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# Review of modelling methods of near-field acid deposition

## Science Report – SC030172/SR4a

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Steve Killeen

Steve Killeen

**Head of Science**

# Executive Summary

The present report reviews the nature of both wet and dry deposition from the perspective of large generating plant and considers the ways in which modelling techniques might be improved. It also examines the conversion of NO to $NO_2$ in plumes over short ranges, which directly affect the amount of $NO_2$ available for deposition to the ground.

The assessment of critical loads for sensitive ecological sites requires the accurate estimation of acid deposition to the ground. There are significant contributions to this from both long and short-range sources. The main research interest has been in the longer range component which has a large particle fraction. Sources at short ranges (up to about 20km), the subject of the present review, produce very variable local concentrations, mainly from the acid gases directly discharged from combustion processes as the time scales are too short for further oxidation to a particulate component.

There is both dry deposition of acid gases from plumes in contact with the ground and wet deposition (washout) by rainfall falling through plumes, which may be on the ground or airborne.

Present short-range modelling of dry and wet deposition uses relatively simple deposition models, based on fixed dry deposition velocities and permanent washout coefficients. These are generally more suitable for particle deposition than the acid gases of interest here and bear little resemblance to the complex multivariate processes that actually constitute gaseous dry and wet deposition. Thus the accuracy and reliability of these deposition models is quite uncertain; the accuracy is thought to lie somewhere between a factor of two and a factor of ten.

This is of particular concern in critical loads estimates for large industrial plant. Recent calculations comparing deposition with critical loads for large power stations (Spanton and Hall, 2000) and for a refinery (Spanton *et al* ., 2001) produced relatively marginal results, that is the calculated acid deposition was relatively close to the critical loads. Thus errors in estimates of acid deposition become a more critical matter of concern.

Two dispersion models are generally used for short-range dispersion calculations: the USEPA AERMOD model and the ADMS3 model. The AERMOD model has only relatively recently offered a direct method of estimating dry and wet deposition. The dry deposition is calculated using a resistance model, as discussed here. The wet deposition model uses a permanent washout based on the gas solubility, which appears to be mainly aimed at soluble organic species. The ADMS model offers calculations of both dry deposition (using a fixed deposition velocity) and wet deposition (using a fixed washout coefficient) including some aspects of plume chemistry (for the washout of $SO_2$ and the oxidation of NO to $NO_2$ by ozone).

For dry deposition calculations, it appears to be possible to account for the effects of the important variables in the dispersion models by suitable pre- and post-processing of the data. This does require a moderate effort, but is practicable.

The report also draws attention to the importance of the contribution of hydrogen chloride (HCl) in the plumes from coal combustion plant to both dry and wet deposition. Despite being a small fraction of the discharged acidity (circa 5%) its contribution to both dry and wet deposition is disproportionately large. It may dominate acid washout in the near field and also affect the washout equilibrium of other acid components, especially $SO_2$. This contribution is presently entirely ignored in acid deposition calculations.

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# 1 Introduction

The EC Habitats Directive places a statutory duty on the Environment Agency (Environment Agency, 1999) to review consents for industrial pollution discharges which affect Habitat Directive sites. There are over 400 of these in England and Wales, either approved or candidate sites. A major concern is their sensitivity to acidic air pollutants, particularly nitrogen and sulphur oxides, both from direct exposure of flora and fauna to ambient concentrations and from acidification and eutrophication from pollutant deposition to the ground (Environment Agency, 1999). Many large air pollution sources regulated by the Environment Agency, such as coal-fired power stations, are major sources of sulphur and nitrogen oxides and annual permitted sulphur emissions are based partly on limiting ecosystem damage. These emissions can contribute both to local pollution and deposition and collectively to national and international background concentrations.

There are threshold criteria for the harmful effects of air concentrations and the deposition of pollutants. The National Air Quality Strategy (DETR, 1997c, 1998) has set objectives for concentrations of $NO_x$ and $SO_2$ for the protection of vegetation and ecosystems. In addition the UK, as part of the UNECE Convention on Long Range Transport of Pollution, has developed procedures for estimating critical loads of acid deposition for different ecosystems (following Posch *et al.*, 1997) which identify the acid deposition rate above which ecosystem damage due to acidification or eutrophication may be occurring.

For critical loads, the major effort has been in estimating the transport and deposition of pollutants on national and international scales and there is now a large body of work dealing with this. Models for calculating long-range transport and deposition, such as HARM (Metcalfe *et al.*, 2001) and FRAME (Singles *et al.*, 1998) in the UK, are in routine use and UK-wide estimates of acid deposition and critical loads are made both on a 1km grid square and on a defined ecosystem area basis. The chemical processes involved in long-range transport and deposition are relatively complex and the models have tended to concentrate on this feature of the modelling.

However, local emitters can also make significant contributions to critical loads at shorter ranges that are not accounted for in the longer range calculations. In a study of deposition and critical loads around UK power stations, Spanton and Hall (2000) found that, though usually small compared with background concentrations, the additional contributions to deposition within a 10-20 km range of the station could be sufficient to generate local exceedences of the critical loads. Substantial areas of sensitive ecosystems around the power stations were observed: between 20% and 90% of the 1km squares in the 20 km by 20 km area around an individual station.

In making these estimates and developing a suitable methodology (Spanton and Hall, 1999), a number of shortcomings in current short-range deposition modelling became apparent. Further, there seemed to be no guidance on the subject. Because of the focus on longer range deposition estimates, the principles used in short-range modelling tended to copy those used at long ranges. However, the fundamental characteristics of acid deposition at long and short-ranges are different, suggesting a different methodology would be needed. The major differences are listed below. The nominal boundary is given as a distance greater than 100 km for long-range sources and less than 20 km for short-range sources, though the elapsed travel time of the plume is also a factor. There is also a long distance indicated by the different boundaries where long and short-range types of plume behaviour overlap. The majority of characteristics attributed to long and short-range sources apply within these limits.

For long-range sources (beyond about 100 km distance):

The dispersing plume fills the boundary layer uniformly in the vertical direction.

The dispersing plume's width is such that over the 5-10 km scale (typically) of a long-range model's calculation grid or mesh, concentrations are likely to be relatively uniform.

All nitric oxide (NO) from combustion plant discharges is oxidised to $NO_2$ or in equilibrium with local ozone levels.

There are complex chemical reactions, especially involving ozone and ammonia. Sulphur and nitrogen oxides ($SO_2$ and $NO_2$) are further oxidised to sulphate and nitrate, which are fine (submicron) particulate species.

Exposure to acid gases and particulates at a site will be relatively uniform over time (from hours to days).

The cumulative effect of exposure to the large number of upwind sources at a given site will further encourage uniformity of exposure over time at any site.

For short-range sources (less than 20 km distance):

The dispersing plume usually occupies only a fraction of the boundary layer depth.

The dispersing plume's width is small within the (typically)10 km scale of the usual long-range calculation grid.

Plume concentrations are high and deposition patterns show a high variability, both spatially and temporally, as the plume's area of contact with the ground varies.

Exposure to acid gases and particles at a site will be highly variable both spatially and temporally, mainly in the form of intermittent (one hour or less) periods of high concentration.

Nitric oxide (NO) from combustion plant discharges will still be oxidising to $NO_2$ within this distance range. Thus the ratio of NO to $NO_2$ will vary over the plume path.

Sulphur and nitrogen oxides are still in gaseous form and there is limited oxidation to sulphate and nitrate particulates within these distances. Chemical processes are also limited, the most important being conversion of NO to $NO_2$.

Deposition rates may show strong diurnal and seasonal variation, due to variations in the discharge rather than to the surface state.

In practice, most sites near significant local sources will be exposed to a combination of these two types of behaviour. There will be a relatively uniform, slowly varying 'background' concentration from the long-range sources, over which there will be an additional intermittent, short-term addition of the high concentration component from sources at shorter range.

These different long and short-range plume chemistry and meteorology characteristics can affect estimates of both wet and dry deposition. Modelling techniques in particular should take account of these differences, but this is not very well done at present and short-range models tend to apply long-range deposition procedures, leading to uncertainty in the accuracy of estimates. Interest in this different short-range behaviour seems to have been largely restricted to a period during the 1980's.

This report analyses these differences and their implications for current modelling techniques and estimates of deposition. For completeness, the report includes work on some aspects of short-term deposition previously reported in Spanton and Hall (1999) and Spanton and Hall (2000).

Since its main concern is critical loads for habitat sites, the report concentrates on dry and wet deposition to the surface, mainly of sulphur and nitrogen oxides. It is mostly concerned with gaseous deposition and washout (below cloud removal), as this is the major short-range component. However, the contribution from hydrogen chloride in plumes from coal combustion is also considered. The residual particulate (fly ash) from heavy oil-fired generation can also be strongly acidic (Primerano *et al*., 1998).

Besides acidic sulphur and nitrogen deposition, it is now recognised that reduced (that is ammoniacal) nitrogen either as $NH_3$ or as $NH_4$ can also contribute to acid deposition, by reactions within the soil and on take-up by plants (NEGTAP, 2001). This behaviour is not presently well understood and is not discussed further here, mainly because it is regarded mostly as coming from long-range sources and is outside the present discussion.

# 2 Present modelling techniques

At present there are two dispersion models mainly used for short-range dispersion modelling in the UK: ADMS and (more recently) AERMOD.

The ADMS3 model will calculate both dry and wet deposition from a dispersing plume. It also has a 'chemistry' module, which will estimate NO to $NO_2$ conversion in a dispersing plume. However this can only be used after the dispersion calculation is completed, so there is no recursive element in the calculation. This is briefly described in the ADMS3 technical documentation (Singles and McHugh, 2000), and is discussed in more detail in Section 7. Most of the basic procedures used in the model follow conventional practice, so the descriptions below are common to many models.

The wet deposition calculation in ADMS3 includes a limit to the uptake of acidic pollutants at high concentrations by the limiting effect of the raindrop pH. This is described in Apsley *et al.* (2000) and more details are given in Appendix B.

Dry deposition in ADMS (Apsley, 2001) is estimated assuming that deposition is proportional to the ambient concentration close to the ground, using a single deposition velocity applied over the whole calculation field. Thus for each point in the calculation field

$$D_d = v_d C \qquad (1)$$

where $D_d$ is the rate of dry deposition, C is the local ambient concentration at ground level and $v_d$ is the deposition velocity.

The deposition velocity is composed of a 'diffusive' component, $v_d$, plus a gravitational settling component, $v_s$. The latter is relevant only to large particle (> ~25 µm aerodynamic diameter) deposition and is not important here. Separate dry deposition velocities can be entered for each pollutant and the same single value is used over the whole calculation field. The ADMS user guide gives recommended values for dry deposition velocities for NO and $NO_2$ of 0.00015 m $s^{-1}$ and 0.0015 m $s^{-1}$ respectively, but the default values in ADMS are zero. The ADMS3 input distinguishes between gaseous and particulate pollutants and, where deposition velocities are not known, gaseous pollutants can be further subdivided into reactive, unreactive and inert gases. In this case Apsley (2001) indicates that surface resistances of 100 s $m^{-1}$, 1000 s $m^{-1}$ and $\infty$ are assumed for the three categories respectively.

The ADMS wet deposition model is described by Apsley *et al.* (2000). It is based on four (commonly used) simplifying assumptions:

- all plume material lies below the precipitation source;
- uptake of pollutants by precipitation is irreversible;
- solution in raindrops does not lead to saturation, except for pH-limited solubility of $SO_2$ and $CO_2$;
- the rainfall rate is uniform over the calculation field, as given by the meteorological data.

The model calculates wet deposition as a proportionate rate of removal of pollutants in the boundary layer using a washout coefficient, $\Lambda$.

The local washout is then given by

$$\Lambda C \qquad (2)$$

where C is the local concentration in the dispersing plume. The local wet deposition, $D_w$ is then given by the integral of ΛC over the depth of the boundary layer, $H_b$, so that

$$D_w = \int_{z=0}^{H_b} \Lambda C \qquad (3)$$

The washout coefficient, Λ, may have either a constant value supplied by the modeller or the modeller can use the expression

$$\Lambda = AP^B \qquad (4)$$

where P is the rate of rainfall (usually in mm $h^{-1}$) and A and B are constants. Values of P are supplied in the meteorological data input. In either case, a single default value (discussed later) is used in the model for all pollutants if no other is entered.

ADMS3 now includes some chemistry specific features of wet deposition, described by Apsley *et al*. (2000), following Singles (1998) who suggested an 'improved treatment of wet deposition'. This mainly covers the dynamic response to the gaseous and chemical equilibrium in the rain droplet as it falls. It includes limiting of the aqueous concentration by liquid/vapour phase equilibria and limits to dissolution due to dissociation and to the pH of acidic components in solution. This model seems to be limited to $SO_2$, but includes the effects of dissolved $CO_2$ in the acid equilibrium. More details are given in Appendix B. Earlier reports by CERC (1998a,b) describe the wet deposition and radioactive decay models and the gravitational settling model; Ellis *et al.* (1998) describe 'deposition in the building effects regime', though this is not included in the present ADMS technical specification. Neither of the latter reports is directly relevant to the present problem.

The ADMS model accounts for plume depletion due to loss of content by deposition, both by modifying the vertical concentration profile to account for loss at the ground and by reducing the effective source strength to account for the total loss. The procedures used are described in CERC (1998b) and are illustrated in Figure 1, taken from this report. They are commonly used in dispersion models. Loss due to washout is similarly accounted for by modifying the effective source strength, as removal of material from the plume is uniform in this model. In fact, for the deposition losses and washout coefficients of interest here, these effects are relatively small in the near field. For example, with the 200 m stack height of a typical power station deposition calculation (Spanton and Hall, 2000), the losses of sulphur and nitrogen to the ground are of the order of 0.3% and 0.01% respectively of their total emissions within the 20 km square of the calculation around the stack.

Until relatively recently, AERMOD had neither a dry nor a wet deposition model: any calculations of deposition had to be devised by the operator, using the model output data. However, the model now includes both wet and dry deposition (Wesely *et al*., 2002). The dry deposition model is a resistance-based model, similar to that discussed here, from which a deposition model is derived, while the wet deposition model uses a permanent removal washout (as with the ADMS model) with washout coefficients derived from the gas solubility via Henry's law coefficient. The model seems mainly aimed at washout of soluble organic species, and appeared during the course of our work so was not used here.

# 3 Exposure to plumes at short ranges

In view of some of the ensuing discussion, it is helpful to review the nature of concentration patterns at the ground from sources at short ranges and its differences from pollutants at longer ranges.

It was noted in the introduction that exposure at a site from the multiplicity of long-range sources, commonly known as 'background' concentrations (though the term is not formally defined), tends to produce relatively slowly changing, low levels of concentration that are persistent over long periods. By contrast, exposure from a single local source is infrequent and intermittent, but with relatively high concentrations during exposure periods.

For example, the sulphur and nitrogen oxide concentrations have been taken from a large power station stack of 200 m height, at the site of the maximum concentration (from Spanton and Hall, 2000). The annual average background concentrations and contribution from the station were:

Table 3.1: Example contribution from a power station (from Spanton and Hall, 2000)

| Pollutant | Background concentrations (µg $m^{-3}$) | | Station contribution |
|---|---|---|---|
| | Urban | Rural | |
| $SO_2$ | 16 | 8 | 1.37 |
| $NO_2$ | 27 | 17 | 0.24* |

*taken as $NO_x$ ($NO + NO_2$)

Table 3.1 shows that annually, the station's average contribution to the total was relatively small. Figure 2 shows the behaviour of rural (background) concentrations from the Ladybower National Network site and the contribution from a power station, at the point of maximum concentration about 4 km from the stack. It shows the hourly averaged concentrations of both sulphur and nitrogen oxides, ordered by value, for a single year. The background and power station data are not directly related; there are only a few rural monitoring sites producing hourly data and none were near any of the power stations in the study. However, both are representative of their type. Both sulphur and nitrogen oxides are present at the rural site at varying levels nearly all the time. The power station plume is present at its site of maximum concentration for only about 8% of the time and for most of this time the contributed concentration is relatively high, comparable to the higher concentrations of the rural measurements.

# 4 Dry deposition

## 4.1 Background

The transfer of acidic gases to the surface is mainly by reaction with the surface material (soil, concrete, brick *etc.*), by dissolving in surface water, by reaction with plant surfaces or by stomatal uptake. Each has different transfer characteristics. The transfer process itself involves, in succession, turbulent transfer of pollutants to the region close to the ground, transfer by molecular diffusion though the laminar sublayer (typically of thickness of the order of millimetres) on the surface and then by reaction, dissolution or absorption at the surface. Each of these processes is dependent on a range of (different) variables. Turbulent transfer to the surface depends on the boundary layer's meteorological parameters that control dispersion and the rate of transfer is proportional to the wind speed. Diffusion through the sublayer depends on molecular diffusion rates (which vary with pollutant and are markedly different for gases and particles) and the aerodynamic conditions defining the sublayer. These conditions include wind speed and, especially, small-scale surface roughness. The rate of diffusion is also proportional to the wind speed. Absorption at the surface may depend on solubility, reactivity and, for stomatal uptake, the active state of the plant. In the case of particles there is an additional deposition mechanism due to small scale inertial impaction. Stomatal uptake is likely to show strong seasonal and diurnal variation, as is dissolution in surface water.

The complexity of dry deposition has led to some difficulty in estimating reliable values of deposition velocities. The present preferred approach is to use the electrical analogy of a deposition resistance, so that the individual components of the transfer process can be assessed and their combined effect estimated. An example of this procedure, taken from the Fourth Report of the Acid Rain Review Group (DETR, 1997a) is shown in Figure 3. The 'resistances' in Figure 3 are:

| | |
|---|---|
| $R_a$ | the atmospheric resistance (due to turbulent transfer), |
| $R_b$ | the sublayer resistance, |
| $R_c$ | the surface resistance, comprising the parallel components of, |
| $R_{soil}$ | the surface soil resistance, |
| $R_w$ | the leaf surface resistance and |
| $R_s$ | the stomatal resistance. |

$R_a$ and $R_b$ are aerodynamic resistances which depend on the wind speed and the form (and roughness) of the surface. There may also be a surface water resistance or other components as desired and some transfer resistance diagrams are complex beyond any bounds of resolution. The units of resistance are s $m^{-1}$, so that the inverse of the overall surface resistance gives a deposition velocity directly. A brief discussion of the determination of the three main resistance components is given in Appendix A, together with some sample calculations of $R_a$ and $R_b$ and some typical values of $R_c$, both measured values and those used in models.

Generally there are pronounced variations in the values of the three resistances and in the subsequent deposition velocities. The most important parameters governing their values are:

- wind speed (to which $R_a$ and $R_b$ are inversely proportional);
- surface type (which affects local wind speed, stomatal and deposition surface area and reactivity);
- presence of surface water from precipitation and seasonal variations (which particularly affects the more soluble gases, $SO_2$, HCl and $NH_3$);

- seasonal and diurnal variations in stomatal activity (which particularly affect NO and $NO_2$ as they are largely taken up stomatally).

Variations in deposition velocity from these causes can be considerable. The examples in Appendix A show that the values of the aerodynamic resistances vary by an order of magnitude over the typical 10-90th percentile wind speed range and the surface resistance can vary from zero to infinity, depending on the pollutant of interest and the type and state of the surface. Figure 4 from Jones (1983) shows his estimates of the aerodynamic resistances of iodine vapour. Figure 5 shows the results of example calculations of the deposition velocities of four gases of interest for different wind speeds and estimates of surface resistances taken from Erisman and Draaijers (1995). The details of the derivation are given in Appendix A. The logarithmic vertical scales of deposition velocity cover two or three decades and show the wide variation in deposition velocity depending on the gas, the surface and the wind speed. The diurnal and seasonal effects, mainly due to variations in stomatal activity, are subsumed into averaged values in this plot, so that shorter term deposition velocities would show considerably greater variation. These are especially great for $NO_2$ (which is largely absorbed stomatally) and $NH_3$ (for which there is a significant rate of surface production in summer and therefore a negative deposition). Later discussions consider these effects.

Useful though the principles of surface resistance are as a means of identifying the separate effects of a complex process, determining the components of the surface resistance remains a difficult matter and estimates usually have a significant level of uncertainty. Overall experimental measurements of deposition are equally difficult to obtain reliably and the problems are discussed by Erisman and Draaijers (1995). A common approach has been the use of flux gradient measurements, in which the vertical concentration gradient above the surface is used in combination with wind speed and/or turbulence measurements to estimate the vertical flux of pollutant to the ground, thus giving a deposition velocity. This effectively uses the plume depletion shown in Figure 1 to determine the deposition. In practice deposition velocities are low, so that the gradient is small and difficult to measure. Figure 6 shows data from experiments by Galmarini *et al*. (1997) of calculated NO and $NO_2$ fluxes over peat grassland, which illustrate the uncertainties involved. Measurements at a height of two metres show normalised values of the flux close to unity, which make the small differences from unity (no net flux) that control the flux difficult to resolve. Measurements at 10 metres height show greater variations from the neutral flux condition, but the scatter in the measurements is large and the flux equally difficult to resolve for this reason. Similarly, estimates using flux gradient turbulence parameters are also hard to determine reliably. Hicks *et al.* (1989) discussed these problems and remarked that there had, at that time, been a tendency to concentrate on the problems of chemical measurement, though uncertainties in the equally essential micrometeorological measurements were just as great and as difficult to resolve. Because of these practical difficulties, there seem to be relatively few direct measurements of any surface resistances.

Partly as a result of the uncertainties in estimating resistances, especially sublayer and surface resistances, there are no standard values in general use and different models have used (occasionally widely) differing values. Because of the wider interest, there is also a tendency for resistances and deposition velocities to be biased towards values for long-range rather than short-range sources, where the effects of more detailed aspects of the deposition process tend to be merged into simpler longer range averaged values. Thus, for example, it is uncommon to see the values of wind speed noted for aerodynamic and sublayer resistances, despite their direct dependence on it. The general argument seems to be that such subtleties are lost in the general level of uncertainty of the calculation. This may be more applicable to deposition at long rather than short ranges. Nor does this assist the systematic investigation of effects due to changes in the control parameters, which can be more important with sources at short ranges.

## 4.2 Dry deposition of nitrogen oxides

### 4.2.1 Background

Of the complex range of nitrogen oxides and nitrate species that are discharged to and produced by reaction in the atmosphere, the deposition of NO and $NO_2$ are of greatest interest at short ranges; further oxidation to nitrate and other oxides occurs mainly over long ranges. Combustion processes generate a variable ratio of NO to $NO_2$ at the point of discharge. The fraction of $NO_2$ depends mainly on the peak combustion temperature; it is about 95% NO and 5% $NO_2$ from boiler plant (such as power stations), but higher in diesel exhaust (about 90% NO to 10% $NO_2$) for example, due to the higher combustion temperatures. However it is also affected by the use of low $NO_x$ burners and exhaust catalysers. For large-scale combustion discharges of interest here, the ratio of 95% NO to 5% $NO_2$ is a reasonable approximation.

A significant fraction of the NO is usually oxidised to $NO_2$ over short ranges, mainly by reaction with atmospheric ozone. This process is considered in more detail in Section 7 with regard to local deposition. However the relatively high proportion of NO in plumes at short ranges means that the deposition and other effects of both NO and $NO_2$ need to be considered.

