On the nitrogen budget for the United Kingdom and north-west Europe

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SUMMARY

The application of a simple trajectory model approach to the emission, transformation and deposition of a coupled series of atmospheric pollutants including SO₂, NO₂ and ammonia is described. A detailed comparison of the model results with observations is provided using United Kingdom monitoring data. Whilst reasonable agreement can justifiably be claimed for some species, whether in the gas phase, aerosol or precipitation, it is clear that for the others there are either severe disagreements or a lack of suitable data for comparison purposes. Background sources of these pollutants are assessed by applying wind sector analysis to precipitation measurements at remote sites. The budgets for the United Kingdom and north-west Europe have a similar balance between wet and dry deposition to that given in the literature for the global nitrogen budget. This is in conflict with some literature budgets for Europe as a whole which have apparently overestimated the dry deposition terms.

1. INTRODUCTION

In this paper, the behaviour of oxidized nitrogen-containing trace gases is examined in air and precipitation over the United Kingdom and north-west Europe. Attention is directed principally to the pollutants nitric oxide (NO), nitrogen dioxide (NO₂), nitric acid vapour (HNO₃) and nitrate aerosol (NA) and to the nitrate anion in precipitation (nitrate). A number of other related nitrogen-containing trace species will be referred to where relevant and these species include nitrogen pentoxide (N₂O₅), ammonia (NH₃) and the ammonium cation in precipitation (ammonium).

Historically, interest in the nitrate and ammonium ion contents of rainwater dates from 1749 but it was the agricultural chemists who started many of the early investigations of nitrogen compounds in rainwater during the later part of the 19th century. Some of the early observations have been reviewed by Eriksson (1952) and show lower concentrations in the remote regions of Scotland compared with northern and central England. Also concentrations in precipitation tended to be higher for ammonium compared with nitrate on a nitrogen equivalent basis. The impression formed in these early studies was that lightning and other natural sources were the most significant. A recent reinvestigation has shown that the mean concentration of nitrate in precipitation doubled at Rothamsted between the 1950s and the 1960s (Brimblecombe and Pitman 1980).

Measurements of the nitrate aerosol were made increasingly from the 1950s and some of the early investigations are described by Junge (1956). Various suggestions were made for the origins of the nitrate content of the atmospheric aerosol particles including interactions between continental emissions and the maritime sea-spray aerosol. Highest aerosol nitrate concentrations were generally associated with aerosol particles of greater than 1 μm in diameter.

Over the thirty or so years since these early studies, understanding of the role and impact of the different atmospheric oxidized nitrogen compounds has changed dramatically. Emissions of nitrogen oxides are now known to arise from fuel combustion

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both in industry and in large electricity-generating power stations together with a contribution from motor vehicle exhausts. Emissions on a European scale increased to a peak somewhere between 1970 and 1985 and are now starting to decrease.

There has been an increasing trend in the nitrate concentration of precipitation over large parts of north-west Europe and the trend has been apparent even at the most remote sites (Rodhe and Rood 1986). Nitrate aerosol concentrations in southern England have been steadily rising over the last three decades (Salmon et al. 1979). This trend can be illustrated by examining the annual mean aerosol nitrate concentrations measured at Harwell, Oxfordshire which were reported to be 0.54 μg N m⁻³ in 1956 compared with 0.78 μg N m⁻³ in 1984 (Atkins and Law 1984).

The global \( \text{NO}_x \) budget calculations have changed over the years to reflect this increasing awareness of the impact of man’s activities. In the first detailed study, Robinson and Robbins (1968) assumed a global mean \( \text{NO}_x \) concentration of 1 p.p.b. (1 p.p.b. represents a volume mixing ratio of 1 part in \( 10^9 \) parts of air), and deduced a turnover of \( 137 \times 10^6 \) tonnes \( \text{N} \) per year, which they assumed to arise largely from biological sources; combustion in comparison was considered to be insignificant. Soderlund and Svensson (1976) adopted lower background concentrations for \( \text{NO}_x \) and derived a global turnover rate of \( 40-120 \times 10^6 \) t N per year. Bottger et al. (1978) refined significantly previous estimates of the global wet deposition of nitrate and now current estimates of the global \( \text{NO}_x \) budget imply a turnover of \( 24-64 \times 10^6 \) t per year (Logan 1983) of which man’s activities through fossil fuel combustion and biomass burning account for the dominant contribution.

Currently, two principal references are available to the nitrogen budget of north-west Europe. These two sources are not strictly comparable because of differences in study area: \( 4 \times 10^6 \text{km}^2 \) (Soderlund 1977); \( 9.1 \times 10^6 \text{km}^2 \) (Bonis et al. 1980). Source area differences may account in part for the markedly different results obtained for export by transport. Both the studies of Soderlund and of Bonis et al. emphasize the importance of fuel combustion as a source of nitrogen oxides and are in broad, general agreement about the relative importance of dry and wet deposition. The ammonia budget does not show the same consistency between the two studies.

In this paper, a simple trajectory model approach is employed to study the emission, transport, transformation and deposition of oxidized nitrogen compounds over north-west Europe. The aim is to evaluate the relative importance of the different elementary processes and to investigate where significant gaps in present understanding remain.

2. The trajectory model

The behaviour of the nitrogen-containing trace gases over north-west Europe has been studied using a simple trajectory model approach. The initial results of this model have been presented elsewhere (Derwent 1986; Derwent and Nodop 1986) where the model philosophy is described and its origins in the pioneering work of Eliassen (1978) have been pointed out. The opportunity has been taken in this study to update some of the model assumptions and techniques employed in the initial work and to attempt a comparison of the model results with the available ambient and precipitation data.

The study employs two models, the first of which represents in some detail the behaviour of nitrogen species over the United Kingdom and the second covers a wider area of north-west Europe. Both models include United Kingdom and European sources and both adopt the same basic representation of the underlying processes. They differ in their output, with the United Kingdom model representing the behaviour of 84 receptor points in the centres of the \( 100 \text{km} \times 100 \text{km} \) ordnance survey grid squares and the
European model representing the behaviour of 36 receptor points within the United Nations Economic Commission for Europe (UN ECE) European Monitoring and Evaluation Programme (EMEP). The 36 receptor points were selected to give an even coverage of about one site per $5 \times 10^4 \text{km}^2$ over the land area of Belgium, Denmark, France, the Netherlands, Norway, the Federal Republic of Germany, the Republic of Ireland, Sweden and the United Kingdom.

