

Modelling land atmosphere exchange of gaseous oxides of nitrogen in Europe

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ABSTRACT

Nitrogen oxides in ambient air in industrial countries result mainly from emissions of nitric oxide (NO) from fossil fuel combustion. In the presence of ozone (O₃), NO is rapidly converted into nitrogen dioxide (NO₂). Further oxidation of NO₂ leads to the formation of a range of compounds, the most important of which are: nitric acid (HNO₃), peroxy acetyl nitrate (PAN) and nitrous acid (HNO₂). The environmental effects of these compounds include eutrophication of natural ecosystems, acidification and photochemical air pollution. It is therefore necessary to understand the dry deposition processes for these compounds and use this understanding to provide estimates of dry deposition inputs to ecosystems across Europe. This review outlines current understanding of the exchange processes and methods used to estimate regional NO_x deposition. Several methods have been used to measure dry deposition. Among these micrometeorological methods provide the best approach for estimating fluxes in the field. However, few field measurements of the deposition velocity of NO₂ to important ecosystems have been reported and the results have not always been conclusive. Measurement artefacts such as non-stationarity caused by local sources, monitors responding to other gases than NO₂ and the influence of photochemical reactions have made field measurement very difficult. More recent field work however has provided strong indications that NO₂ deposition to vegetation is controlled by stomatal opening. This implies that the deposition velocity shows a marked diurnal as well as an annual cycle with maximum values up to 1 cm s⁻¹ during the day in the summer. Few measurements of HNO₂ exchange have been reported, but based on knowledge of its physical-chemical properties it is expected that HNO₂ is taken up via stomata. Measurements of PAN also indicate uptake controlled by stomatal opening. Several measurements have shown that deposition of HNO₃ is limited only by the rate of its aerodynamic transport to the surface leading to deposition velocities as large as 10 cm s⁻¹ to forest. For NO the situation is more complex. Early laboratory studies using high concentrations showed stomatal uptake. However detailed field studies carried out more recently at ambient concentrations show that most ecosystems emit NO. To provide spatial patterns of nitrogen oxide deposition, information on the concentration in air as well as an estimate of the deposition velocity is needed. For the purpose of regional dry deposition estimates, the widely separated rural monitoring stations are adequate to provide broad-scale concentration fields for NO₂. For the other gases, information is scarce and concentrations need to be derived from calculations with long-range transport models. These coarse concentration fields may be combined with statistical information on land use within each grid cell. Deposition to each land-use category within each grid cell can then be calculated using a resistance layer model. An example of this approach is provided for the UK. This exercise showed that the input of NO₂ varies between 1 kg N ha⁻¹ year⁻¹ for remote areas to 10 kg N ha⁻¹ year⁻¹ in more polluted areas, with NO₂ concentrations in excess of 10 ppb.

1. Introduction

Sulphur concentrations and deposition are declining over large areas and concentrations of gaseous nitrogen oxides exceed those of sulphur over most of western Europe. The environmental effects of nitrogen oxides (NO_x)* include regional scale eutrophication of natural ecosystems, acidification and photochemical air pollution. It is therefore essential to understand the deposition process and use this understanding to provide spatial patterns of NO_x deposition (Lövblad and Erisman, 1992).

In Europe, oxidized nitrogen is emitted into the atmosphere by industrial sources and vehicles mainly in the form of nitric oxide (NO). In the presence of typical ambient ozone (O_3) concentrations, NO is converted rapidly into nitrogen dioxide (NO_2) through reaction with O_3 . As a result of photochemical reactions several other gaseous species, including nitrous acid (HNO_2), nitric acid (HNO_3) and peroxy acetyl nitrate (PAN), are formed. During transport nitric acid can be taken up in aerosol particles to form, for example, ammonium nitrate. The surface exchange properties of these products differ dramatically from the original precursor NO. For example, nitrate aerosol deposits very slowly on vegetated surfaces, whereas deposition of HNO_3 is very rapid and is only limited by the rate at which it is transported from the atmosphere to terrestrial surfaces. Deposition of HNO_3 is therefore an important loss process for oxidized nitrogen, whereas nitrate aerosol may be transported over several hundred kilometers.

Regional gaseous NO_x inputs are provided by "models" of the deposition process. At its simplest, a mean deposition rate from the literature for a given vegetation canopy is assumed to apply over (often highly variable) landscape over annual time scales. The product of a concentration field based on measurements and the deposition velocity then provides an estimate of the annual flux. Estimates of dry deposition fluxes to regions in practice are based on calculations with atmospheric transport models. In these models, emission data and

meteorological information necessary to calculate atmospheric transport, are combined with parameterized results of process studies on trace gas exchange. Because the surface exchange characteristics of individual species are so different, conversion processes taking place in the air during transport need to be taken into account.

The objective of this review paper is to describe the current understanding of the exchange of these nitrogen compounds between terrestrial surfaces and the atmosphere, identifying gaps in understanding. The application of current understanding to develop methods of estimating dry deposition inputs to European ecosystems is then discussed.

2. Concentrations of nitrogen oxides in Europe

Nitric oxide (NO) makes up more than 90% of the amount of reactive nitrogen oxides emitted into the boundary layer. In the daytime, with sufficient O_3 present, conversion to NO_2 is rapid, with timescales of several minutes. The NO_2 is converted slowly to HNO_3 mainly by reaction with hydroxyl radicals (OH). Conversion rates for NO_2 depend on solar radiation and vary between 2% per hour in winter to maximum values of 30% per hour on sunny summer days (van Aalst and Diederer, 1985). Peroxy acetyl nitrate (PAN) is formed during the day as a product of reactions of hydrocarbons and aldehydes with OH.

Air concentrations of nitrogen oxides (NO and NO_2) are measured within the EMEP* framework and by more extensive national networks distributed over Europe. The stations for EMEP are distributed typically within 100 km of each other and are selected to be representative for regions. Fig. 1 provides a map of NO_2 concentrations throughout Europe for measurement stations showing a zone of maximum concentration extending from the English midlands through the Netherlands and into central Germany, with annual NO_2 concentrations of 10 to 15 ppbv (5 to $10 \mu\text{g m}^{-3}$). The density of this network is not suf-

* The term NO_x is in principle reserved for the sum of NO and NO_2 , whereas NO_y refers to the sum of all oxidised nitrogen thus including HNO_3 , PAN, etc.

* EMEP = Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe.

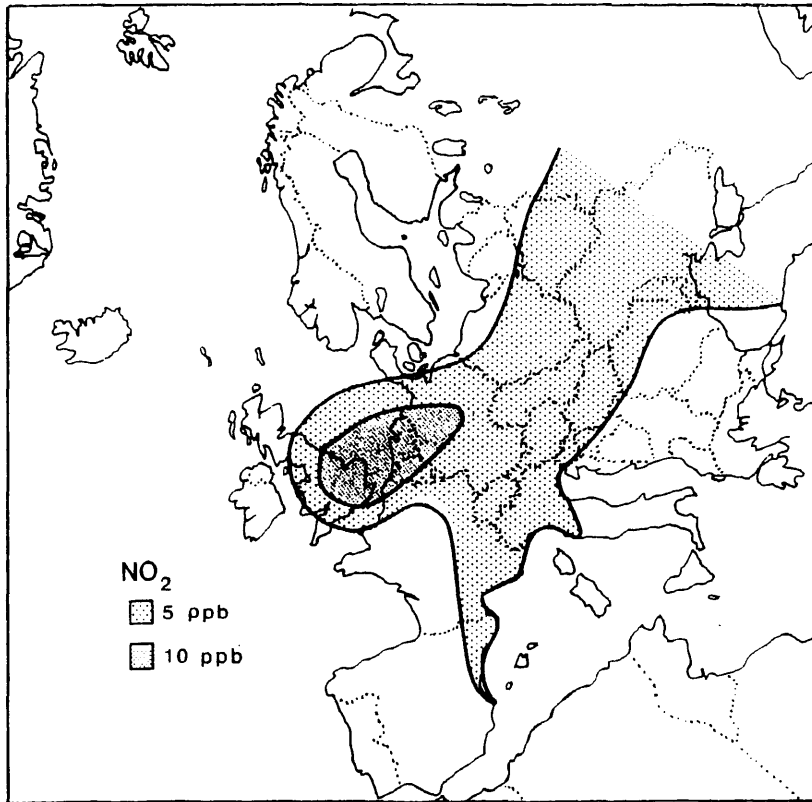


Fig. 1. Annual mean NO_2 concentrations in rural areas of Europe interpolated from rural monitoring stations. 5 ppb NO_2 is roughly equivalent to $3 \mu\text{g N} \cdot \text{m}^{-3}$.

ficient to quantify the large spatial heterogeneity in local concentrations that occur for NO as a result of emissions by low level sources. On a local scale, concentrations of NO and NO_2 can be much higher leading to different deposition patterns in these areas. Other NO_x species are not measured at all on a regular basis. Some species such as PAN are only measured at regular intervals at a few sites, mainly located in western Europe. Concentrations of these species over large regions therefore can only be provided from model calculations.

