The Interpretation of Measurements of Surface Exchange of Nitrogen Oxides: Correction for Chemical Reactions

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The interpretation of measurements of surface exchange of nitrogen oxides: correction for chemical reactions

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The interpretation of measurements of the land–atmosphere exchange of NO and NO_2 is complicated by the interference of chemical reactions in air. In the absence of measurements to test correction procedures a one-dimensional surface layer model was constructed to generate concentrations and fluxes of relevant trace gases in the surface layer to simulate measurement data. The model contains a detailed description of surface exchange processes and a comprehensive submodel describing relevant reactions in air including hydrocarbons. To provide realistic conditions in the simulation runs important parameters and boundary conditions to drive the model were obtained from a large field experiment. The results of calculations with the model were used to test and compare several existing and new procedures to correct flux measurements. In testing the model important parameters such as air concentrations and surface fluxes were varied over an order of magnitude in order to compare the procedures in a broad range of conditions. The calculations showed that the true surface flux of NO and NO_2 may differ from the uncorrected flux by, on average, 20% during the day to 40% at night. Correction procedures from the literature yielded incorrect results with differences as large as 100% between the modelled and true surface fluxes because basic assumptions were not valid.

A new, simple, correction procedure is described which derives fluxes that differ by less than 5% from the true flux during the day and less than 20% at night. All studied procedures were then applied to field data to derive the true surface flux of NO and NO_2 above grassland.

1. Introduction

The exchange of nitrogen oxides between the earth and the atmosphere has been studied for several decades. Micrometeorological methods in which the flux is measured above the surface do not influence the exchange rate and therefore are nowadays considered reference methods. The methods rely on the assumption that under certain conditions regarding homogeneity of the underlying surface, stationarity of the atmospheric conditions and the proximity of sources of the pollutant the vertical flux is constant with height (see, for example, Fowler & Duyzer 1989). Consequently the flux measured a few metres above the surface is equal to the flux crossing the air–surface interface. This assumption, however is

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not valid when the trace gas is produced or destroyed in the layer of air between the observation point and the surface. NO (nitric oxide), NO_2 (nitrogen dioxide) and O_3 (ozone) undergo reactions fast enough to interfere with surface exchange.

Three reactions are most important here:

$$\begin{array}{lcl} (1) & NO_2 + h\nu \rightarrow NO + O & j_{NO_2} \\ (2) & O + O_2 \rightarrow O_3 & k_2 \\ (3) & NO + O_3 \rightarrow NO_2 & k_3 \end{array}$$

Where j_{NO_2}, k_2 and k_3 are the rate coefficients for reaction 1, 2 and 3 respectively and $h\nu$ represents a photon. The second reaction, however, is very fast and is usually considered immediate. The other two reactions have timescales around 30 to 100 s, i.e. $(j_{NO_2})^{-1}$ or $(k_3 O_3)^{-1}$ and may therefore interfere with surface exchange processes with timescales of the same order. As a result, vertical concentration profiles of these gases may deviate from their unreactive equivalents. Moreover, since gases are produced or destroyed between the observation level and the surface, the flux measured at a reference height will differ from the surface flux. Measurements of fluxes of nitrogen oxides have shown confusing results (Wesely *et al.* 1989; Delany *et al.* 1986; Hicks *et al.* 1986; Wesely *et al.* 1982). Part of the variability in these results is probably caused by these reactions.

Several authors have shown quantitatively how exchange rates of nitrogen oxides could be affected by chemical reactions (Gao *et al.* 1991; Fitzjarrald & Lenshow 1983; Duyzer *et al.* 1983; Kramm 1989; Vila *et al.* 1993). Kramm (1989) suggests that even the direction of the vertical apparent fluxes of NO or NO_2 can change between the height of the observations and the surface.

Some authors show how, on a theoretical basis, the true surface flux can be derived from observations in the surface layer over a height range of a few metres (Duyzer 1992; Kramm *et al.* 1991; Lenshow & Delany 1987; Fitzjarrald & Lenshow 1983). Verification of these correction procedures, however, requires flux measurements at multiple heights with an accuracy that cannot be achieved with currently available methods. Moreover, independent methods to assess the ‘true’ surface flux from a site are not available. The lack of validation of these correction methods has led to significant uncertainty in the interpretation of measurements (Duyzer & Fowler 1994).

In the absence of measurements to test correction procedures, a one-dimensional surface layer model is applied to generate concentrations and fluxes of relevant trace gases in the surface layer (0–5 m) to simulate measurement data. These data are then used to test the ability of several correction procedures to derive true surface fluxes from biased concentration gradients. The model combines a full description of turbulent vertical exchange in the surface layer, a detailed description of surface exchange and a comprehensive model describing (photo)-chemical reactions in air between reactive trace gases such as nitrogen oxides, hydrocarbons and several radical species such as the hydroxyl radical. Important input parameters for the model are derived from measurements during a large field experiment over grassland in the Halvergate marshes of Norfolk (U.K.) (see Duyzer *et al.* 1990; Hargreaves *et al.* 1992). The principle objective of the field experiment was to study mechanisms of exchange of trace nitrogen gases and the major variables for the exchange of NO, NO_2 and O_3 were measured during this experiment.

2. Description of the simulation model

(*a*) *General description*

The surface layer model that is used to generate data consists of 20 layers which are logarithmically spaced with the largest density of layers near the surface. The model extends in principle to 700 m height but only the processes in the surface layer not extending above 100 m are important here.

The change of the concentration c_i of trace gas i with time in each layer j is calculated according to

$$\partial c_i/\partial t = -\Delta F_i/\Delta z + Q_{i,j}, \tag{2.1}$$

where $Q_{i,j}$ indicates the chemical production and sink term for each chemical species i in this layer and $\Delta F_i/\Delta z$ is the divergence of the flux F_i across layer j.