Relatively high concentrations of NO can be found in some background concentrations where other sources are relatively close, such as in urban areas, and there is insufficient ozone for complete oxidation to occur. The measurements of $NO_x$ and $NO_2$ at Ladybower, in Figure 2, show little difference (and therefore indicate little NO present) up to about the 90th percentile and 50 $\mu g\ m^{-3}$ concentration, but a greater difference at higher concentrations, where the concentration of NO reaches about 50% of the total $NO_x$. The persistence of NO at a rural monitoring site may be a result of the local NO/$NO_2$/ozone equilibrium or a lack of ozone for further oxidation or contributions from large local sources. For Ladybower (which is about 15 km from Sheffield), the latter seems to be the case as the occurrence of a large proportion of NO is infrequent and only at high $NO_x$ concentrations, consistent with occasional contact from a large local source.

### 4.2.2 Dry deposition of nitric oxide, NO

Both the reports of the Review Group on Acid Rain (DETR, 1997a) and of the Photochemical Oxidants Review Group (DETR, 1997b) discuss the complex relationship between NO, $NO_2$, ozone and deposition to the ground. Their main concern is with the role of NO in the ozone cycle and the production of $NO_2$.

However, NO has a more critical significance in its reaction both with the surface and as a phytotoxic (plant damaging) agent. Figure 7, taken from the Fourth Report of the Review Group on Acid Rain (DETR, 1997a), shows a simplified diagram of this cycle near the surface, which is discussed in more detail in that report. An important feature of this cycle is that the soil acts as a source of NO. This matter is discussed in greater detail by Fowler *et al*. (1998). Soil emissions of NO are a product of biological degradation, and are greater in warm conditions. Figure 8, from Fowler *et al*. (1998), shows some measurements of these fluxes, which appear to be relatively small compared with anthropogenic emissions. However, they do inhibit the deposition of NO to the soil until its atmospheric partial pressure is sufficient to overcome the value in the soil. The authors suggest a simple generalisation for the deposition of NO:

$$\text{NO Flux} = \frac{C_{soil} - C_{air}}{R_a + R_b + R_{soil}} \qquad (5)$$

Proposing a nominal value for $R_{soil}$ of 1000 s $m^{-1}$ leads to an approximate concentration boundary for NO emission/deposition of 10-20 µg $m^{-3}$. Comparison with equation (1) shows that equation (5) is similar to using a fixed deposition velocity, above a reference level corresponding to this emission/deposition boundary, so that the deposition velocity becomes concentration dependent. For the nominal surface resistance of 1000 s $m^{-1}$ quoted, this reference level corresponds (with the addition of about 100 s $m^{-1}$ for the aerodynamic resistances) to a deposition velocity of about 0.9 mm $s^{-1}$. For the example of Ladybower in Figure 2 it would appear that on this basis deposition of NO to the soil due to background concentrations would be quite infrequent, perhaps a few percent of the time. However, the addition of shorter term high concentrations from a power station, for example, would give rise to some deposition of NO to the soil during these periods.

The directly phytotoxic effects of NO on plants seem to be largely unrecognised in short-range air pollution assessments. The Fourth Report of the Photochemical Oxidants Review Group (DETR, 1997b) noted the importance of both NO and $NO_2$ as phytotoxic agents and growing interest in the effects of NO. As a result of this, critical exposure levels for plant damage were being set for $NO_x$ rather than for $NO_2$ alone. Otherwise the report did not consider the significance of NO specifically. Similarly the NEGTAP report (NEGTAP, 2001) recognised the possible significance of NO to plant health, but made no further contribution to the discussion.

The phytotoxic behaviour of NO has been appreciated for some time by plant scientists, generated from experiments (mainly on greenhouse crops exposed to NO from heaters) carried out during the 1970's. Wellburn (1990) reviewed the understanding of the effects of NO at that time, and Mansfield (2002) has reviewed more recent information. The topic was also discussed by Mansfield and Lucas (1996), who remarked that NO might in some circumstances be more toxic to plants than $NO_2$, but that its effects were not well understood. NO is now known to be an important intercellular signalling agent and it is the effects on signalling, rather than any contribution to deposited acidity (which is likely to be small), that is important. NO is largely taken up stomatally and both Wellburn and Mansfield suggest that its rate of dissolution (and therefore its deposition) is greater than in pure water, due to the chemical effects of other agents present in the plant xylem. Deposited in this way, NO directly reduces the growth rate of plants, very markedly at ppm levels. It also appears to have some beneficial effects in that it can encourage the production of chlorophyll and contribute to plant nutrition when soil nitrogen levels are low. However this is still associated with plant damage and neither phenomenon is desirable at habitat sites, as NO is then an agent of change to the existing ecosystem. There seem to be no data on deposition velocities or surface resistances for NO specifically.

In summary, NO is deposited to the soil if concentrations in the plume are above about 10-20 µg $m^{-3}$, a level comparable to background concentrations, otherwise the soil acts as a source of NO. Thus under most circumstances deposition may be marginal or negative, but may occur more readily during high concentration episodes of plumes released from local sources. More importantly, NO is phytotoxic and is taken up stomatally by plants. However, though this phenomenon is now well recognised, there is little useful data to assist short-range deposition assessments, and there are presently no standards for these effects.

### 4.2.3 Dry deposition of nitrogen dioxide, $NO_2$

Unlike NO, the dry deposition of $NO_2$ has been the subject of many investigations and measurement. $NO_2$ is both phytotoxic and a direct contributor to deposited acidity. It is sufficiently soluble and reactive to be taken up by the soil and other surfaces and is also taken up stomatally. However surface take-up other than stomatally is usually regarded as negligible, since when the stomata are very active the surface resistance becomes very low. Because of the relatively high level of stomatal take-up, quoted surface deposition rates of $NO_2$ show a pronounced diurnal and seasonal variation. Figure 9, taken from two figures in the Fourth Report of the Acid Rain Review Group (DETR, 1997a), shows estimates of the overall annual UK deposition and the diurnal variation of the surface resistance. Both show quite marked changes, with negligible deposition in winter, a maximum in summer and low surface resistance in the middle of the day.

The effects of some environmental parameters on $NO_2$ uptake to plants are shown in Figure 10, from Weber and Rennenberg (1996), which are the results of chamber experiments on wheat leaves. The 'conductance' given in the plots is the inverse of the surface resistance, the latter of which varies between about 300 and 2000 s $m^{-1}$. These surface resistances are relatively high compared with those in Figure 9 when the stomata are active.

The essential dry deposition characteristics of $NO_2$ are thus a pronounced diurnal and seasonal variation, closely following the stomatal activity. Surface resistances during summer days can fall to low values, so that deposition is then dominated by the wind speed. The estimated deposition velocities in Figure 5 and Table A3 (taken from Erisman and Draaijers, 1995) do not show such a marked variation with wind speed, partly as they are averaged over the day. However, they are closer to Weber and Rennenberg's values from chamber experiments (1996).

## 4.3 Dry deposition of sulphur dioxide

Dry deposition of sulphur dioxide has been more comprehensively studied than any other gas. $SO_2$ is more reactive and has a higher solubility than $NO_2$, leading to higher dry deposition velocities to soil, other surfaces and especially to surface water. It is also, as with $NO_2$, taken up stomatally. The result is that $SO_2$ shows a diurnal and annual variation in its dry deposition similar to that of $NO_2$, together with a significant fraction deposited to the surface with a smaller variation with time. Figure 11, taken from the Fourth Report of the Acid Rain Review Group, shows two plots of the diurnal and seasonal variation of $SO_2$ deposition and one of surface resistance. The upper two plots of deposition velocity and surface resistance across a day are of experimental measurements. The lower plot is of modelled estimates of the diurnal and seasonal variation of deposition velocity for different ecosystems, based on monthly averages of 30 years of weather data. These values are regarded as less reliable than current estimates, but still show fairly clearly the sort of variation in deposition velocities that occur diurnally and seasonally. The effects of wind speed are subsumed into the plot on an averaged basis. Nominal values of deposition velocity from this plot are given in Table A5 of Appendix A.

As with $NO_2$, the variations in deposition rates are quite marked with surface and wind conditions. Because of its solubility, the surface resistance of $SO_2$ over water or wet surfaces is nominally zero, so that its deposition rate is then dominated by the wind speed. For the UK, this situation applies over vegetation for largely the whole winter period, as the surface is usually wet.

## 4.4 Dry deposition of hydrogen chloride

Hydrogen chloride is emitted from coal combustion at a rate of about 5-10% of that of $SO_2$. It thus apparently makes a small additional contribution to emitted and deposited acidity. However HCl is highly soluble and reactive (even more so than $SO_2$) and, as a result, has a high deposition velocity under almost all circumstances. Tables A2 and A3 show Erisman and Draaijer's (1995) estimates of the surface resistance of HCl as zero for all conditions except for frozen surfaces, and even for these latter conditions the surface resistance quoted is quite low compared with those of other pollutants. Thus deposition velocities of HCl are comparable to those of $SO_2$ over water or wet surfaces, but typically between around three and thirty times higher on dry surfaces in summer or frozen surfaces in winter. Under these latter conditions, HCl deposition would make a significant additional contribution to local acid deposition alongside $SO_2$.

This matter seems to be largely ignored in acid deposition calculations. There are few references to HCl deposition, and its contribution to deposited acidity is ignored in the standard critical load calculations. Laxen and Harrison (1996) refer briefly to its ambient concentration in generating station plumes, but not to its deposition. This lack of interest is partly because the contribution of HCl to long-range deposition estimates is small and there is more limited interest in short-range contributions. However in the UK, coal-fired generation is a major source of the $SO_2$ inventory and it seems surprising that the contribution of HCl has been ignored for so long.

There are few direct measurements of HCl deposition velocities. Harrison *et al*. (1989) describe experimental measurements of surface fluxes of $HNO_3$, HCl and $NH_3$ and also discuss other work up to that time. Both Harrison's work and other studies considered by the authors indicate generally high deposition velocities for both HCl and $HNO_3$, within the ranges given in Appendix A. In discussing the experimental data, Harrison *et al.* (1989) note that, within the uncertainties of measurement, the surface resistances of $HNO_3$ and HCl appear to be effectively zero, in line with Erisman and Draaijer's (1995) estimates.

# 5 Wet deposition

## 5.1 Background

Equations (2) to (4), in Section 2, are typical of short-range acid washout models, in which there is assumed to be a permanent rate of removal of the pollutant in proportion to its concentration, with no loss of already collected material. For pollutants which mainly exist in particle form, as at long ranges, this is a reasonable approximation to the physical processes that occur. Particles captured by collision with raindrops generally remain within the drop and accumulate there during its passage to the ground.

Typical washout coefficients from early studies quoted by Jones (1983) were between $3.10^{-5}$ $s^{-1}$ and $3.10^{-4}$ $s^{-1}$ for both reactive gases and particles up to 10 µm. The values correspond to the value of A in equation (4), for a value of B of unity. The ADMS3 model manual quotes 'default' values of A and B of $10^{-4}$ and 0.64 respectively, so that for the nominal rate of rainfall of 1mm $h^{-1}$ applying to Jones(1983) estimates of washout rates, this default value becomes $10^{-4}$ $s^{-1}$, in the middle of Jones' range of values.

The principles of precipitation scavenging of particles are dealt with in some detail in Slinn's (1984) review and his theories have received some recent experimental justification by Chate and Kamra (1997). A recent review by Underwood (2001) has confirmed Jones' (1983) nominal values and provided a more precise methodology. Underwood preferred a value of the exponent of 0.75 in equation (4) (for which there was some theoretical justification) and provided a range of values of A between $4.10^{-5}$ and $4.10^{-4}$, depending on the particle size.

Particle scavenging is not considered further here. At short ranges the main concern is with gases, as sulphur and nitrogen oxides are still in gaseous form. Different physical principles then apply to the washout. The essential features are:

- Pollutant gases will only dissolve in raindrops until equilibrium is reached between the liquid and gaseous phase vapour pressures. Thus a raindrop falling through a plume containing a high concentration of pollutant gases will absorb these (up to the limit of their solubility) until the vapour pressures in the drop liquid and external gaseous phases are in equilibrium.

- This process is also reversible. In passing below the maximum concentration within a plume, or out of it altogether, the drop can equally desorb the gases until a new equilibrium is reached with the much lower (if any) concentrations outside the plume. Thus if there is no pollutant gas concentration outside the plume, the droplet may in principle eventually desorb all of its dissolved gas.

- This liquid/gas vapour pressure equilibrium can be modified by the pH in the droplet and this can limit the solubility of gases to levels below the theoretical maximum.

- Dissociation and chemical reaction within the droplet may alter the constituents of the liquid phase and thus the liquid/vapour pressure equilibrium. Particularly, it may increase the droplet concentrations and inhibit desorption.

- The rates of gaseous absorption/desorption and of chemical reaction within the droplet have timescales. These may be significant compared with those of the passage of a drop through the plume and to the ground or with the timescales of the plume dispersion.

- The equilibrium state may also be modified by low concentrations of some ambient gases, especially ozone and $H_2O_2$. Also the presence of trace metals may catalyse some reactions.

- In general, the chemical equilibria in a droplet cannot be considered in isolation; for example the effects of pH in limiting gas solubility can result from all contributions to droplet acidity from different dissolved species.

These effects are considered briefly below. Slinn's (1984) review includes a detailed treatment of gas scavenging by raindrops. Apsley *et al*. (2000) and Singles (1998) also contribute useful data on gas scavenging, though the relative importance of the processes described in these papers is not always clear. Brimblecombe (1996) describes the basic processes very clearly. Most recently, Hewitt (2001) has reviewed the atmospheric chemistry of power station plumes.

The discussion here considers only falling rain of relatively large drop size, rather than cloud droplets and fogs.

## 5.2 Washout by simple dissolution

If there are no chemical effects on the dissolution process, then the concentration of pollutant in a raindrop will be in a simple equilibrium with the ambient concentration following Henry's law, which at concentrations well below saturation is:

$$H = \frac{C_{aq}}{p_v} \qquad (6)$$

where $C_{aq}$ is the aqueous concentration of the vapour, $p_v$ is its ambient partial pressure and H is the Henry's law coefficient.

Henry's law thus provides the equilibrium drop concentration directly if the ambient concentration is known and no secondary chemical reactions affect the equilibrium. This parameter is sometimes also called the washout ratio or the scavenging ratio. Units of H are quite variable according to Slinn (1984), but are usually in some form of mol $l^{-1}$ $atm^{-1}$ or similar. In practice there is a pronounced effect of temperature on H which varies with the gas, the liquid phase solubility reducing rapidly with increases in temperature. Seinfeld and Pandis (1996) give details of this, but typically a variation of 10°C in the ambient range will alter the dissolved gas concentration by a factor of between 1.25 and 2. Table 5.1 shows values of the Henry's law coefficients for some ambient gases of interest, taken from Brimblecombe (1996) and from Seinfeld and Pandis (1996). Also given are their relative values against $SO_2$. In the case of Brimblecombe's value for HCl, the definition of the Henry's law coefficient is modified by its dissociation, so that equation (6) then becomes:

$$H = \frac{C_{aq}(H^+)C_{aq}(Cl^-)}{p_v} = \frac{C_{aq}^2}{p_v} \qquad (7)$$

so that the liquid/vapour equilibrium becomes non-linear with concentration. The value of H given in Table 5.1 corresponds to an ambient HCl concentration of about 0.5 ppm if used as in equation (6).

**Table 5.1 Some values of Henry's law coefficients from different references**

| Species | Brimblecombe (1996) | | Seinfeld and Pandis (1996) | |
|---|---|---|---|---|
| | Henry's law coefficient, H (mol$^{-1}$ l$^{-1}$ atm$^{-1}$) at 15°C | Ratio against $SO_2$ | Henry's law coefficient, H (mol$^{-1}$ l$^{-1}$ atm$^{-1}$) at 25°C | Ratio against $SO_2$ |
| Carbon dioxide ($CO_2$) | 0.045 | 1/120 | 0.034 | 1/36 |
| Ammonia ($NH_3$) | 90 | 16.6 | 62 | 50 |
| Sulphur dioxide ($SO_2$) | 5.4 | 1 | 1.23 | 1 |
| Formaldehyde (HCHO) | 1.7 | 1/3 | 2.5* | 2.0 |
| Nitric oxide (NO) | 0.0023 | 1/2400 | 0.0019 | 1/650 |
| Nitrogen dioxide ($NO_2$) | - | - | 0.01 | 1/123 |
| Ozone ($O_3$) | 0.02 | 1/270 | 0.0113 | 1/109 |
| Hydrogen fluoride (HF) | $1.4 \times 10^4$ | 2600 | - | - |
| Hydrogen chloride (HCl)** | $2.04 \times 10^6$ | 380,000 | 727 | 590 |

* $6.3 \times 10^3$ if diol formation is included

** For an ambient concentration of 0.5 ppm. See text and equation (7) for modified definition of H.

After noting the difficulties in obtaining reliable gas solubility data, due to a number of problems including a wide variety of units and definitions (with which the authors are in sympathy), Slinn quotes calculated gas solubilities for a wide range of gases in pure water. Values for the gases of interest here are given in Table 5.2. These solubilities are the ratio of gas concentration in water to gas concentration in air at the equilibrium state, which is also the Henry's law coefficient. The units are uncertain from the text, but are clearly not the same as in Table 5.1. The variations in Henry's law coefficients between Brimblecombe and from Seinfeld and Pandis in Table 5.1 are partly because the values are given at different ambient temperatures, but mainly because Brimblecombe's values include the effects of hydrolysis and dissociation in solution, whereas Seinfeld and Pandis' data are solely for simple dissolution. Slinn's data appear to be on the same basis as Seinfeld and Pandis, as his ratios of Henry's law coefficients against sulphur dioxide are very similar. The effect of dissociation on HCl absorption is particularly pronounced, leading to an effective value of the Henry's law coefficient around three thousand times that for simple dissolution.

**Table 5.2 Solubilities of some plume gases at equilibrium (from Slinn (1984), Table 11.8)**

| Gas | Solubility* | Ratio against $SO_2$ |
|---|---|---|
| NO | 0.046 | 1/650 |
| $NO_2$ | 0.24 | 1/125 |
| $O_3$ | 0.32 | 1/94 |
| $SO_2$ | 30 | 1 |
| HCl | 510 | 17 |

* See text above.

## 5.3 Effects of pH on gas solubility in raindrops

A consequence of the dissociation of acid gases in raindrops is a reduction of pH in the raindrop. One effect of this is to limit the total quantity of dissolved gas; for $SO_2$, the values of Henry's law coefficient decrease rapidly with increasing acidity. The main concern has been with the effect of this on the rate of washout of $SO_2$. Seinfeld and Pandis (1996) quote a reduction in Henry's law coefficient for $SO_2$ of about three orders of magnitude when the pH in raindrops decreases from 5.6 for clean atmospheres (where there is only $CO_2$ in solution) down to a pH of 1-2. The upper plot in Figure 12 (from Slinn, 1984) shows this behaviour. The values of Henry's law coefficient for $SO_2$ quoted in Tables 5.1 and 5.2 correspond to a droplet pH of around 2 and are close to the lower bounds of $SO_2$ solubility quoted by Seinfeld and Pandis.

Acidity in rain droplets may be altered by the absorption of other acid or basic species besides sulphur dioxide. The increased acidity due to HCl absorption from coal-fired plants is probably the most significant here, but other ambient background pollutants, such as $NH_3$, can also be adsorbed. These directly affect the pH balance and in turn the Henry's law coefficient for $SO_2$. The significance of HCl washout is considered in more detail in Section 6.6.

Washout of $NO_2$ seems to be less affected by the pH. Ponche *et al*. (1993) noted in experiments on gaseous absorption into droplets that the gas transfer coefficient for $NO_2$ was largely unaffected by the droplet pH.

## 5.4 Effects of chemical reaction and dissociation on washout at short ranges

The effects of dissociation of dissolved gases in raindrops have already been noted for the resultant Henry's law coefficients from the two references in Table 5.1. Generally, dissociation or reaction of adsorbed gases in solution unbalances the liquid vapour equilibrium in favour of a higher concentration in solution. The example of hydrogen chloride (already discussed), which is almost completely dissociated in solution, is very marked as Brimblecombe's (1996) dissociated and Seinfeld and Pandis' (1996) undissociated values of Henry's law coefficient for hydrogen chloride are different by a factor of 3000.

In species with significant dissociation and/or reaction (as with $SO_2$, $NO_2$ and HCl), there may be a resultant asymmetry in the adsorption/desorption behaviour. For simple adsorption the process is essentially symmetrical for similar increases or decreases in the external concentration. In the presence of reaction and dissociation, desorption usually decreases so that gases are more readily absorbed than desorbed.

A variety of complex reactions are possible in raindrops, depending on the species present. $SO_2$ may oxidise to $SO_4$, though this reaction is regarded as relatively slow by the standards of short-range dispersion. However it can be much faster in the presence of adsorbed atmospheric ozone or $H_2O_2$. The lower plot in Figure 12 shows the change in $SO_2$ oxidation rate with solution pH for typical levels of ambient ozone and $H_2O_2$ (there is no effect of solution acidity on the behaviour of $H_2O_2$). However if $O_3$ and $H_2O_2$ in the plume are removed during oxidation of NO (see Section 7), this reaction in solution may be negligible. Brimblecombe (1996) notes that small traces of iron or manganese (both present in combustion plumes) can also catalyse the forward reaction. Wright (2001) has reviewed the rates of many of these secondary reactions, which seem to be relatively slow compared with the timescales of short-range dispersion. They may therefore have only limited effects on wet deposition at short ranges.

$NO_2$ in solution dissociates to produce nitrate or (in combination with NO) nitrite. This in turn can be converted to nitrate ion in the presence of chlorine. Brimblecombe notes that this reaction frees any chloride for desorption as HCl, normally in conditions with low ambient levels of HCl, rather than the relatively high concentrations that can occur in plumes from coal combustion. In this latter case, it seems probable that all nitrate is converted to the nitrate ion. The end result of reactions of this sort in solution is to remove these species from the gas/liquid equilibrium so that their removal is permanent, and therefore that further adsorption of acid species is possible to maintain the gas/liquid equilibrium. Gaseous washout then more resembles the permanent removal behaviour of particles. As with $SO_2$ it is uncertain whether these reactions are important at the short timescales of short-range dispersion.

## 5.5 Timescales of drop solution equilibrium

In long-range washout calculations, the ambient concentrations of contaminants are uniformly distributed vertically through the mixing layer. Thus there is only a single equilibrium state for a raindrop to attain where there is no permanent removal of contaminants and a significant amount of time, of the order of a minute or so, for a raindrop to achieve this state before it reaches the ground. However, over short ranges there is commonly a strong vertical non-uniformity, so that a raindrop in its passage to the ground may experience a rapidly changing external concentration over timescales of seconds. A raindrop passing though an elevated plume may pass though regions of low, then high, then again low concentrations of contaminants before reaching the ground. Thus both adsorption and desorption of contaminant gases is possible. The time required for a drop to reach a liquid/vapour equilibrium with its surroundings is much more critical to estimating the droplet constituents at the ground.