In Table 1, order of magnitude estimates of air concentrations of those nitrogen oxides that occur in significant concentrations over regions in Europe are presented. These estimates are to a large extent derived from calculations with the EMEP model (Sandness and Styve, 1992) The concentrations for NO and NO_2 have been validated with measurements at EMEP stations.

For HNO_3 and PAN, hardly any measurements are available. For these gases the figures in Table 1 therefore rely heavily on the model assumptions. For example the estimated concentration of

Table 1. Concentration of relevant nitrogen compounds in air; figures given are annual average concentrations for 1990 ($\mu\text{g N m}^{-3}$), derived from calculations using the EMEP model (Sandness and Styve, 1992) ($1 \mu\text{g N m}^{-3} \equiv 1.7 \text{ ppbv}$ at 20°C)

Compound	Polluted areas	Remote
NO	0.1–0.7	0.04–0.1
NO_2	1.0–10	0.25–1.0
HNO_3	0.1–0.5	0.02–0.1
PAN	0.1–0.4	0.04–0.07
$\text{HNO}_2^{\text{a)}}$	0.05–0.3	0.05–0.3

^{a)} The HNO_2 concentration is relatively uncertain.

HNO_3 depends heavily on the concentration assumed for other gaseous compounds such as the hydroxyl radical, ammonia and the concentration of sub micron aerosol, and is therefore uncertain. Slanina et al. (1990) report measurements of HNO_2 and HNO_3 with a wet denuder system carried out over a forest in the Netherlands. The average concentrations for HNO_3 and HNO_2 for 1989 were $0.13 \mu\text{g N m}^{-3}$ and $0.19 \mu\text{g N m}^{-3}$ respectively. The concentration of HNO_3 is slightly larger than those calculated with the EMEP model. Long time series of PAN measurements are available for Delft (the Netherlands) and Harwell (England) (Guicherit, 1988; Dollard et al., 1991). For these sites the model calculations are in reasonable agreement with model values. Little information is available on HNO_2 concentrations and how they vary over Europe. Sjodin (1989) showed that HNO_2 concentrations are usually not more than 10% of the concentration of NO_2 . Kitto and Harrison (1992) observed that the HNO_2 concentration shows a strong diurnal cycle with peak concentrations at night and minima around midday.

From Table 1 it is clear that at present NO_2 is the dominant oxidized N compound in the boundary layer over Europe. The concentration of HNO_3 is much smaller but because the deposition velocity of HNO_3 may be a factor of ten larger than that of NO_2 , the deposition of HNO_3 could still be significant. The deposition velocities of PAN and HNO_2 are smaller than that of HNO_3 . Deposition of these compounds is therefore also considered less important. It should be realized, however, that these values are approximate and measurements are required to confirm the present assessment.

3. Measurements of exchange of oxidized nitrogen compounds

There are three main methods: surface collection methods (throughfall/stemflow), micrometeorological methods and enclosure methods have been applied to study exchange of NO_x . These will be discussed below.

3.1. Surface collection methods (throughfall/stemflow)

Inputs of a range of ionic species by dry deposition to canopies of vegetation and in particular to

forest canopies have been estimated by measuring the increase in deposition below the canopy relative to those in bulk precipitation. For some mobile ionic species, notably SO_4^{2-} , these methods have been shown to provide a good estimate of total inputs (Lindberg and Garten, 1988; Lindberg et al., 1986). However, when the same methods are applied to nitrogen compounds the exchange of ammonium (NH_4^+) and nitrate (NO_3^-) between surface water and foliage frequently lead to the throughfall plus stemflow (TF + SF) nitrogen flux being smaller than the above canopy precipitation input of nitrogen. The canopy uptake has been reported for a range of sites (Lovett and Lindberg, 1993) and shows that for inorganic nitrogen inputs, throughfall-stemflow methods do not generally provide good input estimates.

There are some situations where throughfall methods have provided valuable input data for inorganic nitrogen. For example, in the case of short heathland vegetation in The Netherlands, Heil et al. (1988) have shown that the large inputs of ammonia dry deposited on to the canopy may be estimated using throughfall collectors. In this case, the input is greatly in excess of nutritional requirements of the vegetation. However, where inputs are smaller and quantitatively similar to the nutritional requirements of the plants, foliar uptake becomes much more important. There is evidence from work within the Integrated Forest Study in North America that at some locations the net input to forests of NO_3^- may be used to estimate dry deposition. The relationship appears to result from gaseous HNO_3 deposited onto the forest canopy which is subsequently washed to the forest floor (Lovett and Lindberg, 1993). The same study also shows that organic N in throughfall may represent a significant fraction of the total, and that at some sites, the inorganic N and organic N in throughfall and stemflow is linearly related to total N deposition from measured wet deposition and dry deposition inferred for air concentrations of particulate and gaseous nitrogen compounds and deposition velocity. These recent studies show that measurements of throughfall and stemflow nitrogen in inorganic and organic form are of value in estimating ecosystem inputs. However, there is a degree of circularity in the arguments underpinning the studies. In estimating dry deposition from air concentrations of HNO_3 , aerosol and NO_2 , the authors calculate input on the basis of

literature values of deposition velocity or calculation schemes based on them. The details of these processes are therefore assumed to be known; for example, it is assumed that there is no cuticular uptake of NO_2 and that the size dependence of aerosol deposition velocity is known and so on.

If current understanding of the deposition process for each of the contributing nitrogen containing species was sufficient to provide a scheme to convert concentration measurements of a fraction of the species into dry deposition with an uncertainty of less than 30%, this exercise would be entirely satisfactory. There are many processes for which we have only a rudimentary understanding and it is likely that the uncertainty is closer to 100%.

The growing need to link inputs to ecosystems with environmental effects and the demand for more resolution in spatial patterns will lead to more research on throughfall and stemflow methods and in time a mechanistic basis to link the measurements with ecosystem inputs will emerge.

3.2. Enclosure methods

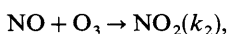
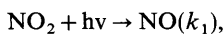
In the laboratory, soil samples, leaves and whole plants have been exposed to trace gas concentrations under well controlled conditions (Hill, 1971; Taylor and Tingey, 1983; Parish et al., 1987). This allows studies of the influence of process parameters such as temperature, moisture status etc. on trace gas exchange. In the field, enclosures have been successfully applied to branches (Johansson, 1987) and small surfaces (Slemr and Seiler, 1984). It is, however, not easy to translate the results of these studies to ambient conditions and whole ecosystems. For monitoring purposes, enclosure methods do not seem to be useful. The influence of the enclosure on the plants in prolonged exposure experiments creates bias in the results that may not be readily compensated.

3.3. Micrometeorological methods

These methods rely on the assumption that under certain conditions with respect to stationarity, the homogeneity of the underlying surface and the proximity of pollutant sources, the vertical flux of trace gases in the boundary layer is constant with height. Under these conditions the flux measured at a certain height (usually less than 10 m) over the surface is equal to the surface flux.

