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The divergence of the turbulent diffusion flux in the surface layer due to chemical reactions: the $NO-O_3-NO_2$ system

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ABSTRACT

The concentration profiles and fluxes in the atmospheric surface layer are studied for the case that the time scales of the chemical reactions and the turbulent diffusion are of similar order. A model which includes both processes, turbulent diffusion and chemical transformations, is developed and applied to the $NO-O_3-NO_2$ system. The governing equations of the model are presented in a non-dimensional way which allows a more compact and elegant formulation of the problem. The concentration and fluxes of the three chemical species are correctly calculated for the whole surface layer. The model results show that the turbulent diffusion flux diverges due to the non-equilibrium state of the chemical species. Thus, the concentration profiles of the chemical species deviate from the logarithmic profile which would be obtained for non-reactive species. The divergence of the turbulent flux of ozone is calculated with the model and compared with observations taken at Pawnee site by Zeller et al. Both show a good agreement and point out the necessity to take into account chemical reactions when calculating concentration and fluxes of chemically active species. The deposition velocities of the chemical species and the photostationary state relation, two parameters which are affected by the divergence of the turbulent flux, are calculated. The model results show a variation of deposition velocities with height, which implies a shortcoming in the classical definition of the deposition velocity based on the ratio of a constant flux to the concentration. The photostationary state relation ($R(z)$), the ratio of production and depletion of NO_2 due to chemistry, also shows a variation with height. For an upward flux of NO the model results are supported by observations, both showing an increase of $R(z)$ towards the surface.

1. Introduction

In surface layer theory, the vertical turbulent diffusion flux is constant with height for inert chemical species. Consequently, in the neutral surface layer, vertical concentrations profiles follow a logarithmic function. However, when reactive species with second-order chemical reactions are involved (non-linear systems), it can be shown that the turbulent diffusion flux is disturbed by the chemical transformations; this leads to concentration profiles for the reactive species which deviate from the logarithmic profile. The chemical system chosen to study this effect is the $NO-O_3-NO_2$ cycle under the influence of solar radiation. Experimental studies by van Aalst (1982), Duyzer et al. (1983), Delany et al. (1986) and Zeller (1990) have already pointed to the influence of chemical reactions on concentration profiles and turbulent fluxes. In an up-to-date review of dry deposition of nitrogen compounds, Hanson and Lindberg (1991) mentioned the necessity to correct the measurements to take into account chemical reactions.

Analytical models for studying the same chemical system were developed by Thompson and Lenschow (1984) and Lenschow and Delany (1987). In these papers, it is assumed that at least one species (O_3 or NO) is constant with height.

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This implies that the only non-linear chemical term in the equations becomes linear. Therefore, it can be shown that the only possible solution which satisfies all three differential equations is a logarithmic function with height. A numerical model which solved the three differential equations was developed by Fitzjarrald and Lenschow (1983). A drawback of their model is that the concentrations and fluxes increase dramatically after a certain height (around 25 m above surface), giving non-physical solutions. Kramm (1989) and Kramm et al. (1991) also solve numerically the same triad. However, they found similar results to Fitzjarrald and Lenschow (1983) concerning the behaviour of fluxes for large values of z. In this paper, this problem is circumvented by prescribing chemical equilibrium, i.e., photostationary state equilibrium, at the top of the surface layer.

In the absence of advection, the main processes that govern the rate of change of the chemical species in the surface layer are turbulent diffusion and chemical reactions. The former brings together the different species so that they can react, whereas the latter transforms the species. A strong coupling of these two processes is expected when the time scale of chemical transformations is of similar order to the time scale of turbulent diffusion. An important process that is affected by this interaction is the removal of (reactive) species by dry deposition. The importance of a correct parametrization of the process of dry deposition is required because dry deposition is the most important sink for ozone in the atmospheric boundary layer (Finlayson-Pitts and Pitts, 1986). A standard and simple way to parametrize dry deposition is to define the deposition velocity as the ratio of the flux and concentration at a certain height. However, because the turbulent diffusion flux for reactive species is not constant with height in the surface layer due to chemical transformations, it is difficult to define an appropriate deposition velocity. Fitzjarrald and Lenschow (1983) already questioned the validity of this deposition velocity concept. They suggested a more rigourous definition of the deposition velocity. In their view deposition velocity should be calculated at a height equal to the roughness length and be based on the measurements of concentrations and fluxes at two different height levels. Concentration and fluxes profiles should first be calculated with a model.

The ratio of the chemical production/depletion of nitrogen dioxide is commonly known as the photostationary state relation (Leighton, 1961). With constant solar radiation this ratio is expected to be a constant (chemical equilibrium). However, diverse chemical and physical factors can cause this parameter to deviate from an equilibrium state (Calvert and Stockwell, 1983). For this study, the photostationary state ratio is an estimator of the balance of the chemical terms.

Examples of the disturbances in the turbulent flux due to chemical reactions are presented as well as a discussion comparing model results with observations taken above grass. The model equations are expressed in a non-dimensional form which can be solved for convective and neutral stability conditions in the surface layer. Particular attention is given to the the deposition velocity and the photostationary state relation, all of which are studied for two different cases: an upward and a downward flux of NO.