Air chemistry in each layer is simulated using a reaction scheme described by Hough & Derwent (1987). This model contains 85 reactions and 43 chemical species. Reaction rate constants are calculated as a function of air temperature and zenith angle. Hydrocarbons are treated in lumped classes such as isobutylene for olefinic species and N-butane for aliphatic hydrocarbons. Turbulent exchange between the layers of trace gas i is calculated using classical K-theory similar to Thompson & Lenshow (1984), namely,

$$F_{i,j} = -k_z \frac{c_{i,j} - c_{i,j-1}}{z_j - z_{j-1}}, \tag{2.2}$$

where k_z is the turbulent exchange coefficient at height z of layer j calculated as

$$k_z = \kappa u_* z/\Phi(z/L), \tag{2.3}$$

in which u_* is the friction velocity, κ is von Karman's constant (0.4), $\Phi_c(z/L)$ the flux profile function for gases derived from Φ_h the flux profile function for heat (Dyer & Hicks 1970) and L the Monin–Obukhov stability parameter. Trace gas exchange between the lowest layer of air and the surface, at a height equal to the roughness length z_0, is parametrized according to the resistance layer model described by Wesely (1989), i.e.

$$F_{i,0} = -\frac{c_{i,1} - c_{i,0}}{R_b + R_c}, \tag{2.4}$$

where $c_{i,1}$ and $c_{i,0}$ denote the concentration of the trace gas i in the lowest layer of air (at a height of 0.5 mm above z_0) and the model boundary (the soil-vegetation level) respectively. R_b is the pseudo-laminar boundary layer calculated as

$$R_b = \frac{2}{\kappa u_*}\left(\frac{Sc}{Pr}\right)^{2/3}, \tag{2.5}$$

where Sc represents the Schmidt number (the ratio between the molecular diffusion coefficient and the kinematic viscosity) and Pr the Prandtl number (0.72). The canopy resistance R_c is controlled by global radiation G in W m^{-2} and air temperature (T in °C) according to Wesely (1989):

$$R_c = 0.8788\left[1 + \left(\frac{200}{G}\right)\right]^2 \left(\frac{400}{T(40-T)}\right) R_{c,\min}. \tag{2.6}$$

Table 1. *Concentration of precursor trace gases in the base run with hydrocarbons*

(The concentration of these gases is kept constant throughout the run and in all layers.)

gas	concentration (ppm)
CH_4	1.75
CO	0.3
H_2O	1.6×10^4
butane	0.45
butylene	0.01
CO_2	353

The minimum canopy resistances $R_{c,min}$ for O_3 and NO_2 were given values of $160\ s\ m^{-1}$. All other gases were given canopy resistances similar to Wesely (1989). Radicals were given a low canopy resistance of $100\ s\ m^{-1}$.

Emission of NO is prescribed throughout the day and simulated by using a soil resistance and a concentration of NO in the soil ($c_{NO,0} = 4$ ppb in the base run). This leads to an emission of NO between 5 and 10 ng N NO $m^{-2}\ s^{-1}$ which is of the same order as (uncorrected) fluxes of NO observed by micrometeorological measurements during the experiment (Duyzer *et al.* 1990). At the same site Remde *et al.* (1993) observed fluxes between 7 and 14 ng N $m^{-2}\ s^{-1}$ using flux chambers. We therefore assume that surface exchange processes are modelled in a realistic way in the simulation program.

Boundary conditions are also prescribed at the top of the boundary layer where the NO_x concentration ($NO_x = NO + NO_2$) is maintained at a constant value. The concentrations of NO and NO_2 in this layer are calculated by using a simplified chemical scheme with only reactions (1) and (3). Turbulent exchange with this layer is simulated by diffusive transport. Several sensitivity runs showed that the method used to model the exchange at the top of the boundary layer and the treatment of chemical processes in the top layer are not critical for the processes in the region of interest near the surface.

In the runs including hydrocarbons the concentration of water vapour, precursor hydrocarbons, carbon monoxide and methane was the same in all layers and was maintained at a constant value (given in table 1) throughout the simulation. The concentrations of all other gases were variable and calculated according to equation (2.1). Starting concentrations for NO, NO_2 and O_3 were 5, 13 and 37 ppb in the base run.

The set of coupled differential equations (2.1) and (2.2) for each layer is solved by using the FACSIMILE program described by Curtis & Sweetenham (1988). To test the correction procedures in all relevant conditions a complete diurnal cycle is simulated. Model output, i.e. concentrations and fluxes at various heights in the surface layer, is generated every model half hour in a form which can be used directly in the correction procedures described above.

(*b*) *Base run*

In the base run the NO_x ($NO + NO_2$) concentration in the free troposphere was 10 ppb. Diurnal cycles of micrometeorological parameters necessary to calculate k_z were derived from observations on 20 September 1989. These included friction

Table 2. *Midday and midnight values of important parameters*
(R_c is given for O_3 and NO_2.)

	midday	midnight
$T_{air}/°C$	23	9
$u^*/(m\ s^{-1})$	0.55	0.05
L/m	−155	20
j_{NO_2}/s^{-1}	5.5×10^{-3}	0
$G/(W\ m^{-2})$	600	0
$R_c/(s\ m^{-1})$	160	650