The advantages are that whole ecosystems can be studied on scales of several hectares without any interference with the actual exchange process (Fowler and Unsworth, 1989; Wesely et al., 1982). Moreover, generalized results can directly be applied in transport models. An important problem however is that relatively complex, expensive and delicate instrumentation is required. In addition there may be classical micrometeorological problems related to advection of pollutants from nearby sources, non-stationarity of environmental conditions during the measurements, the homogeneity of the site etc. (Fowler and Duyzer, 1989). Because of the large number of sources of NO_x these problems are not easily overcome under field conditions.

For reactive gases such as NO and NO_2 chemical reactions in the atmosphere complicate the interpretation of field measurements even further: For example the surface exchange of nitrogen oxides NO and NO_2 is influenced by chemical reactions. Reactions in the photochemical triad between NO , NO_2 and O_3 are fast enough to interfere with both measurement of and the actual fluxes at the surface. These reactions are described by:



where k_1 and k_2 are the reaction rate coefficients and $\text{h}\nu$ represents a photon.

Under the assumption of stationary conditions and horizontal homogeneity, the boundary layer budget of a non-conserved entity reduces and the flux divergence at height z is equal to:

$$\left(\frac{\partial \text{flux}}{\partial z} \right)_{\text{NO}_2} = k_2[\text{NO}][\text{O}_3] - k_1[\text{NO}_2]. \quad (1)$$

Consequently, the flux measured above the surface is not equal to the surface flux. Fig. 2 gives an illustration of the surface exchange and air chemistry interactions of NO_x and O_3 . In this example NO is emitted from the soil and reacts with O_3 in air. As a result the NO flux decreases with height.

Several methods have been described to solve the flux divergence term in the boundary layer and account for the effect of chemical reactions on vertical fluxes and concentration gradients

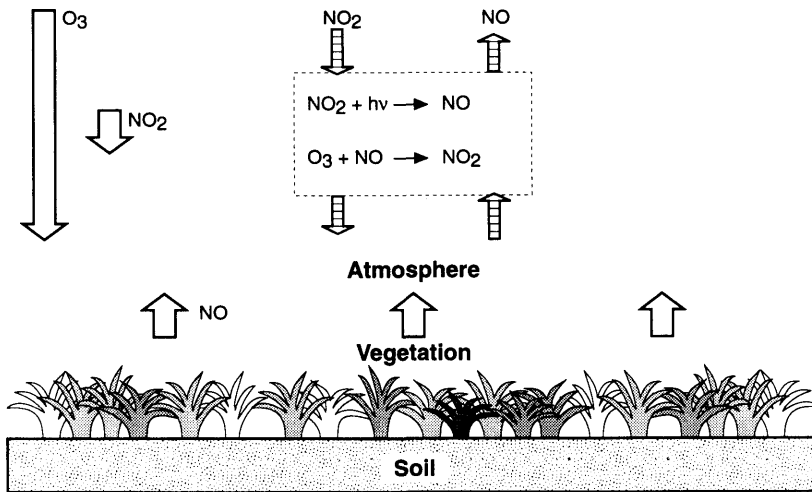


Fig. 2. An illustration of the influence of chemical reactions in air on surface exchange.

(Fitzjarrald and Lenschow, 1983; Lenschow and Delany, 1987; Kramm, 1989; Vila et al., 1993; Gao et al., 1991; Duyzer, 1992). It was shown that these reactions could have an important effect on fluxes derived from observed gradients. In some cases even the apparent direction of the vertical flux of NO or NO₂ could be influenced by these reactions. Verification of the applied correction procedures requires flux measurements at multiple heights with an accuracy that cannot be achieved with current methods. The results of field measurements using micrometeorological methods may therefore still be biased by chemical reactions and must be interpreted with care.

3.4. Monitoring of fluxes

It does not appear practical to apply any of these measurement methods to monitor trace gas deposition over large areas in Europe. They are therefore used primarily to study processes and develop mechanisms describing trace gas exchange. Such mechanisms are used in atmospheric transport models to describe trace gas exchange in increased detail. To validate these model based assessments there is also a need to monitor trace gas fluxes. In principle micrometeorological methods are suitable for monitoring purposes. First attempts to measure sulphur dioxide and nitrogen dioxide fluxes

(Erisman et al., 1994) by micrometeorological methods over extended periods have been described.

4. Parameterization of dry deposition: the resistance model

In most early experimental studies it was found that the uptake of gases was proportional to the concentration of the trace gas (Hill, 1971; Chamberlain, 1966). This allows a very simple generalisation of results of flux measurements by introduction of the deposition velocity v_d defined in:

$$\text{flux} = -v_d(C_{\text{air}} - C_{\text{surface}}). \quad (2)$$

For gases that are continuously deposited C_{surface} is taken equal to zero thus reducing the above equation to:

$$\text{flux} = -v_d C_{\text{air}}. \quad (3)$$

In the case of a depositing gas the concentration is not constant with height. In a constant flux layer the flux is constant and v_d is therefore dependent on height. The deposition velocity is given at a reference height, for example one metre. This formulation can be used for all depositing gases

except for gases that may also be emitted. With these gases C_{surface} is equal to the so-called compensation point. At air concentrations above this compensation point deposition is the main process, while at lower concentrations emission is dominant.

In a further development of results of measurements, a surface layer resistance model is used in which the specific chemical-physical interaction between one chemical compound and the plant can be separated from the atmospheric transport process. The transfer between the surface and the atmosphere is treated as an analogue of electrical current flow through resistances in parallel and in series. In this model, described by Monteith and Unsworth (1990) for water vapour, the difference in the concentration in air (C_{air}) and the concentration at a level inside the plant or soil (C_{surface}) acts as a potential difference to drive the flux. The total resistance to transport is equal to $1/v_d$ and includes atmospheric and surface processes. An example of a simple resistance layer model is displayed in Fig. 3.

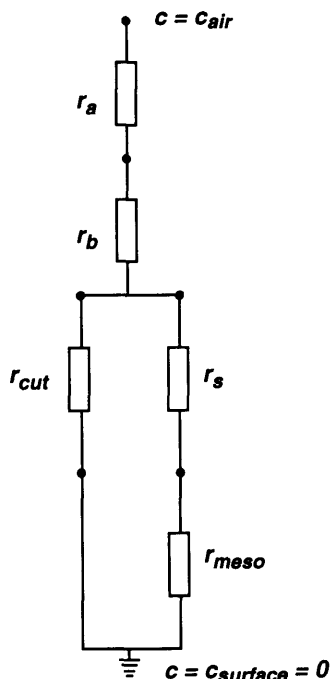


Fig. 3. Example of a simple resistance layer model. In this example $C_{\text{substrate}}$ is zero.

In the basic form the total resistance is composed of a series of three resistances:

$$v_d = \frac{1}{r_a + r_b + r_c}, \tag{4}$$

where the r_a and r_b represent the aerodynamic resistances and r_c the resistance operating at the sites of uptake.

4.1. The aerodynamic resistance r_a and the pseudo laminar resistance r_b

The aerodynamic resistance r_a represents the resistance to transport through the turbulent layer of air between the reference level and the vegetation. The value of r_a is determined by the intensity of the turbulence in the layer of air above the vegetation and therefore is related to windspeed, surface roughness and atmospheric stability. The resistance r_b represents the resistance to transport through the quasi-laminar layer of air surrounding the vegetation elements. Whereas r_a is assumed to be equal for all gases, the boundary layer resistance r_b is weakly dependent on the molecular diffusivity of the gas.

r_a and r_b can be estimated from windspeed, surface roughness (z_o) and sensible heat flux (Thom, 1972).

$$r_a = \frac{1}{ku_*} \left(\ln \left(\frac{z}{z_o} \right) - \psi_c \right), \tag{5}$$

where u_* is the friction velocity and ψ_c a correction for stability. u_* relates to the windspeed u_z at level z according to:

$$u_z = \frac{u_*}{k} \left(\ln \frac{z}{z_o} - \psi_m \right), \tag{6}$$

where ψ_m is a correction factor for stability.

r_b is calculated from:

$$r_b = \frac{2}{ku_*} \left(\frac{Sc}{Pr} \right)^{2/3} \tag{7}$$

with Sc and Pr the Schmidt and Prandtl numbers respectively (Hicks et al., 1987).