The description of the behaviour at each receptor point was obtained by averaging over the results obtained for 24 separate trajectories arriving at that point, suitably weighted by the frequencies of winds in each 15° sector. The complex interplay between the individual atmospheric processes was described by considering a column of air of arbitrary cross-section, extending from the surface to the top of the boundary layer. Within this ‘air parcel’, mixing was assumed to be instantaneous so that vertical and horizontal gradients could be neglected. The ‘air parcel’ moved over the emission grid following a single trajectory for the whole boundary layer depth, that is, vertical wind shear was neglected. Furthermore, the trajectories were assumed to be straight lines over a travel period of between 48 and 96 hours. This is clearly a gross approximation in most circumstances and even more so where mountains would cause large-scale flow diversion. The model region therefore only extended as far as the Pyrenees, Alps and Ural mountains.

The basic assumptions and input parameters adopted in the simple trajectory model are detailed in Table 1. The same wind rose was adopted for all the receptor points in the United Kingdom model and was taken from Jones (1981). This reference gives four wind roses with a resolution of 30°, one for each wind speed range. The wind rose for the most frequently observed wind speed range ($5-10 \text{ m s}^{-1}$), accounting for 32-75% of the time, was adopted in this study. For the European model, the wind speed, 7-5 m s$^{-1}$, and boundary layer depth, 800 m, have been retained. The wind roses for the 36 receptor points have been taken from the daily sector analysis carried out by the Meteorological Synthesizing Centre-W (MSC-W) for the 636-day period from 1 February 1981 to 29 October 1982 (Lemhaus et al. 1985). This analysis provides wind roses with a resolution of 45° and provides an additional category where no allocation has been possible. In both models, the resolution of the wind roses has been artificially improved by taking two or three trajectories equally spaced at 15° apart in the 30 degree or 45 degree sectors respectively.

**TABLE 1. INPUT PARAMETERS ADOPTED IN THE SIMPLE TRAJECTORY MODEL CALCULATIONS**

<table>
<thead>
<tr>
<th>Input parameter</th>
<th>Adopted value</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Windspeed, $u$</td>
<td>$7.5 \text{ m s}^{-1}$</td>
<td>Jones (1981) (a)</td>
</tr>
<tr>
<td>Boundary layer depth, $h$</td>
<td>800 m</td>
<td>Jones (1981)</td>
</tr>
<tr>
<td>Tropospheric baseline ozone concentration, $O_3$</td>
<td>30 p.p.b.</td>
<td>(b)</td>
</tr>
<tr>
<td>Hydroxyl radical concentration</td>
<td>$0.8 \times 10^4 \text{molecule cm}^{-3}$</td>
<td>(see text)</td>
</tr>
<tr>
<td>‘Constant drizzle’ wet removal rate coefficients:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HNO$_3$, NH$_3$</td>
<td>$9 \times 10^{-6} \text{s}^{-1}$</td>
<td>Derwent (1987)</td>
</tr>
<tr>
<td>Nitrate and sulphate aerosol</td>
<td>$1.3 \times 10^{-3} \text{s}^{-1}$</td>
<td>Derwent (1987)</td>
</tr>
<tr>
<td>Sulphur dioxide oxidation rate coefficient</td>
<td>$1.0 \times 10^{-2} \text{h}^{-1}$</td>
<td>Eliassen (1978)</td>
</tr>
</tbody>
</table>

(a) Representative value for $5-10 \text{ m s}^{-1}$ wind speed range from the wind rose for use in long-range dispersion calculations, Table 6 of Jones (1981)

(b) A value selected on the basis of the ozone data presented in PORG (1987)
The concentrations of NO, NO$_2$, HNO$_3$, NH$_3$ and nitrate aerosol together with the dry and wet deposition rates of the nitrogen compounds were obtained by solving the coupled differential equations describing their production and loss in the moving air parcel. The differential equations representing the concentrations, $C_i$, of each species, $i$, had the general form

$$\frac{dC_i}{dt} = \frac{E_j}{A_j} + P_i - Q_i C_i - \frac{(V_i/h)C_i}{L_i}$$

where $E_j$ is the annual pollutant emission rate in mass units on the chosen grid, $j$; $A_j$ is the conversion factor between mass units per year and p.p.b.s$^{-1}$ for the chosen grid taking into account the respective grid sizes; $P_i$ is the total production rate of the species by chemical conversion processes; $Q_i C_i$ is the total removal rate by chemical conversion processes; $V_i$ is the dry deposition velocity of the species at some standard reference height, typically 1 m above the surface; and $L_i C_i$ is the total removal rate by wet processes.

The pollutant emissions of nitric oxide from man's activities were taken from the Warren Spring Laboratory studies (PORG 1987) for the United Kingdom and aggregated up to 100 km$\times$100 km grid squares. For the remaining countries of north-west Europe, the NO emissions for the 150 km$\times$150 km squares of the EMEP grid were based on the study Semb and Amble (1981) but with updated national total emissions. This latter inventory shows a pattern of significant emissions starting in southern Scotland, passing through England into Belgium, the Netherlands and the Federal Republic of Germany and then out through to the German Democratic Republic and Poland in the east.

The emissions of ammonia over the study region were taken from Buijsman et al. (1985). The spatial distributions of the ammonia and nitric oxide emissions are distinctly different, the former following the broad pattern of agriculture and the latter of urban industrialization. Over north-west Europe as a whole, cattle rearing accounts for the largest contribution to total ammonia emissions. For the United Kingdom, total ammonia emissions are estimated to be 405 thousand tonnes per year (Buijsman et al. 1985) compared with the estimate by Kruse et al. (1986) of 451.3 thousand tonnes of NH$_3$ per year. In the study reported here, the lower NH$_3$ emissions of Buijsman et al. have been employed. The emissions of sulphur dioxide disaggregated over the United Kingdom were taken from Warren Spring Laboratory studies (RGAR 1987) and for the EMEP grid from Dovland and Saltbones (1986).

The chemical scheme used to describe the behaviour of the atmospheric nitrogen compounds is illustrated in Fig. 1, from which the respective $P_i$ and $L_i C_i$ terms in Eq. (1) have been constructed. Table 2 summarizes the rate coefficient data for the processes employed in the model and highlights the simple scheme for ammonia. Little is known about the chemical kinetics of this species and there are too few studies available upon which reliable estimates of rate coefficients can be based. This is a major barrier to further progress in this area.

The initial concentrations for most of the model species were set to zero either at the start of the trajectory or when the ‘air parcel’ crossed the boundaries of the EMEP grid. The initial ozone concentration was set to 30 p.p.b., see Table 1, representing the surface baseline concentration in north-west Europe based on U.K. ozone measurements (PORG 1987). Ozone was assumed to be replenished by vertical exchange through the upper surface of the ‘air parcel’ at a rate which would exactly balance dry deposition removal in the absence of nitric oxide pollution sources. No loss by vertical exchange was allowed for in the differential equations representing other model species.

