equilibrium (TCE) as the condition in which the chemistry term (12) is smaller than the leading terms in the flux equation ($\tilde{G}$, $\tilde{B}$, $\tilde{P}$, non-dimensional forms of $\tilde{G}$, $\tilde{B}$, $\tilde{P}$ indicated in (3)) or, since we considered non-dimensional expressions, as the condition that occurs when the chemistry term is smaller than $O(1)$.

4. Equation hierarchy

As anticipated in section 2, when a second-order closure model is used to close the mean equation, other second-moment variables (namely velocity variances, temperature-concentration covariances, concentration variances) are needed in order to obtain a closed system of equations. In Fig. 1 we summarize the hierarchy of equations needed to obtain a closed problem in the case of chemically reactive species. For simplicity, we indicate only the name of the equations; the explicit formulation of the mean equation is given by (6)
and the second-moment equations can be found in Vilà-Guerau de Arellano et al. (1995) together with the closure constants.

Figure 1 has three main areas of interest. The top one (group CI) contains all the differential equations for the mean concentrations of the species considered (Eq. (6)); the following one (group CII) includes all second-moment equations involving the concentration fluctuations; the third one (group D) groups all the second-moment equations relating to velocity and temperature fluctuations. This last group contains the equations that determine the turbulent character of the flow (i.e. the momentum and the heat flux). Figure 1 shows that group D forms a separate closed set of equations for calculating the chemistry-related turbulent variables. The group contains a fixed number of equations and the dimensionless variables depend only on the atmospheric stability $\zeta$.

In group CII, the concentration–flux equation is needed to close the flux in the mean equations. However, since the pressure term and the buoyancy term are included in the equations, the temperature–concentration covariance equation ($\theta c_l$) and the horizontal concentration–flux equation ($u c_l$) have to be added to the group.

The concentration covariance equation is also needed to close the mean concentration equation; so, in order to close the system, it has to be combined with the concentration–variance equation (see (5)) and the flux equation. The equations of group CII depend on those of group D from which they acquire the turbulent characteristics of the flow (momentum and temperature flux, velocity and temperature variances, etc.). Since the second-moments of group CII relate to chemical variables, each equation of group CII includes a chemical term that accounts for the chemical production or depletion of the second moments. A model that assumes a flux–gradient relationship that is not corrected for the chemistry (Thompson and Lenschow 1984; Lenschow and Delany 1986; Kramm 1989; Vilà-Guerau de Arellano et al. 1993) and/or disregards the concentration covariance (Thompson and Lenschow 1984; Lenschow and Delany 1986; Kramm 1989; Gao et al.
1991; Hamba 1993; Vilà-Guerau de Arellano et al. 1993; Gao and Wesely 1994) would also neglect the effect that the chemistry has upon all the variables described by the equations of group CII. The chemical terms of the equations in this group are given in summation notation in appendix A for an undefined number of chemical reactions.

5. A CASE STUDY

In this section we present the results obtained with our model under various regimes of turbulence and chemistry. Subsection (a) concerns the influence of chemical transformation on the fluxes of the chemical triad NO–NO₂–O₃ when transported in a neutral surface-layer. In subsection (b) we shall consider the flux of three species in stratified conditions (stable and unstable) in order to determine the differences between a reactive and a passive tracer under different stratifications. The effect of concentration covariances on the mean concentration profile for NO under various stability conditions is presented in subsection (c). In subsection (d) we apply the generalized expression for the chemical terms of appendix A to determine the fluxes and the intensity of segregation for a typical nocturnal-chemistry scheme.

(a) Turbulent transport in a neutral surface-layer

The NO–NO₂–O₃ scheme consists of a second-order chemical reaction between NO and O₃, which produces NO₂ (reaction rate \( k_1 = 0.25 \) parts per million min⁻¹) and a first-order chemical reaction (photodissociation) in which NO₂ is transformed back to NO and O₃ by interaction with solar radiation (reaction rate \( j = 25 \) min⁻¹). This scheme has been chosen because it is simple (only three species), complete (a first- and a second-order chemical reaction) and closed (a forward and a backward reaction). The aim of the simulation is to identify the parameters that cause the chemical species to behave differently from inert tracers rather than to study the specific chemical system.