Through the Schmidt number r_b is slightly

Table 2. Typical values of $r_a + r_b$ for NO_2 in s m^{-1} and v_{max} in mm s^{-1} at one meter over forest and grassland for different atmospheric conditions; windspeed at 100 m was assumed 8 m s^{-1} in all cases

Atmosphere vegetation	Stable		Neutral		Unstable	
	$r_a + r_b$	v_{max}	$r_a + r_b$	v_{max}	$r_a + r_b$	v_{max}
grassland	100	10	50	20	40	25
forest	35	30	10	100	5	200

dependent on the diffusion coefficient of the gas in question. For the nitrogen oxides discussed here the difference in r_b between the various species is less than 10%.

Voldner et al. (1986) provide an overview of roughness lengths over several vegetation types. For a given windspeed at 100 m over the surface some examples are given in Table 2.

Values of $r_a + r_b$ based on the above may vary between 10 s m^{-1} a few m over forest to 50 s m^{-1} over grassland. The effect of nocturnal stability may increase the atmospheric resistance $r_a + r_b$ over forest to for example 60 at night and more than 100 s m^{-1} over grass. For gases such as HNO_3 , and, for some surfaces, NH_3 , that are very efficiently absorbed by foliage, transport through the air and the laminar boundary layer is rate determining. The maximum deposition velocity v_{max} is then equal to $1/(r_a + r_b)$ and v_{max} varies from 6 mm s^{-1} over grass at night to 0.2 m s^{-1} over forest in the daytime (Table 2). On an annual basis v_{max} varies typically between $10\text{--}20 \text{ mm s}^{-1}$ over low vegetation and $20\text{--}40 \text{ mm s}^{-1}$ over forest (Duyzer, 1994; Duyzer et al., 1992).

The understanding of the physical processes underlying r_b however is limited. The resistance of the sublayer r_b was introduced to allow for the difference between momentum transfer between the atmosphere and terrestrial surfaces and other entrained quantities such as heat, water vapour and trace gases and is equivalent to transport through an additional layer. The approaches commonly used to estimate r_b rely on empirical relationships published by e.g., Garrat and Hicks (1973), Thom (1972) or Chamberlain (1966). For gases with appreciable surface resistances (e.g., NO_2 and O_3) the choice of empirical relationship

is not very important as the canopy resistance is typically an order of magnitude larger than r_b . However, for gases with very small values for r_c choosing the correct formulation for r_b is both very important and presents considerable problems. This lack of understanding contributes to the uncertainty in estimates of v_d especially for efficiently absorbed gases, such as nitric acid for which r_c is small.

Over smooth, homogeneous surfaces r_a can be estimated with reasonable accuracy. In inhomogeneous terrain, however, for example near forest edges, turbulence is increased. For these forest edges the aerodynamic resistance is small and has even been assumed to be zero by some (McMillen, 1990). As little experimental evidence is available to support this assumption the uncertainty is significant. This uncertainty is again especially relevant for HNO_3 .

4.2. The surface resistance r_c

Finally the gas is absorbed within or on the surface of the vegetation. The rate of this process may be quantified by the canopy resistance r_c . In field measurements using micrometeorological methods the total resistance r_t , r_a and r_b can be measured directly and r_c obtained by subtracting these quantities from the total resistance $r_t = (1/v_d)$.

At its simplest, uptake at the foliage level may be via one of two parallel routes.

4.2.1. Uptake onto the leaf cuticle (r_{cut}). The first step in this process can be the physical absorption at the surface followed by transport through cuticles or chemical reactions with epicuticular waxes. Few experimental data are available on these reactions. Transport through the cuticle is assumed to be slow for most trace gases and the absorption capacity is probably low. However dew or rain may change cuticular characteristics drastically. For gases such as NH_3 and HNO_3 absorption onto the cuticle is probably the dominant process. For NH_3 it has been shown that deposition is especially efficient when the canopy is wet (Duyzer, 1994; Van Hove et al., 1990). For other gases, deposition to the cuticle needs to be taken into account as the only uptake mechanism at night when the stomata are closed.

4.2.2. Stomatal uptake (r_s). Stomatal opening or closure is controlled primarily by light intensity, humidity, temperature and leaf water potential.

Once inside the stomatal cavity the molecules may enter and react with intercellular fluids or be transported across cell membranes. Both reactivity and solubility of the compound are important here as was shown by Hill (1971). For sulphur dioxide and ozone the two trace gases studied in most detail the resistance to transport through the mesophyll cells was found to be zero for many plants in many conditions. Law and Mansfield (1982) discuss possible routes of NO_x conversion by plants. Enzymes that act upon dissolved nitrate and nitrite are normally involved in the pathway by which nitrogen is assimilated. Some plants may therefore benefit from foliar uptake from the air first by preventing the accumulation of nitrite and nitrate but also by providing nitrogen if this is limiting. On the other hand the combination of stresses of resisting cellular acidification and enhanced levels of nitrite and the interference of the free radical ($\text{N}=\text{O}$) on critical enzymes and regulatory mechanisms may be the main reason why nitrogen oxides inhibit growth (Wellburn, 1990).

Several dry deposition models of variable detail (Hicks and Matt, 1988; Wesely et al., 1989; Fowler et al., 1991) have been developed. Wesely (1989) describes a more detailed structure for the canopy resistance which consists of 4 parallel resistances describing uptake by the leaves (cuticles and stomata), uptake in the lower canopy (twigs, bark etc.) and uptake to the ground. To simulate the deposition of SO_2 to a deciduous forest Baldocchi (1988) uses a model consisting of a large number of layers with a very detailed treatment of the light distribution within the canopy.

In any form, the resistance model has important limitations, and for trace gases it is unable to simulate the transfer of combinations of gases with different sources and sinks in plant canopies. This may be important for gases that may interact within the canopy such as sulphur dioxide and ammonia or nitric oxide and ozone. For such gases new formulations may need to be developed. Nevertheless the resistance layer model is a useful tool to generalize the results of a limited number of field measurements because of its ability to quantify the importance of surface processes relative to those in the atmosphere. The resistance model can be used directly in atmospheric transport models to parameterize surface exchange. In the following section the model will be used as a framework to interpret results of measurements.

5. Mechanistic studies for individual compounds

Several comprehensive reviews dealing with surface exchange of NO_x have been published recently (Hanson et al., 1989; Wesely, 1989; Voldner et al., 1986; Van Aalst, 1982; Johansson, 1989).

5.1. Nitric oxide NO

On the basis of the solubility of NO in water the deposition of NO to vegetated surfaces is expected to be slow relative to NO_2 . Reported deposition velocities range from 10^{-4} to 2 mm s^{-1} for several soils. For vegetated surfaces deposition velocities are usually lower than 1 mm s^{-1} (Van Aalst, 1982). Stomatal as well as cuticular uptake has been documented (Hanson and Lindberg, 1991). At concentrations over $30 \mu\text{g N m}^{-3}$, deposition, probably governed by stomatal control, is the main process. Such large concentrations may only be found in source areas. At smaller concentrations however, emission is more frequently observed. Emission of NO or NO_2 from plants has not been documented in typical field conditions and emission of NO_2 has been observed only from herbicide treated plants.

NO emission from soils however has been shown to be important at various sites (Slemr and Seiler, 1984). The emissions, generally produced during microbial nitrification and denitrification processes, are influenced by soil temperature, soil moisture, plant cover and soil nutrient content. In mid latitude ecosystems emissions from natural and cultivated soils may vary between 0.1 and $100 \text{ ng N m}^{-2} \text{ s}^{-1}$ (Johansson, 1989). At the canopy level the situation could be quite complicated. NO emitted from forest soil can be converted by O_3 present in the air within or below the canopy and subsequently be absorbed as NO_2 . These emissions may contribute to the background NO_x in remote areas*.