A fixed hydroxyl radical concentration was employed in the calculations and was estimated using the following assumptions. In the initial investigations of the budget over north-west Europe (Eliassen 1978) a constant transformation rate of 1.3% per hour was
Figure 1. The coupled life cycles of the sulphur- and nitrogen-containing trace gases.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate coefficient</th>
<th>Units</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO + O₃ = NO₂ + O₂</td>
<td>1.8×10⁻¹³ exp(-1370/T)</td>
<td>cm³molecule⁻¹s⁻¹</td>
<td>(a)</td>
</tr>
<tr>
<td>NO₂ + hν = NO + O</td>
<td>1.45×10⁻² exp(-0.4 sec θ)</td>
<td>s⁻¹</td>
<td>(b)</td>
</tr>
<tr>
<td>O + O₂ + M = O₃ + M</td>
<td>5.8×10⁻²² (T/300)⁻²⁶</td>
<td>cm³molecule⁻²s⁻¹</td>
<td>(a)</td>
</tr>
<tr>
<td>OH + NO₂ + M = HNO₃ + M</td>
<td>1.5×10⁻¹¹</td>
<td>cm³molecule⁻¹s⁻¹</td>
<td>(a)</td>
</tr>
<tr>
<td>O₃ + NO₂ + M = NO₃ + O₂ + M</td>
<td>1.2×10⁻¹⁵ exp(-2450/T)</td>
<td>cm³molecule⁻¹s⁻¹</td>
<td>(a)</td>
</tr>
<tr>
<td>NO₃ + hν = NO₂ + O</td>
<td>8.94×10⁻³ exp(-0.06 sec θ)</td>
<td>s⁻¹</td>
<td>(c)</td>
</tr>
<tr>
<td>NH₃ + HNO₃ = NH₄NO₃</td>
<td>1.0×10⁻¹⁴</td>
<td>cm³molecule⁻¹s⁻¹</td>
<td>(d)</td>
</tr>
<tr>
<td>HNO₃ = nitrate aerosol</td>
<td>3.0×10⁻₅</td>
<td></td>
<td>(e)</td>
</tr>
<tr>
<td>NO₃ + NO₂ + M = N₂O₅ + M</td>
<td>2.3×10⁻¹³ exp(-1000/T)</td>
<td>cm³molecule⁻¹s⁻¹</td>
<td>(a)</td>
</tr>
<tr>
<td>N₂O₅ = nitrate aerosol</td>
<td>3.0×10⁻³</td>
<td>s⁻¹</td>
<td>(e)</td>
</tr>
</tbody>
</table>

Notes:
Temperature 288 K.

assumed. In subsequent studies (Eliassen and Saltbones 1983) this approach has been modified but nevertheless as a working hypothesis it represents a reasonable basis with which to begin the present investigation of the nitrogen budget. Imagining all this conversion to be driven by hydroxyl radical oxidation, which it most certainly is not because of the well-established oxidation mechanisms for sulphur dioxide in cloud droplets, allows the estimation of a hydroxyl radical concentration using the literature OH + SO₂ rate coefficient of 1.35×10⁻¹² cm³molecule⁻¹s⁻¹ (Baulch et al. 1984). This gives a first estimate of 2.7×10⁶ OH radicals per cm³ which was adopted in our first studies (Derwent 1986; Derwent and Nodop 1986). In this paper, a much lower value
was adopted (see Table 1) of \(0.8 \times 10^6\) molecules cm\(^{-3}\) taken from the results of tropospheric two-dimensional model studies of the isotopic distribution in atmospheric carbon monoxide (Volz et al. 1981).

Dry deposition plays an important role in removing nitrogen species from the atmosphere. It occurs in a sequence of processes which involves turbulent transport through the boundary layer towards the surface, transport across the surface layer and chemical or physical capture of the pollutant at the surface. As implied by Eq. (1), dry deposition has been modelled by assuming that the dry deposition flux is directly proportional to the model concentration averaged over the entire boundary layer depth. The constant of proportionality between deposition flux in p.p.b. s\(^{-1}\) in Eq. (1) and concentration in p.p.b. is species dependent and is given by \(V_d/h\), where \(h\) is the boundary layer depth. It is assumed in this study that the parameters \(V_i\) can be represented approximately by the deposition velocities, \(V_g(z)\), determined at particular reference heights \((z)\) above ground for each pollutant–surface combination.

Having made these assumptions, the next step is to choose appropriate \(V_i\) values based on literature surveys for the study region. This is not a particularly easy task because of the wide variety of surfaces involved, the problems of dealing with seasonal factors of snow cover and vegetation growth, the paucity of field experimental data, problems of soil exhalation and measurement unreliability, apart from the problems of averaging aerodynamic resistances over diurnal and seasonal cycles (Voidner et al. 1986). Table 3 summarizes the \(V_i\) values adopted in this study for the long term representation of dry deposition on the regional, 100–1000 km, spatial scale.

The removal of nitrogen compounds by precipitation has received some attention and a review of the likely significant processes (Asman 1982) points to wet removal of nitrate aerosol through a cloud condensation nucleus mechanism and below-cloud

<table>
<thead>
<tr>
<th>Pollutant</th>
<th>Parameter value, (V_i) (cm s(^{-1}))</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitric oxide (NO)</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Nitrogen dioxide (NO(_2))</td>
<td>0.15</td>
<td>(a)</td>
</tr>
<tr>
<td>Gaseous nitric acid (HNO(_3))</td>
<td>4.0</td>
<td>(b)</td>
</tr>
<tr>
<td>Ammonia (NH(_3))</td>
<td>1.0</td>
<td>(c)</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>0.5</td>
<td>(d)</td>
</tr>
<tr>
<td>Nitrate and sulphate aerosol</td>
<td>0.1</td>
<td>(e)</td>
</tr>
</tbody>
</table>

(a) Field studies usually report difficulties in observing NO\(_2\) deposition as both upward and downward fluxes can be reported over the same surface.
(b) Deposition of this reactive gas is largely controlled by aerodynamic factors, but may be influenced by reaction with ammonia to form aerosol nitrate with the flux divergence into the aerosol, giving a higher deposition than expected from consideration of the atmospheric resistance alone. It is unlikely to be affected by soil moisture and is only restricted over water and snow because of the flow conditions over smooth surfaces.
(c) Behaves similarly to sulphur dioxide, except that soils can sometimes emit ammonia. In nitrogen-deficient regions and areas where soils are not managed NH\(_3\) would be strongly absorbed. However, in managed systems where fertilisers are in use, ammonia emission could be expected. This value could be too high and a somewhat smaller value may be more appropriate for a wide range of soil types, land and sea surface and different seasons.
(d) RGAR (1987)
(e) This value is appropriate for a predominantly submicron aerosol. However, the presence of coarse nitrate particles would indicate a deposition velocity of about 0.1 cm s\(^{-1}\).
scavenging of gaseous nitric acid as being important. Both of these processes have been included in the present study, see Fig. 1. It is one thing to establish the nature of the important mechanism, it is another to represent such a complex process as wet removal in a simple model. It has not been possible to develop a detailed representation of precipitation removal over the spatial scale of north-west Europe within this study. The adopted approach can at best be described as broadly descriptive and is intended only as a zero-order estimate.