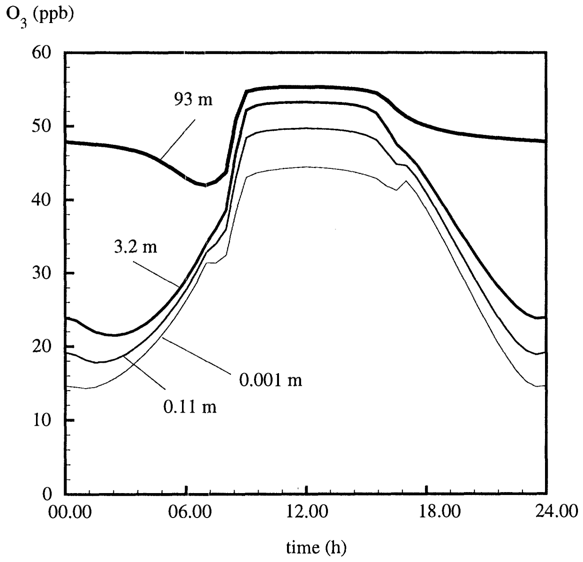

Figure 1. The concentration of O_3 at several heights during the day calculated in the base run.

velocity (u_*), air temperature (T_{air}), atmospheric stability (L), global radiation (G) and NO_2 photolysis rate (j_{NO_2}). The latter was measured by using a special NO_2 actinometer. Multiparameter functions, often of sinusoidal shape, describing the course of these parameters on the 20th were obtained from least-square fits to the observations. These continuous functions, were used in the simulation runs to calculate values of these parameters in every timestep and calculate values for turbulent exchange rates, temperature-dependent reaction rates and canopy resistances. The major micrometeorological values at midday and midnight are given in table 2.

The course of O_3 concentrations at several heights during the day as calculated in the base-model runs is shown in figure 1. The concentration of NO during the day was around 2 ppb and nearly zero at night while NO_2 concentration reached 10 ppb at night and 6 ppb during the day. The O_3 concentrations reached 50 ppb on the middle of the day and dropped to 10 ppb at night. No hydrocarbons were assumed present in the air for the base run.

In figure 2 the fluxes of NO and NO_2 calculated at several heights in the base

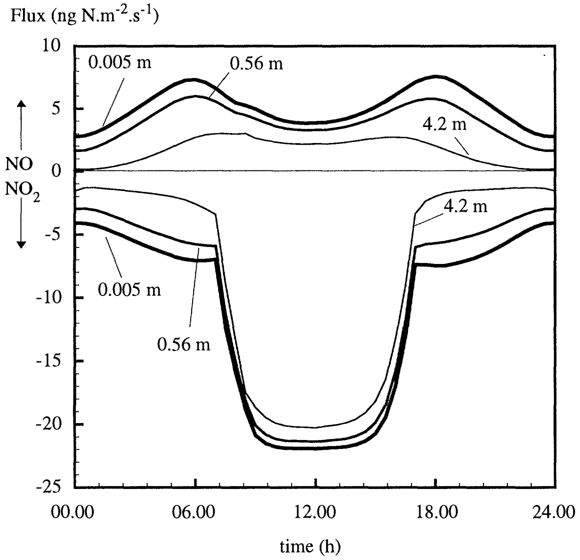

Figure 2. The flux of NO and NO_2 at several heights in the base run with no hydrocarbons added.

run are shown. The fluxes are largest near the surface. At higher levels in the surface layer the fluxes become very small. At night when turbulent mixing rates are small the flux divergence is quite large. During the day mixing is more intense which reduces flux divergence. In addition, the reaction between O_3 and NO which causes the large divergence at night by acting as a sink for NO and as a source for NO_2 is compensated by the photolysis of NO_2 during the day. Figure 3 illustrates the height dependency of the flux divergence $\Delta F/\Delta z$, which is largest near the surface and declines to a small value at a height of 10 m. It is hard to measure a divergence of this size with currently available methods such as eddy correlation. It is also clear from these simulations that corrections are required: the flux of NO at the surface may differ by as much as 100% from the flux at 10 m. The flux measured above the surface therefore differs from the surface flux. Moreover, the vertical concentration gradients of these gases cannot be used to estimate surface fluxes. Since the concentration near the surface is changed by these reactions even the actual flux of gases entering stomata differs from the 'unreactive' case.

3. Procedures to derive surface fluxes of reactive trace gases from concentration profiles

In this section several procedures to derive surface fluxes from vertical concentration profiles are discussed briefly. These procedures will be applied to the output of model calculations. To treat the data exactly as if they were measured values only the concentrations of NO, NO_2 and O_3 at four measurement heights (0.5, 1, 2 and 4 m) and the values of u_*, L and j_{NO_2} used in the simulation are given as input to the correction procedures described below. These data are usually available from field experiments such as the Halvergate experiment mentioned above. In a similar way the 'uncorrected' fluxes (as well as the 'corrected fluxes') are calculated from the simulation runs by using only the concentrations at these heights.

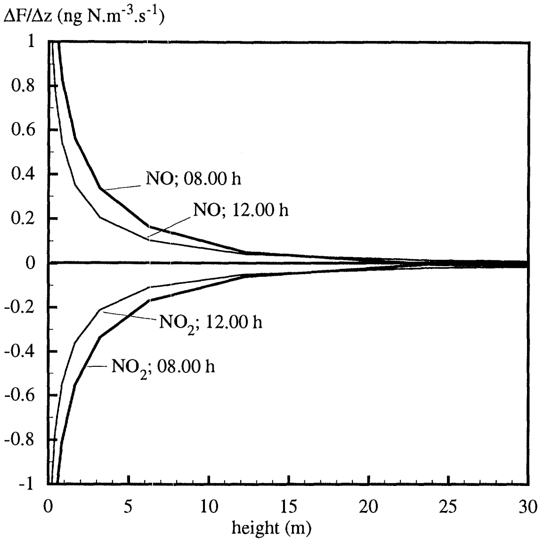

Figure 3. The flux divergence of NO and NO_2 as a function of height calculated from the base run.