Wesely et al. (1989) report measurements over grasslands in the USA using the eddy correlation

* Grid square averaged emissions estimated in the EMEP framework range from almost 1000 kton NO_2 per annum in densely populated areas to one kton per annum in remote areas. The emission from natural sources may be as high as several ktons and needs to be taken into account for remote areas.

method. Surface uptake was found to be small. Instead emission at rates between 1 and 4 ng N m⁻² s⁻¹ was observed. An extensive linear regression analysis between the NO-flux and several parameters was carried out, which indicated a strong correlation between the flux and photochemical reactions involving NO₂ and O₃. This observation is consistent with the findings of Lenschow and Delany (1987) who showed, on a theoretical basis, that above a certain height (determined by the turbulence intensity and the reaction rates k_1 and k_2), the flux is determined by chemical reactions in air rather than by surface exchange.

Duyzer (1992) and Hargreaves et al. (1992) report emission rates around 10 ng N m⁻² s⁻¹ measured over unfertilized, grazed pasture. Micrometeorological methods were applied very close to the vegetation thus limiting the influence of photochemical reactions. Laboratory studies carried out with soil samples taken from the same site showed that these emissions are caused by microbial processes in the top 5 cm of the soil (Remde et al., 1993).

The simulation of surface exchange of NO using a model is not simple because fluxes can be directed to the surface as well as away from the surface and, in the condition of very large gradients or changes in NO-concentration with time, cause large advection and/or storage errors in measured fluxes. Deposition to vegetated and non-vegetated surfaces is most likely to be slow at ambient concentrations with deposition velocity generally smaller than 1 mm s⁻¹. For most cultivated and uncultivated soils however emission is probably the main process. In a generalized, simplistic form the flux may be estimated using equations of the form:

$$\text{flux} = \frac{C_{\text{soil}} - C_{\text{air}}}{r_a + r_b + r_{\text{soil}}}, \quad (8)$$

where C_{soil} is the equilibrium concentration existing in the soil as a result of microbial processes and C_{air} is the concentration in the air near the surface. In many cases C_{air} is so low that emission is the main process. For vegetated areas, r_a includes the resistance to transport through the canopy to the soil level. Wesely (1989) shows a crude parameterization for r_a in those cases. The value of the soil resistance, r_{soil} , is not easy to assess,

because of its dependency on soil texture, soil moisture content, effective depth of relevant production processes etc. A reasonable value of 1000 s m⁻¹ (constant throughout the day) for r_{soil} combined with a constant equilibrium concentration in the soil C_{soil} of 20 μg N m⁻³ (as NO) would be adequate to mimic experimental observation that NO is deposited at high NO concentrations in the air and emitted at smaller concentrations. Deposition of NO would take place at concentrations larger than 20 μg m⁻³ and the maximum emission rate of about 20 ng N m⁻² s⁻¹ when the air concentration of NO is near to zero.

In practice, the dependence of NO emission on temperature, soil nitrate content and soil water has been shown to control NO emission through regulating C_{soil} and these factors will need to be included in any process-based formulation. Although this parameterization could be valuable in describing emissions from low vegetation, some corrections may be necessary for emissions from the forest floor. Due to reactions with O₃ below the canopy, emitted NO molecules may never be released from the canopy into the atmosphere as they could be converted to NO₂ and absorbed within the canopy.

When more information is available a more sophisticated approach can be justified. Williams et al. (1991) for example derived land use specific emission factors for the northern United States. With some changes their approach could also be applied to European ecosystems.

5.2. Nitrogen dioxide NO₂

Early chamber studies of dry deposition at NO₂ concentrations ranging from 10 to 60 μg N m⁻³ provided results showing dry deposition rates of NO₂ uptake by crops, conifers and broad leaved plants to be strongly influenced by light (Hill, 1971). The metabolism of NO₂ taken up in the leaves was also shown to be quite efficient (Rogers et al., 1979A). Hanson et al. (1989) and several other authors (Rondón, 1993) conclude that the uptake of NO₂ by plants is under stomatal control. Hanson and Lindberg (1991) conclude that cuticular conductance is 1 to 2 orders of magnitude smaller than stomatal conductance. On the basis of several studies of the deposition of NO₂ to water surfaces one would also expect the deposition to wet cuticles to be slow and similar to uptake on dry canopies (Schwartz and White, 1983).

Using chambers, Hanson et al. (1989) showed that the uptake rate of several tree species may vary by an order of magnitude. Deposition to broadleaves at a concentration level around $18 \mu\text{g N m}^{-3}$ was greater than to conifers. Litter showed very little uptake of NO_2 . Deposition onto soil from the forest floor was disproportionately large relative to bark or foliage surfaces. The conductance ($v_d \approx 1/r_c$) to NO_2 deposition of forest floors and soil was around 5 mm s^{-1} . Large deposition velocities were also found to sand and clay soils and cement ranging from 3 to 7 mm s^{-1} (Judeikis and Wren, 1978). In a real forest, however turbulence below the canopy is suppressed and the actual deposition velocity to the forest floor is probably very small. At night, however the forest floor may present the only significant sink for NO_2 in forest ecosystems.

In most studies, NO_2 deposition has been shown to be proportional to NO_2 concentration (Law and Mansfield, 1982; Hill, 1971; Rogers et al., 1979B; Grennfelt et al., 1983). Many of these studies, however, were carried out using much higher concentrations than ambient. Johansson (1987) also found a linear dependence of the uptake rate of NO_2 by Scots Pine branches at concentrations higher than $6 \mu\text{g N m}^{-3}$ and reported indications of a mesophyll resistance. At concentrations between 0.5 and $2 \mu\text{g N m}^{-3}$ no uptake was found. These findings would be indicative of a compensation point around $1 \mu\text{g N m}^{-3}$. Fowler et al. (1991) also report a low deposition velocity (2 mm s^{-1}) to cotton grass at concentrations around $0.3 \mu\text{g N m}^{-3}$.

Whole canopy measurements of NO_2 deposition using micro meteorological methods have proved much more difficult and have produced less consistent results (Delany and Davies, 1983; Duyzer et al., 1983; Hicks et al., 1986; Delany et al., 1986). Since NO_2 fluxes are usually small such measurements are very sensitive to artefacts such as instrumental noise, sensitivity of NO_2 monitors to other gases such as HNO_3 , PAN etc., non-stationarity or advection from nearby sources. As already discussed, fluxes measured in the air above the canopy may differ from surface fluxes as a result of chemical reactions in air. In several field studies, the effect of these processes hindered simple evaluation of field data. Duyzer et al. (1983) derived estimates of deposition velocities for NO_x of up to 15 mm s^{-1} . In some cases, however, fluxes

were away from the surface. Similar phenomena were also observed by Hicks et al. (1986). Wesely et al. (1982) measured NO_x fluxes by eddy correlation over soybean and found that the deposition velocity was about 70% of that for O_3 . The concentration of NO_x (of which 90% was NO_2) was usually around $6 \mu\text{g N m}^{-3}$. The surface resistance of NO_2 correlated with stomatal resistance but the actual value was substantially larger indicating a mesophyll resistance around 50 s m^{-1} . Hargreaves et al. (1992) measured NO_2 deposition to grass by micrometeorological methods. An example of their results is shown in Fig. 4. Minimum surface resistances for NO_2 were in the range of 60 – 100 s m^{-1} increasing to around 1000 s m^{-1} in the early afternoon suggesting that the same mechanism, almost certainly stomatal resistance, was controlling both O_3 and NO_2 uptake. NO_2 fluxes measured over heathland also showed strong indications of stomatal uptake (discussed in Erisman et al., 1994). Whole canopy measurements over forest reported by Hicks et al. (1983) are, however, of much lower quality.