Without any dissociation or reaction within the drop, the time taken to reach equilibrium is mainly controlled by contaminant diffusion, both between the atmosphere and the drop surface and within the drop. Liquid diffusion is normally by far the slowest process and usually controls the time to the drop equilibrium. Even so, for small droplets the times can be quite short. Brimblecombe (1996) quotes a sample calculation for a 50 µm droplet reaching 50% saturation in 0.3 seconds. Larger raindrops should in principle have much longer times to equilibrium, but these are greatly reduced in practice by recirculating flows in the droplet, driven by the external ambient skin friction on the falling drop, which greatly enhances the internal mixing. As result of this, Walcek and Pruppacher (1984a) note that for large drops (>1 mm) and $SO_2$ concentrations at ambient levels, the adsorption is largely controlled by diffusion in the gas phase.

Both experiments and theoretical models have been used to study this behaviour. Some early Russian experimental work on hydrogen fluoride (HF) by Zaytsev *et al.* (1970) involved experiments in which water droplets fell down a tube through which there was a gentle upward flow of an HF/air mixture. Both the drop exposure time and the resultant liquid concentration of HF could then be easily determined. The authors found that the approach to a gas/liquid equilibrium was quite rapid in relatively low air concentrations of HF. For 3.6 mm diameter droplets, the time to 90% of the equilibrium state was about 0.15 to 0.2 seconds. This would correspond to a falling distance for a 3.6 mm drop of about 1.5 m.

Slinn (1984) describes the droplet absorption process in some detail and notes that the rate at which pure water drops reach a solution equilibrium with atmospheric trace gases depends on both the solubility of the gas and the droplet size. The time to equilibrium reduces as the solubility of the gas and the droplet size decrease. This is simply because a gas with lower solubility requires a smaller mass to be transferred to the droplet before liquid/vapour equilibrium occurs. Droplet size controls the ratio of the surface area, across which the gas transfer occurs, to the liquid mass, into which it dissolves. Since this ratio is inversely proportional to drop diameter, the time to equilibrium (to first order) increases in direct proportion to the drop diameter. This is the correct description for simple dissolution, though both Ponche *et al*. (1993) and Walcek and Pruppacher (1984a) note that the process is modified by a number of factors, including the internal recirculating flows driven in larger droplets. Slinn also includes these effects in his calculations.

Slinn estimated the distance of fall of a drop within which it reached the equilibrium state, and quoted for a 2 mm drop diameter (which has a falling speed of about 6 m $s^{-1}$).

For low solubilities (NO, $NO_2$, $O_3$) $\simeq$ 1 m

For moderate solubilities (HCl) $\simeq$ 10 m

For $SO_2$, whose solubility falls between these values, the fall distance to equilibrium would be a few metres. These values were derived theoretically and the characteristic time to the equilibrium state is not perfectly clear, but is probably the time to 61% (1/e) of the equilibrium state. By the standards of industrial plumes, these scales are relatively small and raindrops could be considered as being close to equilibrium with their surroundings.

On the basis of his own estimates, Slinn (1984) remarked that if washout is controlled solely by solubility in this way, then washout calculations for acid gases become relatively trivial. The droplet is in virtually instantaneous equilibrium with its surroundings in large dispersing plumes, even at the short ranges considered here. Deposition is then solely dependent on ambient concentrations within a few metres of the ground and can be calculated on this basis. The upper plot of Figure 13, taken from Slinn's review, shows some calculations by Hales of the concentration of $SO_2$ in water drops falling through a plume. This is calculated assuming solely a liquid/vapour $SO_2$ equilibrium with the response characteristics from Slinn's work described above. The plume has a height of about 40 m, small by the standards of generating station plumes. The plot shows curves of the local ambient concentration (the broken lines) and the resultant estimated $SO_2$ concentration in three different sizes of droplet (the solid lines). The deviations from the equilibrium state of the drop at the ground are relatively small. For $NO_2$ , or for a larger or higher plume, differences from the equilibrium state would be negligibly small at the ground. Equally, if Slinn's estimates of times to the equilibrium state are high, the differences from the equilibrium state would be less.

Similar experiments to Zaytsev *et al*. (1970) on gas absorption into drops have been carried out by Walcek and Pruppacher (1984b) (for $SO_2$), by Amokrane *et al.* (1991) (for $SO_2$) and by Ponche *et al*. (1993) (for $SO_2$ $HNO_3$, $NO_2$ and $NH_3$). Walcek's experiments covered both the absorption and desorption of $SO_2$ from water drops up to 4mm in diameter and also included the effects of $H_2O_2$ on inhibiting the desorption in clean air. The results generally agreed with Walcek and Pruppacher's (1984a) theoretical model for $SO_2$, provided that the enhanced absorption of larger drops observed (due to recirculating flows within the droplet) was accounted for by increasing the apparent liquid diffusivity by a factor of 20. Their model quotes equilibrium times of the order of seconds, depending on droplet size and ambient concentration. Figure 14 shows their plot of estimated times of transfer of $SO_2$ into droplets, showing the effects of droplet size and ambient $SO_2$ concentration. The addition of $H_2O_2$ markedly increased the $SO_2$ retention, largely following their theoretical model. Amokrane *et al*. (1991) also described experiments on droplets falling through a column of air containing traces of $SO_2$. Their experimental data showed gas transfer times of the same order but faster (by varying amounts of around 10-30%) than Walcek and Pruppacher's (1984a) theoretical estimates. Ponche *et al*. (1993) used a stream of small droplets (around 100 µm) in low pressure gas streams containing $SO_2$, $HNO_3$, $NO_2$ and $NH_3$. All their quoted characteristic transfer times are less than 0.2 seconds.

Slinn (1984) also remarked on the rapid adsorption and desorption of acid gases from raindrops having the ability to lower the height of a plume. Similar calculations are presented by Walcek and Pruppacher (1984a,b,c). The lower plot in Figure 13 shows an example calculation of this sort in Slinn's review (from his own paper, Slinn (1974)). For $SO_2$ this behaviour seems unlikely to be important unless the plume is relatively small and the equilibrium relatively slow. It may be more important for HCl; this is discussed in Section 6.6. The timescales for significant downwash of $SO_2$ are relatively large from the plot, in excess of 1000 s, which indicates plume travel distances of 2-10 km.

Some of the experimental data indicate significantly faster equilibrium times than Slinn's calculations, especially that of Zaytsev *et al*. (1970). Considering the larger drop size in this work than that used in Slinn's calculations, and that the solubility of HF is greater than of $SO_2$, this equilibrium time is about an order of magnitude less than that calculated theoretically by Slinn. On this basis the fall distances within which gaseous equilibrium is achieved would be proportionately smaller, of the order of a metre or two at most for HCl and $SO_2$ rather than Slinn's estimate of about 10 m. On the same basis the equivalent distances and times for $NO_2$ would be about a tenth of these values.

The only experimental measurements described here for desorption and the presence of other contaminants ($H_2O_2$) are by Walcek and Pruppacher (1984b). Otherwise there seem to be no experiments which have used gas mixtures related to any other exposure (including to ozone) that a droplet might experience in reality. These have the property of modifying the dissociation and species content of a droplet by reaction, and thus the resultant absorption and, especially, the desorption behaviour of dissolved gases in the droplet.

## 5.6 Washout of hydrogen chloride from coal combustion

As noted in Section 5.4, coal combustion generates hydrogen chloride which is emitted along with $SO_2$ and nitrogen oxides. For UK coal with a nominal chloride content of 0.2% and a sulphur content of 2%, the emitted HCl would contribute about 5% of the total emitted acidity. On the basis of Henry's law coefficients in Table 5.1, the relative concentrations washed out in a raindrop would be 380,000:1 for an ambient concentration of 0.5 ppm and about 78,000:1 for an ambient concentration of 10 ppm. In these cases the relative contributions of HCl and $SO_2$ to acidity in rainfall in the near field would be in the ratio of about 20,000:1 and 100:1 respectively. In practice it seems likely that removal of ambient HCl on these scales would be constrained by gaseous transfer to the droplet. Nonetheless, the potential droplet acidity due to HCl is extremely high and implies a high rate of washout in the near field.

There are further ramifications of the absorption of HCl into raindrops on this scale. Firstly, since the absorption of $SO_2$ is pH-limited, this high additional contribution to droplet acidity would likely inhibit the absorption of $SO_2$ in the near field, making droplet acidity further weighted towards HCl. Secondly, the oxidation of $NO_2$ in solution is encouraged by the presence of HCl, so that the additional HCl in solution might encourage permanent retention of ambient NO as nitrate. Thirdly, though in principle HCl can be desorbed below a plume, the balance of the Henry's law coefficient is so heavily weighted towards the aqueous fraction that it would only require low ambient residual concentrations of HCl for a significant fraction to remain in solution. Finally, present acid deposition and critical loads methodology takes no account of any acidic contribution from HCl, being based solely on deposition of $SO_2$ and $NO_2$.

There has been only limited interest in this matter, with little discussion of HCl's contribution to coal combustion plume acidity. The, then, CEGB investigated HCl deposition in the early 1980's, but most of the work was not publicised. Clark (1984) analysed the characteristics of HCl washout at both short and long ranges. The work was concerned mainly with longer range deposition, but confirmed a number of important features of shorter range deposition. Clark noted that in a simple equilibrium, the liquid/vapour fractions were such that nearly all HCl was in solution. Also in some cases washout could be effectively irreversible, though this assumption was uncertain in the near field with elevated plumes. Equilibrium times were of the order of seconds for small cloud or fog droplets, but longer for raindrops, partly due to the amount of HCl that must be transferred to a drop to reach equilibrium. Clark also noted the rapid rates of HCl depletion from a plume that could occur in moderate rainfall. Some related experiments on wet deposition under power station plumes indicated that there could be a substantial component of HCl in precipitation at the ground, especially in drizzle.

Fenton *et al*. (1980), described experiments on HCl washout from rocket plumes. These were concerned with relatively high concentrations of HCl which formed their own acid mists. The authors' theoretical model predicted very high washout rates, especially at high humidity, though these were not confirmed by experiments (due, it was thought, to the presence of other chemical species in the exhausts). After comparing with experiments, the authors quoted the following washout formula:

$$\Lambda = 5.12.10^{-5}\frac{P^{0.773}}{c^{0.176}} \tag{8}$$

where P is the rainfall rate in mm $h^{-1}$ and c is the ambient concentration of HCl in g $m^{-3}$.

For a rainfall rate of 1mm $h^{-1}$, this gives a washout coefficient of 2.1 x $10^{-4}$ for an HCl concentration of 500 $\mu$g $m^{-3}$. This is close to the upper bounds quoted by Jones (1983) and by Underwood (2001) for $SO_2$. However, the relative Henry's law coefficients suggest a much higher proportionate washout.

# 6 Oxidation of NO to $NO_2$ in dispersing plumes

As noted in Section 5.2.1, conventional combustion plants discharge nitrogen oxides mainly as nitric oxide, NO and nitrogen dioxide, $NO_2$ in the ratio of about 95% NO (or more) to 5% $NO_2$. Some (probably most) of this NO can be oxidised to $NO_2$ during the life of the plume, and its significantly higher acidity and deposition velocity directly affects the acidic nitrogen deposition, both wet and dry, from the plume.

The NO in the plume is oxidised only quite slowly to $NO_2$ by atmospheric oxygen and the ratio of NO to $NO_2$ would be little affected by this over the timescales of plumes dispersing at short ranges. However, atmospheric ozone oxidises NO much more rapidly. Varey *et al*. (1984) quote reaction rate constants for the three reactions of greatest interest in this conversion as:

| | | |
|---|---|---|
| $k = 1.0\ ppm^{-1}\ s^{-1}$ | for | $NO + O_3 \rightarrow NO_2 + O_2$ |
| $k = 1.5 \times 10^{-11}\ ppm^{-2}\ s^{-1}$ | for | $2NO + O_2 \rightarrow 2NO_2$ |
| $k = 5.6 \times 10^{-3}\ s^{-1}$ | for | $NO_2 + hv \rightarrow NO + O$ and |
| $k = 2.5 \times 10^{4}\ s^{-1}$ | for | $O + O_2 + M \rightarrow O_3 + M$ |

The last two equations are the reverse process in the ozone cycle, the conversion of $NO_2$ to NO and ozone in the presence of solar radiation, hv. M is an arbitrary balancing air molecule in the equation. This clearly only occurs in the presence of significant solar radiation, a minority of the time diurnally and especially infrequent in the UK.

The relative rates of reaction are in proportion to the constituent concentrations, but for plausible ambient concentrations of 100 ppb of NO in a plume and 25 ppb of ozone in the atmosphere, the rates of conversion of NO (or its reverse conversion from $NO_2$) are:

| | | |
|---|---|---|
| about* $2.5\%\ s^{-1}$ | for | $NO + O_3 \rightarrow NO_2 + O_2$ |
| about $3 \times 10^{-7}\%\ s^{-1}$ | for | $2NO + O_2 \rightarrow 2NO_2$ |
| about $0.5\%\ s^{-1}$ | for | $NO_2 + hv \rightarrow NO + O$ and |
| about** $2.5 \times 10^{4}\%\ s^{-1}$ | for | $O + O_2 + M \rightarrow O_3 + M$ |

*Seinfeld and Pandis (1996, p1299) give a reaction rate constant that corresponds to a rate of conversion of about $1\%\ s^{-1}$ at 298K.
**This assumes a concentration of O of $10^{-8}$ (10 ppb). The removal of free oxygen is normally regarded as instantaneous.

At combustion plant stack exit conditions, where the concentration of NO is about 100-200 ppm, the rates of the first two reactions are higher, about $2{,}500\%\ s^{-1}$ and $0.03\%\ s^{-1}$ respectively for 100 ppm NO.

The full NO/ozone photochemical cycle is relatively complex and is discussed in detail by Seinfeld and Pandis (1996) and in the Acid Rain Review Group and Photochemical Oxidants Review Group reports. There are also discussions of the $NO/NO_2/O_3$ reactions in plumes by

Janssen (1986) and more recently by Hewitt (2001). These do not particularly affect the discussion below. For the purposes of this report a simpler view is probably acceptable, as Varey *et al*. (1984) note, and the main features of the process are:

The conversion of NO to $NO_2$ is dominated by the reaction with ozone; natural conversion by atmospheric oxygen is very slow by the timescales of dispersing plumes, even at stack discharge concentrations.

The reverse photochemical reaction, producing ozone, is significantly slower compared with the forward oxidation of NO by ozone.

Thus, if the NO/ozone equilibrium is disrupted by the introduction of a high concentration of NO, as in the case of a dispersing combustion plume, the atmospheric ozone is used up relatively rapidly in oxidising NO. Even when sufficient solar radiation is present to drive the reverse reaction, this will only reconstitute NO relatively slowly.

There is an additional time delay in the forward reaction due to the need for intimate mixing of NO and atmospheric ozone which is entrained into the plume with ambient air. At long ranges the plume fills the whole boundary layer depth, the times for turbulent mixing are long and intimate mixing can be assumed. At smaller scales this is not the case and this additional mixing time must be considered.

Initial mixing in the plume is by larger eddies, but it is mixing by smaller eddies, followed by molecular diffusion, which intimately mix the gases and this process is slower than that of the larger eddies. The relative importance of the reaction rate and the plume mixing are indicated by the dimensionless Damkohler number (Cussler, 1984; Brown and Bilger, 1998a,b), which is a dimensionless time of the form:

$$\frac{k_c L}{U} \qquad (9)$$

where L and U are related length and velocity scales of the turbulent mixing and $k_c$ gives the reaction rate as in the list immediately above. If the Damkohler number is small, the reaction is controlled by the chemical reaction rate; if it is large, by the rate of mixing of the gases. For dispersing plumes, the plume height and wind speed are reasonable indicators of the turbulent velocity and length scales experienced by a plume dispersing to the ground. Taking nominal values for a large generating station plume of 100 m for L (the order of the vertical scale) and 5 m $s^{-1}$ for U, the Damkohler number is about unity for the NO/ozone reaction at 100 ppb concentrations of NO, but of the order of 1000 at stack discharge concentrations of NO. It is very small for the $NO/O_2$ reaction. Thus the NO oxidation process in a plume passes from being controlled more by the rate of mixing in the initial stages towards being controlled more by the reaction rate at longer ranges.

In practice the relative importance of the mixing time and reaction rate depends on the scale of the dispersing plume and whether it is dry or wet deposition that is of interest. In the case of dry deposition, it is only the gas mixture in contact with the ground that is important and in this case, it is reasonable to assume that intimate mixing has occurred. There are two reasons for this. Firstly, the considerable reduction in wind speeds close to the ground allows increased mixing and reaction times. Secondly, the pronounced wind shear at the surface encourages intimate mixing of the gases. This initially allows the forward reaction to complete, but also allows further time for the reverse reaction to develop. In practice the final stages of the dry deposition process must be at the ground and within the canopy, but this region is also subject to shading by the canopy, which again suppresses the reverse reaction. Uncertainty over ozone damage to vegetation is partly for this reason. For wet deposition it is the conversion process within the whole plume that is of concern and this is more complex. In large plumes, there is generally adequate time for efficient mixing, but conversion of NO to $NO_2$ initially occurs more completely at the edges of the plume, where the relative ratio of $O_3$ to NO is high.

A diagram of the simple model of NO to $NO_2$ conversion is shown in Figure 15. This assumes that only the forward reaction, driven by the presence of ambient ozone, occurs and that this reaction is instantaneous (that is, there is no delay for intimate mixing). The upper plot shows along-wind plume concentrations, the lower plot plume cross-wind concentrations.

On the upper (along-wind) log-log plot, concentrations in a plume with distance are approximately represented by a straight line and the three broken straight lines show the unreacted concentrations of NO, $NO_2$ (in the ratio 95%:5%) and their sum, the total nitrogen oxides, $NO_x$. There is also a horizontal line indicating an assumed ambient concentration of $O_3$. As concentrations of nitrogen oxides in the dispersing plume reduce, the proportionate concentration of $O_3$ in the diluting ambient air increases and steadily more NO is oxidised to $NO_2$. The two bold lines on the plot are of the resulting NO and $NO_2$ concentrations. Once the NO and $O_3$ concentrations in the plume are equal, all NO is assumed to be converted to $NO_2$. The concentrations are represented simply by:

$$
\begin{aligned}
&[NO_2] = \frac{n}{100}[NO_x] + [O_3], \text{ for } [NO] > [O_3], \\
&[NO_2] = [NO_x], \text{ for } [NO] < [O_3] \qquad\qquad (10) \\
&\text{and} \\
&[NO] = [NO_x] - [NO_2],
\end{aligned}
$$

where n is the percentage of $NO_2$ in the plume $NO_x$.

The lower plot of Figure 15 represents the same process applied across a plume. Equations (10) also apply here. As concentrations are lower at the plume edges, complete conversion of NO to $NO_2$ occurs there initially and spreads into the centre of the plume with increasing distance as it disperses. Thus the NO and $NO_2$ concentration profiles become non-Gaussian, until there is complete conversion of all NO at longer distances.

For dry deposition, which requires only concentrations at the ground, equations (10) generate a quite straightforward calculation applied to the ground-level concentrations. This can be made either within a model calculation, once an ambient concentration of $O_3$ is assumed, or it can be post-processed from the output ground-level concentrations. For wet deposition, the calculation is more complex if, as seems likely, the washout of $NO_2$ is a permanent process due to further reactions within the droplet. A washout calculation must in this case calculate the integrated absorption of $NO_2$ through the plume, and this must be done as part of the dispersion calculation.

The ADMS3 model contains an NO to $NO_2$ conversion procedure (Singles and McHugh, 2000), which includes the effects of the reverse reaction. However, there is no indication of its performance and how it compares with the simple model. The calculation is based on conditions in the centre of the plume rather than at the ground. Some example calculations using this model are shown in Figures 16 and 17, which show plume centreline concentrations (at the ground) for four specific weather conditions. The calculations have used the plume discharge conditions shown in Table 6.1.

**Table 6.1 Source details for example calculations of NO oxidation model**

| | |
|---|---|
| Source height | 0 m |
| Source diameter | 12 m |
| Exit velocity | 0 m $s^{-1}$ |
| Exit temperature | 15°C |
| $NO_x$ emission rate | 500 g $s^{-1}$ |
| % of $NO_x$ as $NO_2$ (by volume) | 5% |

These are comparable with a large generating station, except that the source is at the ground and there is no buoyancy or momentum in the discharge. This was done in order to examine the effects of the conversion process alone, without additional confusion caused by varying plume rise and a rising and falling ground-level concentration pattern.

The first calculation used cloudy night conditions, chosen to eliminate effects of solar radiation. This was then repeated for midday on the same day, firstly with complete cloud cover and then with no cloud, to increase the effects of solar radiation and the conversion of NO to $NO_2$. Finally a summer's day at midday was used to show the effects with maximum solar radiation. It is not possible, in ADMS3, to input specific values of the surface heat flux when using the chemistry module, so suitable hours and days of the year were chosen, as shown in Table 6.2. The calculations were also made with a high wind speed of 10 m $s^{-1}$. This resulted in a nearly neutral stable atmosphere in all cases, so that the choice of particular weather conditions (day/night and high/low solar radiation) did not additionally alter the rate of dispersion due to varying atmospheric stability. The plots then followed a similar pattern to that for the simple model in Figure 15. Examination of the curves for 'no chemistry' in the figures shows that the dispersion calculations were similar, but not identical. The calculations were made for an assumed $O_3$ ambient concentration of 50 ppb, at the upper bound of most UK measurements and sufficient to show any conversion effects clearly.

Figure 16 shows the calculations for no (cloudy night) or low (cloudy day) solar radiation and Figure 17 for moderate (clear day) and high (clear summer day) levels of solar radiation. Each plot shows the downwind profiles of NO and $NO_2$ obtained firstly with no chemical conversion, then using the simple model and finally using the ADMS3 chemistry module.

**Table 6.2 Meteorological data used in ADMS oxidation model calculations**

| Parameter | Cloudy night | Cloudy day | Clear day | Clear day (summer) |
|---|---|---|---|---|
| Date | 31 March | 31 March | 31 March | 21 June |
| Hour | 23 | 12 | 12 | 12 |
| Cloud cover (oktas) | 8 | 8 | 0 | 0 |
| Boundary layer height (m) | 2000 | 2000 | 2000 | 3000 |
| Temperature (°C) | 5 | 5 | 5 | 20 |
| Wind speed (m $s^{-1}$) | 5 and 10 | 5 and 10 | 5 and 10 | 5 and 10 |
| Solar radiation (W $m^{-2}$) | 0 | 150 | 675 | 850 |

Figure 16, for no solar radiation (cloudy night), shows very little difference in predicted $NO_2$ levels between the ADMS3 calculations and the simple model. With a little solar radiation (cloudy day), the ADMS3 calculation shows a slightly slower oxidation rate around 7-8 km distance than the simple model. In Figure 17, with moderate and high solar radiation, there is a more marked departure between ADMS3 and the simple model, due to higher rates of the $NO_2$ reverse reaction. The greatest difference between the two calculations (around a factor of 2-3 in calculated $NO_2$ concentrations) occurs at around 4km distance. Beyond this distance the difference decreases and at long ranges there remains a small residual difference between the two models of about 30% in $NO_2$ concentrations.