The first case considered is that of a 100 m deep neutral surface-layer (\( L = \infty \)) characterized by a friction velocity \( u_* \) of 0.25 m s⁻¹ (turbulence boundary conditions). The three species NO, NO₂ and O₃ are prescribed with their concentration at the bottom of the domain. The fluxes, on the other hand, are prescribed at the bottom for NO and NO₂ and at the top for O₃. Table 1 shows the surface concentration ratios (10), the Damköhler numbers (9) for the three species at the reference height \( z_0 = 0.1 \) m and the concentration scales (13) used as chemistry boundary condition of the simulation.

From Table 1 and (13) we can see that NO is assumed to be emitted at the surface, whereas NO₂ and O₃ are deposited in accordance with experimental evidence (Delany et al. 1986). The values for the Damköhler numbers in Table 1 are very small since they are calculated in the lowest part of the domain (\( z = z_0 \)) and therefore very close to the surface.

The model calculations show that the Damköhler numbers of NO, NO₂ and O₃ increase linearly with height, reaching values of 2.9, 0.7 and 0.05 respectively at the top of the domain.

The flux–gradient relationship profile of the three chemical species is presented in Fig. 2. For an inert tracer in a neutral surface-layer, the flux–gradient relationship is ex-

<table>
<thead>
<tr>
<th>( \varphi_{\text{NO,NO₂}} )</th>
<th>( \varphi_{\text{NO₂,O₃}} )</th>
<th>( \varphi_{\text{NO₂,NO}} )</th>
<th>( D_{\text{NO}} )</th>
<th>( D_{\text{O₃}} )</th>
<th>( D_{\text{NO₂}} )</th>
<th>( NO_{eb} )</th>
<th>( O_{eb} )</th>
<th>( NO_{2eb} )</th>
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<tr>
<td>( 4 \times 10^{-1} )</td>
<td>( 1.3 \times 10^{-1} )</td>
<td>( 2.5 \times 10^{6} )</td>
<td>( 1.8 \times 10^{-3} )</td>
<td>( 8.7 \times 10^{-5} )</td>
<td>( 6.9 \times 10^{-3} )</td>
<td>( -4 \times 10^{-3} )</td>
<td>( 7.2 \times 10^{-1} )</td>
<td>( 8 \times 10^{-2} )</td>
</tr>
</tbody>
</table>

The italic form of the species name, e.g. NO, O₃, NO₂, denotes the concentration of the species, as in Eqs. (9), (10) and (11).
Figure 2. Vertical profile of the flux-gradient relationship of NO, NO$_2$, O$_3$ and heat in a neutral surface-layer.

pected to equal unity throughout the surface layer, as indicated by the vertical line in the figure that represents the flux-gradient relationship of heat $\Phi_h$. The flux-gradient relationships of NO, NO$_2$ and O$_3$ in Fig. 2 tend to deviate from $\Phi_h$ at various heights of the domain. The figure shows clearly that the larger deviations are obtained for NO and NO$_2$, whereas the flux-gradient relationship of O$_3$ tends to equal unity for most of the domain; it then reduces gradually at the top of the domain where it reaches a minimum value of 0.4. The reason why the flux-gradient relationships of the three species deviate from the flux-gradient relationship of an inert tracer is that the chemical transformation acts as a production or depletion term in the budget of the flux of the species, as explained previously. In order to show this dependence, in Fig. 3 we present the vertical budget of the flux equation of NO. For an inert tracer, the flux budget consists (in steady-state conditions) of the production due to the mean-concentration gradient $\nabla \bar{c}$ and the depletion due to the pressure term $\bar{P}$. The buoyancy term $\bar{B}$ is zero since we are considering a neutral surface-layer. In the case of a chemically reactive species the chemistry term $\tilde{R}_{w,na}$ is added to the budget as a production or depletion term. Figure 3 shows that in the first 50 m the chemistry term does not play an important role in the budget; this confirms the small deviation of $\Phi_{NO}$ from $\Phi_h$ shown in Fig. 2. On the other hand, at 40–50 m the value of $\tilde{R}_{w,na}$ increases and becomes comparable to the other two terms of the budget. As a consequence, the chemical transformation makes the flux-gradient relationship deviate from unity, as shown in Fig. 2.