2. Model formulation

The chemical system chosen as the basis for this study is the production/depletion of ozone by nitrogen oxides. This is one of the more important cycles in atmospheric chemistry. To keep the chemistry as simple as possible, hydrocarbons have not been included in the model formulation. The $NO\text{-}O_3\text{-}NO_2$ cycle can be described by the following chemical reactions:

$$O + O_2 + M \rightarrow O_3 + M, \tag{1}$$

$$NO + O_3 \rightarrow NO_2 + O_2, \tag{2}$$

$$NO_2 + h\nu(\lambda \leqslant 420\ \text{nm}) \rightarrow NO + O, \tag{3}$$

where the chemical reactions rate constants are k_1, k_2 and k_3, respectively. M is a molecule, normally nitrogen or oxigen, that absorbs the excess energy produced by the reaction.

The continuity equations for the concentrations of the chemical species are:

$$\frac{\partial O}{\partial t} + u_i \frac{\partial O}{\partial x_i} = -k_1 O_2 O + k_3 NO_2 + \gamma_O \frac{\partial^2 O}{\partial x_i \partial x_i}, \tag{4}$$

$$\frac{\partial O_3}{\partial t}+u_i\frac{\partial O_3}{\partial x_i}=k_1O_2O-k_2NOO_3 + \gamma_{O_3}\frac{\partial^2 O_3}{\partial x_i\,\partial x_i}, \quad (5)$$

$$\frac{\partial NO}{\partial t}+u_i\frac{\partial NO}{\partial x_i}=-k_2NOO_3+k_3NO_2 + \gamma_{NO}\frac{\partial^2 NO}{\partial x_i\,\partial x_i}+S_{NO}(x,t), \quad (6)$$

$$\frac{\partial NO_2}{\partial t}+u_i\frac{\partial NO_2}{\partial x_i}=k_2NOO_3-k_3NO_2 + \gamma_{NO_2}\frac{\partial^2 NO_2}{\partial x_i\,\partial x_i}, \quad (7)$$

where u_i is the wind velocity, γ_O, γ_{O_3}, γ_{NO} and γ_{NO_2} are the molecular diffusivities and $S_{NO}(x, t)$ is the source term. Reaction (1) can be considered a pseudo first-order reaction due to the fact that O_2 has a much higher concentration (2×10^5 ppm) than the other chemical species involved. Therefore, for the time being k_1 can be written as

$$k_1' = k_1O_2. \quad (8)$$

The O radical is highly reactive, and, consequently concentrations of O are expected to be lower than concentrations of NO, NO_2 and O_3. Therefore, the most important terms in equation (4) are the chemical terms, yielding the following equilibrium

$$k_1'O = k_3NO_2. \quad (9)$$

The eqs. (5)–(7) are made dimensionless. The derivation of these non-dimensional equations is given in the Appendix. The stability function for convective conditions (ϕ_c) is included. Eqs. (5)–(7) can be written as three dimensionless second-order differential equations:

$$\frac{1}{\phi_c}\frac{\partial^2 O_3^*}{\partial x^2}-\frac{aU}{\phi_c^{1-a}}e^x\frac{\partial O_3^*}{\partial x} + e^x\tau R_{O_x}(NO_2^*-RNO^*O_3^*)=0, \quad (10)$$

$$\frac{1}{\phi_c}\frac{\partial^2 NO^*}{\partial x^2}-\frac{aU}{\phi_c^{1-a}}e^x\frac{\partial NO^*}{\partial x} + e^x\tau R_{NO_x}(NO_2^*-RNO^*O_3^*)=0, \quad (11)$$

$$\frac{1}{\phi_c}\frac{\partial^2 NO_2^*}{\partial x^2}-\frac{aU}{\phi_c^{1-a}}e^x\frac{\partial NO_2^*}{\partial x} + e^x\tau RNO^*O_3^*-e^x\tau NO_2^*=0, \quad (12)$$

(a) (b) (c)

where x is equal to the dimensionless variable $\ln(1+z/z_0)$ and O_3^*, NO* and NO_2^* are non-dimensional concentrations in terms of the respective concentrations at the top of the surface layer (z_t). The other dimensionless parameters are defined in the following way:

$$R=R(z_t)=\frac{k_2^*\langle O_3(z_t)\rangle\langle NO(z_t)\rangle}{k_3\langle NO_2(z_t)\rangle}, \quad (13)$$

$$R_{NO_x}=\frac{\langle NO_2(z_t)\rangle}{\langle NO(z_t)\rangle}, \quad (14)$$

$$R_{O_x}=\frac{\langle NO_2(z_t)\rangle}{\langle O_3(z_t)\rangle}, \quad (15)$$

$$\tau=\frac{k_2^*\langle O_3(z_t)\rangle\langle NO(z_t)\rangle z_0}{\langle NO_2(z_t)\rangle\kappa u_*}, \quad (16)$$

where κ is the von Karman constant equal to 0.4, u_* is the friction velocity, z_0 is the roughness length and k_2^* is the effective chemical constant rate defined by equation (A5).