The precipitation model employed is a 'constant drizzle' approximation and has the advantage of being simple, yet mass conserving. The first-order removal coefficients used in the model are given in Table 1 and have been derived from a statistical model of NOx behaviour under idealized model conditions (Derwent 1987). The patterns of gaseous nitric acid and nitrate aerosol wet removal were simulated using a random distribution of wet and dry periods and the removal coefficients were obtained by fitting the spatial patterns obtained.

The representation of the sulphur cycle is based on our earlier study of the behaviour of sulphur in north-west Europe (Buckley-Golder and Derwent 1986). The assumptions are illustrated in Fig. 1. The 'constant drizzle' removal coefficients for the sulphur species were obtained from a statistical model.

The system of differential equations representing the conservation of mass for the model species was solved using FACSIMILE, a variable-order Gear's method program (Curtis and Sweetenham 1987) on an IBM PC XT microcomputer, or integrated with a first-order forward difference Euler's method using a fixed time step of 120 seconds in a PASCAL program on the Harwell IBM 3084Q mainframe computer.

3. RESULTS WITH THE TRAJECTORY MODEL FOR GASEOUS AND AEROSOL SPECIES

The pattern of long-term mean concentrations of nitric oxide calculated with the trajectory model closely follows that of the emissions. Nitric oxide concentrations show a double maximum in the midlands and south-east England, spreading northwards towards Tyneside and Lancashire and westwards to include south Wales and southern England. The pattern of nitric oxide concentrations over the United Kingdom is illustrated in Fig. 2 and is part of a larger feature covering the whole of north-west Europe. The maxima over England are part of a broad maximum which covers the Rhine, the Netherlands and Belgium.

The broad features of this spatial distribution over the United Kingdom are confirmed by the available ambient measurements, see Fig. 2 (Martin and Barber 1981, 1984; Apling et al. 1981; Cox et al. 1976; Sandalls and Leonard 1986; RGAR 1987). The overall agreement between model and measurement is, however, not particularly good. In particular, the model significantly underpredicts the observations in the east Midlands at Bottesford, Leicestershire and Jenny Hurn, Lincolnshire. This highlights a particular deficiency in the model, which aims at addressing sources of pollution on the regional scale, 100–1000 km. The concentration of nitric oxide in rural areas can be significantly influenced by local vehicle traffic and combustion sources. These small-scale features are not adequately represented in the trajectory model.

In addition to pronounced spatial variations, the trajectory model predicts pronounced variations in nitric oxide concentrations with time of day about the average concentrations reported in Fig. 2. The model nitric oxide concentrations drop to exceedingly low values during nighttime as the nitric-oxide-ozone reaction goes through to completion: \( \text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_3 \). Nitric oxide concentrations in the model are apparently only significant in the atmospheric boundary layer during daylight, see Fig. 3.
Figure 2. The spatial pattern of the nitric oxide concentrations calculated and observed for the United Kingdom in p.p.b.

Figure 4, in contrast, shows the observed diurnal variations in nitric oxide concentrations at Harwell, Oxfordshire, a rural site in southern England. The observed nitric oxide concentrations fall to a value which approaches the minimum detectable for the instrumental method employed, confirming the trajectory model predictions.

Nevertheless, ambient measurements reveal the presence of nitric oxide, at times, albeit at a low concentration, in most rural sites at night. This apparent conflict with the trajectory model is due to the assumption in the model of complete instantaneous mixing over the regional scale. Local sources of nitric oxide pollution are not necessarily completely mixed and completely oxidized during travel to the measuring sites. This effect is particularly noticeable at nighttime when nitric oxide concentrations should be extremely low if chemical reactions and atmospheric mixing are assumed to be complete in rural areas. The model will therefore consistently underestimate nighttime nitric oxide concentrations in any rural area with close-by nitric oxide pollution sources from local vehicle traffic.

The illumination conditions assumed in the model are consequently of some importance, judging by Figs. 3 and 4. It would take an unreasonable amount of computer time to simulate the full diurnal cycle in the present calculations and perform a series of calculations arriving at each receptor point for each hour of the day. Simplifications have
Figure 3. The calculated diurnal variations in nitric oxide and nitrogen dioxide concentrations for a rural site in southern England.

Figure 4. The observed diurnal variations in nitric oxide and nitrogen dioxide concentrations at a rural site in southern England, Harwell, Oxfordshire, taken from Cox et al. (1976).

decided to implement the treatment of time-dependent photolysis rates. The results presented in Fig. 2 are based on constant illumination conditions; that is, the photolysis rate for nitrogen dioxide has been averaged over a complete 24-hour cycle and an annual cycle of summer–autumn–winter–spring for clear sky conditions. The 24-hour-mean nitric oxide concentration calculated for Fig. 4 is 1.6 p.p.b. compared with the value of 1.9 p.p.b. obtained using the 'constant-sun' approximation. The error thus committed is significant.
in absolute terms, amounting to an overestimate approaching 20%. However, when viewed against the larger factor of 2 to 4 underprediction by the model of ambient nitric oxide concentrations, the 'constant sun' approximation can be viewed as not too unreasonable.

The calculated distribution of nitrogen dioxide shows a double maximum, see Fig. 5, with centres over the midlands and south-east England, reflecting strongly the spatial pattern of nitric oxide emission sources. A pronounced concentration gradient across the United Kingdom is obtained and this is part of a larger-scale distribution pattern across north-west Europe. The maxima over the United Kingdom represent the extension northwards and westwards of the maxima which lie over Belgium, the Netherlands and the Federal Republic of Germany.

The comparison of model results and ambient measurements (Martin and Barber 1981, 1984; Harrison and McCartney 1980; Cox et al. 1976; Apling et al. 1981; RGAR 1987; Goldsmith 1986) for nitrogen dioxide is detailed in Fig. 5. The spatial patterns have been reproduced in a broad manner by the model but the absolute magnitudes in the model and observations are significantly different. The discrepancies are smallest, 20–60% underprediction, at the least polluted sites, Sibton and Lough Navar. However,
at the rural sites in the midlands, the underprediction approaches a factor of three. This poor level of agreement is considered to be a serious weakness of the trajectory model and warrants further detailed scrutiny. The presence of local sources of pollution in combination with a shallow nocturnal boundary layer may be a plausible explanation. Local vehicle traffic and combustion sources may play a role. There is also the nighttime exhalation of NO from soil which may be significant over grazed pasture.

The ambient measurements at Bottesford, Leicestershire, show significant year-by-year variations which amount to about a factor of 2–4 between the highest and lowest annual mean concentrations. The origin of this variability has not been explained. Nevertheless, even at the lowest annual concentrations found, ambient measurements are still about 30% higher than the model calculations.