Figure 18 shows bar charts of the differences between the ADMS3 and simple model calculations at three distances. At 1km distance in all cases and at all distances for the cloudy night case, there is little difference between the ADMS3 and simple model calculations. For the other cases with some solar radiation, there are differences between the ADMS3 and simple model calculations. These are relatively small for the low solar radiation ‘cloudy day’ case (about 10%), but larger for the cases with more solar radiation (about 25%).

Overall, considering that there is no solar radiation for half the time (at night) and clear days with high solar radiation are relatively infrequent in the UK (the average hourly sunshine is around 3-4 hours per day), the simple oxidation model would seem to agree with the ADMS3 calculation within about 10% for most of the time. If the overall oxidation predicted by the simple model were increased by 10% for daylight hours, it would be within 10% of the ADMS3 model calculation nearly all the time.

# 7 Analysis and discussion

## 7.1 General

The purpose of this report was to review briefly the dry and wet deposition processes for acid gases and consider these in the light of current methods for assessing industrial plumes, both in terms of their accuracy and of reasonable improvements that might be made.

The physical processes involved in deposition are complex and are subject to the influence of a relatively large number of variables, so that neither wet nor dry deposition will ever be calculated precisely. However the limited approximations presently used in short-range modelling seem something of a travesty of the physical processes involved, and it is not certain that these provide much more than token indications of the actual deposition. The uncertainty of current estimates of wet and dry deposition is not better than a factor of two and in some cases not better than an order of magnitude. Variations in this range can have marked effects on calculations of critical loads.

Improving the methodology will depend both on the availability of adequate additional information and the degree to which improved calculations can be made using existing models, for example by changing coefficients or by pre- and post-processing the input and output data of existing models; in some cases, the models themselves may need to be modified to make significant improvements. The discussion here considers a hierarchy of increasing complexity to improve the methodology.

## 7.2 Hydrogen chloride

Both dry and wet deposition of hydrogen chloride from coal combustion is likely to be significant. Despite its relatively small contribution to the total emitted acidity from unabated emissions (perhaps 5% of the total), its dry and wet deposition in the near field is proportionately much greater and in some conditions may be the dominant contribution to deposited acidity. HCl may also affect the wet deposition of other acid gases, for example by inhibiting the dissolution of $SO_2$. Its contribution to acid deposition and to critical load estimates is currently ignored.

## 7.3 Possible improvements to dry deposition modelling

### 7.3.1 Controlling parameters

The current short-range modelling assumption of a fixed overall deposition velocity for each gas, used in the ADMS model, bears little resemblance to actual behaviour. It is more suitable (though not entirely satisfactory) for particle deposition. For gaseous deposition there are marked variations in deposition velocity with the:

gas;
type of surface (both biologically and physically);
aerodynamic roughness;
wind speed;
amount of surface water;
diurnal changes in plant stomatal activity and other factors (such as cloud cover and temperature);
seasonal changes in the state and biological activity of the surface.

Since deposition and critical loads are normally estimated on an annual basis, any of these variables may affect the deposition calculation. For $NO_2$, where deposition is mainly stomatal, all the variables except the surface water can significantly affect the calculation. For $SO_2$ deposition, all the variables are important as it is taken up both stomatally and by reaction and dissolution at the surface. For hydrogen chloride, where the surface resistance is always close to zero, the effects of wind speed and surface roughness tend to dominate and the nature and condition of the surface is relatively unimportant.

It is also a general feature of short-range dispersion modelling at power station scales, which typically cover a surface area 30-40 km square, that the surface characteristics are variable within this area, so that the use of overall values of deposition velocity in a calculation is not satisfactory.

In principle it would be practicable to include all these effects into one of the short-range dispersion models using relatively simple assumptions of the effects of the governing parameters. However, it is also possible to account for some of these variables by pre- and post-processing of data in the existing models. A hierarchy of possible improvements to the current methodology is discussed below.

### 7.3.2 Varying local values of the overall annual deposition velocity

Deposition to different surface types (forest, grassland, water *etc*.) within the model calculation area can be accounted for to first order by varying the overall assumed annual deposition velocity over the calculation grid. This is a common procedure in long-range deposition models such as FRAME and HARM. Though this cannot be done directly within any of the present short-range dispersion models, it is relatively simple to post-process the values of the output ground-level concentration or deposition grid. Since the deposition is directly proportional to the assumed deposition velocity, if the deposition is calculated for a single reference deposition velocity (say 10 mm $s^{-1}$), then the local deposition can simply be scaled by the ratio of this to the required value.

This procedure requires only a single model calculation and the post-processing is relatively easy to do. An alternative approach is to carry out separate model calculations for the different deposition velocities required (or to treat these as separate gases with different deposition velocities, which the ADMS model allows) and pick appropriate values off the different calculation grids as required. However this is likely to be more time consuming than simply applying a varying deposition scaling factor to a single calculation grid.

### 7.3.3 Varying local values of the overall annual deposition velocity on a diurnal and seasonal basis

For $NO_2$ and to a lesser extent $SO_2$, there are significant seasonal and diurnal variations in deposition velocity. These can be accounted for in several ways, for example by splitting the annual dispersion calculation into four segments, for winter/summer and day/night conditions, using different deposition velocities for each segment as desired. The meteorological input data for the model calculation are divided appropriately and the four segments run separately. On an annual basis, the total deposition is simply the sum of the four components.

This type of calculation was made recently in a study of the New Forest (Barrowcliffe *et al*. 2003). The deposition velocities of $SO_2$ and $NO_2$ were varied as in Table 7.1, so that the overall time-weighted value matched the required annual value used by Spanton and Hall (1999) for power station plume calculations. The values were based on those provided for this work, as used by the Centre for Ecology and Hydrology in long-range modelling studies. $SO_2$ deposition was varied by only a limited amount, as high deposition stomatally and onto dry vegetation surfaces in summer was balanced by higher deposition to a wetter ground surface in winter. Varying but significant changes in both $SO_2$ and $NO_2$ deposition resulted. Tall stack calculations produced values of the maximum deposition of sulphur only a few percent higher, but an increase in $NO_2$ deposition of about 50%.

**Table 7.1 Assumed variable deposition velocities of $SO_2$ and $NO_x$**

| Period | Months | Hours | Assumed dry deposition velocities (mm $s^{-1}$) | | | |
|---|---|---|---|---|---|---|
| | | | Variable | Constant | Variable | Constant |
| | | | $SO_2$ | | $NO_x$ | |
| Summer day | Apr – Sep | 04:00 - 19:00 | 6 | 5 | 2.8 | 1 |
| Summer night | | 00:00 - 03:00<br>20:00 - 23:00 | 4 | | 0 | |
| Winter day | Oct – Mar | 08:00 - 15:00 | 5 | | 0.4 | |
| Winter night | | 00:00 - 07:00<br>16:00 – 23:00 | 5 | | 0 | |

This procedure requires five separate model calculations: one for the whole year, to find annual ambient concentrations, and four seasonal calculations, to find the overall annual deposition. Also, since the assumed seasonal and diurnal variations in deposition velocity may vary with the surface type, separate calculations may be required for the five different surface categories in current use. However, in the ADMS model, these may be treated as different gases for which the deposition velocity may be altered.

### 7.3.4 Varying the assumed emission rate to account for varying deposition velocity due to seasonal and diurnal changes, wind speed and other parameters

Equation (1) notes that the dry deposition, $D_d$, is given by

$$D_d = v_d C \tag{11}$$

where $v_d$ is the assumed dry deposition velocity and C is the concentration at the ground. The options for improved modelling have so far considered methods of varying $v_d$ in the model input or output to account for the effects of the governing parameters. However it is possible to achieve the same effect on the calculated deposition by altering the ambient pollutant concentration, C, instead by an equivalent amount. This can be achieved by altering the pollutant emission rate in direct proportion, in the model input file, rather than by scaling the data in the output file.

The advantage of this approach is that the effects of most of the relevant parameters controlling deposition velocity, including wind speed, can be accounted for. This is especially important for the effects of wind speed as, for at least part of the time for $SO_2$ and $NO_2$ and all of the time for HCl, the surface resistance is effectively zero and the deposition velocity is then directly proportional to wind speed.

The ADMS model input includes an option for an hourly input file for the whole year, so that the pollutant emission rate can be varied on an hourly basis over the year. This input file can also be allied to the hourly input file of meteorological data, which includes wind speed and other parameters affecting the surface resistance. Using these two input files, most of the input variables affecting the aerodynamic and surfaces resistances, and thus the deposition velocity, can be accounted for on an hourly basis through the year. The AERMOD model allows an emission rate variation on the basis of month or year, wind speed and hour of day, so that a similar, but slightly more constrained, variable input could also be used.

Using this methodology allows:

- calculation of all three surface resistances separately and the resultant deposition velocity on an hourly basis;
- correction of aerodynamic resistances for the effects of wind speed and local surface roughness;
- correction of surface resistance for the effects of surface water (by season and during and after precipitation) and stomatal activity (by hour of day, season, surface solar radiation (including reduction due to cloud cover) and temperature).

This can all be done in combination with varying pollutant emission rates, a common feature of power generator emissions.

Due to the habitat specific nature of many of the parameters that control deposition velocity, a dispersion calculation would have to be repeated for each habitat type of interest, along with a normal calculation to obtain the ambient concentrations. The effort required to develop a systematic procedure for producing the variable input files would be significant. However this is by far the most versatile of the input options for estimating dry deposition.

## 7.4 Possible improvements to wet deposition modelling

Gaseous washout is the most complex of the deposition processes and the most difficult to deal with reliably in a simplified way. The wet deposition process is probably partly one of permanent removal by rainfall (resembling particle washout) and partly a liquid/vapour gaseous equilibrium. There are also interactions between the different components of the process and the different gaseous species involved. This makes it difficult to assess and recommend simple improvements to washout modelling without modelling the adsorption/desorption and internal reactions within raindrops descending through a plume. Research on washout from concentrated plumes at short ranges is limited compared with that for long-range dispersion, for which the atmospheric concentrations, distribution and the balance with other ambient gases that affect the process is different. Thus many descriptions of gaseous washout are not appropriate for the chemical species balance of short-range processes.

The main components of the washout process for $NO_2$, $SO_2$ and HCl in relatively high concentrations in plumes at short ranges is probably as follows.

Some $NO_2$ may be permanently removed by washout, where reactions within the droplet convert it to $NO_3^-$. The removal mechanism will be similar to that of particles and a washout coefficient in the form of equation (4) could probably be used. However the washout coefficients are unlikely to be similar and must be determined. The remaining $NO_2$ in solution should exhibit a local liquid/vapour equilibrium. This equilibrium should not to be influenced by droplet acidity.

Some $SO_2$ may be permanently removed by reaction with dissolved ambient $H_2O_2$ and $O_3$ to produce $SO_4^{--}$. This process can probably be described in terms of a washout coefficient as above. However, the high concentrations of $SO_2$ in plumes at short ranges suggest that there is additional removal of $SO_2$ following a liquid-vapour equilibrium governed by Henry's law. Also if $O_3$ and $H_2O_2$ entrained into the plume are lost in oxidising the plume NO, there may be no significant residue for reactions within droplets and this permanent removal mechanism for $SO_2$ will be lost. Further Wright (2001) indicates that this type of reaction may be slow at the scales of short-range dispersion. Other $SO_2$ in solution should also follow a liquid-vapour equilibrium.

The absorption of $SO_2$ into raindrops is additionally pH-limited (see Appendix B), at levels which are readily attained within plumes at short ranges. The limiting pH includes acidic contributions due to dissolved (and reacted) $NO_2$ and, where present, HCl as well as from dissolved $SO_2$. Thus, for example, where there is significant dissolved HCl in the near field of a dispersing plume, there may be relatively little $SO_2$ at this pH limit.

The liquid/vapour equilibrium around droplets occurs quickly, with timescales of the order of seconds or less. At the scale of power station plumes this can reasonably be regarded as an instantaneous local equilibrium. One consequence of this is that, for airborne plumes, there should be little or no washout to the ground of gaseous $SO_2$, as droplets below a plume will desorb their contents relatively quickly, leaving only those components permanently removed by reaction within the raindrops. For plumes in contact with the ground, the wet deposition of dissolved species in liquid/vapour equilibrium is then controlled by the equilibrium condition at the ground, the previous history of a raindrop having no effect.

It is possible that desorption of dissolved HCl below a plume will follow a slower equilibrium, where the high Henry's law coefficient for HCl (due to its dissociation) balances the equilibrium very heavily in favour of dissolved HCl. Thus even the release of small amounts of HCl to the atmosphere in a descending air mass attached to a region of precipitation may be sufficient to allow significant amounts of HCl to remain in solution and deposit to the ground. The effect is similar to that described by Slinn (1984) and Hales of rainfall lowering the height of a plume, illustrated in Figure 13b, but the effect is far more pronounced with HCl than with $SO_2$.

As noted above, it is difficult to derive a simple washout model incorporating this collective behaviour without attempting a calculation of the history of a rainfall through a plume to the ground. There is also a good case for further experiments of the type described by Walcek and Pruppacher and others, on the liquid-vapour equilibrium of droplets falling though gas mixtures. These experiments have so far tended to use single gases or limited gas mixtures. The main difficulty with applying this work to the present problem is the effect of the specific gas mixtures of interest here on adsorption, retention in and desorption from a falling droplet.

Based on what is presently known, a possible methodology would be as follows.

Washout of most $NO_2$ is probably via a local liquid/vapour equilibrium, possibly in combination with some permanent removal. The present methodology of the ADMS3 model, using washout coefficients, could be used only to deal with the permanent removal component, provided that a plausible washout coefficient could be determined. The remaining component of the washout could be determined from the local equilibrium at the ground, knowing the rate of rainfall and the ambient $NO_2$ concentration at the ground from the normal dispersion calculation.

Permanent washout of a fraction of $SO_2$ due to reaction with ambient $H_2O_2$ and $O_3$ would depend both on the reaction rates and the presence of residual components of these gases after reaction with plume NO. This might be unlikely while there was a residue of unoxidised NO in the plume. Beyond this point (at longer distances) some permanent washout of $SO_2$ could occur. Removal of this fraction could be treated using a washout coefficient, provided this could be determined.

Additional washout of residual $SO_2$ and of HCl in gaseous equilibrium could be found from a Henry's law equilibrium calculation for ambient concentrations at the ground. The pH limit for dissolution of $SO_2$ would need to be observed, including contributions to $H^+$ from dissolved HCl and $NO_2$, together with that due to acidic $SO_4$ from permanently removed $SO_2$. Assumptions would need to be made concerning residual ambient HCl falling with the precipitation and encouraging retention of HCl in solution. The end result of this might be that HCl washout would not be dissimilar from a permanent washout model.

The ADMS3 model incorporates an $SO_2$ chemistry model in which the dissolution of $SO_2$ is pH-limited (see Appendix B). Since this model is one of permanent removal, an end result is the prediction of high concentrations of $SO_2$ in the near field, very close to the source, where the plume is still airborne. The model also assumes permanent removal of $SO_2$ in solution, but accounts for no other pollutants.

## 7.5 Possible improvements to modelling NO to $NO_2$ conversion

The ADMS3 model's calculation of NO to $NO_2$ conversion appears to be largely indistinguishable from the simple model for the majority of the time, that is when there is no strong solar radiation. As such the simple model represents a reasonable first approximation to the full calculations. Any errors are essentially conservative. The simple model can also be post-processed from the output ground-level concentration grid in either the ADMS or AERMOD models. The only additional requirement is an assumed $O_3$ concentration. Since $O_3$ concentrations show some diurnal and seasonal variation, this should either be approximated by an annual average, or the calculation should be split into day/night and summer/winter fractions or similar as discussed for dry deposition in Section 8.2. Alternatively, ADMS allows hourly background values of ozone concentrations to be input.

This simple model would represent a significant improvement to the present approach, which is essentially to assume that a fixed fraction of NO is converted, usually 50% or (more conservatively) 100%. An alternative would simply be to use the ADMS 3 model as it stands, though it calculates the equilibrium in the plume centre rather than at the ground, which is needed for deposition estimates.

Amended values of $NO_2$ concentrations from ADMS3 or the simple model could be used directly in dry deposition calculations, but it would be more difficult to incorporate them into wet deposition calculations. In ADMS3, the NO to $NO_2$ conversion calculation is post-processed from the dispersion data and cannot be fed back into a washout calculation which integrates the washout through the plume. Given a correction to the $NO_2$ concentration and an associated plume depth and maximum concentration associated with a calculation grid, it would be relatively simple to estimate the total washout. This information could be obtained from the ADMS model calculations, but the calculations would have to be done on an hourly basis when precipitation occurred. This would thus require a significant amount of post-processing of the dispersion data.

# 8 Conclusions

1. Current modelling methods, using fixed dry deposition velocities and washout coefficients, bear little resemblance to the physical processes involved, take little or no account of the dependent variables and are of quite uncertain accuracy (probably somewhere between a factor of two and a factor of ten).

2. Though it is conceivable that current methods provide a reasonable indication of deposition on the annually averaged basis for which deposition is usually calculated, it also seems unlikely. However, without detailed calculations taking more note of the true characteristics of deposition against which to compare them, any possible differences between the two types of calculation remain uncertain.

3. Dry deposition varies significantly with different gases and is dependent on a range of meteorological, biological and surface variables, all of which can significantly affect the resultant deposition velocity. There is an adequate methodology in the literature from which this parametric dependence can be calculated. There are, however, some uncertainties and deficiencies, especially since dry deposition is quite difficult to measure directly.

4. Wet deposition is controlled by a number of different processes including the gas/liquid concentration equilibrium, dissociation and reaction in solution. There are also interactions between the main species in solution ($SO_2$, $NO_2$ and HCl) and with other ambient gases, especially $H_2O_2$ and $O_3$. The overall process can be quite complex.

5. Some $NO_2$ may be permanently removed by washout, via dissociation and reaction to form $NO_3^-$ in solution. The remaining $NO_2$ in solution would follow a local liquid-vapour equilibrium.

6. Some $SO_2$ may be permanently removed by washout, by reaction in solution. However, this probably does not occur while there is residual NO in the plume which removes $H_2O_2$ and $O_3$ during its oxidation. Reaction rates of these processes seem to be relatively slow by the timescales of short-range dispersion. Otherwise the $SO_2$ is probably in liquid/vapour equilibrium and may be both adsorbed and desorbed to and from raindrops in equilibrium with the external concentration. The dissolution of $SO_2$ is also pH-limited.

7. The important contribution of hydrogen chloride (HCl, usually present in plumes from coal combustion) to acid deposition is at present largely ignored. This seems an entirely unsatisfactory position. Because of its high solubility, strong dissociation in solution and reactivity, its contribution to both wet and dry deposited acidity may be quite disproportionate to its small fraction (ca 5%) of the acid components of the plume. HCl can also affect the washout of other acid gases, especially of $SO_2$.

8. The oxidation of NO to $NO_2$ in plumes, which governs the amount of $NO_2$ available for deposition, is largely controlled by the level of ambient $O_3$ . The simple oxidation model from Varey *et al*. (1984) is largely indistinguishable from the ADMS3 NO chemistry model, which includes the effect of the reverse reaction due to solar radiation. The simple model can be post-processed from the ground-level $NO_2$ concentration grid from the dispersion calculation, once an ambient $O_3$ concentration is assumed.

9. The ADMS3 model does not account directly for the effects of the multiple governing variables on dry deposition. However they can be accounted for by pre- and post-processing data in either ADMS3 or AERMOD. The ADMS3 model is probably the easiest to use in this respect, but the level of data processing required is significant.

10. There was originally no treatment of gaseous washout or dry deposition in the AERMOD model. However it now contains a resistance-based dry deposition model and a permanent washout model with washout based on species solubility. The washout model seems mainly aimed at soluble organic species. The ADMS3 model has a limited treatment of some aspects of $SO_2$ washout chemistry. Some aspects of gaseous washout can be dealt with by pre- and post-data processing, but is inherently more difficult than handling dry deposition due to the complex wet deposition chemistry. It is probably possible to devise an improved washout model on this basis.