Eq. (13) is the photostationary state relation or dimensionless Leighton relationship (Finlayson-Pitts and Pitts, 1986). Under chemical equilibrium conditions R is equal to 1 which means the same production and depletion rate of nitrogen dioxide. Other chemical species, i.e., hydrocarbons, can break this chemical equilibrium. However, to keep chemistry simple these chemical species have not been included in this study. The ratio of the time scales of turbulent diffusion and the chemical reactions is represented by eq. (16).

The stability function for heat for the convective case (ϕ_c) in the x-coordinate is taken from Dyer (1974)

$$\phi_c=(1-\xi_0e^x)^{-a}. \quad (17)$$

ζ_0 is a dimensionless parameter proportional to the Obukhov length scale L and equal to

$$\xi_0=\frac{\gamma_c z_0}{L}. \quad (18)$$

The constants a and γ_c are 0.5 and 16, respectively.

The six boundary conditions, three fluxes and three concentrations, are prescribed at the bottom and the top of the surface layer. At the bottom it is assumed that the only quantity known is the flux of NO. Measurements collected above grass by Duyzer et al. (1983) show that upward fluxes are generally to be expected. The O_3 and NO_2 fluxes are specified at the top of the surface layer. As a result of entrainment from the mixed layer the flux of O_3 is downward. Recent measurements of NO_2 fluxes also show predominant downward fluxes (Hicks and Matt, 1988), although this behaviour is not as clear as it is for ozone. The concentrations of O_3, NO and NO_2 are prescribed at the top of the surface layer. At the top of the surface layer (z_t), R is assumed to be equal to 1, i.e., photostationary equilibrium. The prescription of five boundary conditions at the top and one at the bottom of the surface layer and the assumption $R = 1$ at the top of the surface layer are the two main differences with respect to the model of Fitzjarrald and Lenschow (1983), in which the six boundary conditions are all imposed at the lowest level when the model is integrated for all the surface layer. The Runge-Kutta method and a Newton iteration in a shooting and matching technique are used to solve the differential equations.

3. Results

Before the model results are analysed, it is convenient to mention the concentration profile for the case of inert species. As is well-known, in surface layer theory the turbulent flux divergence is equal to zero and as a result logarithmic concentration profiles are obtained. The introduction of chemical terms into the continuity equation, for the case of reactive species, will produce a divergence in the turbulent diffusion flux which, obviously, will lead to deviations from the logarithmic profile.

Table 1 summarizes the boundary conditions and the constants used in the model runs as well as the dimensionless parameters (eqs. (13)–(16)). Flux values are chosen on the basis of measurements taken by Duyzer et al. (1983) and Duyzer (1991). The values for the chemical reaction rate constants are taken from Finlayson-Pitts and Pitts (1986), assuming a free-cloudy sky for k_3. Two different cases are studied for a neutral surface layer: a case with an upward (case 1) and a downward (case 2) flux of NO. Fig. 1a shows the concentration profiles for O_3, NO and NO_2 for case 1. The logarithmic concentration profile is also plotted; this profile is the expected one if the NO_2 is an inert species. A logarithmic profile is also obtained for the $NO_x(NO + NO_2)$ concentration profile (not plotted) because when equations (11) and (12) are added it is obvious that NO_x is chemically inert. The same logarithmic profile is obtained for $O_x(O_3 + NO_2)$. As the figure shows, deviations from the logarithmic profile are found for the three pollutants considered. The variation of the photostationary relationship with height ($R(z)$) (variation with height of equation 13) is also calculated. Large deviations (27%) from the equilibrium state are found close to the height ($z = 1$ m) where dry deposition measurements are normally carried out. For case 1 the NO_2 production is more important than the depletion.

Fig. 1b shows the dimensionless fluxes of O_3, NO, NO_2, NO_x and O_x. The fluxes are made non-

Table 1. *Boundary conditions, constants and dimensionless parameters used in the model runs*

Boundary conditions		
O_3 (ppb)		25
NO_2 (ppb)		10
NO (ppb)		8
F_{O_3} (ppb m s^{-1})		−0.125
F_{NO_2} (ppb m s^{-1})		−0.05
F_{NO} (ppb m s^{-1})	Case 1	0.08
	Case 2	−0.04
Constants		
u_* (m s^{-1})		0.25
z_0 (m)		0.1
k_2 (ppm^{-1} min^{-1})		25
k_3 (min^{-1})		0.5
Dimensionless parameters		
R		1
R_{NO_x}		1.25
R_{O_x}		0.4
τ		0.08

All the values are prescribed at the top of the surface layer ($z_t = 110$ m), except the flux of NO which is prescribed at the roughness length (z_0).