To parameterize surface exchange of NO_2 it is necessary to show the degree to which cuticular resistance varies with plant and environmental conditions and the magnitude of any mesophyll resistance. However few authors have been able to separate these two components from the bulk value of r_c determined from measurements. It is necessary therefore, first to examine the variability on the most commonly reported parameter v_d .

In Table 3, estimations given by Voldner et al. (1986) based on a literature survey are listed. Day and night values are presented for four seasons thus taking into account leaf fall in winter and the observed dependence of the stomatal resistance on light intensity. The lack of detail in the values given by Voldner reflects the weakness in understanding NO_x exchange at vegetated surfaces at that time. There was very little experimental evidence for a more detailed parameterization. As discussed above the results of more recent field studies seem more consistent in indicating stomatal uptake to be dominant. When these results are taken into account, more scientific knowledge on stomatal dynamics, canopy structure etc. can be applied.

Wesely (1989) gives an extensive overview of the parameterization scheme applied in the US Regional Acid Deposition Model (RADM). Canopy resistances for NO_2 , PAN and HNO_2 can

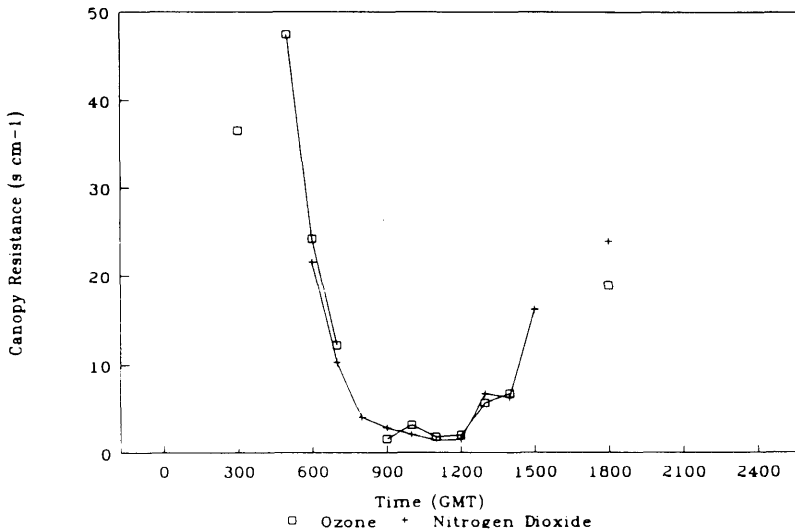


Fig. 4. Halvergate, 15 September 1989: canopy resistances to the deposition of NO₂ and O₃.

be calculated for 11 land use categories, i.e., urban, agricultural, range land, deciduous and coniferous forest, mixed forest including wetland, water, barren land (desert), non-forested wetland, mixed agricultural and range land and rocky open terrain with low shrubs. Five seasonal categories are considered, i.e., midsummer with lush vegetation, autumn with unharvested cropland, late autumn after frost but with no snow, winter snow and sub-freezing, and transitional spring with partially green short annuals. The canopy stomatal resistance is calculated as a function of solar radiation, surface air temperature, humidity and plant water status. In addition to that, deposition to lower canopy and the ground is accounted for. The

effect of temperature on deposition to snow-covered surfaces is accounted for as well as penetration of wind into canopies on hill sides.

An example of modelled canopy conductance ($1/r_c$) to dry deposition of NO₂ to deciduous forest as a function of light intensity is given in Fig. 5. Significant deposition can only take place in mid-summer and spring. The maximum deposition velocity is around 8 mm s⁻¹. In other seasons the canopy resistance is larger than 1500 s m⁻¹, equivalent to a maximum deposition velocity around 0.6 mm s⁻¹. The influence of light intensity and season is clearly demonstrated. The method

Table 3. Surface resistances (s cm⁻¹) NO₂ uptake for land use types after Voldner et al. (1986); in each column day and night values are presented respectively (day/night)

surface type	winter	spring	summer	fall
coniferous forest	10/10	1/5	1/5	1/5
deciduous forest	20/20	2/5	1/5	3/6
cultivated land	50/50	2/5	4/6	5/10
grassland	50/50	2/5	3/4	2/10
urban	10/10	10/10	10/10	10/10
swamp	50/50	10/15	10/15	10/15

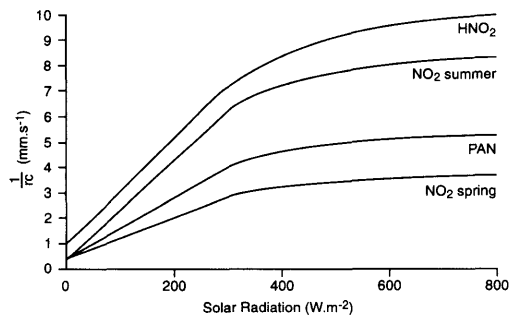


Fig. 5. Canopy conductance ($1/r_c$) for day deposition of nitrogen oxides to deciduous forest as a function of light intensity (after Wesely, 1989).

described by Wesely is attractive because differences in light intensity, temperature and humidity as they vary across latitudes can be quantified. Moreover the difference between deposition to wet or dry canopies is accounted for. This method is also attractive for validation since the model can be used to estimate fluxes in specific conditions where more information on the vegetation is available.

5.3. Nitric acid (HNO_3)

Most information is available from field studies using micrometeorological methods over grass (Müller et al., 1993; Dollard et al., 1987; Dollard et al., 1990; Huebert and Robert, 1985; Harrison et al., 1989) and coniferous forest (Meixner et al., 1988). These experiments have shown that the canopy resistance to uptake of gaseous nitric acid is negligible. Chamber studies to coniferous and deciduous trees gave similar results (Hanson and Lindberg, 1991). On the basis of its chemical properties one would expect deposition of HNO_3 to the cuticle to be very efficient and dominant over stomatal uptake. This expectation was confirmed in several experimental studies (referred to in Hanson and Lindberg, 1991). Only to snow covered surfaces at temperatures below -5°C could a surface resistance be detected (Johansson and Granat, 1987). At -18°C , r_c was 5 s mm^{-1} and at -3°C , 1 s mm^{-1} .

It is clear that the canopy resistance to nitric acid vapour is close to zero for most non frozen surfaces. To account for the temperature effect, Wesely (1989) uses a correction factor which leads to a small increase of r_c at temperatures lower than -2°C . Using the resistance layer model it is straight forward to obtain the deposition velocity. If the surface resistance for HNO_3 deposition is effectively zero, then calculating rates of deposition onto a wide range of surface requires only the atmospheric resistances to be estimated (r_a and r_b). A major problem then arises in providing an appropriate formulation for r_b , the majority of which are based on wind tunnel studies for surfaces which are not necessarily representative of canopies of vegetation in the field (Brutsaert, 1982). For the other oxides of nitrogen the laminar sub-layer term has only a minor influence on the overall rate of deposition, but for HNO_3 and especially in very turbulent conditions, such as over a forest, the rate of HNO_3 deposition is very sensitive to r_b .

Recognizing this weakness in our understanding of the r_b -term, Müller et al. (1993) used flux measurements from a number of field campaigns to estimate the values of the sub-layer Stanton number from which r_b may be calculated. The field measurements were all obtained at small HNO_3 concentrations, and with the techniques available the fluxes were subject to uncertainties sufficiently large to introduce large uncertainties in the values of the sub-layer Stanton number. The measurement of HNO_3 fluxes with a much more sensitive technique would provide the necessary values for the Stanton number in field conditions and provide a more satisfactory basis for modelling fluxes of a range of very reactive species (HNO_3 , HCl and some radical species). In complex terrain near forest edges where turbulence is even more increased, the resistance to transport at these edges will be very small leading to high deposition fluxes for HNO_3 . In model exercises this effect could in principle be accounted for using landuse information and applying a correction factor to r_a and r_b .