The variation of the chemistry term in the flux equation is the result not only of the increase in the Damköhler number with height, as generally believed, but also of the variation in the concentration scales (i.e. the local fluxes) with height as shown in (12). To show this behaviour in detail we plot, in Fig. 4, the separate components of the chemistry terms in the flux equation of NO. The explicit non-dimensional chemistry term in the flux equation of NO is

$$\tilde{R}_{w,na} = D_{NO2} \frac{NO_{2\ast}}{NO_{\ast}} - D_{O3} \frac{O_{3\ast}}{NO_{\ast}} - D_{NO},$$

where the first term on the right-hand side accounts for the contribution of the photodis-
Figure 3. Vertical budget of the non-dimensional flux equation of NO. The terms in the figure are: \( \tilde{G} \) = mean-gradient production, \( \tilde{P} \) = pressure term, \( \tilde{B} \) = buoyancy term, \( \tilde{R}_{\text{wno}} \) = chemistry term.

Figure 4. Vertical profiles of the chemistry term (see Fig. 3) in the flux equation of NO and of the three contributions to this term (expression (16)).

Association of NO\(_2\) and the other two terms account for the reaction between NO and O\(_3\). In Fig. 4 the three components of (14) are plotted together with the total value of the chemical term. From the figure we can deduce that values of the three terms differ from zero in the first 50 m but almost balance each other, i.e. the species are in TCE. Above 50 m, the third term in (14) dominates the other two, and causes the overall chemistry term to increase with height. The figure also shows that the two components of the second-order chemical
reaction, a sink of NO, act as a depletion and production term of the flux. This is because of the sign of the ratio of the scales of concentration. The ratio \( O_{3e}/NO_{e} \) is negative since NO is emitted and O\(_3\) is deposited and \( D_{NO} \) is positive by definition. An example of the limited information provided by the Damköhler number is also given by the flux–gradient relationships of NO\(_2\) and O\(_3\) shown in Fig. 2. Despite the Damköhler numbers being less than unity, the flux–gradient relationships deviate from that of an inert tracer.

The results shown in Figs. 2, 3 and 4 indicate that, in the end, a deviation of the flux–gradient relationship of a chemically reactive species from that of an inert tracer depends on the overall value of the chemistry term compared to the values of the other terms in the flux equation. The flux–gradient relationship of a species can deviate from that of a tracer, even at shorter distances, as a function of the Damköhler numbers, the flux ratios and the way in which these factors contribute to determine the overall value of the chemistry term in the flux equation. An a priori estimation of the effect of the chemistry on the flux of a species may be obtained by evaluating the chemistry term in the flux equation ((14) for NO). If this term is equal or close to zero (TCE), we can expect the flux–gradient relationship of the species to equal \( \Phi_{n} \).

(b) Turbulent transport in a stratified surface-layer

By fixing the height \( z \) at 50 m and varying the Monin–Obukhov length \( L \), we can obtain the non-dimensional flux-budget for the species as a function of the stability parameter \( \zeta \). In Fig. 5, the four components of the flux–gradient relationship budget of NO, namely the mean-gradient production (Fig. 5(a)), the pressure redistribution (Fig. 5(b)), the buoyancy term (Fig. 5(c)) and the chemistry term (Fig. 5(d)) are shown as functions of stability. The dashed line represents the same budget terms for an inert species for which the chemistry term is equal to zero. The chemistry term (Fig. 5(d)) is constant because we have fixed the height (and consequently also the mean concentration and the local fluxes of the species at that height); the values for the Damköhler numbers and the local fluxes are those obtained at 50 m from the results of the simulation of subsection (a). In comparing the inert-tracer budget with the NO budget, we notice that the presence of a non-zero chemistry term in the equation produces a variation in the other three terms for every stability range. From Fig. 5(b), we can see that in neutral and near-neutral conditions the buoyancy term is equal or close to zero. Moreover, the pressure term assumes the same values as for an inert tracer in these conditions, indicating that the chemistry term present in the horizontal-flux equation (used to parametrize the pressure term, see Fig. 1) is not affecting its value. This confirms that, in neutral conditions, the deviations of the flux–gradient relationship of a species from that of a tracer are due only to the chemistry term in the flux equation. Because of this, a deviation of the chemistry term from the TCE can indeed be used to estimate the possible influence of chemistry on the flux of the species. On the other hand, this cannot be done for stable or unstable conditions because the deviation of the pressure and buoyancy terms from the values for a tracer show that the chemistry terms in the equations for the covariance of temperature and concentration and for the horizontal flux of concentration also affect the value of the flux–gradient relationship of the species.