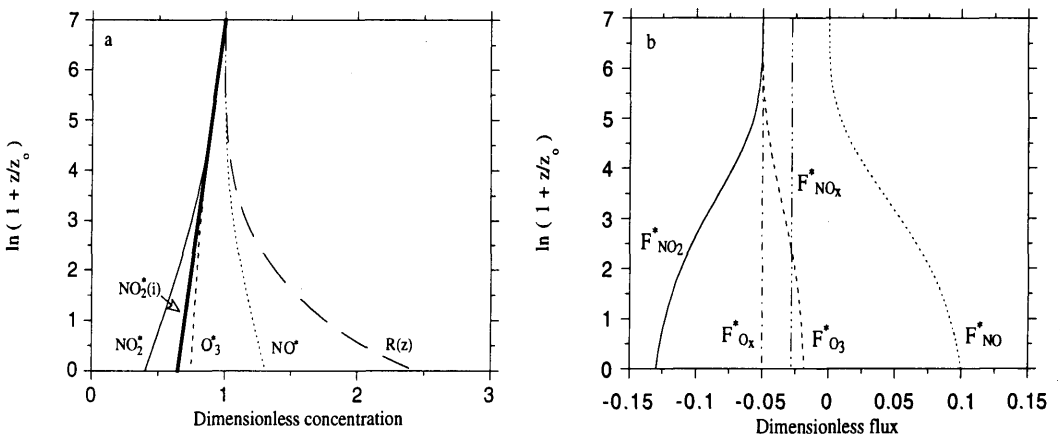

Fig. 1. (a) The dimensionless concentration profiles O_3^*, NO* and NO_2^* (made non-dimensional in terms of the respective concentrations at the top of the surface layer (z_t)), the logarithmic concentration profile of NO_2 (i) if it was acting as an inert species and the dimensionless number $R(z)$ (eq. (13)) as a function of height for an upward flux of NO (case 1). (b) The dimensionless fluxes $F^*_{O_3}$, F^*_{NO}, $F^*_{NO_x}$ and $F^*_{O_x}$ (made non-dimensional in terms of their respective concentrations at the top of the surface layer (z_t), the friction velocity (u_*) and the von Karman constant (κ)) for an upward flux of NO (case 1). Positive values indicate upward dimensionless fluxes.

dimensional by dividing the flux by their respective concentrations at the top of the surface layer and by κu_* in the following way

$$F_i^* = \frac{\langle w'c_i' \rangle}{\langle c_i(z_t) \rangle \kappa u_*}, \tag{19}$$

where F_i^* is the dimensionless flux. Without chemistry (non-reactive species like NO_x and O_x) the turbulent fluxes are constant with height. Here, the fluxes of O_3, NO and NO_2 clearly vary with height. The upward flux of NO decreases with height until it reaches zero at the top of the surface layer. The downward ozone flux increases with height, whereas the downward NO_2 flux decreases with height. Therefore the turbulent flux divergence is not zero and as a result the NO_2

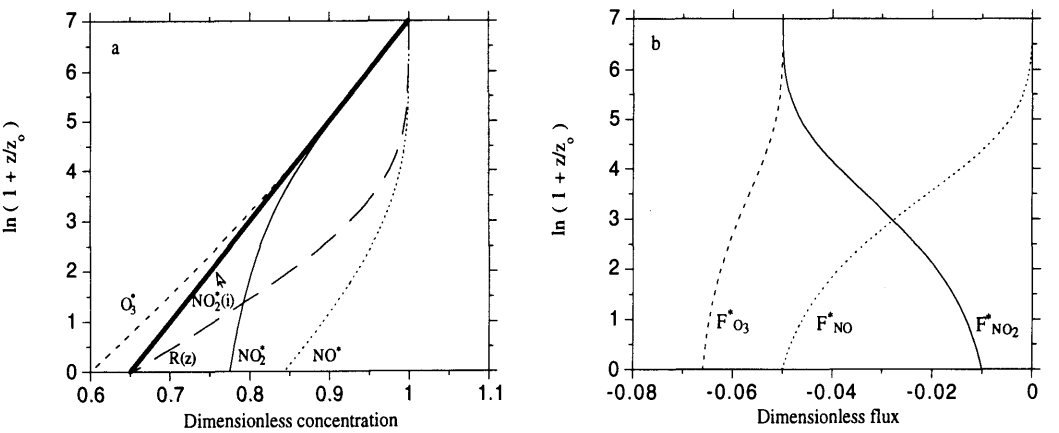

Fig. 2. (a) The dimensionless concentration profiles O_3^*, NO* and NO_2^*, the logarithmic concentration profile if NO_2 (i) was acting as an inert species and the dimensionless number $R(z)$ (eq. (13)) for a downward flux of NO (case 2). Non-dimensional concentrations as in Fig. 1a. (b) The dimensionless fluxes $F^*_{O_3}$, F^*_{NO} and $F^*_{NO_2}$ for a downward flux of NO (case 2). Non-dimensional fluxes as in Fig. 1b.

production and depletion due to chemistry are not in balance.