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# Figures

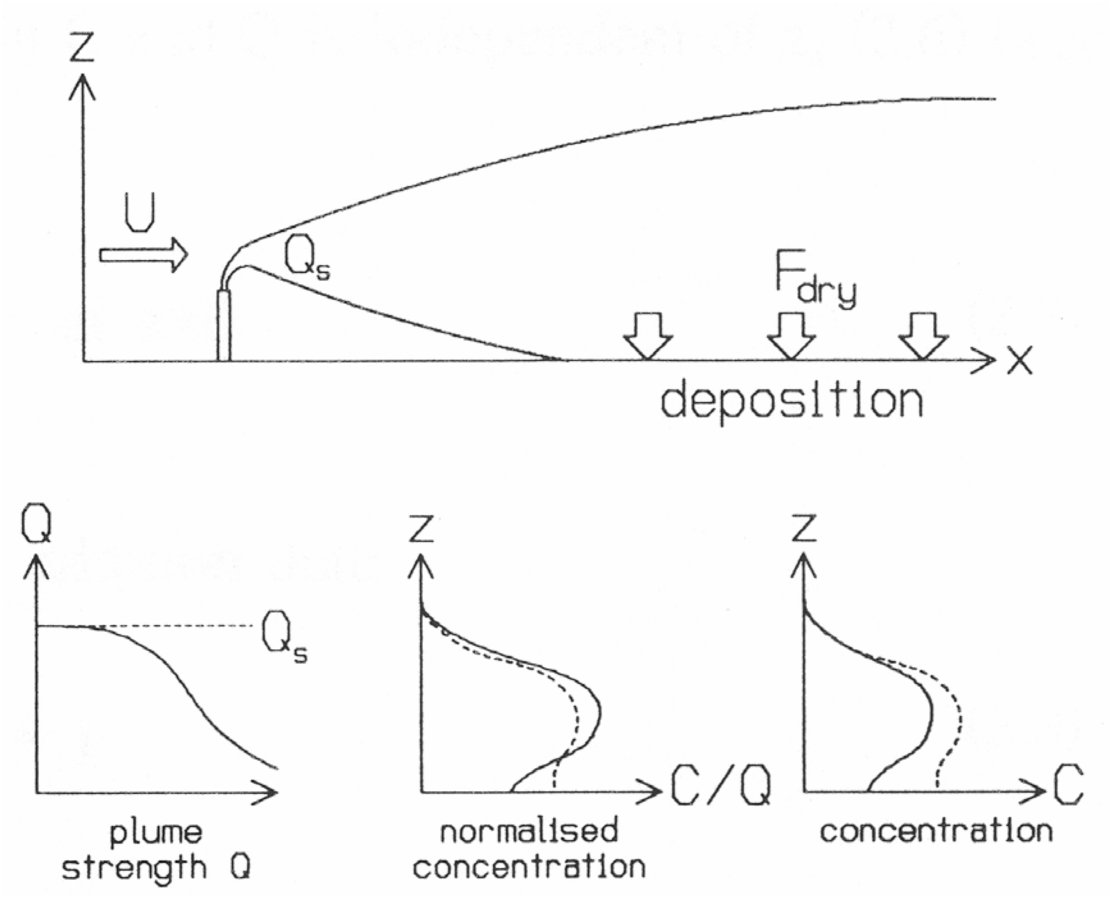


**Figure 1. Corrections for plume depletion due to deposition losses in ADMS model. From ADMS specification for deposition and radioactive decay (CERC, 1999).**

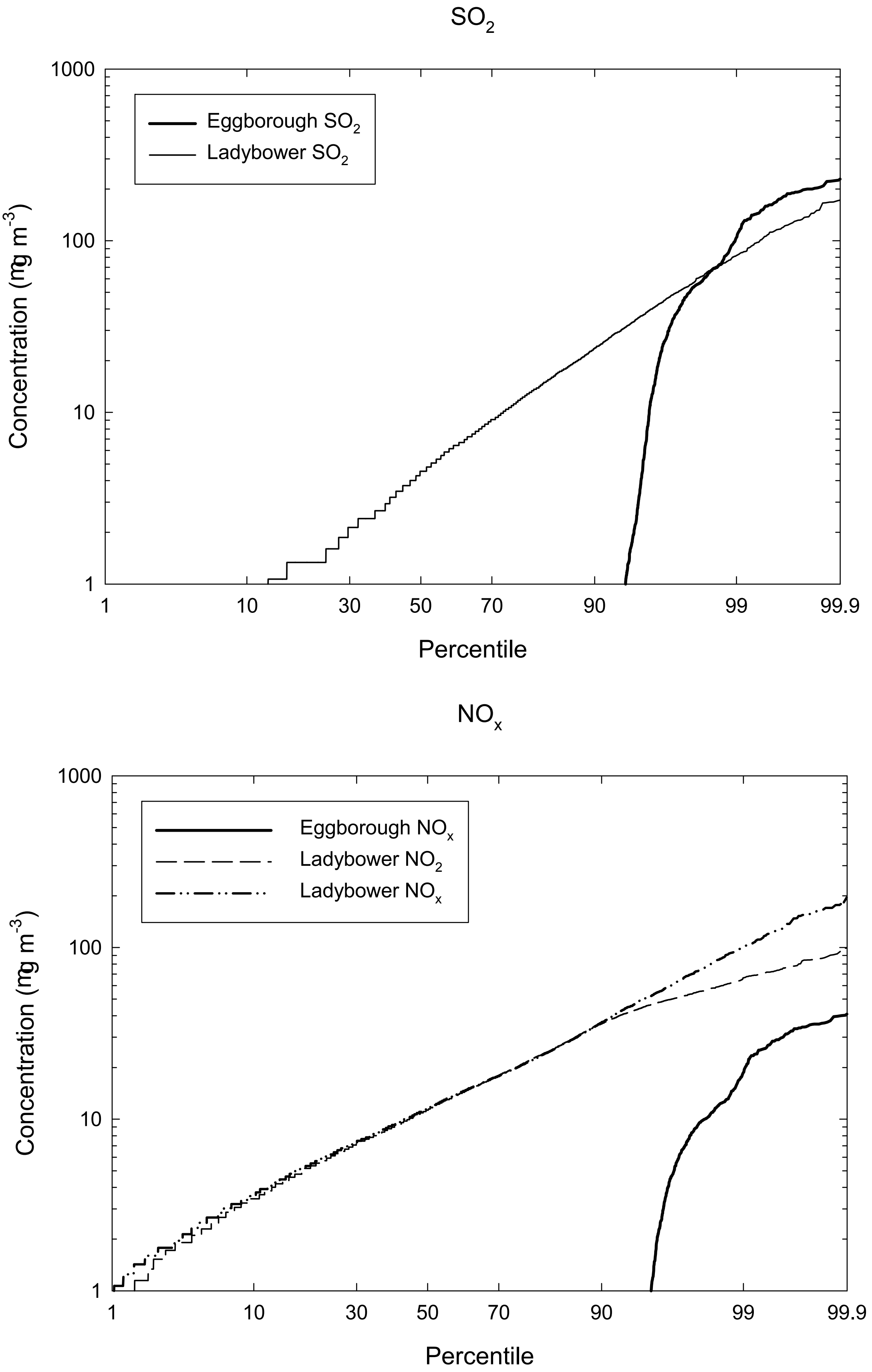


Figure 2. Concentrations frequency distributions from ‘background’ concentrations (Ladybower) and from a tall (200 m) power station discharge at the point of maximum concentration.

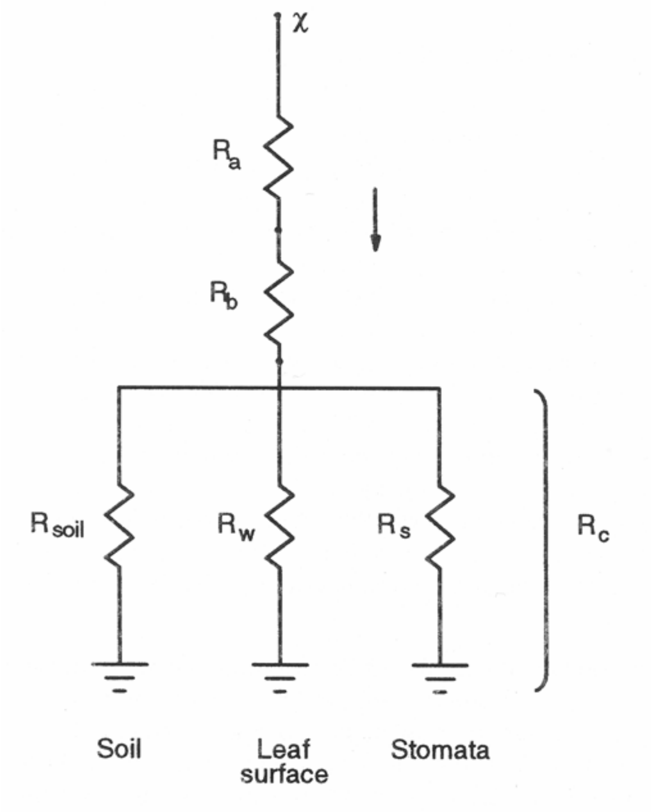
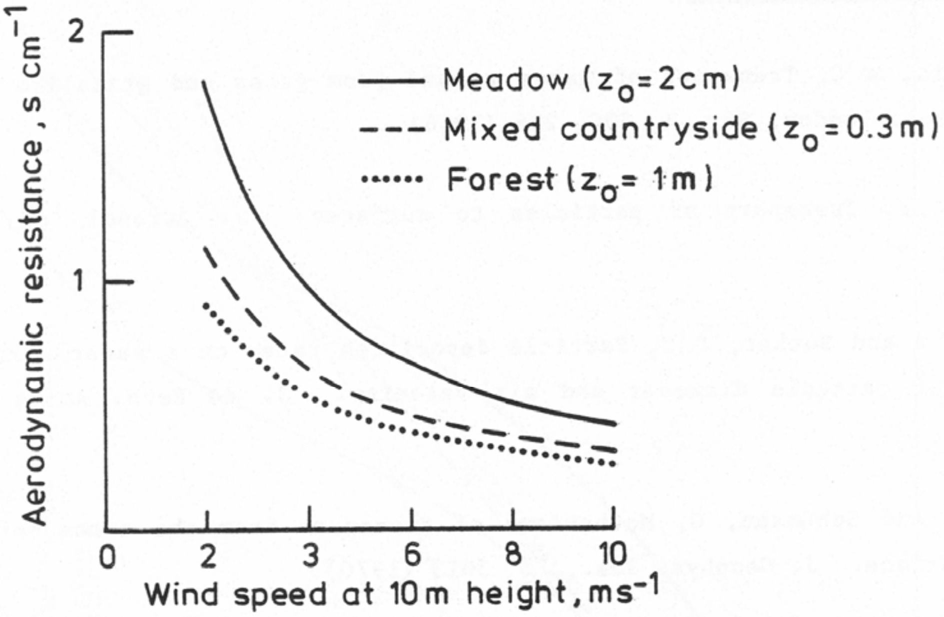
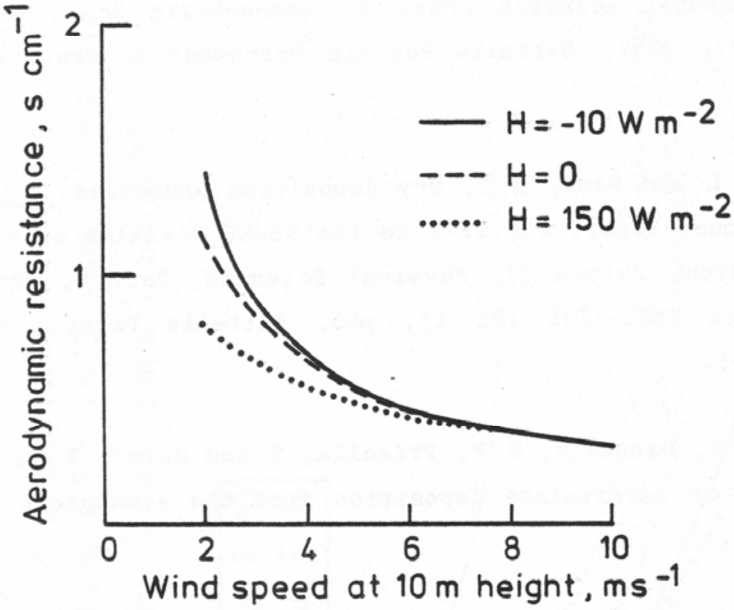


Figure 3 The principle of estimating deposition velocity using the 'surface resistance' analogy. From the Fourth Report of the Review Group on Acid Rain (DETR, 1997a).



a) Variation of aerodynamic resistance for iodine vapour at various surfaces in neutral conditions



b) Variation of aerodynamic resistance for iodine vapour with wind speed for mixed countryside (z =0.3 m), showing the effect of surface heat flux in conditions of moderate daytime heating (H = 150 W m$^{-2}$), neutral and moderate nocturnal cooling (H =-10 W m$^{-2}$)

Figure 4. Estimates of the aerodynamic resistance of iodine vapour. From Jones (1983).

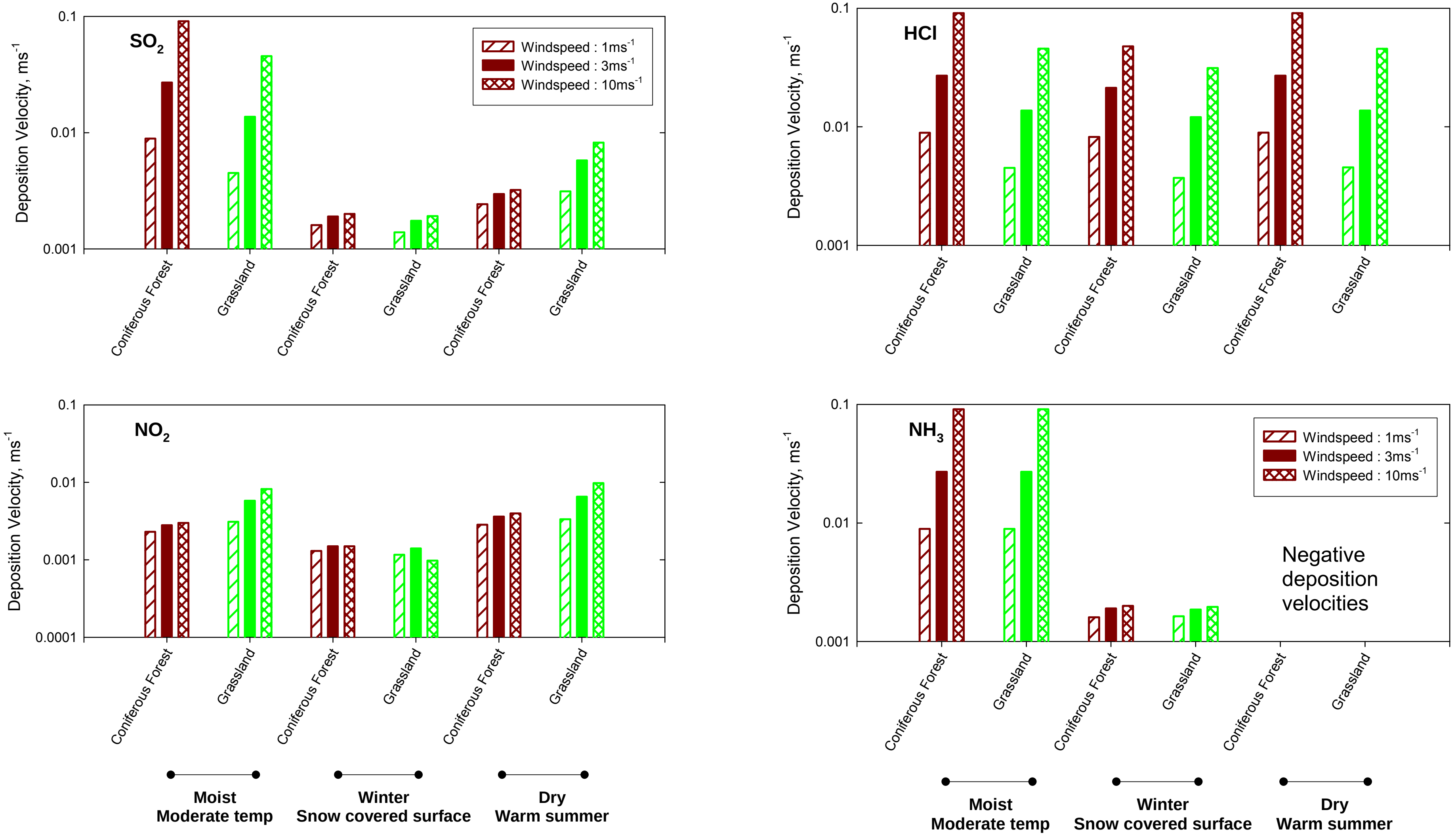


Figure 5. Example calculations of deposition velocities, derived from Tables A1 and A2.

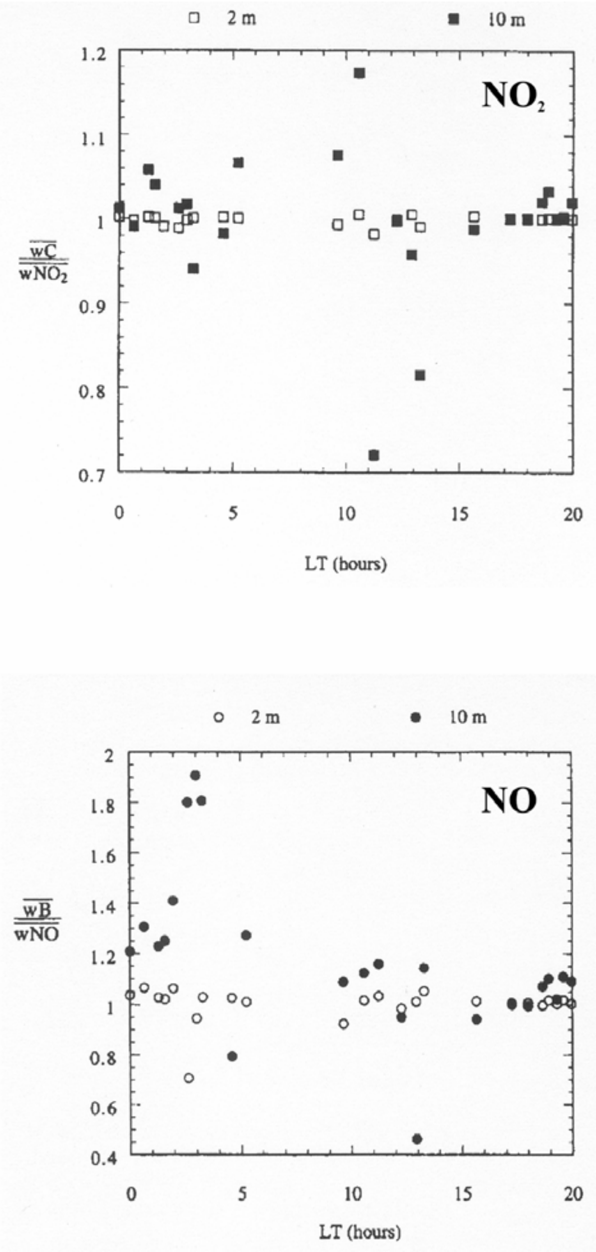


Figure 6. Estimates of normalised fluxes of NO and $NO_2$ over peat grassland using a modified flux gradient method. From Galmarini *et al.* (1997).

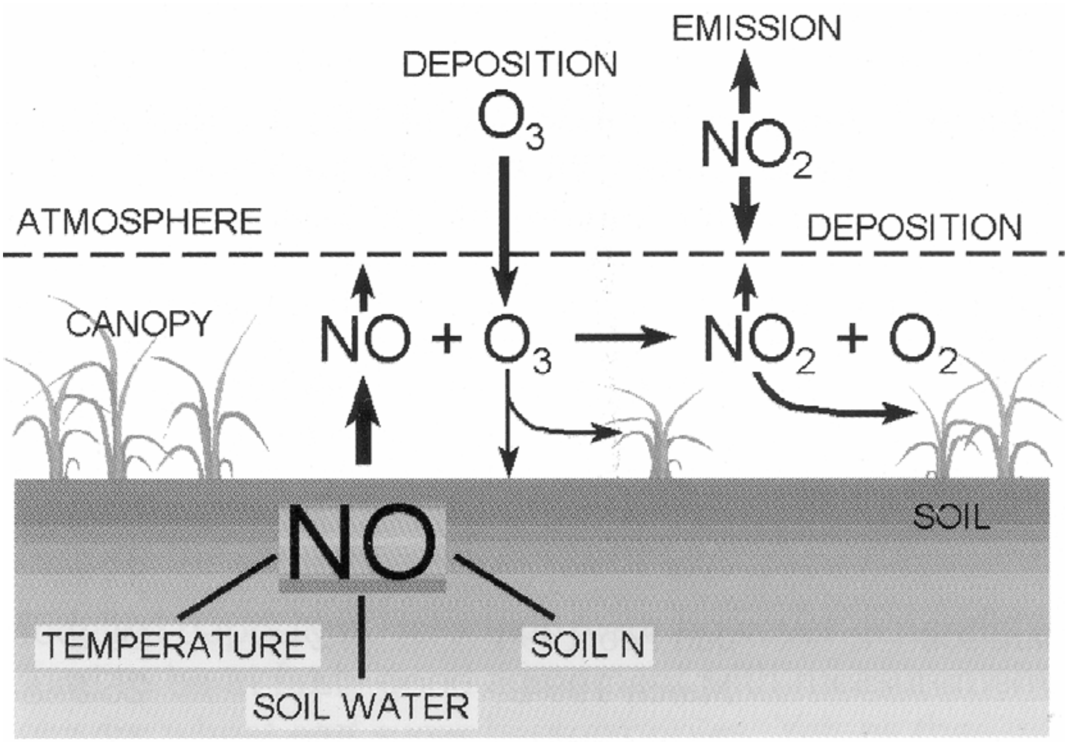


Figure 7. Relationship between NO, $NO_2$ and ozone near the surface. From the Fourth Report of the Review Group on Acid Rain (DETR, 1987a).

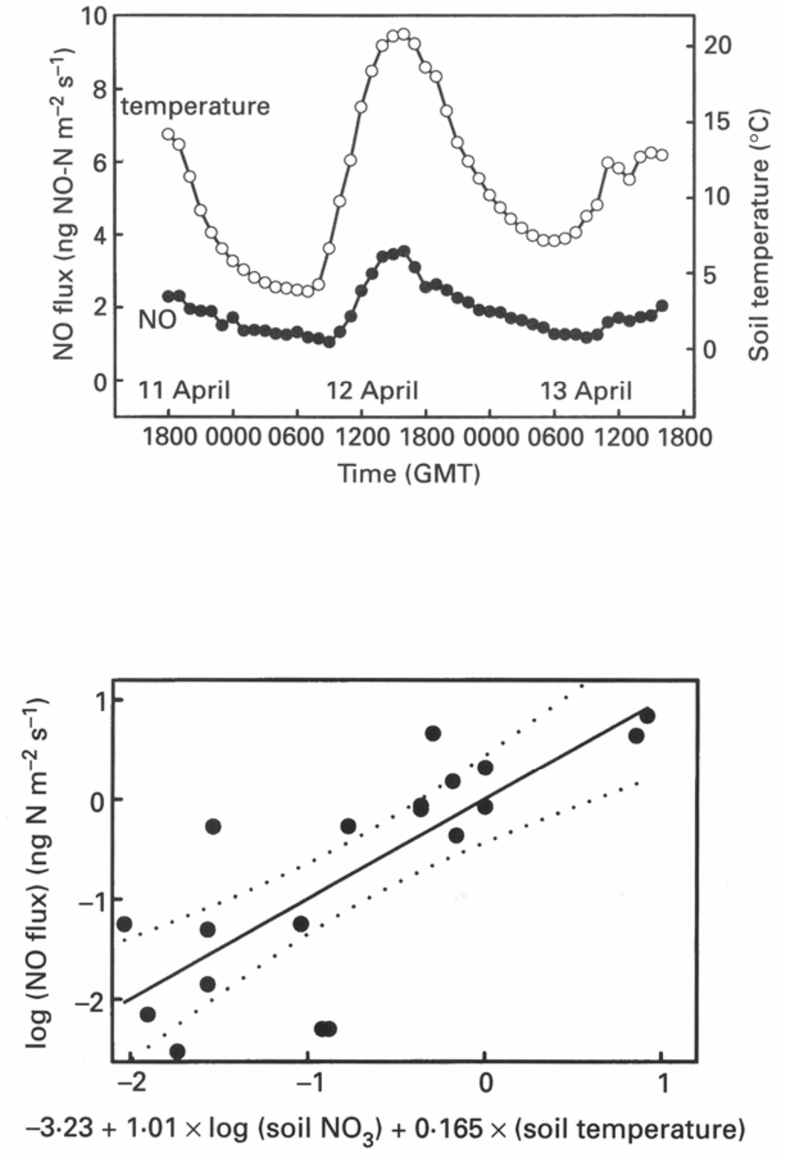


Figure 8. NO emissions from a loam soil by time of day (upper) and from woodland and moorland soils as a function of acidity and temperature (lower). From Fowler *et al.* (1998).