5.4. Peroxy acetyl nitrate (PAN)

Only a limited number of chamber studies have been reported for PAN. Garland and Penkett (1976) measured PAN deposition over grass and calculated an average deposition velocity of 2 mm s^{-1} . Hill (1971) reported results from enclosure studies in which a deposition velocity of 8 mm s^{-1} to alfalfa, significantly slower than that for NO_2 for which nearly 13 mm s^{-1} was found. The values obtained by Hill are relatively high, possibly related to the large leaf area index of the exposed plants. Dollard et al. (1990) studied dry deposition of PAN to several soil types and found PAN deposition velocity to range from 0.9 mm s^{-1} for acidic moorland to 2 mm s^{-1} for calcareous soil-grass.

The estimate by Wesely (1989) is given in Fig. 4. The maximum deposition velocity predicted to deciduous forest is close to 5 mm s^{-1} . However, there have not been any measurements of PAN deposition on forest to confirm these predictions.

5.5. Nitrous acid (HNO_2)

Very few measurements of HNO_2 deposition have been reported. On the basis of the chemical properties Wesely (1989) expects the same behaviour as sulphur dioxide, i.e., uptake via

stomata. The canopy conductance to deciduous forest according to Wesely is given in Fig. 5. The maximum deposition velocity to deciduous forest is 10 mm s^{-1} . The deposition to a canopy wetted by dew or rain is also around 10 mm s^{-1} .

6. Modelling NO_x deposition to regions

To estimate the dry deposition flux of a gas i to an ecosystem j at a certain location (x, y) and time t , the concentration c at height z in the air above this ecosystem needs to be available as well as the deposition velocity v_d to this ecosystem at that time:

$$\text{flux}(i, j, x, y, t) = v_d(i, j, x, y, z, t) \times c(x, y, z, t). \quad (9)$$

The concentration and deposition velocity are needed at a reference height z in the surface layer at time scales of typically on hour. In large areas in Europe, measurements of air concentrations of relevant nitrogen oxides are not available. In the absence of measurements, atmospheric transport models are used to calculate the air concentration over regions (Sandness and Styve, 1992). In these models, all processes affecting air concentrations of nitrogen oxides such as emission, transport, formation and conversion as well as surface exchange are described, introducing an element of circularity in the approach. The grid size used in these models is usually around 100 km. Calculations using an atmospheric model for Europe with a grid size based on the scale of ecosystems (10 to 50 km) would require an impractically large input of data and prohibitively large computing effort.

For the purposes of regional dry deposition estimates the widely separated rural monitoring stations are adequate to provide broad scale concentration fields, e.g., Fig. 1. These data may be scaled in time for seasonal or diurnal cycles in NO_2 concentration (see Fig. 6) as inputs for the modelling. An example of the use of this approach will be given below.

Except close to sources, annual average rural concentrations of the most important gaseous species NO_2 usually vary by less than 50% over scales of 100 km (Campbell et al., 1994). Strong gradients on these scales are not expected for secondary products such as HNO_2 , HNO_3 or

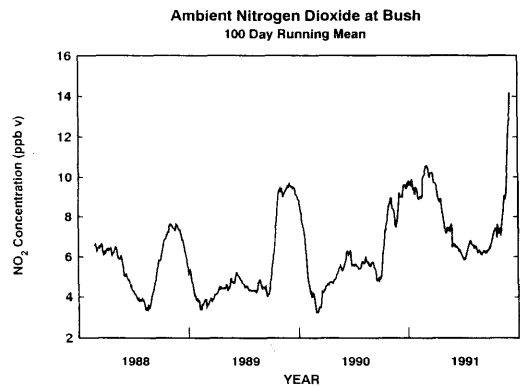


Fig. 6. Concentration of NO_2 over recent years at a site in Scotland (1 ppbv is $0.58 \mu\text{g N} \cdot \text{m}^{-3}$).

PAN. So for concentrations fields of important nitrogen oxides over Europe, a grid size with a resolution between 50 to 150 km should be adequate. This scale however does not match the 10 to 50 km scale over which ecosystems change. It is therefore appropriate to separate the resolution required to estimate the air concentration from that required to calculate the deposition velocity. It is possible to use a coarse grid to estimate concentration fields and combine these fields with statistical information on the landuse types within each grid cell. In each grid cell deposition to each landuse type is calculated. This method is attractive because it can easily be combined with existing atmospheric models. An alternative method is to combine a coarse concentration grid with a second finer grid with a resolution adequate to cover only a few major ecosystems. Deposition to each grid cell can then be calculated using information on these ecosystems and the concentration field.

To calculate the deposition velocity, a resistance model is proposed. The aerodynamic resistances are calculated from windspeed data, atmospheric stability and roughness lengths for the specific landuse-category. The canopy resistances for the compounds can be calculated on the basis of the overview given above. A starting point could be the parameterization given by Wesely (1989). For NO_2 , PAN and HNO_2 , stomatal uptake is most important. For HNO_3 the canopy resistance is zero whereas for NO uptake is negligible. To estimate the canopy resistance, r_c , information on solar radiation, air and surface temperature, air

humidity and leaf area index is needed. Using this approach hourly fluxes for representative land uses may be calculated and summed to provide seasonal or annual values.

6.1. Example estimate of current inputs of NO_2 by dry deposition within the UK

Current inputs of NO_2 by dry deposition were estimated within the UK. The ambient concentration for the UK has been monitored using both chemiluminescent analysers to provide detailed temporal resolution, and passive diffusion samplers to provide detailed spatial resolution using 350 monitoring stations throughout the country (Campbell et al., 1994). The concentration field is used to provide $10 \text{ km} \times 10 \text{ km}$ grid based maps of NO_2 concentration throughout the year as inputs for the modelling exercise.

Land use data are used to define the major vegetation types within each grid square from which appropriate characteristics may be used within the model to calculate, e.g., roughness length and leaf area index. As was discussed above, available literature provides a very limited understanding of the differences in NO_2 exchange of different species. However, it is appropriate to treat the major classes of vegetation differently according to published stomatal light response relationships and phenology. The vegetation classes used include forest, permanent grassland, moorland, arable land (cereal) and urban areas. For each grid square the population of each land use class is provided. Forest for the UK is treated as conifer spruce, *Picea sitchensis* (Bong), grassland is treated as *Lolium perenne*, and moorland as *Calluna vulgaris*. For each month of the year, vegetation height and leaf area index are defined from published work defining the morphology and growth rates (see, e.g., Biscoe et al., 1975).

Climatological temperature and solar radiation are used to drive stomatal response function for each species from published work (e.g., Jarvis, 1981). The uptake of NO_2 has been assumed for this exercise to be entirely stomatal and the model calculates for each hour the flux to each land class in each grid element and accumulates deposited nitrogen throughout the year. The resulting map of NO_2 deposition within the UK may be used to calculate deposition velocity averaged across the country and yields a value of about 3.5 mm s^{-1} .

The average deposition velocity to forest was 4 mm s^{-1} and 2 mm s^{-1} to grassland and arable land. The deposition velocity to moorland was only 1 mm s^{-1} . Because of the slow stomatal uptake the deposition flux was low in the winter and much higher in summer. Most NO_2 is taken up during the growing season.

In Fig. 7, the nitrogen input from NO_2 deposition is presented for the UK (see PORG, 1993). The input varies from $1 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in remote areas in northern Scotland to more than $10 \text{ kg N ha}^{-1} \text{ yr}^{-1}$ in more densely populated areas.

However, this approach may also be used to provide an input for regions or the entire country which may be compared with estimates based on long range transport models.

6.2. Deficiencies in current model approaches

6.2.1. *Conversion of boundary layer concentration to ground concentrations for reactive gases.* Depending on the vertical resolution available in a simulation model, conversion from boundary layer average concentrations in a long range transport model to the ground level concentrations necessary for deposition estimates, present a problem. Chemical reactions in air affect the relation between these two concentrations. When vertical resolution is applied in the transport and chemistry model the influence of photochemical processes (photolysis of NO_2 , conversion of NO by O_3) is in principle automatically accounted for. It is important however to note that the corrections apply only within the turbulent boundary layer and not within the plant canopy. Thus, within the trunk space and foliage of forests, large changes occur in, e.g., NO emission from underlying soil.