(*a*) *Unreactive gases*

The gradient and eddy correlation methods are the two most important micrometeorological techniques used (Fowler & Duyzer 1989). In the gradient method the flux is estimated from the vertical gradient of the pollutant concentration and a vertical exchange coefficient k_z. The vertical concentration gradient $\partial c/\partial z$ at height z and the vertical flux F_z of a compound are related according to the flux profile assumption:

$$F_z = -k_z(\partial c/\partial z)_z. \tag{3.1}$$

If the flux is constant with height, F_z is equal to the surface flux F_0.

In practice the surface flux F_0 (at the roughness length z_0) of an inert compound can easily be derived from the integrated form of equation (3.1):

$$c_{z_2} - c_{z_1} = -\frac{F_0}{\kappa u_*}\left[\ln\left(\frac{z_2}{z_1}\right) - \Psi_{\mathrm{c}}\left(\frac{z_2}{L}\right) + \Psi_{\mathrm{c}}\left(\frac{z_1}{L}\right)\right], \tag{3.2}$$

with $\Psi_{\mathrm{c}}(z/L)$ the integrated flux profile function Φ_{c} (calculated from Φ_{h}). The surface flux is calculated for example from a least square fit of the straight line between the concentration measured at heights z and the function, $\ln(z) - \Psi_{\mathrm{h}}(z/L)$.

(*b*) *Reactive gases*

As already discussed concentrations and fluxes of some gases are influenced by chemical reactions in air. As a result the vertical profiles of each of these gases may depart from the classical description provided by Monin–Obukhov similarity theory describing the transport of conserved (non-reactive) species. Fitzjarrald & Lenshow (1983) derive new flux profile functions for reactive trace gases but indicate that the classical functions may be used in most cases.

The magnitude of the influence of the reactions on exchange processes can be assessed from the boundary layer budget of the trace gas. Under stationary conditions ($\partial c/\partial t = 0$) the flux divergence of NO_2 at height z is equal to

$$(\partial F/\partial z)_{NO_2} = Q_{NO_2}. \tag{3.3}$$

Considering only reactions (1) and (3) gives

$$(\partial F/\partial z)_{NO_2} = k_3[NO][O_3] - j_{NO_2}[NO_2]. \tag{3.4}$$

The magnitude of the flux divergences of NO and O_3 are then equal to (3.4) but they have an opposite sign. As was pointed out by Fitzjarrald & Lenshow (1983), micrometeorological variables (u_*, L), reaction rate constants and measurements of at least six independent parameters such as fluxes and concentrations at two heights are required to infer the exact surface flux. To derive the true surface flux from biased concentration profiles numerical methods can be used to solve the differential equations describing the flux divergences (3.4) and the flux gradient relations (3.1) in the boundary layer.

Lenshow & Delany (1987) present an analytical solution to solve the set of coupled differential equations (3.1) and (3.4) taking the concentration of ozone constant with height and ignoring stability effects. They provide an analytical description of the NO flux as a function of height. This solution contains two Bessel functions. One of these however causes the NO flux to become infinite at higher levels. Since this is obviously not realistic the authors omit the latter Bessel function from the solution. This results in a stable solution throughout the boundary layer. From the theory given in Lenshow & Delany (1987) we constructed a correction procedure that fits these analytical functions to the observed concentration profiles by varying the surface flux. The solution based on a single Bessel function is labelled LD1 here, LD2 is the solution based on two Bessel functions.

The procedure described in detail in Duyzer (1992), hereafter labelled ‘JD91’ takes chemical reactions and atmospheric stability into account and solves the coupled differential equations (3.1) and (3.4) numerically. In an iterative process the surface-fluxes of the reactive gases are varied until an optimal fit of the calculated profile to the observed profiles of NO, NO_2 and O_3 is obtained.

(c) *An empirical method*

The application of only two reactions in (3.4) to characterize chemical modification of the concentration profiles implicitly assumes that other reactions are not important. It will be shown below that the interference of other gases reacting with NO and NO_2 could also be important. It appears that under realistic conditions the procedures discussed above lead to biased corrections. Therefore new methods were developed in which these assumptions are not necessary. In these procedures the flux divergence is derived from the observations directly.

A new method (hereafter called the ‘empirical method’) has been developed which does not use the flux divergence equations (3.4). The development of the flux divergence $\partial F/\partial z$ for NO, NO_2 and O_3 with height is approximated with a logarithmic function of height. From figure 3 this seems a reasonable approximation. Moreover using the simple equations for the flux derived by Lenshow & Delany it can be demonstrated that at heights lower than 4 m the flux divergence can be described with a function of the form:

$$(\partial F/\partial z)_z = a\ln(z) + b. \tag{3.5}$$

Integrating these functions for NO, NO_2 and O_3 independently yields expressions for the flux as a function of height, i.e.

$$F_z = F_0 + \int_{z_0}^{z} \left(\frac{\partial F}{\partial z}\right)_z \mathrm{d}z = F_0 + (a-b)(z-z_0) + b[z_0 \ln(z_0) - z\ln(z)]. \quad (3.6)$$

The flux is related to the concentration profile according to (3.1). These equations can be used to derive the concentration profiles for the reactive gases:

$$c_z = c_{z_1} - \int_{z_1}^{z} \frac{\Phi(z/L)}{\kappa u_*} F_z \,\mathrm{d}z, \quad (3.7)$$

$$c_z - c_{z_0} = -\frac{F_0}{\kappa u_*}\int_{z_0}^{z} \frac{\Phi(z/L)}{z}\,\mathrm{d}z - \frac{a-b}{\kappa u_*}\int_{z_0}^{z} \Phi(z/L)\,\mathrm{d}z - \frac{b}{\kappa u_*}\int_{z_0}^{z} \Phi(z/L)\ln z\,\mathrm{d}z. \quad (3.8)$$

The solution to the integrals in (3.8) can be found in Peirce (1929). The parameters a and b and the surface flux F_0 for each of the three gases NO, NO_2 and O_3 and the concentrations at the surface are now determined from a least square fit of the measured profiles to equation (3.8).