Figs. 2a and 2b show the dimensionless concentration profiles and fluxes for case 2. Departures from the logarithmic profile are found and the fluxes are certainly not constant with height. For a downward flux of NO, $R(z)$ values lower than 1 are obtained throughout the surface layer. For example, the value of $R(z=1\text{ m})$ is about 0.7, which indicates more depletion than production of NO_2.

Figs. 1 and 2 show that the model performs correctly in the whole surface layer. In other words, physical solutions for large z can be obtained for the three concentrations and fluxes, i.e., they converge to an asymptotic boundary condition. This correct behaviour is obtained after imposing the photostationary equilibrium state ($R=1$) at the top of the surface layer where the time scale of turbulent mixing is larger than the chemical reaction time scale. These results are in contrast with the model results presented by Fitzjarrald and Lenschow (1983) where singularities were found at 25 m above ground level, fluxes and concentrations increased exponentially (Lenschow and Delany, 1987), due to the non-linearity of the second-order chemical reaction term.

Fig. 3 shows in more detail the turbulent diffusion flux divergence and the chemical production and destruction (terms *a*, *b* and *c* in equation (12) divided by e^x) for NO_2 (case 1) as a function of height. As was mentioned above, close to the reference level chemical production is greater than chemical destruction ($R(z)>1$) reaching an equilibrium at the top of the surface layer where the photostationary state relationship was prescribed ($R(z_t)=1$). The divergence in the turbulent flux is produced by the non-equilibrium between chemical production and destruction. Once this equilibrium is established, the turbulent flux divergence becomes zero and thus the turbulent flux becomes constant. Here the photostationary equilibrium is modified by the mean concentration term. It is also possible that the photostationary equilibrium is altered by the fluctuating components, in this case the term $\langle NO'O_3' \rangle$ will be important. The importance of this term can be estimated with the intensity of segregation (I_s) (eq. (A6) in the appendix). For the two cases studied, values of I_s close to zero are obtained, i.e., k_2^* is equal to k_2 (eq. (A5) in the appendix). Therefore, it is only the product of the mean concentrations that creates the flux divergence. This is a consequence of the non-linear terms (in eqs. (10) to (12)) due to second-order chemical reactions.

The O_3, NO and NO_2 fluxes as a function of the Obukhov length scale are shown in Fig. 4 for case 1. The introduction of the stability correction (eq. (17)) introduce minimum changes in the values of the fluxes. Therefore, Figs. 2a, b,

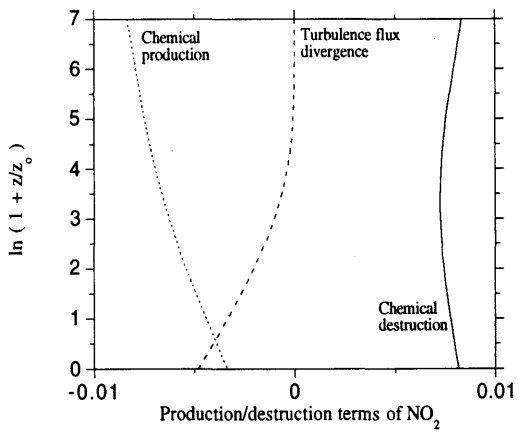

Fig. 3. The non-dimensional turbulent flux divergence, chemical production and destruction (terms (*a*), (*b*) and (*c*) in eq. (12)) as a function of height for the case of an upward flux of NO (case 1).

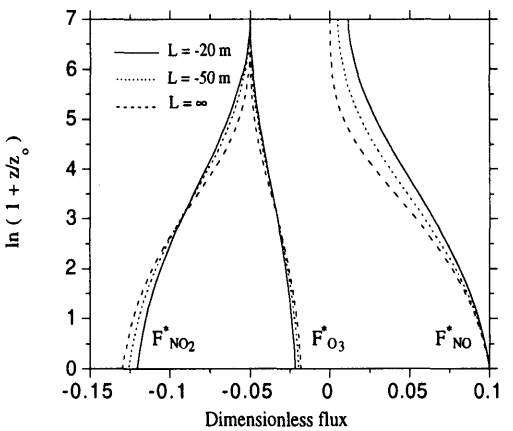

Fig. 4. The dimensionless fluxes $F^*_{O_3}$, F^*_{NO} and $F^*_{NO_2}$ as a function of the Obukhov length scale. The boundary conditions are taken from case 1.

calculated with neutral stability conditions, are representative for the behaviour of the fluxes in the whole surface layer. However, less divergence in the turbulent fluxes are calculated for the convective cases. For instance for ozone, the maximum divergence for $L = -20$ m is equal to 57% and for the neutral case is equal to 65%. Turbulent time scales in the convective situations are smaller than in the neutral case. Consequently, the effect of chemistry is less important and fluxes have a tendency towards the constant value prescribed as boundary condition.