In Fig. 6, continuous lines show the vertical profiles (integrated up to 20 m) of the flux–gradient relationships for NO for unstable and stable air \( (L = -20 \) and \( L = +20 \) respectively); for both regimes of stability the boundary conditions were those used in subsection (a). Pecked lines in Fig. 6 show the corresponding profiles for a tracer (heat). Under both regimes, even in stable air where buoyancy forces work to suppress turbulence produced by shear, the profile of the flux–gradient relationship for NO differs from that for the tracer.
The non-dimensional production and depletion terms in the flux equation of NO as a function of the stability parameter $\zeta$; (a) $\hat{G}$; (b) $\hat{F}$; (c) $\hat{B}$; (d) $\hat{R}_{\text{NO}}$. The pecked lines in the panels represent the values of the four terms for an inert tracer, namely heat.

(c) The mean concentration profiles and the intensity of segregation

Figure 7 shows the profile of the mean concentration of NO, normalized with the surface value, under stable, unstable and neutral conditions (as in subsection (a)). The pecked line represents the mean concentration obtained by assuming the flux–gradient relationship to be that of heat in (6) and by neglecting the intensity of segregation in the chemistry term (8). For the NO–NO$_2$–O$_3$ scheme, the intensity of segregation is that generated by the second-order chemical reaction between NO and O$_3$ and is defined as

$$I_8 = \frac{\langle \Delta N_0 \Delta O_3 \rangle}{N_0 \langle O_3 \rangle},$$

where the lower case italic forms of the species ‘$n_0$’ and ‘$o_3$’ denote the fluctuations of NO and O$_3$.

Figure 8 shows the vertical profile of $I_8$ in the three stability conditions. The sign of $I_8$ is negative since NO and O$_3$ have opposite fluxes, so that the species are negatively correlated. The intensity of segregation thus tends to slow down the chemical transformation. As we can see from Fig. 8, the order of magnitude of the intensity of segregation obtained is very small; this is consistent with the small variation in the mean concentration shown in Fig. 7.
Figure 6. Vertical profile of the flux–gradient relationship of NO in stable \( (L = 20) \) and unstable \( (L = -20) \) conditions. The pecked lines represent the flux–gradient relationship of an inert tracer.

Figure 7. Normalized NO concentration profiles. Thick line: result obtained including the chemistry terms in the second moments equations. Pecked line: result obtained neglecting the chemistry terms.
Figure 8. Vertical profiles of the intensity of segregation $I_s$ of NO and O$_3$ under stable, neutral and unstable conditions.

(d) Extension of the chemistry

The non-dimensional formulation of the second-moment equations presented above allows us to consider a larger chemical scheme. By means of the general chemistry terms in the second-moment equations presented in appendix A, we can calculate the flux–gradient relationship and the intensity of segregation for a more extended chemical scheme than NO–NO$_2$–O$_3$. The scheme is presented in appendix B; it is the so-called ‘night-time’ chemical cycle of nitrogen oxides. The cycle includes the depletion of NO and O$_3$ and the production of NO$_2$, NO$_3$ and N$_2$O$_5$ which constitute the reservoir species during the night. The reaction rates, Damköhler numbers and concentration scale for the five species are presented in the appendix. The lack of fast-response measurements of the fluxes of these species makes it difficult to choose realistic values for the flux. Nevertheless, an estimate has been made on the basis of deposition velocities of the species (Gao and Wesely 1994).

Figure 9 presents the flux–gradient relationship of the five chemical species normalized with that of heat as a function of stability. When the ratio of the flux–gradient relationships is equal to one the species behave like an inert tracer and any deviation from unity represents the effect of the chemical transformation. In Fig. 9, we see that the flux–gradient relationship of O$_3$ does not differ substantially from that for heat in any stability regime. The flux–gradient relationships of all other species, however, deviate from that for heat throughout the stability range. In the stable regime ($\xi > 0.5$) the flux–gradient relationships for NO, NO$_2$, NO$_3$ and N$_2$O$_5$ slowly approach the flux–gradient relationship for heat.