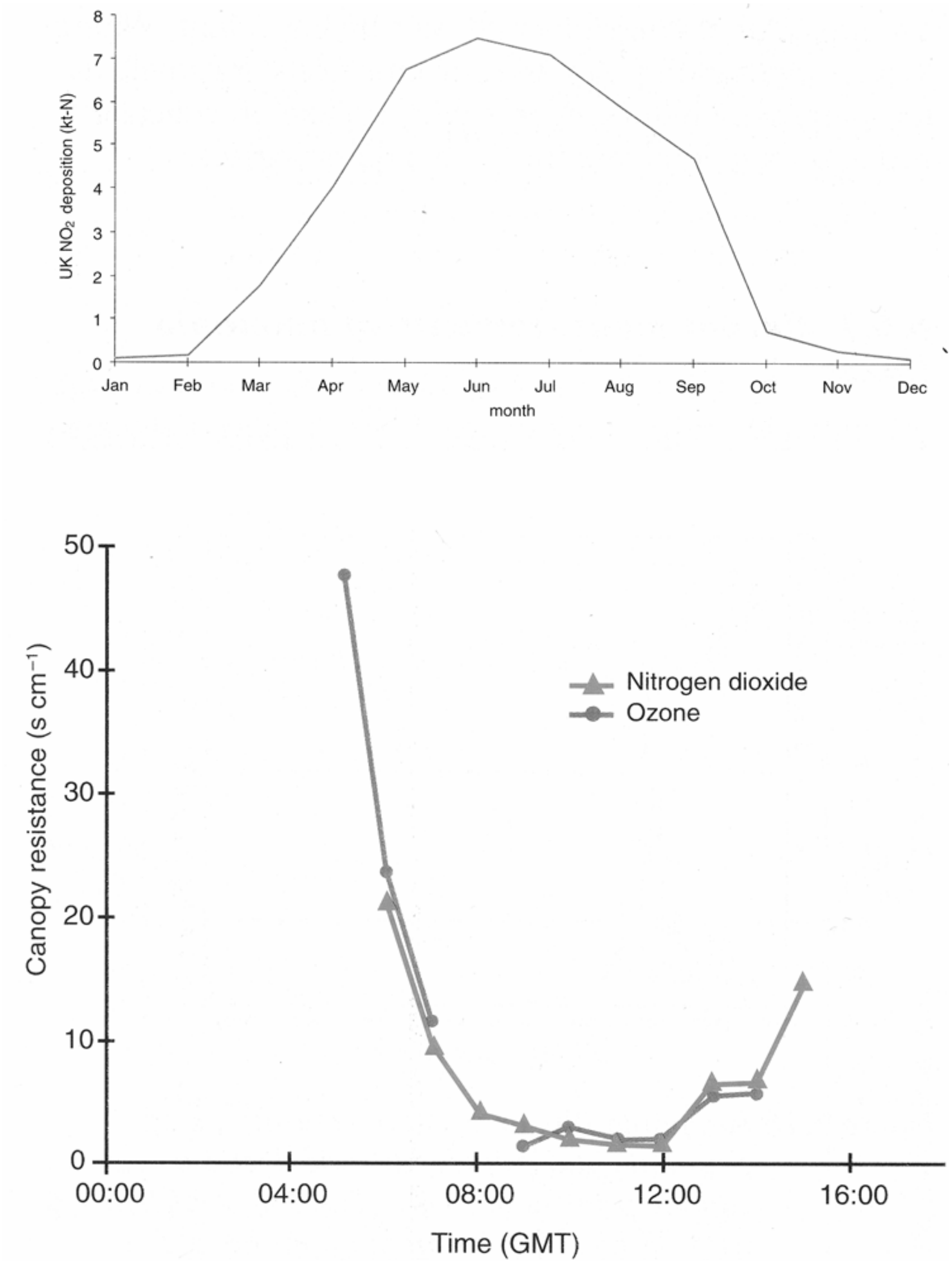


Figure 9. Diurnal and annual variations of dry deposition of $NO_2$. From the Fourth Report of the Review Group on Acid Rain (DETR, 1987a).

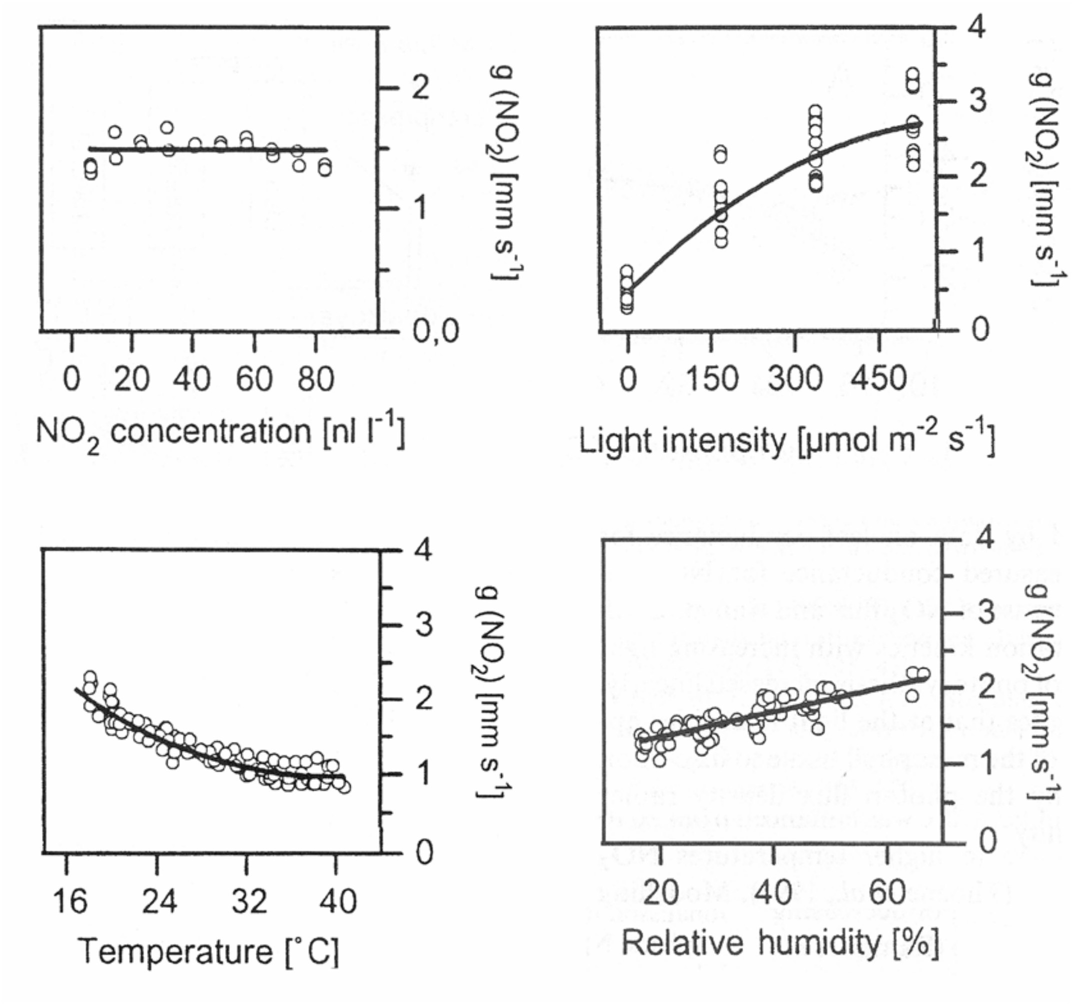


Figure 10. Dependence of measured and predicted surface conductance, g, of $NO_2$ on to wheat leaves as a function of temperature, $NO_2$ concentration, light intensity and relative humidity. From Weber and Rennenberg (1996).

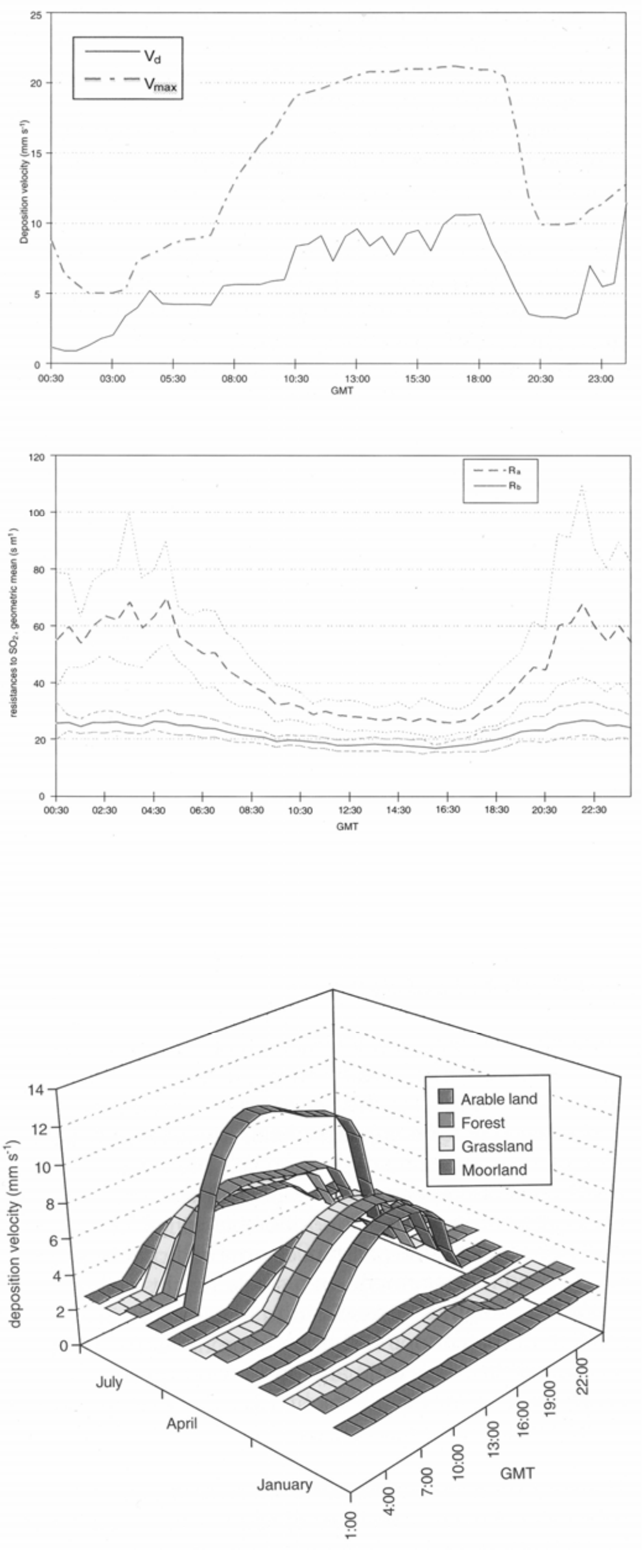


Figure 11. Dry deposition properties of $SO_2$. Upper plot - Measured deposition over a wheat canopy. Middle plot - Aerodynamic resistances ($R_a$ and $R_b$) over a wheat canopy. Lower plot - Modelled values of deposition velocity over different surfaces, obtained using monthly averages from 30-year weather data. From the Fourth Report of the Review Group on Acid Rain (DETR, 1987a).

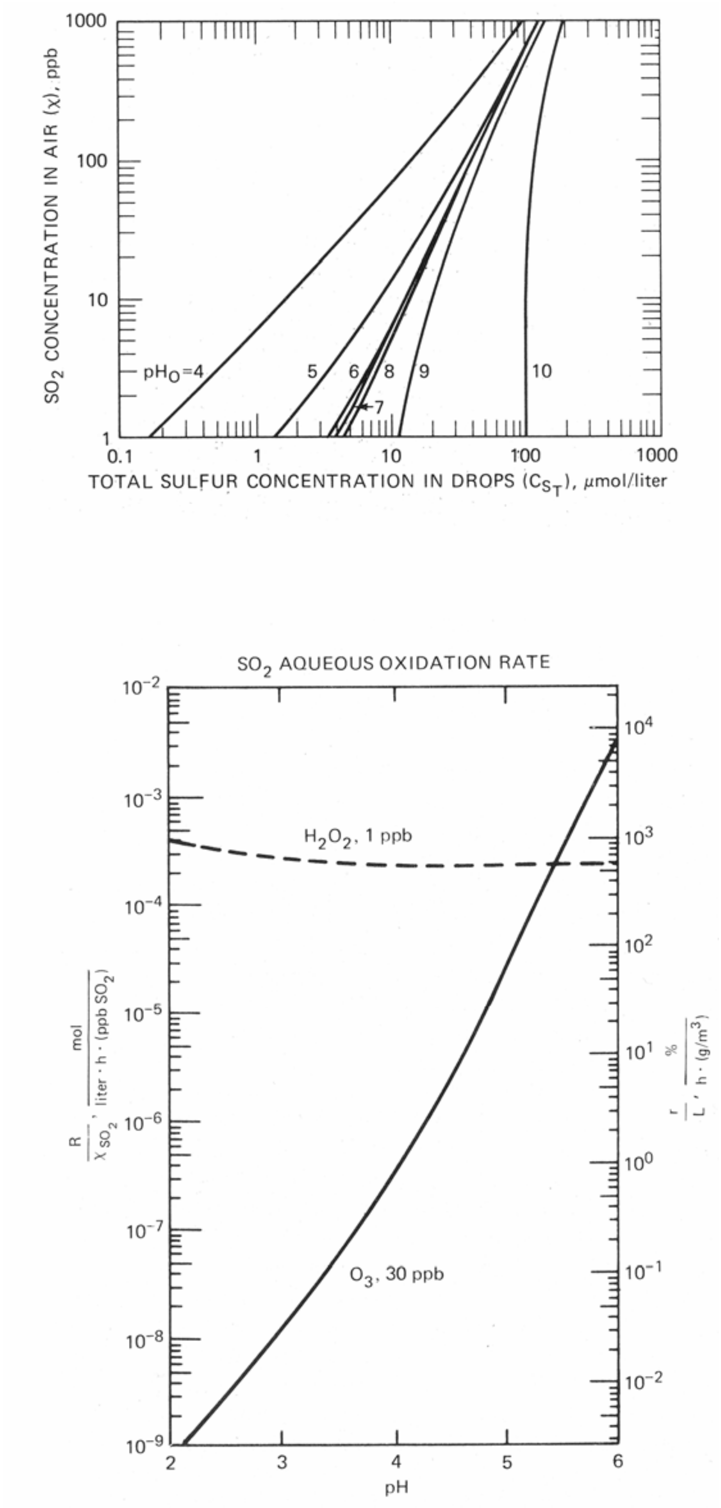


Figure 12. Some characteristics of $SO_2$ in solution in atmospheric droplets. Upper plot - Effect of droplet pH on solubility of $SO_2$. Lower plot - Effect of atmospheric ozone and $H_2O_2$ on $SO_2$ oxidation in solution. From Slinn (1984).

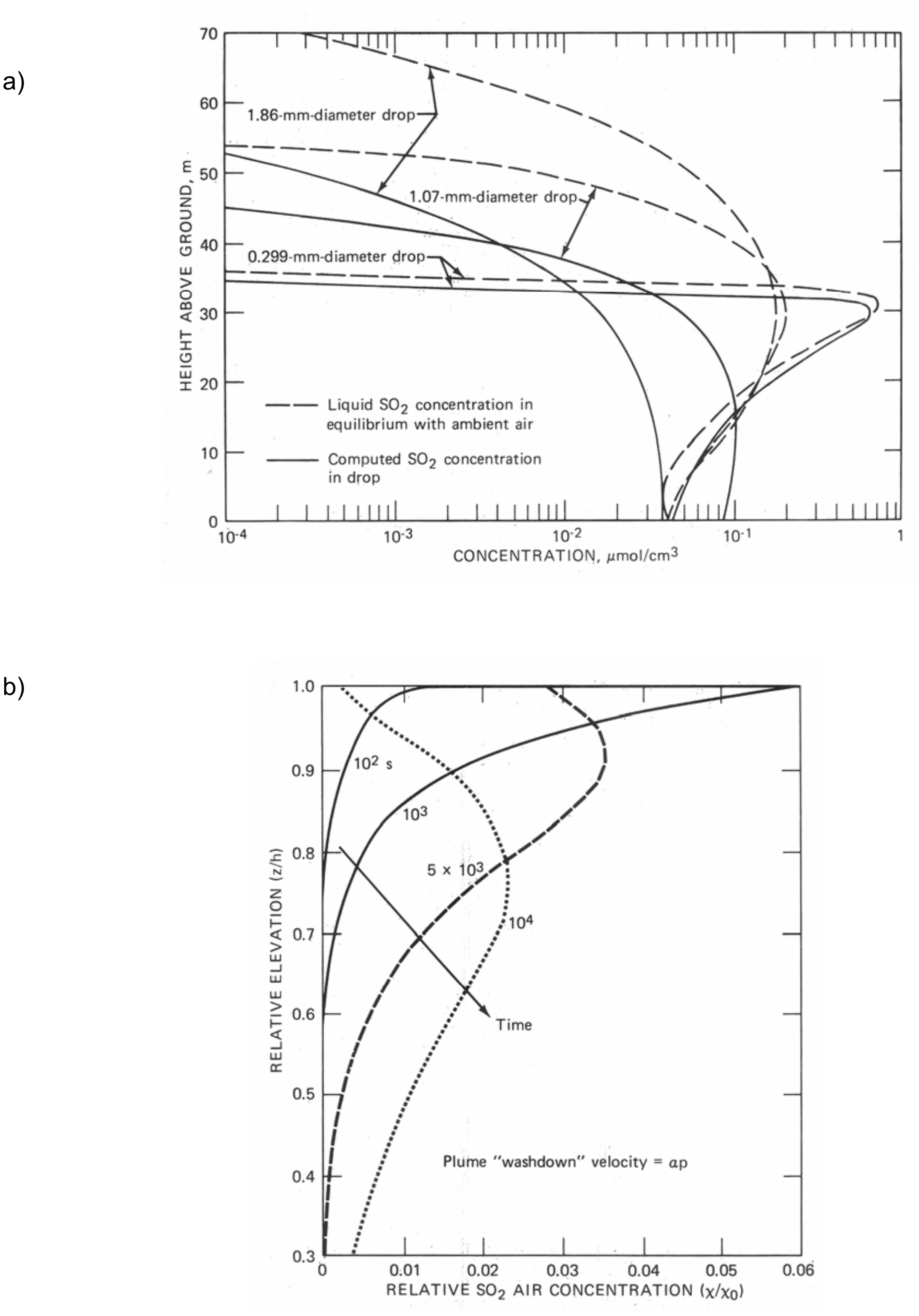


Figure 13a) Concentration of $SO_2$ in raindrops falling through a plume, calculated by Hales.
b) Effect of absorption/desorption of $SO_2$ on plume height, from Slinn (1984), assuming $SO_2$ liquid/vapour equilibrium governs the drop concentration.

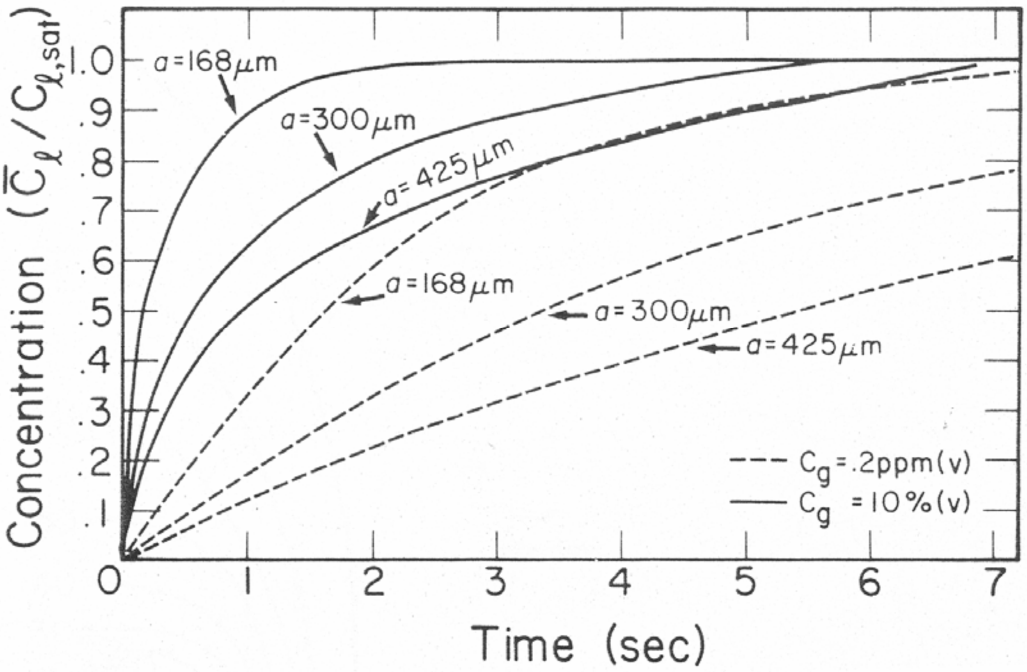


Figure 14. Theoretical estimates of the time history of $SO_2$ concentrations in different droplet sizes at varying ambient concentrations. From Walcek and Pruppacher (1984a).