A comparison of the divergence of the turbulent flux between observations and model results is depicted in Fig. 5. The data were collected above short grass ($z_0 = 4 \times 10^{-2}$ m) by the U.S. Forest Service Rocky Mountain Forest and Range Experiment Station's Pawnee Grassland in Colorado (USA) between June 15 through June 19, 1989. A description of the measurements and data treatment can be found in Zeller (1990) and Zeller et al. (1990). Eddy correlations measurements of ozone were taken at 3 m and 8 m and were averaged in half-hour period. The flux measurements were only corrected for sensible heat flux, but not for the sensor response and the separation between measurements. These corrections reduce the divergence of ozone flux because the corrections for 3 m are greater than for 8 m (Zeller, personal communication). The model results are calculated from the standard case 1 increasing/decreasing simultaneously the values of the O_3, NO and NO_2 fluxes. Although observations are rather scatter and the boundary conditions used are general standard values, both, model calculations and measurements clearly show the divergence of the turbulent flux for ozone. For these model calculations, the maximum divergence is 20% between the ozone flux at 8 m and at 3 m. This divergence also shows the different behaviour of the chemical species in the surface layer with respect to other fluxes, for instance momentum or heat, and the necessity to include the chemical reactions terms in the flux equations.

Fig. 6 show the variations with height of the O_3, NO and NO_2 deposition velocities for case 1. Strong curvatures are found close to the surface. Similar results are also found for case 2 (not plotted). Dry deposition measurements are usually taken in the first 10 m above the surface and therefore observations can be strongly affected by chemical transformations. A better approach to calculate the deposition velocity of chemical species, already suggested by Fitzjarrald and Lenschow (1983), could be to calculate the flux and concentration profiles with equations (10)–(12) using measured concentrations and fluxes as boundary conditions. Thus, if chemical reactions and the turbulent mixing have a similar time scales the deposition velocity will vary with height.

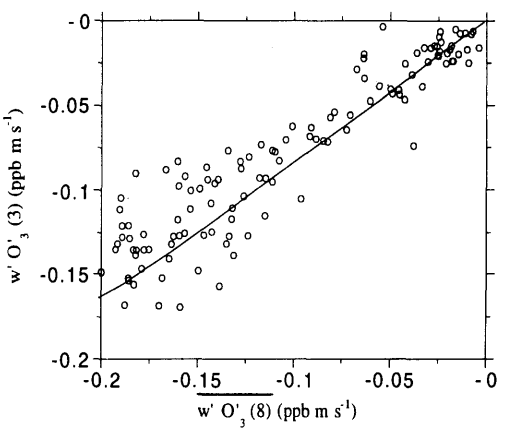

Fig. 5. The ozone turbulent flux at 3 and 8 m height: observations (o) were collected at Pawnee site by Zeller et al. (1990) and the model results (full line) are calculated varying the flux values of case 1.

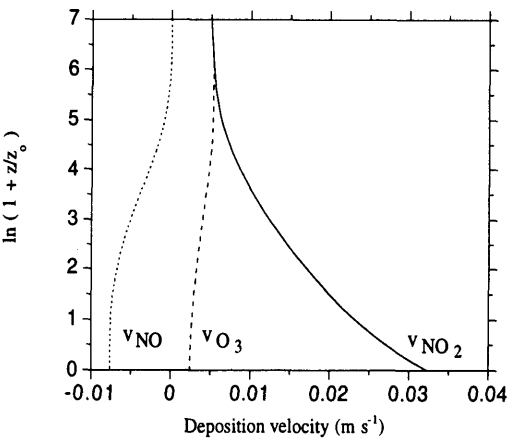

Fig. 6. The deposition velocities of O_3, NO and NO_2 calculated for the case of an upward flux of NO (case 1). Negative values indicate an upward flux.

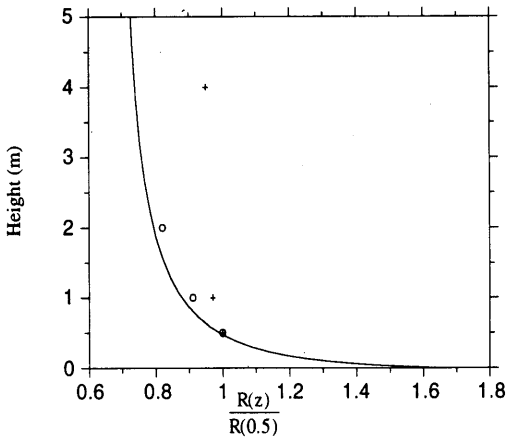

Fig. 7. The photostationary state relation $R(z)/R(0.5)$ as a function of height for an upward flux of NO (case 1). The model results are shown as a full line and the observations as (+) for data set 1 and (o) for data set 2.

The model calculates the variation of $R(z)/R(0.5)$ with height as is shown Figure 7. Two sets of half-hourly average concentration profiles measured above grass in Halvergate (UK), provided by Duyzer (Duyzer, 1991), are compared to the model results. The two data set were measured under the following meteorological conditions: in the first data set u_* is 25 cm s^{-1} and L is -40 m and in the second data set u_* is 29 cm s^{-1} and L is -56 m. The model results show that there is a clear decrease in the photostationary state relationship with height. This correspond to the observations of Duyzer and Bosveld (1988) who also found a significant flux divergence for NO. Therefore, for an upward flux of NO, the chemical balance of the chemical reactions (2) and (3) shifts towards production of NO_2.