The chemical scheme considered includes four second-order chemical reactions. These give rise to four intensities of segregation which can affect the efficiency of the mean chemical reactions. These intensities are

$$I_{s1} = \frac{n_0 \sigma_5}{NO \ O_3}; \ I_{s2} = \frac{n_0 \sigma_2 \sigma_3}{NO_2 \ O_3}; \ I_{s3} = \frac{n_0 \sigma_5}{NO \ NO_3}; \ I_{s4} = \frac{n_0 \sigma_2 \sigma_3}{NO_2 \ NO_3}. \quad (16)$$
In Fig. 10, we present the intensities of segregation of (16) as functions of \( \zeta \); all the intensities of segregation are negative and tend to larger negative values as \( \zeta \) increases. In the case considered, the absolute values are very small, reaching a maximum of almost 1% for the reaction between \( \text{NO}_2 \) and \( \text{NO}_3 \).

Vilá-Guerau de Arellano and Duykerke (1993) obtained large values for the intensity of segregation by solving the covariance equation of \( \text{NO} \) and \( \text{O}_3 \) for various ranges of concentration and flux. They found large values for \( I_s \) only for Damköhler numbers larger than 0.1 and very large fluxes of \( \text{NO} \) and \( \text{O}_3/\text{NO} \) ratio. We carried out sensitivity analyses for the \( \text{NO}–\text{NO}_2–\text{O}_3 \) scheme and for the night-time scheme. In both, we used fluxes and concentrations which were typical of non-polluted surface-layers. The resulting values of \( I_s \) were never larger than a few per cent of the mean concentration. In general, we may conclude from the results presented in subsection (c) and in this subsection that, in the surface layer, we can expect the intensity of segregation to have only a small or negligible effect on the mean concentration. This result is applicable to all stability conditions with typical values of surface-layer flux.

6. Conclusions

We have presented a non-dimensional model for calculating vertical profiles of the mean concentration, of the flux and of the concentration covariance under any stratification regime. The flux and the concentration covariances are calculated by means of a second-order closure model. All relevant contributions to the production and depletion of first- and second-order moments of chemical species have been taken into account. The model can be applied to any chemical scheme. In order to show the effect of the combined action of turbulent transport and chemical transformation on the flux and on the mean concentration of chemical species, we have selected the case of turbulent transport of \( \text{NO}–\text{NO}_2–\text{O}_3 \). In addition, we have investigated a more extended chemical scheme representing the night-time chemistry of nitrogen oxides. Some of our results confirm those obtained in the past.
Figure 10. Intensities of segregation $I_5$ for the night-time chemical scheme of nitrogen oxides as a function of the stability parameter $\zeta$. The explicit expressions are given in the text in Eq. (18).

by authors using models which have partially analysed the vertical transport of chemically reactive species. Application of the present model to the two cases mentioned above leads to the following conclusions:

- a simple evaluation of the Damköhler number of a chemical species is not enough to allow an estimation to be made of the possible influence of the chemical reaction on the flux of a species. The ratios of the fluxes of species (explicit within the chemistry term of the flux equation) can reduce or enhance the chemical transformation of each of the several species in flux;
- the dependence of the chemistry term on Damköhler numbers and the local flux ratios makes it difficult to define the range of heights over which the effect of the chemical transformation can be neglected or should be considered;
- the linear dependence of the Damköhler number on height $z$ means that the effects of chemical production or depletion on the fluxes are less likely to occur close to the surface;
- we have defined turbulence–chemistry equilibrium (TCE) as the condition in which the chemistry term of the flux equation is small or close to zero. This condition generally differs from the condition of chemical equilibrium in the mean equation since the TCE is governed not only by the chemical transformation but also by the turbulent state of the flow. An example of this condition has been given for the NO–NO$_2$–O$_3$ scheme;
- the vertical budget of the flux–gradient relationship of a chemical species in neutral conditions reveals that, when the chemistry term increases and becomes comparable to the other terms in the equation, the flux–gradient relationship deviates from that of an inert tracer. A more detailed analysis of the flux budget as a function of stability reveals that simple evaluation of the non-dimensional chemistry term and its deviation from the TCE can be used to estimate qualitatively the possible influence of the chemical transformation on the fluxes;