Since four parameters need to be fitted, the concentration of the three reactive gases at, at least, four heights in the lowest metres of the atmosphere need to be available. It is important to note that the surface flux of, for example, NO can be calculated from the concentration profile of NO only. Information on the fluxes and profiles of other trace gases is not required.

(*d*) *A correction factor*

Apart from these methods that require sophisticated iterative procedures and low-noise data it would be desirable to be able to estimate the correction ‘directly’ from measured quantities. With some sacrifice in accuracy this can be accomplished.

First the flux F_z at the measuring height l_1 is approximated by the uncorrected flux (F^*) at this level. F^* is calculated from the measurements at this height by simply using equation (3.2) for unreactive gases thereby implicitly ignoring the influence of chemical reactions on the gradient between 0.5 and 4 m. This seems to be a reasonable assumption during the day when mixing is efficient.

From above, it is also reasonable to approximate the flux divergence by a logarithmic function according to equation (3.5). The factor a for NO_2 can then simply be calculated from

$$a_{NO_2} = z\left(\frac{\partial^2 F_z}{\partial z^2}\right)_{NO_2} = z\left[k_3\left(NO\frac{\partial O_3}{\partial z} + O_3\frac{\partial NO}{\partial z}\right) - j_{NO_2}\frac{\partial NO_2}{\partial z}\right]. \quad (3.9)$$

It is interesting to realize that the gradients $\partial c/\partial z$ are related to the ‘uncorrected’ fluxes F^* and therefore

$$a_{NO_2} = -\frac{\Phi_c(z/L)}{\kappa u_*}[k_3(NO F^*_{O_3} + O_3 F^*_{NO}) - j_{NO_2}F^*_{NO_2}]. \quad (3.10)$$

As shown by Lenshow & Delany it can also be assumed that the flux divergence $\partial F/\partial z$ approaches zero at higher levels. At a height l_2 (taken as 4 m, our highest measurement point) $\partial F/\partial z$ is equal to zero, therefore $b = -a\ln(l_2)$. The parameters a and b can be calculated for NO, NO_2 and O_3 from the uncorrected F^*. Both

F_z and $\partial F/\partial z$ are known and the surface flux F_0 for NO_2 can be approximated as

$$F_0 = F_{l_1} + \int_{l_1}^{z} \left(\frac{\partial F}{\partial z}\right)_z \mathrm{d}z = F^* + a_{NO_2} l_1 (1 + \ln(l_2/l_1)). \qquad (3.11)$$

The attractive feature of this approach is that a direct relation between the 'uncorrected' gradient (or flux) and the true surface flux is obtained. It appears that this method does not have the low noise data requirement of the empirical method. In addition, it will appear that although the 'two-reaction scheme' is used to estimate the pre-logarithmic factor a the method does not suffer from the limitations typical of the 'two-reaction scheme' methods. This scheme also provides reasonable results in cases that the two-reaction schemes fail.

4. Calculation of the surface flux from biased profiles

(a) *Base run*

As outlined above, the concentrations of NO, NO_2 and O_3 at four heights calculated in the simulation model run are used as input to the correction procedures. The surface fluxes calculated in this procedures are shown in figure 4 together with the 'true' surface flux from the simulation. A perfect correction procedure is capable of deriving the true surface flux from the biased concentration profiles calculated in the simulation. The surface flux calculated from the concentrations directly by using equation (3.2), thereby assuming a flux constant with height (i.e. no influence of chemical reactions), is also shown as the 'uncorrected flux'. The difference between the uncorrected flux and the true flux illustrates how large errors can be if field measurements are not corrected for chemical reactions. The surface flux of NO differs from the flux calculated directly from the data (i.e. the 'uncorrected' flux) by a factor of three at night. During the day the difference is smaller but the uncorrected flux is still about 70% of the true flux.

The analytical solution presented by Lenshow & Delany (1987) labelled LD1 gives results that differ strongly from the other methods. The exact cause of this result was not investigated in detail. Probably the use of only one Bessel function, although necessary to obtain realistic solutions at higher levels is not correct at low levels. In our tests this method however gives unrealistic results in all cases and is therefore no longer used here. The surface flux calculated from the data by using the method described by L&D (LD2) gives good results during the day but gives unrealistic results at night probably because of stability effects. In runs with a neutral atmosphere (not reported here) the LD2 procedure gave much better results indicating that stability effects cannot be ignored at night. The correction procedures described in Duyzer (1992) as well as the empirical solution yield satisfactory results. Under these conditions the corrections for O_3 are small.

(b) *Model runs with complete chemistry including hydrocarbons*

In a more realistic example hydrocarbons are added to the surface layer air (see table 1). In the base run 0.3 ppm CO, 1.75 ppm CH_4, 0.45 ppm n-butane and 0.01 ppm butylene were added.

None of the above procedures except the 'empirical method' are able to estimate the surface flux of NO and NO_2 correctly. This result is displayed in figure 5

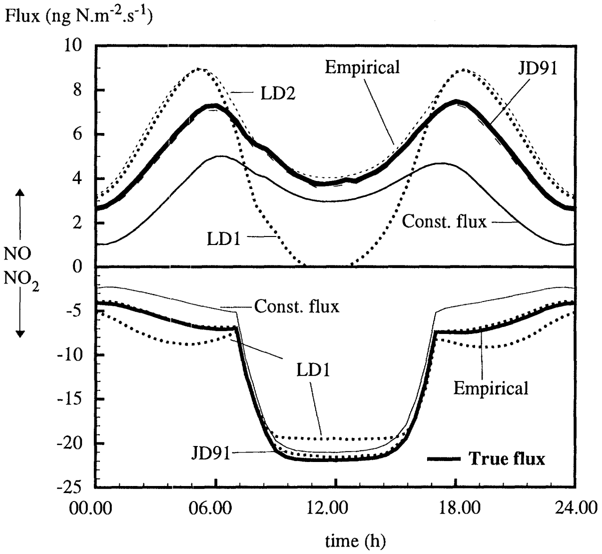

Figure 4. The true surface flux of NO and NO_2 from the base run and the surface fluxes calculated from the concentrations at 0.5, 1, 2 and 4 m using the classical gradient approach (equation (3.2)) and the correction-procedures described in the text.