4. Conclusions

Using numerical methods to solve the continuity equations for reactive species, the interaction between turbulent diffusion and chemical transformation for the NO-O_3-NO_2 system has been investigated in the atmospheric surface layer. The model equations are made non-dimensional in terms of the respective concentrations at the top of the surface layer, the friction velocity (u_*) and the von Karman constant (κ). As a result, the fluxes and concentrations are only a function of five non-dimensional parameters: the photostationary state relation (R), two ratios of concentrations (R_{NO_x} and R_{O_x}), the ratio of the time scale of turbulent diffusion and chemical transformation (τ) and the stability (ζ_0). From the six boundary conditions required, five are prescribed at the top of the surface layer and one at the bottom. At the top of the surface layer, where the time scale of turbulent mixing is larger than the chemical reaction time, the photostationary state equilibrium ($R(z_t) = 1$) is imposed, i.e., the chemical terms are balanced, and consequently the turbulent flux divergence becomes zero. The model calculates correctly the concentrations and fluxes for the three chemical species for the whole surface layer and approach the asymptotic boundary condition, i.e., photostationary state equilibrium. This is in contrast to previous numerical model which prescribed all the boundary conditions at the lowest level and consequently one or more of the concentration profiles become negative for large z (Fitzjarrald and Lenschow, 1983). This problem was also discussed by Lenschow and Delany (1987).

According to surface layer theory for inert species, the divergence of the turbulent diffusion flux is equal to zero in the whole surface layer. It is expected, however, that this flux will be altered when chemical species are introduced which react with similar time scales to the turbulent diffusion time scale. The model results do indeed show a non-constant turbulent flux which agree with the ozone eddy correlations measurements collected by Zeller et al. (1990). This is due to the non-linear terms of the second-order chemical reactions. In this paper, the only second-order chemical reaction is the conversion of NO to NO_2 by oxidation with ozone. Therefore the non-linear terms are the product of mean concentrations $\langle NO \rangle \langle O_3 \rangle$ and the concentration fluctuation covariance $\langle NO' O_3' \rangle$. A ratio of these two terms (intensity of segregation) has been calculated using concentration and fluxes calculated with the model. The results yield negligible values for the concentration fluctuations.

The calculated value of the photostationary state ratio ($R(z)$) also confirms the non-equilibrium between production and depletion of the chemical terms. Assuming always a downward flux for ozone and nitrogen dioxide two different situa-

tions, an upward and downward flux of NO have been analysed. For both cases large deviations from the photostationary equilibrium ($R(z)=1$) have been found, especially close to the surface. For an upward flux of NO the model results are in the line with the observations, showing that chemical production is higher than chemical destruction ($R(z)>1$).

The model results show the importance of chemical transformations on mean concentration profiles, turbulent fluxes and deposition velocities. Usually the measurements of concentrations and turbulent fluxes are taken at the height between 0.5 and 10 m above ground. These can be used as the boundary conditions for the model to determine more accurately the dry deposition of chemical species at the surface.

5. Appendix

The wind velocity u_i and the concentrations c_i can be described by an ensemble (time/space) average and a fluctuating term. Thus, if $c_i = O_3$, NO and NO_2 ($i=1, 2, 3$), the following decomposition is assumed

$$u_i = \langle u_i \rangle + u_i', \tag{A1}$$

$$c_i = \langle c_i \rangle + c_i', \tag{A2}$$

where the ensemble average of the fluctuating term is:

$$\langle u_i' \rangle = \langle c_i' \rangle = 0. \tag{A3}$$

Applying this decomposition, the relation obtained in (9) and ensemble averaging, the governing equations for O_3, NO and NO_2 can be written in the following way

$$\frac{\partial \langle c_i \rangle}{\partial t} + \langle u_j \rangle \frac{\partial \langle c_i \rangle}{\partial x_j} + \frac{\partial}{\partial x_j}\left\{ \langle u_j' c_i' \rangle - \gamma_i \frac{\partial \langle c_i \rangle}{\partial x_j} \right\}$$
$$= v_i \left(\sum_{m,n}^{2} (1-\delta_{mn}) \frac{k_2}{2} (\langle c_m \rangle \langle c_n \rangle + \langle c_m' c_n' \rangle) - k_3 \langle c_3 \rangle \right) + \delta_{i2} S_i(x, t), \tag{A4}$$

where v_i is the vector $(-1, -1, 1)$ and δ_{mn} is Kronecker's delta equal to 1 if $m=n$ and 0 if $m \neq n$.