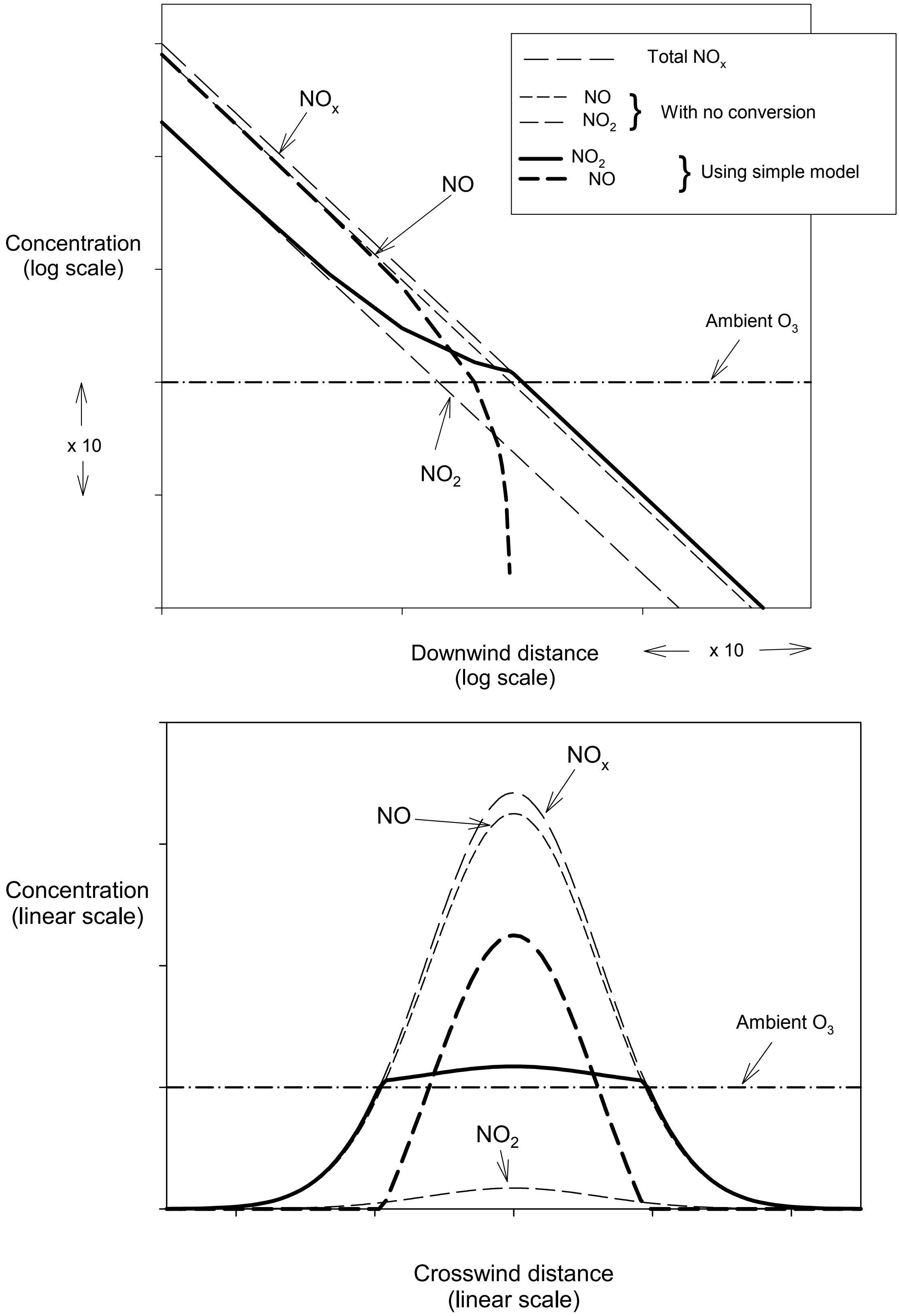
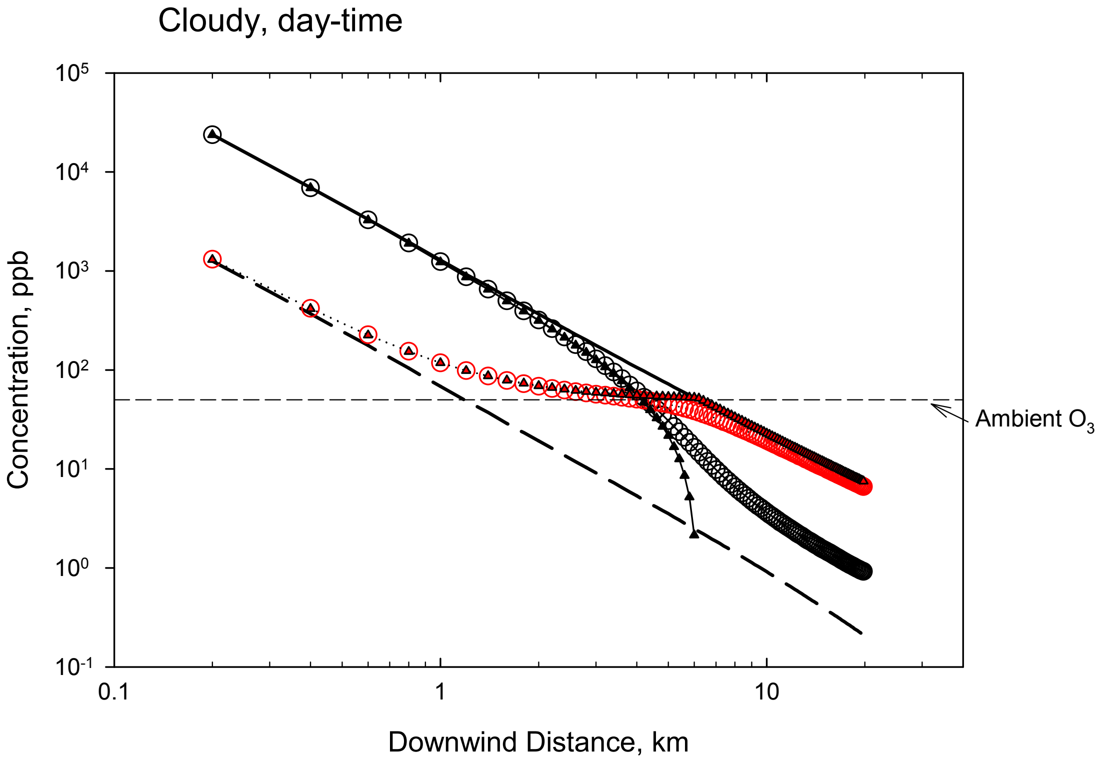


Figure 15. Diagram of the simple model for NO to $NO_2$ conversion in a plume. After Varey *et al*. (1984). Upper plot: along wind. Lower plot: across wind.



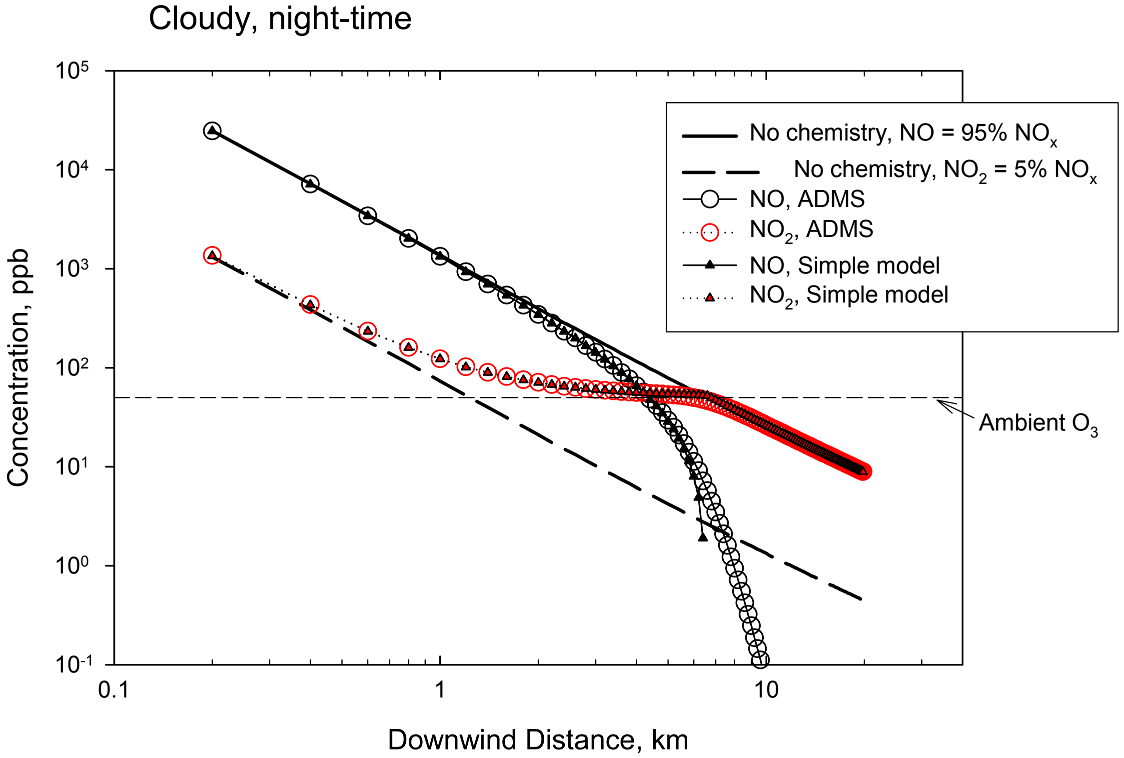
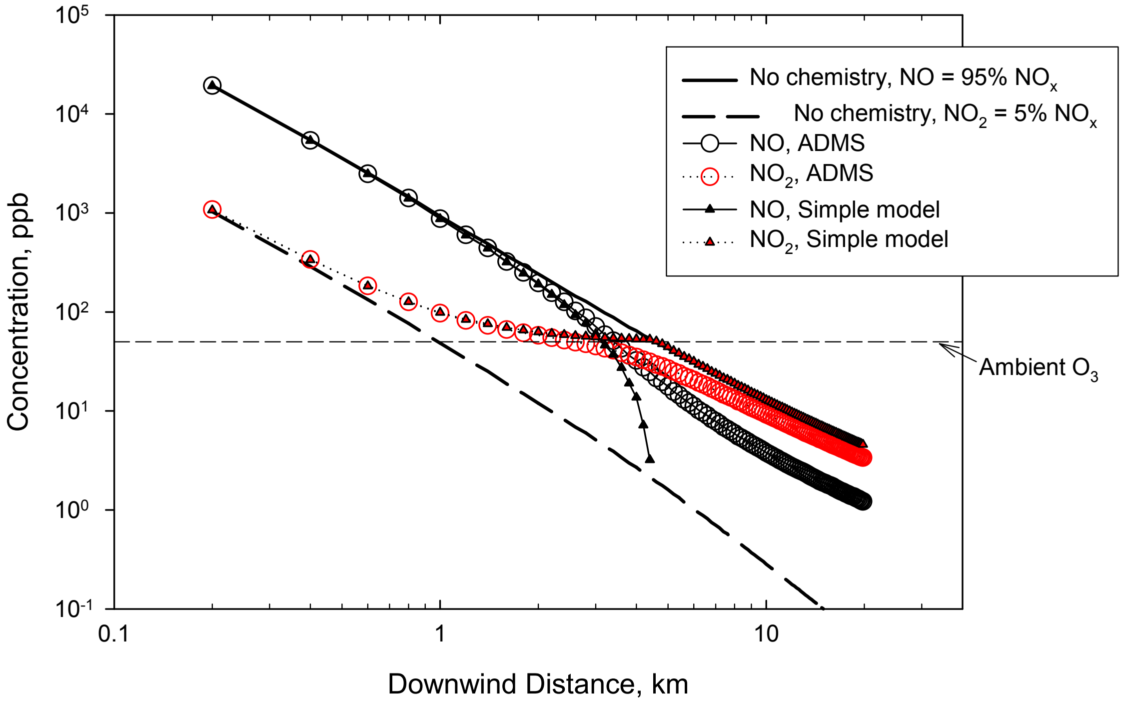


Figure 16. Comparison of ADMS3 chemistry module with simple oxidation model. Low solar radiation.

Clear, day-time



Clear, Summer's day

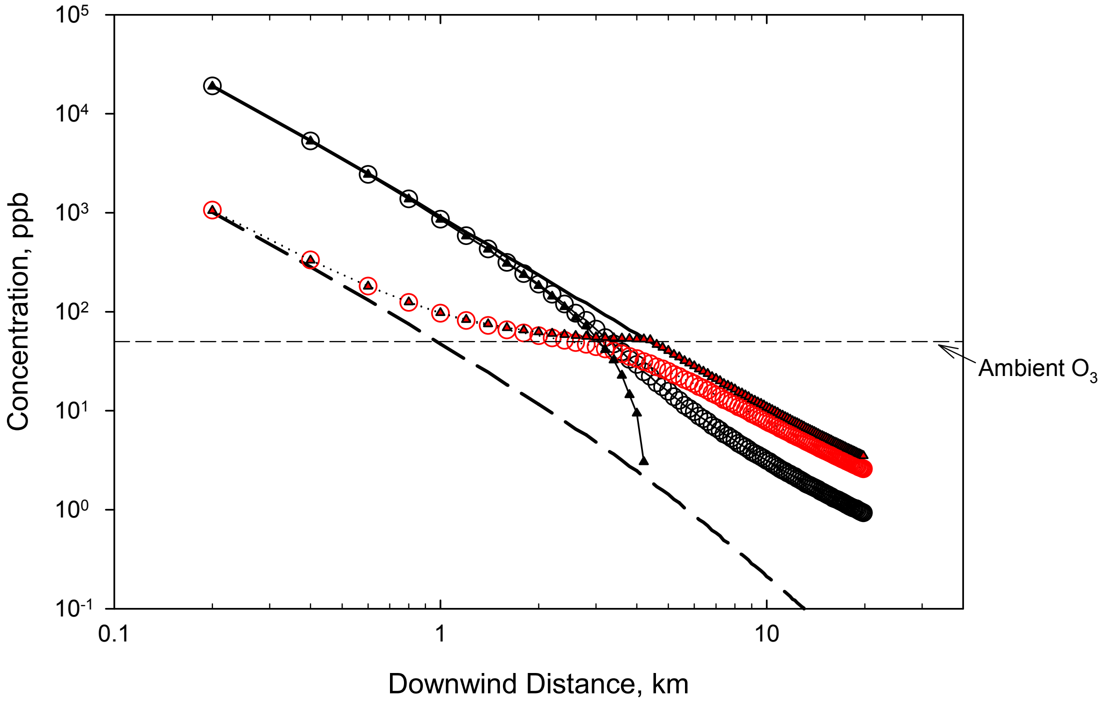


Figure 17. Comparison of ADMS3 chemistry module with simple oxidation model. High solar radiation.

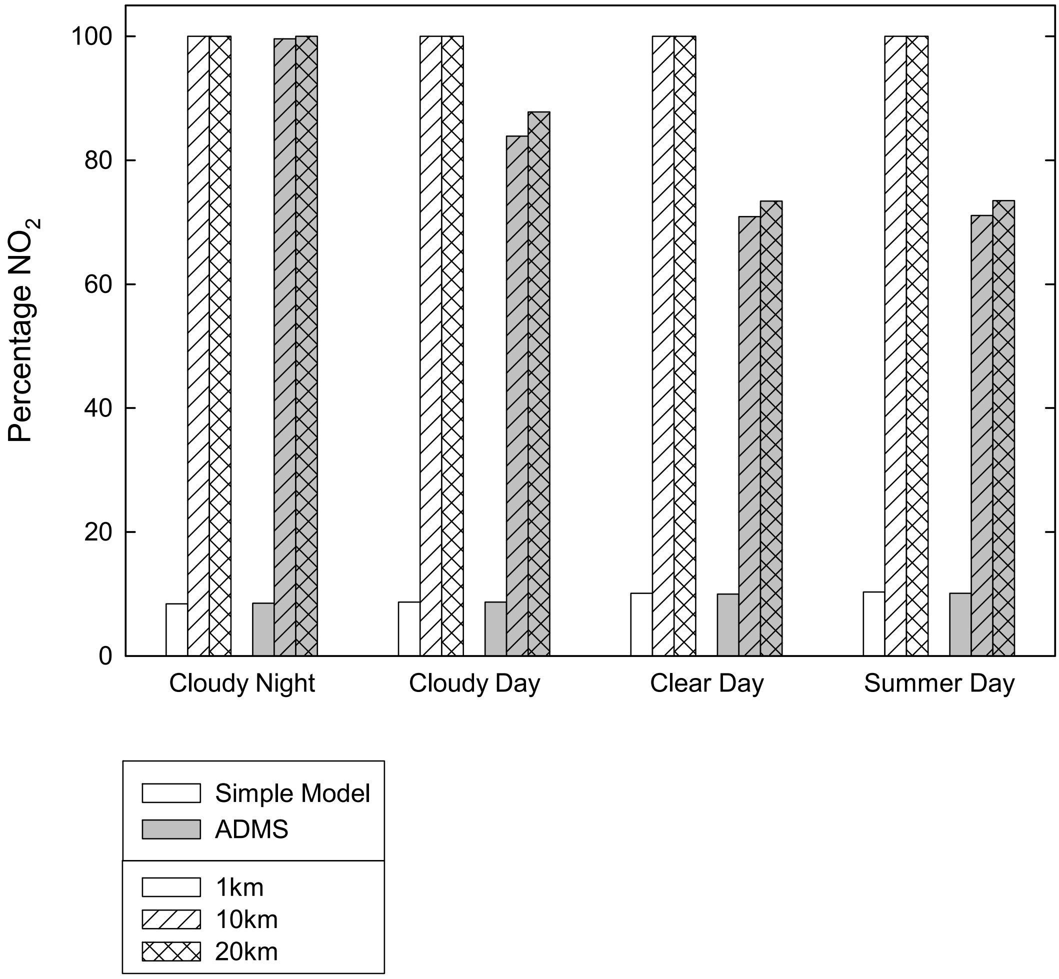


Figure 18. Variation in percentage $NO_2$ calculated by the simple model and ADMS3, for 10 m $s^{-1}$ wind speed and 50 ppb background ozone concentration.

# Appendix A

## Values of gaseous transfer resistances and dry deposition velocities from various sources

This appendix is not intended to be a detailed description of the problems of estimating dry deposition calculations. It provides a brief description of the methods and some sample calculations, which are compared with some experimental estimates of dry deposition velocities and values used in some long-range models. Reviews of the problems of estimating dry deposition can be found in the Fourth Report of the Review Group on Acid Rain (DETR, 1997a) and of the Photochemical Oxidants Review Group (DETR, 1997b), and in Erisman and Draaijers (1995); also more recently by Wesely and Hicks (2000).

Erisman and Draaijers (1995) give a good brief review of the determination of surface resistances. They suggest a formula for the aerodynamic resistance, $R_a$, due to Garland (1978):

$$R_a(z) = \frac{1}{\kappa u_*}\left[\ln\left(\frac{z-d}{z_o}\right) - \Psi_h\left(\frac{z-d}{L_{mo}}\right) + \Psi_h\left(\frac{z}{L_{mo}}\right)\right] \tag{12}$$

where z is height above the ground,
d is the surface displacement height,
$z_o$ is the aerodynamic surface roughness,
$L_{mo}$ is the Monin-Obukhov length scale,
$\kappa$ is Von Karman's constant and
$\Psi_h$ is a function classifying the effects of atmospheric stability on the wind profile.

The right hand side of equation (12) is essentially the usual boundary layer logarithmic velocity profile equation, scaled by $1/u_*$, so that effectively:

$$R_a = \frac{u(z)}{u_*^2} \tag{13}$$

where u(z) is the wind speed at the chosen reference height. Thus $R_a$ is inversely proportional to wind speed (which scales with $u_*$) and reduces with the chosen reference height above the ground and with increasing surface roughness (which increases $u_*$).

Estimates of aerodynamic resistance for iodine vapour and the effects of wind speed (the choice of gas or vapour does not affect the value) taken from Jones (1983) are shown in Figure 4.

Erisman and Draaijers (1995) also suggest an expression for the sublayer resistance, $R_b$, from Hicks *et al*. (1987), of the form:

$$R_b = \frac{2}{\kappa u_*}\left(\frac{S_c}{P_r}\right)^{\frac{2}{3}} \tag{14}$$

where $S_c$ and $P_r$ are the Schmidt and Prandtl numbers, which vary with the gas. It can be seen that $R_b$ is also inversely proportional to wind speed (through its proportionality to $u_*$). Erisman and Draaijers give the following values for $(S_c/P_r)^{2/3}$, which is constant (though temperature dependent) for a given gas, also from Hicks *et al*. (1987):

| | |
|---|---|
| $SO_2$ | 1.44 |
| $NO_2$ | 1.3 |
| $HNO_3$ | 1.44 |
| $O_3$ | 1.3 |
| $H_2O$ | 0.96 |

Thus there will be little variation in $R_b$ between the pollutants of interest. There will, however, be a much greater difference in $R_b$ between gases and particles, as $S_c$ is of the order of unity for gases and proportionately very large for particles (it has a value of around $10^6$ for 1 μm particles). However, there are additional deposition mechanisms for particles which increase the effective deposition velocity.

Taking a value of 1.4 for $(S_c/P_r)^{2/3}$ as representative of the pollutants of interest and using $\kappa = 0.4$, equation (14) approximates to

$$R_b = \frac{7}{u_*} \tag{15}$$

The Meteorological Office NAME model uses both equations (13) and (15), with a factor of 8 for both $SO_2$ and particles in equation (15). No reason is given for this particular choice.

Except for very smooth surfaces, such as water or mud flats, the $u_*$ terms in equations (13) and (14) are not formally the same. The value of $u_*$ in equation (12) is that usually used in meteorology, related to the overall characteristics of the surface roughness as seen by the atmospheric boundary layer. However for other more complex surfaces, such as grass or leaves, the value of $u_*$ in equation (14) should be that related to the thin (possibly laminar) boundary layer and its associated sublayer on these surfaces, which is quite different. One of the difficulties in determining $R_b$ for complex surfaces is in estimating, in effect, this value of $u_*$ in terms of some reference wind speed at higher levels. In order to avoid this problem with complex surfaces such as plants, the overall $u_*$ for the surface (as in equation (12)) can be substituted in equation (14), provided that the value of $R_b$ is suitably modified to account for the different values of $u_*$ in equations (13) and (14), which should be in an approximate constant ratio. It is usually the only practicably measurable value and both values of $u_*$ should be proportional to wind speed. The value of $R_b$ is then an 'apparent' value for the surface.

This was accounted for by Hicks *et al*. (1987) in deriving equation (14), in which the factor of 2 was a correction of this sort, so that $u_*$ in equations (14) and (15) is then the usual meteorological value. The factor of 2 was based not on gaseous transfer measurements, which tended to show anomalous behaviour, but inferred from a general limit value of the sublayer transfer resistance derived from sensible heat and water vapour transfer measurements over vegetation. There must, however, be significant variations in this estimate of $R_b$ both for different types of vegetation and its surface area and on a seasonal basis. The value of $R_b$ defined in this way can only be obtained experimentally. The literature is not always clear on this point and the universal accuracy of equation (15) must be uncertain.

There seems to be no single published source of transfer resistances and the resultant deposition velocities for the gases of interest here, mainly NO, $NO_2$, $SO_2$ and HCl. The major interest has been in $SO_2$ deposition, but there is some surface resistance data for $NO_2$. There is only limited information on HCl (see Harrison *et al*.,1989), but because of its high solubility and reactivity, its surface resistance appears to be zero or nearly so.

The aerodynamic and sublayer resistances remain nominally similar for all gases. Some values calculated from equations (13) and (15) are given in Table A1. As the aerodynamic resistance reduces with the height at which it is calculated, a suitable reference height must be chosen. The literature is usually somewhat vague on this subject, so it has been taken here as $10z_0$, which is close to the top of the surface roughness, below which transfer through the sublayer starts to take over. The stability terms in equation (12) have therefore been ignored, as at the low heights of the calculation the boundary layer always appears nearly neutrally stratified, irrespective of conditions at greater heights. For a transfer height of $10z_0$, equation (13) then becomes simply

$$R_a = \frac{5.76}{u_*} \tag{16}$$

and as

$$R_b = \frac{7}{u_*} \tag{17}$$

the total aerodynamic and sublayer resistances (subject to the caveats over $R_b$) become simply

$$R_a + R_b = \frac{12.76}{u_*} \tag{18}$$

This value of $R_a$ (from equation (16)) is a lower bound of the possible values due to the chosen reference height, but rational in terms of transfer to the ground. For gaseous deposition velocities of the order of 0.01 m $s^1$ from large plumes, plume depletion is quite small (as noted in Section 3) and there will be little effective constraint on the transport of contaminants to the ground from higher up.

Calculated values of $R_a$ + $R_b$ for varying conditions are shown in Table A1. The range is about 60:1, over the range of wind speeds (roughly the 10th percentile to 90th percentile range in the UK at 10 m height) and surface roughness covering most natural surfaces. Similar calculations were published by Voldner (1986) and showed similar results within the range of options for reference velocities and surface roughness.

Values of the surface resistance vary considerably depending on the pollutant gas, whether to plant surfaces (stomatally or otherwise) or to wet or dry ground surfaces. Smith *et al*. (2000), Baldocchi *et al*. (1987) and Erisman and Draaijers (1995) discuss these complexities in some detail. Erisman and Draaijers quote nominal values of daytime surface resistances of various gases in their synopsis of results. Some of the content of their Table 4.7 is reproduced in Tables A2 and A3 for the pollutants of interest here, for grassland and deciduous forest in Table A2 and for some ground surfaces in Table A3. A nominal 'stomatal resistance' is also given, the derivation of which is relatively complex and in practice varies considerably with the gas of interest. Daytime conditions nominally correspond to stomatally active conditions, but in some cases, as in winter conditions in the table, the stomatal activity may be low or zero. Negative values of surface resistance for $NH_3$ imply production at the surface rather than deposition from the atmosphere. Table A2 shows gaseous resistances both above and below the quoted stomatal resistance, depending on the gas and the degree to which the surface deposition is stomatally controlled. The zero surface resistances given for acid gases are for conditions with absorption on to surface water, which then dominates the overall deposition. HCl is so reactive that it also deposits efficiently onto many dry surfaces.