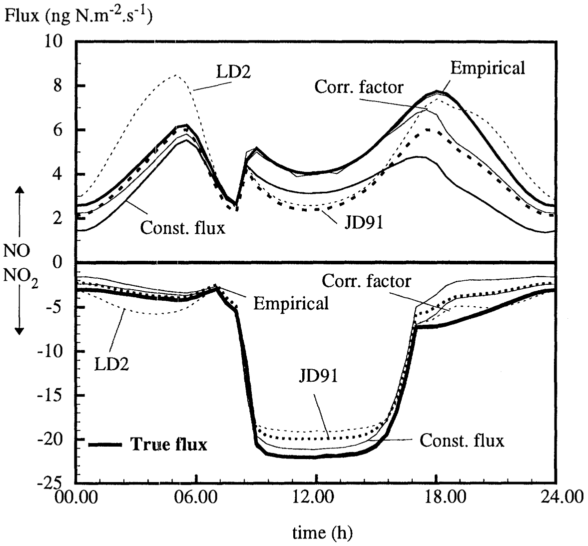

Figure 5. The true surface flux of NO and NO_2 in the run including hydrocarbons and the surface fluxes calculated from the concentrations at 0.5, 1, 2 and 4 m using the classical gradient approach (equation (3.2)) and the correction procedures described in the text.

showing that large errors can be made if a simple two-reaction scheme is used. The empirical model gives good results because no assumptions regarding the cause of the flux divergence were made. The correction factor approach gives good results during the day, but differs by up to 10% from the true flux at night.

The reason for the erroneous results of most correction procedures based on two-reaction schemes must be that the other sources and sink processes of these gases are ignored. Other reactions converting NO and NO_2 should be taken into

Table 3. *Range of values of important parameters in several simulation runs*
(The maximum surface fluxes are given.)

parameter	range
C butane (ppb)	0–450–1350
C butylene (ppb)	0–10–30
NO_x (ppb)	10–20–40
$F_{NO}/(\mathrm{ng\ N\ m^{-2}\ s^{-1}})$	7–25
$F_{NO_2}/(\mathrm{ng\ N\ m^{-2}\ s^{-1}})$	2–80
$F_{O_3}/(\mathrm{ng\ m^{-2}\ s^{-1}})$	0–800
$u^*/(\mathrm{m\ s^{-1}})$	0.28–0.55

account in order to derive surface fluxes for NO and NO_2 correctly. Focusing on NO_2 in our comprehensive model several reactions could be important. Inorganic species such as O_3, NO_3 and NO may react with NO and form nitric or nitrous acid. Organic radicals, products of the reactions between hydrocarbons and ozone or OH radicals may react with NO to form NO_2. Which reactions are responsible was not investigated in detail. Calvert & Stockwell (1983) as well as Thompson & Lenshow (1984) investigated the importance of other reactions and non-stationarity ($\partial c/\partial t$) on production and destruction rates of nitrogen oxides. In any case it is clear that it will not be possible to determine all factors responsible for the additional terms in the flux divergence equations in the field. Therefore the empirical correction procedures and the correction factor method are probably more useful.

Several additional sensitivity runs in which parameters were changed were completed. Table 3 shows the range within which each parameter was varied in the various sensitivity runs. In the table the maximum true surface fluxes are given. This is usually the flux at the middle of the day. By changing the concentration of NO in the soil ($c_{NO,0}$) the complete diurnal cycles of the NO flux and of other gases are also changed.

In all of these runs the concentration of NO varied between 0.2 and 8 ppb, the NO_2 concentration varied between 2 and 35 ppb and O_3 varied between nearly zero and 50 ppb. Moreover the range of the fluxes of NO, NO_2 and O_3 in the simulation runs encompasses the range in which these fluxes varied during the Halvergate experiment. It therefore seems reasonable to assume that conclusions concerning the ability of correction procedures are also valid for the field results.

The results of all runs are summarized in table 4 showing the magnitude of the corrections to the flux calculated by using equation (3.2). For NO the uncorrected flux is always an underestimation of the true surface emission. NO_2 deposition fluxes are underestimated by the uncorrected flux whereas the uncorrected deposition flux of O_3 is an overestimation of the true deposition flux. Daytime corrections are usually of the order of 20% for NO and NO_2 for O_3 corrections are small. Corrections are usually larger at night because of reduced mixing. Even for O_3 corrections may be significant.

All runs yielded similar results, i.e. incorrect estimates (up to 100%) of the surface flux using the simple two-reaction procedures (LD2 and JD1). Using the

Table 4. *Representative results from all sensitivity runs in* ng m^{-2} s^{-1}

(A, average true surface fluxes; C, average correction to uncorrected flux equal to the difference between the true surface flux and the flux calculated according to equation (3.2) ($F_{\text{uncorrected}} - F_{\text{true}}$). C_{rel}, average relative corrections.)

	A day	A night	C day	C night	C_{rel} day (%)	C_{rel} night (%)
NO	8.1	5.8	−2.0	−2.2	−22	−38
NO_2	−16	−5.6	1.9	2.4	16	42
O_3	−320	−34	−10	−5.4	−7	−23

empirical method the true surface flux could be estimated from the biased concentration profiles within a few percent throughout the diurnal cycle. Using the correction factor approach the surface flux could be estimated within a few percent during the day and within roughly 20% during the night. It is also important to note that in many cases corrections using the two-reaction schemes do not lead to improved estimates of the flux compared to the ‘uncorrected’ flux.