The rapid apportioning of the NO$_x$ species between NO and NO$_2$ during daylight is an important aspect of the overall behaviour of nitrogen-containing trace gases in the boundary layer. The daytime production of nitric oxide acts to promote long-range transport by acting as a temporary reservoir for NO$_x$, since the bulk of the removal processes act either on NO$_2$ or its subsequent reaction products. It is interesting to note that the ability of nitric oxide to act as a temporary reservoir is progressively reduced as ozone concentrations increase, particularly during photochemical ozone episodes.

Figure 6. The spatial pattern of the gaseous nitric acid concentrations calculated and observed for the United Kingdom in p.p.b.
The model-calculated distribution of gaseous nitric acid is shown in Fig. 6, revealing a tongue extending into the United Kingdom from continental Europe passing up through the south and east to the midlands. The extent of any agreement with the few available ambient observations (Harrison and Pio 1983; Dollard et al. 1987) is addressed in Fig. 6. The model and measurements appear to be in reasonable agreement although a larger database would be required before a more detailed comparison could be attempted. However, the gross underprediction observed above for NO and NO₂ is not as apparent here for HNO₃.

The distribution of aerosol nitrate over the United Kingdom calculated by the trajectory model reveals the dominant influence of sources in continental Europe. A tongue of high concentration extending into south and east England is apparent in Fig. 7. Sources in the United Kingdom also make an additional contribution over a large, 500–1000 km, horizontal scale.

![Figure 7](image_url)
The extent of agreement between the model and ambient measurements (Cawse 1974; RGAR 1987) for aerosol nitrate is considered in some detail in Fig. 7. The model overestimates observed particulate nitrate concentrations at all sites. At the remote site, Lerwick, concentrations have been overestimated by a factor of approaching 4. At all other sites, the model performs significantly better, being about a factor of 2 or less higher than observations. The extent of the model overestimation of particulate nitrate concentration for the Harwell, Oxfordshire site is illustrated in Fig. 8 using the complete time series of observations. Only during one period have observed levels exceeded the calculated particulate nitrate concentrations, during the exceptional summer of 1976. This strongly suggests that the model is overestimating the conversion of oxidized nitrogen compounds into aerosols.

![Graph showing concentration of aerosol sulphate and nitrate over time](image)

Figure 8. The time series of quarterly running means of aerosol sulphate and nitrate concentration observed at Harwell, Oxfordshire from 1954 to 1985 (Atkins and Law 1984; Atkins 1987) and the model calculations in \( \mu g \text{S m}^{-3} \) and \( \mu g \text{N m}^{-3} \).

The level of agreement found between the model and measurements for nitric oxide and nitrogen dioxide over the United Kingdom is not striking. This is in slight conflict with the behaviour found for gaseous nitric acid and aerosol nitrate, where better agreement is found. Before the results for precipitation are presented it is worth examining the model results for the ammonia- and sulphur-containing species. Although they are not the main preoccupation of this study, they nevertheless provide a source of ambient measurements against which the trajectory model results can be compared.

The calculated distribution of sulphur dioxide concentrations in the model is illustrated in Fig. 9 and compared against the available ambient measurements in rural areas (Cox et al. 1976; RGAR 1987). The trajectory model parameters employed for the sulphur species are listed in Tables 1 and 2; in all other respects, besides emissions, the nitrogen and sulphur models are analogous. The agreement between model and measurement for sulphur dioxide is satisfactory both in absolute magnitude and spatial variation.

The calculated distribution of particulate sulphate shows a broad maximum over the United Kingdom with a spatial scale of about 500 km, see Fig. 10, which is a part of a larger feature covering north-west Europe. The model results are compared with the available rural measurements (RGAR 1987) and the agreement is most heartening. For most sites, the discrepancies between model and observation amount to \( \pm 30\% \), except
Figure 9. The spatial pattern of the sulphur dioxide concentrations calculated and observed for the United Kingdom in p.p.b.

Figure 10. The spatial pattern of the particulate sulphate concentrations calculated and observed for the United Kingdom in \( \mu g \text{Sm}^{-3} \).
for Ludlow and Eskdalemuir where there seems to be a significant underestimation in the model. This underestimation could be improved by the addition of a background particulate sulphate aerosol concentration. The addition of 0.25 µg S m\(^{-3}\) background to the model concentrations minimizes the sum of squares of the deviations between model and observations over the entire table. There could, however, be other explanations of this model underestimation.

In contrast to the case for particulate nitrate, the comparison of particulate sulphate with a long-running time series (Atkins and Law 1984; Atkins 1987) illustrates the model underprediction. Adding in 0.25 µg S m\(^{-3}\) clearly improves the agreement over the 1980–1986 period.

Ammonia shows a completely different distribution across the United Kingdom from the other pollutants discussed so far. Figure 11 shows how the model-calculated ammonia concentrations peak over Wales and south-west England. This distribution reflects the combined effect of the ammonia sources and rapid chemical removal following sulphur dioxide and nitrogen oxide oxidation. There are no published measurements of gaseous ammonia against which to compare the model calculations.

Some unpublished ammonia concentrations (Dollard et al. 1987; Atkins 1987) determined using oxalic-acid-coated denuder tubes have been added to Fig. 11. The few

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Figure 11. The spatial pattern of the gaseous ammonia concentrations calculated and observed (see Atkins (1987)) for the United Kingdom in p.p.b.
measurements available indicate reasonably good agreement with the model calculations in the north-west and central southern sites in England. However, at the relatively polluted sites in the midlands, agreement between the model and observations is poor. This level of disagreement reflects a serious weakness in the model which will require further attention. In Table 3 it is noted that a somewhat lower deposition velocity for ammonia may be appropriate for such a regional-scale model. However, adopting such a lower value would not significantly improve model agreement.

4. RESULTS WITH THE TRAJECTORY MODEL FOR VARIOUS SPECIES IN PRECIPITATION

The calculated pattern of the nitrate content of precipitation is shown in Fig. 12 revealing a broad maximum spreading over the United Kingdom from the continent of Europe. The north–south east–west gradient in the model concentrations of nitrate in precipitation are also apparent in the observations (RGAR 1987). The agreement revealed in Fig. 12 is most heartening, with the most serious discrepancy amounting to less than 20%, at Bottesford, Leicestershire, the most polluted site.

The addition of a background precipitation concentration to the model results would remove many of the discrepancies between the model and observations. A background correction of 0-05 mg N l⁻¹NO₃ minimized the sum of the squares of all the discrepancies but there may, however, be other causes for the small deviations apparent between model and observations.

Interest in the life cycle of ammonia and its compounds has developed only recently. The model in Fig. 13 is able to reproduce a broad maximum of 0-4 mg N l⁻¹NH₄ over the United Kingdom in reasonable agreement with the contours of ammonia in precipitation compiled by the EMEP CCC (Nodop et al. 1985) from available measurements. However, the model is not able to account for much of the spatial variability of ammonium in precipitation. The main points are as follows:

For the sites with the highest concentrations, Bottesford, Stoke Ferry and Chilton, the observations (RGAR 1987) are underestimated by between one third and one half, 0-2–0-5 mg N l⁻¹NH₄.