**Table A1 Aerodynamic and sublayer resistances. Calculated from equations (16), (17) and (18).**

| Surface roughness $z_0$ (m) | Typical surface type | Reference wind speed u at 10 m height ($m\ s^{-1}$) | Wind speed u at $10z_0$ height ($m\ s^{-1}$) | u* ($m\ s^{-1}$) | $R_a$* ($s\ m^{-1}$) | $R_b$** ($s\ m^{-1}$) | $R_a+R_b$*** ($s\ m^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | | | | | |
| 0.001 | Water etc. | 1 | 0.25 | 0.043 | 133 | 161 | 294 |
| 0.01 | Short grass | 1 | 0.33 | 0.058 | 100 | 121 | 220 |
| 0.1 | Open country | 1 | 0.50 | 0.087 | 66 | 81 | 147 |
| 0.3 | Rough/forest | 1 | 0.66 | 0.114 | 51 | 61 | 112 |
| | | | | | | | |
| 0.001 | Water etc. | 3 | 0.75 | 0.130 | 44 | 54 | 98 |
| 0.01 | Short grass | 3 | 1.00 | 0.174 | 33 | 40 | 73 |
| 0.1 | Open country | 3 | 1.50 | 0.260 | 22 | 27 | 49 |
| 0.3 | Rough/forest | 3 | 1.97 | 0.342 | 17 | 20 | 37 |
| | | | | | | | |
| 0.001 | Water etc. | 10 | 2.50 | 0.434 | 13 | 16 | 29 |
| 0.01 | Short grass | 10 | 3.33 | 0.579 | 10 | 12 | 22 |
| 0.1 | Open country | 10 | 5.00 | 0.868 | 7 | 8 | 15 |
| 0.3 | Rough/forest | 10 | 6.57 | 1.140 | 5 | 6 | 11 |

* From equation (16). Assumed neutral stability and zero displacement, d.
** From equation (17).
*** From equation (18).

The results in Tables A1 and A2 were used to estimate total transfer resistances and the resultant deposition velocities, which are given in Table A4 for grass and coniferous forest surfaces. The same results are shown plotted as bar charts in Figure 5. Since they are for daytime conditions, they represent an upper bound for gases where stomatal deposition is important. This is most important for $NO_2$, which compared with the other acid gases and $NH_3$ is relatively insoluble and whose surface uptake is considered to be mainly stomatal. The acid gases $SO_2$ and HCl are so soluble and reactive that stomatal uptake tends to be a small (though important) fraction of the total. It is of interest that, for $NO_2$, Table A4 predicts higher deposition velocities for grassland than for forest under some conditions, due to the proportionately higher values of $R_a+R_b$ and lower values of $R_s$ over grassland. This is contrary to many models and some measurements, which indicate higher deposition velocities over forest.

Table A4 is representative of the effects of the relevant variables on deposition velocity rather than precise estimates. However it does show the salient features and it is clear that the conventional short-range approximation of a constant deposition velocity is a poor approximation to reality. It is also clear that the effects of wind speed on deposition cannot be ignored without evidence that its practical effects are small. Though Jones (1983) notes its importance and Smith *et al*. (2000) remark on the lack of wind speed data associated with dry deposition measurements, it is not usually accounted for in short-range deposition calculations and the effects are little referred to in longer range calculations. This is to some extent due to difficulties in determining local wind speeds in some calculations, especially in long-range hazard assessments (such as the Chernobyl release). However in typical short-range calculations wind speeds are relatively accurately known on an hourly basis, so could be readily accounted for.

# Other estimates of deposition velocities

Comparison can be made between Table A3, experimental data and currently used deposition velocities in some models. There are generally no comprehensive sets of experimental data or formally published values of the transfer resistances that are generally accepted for modelling purposes. However, published values and those used in various models tend to be broadly similar (though the variations in many chosen values easily exceed a factor of two). Because of the difficulties in making such measurements, experimental data are usually associated with high levels of uncertainty. Almost universally, data on wind speeds during experiments are not provided in detail. The greatest interest has been in deposition of $SO_2$, though some experimental data on $NO_2$ deposition are available. There have been comprehensive reviews of deposition data by Sehmel (1984) and by Voldner (1986), and also by Smith *et al*. (2000) who describe the characteristics of surface transfer mechanisms fairly comprehensively. Erisman and Draaijers (1995) summary data of surface resistances, reproduced in Tables A2 and A3, represent a good summary of typical values. A few comparisons are given below. Most of the interest has been in long-range modelling and, as before, the effects of wind speed on deposition velocity are generally not accounted for.

**Table A2 Surface resistances (in s $m^{-1}$) over vegetation for different gases during daytime under different pollution climates. From Erisman and Draaijers (1995).**

| Gas | Moist<br>(rain or RH > 90%)<br>moderate temperature | | Winter, snow-covered surface | | Dry, warm summer | |
|---|---|---|---|---|---|---|
| | Coniferous forest | Grassland | Coniferous forest | Grassland | Coniferous forest | Grassland |
| Stomatal resistance | 200 | 60 | 400 | - | 150 | 50 |
| $SO_2$ | 0 | 0 | 500 | 500 | 300 | 100 |
| $NO_2$ | 320 | 100 | 640 | 1000 | 240 | 80 |
| HCl | 0 | 0 | 10 | 50 | 0 | 0 |
| $HNO_2$ | 0 | 0 | 500 | 500 | 300 | 100 |
| $HNO_3$ | 0 | 0 | 10 | 50 | 0 | 0 |
| $NH_3$ | 0 | 0 | 500 | 500 | -500 | -500 |
| $O_3$ | 320 | 100 | 640 | 1000 | 240 | 80 |

**Table A3 Surface resistances (in s $m^{-1}$) of soil and water for different gases. From Erisman and Draaijers (1995).**

| Gas | Surface | | | | | |
|---|---|---|---|---|---|---|
| | Dry soil | Wet soil | Water | For pH | Snow-covered | At temperature (°C) |
| $SO_2$/$HNO_2$ | 1000 | 0 | 0 | >4 | 70 | 1<T<-1 |
| | 5-400* | 500 | 500 | <4 | 500 | T<-1 |
| $NH_3$ | -500 | 250 | 500 | >8 | 70 | 1<T<-1 |
| | 50 | 0 | 0 | <8 | 500 | T<-1 |
| NO | -1000 | -1000 | 2000 | - | 2000 | - |
| $NO_2$ | 1000 | 2000 | 2000 | - | 2000 | - |
| $HNO_3$/HCl | 0 | 0 | 0 | >2 | 0 | T>-5 |
| | | | | | 100 | T<-5 |
| $O_3$ | 100 | 500 | 2000 | - | 2000 | - |

* Variable with relative humidity. Typically 5 at 100%, 80 at 90%, 100 at 80%, 200 at 70%, 400 at 60%, 800 at 50%

**Table A4 Deposition velocities (m $s^{-1}$) derived from Tables A1 and A2. For daytime.**

| Gas | Wind speed (m $s^{-1}$ at 10 m height) | Moist (rain or RH > 90%) moderate temperature | | | | Winter, snow-covered surface | | | | Dry, warm summer | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Coniferous forest | | Grassland | | Coniferous forest | | Grassland | | Coniferous forest | | Grassland | |
| | | $R_{total}$ | $v_d$ | $R_{total}$ | $v_d$ | $R_{total}$ | $v_d$ | $R_{total}$ | $v_d$ | $R_{total}$ | $v_d$ | $R_{total}$ | $v_d$ |
| $SO_2$ | 1 | 112 | 0.0089 | 220 | 0.0045 | 612 | 0.0016 | 720 | 0.0014 | 412 | 0.0024 | 320 | 0.0031 |
| | 3 | 37 | 0.0270 | 73 | 0.0137 | 537 | 0.0019 | 573 | 0.0017 | 337 | 0.0030 | 173 | 0.0058 |
| | 10 | 11 | 0.0909 | 22 | 0.0455 | 511 | 0.0020 | 522 | 0.0019 | 311 | 0.0032 | 122 | 0.0082 |
| $NO_2$ | 1 | 432 | 0.0023 | 320 | 0.0031 | 752 | 0.0013 | 860 | 0.0012 | 352 | 0.0028 | 300 | 0.0033 |
| | 3 | 357 | 0.0028 | 173 | 0.0058 | 677 | 0.0015 | 713 | 0.0014 | 277 | 0.0036 | 153 | 0.0065 |
| | 10 | 331 | 0.0030 | 122 | 0.0082 | 651 | 0.0015 | 1022 | 0.0010 | 251 | 0.0040 | 102 | 0.0098 |
| HCl | 1 | 112 | 0.0089 | 220 | 0.0045 | 122 | 0.0082 | 270 | 0.0037 | 112 | 0.0089 | 220 | 0.0045 |
| | 3 | 37 | 0.0270 | 73 | 0.0137 | 47 | 0.0213 | 83 | 0.0120 | 37 | 0.0270 | 73 | 0.0137 |
| | 10 | 11 | 0.0909 | 22 | 0.0455 | 21 | 0.0476 | 32 | 0.0313 | 11 | 0.0909 | 22 | 0.0455 |
| $NH_3$ | 1 | 112 | 0.0089 | 112 | 0.0089 | 612 | 0.0016 | 612 | 0.0016 | -388 | -0.0026 | -388 | -0.0026 |
| | 3 | 37 | 0.0270 | 37 | 0.0270 | 537 | 0.0019 | 537 | 0.0019 | -463 | -0.0022 | -463 | -0.0022 |
| | 10 | 11 | 0.0909 | 11 | 0.0909 | 511 | 0.0020 | 511 | 0.0020 | -489 | -0.0020 | -489 | -0.0020 |

## Estimates of deposition velocities for $SO_2$

Hicks *et al*. (1989) quote surface resistances and deposition velocities for $SO_2$ over a crop during summer days. The averaged values from about twenty scattered measurements were:

| | | |
|---|---|---|
| $R_a$ | 50 s $m^{-1}$ | (20) |
| $R_b$ | 28 s $m^{-1}$ | (11) |
| $R_s$ | 70 s $m^{-1}$ | (52) |
| $v_d$ | 0.0068 m $s^{-1}$ | |

Values in parentheses are the standard deviations of individual measurements, showing that the variability of the data was high. No wind speeds were quoted for the data, but should have been effectively subsumed into the values of $R_a$ and $R_b$. Some of this variability is not due to experimental error, but to natural variations in the behaviour of the wind and of the surface. The values are generally consistent with Tables A1, A2 and A4. This result is typical of field experiments of this sort and indicates the difficulty of obtaining good measurements.

Some values of $v_d$ for $SO_2$ from a variety of sources are given in Table A5. Table A6, taken from Sorteborg and Hov (1996), shows the importance of the surface condition, especially the presence of surface water, to the deposition velocity.

## Estimates of deposition velocities for $NO_2$

There are generally fewer measurements of $NO_x$ deposition than for $SO_2$. Besides Erisman and Draaijers (1995) summary values, some values from other sources are given in Table A7. Erisman and Draaijers note a calculation by Lee and Schwartz (1981) which estimates that "*due to the low solubility of $NO_2$ in water and the rate of subsequent reactions, deposition velocities of $NO_2$ cannot exceed about 0.001 m $s^{-1}$*". A number of the values in Table A7 are well in excess of this, partly due to additional stomatal adsorption.

### Table A5 Some estimates of $v_d$ for $SO_2$ from various sources

| Source | Surface/conditions | $v_d$ (m $s^{-1}$) |
|---|---|---|
| Erisman and Draaijers (1995) | Averaged overall | 0.002-0.02 |
| | Daytime | 0.008-.012 |
| | Water | >0.02 |
| | Bare soil/snow | <0.0013 |
| | Forest | 0.0025-0.006 |
| Fowler and Smith (1991) | Forest (diurnal range) | 0.0025-0.006 |
| HARM model (Metcalfe, 2001) | Grassland/arable | 0.009 |
| | Heathland | 0.008 |
| | Coniferous woodland | 0.007 |
| | Deciduous woodland | 0.006 |
| | Water | 0.004 |
| | Sea water | 0.005 |
| | Urban | 0.001 |
| *FRAME model (Smith *et al*., 2000) | Low vegetation -average | 0.0054 |
| | Low vegetation - winter | 0.0051-0.0055 |
| | Low vegetation - summer | 0.0052-0.0066 |
| | Forest (average) | 0.007 |
| | Forest - winter | 0.0069-0.0072 |
| | Forest - summer | 0.0059-0.0083 |
| | Moorland (average) | 0.006 |
| From ITE Annual Report (1991)<br>(Approximate, derived from Figure 11) | Arable - summer day | 0.01 |
| | Arable - summer night | 0.0035 |
| | Arable - winter day | 0.0035 |
| | Arable - winter night | 0.0035 |
| | Forest - summer day | 0.005 |
| | Forest - summer night | 0.0035 |
| | Forest - winter day | 0.0045 |
| | Forest - winter night | 0.004 |
| | Grassland - summer day | 0.004 |
| | Grassland - summer night | 0.003 |
| | Grassland - winter day | 0.0035 |
| | Grassland - winter night | 0.003 |
| | Moorland - summer day | 0.004 |
| | Moorland - summer night | 0.003 |
| | Moorland - winter day | 0.0035 |
| | Moorland - winter night | 0.003 |

*From model calculations

**Table A6 Estimates of dry deposition velocities of $SO_2$ (m $s^{-1}$), from Sorteborg and Hov (1996). Daytime conditions and winter temperatures above 1°C.**

| Surface | No precipitation | | | | During precipitation | |
|---|---|---|---|---|---|---|
| | Clear | | Overcast | | | |
| | Summer | Winter | Summer | Winter | Summer | Winter |
| Crop and grass | 0.011 | 0.003 | 0.009 | 0.003 | 0.018 | 0.009 |
| Conifer | 0.008 | 0.003 | 0.007 | 0.003 | 0.028 | 0.028 |
| Deciduous | 0.008 | 0.003 | 0.007 | 0.003 | 0.014 | 0.014 |
| Moorland | 0.005 | 0.003 | 0.004 | 0.003 | 0.011 | 0.009 |
| Desert | 0.002 | 0.002 | 0.002 | 0.002 | 0.005 | 0.005 |
| Water | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 | 0.006 |
| Ice | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 | 0.001 |

**Table A7 Estimates of $v_d$ for $NO_2$ from various sources**

| Source | Surface/conditions | $v_d$ (m $s^{-1}$) |
|---|---|---|
| Quoted by Erisman and Draaijers(1995) | Water/sea water | 0.0001-0.0002 |
| | Snow | <0.003 |
| | Deciduous forest (daytime) | 0.001-0.028 |
| Fowler and Smith (1991) | Forest (diurnal range) | |
| Neubert *et al.* (1993) (Chamber experiments) | Sunflower (light) | 0.0015 |
| | Sunflower (dark) | 0.0009 |
| | Tobacco (light) | 0.0017 |
| | Tobacco (dark) | 0.0005 |
| HARM model (Metcalfe, 2001) | Grassland/arable | 0.0011 |
| | Heathland | 0.001 |
| | Coniferous woodland | 0.001 |
| | Deciduous woodland | 0.004 |
| | Water | 0.00005 |
| | Sea water | 0.00005 |
| | Urban | 0.0006 |
| *FRAME model (Smith *et al.*, 2000) | Low vegetation -average | 0.0009 |
| | Low vegetation - winter | 0.0005 |
| | Low vegetation - summer | 0.0051 |
| | Forest (average) | 0.0012 |
| | Forest - winter | 0.0009 |
| | Forest - summer | 0.005 |
| | Moorland (average) | 0.0008 |

*From model calculations

# Appendix B

## The ADMS plume chemistry calculation for pH limiting of $SO_2$ in raindrops

This is noted briefly in Section 3, and is described in more detail below. The main description of the model is in Singles (2000). It appears to be quite similar to the model proposed by Walcek *et al.* (1984b). The model deals solely with the $SO_2$ solution equilibrium, including pH-limited absorption, and some effects of $CO_2$. It does not account for any other species in solution, $O_3$, $H_2O_2$ or HCl in the case of coal combustion.

Wet deposition in ADMS3 uses a washout coefficient, $\Lambda$, such that the mass of pollutant incorporated into the rainfall is

$$\Lambda C \tag{19}$$

per unit volume per unit time, where C is the local airborne concentration. $\Lambda$ can be input directly by the user or can take the form

$$\Lambda = AP^B \tag{20}$$

where P is the rate of rainfall and A and B are constants for a specific gas. The default values are $A = 1.0 \times 10^{-4}$ and $B = 0.64$.

In ADMS3, the uptake of acidic pollutants into the raindrop is limited by the pH of the raindrop. The scheme is applied only to $SO_2$ and $CO_2$. It is modelled by considering the aqueous concentration of pollutant in the rain that has passed through the plume without any limiting effect of pH, $M_1$, and comparing this to the amount, $M_2$, including the limiting effect. If $M_2 < M_1$, then the washout coefficient in equation (19) is replaced by $\Lambda M_2/M_1$. $M_1$ is calculated as a plume-averaged value, whereas $M_2$ is calculated for the plume centreline concentration. The limiting effect is applied near to the source; if $M_2 > M_1$ at a distance from the source, then $\Lambda$ is not pH-limited downwind from that point.

The aqueous concentration, $M_1$, in the raindrop is calculated from

$$M_1 = \frac{Q(x)\Lambda}{MW_{SO_2}\left(P / 3.6 \times 10^6\right)U\sqrt{2\pi}\sigma_y} \times 10^{-3} \tag{21}$$

where

$Q(x) =$ total mass flux of source material (g $s^{-1}$) in the plume at a downwind distance, x,

$P =$ precipitation rate in mm $h^{-1}$,

$MW_{SO_2} =$ molar mass of pollutant ($SO_2$) in g $mole^{-1}$,

$U =$ windspeed (m $s^{-1}$),

$\sqrt{2\pi}\sigma_y =$ lateral plume scale (m) and

the constants, $(3.6 \times 10^6)$ and $(10^{-3})$, are used to convert mm $h^{-1}$ to m $s^{-1}$ and moles $m^{-3}$ to moles $l^{-1}$ respectively.

The pH-limited aqueous concentration, $M_2$, is calculated by an iterative procedure starting with an initial pH of 5.6 to account for absorption of $CO_2$ by the raindrop. From this an initial concentration of hydrogen ions, $[H^+]$ can be calculated ($= 10^{(-pH)}$) and then the effective solubility of $SO_2$, $K_{SO2}$, (mole $l^{-1}$ atm$^{-1}$) is given by

$$K_{SO_2} = K_1\left\{1 + \frac{K_3}{\left[H^+\right]}\right\} \qquad (22)$$

where $K_1$ (moles $l^{-1}$ atm$^{-1}$) and $K_3$ (moles $l^{-1}$) are the reaction constants for the following reactions, taken from the ADMS documentation (Apsley *et al.*, 2000) and originally given by Bower *et al.* (1991):

$$SO_{2(g)} + H_2O \leftrightarrow SO_2 \cdot H_2O; \quad K_1 = 1.23 \times 10^0 \exp(3120T') \qquad (23)$$

and

$$SO_2 \cdot H_2O \leftrightarrow H^+ + HSO_3; \quad K_3 = 1.70 \times 10^{-2} \exp(2090T') \qquad (24)$$

where $\quad T' = \left(1/T - 1/298\right)$

Then the partial pressure of the pollutant, $p_{SO2}$, is given by

$$\frac{p_{SO_2}}{p_{cl}} = \frac{N_{SO_2}}{\left(\dfrac{L_w K_{SO2} p_{cl} \cdot 1000}{\rho_w \cdot 1.01325 \times 10^5} + \dfrac{p_{cl}}{RT_{cl}}\right)} \qquad (25)$$

where

$p_{cl} =$ the atmospheric pressure on the centreline (Pascals),

$N_{SO_2} =$ total number of moles of $SO_2$ in $1m^3$ of atmosphere,

$L_w =$ the liquid water content of raindrops in the atmosphere (kg m$^{-3}$),

$$= \frac{\rho_w \left(P/3.6 \times 10^6\right)}{w_t},$$

$\rho_w =$ density of water, 1025kg m$^{-3}$,

$w_t =$ terminal velocity of droplet (m/s),

$R =$ molar gas constant, 8.3143kJ/(kmole K),

$T_{cl} =$ the temperature on the plume centreline (K)

and the constants 1000 and 1.01325 x $10^5$ are the conversion factors from $m^3$ to litres and atmospheres to Pascals respectively.

From the electroneutrality equation, the concentration of hydrogen ions is given by

$$\left[H^+\right] = \sqrt{\left(K_w + K_1 K_3 p_{SO2}\right)} \qquad (26)$$

where $K_w$ is the equilibrium constant for water ( $= 1.0\times10^{-14}\exp(-716T')$ ) and equations (22) to (26) are solved by iteration.

The pH-limited aqueous concentration, $M_2$, is then given by

$$M_2 = K_{SO2} p_{SO2} \tag{27}$$

For a rainfall rate of 2 mm $h^{-1}$ and a raindrop of 2 mm diameter with a terminal velocity of 6 m $s^{-1}$ (as given by Slinn (1984), see Section 6.5), if a plume centreline concentration of 200 $\mu$g $m^{-3}$ at a temperature of 15°C is assumed, then the limiting pH becomes 1.8.

# Notation

| | |
|---|---|
| $A$ | Constant in equation (4). |
| $B$ | Constant in equation (4). |
| $c$ | Concentration in equations (8) and (9). |
| $C$ | Ambient pollutant concentration. |
| $C_{aq}$ | Pollutant concentration in aqueous solution and in vapour equilibrium in raindrop, in equations (6) and (7). |
| $d$ | Surface displacement in boundary layer wind profile, equation (12). |
| $D_d$ | Rate of dry deposition. |
| $D_w$ | Rate of wet deposition. |
| $H_b$ | Depth of atmospheric boundary layer. |
| $H$ | Henry's law coefficient. |
| $k$ | Reaction rate constant for NO conversion in equation (9). |
| $L$ | Length scale. |
| $L_{mo}$ | Monin-Obukhov length scale. |
| $p_v$ | Partial pressure of dissolved gas. |
| $P$ | Rate of rainfall. |
| $P_r$ | Prandtl number. |
| $R_a$ | Aerodynamic transfer resistance. |
| $R_b$ | Sublayer transfer resistance. |
| $R_c$ | Surface transfer resistance (see page 13). |
| $R_s$ | Stomatal resistance. |
| $R_{soil}$ | Surface resistance of soil. |
| $R_w$ | Leaf surface resistance. |
| $S_c$ | Schmidt number. |
| $u$ | Wind speed. |
| $u_*$ | Friction velocity. |
| $v_d$ | Dry deposition velocity of gases or particles. |
| $v_s$ | Gravitational settling velocity of particles. |
| $z_0$ | Aerodynamic surface roughness length. |
| $\kappa$ | Von Karman's constant, taken here as 0.4. |
| $\Lambda$ | Washout coefficient. |
| $\Psi$ | Atmospheric stability function in equation (12). |

We are The Environment Agency. It's our job to look after your environment and make it **a better place** – for you, and for future generations.

Your environment is the air you breathe, the water you drink and the ground you walk on. Working with business, Government and society as a whole, we are making your environment cleaner and healthier.

The Environment Agency. Out there, making your environment a better place.

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