• the flux budget shows that, under unstable and stable conditions, all contributions
to the production and depletion of the flux of a chemical compound (expressed by the
mean gradient production term, the pressure term and the buoyancy term) are affected by
the chemical reaction;
• we find that the flux–gradient relationship continues to be affected by the chemistry
under conditions of stable stratification. This underlines the fact that chemistry can also
play an important role in conditions of suppressed turbulence;
• for typical surface-layer values of flux and concentration, the intensity of segrega-
tion is of the order of a few per cent of the mean concentration. The large value of the
mean concentration of chemical species in the surface layer reduces the influence that
the formation of concentration covariances has on the chemical reaction. This result is
independent of the stability of the surface layer; the intensity of segregation can then be
considered negligible;
• the formulation presented allows one to take extensive chemistry into account;
• a well-structured hierarchy of equations has been derived which can be used for a
comprehensive description of the turbulent transport of chemically reactive species in the
surface layer.

The model can be applied to any case to which similarity theory can be extended, including,
for example, the study of the turbulent transport of chemically reactive species in the
nocturnal boundary-layer. Furthermore, it is a useful tool for the planning of experimental
campaigns as well as the determination of emission and deposition fluxes in large-scale
models.

APPENDIX A

In this appendix we present the general non-dimensional form of the chemical terms
of the equations for fluxes, variances and co-variances of chemical species (equations in
group CII in Fig. 1). The terms are indicated in a non-dimensional formulation for first- and
second-order chemical reactions (I-ord. and II-ord. respectively). By means of summation
notation, we indicate the reactants by subscripts $i$ and $j$ and the products by subscripts $m$
and $n$. This distinction is justified, for example, by the chemical term of the concentra-
cion covariance equation being expressed differently depending on whether the reaction occurs
between reactant–reactant, reactant–product and product–product. The chemical term of a
species which participates in more than one chemical reaction can be obtained by a linear
combination of the terms indicated below.

List of symbols:

$$c_{m*} = \frac{wc_m}{u*}; \quad \theta* = \frac{w\theta}{u*}; \quad r_{u cm} = \frac{\theta c_m}{c_{m*} u*}; \quad r_{1 cm} = \frac{wc_m}{c_{m*} u*}; \quad r_{cm*n} = \frac{c_n c_m}{c_{m*} c_{n*}}.$$  

Vertical flux equation

I-ord.:

$$\tilde{R}_{w c_i} = D_{cm} \frac{c_{m*}}{c_{i*}}$$

II-ord.:

$$\tilde{R}_{w cm} = -D_{cm}$$

$$\tilde{R}_{w c_i} = D_{cm} \frac{c_{m*}}{c_{i*}} - D_{ci}$$
\[ \tilde{R}_{\text{ucm}} = -D_{c_j} \frac{c_j}{c_m} - D_{c_j} \frac{c_j}{c_m} \]

**Horizontal flux equation**

I-ord.:
\[ \tilde{R}_{\text{ucj}} = D_{c_j} \frac{c_j}{c_j} r_{ucj} + D_{c_j} r_{ucj} \]
\[ \tilde{R}_{\text{ucm}} = -D_{c_m} r_{ucm} \]

II-ord.:
\[ \tilde{R}_{\text{ucj}} = D_{c_j} \frac{c_j}{c_j} r_{ucj} + D_{c_j} r_{ucj} \]
\[ \tilde{R}_{\text{ucm}} = -D_{c_j} \frac{c_j}{c_m} r_{ucj} - D_{c_j} \frac{c_j}{c_m} \]

**Temperature-concentration co-variance equation**

I-ord.:
\[ \tilde{R}_{\theta c_j} = D_{c_m} \frac{c_m}{c_j} r_{\theta cm} \]
\[ \tilde{R}_{\theta c_m} = -D_{c_m} r_{\theta cm} \]