In figure 6 the results of all of our calculations for NO and NO_2 are given. It appears that the uncorrected flux may differ from the true flux by up to 50% depending on several factors such as turbulence intensity, photolysis rates, the ratio of the concentration and the flux of trace gases factors affecting the photostationary state. The correction factor can significantly improve estimates with a maximum deviation of approximately 15% for NO.

5. Using the correction procedures on real data

During the field campaign on the Halvergate marshes vertical profiles of NO, NO_2 and O_3 were measured between 0.5 and 4 m. A sonic anemometer at 4 m was used to measure momentum, heat and ozone fluxes by the eddy correlation method. Several other parameters (including radiation) were measured by other groups (see also Hargreaves *et al.* 1992). More detail about the instrumentation is given in Duyzer (1992).

In figure 7 the results of measurements of the NO and NO_2 fluxes on 20 September 1989 are presented. Corrections are calculated by using the methods described by LD2, JD91 and the correction factor.

Calculations with the empirical method gave unrealistic results. These are caused by the high random noise error in the concentration measurements at the four levels. A sensitivity analysis with the empirical method showed that the random error in the average concentration at each of the four levels needs to be less than 0.5% to estimate the surface flux with an error of less than 100%. The requirement for data with a low noise limits the use of the empirical method because NO_x instruments with adequate sensitivity and response time may only be available in a specifically designed experiment.

The sensitivity of the empirical method can be understood if one realizes that in this approach the flux divergence is actually derived from the measurements directly. Measurements were only made at four heights therefore providing only two independent estimates of the flux and consequently only one estimate of the

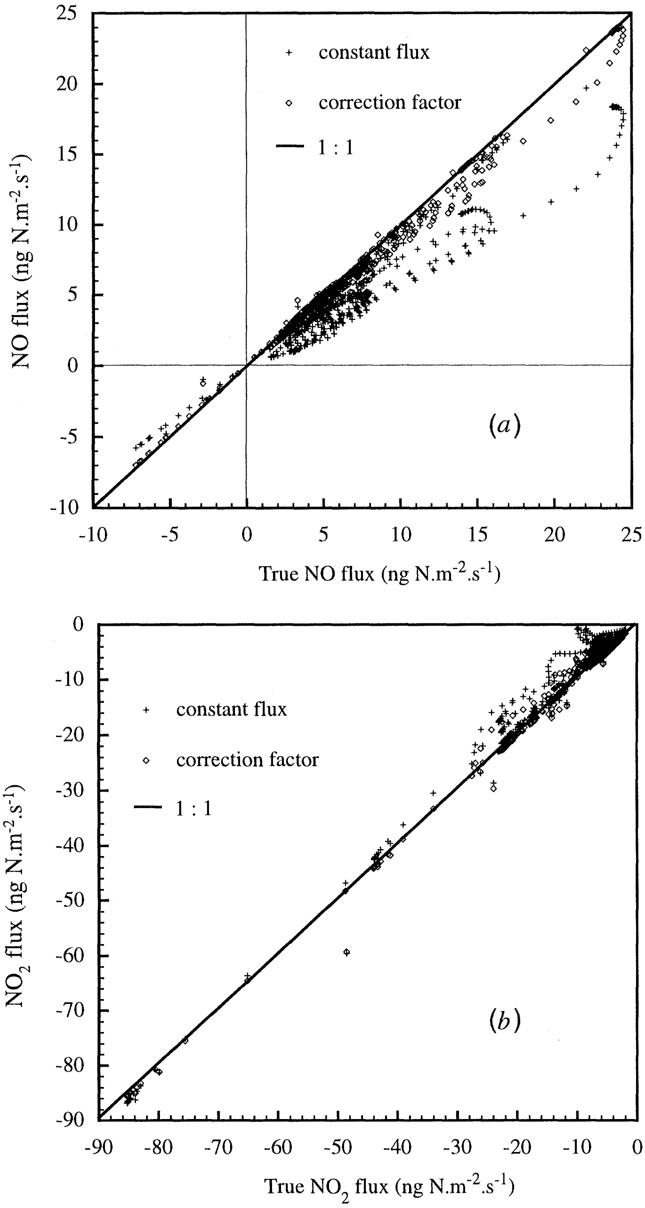

Figure 6. The surface flux of NO and NO_2 in several runs compared with the uncorrected flux calculated directly from equation (3.2).

divergence can be calculated. The random error in the flux divergence calculated from noisy concentration measurements is therefore very large.

For NO and NO_2 the corrections according to LD2 and JD91 are small but often in the opposite direction. As was outlined above the two-reaction procedures could be wrong because the influence of other reactions are not included. For NO_2 it is interesting to see how the correction factor is converting the apparent emission of NO_2 around noon to a deposition flux. The corrected flux of NO_2 leads to a normal cycle of the canopy resistance of NO_2 with a minimum value of approximately