For six widely-spaced sites (Achnagoichan, Torlundy, Eskdalemuir, Waterhead, Loch Dee and Goonhilly) reasonable agreement between model and measurement (RGAR 1987) can be claimed.

For six sites in the more northern regions (Inverpolly, Peterhead, Lochnagar, Faskally, Whiteadder, Redesdale) the observations (RGAR 1987) are underestimated by about 0-09–0-29 mg N l⁻¹NH₄, whilst other sites within 100–200 km do not share such underestimation.

The addition of a background ammonium in precipitation of 0-1–0-3 mg N l⁻¹NH₄ would help resolve some of the discrepancies found between model and observations. However, this explanation does not account for all the problems noted. Significant underestimation will still remain at Bottesford and Stoke Ferry, with slight overestimation at Goonhilly. This points to serious problems with the representation of the ammonia life cycle or its emissions in the model.

It has been noted in Table 3 that the deposition velocity assumed for ammonia in this study may be too high for such a regional model investigation. This would lead to an underestimation of gaseous ammonia concentrations and hence an underestimation of the amount of ammonia passing into the aerosol and hence into wet deposition. However, the supply of oxidized and acidic sulphur and nitrogen species controls the
Figure 12. The spatial pattern of the nitrate concentration in precipitation calculated and observed (RGAR 1987) for the United Kingdom in mg N\(^+\)NO\(_3\)\(^-\).

Figure 13. The spatial pattern of the ammonium concentration in precipitation calculated without background and observed (RGAR 1987) for the United Kingdom in mg N\(^+\)NH\(_4\).
flux of ammonia into aerosol in the present model and there is apparently an adequate supply of ammonia even with the high deposition velocity assumed. The feedback between ammonia supply and sulphur oxidation rate has not been described and this itself may be a significant source of model discrepancy.

The distribution of sulphur in precipitation obtained in the model calculations is shown in Fig. 14, revealing a pattern of high concentration over south and east England, decreasing towards Scotland. This pattern is apparent in the observations (RGAR 1987) but there is considerable disagreement concerning the absolute concentrations. The highest measurements reach nearly 2 mg S\(^{-1}\)SO\(_4\) whereas the corresponding model precipitation concentrations are at least a factor of five lower. In Scotland, the observations indicate lower concentrations, yet there are significant spatial variations. The four sites in central Scotland (Agnagoichan, Torlundy, Faskally and Lochnagar) show remarkable differences over such a small spatial scale for which the model has no explanation at all.

The addition of a background concentration of sulphate in precipitation would help bring the model results into closer agreement with observations. This would need to be of the order of 0.4–0.5 mg S\(^{-1}\)SO\(_4\).

Figure 14. The spatial pattern of the sulphate concentration in precipitation calculated without background and observed (RGAR 1987) for the United Kingdom in mg S\(^{-1}\)SO\(_4\).
5. BACKGROUND AEROSOL PRECIPITATION CONCENTRATIONS AND MODEL DISCREPANCIES

The model does not include all sources of nitrogen- and sulphur-containing aerosol and precipitation species. Allowance should be made for the trace constituents in the air and rain at the start of each 96-hour trajectory, whereas in the model these are set to zero. Important sulphur and nitrogen sources outside the EMEP region, for example the North American continent and the remote areas of the Asian continent, should be included. However, not all the 96-hour back trajectories are initiated outside the EMEP grid; some start within the grid. Again, the model concentrations should be initialized to the appropriate values for the starting region. It is difficult to assess how these initial values are to be selected.

Furthermore, the model does not specifically treat natural sources of sulphur and nitrogen within the EMEP or the U.K. model grids. They are expected to be small in comparison with the man-made sources but, nevertheless, they cannot be wholly neglected.

Either of these sources — extra long-range transport of man-made pollutants or natural emissions — could lead to significant, measurable concentrations of sulphur- and nitrogen-containing pollutants in the atmosphere, aerosol and precipitation over the United Kingdom. These would not be included in the model and their inclusion would partially account for some of the discrepancies between the model and observations which have been noted already in this study.

Discrepancies between model and observations could also arise because of inadequacies in the model formulation, emission data or through the inappropriate choice of model parameters. In the following paragraphs, the magnitudes of apparent background concentrations anticipated from the modelling studies are compared with estimates of background concentrations based on measurements at the more remote sites in north-west Europe.

The background concentrations of nitrate and ammonium in precipitation have been assessed using the technique of sector analysis using the daily precipitation measurements at remote EMEP sites. This analysis employed the daily wind sector allocation performed by the MSC-W, using 45° wind sectors (Lemhaus et al. 1985); the daily nitrate concentrations in precipitation, together with precipitation amount, reported by the EMEP CCC (Nodop et al. 1985); and precipitation-weighted mean concentration data for the period October 1981 to September 1982.

Table 4 summarizes the precipitation-weighted mean concentrations found for each 45° wind sector at each site for each species. Taking the four sectors forming the semi-circle from west to north-west inclusive as representative of relatively unpolluted precipitation, it is possible to estimate the background precipitation concentrations in Table 5. Placed alongside are the assumptions made in the EMEP model for sulphate in particulates and precipitation (Eliassen and Saltbones 1983). The particulate nitrate concentration was estimated from the precipitation concentration using the observed washout ratio determined over the United Kingdom of 1170 mg N per kg rain per mg N per m² air.

A comparison of these observed background concentrations with the corresponding concentrations that would minimize model discrepancies is given in Table 5. The conclusions that can be drawn from Table 5 differ somewhat from species to species. For nitrate in precipitation and particulate nitrate, there is almost certainly a real contribution to pollutant levels in the model from sources outside our consideration. The inclusion of this small contribution would significantly improve agreement between model and
TABLE 4. Precipitation-weighted mean concentrations found for nitrate and ammonium at three remote EMEP sites based on the measurements of Nodor et al. (1985)