II-ord.:
\[ \tilde{R}_{\theta c_j} = D_{c_j} \frac{c_j}{c_j} r_{\theta cj} + D_{c_j} r_{\theta cj} \]
\[ \tilde{R}_{\theta c_m} = -D_{c_j} \frac{c_j}{c_m} r_{\theta cj} - D_{c_j} \frac{c_j}{c_m} r_{\theta cj} \]

**Concentration variance equation**

I-ord.:
\[ \tilde{R}_{\text{cjcj}} = -D_{c_j} r_{cjcj} \]
\[ \tilde{R}_{\text{cmcm}} = D_{c_j} \frac{c_j}{c_m} r_{cjcj} \]

II-ord.:
\[ \tilde{R}_{\text{cjcj}} = -D_{c_j} \frac{c_j}{c_j} r_{cjcj} - D_{c_j} r_{cjcj} \]
\[ \tilde{R}_{\text{cmcm}} = D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} \]

**Concentration co-variance equation**

I-ord.:
\[ \tilde{R}_{\text{cjcj}} = -D_{c_j} \frac{c_j}{c_m} r_{cjcj} - D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} \]
\[ \tilde{R}_{\text{cmcm}} = D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} \]

II-ord.:
\[ \tilde{R}_{\text{cjcj}} = D_{c_j} \frac{c_j}{c_j} r_{cjcj} + D_{c_j} \frac{c_j}{c_j} r_{cjcj} - D_{c_j} r_{cjcj} \]
\[ \tilde{R}_{\text{cmcm}} = D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} + D_{c_j} \frac{c_j}{c_m} r_{cjcj} \]
TABLE B.1.  DAMköHLER NUMBERS, REACTION RATES AND CONCENTRATION SCALES

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(B.1)</th>
<th>(B.2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{C_1}$</td>
<td>NO</td>
<td>$3.19 \times 10^9$</td>
</tr>
<tr>
<td>$c_{ai}$</td>
<td>NO</td>
<td>$-5 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(B.3)</th>
<th>(B.4)</th>
<th>(B.5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{C_1}$</td>
<td>NO</td>
<td>$1.16 \times 10^6$</td>
<td>$21.12 \times 10^6$</td>
</tr>
<tr>
<td>$c_{ai}$</td>
<td>NO</td>
<td>$2 \times 10^{-3}$</td>
<td>$2.2 \times 10^{-1}$</td>
</tr>
<tr>
<td>$k_i$</td>
<td>NO</td>
<td>$2 \times 10^{-3}$</td>
<td>$2.2 \times 10^{-1}$</td>
</tr>
</tbody>
</table>

These values are used in subsection 5(d) of the text.

APPENDIX B

In this appendix we present the extended chemical scheme used in subsection 5(d). The reactions presented below represent a typical night-time chemical scheme for the production and depletion of nitrogen oxides. In addition, we present the Damköhler numbers and the concentration scales used to obtain the results presented in Figs. 9 and 10.

\[
\begin{align*}
\text{NO} + \text{O}_3 & \xrightarrow{k_1} \text{NO}_2 + \text{O}_2 \\
\text{NO}_2 + \text{O}_3 & \xrightarrow{k_2} \text{NO}_3 + \text{O}_2 \\
\text{NO} + \text{NO}_3 & \xrightarrow{k_3} 2 \text{NO}_2 \\
\text{NO}_2 + \text{NO}_3 & \xrightarrow{k_4} \text{N}_2\text{O}_5 \\
\text{N}_2\text{O}_5 + M & \xrightarrow{k_5} \text{NO}_2 + \text{NO}_3
\end{align*}
\]  

(B.1) \hspace{2cm} (B.2) \hspace{2cm} (B.3) \hspace{2cm} (B.4) \hspace{2cm} (B.5)

The species considered are involved in more than one chemical reaction. Each of them will thus have more than one Damköhler number. Assuming a friction velocity $u_* = 0.2 \text{ m s}^{-1}$ and a height $z = 30 \text{ m}$, the non-dimensional numbers used in subsection 5(d) are as in Table B.1.

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Vilà-Guerau de Arellano, J., Duyzer, J. and Builtes, J. P. H. 1993 The divergence of turbulent diffusion flux due to chemical reaction in the surface layer: the NO–O₃–NO₂ system. Tellus, 45B, 23–33