Several studies (Donaldson and Hilst (1972), Builtjes and Talmon (1987), Schumann (1989)) have shown the importance of the concentration fluctuation term ($\langle c_m' c_n' \rangle = \langle NO' O_3' \rangle$). This term is often neglected in model calculations. However, the inclusion of this term provides an estimation of the interaction between turbulence, which brings together the different chemical species through the mixing, and the chemical reaction (2). First-order reactions are unaffected by the presence of concentration fluctuations (Lamb, 1975). In this study, $\langle NO' O_3' \rangle$ has been included, after an effective chemical constant rate k_2^* has been defined in the following way:

$$k_2^* = k_2(1 + I_s), \tag{A5}$$

where I_s is the intensity of segregation defined by

$$I_s = \frac{\langle NO' O_3' \rangle}{\langle NO \rangle \langle O_3 \rangle}. \tag{A6}$$

Values of this parameter can range from 0 to -1 depending on the concentration of chemical species and the atmospheric stability (Vilà-Guerau de Arellano et al., 1990). The concentration fluctuation covariance is estimated using the following relation

$$\langle NO' O_3' \rangle = C_1 \sigma_{NO} \sigma_{O_3} \tag{A7}$$

where σ_{NO} and σ_{O_3} are the standard deviations of the mean concentrations of NO and O_3 and C_1 is the correlation coefficient. I_s can be calculated from the correlation coefficient multiplying by the NO and O_3 standard deviations and dividing by the NO and O_3 means. Aircraft measurements (Vilà-Guerau de Arellano et al. (1990) and Vilà-Guerau de Arellano et al. (1992)) and wind-tunnel measurements (Builtjes and Talmon, 1987) obtained a value of about -0.7 for the correlation coefficient. For a NO reacting plume in the surface layer, Komori et al. (1991) reported minimum values of the intensity of segregation equal to -0.27, which suggests that the value -0.7 for the correlation coefficient can be a good estimation. In a second-order closure study, Vilà-Guerau de Arellano and Duynkerke (1992) studied the intensity of segregation and the correlation coefficient. In relation with the correlation coefficient, the values always range from -0.6 to -0.8 depending on the fluxes and the ratio of initial concentrations.

From surface layer theory, the standard deviations are proportional to the ratio of the reactive species flux and the friction velocity u_* (Stull, 1988). Thus, for the chemical species i:

$$\sigma_i = C_2 \left| \frac{\langle w' c_i' \rangle}{u_*} \right|. \tag{A8}$$

Typical values for C_2 (reciprocal of the correlation coefficient between w and c_i multiplied by the ratio u_*/σ_w) estimated for temperature fluctuations in the neutral surface layer are around 2.5 (Nieuwstadt, 1984).

Equations (A4) are solved in the atmospheric surface layer assuming that:

(a) molecular diffusivity is neglected ($\gamma_i = 0$);
(b) the processes are stationary;
(c) the ensemble average quantities are independent of the horizontal coordinates;
(d) turbulent fluxes are modelled using K-theory:

$$\langle w' c_i' \rangle = -\frac{K(z)}{\phi_c} \frac{\mathrm{d}\langle c_i \rangle}{\mathrm{d}z}, \tag{A9}$$

where the exchange coefficient ($K(z)$) for neutral stable conditions can be expressed as

$$K(z) = \kappa u_* (z + z_0), \tag{A10}$$

and the stability correction for convective case (Dyer, 1974) is

$$\phi_c = \left(1 - \gamma_c \left(\frac{z + z_0}{L}\right)\right)^{-a}. \tag{A11}$$

The von Karman constant (κ) is equal to 0.4, u_* is the friction velocity, z_0 the roughness length, z is the height above the roughness length, L is the Obukhov length and γ_c and a are experimental constants equal to 16 and 0.5, respectively. The exchange coefficient is assumed equal for O_3, NO and NO_2. The use of the standard Monin–Obukhov (M–O) similarity theory is still a matter of discussion when the chemical reactions have a similar time scale to the turbulence. Fitzjarrald and Lenschow (1983) showed that for ozone M–O similarity theory is a good approximation, whereas departures from the theory could be expected for nitric oxide and nitrogen dioxide. Using a different chemical species triad, Brost et al. (1988) suggested that M–O similarity theory might hold for linear systems when chemical species remain close to equilibrium, and consequently are produced and destroyed by chemical reaction.

(e) sources of NO are neglected, i.e., $S_{NO}(x, t) = 0$.

After the assumptions (a), (b), (c), (d) and (e) are applied, the eqs. (A4) can be written in the following way

$$\frac{\partial}{\partial(z + z_0)} \left(\frac{1}{\phi_c} (z + z_0) \frac{\partial \langle c_i \rangle}{\partial(z + z_0)} \right) + v_i \left(\sum_{m,n}^{2} (1 - \delta_{mn}) \left(\frac{k_2^*}{2\kappa u_*} \langle c_n \rangle \langle c_m \rangle \right) + \frac{k_3}{\kappa u_*} \langle c_3 \rangle \right) = 0. \tag{A12}$$

In order to make (A12) dimensionless, the equations are multiplied by the variable $(z + z_0)$ and divided by the respective concentrations at the top of the surface layer, i.e., $c_i(z_t)$. With the variable change $x = \ln(1 + z/z_0)$, the eqs. (10), (11) and (12) are obtained with the non-dimensional parameters (13)–(16) and (18).

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