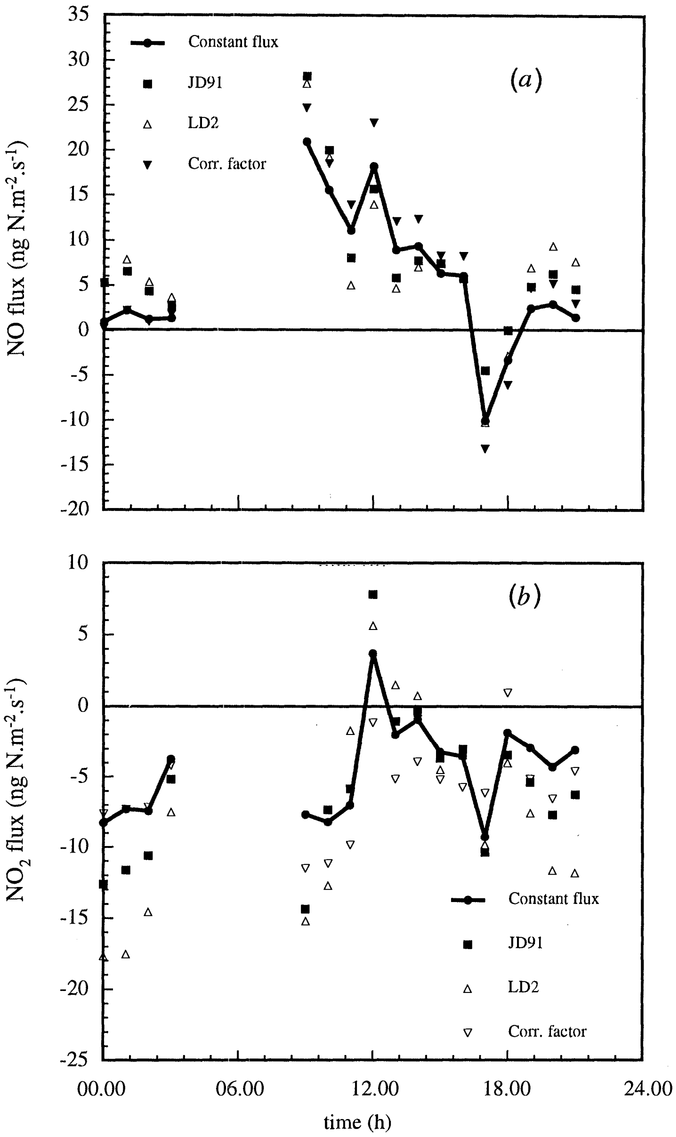

Figure 7. The surface flux of NO and NO_2 calculated using equation (3.2) (constant flux) from measurements carried out on the Halvergate marshes on 20 September 1989. Correction methods are described in the text.

200 s m^{-1} which could very well be linked to stomatal uptake. It is important to note that the 'uncorrected' fluxes derived directly from the measurements lie well within the range of values of uncorrected fluxes studied with the simulation model. Within this range the correction factor gave good results.

6. Discussion and conclusions

It is not easy to provide guidelines for interpretation of flux measurements of NO and NO_2. The calculations carried out with our model show that the flux of NO and NO_2 measured by micrometeorological methods a few metres above the surface may differ considerably from the true flux at the surface. Therefore corrections of the observations for chemical reactions in air are necessary. However, procedures described in the literature may give false corrections because several important chemical reactions of other species with NO, NO_2 and O_3 are not taken into account. In many cases the corrected fluxes differ more from the true flux than the uncorrected flux. It is generally not possible to measure the concentrations of all of these important species (radicals, etc.) to determine the flux divergence for NO and NO_2 more accurately during field experiments. Usually only NO, NO_2 and O_3 concentrations and an estimate of j_{NO_2} and k_3 are available.

Measurements of concentrations of NO, NO_2 and O_3 at levels higher than for example 10 m may give some insight in the importance of other chemical reactions. At these heights the timescales of the important chemical reactions are small compared to the timescales of turbulent mixing. The concentrations of these gases are then related according to the photostationary state (PSS) ratio R which approaches an asymptotic value (R_{eq}) of unity at these heights:

$$R = \frac{k_3[O_3][NO]}{j_{NO_2}[NO_2]} \approx 1 = R_{eq}. \qquad (6.1)$$

Near the surface, however, R may deviate from unity because of surface exchange processes. If the two-reaction case is considered rewriting equation (3.4) and (6.1) into (6.2) gives insight into the link between the PSS and the flux divergence for NO_2:

$$\left(\frac{\partial F}{\partial z}\right)_{NO_2} = j_{NO_2} NO_2 (R - 1). \qquad (6.2)$$

From (6.2) it becomes clear that when large deviations from the PSS (meaning $R \neq 1$) are found at the observation level, the differences between the flux at this level and the flux at the surface is large. Consequently the observed flux will be corrected by a large factor if a simple two-reaction scheme such as LD1&2 or JD91 is used.

In the simple, two-reaction scheme, correction procedures discussed above, deviations from photostationary state ($R = 1$) can only be caused by surface exchange processes ($R_{eq} = 1$). In field measurements, however, large deviations from photostationary state ($R = 1$) are observed (see Parish *et al.* 1986). During the Halvergate experiment also significant deviations of R from unity (from 0.7 to 2) at heights between 0.5 and 4 m were observed. Similar to the model calculations the photostationary state ratio was also found to decrease with height. Apart from surface exchange processes these deviations could be related to small measurement errors or the influence of sources or instationarity (such as the change of the radiation intensity at dawn or dusk). Chemical reactions of NO, NO_2 or O_3 with other compounds also cause deviations from photostationary state (Calvert & Stockwell 1983). These reactions cause a systematic shift of R at low heights as well as the asymptotic values R_{eq} aloft. Measurements of R_{eq} may give insight in the influence of other chemical reactions on the flux divergence. In cases where R_{eq} deviates from one simple two-reaction schemes will not be able to derive true surface fluxes from biased profiles. Therefore the empirical methods described here in which the flux divergence is determined from the gradients only seem more valuable. This method, however, requires rather low-noise concentration measurements at four heights above the surface.

The uncorrected fluxes of NO, NO_2 and O_3 and estimates of reaction rate constants can be used with the correction factor (3.11) to obtain a first estimate of the corrections. It is important to use this method only for measurements carried out between 0.5 and 4 m and only when fluxes are of similar magnitudes as the fluxes studied here. These equations may also be used to identify conditions in which corrections are small. When large corrections are calculated with the correction factor the measurements must be interpreted with great care.

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