<table>
<thead>
<tr>
<th>Precipitation-weighted mean concentration by wind direction sector</th>
<th>N</th>
<th>NE</th>
<th>E</th>
<th>SE</th>
<th>S</th>
<th>SW</th>
<th>W</th>
<th>NW</th>
<th>(a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate in precipitation (mg N(^{14})NO(_3))</td>
<td>0.025</td>
<td>0.062</td>
<td>0.169</td>
<td>0.156</td>
<td>0.115</td>
<td>0.099</td>
<td>0.042</td>
<td>0.049</td>
<td>0.113</td>
</tr>
<tr>
<td>Kaarvatin, Norway</td>
<td>0.017</td>
<td>0.048</td>
<td>0.304</td>
<td>0.324</td>
<td>0.690</td>
<td>0.211</td>
<td>0.049</td>
<td>0.453</td>
<td>0.104</td>
</tr>
<tr>
<td>Faeroes, Denmark</td>
<td>0.108</td>
<td>0.040</td>
<td>0.024</td>
<td>0.029</td>
<td>0.055</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Braganca, Portugal</td>
<td>0.048</td>
<td>0.062</td>
<td>0.060</td>
<td>0.087</td>
<td>0.132</td>
<td>0.132</td>
<td>0.11</td>
<td>0.082</td>
<td>0.130</td>
</tr>
<tr>
<td>Faeroes, Denmark</td>
<td>0.039</td>
<td>0.221</td>
<td>0.471</td>
<td>0.333</td>
<td>0.274</td>
<td>0.291</td>
<td>0.588</td>
<td>0.691</td>
<td>0.172</td>
</tr>
<tr>
<td>Braganca, Portugal</td>
<td>0.065</td>
<td>0.070</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a): Unattributed

TABLE 5. A comparison of background concentrations estimated from observations together with the corresponding concentrations that would minimize model discrepancies

<table>
<thead>
<tr>
<th>Species</th>
<th>Concentration to minimize model discrepancies</th>
<th>Concentration from sector analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate aerosol (µg N m(^{-3}))</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>Sulphate aerosol (µg S m(^{-3}))</td>
<td>0.25</td>
<td>0.2*</td>
</tr>
<tr>
<td>Ammonium in precipitation (mg N(^{14})NH(_3))</td>
<td>0.1-0.3</td>
<td>0.2</td>
</tr>
<tr>
<td>Nitrate in precipitation (mg N(^{14})NO(_3))</td>
<td>0.05</td>
<td>0.04</td>
</tr>
<tr>
<td>Sulphate in precipitation (mg S(^{13})SO(_4))</td>
<td>0.4-0.5</td>
<td>0.4*</td>
</tr>
</tbody>
</table>

* Eliassen and Saltbones (1983), from EMEP study.

observations. It is noted that the adopted background concentration of nitrate in precipitation is in good agreement with historical nitrate levels.

For ammonium in precipitation, the likely contribution from sources outside our consideration is slightly below the level required to minimize the discrepancies between model and observations. Clearly, its inclusion will help to improve agreement but other more serious sources of discrepancy still remain. Again, the adopted background concentration for ammonium in precipitation is consistent with historical levels.

For particulate sulphate and sulphate in precipitation, the likely contributions estimated within the EMEP study from sources beyond consideration by the routine sulphur model (Eliassen and Saltbones 1983) are in good agreement with the discrepancies noted in the present study between model and observations. Clearly, the addition of background particulate sulphate and sulphate in precipitation will markedly improve the apparent performance of the model.

In summary, therefore, careful attention to background contributions has removed many of the remaining discrepancies for particulate nitrate and sulphate and for nitrate and sulphate in precipitation. Problems undoubtedly remain with ammonium in precipitation, where a background contribution large enough to balance model and observations cannot be supported by sectoral analysis of the precipitation composition at remote sites. Background contributions appear to be much more important for sulphur and ammonium in precipitation compared with nitrate. This conclusion should be reflected in the budgets for the United Kingdom and Europe described in the next section.
6. SULPHUR AND NITRATE BUDGETS

The budgets for the United Kingdom were obtained by integrating the wet and dry deposition rates for each pollutant in the model over the 244 796 km² area of the country. The background or unattributed contribution was obtained using only the observed background precipitation concentrations in Table 5 and no specific contributions from aerosol species have been included. Table 6 summarizes the results for sulphur- and nitrogen-containing pollutants, split into dry and wet deposition, attributed and unattributed contributions.

The sulphur budget is heavily dominated by the dry deposition of sulphur dioxide, almost wholly of United Kingdom origin. There is a smaller contribution from the wet deposition of material of unattributed or background origins. Dry deposition accounts for about three quarters of the total sulphur deposition. The remaining quarter is highly model-dependent being influenced by the model parametrization of sulphur oxidation and wet removal.

The budget of oxidized nitrogen compounds is fairly evenly balanced between dry deposition of nitrogen dioxide and gaseous nitric acid and wet deposition of gaseous nitric acid and nitrate aerosol. The background or unattributed contribution is much smaller for oxidized nitrogen (7%) than for sulphur (20%).

A similar balance between dry and wet deposition is found in the budget for the reduced nitrogen compounds for the United Kingdom. However, the model considerably underestimates wet deposition of ammonium and this is presumably reflected in Table 6. Whether or not dry deposition is also underestimated cannot be judged at present because of the absence of widespread gaseous ammonia measurements. Background deposition appears to be particularly significant for reduced nitrogen, contributing 30% of the model budget.

The background contributions over the United Kingdom for ammonium and sulphate amount to $50 \times 10^9 \text{g N y}^{-1}$ and $100 \times 10^9 \text{g S y}^{-1}$, respectively. These are in the mass ratio of 1:2 which is consistent with the wet deposition of background NH$_4$(HSO$_4$) rather than of (NH$_4$)$_2$SO$_4$.

**TABLE 6. SULPHUR AND NITROGEN BUDGETS FOR THE UNITED KINGDOM**

<table>
<thead>
<tr>
<th></th>
<th>Sulphur: SO$_2$ and sulphate aerosol ($10^9$ g S y$^{-1}$)</th>
<th>Oxidized nitrogen: NO$_2$, HNO$_3$ and nitrate aerosol ($10^9$ g N y$^{-1}$)</th>
<th>Reduced nitrogen: ammonia and ammonium ($10^9$ g N y$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry deposition</td>
<td>361 Attributed</td>
<td>58 Attributed</td>
<td>50 Attributed</td>
</tr>
<tr>
<td>Wet deposition</td>
<td>40 Attributed</td>
<td>67 Attributed</td>
<td>68 Attributed</td>
</tr>
<tr>
<td></td>
<td>100 Background</td>
<td>10 Background</td>
<td>50 Background</td>
</tr>
<tr>
<td></td>
<td>501 Total</td>
<td>135 Total</td>
<td>168 Total</td>
</tr>
</tbody>
</table>
Over the land areas of north-west Europe, the budget of oxidized nitrogen is heavily dominated by wet deposition, see Table 7, which accounts for about three quarters of the total deposition. Background or unattributed deposition is apparently quite unimportant on the regional scale.

A different picture is found for ammonium depositions, where background or unattributed deposition accounts for one third of the total deposition of reduced nitrogen compounds. Wet deposition nevertheless contributes a similar fraction of the total deposition, as with oxidized nitrogen compounds.