6.2.2. *Complex terrain.* Forest edges are believed to receive increased amounts of deposition. Although the causes of these effects are reasonably well understood, correction factors still need to be developed. The linear extent of forest edges and the leaf area index are key parameters. Deposition to hillsides may also require special treatment.

6.2.3. *Subgrid scale effects.* When the purpose of modelling exercises is to assess exceedance of critical loads to sensitive ecosystems, subgrid effects may be important. Although critical loads may not be exceeded on an average grid basis,

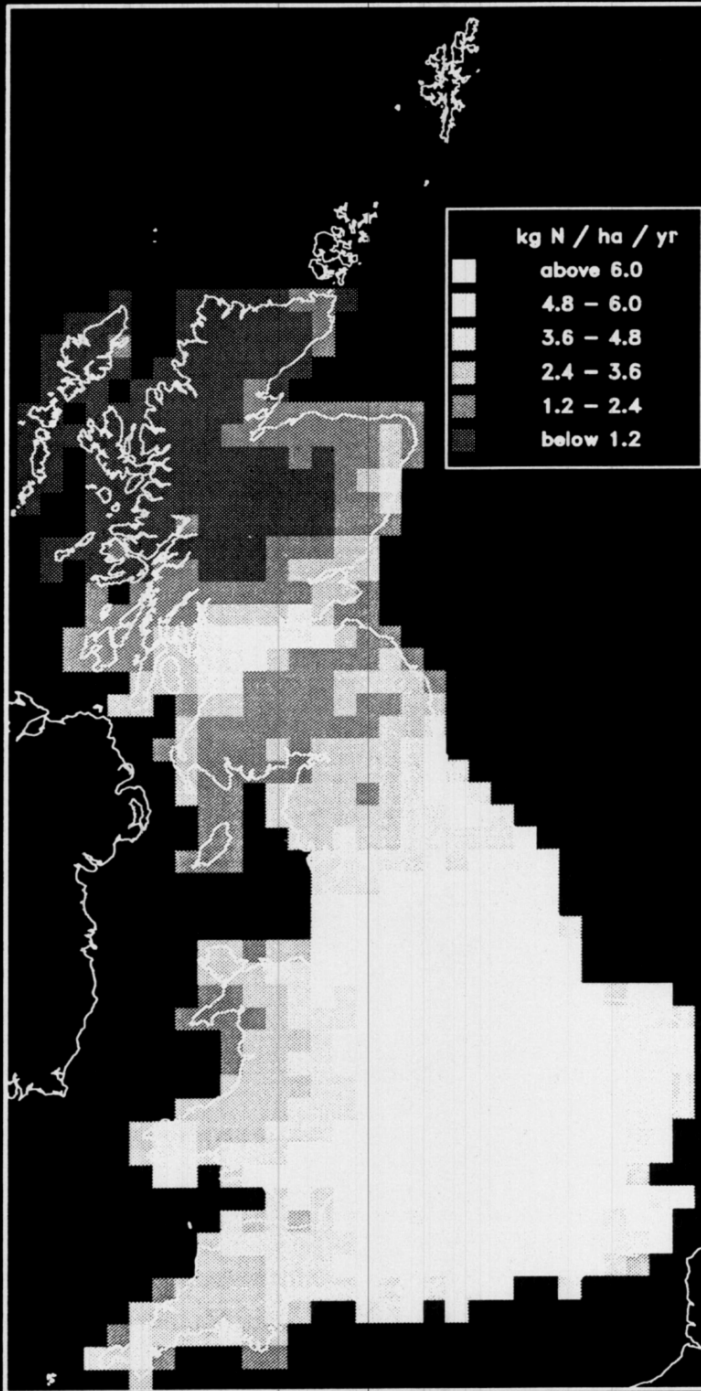
Dry deposition of N02 (89-92)

Fig. 7. Deposition of nitrogen dioxide to ecosystems in the UK.

deposition on a local scale may be higher (Lövblad and Erisman, 1992). Deposition related to local sources of NO may contribute significantly to deposition especially in densely populated areas in Western Europe. Although the deposition rate of NO is small, it is converted into NO₂ on scales of a few kilometres. With grid squares of larger scales correction factors need to be developed to account for the impact of local emissions. Progress can be made using Gaussian plume models including chemical conversion processes, but little progress in this area has been made and a critical loads approach will almost certainly require information at this scale.

7. Validation of estimated fluxes from long range transport models

In the process of validation of estimated fluxes, it is valuable to separate the air concentration and the dry deposition velocity. A first step in the validation of results of long range transport models (LRTM) is the comparison of estimated and measured concentrations. For NO₂ and NO, information on air concentrations is available, for example, from the EMEP network. The result of a comparison of air concentrations with measured concentrations in the EMEP framework was reasonably good (Sandness and Styve, 1992). The correlation coefficient between measured and modelled daily averaged concentrations was better than 0.4 for 80% of the stations. So the concentration of these gases can be estimated quite well for large regions in Europe. For HNO₃, HNO₂ and PAN time series of concentrations at remote locations are completely lacking, so there is no data base for comparison. For these gases concentration measurements are therefore the first priority.

For NO and NO₂ there is also a need to validate estimated deposition velocities as for, e.g., in the example above where an independent modelling exercise is used to check the results of LRTM. Only for O₃ have attempts to validate estimates of dry deposition velocities in large scale models have been reported. Eliassen et al. (1982) varied the deposition velocity for O₃ from 0 to 6 mm s⁻¹ in calculations with a Lagrangian model. The result of this variation was a difference of 50 to 140% in O₃ concentrations. Only large deviations in deposition variables can be identified using this

method. It is difficult, however, to attribute differences between observations and model calculations to errors in one process such as deposition only.

Godowitch (1990) describes measurements of O₃ fluxes over regions using eddy correlation techniques from an aircraft. It was found that the fluxes from flights over areas where deciduous forest dominated, did not differ significantly from those for areas dominated by agricultural cropland. These results generally supported the estimates made using a dry deposition parameterization module of RADM.

Padro et al. (1990) compared eddy correlation measurements of O₃ with estimates of dry deposition fluxes with the dry deposition module in the Acid Deposition and Oxidant Model (ADOM). It appeared that the module overpredicted deposition fluxes by 70%. In addition, several weaknesses in the model formulation were identified.

To validate model assessments more completely for NO₂, specific large scale experiments are necessary.

8. Gaps in present knowledge

It is less a question of defining gaps as describing the skeletal picture of the deposition process we have obtained to date, which requires field and laboratory data to complete. The subject is poorly understood, and could reasonably be described as "mainly gaps". However, the limited skeleton we have sketched here is already valuable to test LRTM and the methods we have described appear to be appropriate for the remaining tasks.

Some specific requirements are already clear.

- More information is required to support present estimates of air concentrations of HNO₃, PAN and HNO₂. Measurements of concentrations of these gases would be necessary to validate current model estimates. In general, methods to validate deposition estimates for regions resulting from calculations with long range transport models still need to be developed.

- According to present calculations, NO₂ is the dominating species in most areas of Europe. Although there is some evidence that in some areas deposition is slow at low concentrations, uptake of NO₂ by plants seems to be via stomata. However the number of measurements over whole

canopies to support the parameterization schemes described here is very limited. For important and sensitive ecosystems such as coniferous forest, measurements are completely lacking. There is a need therefore for a long series of well documented measurements of NO₂ deposition. It is relevant to study at the same time subcanopy exchange processes and the influence of chemical reactions in air.

- The use of parameterized results in models requires the development of procedures to convert mixed layer average concentrations of reactive gases to ground level concentrations, e.g., at one meter.

- For trace gases which are deposited efficiently to vegetation (HNO₃) more information on

aerodynamic resistances and how they are affected by complex terrain is necessary. The net effect of forest edges need to be quantified at the landscape scale.

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