It is interesting to compare the present model nitrogen budgets for north-west Europe with the literature studies of Soderlund (1977) and Bonis et al. (1980). Considering first the oxidized nitrogen compounds, the present model indicates an integrated wet deposition which amounts to about three times the integrated dry deposition term. Both studies have wide margins on their respective dry deposition terms but they are both comparable with or considerably larger than their wet deposition terms.

The agreement between model and observation for nitrate in precipitation detailed in sections 4 and 5 above has been achieved by converting NO, NO\textsubscript{2} and HNO\textsubscript{3} into species which may be efficiently removed by wet deposition in competition with dry deposition. The model nitrogen budget is thus not as heavily dominated by the dry deposition of gaseous nitric acid and nitrogen dioxide as the earlier literature budgets have suggested. Further studies are clearly required to resolve the remaining model discrepancies, particularly for NO and NO\textsubscript{2}, before discussion of the oxidized budgets for north-west Europe can be considered closed.

The reduced nitrogen budget in the present model has an integrated wet deposition term which is three times the integrated dry deposition term. The literature dry deposition budgets (Soderlund 1977; Bonis et al. 1980) are generally comparable with the wet depositions budgets for the reduced nitrogen species. Again, there is an apparent conflict with the present model study which, if anything, has almost certainly underestimated the wet deposition term. Measurements of ammonia in the atmospheric boundary layer would clearly help to remove the uncertainty in the dry deposition contribution to the reduced nitrogen budgets.

Taken together the present model appears to give a radically different picture of the nitrogen budgets of north-west Europe compared with literature studies. This may be an artefact of some regional-scale budget studies which use the dry deposition term to balance the difference between an uncertain emission term and a well-characterized wet deposition term. Emissions, particularly from natural sources, have been overestimated in the past, and this may account for the overestimation of the dry deposition terms in the nitrogen budgets.

In comparison with the global nitrogen budget study of Logan (1983), the present modelling study is giving a most acceptable apportioning between the wet and dry deposition terms. Since the source and sink terms have been carefully examined in some detail in the global study, the agreement with the present model is probably not fortuitous and is most encouraging.

7. Conclusions

A simple trajectory model approach has been developed to address the emission, transformation and deposition of a coupled set of pollutants, including SO\textsubscript{2}, NO\textsubscript{2} and ammonia. The main purpose has been to compare the model results with the available observations for the United Kingdom and then to proceed with an examination of the nitrogen budgets for the United Kingdom and north-west Europe.
<table>
<thead>
<tr>
<th></th>
<th>Belgium</th>
<th>Denmark</th>
<th>France</th>
<th>Federal Republic of Germany</th>
<th>Republic of Ireland</th>
<th>Netherlands</th>
<th>Norway</th>
<th>Sweden</th>
<th>United Kingdom</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Oxidized nitrogen (10^9 g N y^-1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry deposition</td>
<td>10.1</td>
<td>5.6</td>
<td>63.5</td>
<td>95.5</td>
<td>2.0</td>
<td>8.8</td>
<td>10.7</td>
<td>30.1</td>
<td>58.2</td>
<td>284.5</td>
</tr>
<tr>
<td>Wet deposition, attributed unattributed</td>
<td>24.0</td>
<td>20.8</td>
<td>231.4</td>
<td>213.3</td>
<td>6.8</td>
<td>22.6</td>
<td>55.1</td>
<td>117.8</td>
<td>67.3</td>
<td>759.1</td>
</tr>
<tr>
<td></td>
<td>1.3</td>
<td>1.8</td>
<td>22.4</td>
<td>10.2</td>
<td>2.9</td>
<td>1.4</td>
<td>13.3</td>
<td>18.4</td>
<td>10.0</td>
<td>81.7</td>
</tr>
<tr>
<td><strong>Total deposition</strong></td>
<td>35.4</td>
<td>28.2</td>
<td>317.3</td>
<td>319.0</td>
<td>11.7</td>
<td>32.8</td>
<td>79.1</td>
<td>166.3</td>
<td>135.5</td>
<td>1125.3</td>
</tr>
<tr>
<td><strong>Reduced nitrogen (10^9 g N y^-1)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dry deposition</td>
<td>10.8</td>
<td>14.9</td>
<td>124.3</td>
<td>66.8</td>
<td>2.0</td>
<td>7.6</td>
<td>7.8</td>
<td>33.3</td>
<td>50.2</td>
<td>318.7</td>
</tr>
<tr>
<td>Wet deposition, attributed unattributed</td>
<td>14.2</td>
<td>13.8</td>
<td>143.3</td>
<td>125.1</td>
<td>4.3</td>
<td>13.1</td>
<td>25.9</td>
<td>65.7</td>
<td>68.3</td>
<td>473.7</td>
</tr>
<tr>
<td></td>
<td>6.3</td>
<td>8.8</td>
<td>112.0</td>
<td>50.9</td>
<td>14.4</td>
<td>6.9</td>
<td>66.4</td>
<td>92.1</td>
<td>50.1</td>
<td>407.9</td>
</tr>
<tr>
<td><strong>Total deposition</strong></td>
<td>31.3</td>
<td>37.5</td>
<td>380.6</td>
<td>242.8</td>
<td>20.7</td>
<td>27.6</td>
<td>100.1</td>
<td>191.1</td>
<td>168.6</td>
<td>1200.3</td>
</tr>
</tbody>
</table>
The principal conclusions are given below:

Model and observations are in striking conflict over rural nitric oxide and nitrogen dioxide concentrations, whereas good agreement can be claimed for sulphur dioxide concentrations at the same or similar sites.

Nighttime motor vehicle, combustion and soil exhalation NO₂ emissions in rural areas in combination with shallow nocturnal boundary layer depths may partially explain the large underestimation of rural NO and NO₂ concentrations in the model.

The observational database for gaseous ammonia and nitric acid is inadequate to test model calculations.

The model and observations are in good agreement for sulphate and nitrate aerosol but the observational database for ammonium in aerosol is not adequate to allow any firm conclusions to be drawn.

Model precipitation concentrations require correction for background sources not considered in the model formulation. Model nitrate and sulphate concentrations in precipitation appear to be in good agreement with observations, whereas ammonium concentrations are underpredicted.

Washout of sulphur dioxide may account for the high precipitation sulphate concentrations observed in some areas close to the major SO₂ sources.

Additional ammonia sources may be required to balance the observed regional wet deposition of ammonium.

The model budgets of oxidized nitrogen show a negligible contribution from background, unattributed sources in contrast with the sulphur and reduced nitrogen budgets.

Wet deposition predominates over dry deposition by an appreciable factor in the model nitrogen budgets but not in the regional nitrogen budgets given in the literature.

The model suggests that the scavenging of pollutants from the gas phase into aerosol and precipitation may compete efficiently against dry deposition as a removal process for both oxidized and reduced nitrogen-containing trace gases.

The model and its comparison with observations require further extension to address the contributions from each wind direction sector and seasonal variation. This work is the subject of a continuing study.

Acknowledgments

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