

Modelling the Deposition and Concentration
of Long Range Air Pollutants:
Final Report

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Executive Summary

- The FRAME Atmospheric Transport Model has been developed as a flexible multiple scale tool. The model can be applied to estimate the concentration and deposition of sulphur and nitrogen compounds at resolutions of 1 km and 5 km over the UK and at 50 km resolution over the EMEP European domain. The European simulation was used to generate the boundary conditions for the UK simulations.
- The model demonstrated good agreement with measurements of aerosol concentrations (sulphate, nitrate and ammonium) and gas concentrations (SO₂ and NO₂) from the UK Eutrophying and Acidifying Pollutants monitoring network. Reasonable agreement was also obtained with wet deposition measurements. A greater scatter was apparent in the correlation with measurements of NH₃ concentrations, due to the highly localised nature of their emissions.
- The development of a fine scale (1 km resolution) version of FRAME over the UK represents an important step forward in improved spatial representation of concentrations and dry deposition of both oxidised and reduced nitrogen. Improvement in spatial disaggregation of ammonia emission sources and nature reserves at 1 km resolution was found to be highly significant in assessment of exceedance of the critical level for ammonia concentration at Special Areas of Conservation and Special Protection Areas.
- The deposition of sulphur, oxidised nitrogen and reduced nitrogen in the UK is estimated to have decreased between 1990 and 2005 by 56%, 20% and 14% respectively. A strong inter-annual variability in sulphur and nitrogen deposition occurs due to changes in general circulation and precipitation which can result in fluctuations of annual deposition of +/- 10%.
- The deposition of sulphur, oxidised nitrogen and reduced nitrogen in the UK is predicted to decrease between 2005 and 2020 by 47%, 32% and 16% respectively. Reduced nitrogen deposition will become relatively more significant than oxidised nitrogen and sulphur deposition. Policy to further reduce nitrogen deposition and acid deposition will need to focus on control of emissions of ammonia.
- Emissions from international shipping currently contribute 18% and 19% respectively of the deposition of oxidised nitrogen and sulphur in the UK. With the implementation of Annex VI of the MARPOL convention, sulphur deposition from international shipping will be greatly reduced by 2020 whereas shipping emissions are likely to remain a significant source of nitrogen deposition.
- A version of FRAME has been developed to include calculation of PM₁₀ concentrations. A preliminary comparison with measurements from the UK monitoring network shows that concentrations are generally under-estimated by the model by approximately 50%. The reasons for this are thought to be due to missing chemical components (i.e. secondary organic aerosol and base cations) as well as the presence of water associated with aerosol in the measurements.

1. Background

The emission of pollutant gases (SO₂, NO_x and NH₃) from the United Kingdom, from European sources and from international shipping results in the deposition of acidifying and eutrophying species to sensitive ecosystems. The emitted gases are chemically transformed in the atmosphere to particulate matter, comprising sulphate, nitrate and ammonium aerosol, which is subject to long range transport. Deposition exceeding the critical loads for acidification and eutrophication may occur, even in regions remote from the source of emissions, such as the Scottish Highlands. Acidification affects soils and freshwater, particularly in upland areas where soils tend to be derived from base-poor rocks and annual precipitation is high. Deposition of both reduced and oxidised nitrogen results in eutrophication leading to changes in plant species composition and water quality in semi-natural habitats. In addition, secondary aerosols are of concern both regarding their potential impacts on human health (COMEAP, 2001) and their effect on visibility and the global radiative balance.

Emissions of SO₂ and NO_x in the United Kingdom have fallen by 89% and 48% during the period 1970-2005 (Dore *et al.*, 2005), with further reductions of 44% and 38%, respectively, forecast over the next 15 years (Grice *et al.*, 2005). Despite these improvements to the quality of the atmosphere, deposition of sulphate and nitrate by precipitation has responded with smaller changes than those in land-based emissions (Fowler *et al.*, 2005). One possible explanation of this observation is the role of shipping emissions of SO₂ and NO_x which, in contrast to land based emissions, have shown increases over recent decades of approximately 2.5% per year (Endresen *et al.*, 2003). The role of emissions from international shipping has been estimated to make a major contribution to levels of pollutant concentrations in Europe (Johnson *et al.*, 2000; Vestreng and Fagerli, 2005; Dore *et al.*, 2007). Furthermore, emissions of ammonia in the UK have shown more modest decreases of 18% between 1990 and 2005 (Dore *et al.*, 2005). Emissions of SO₂ and NO_x from Europe have shown similar decreases to those from the UK. However, estimating their role in contributing to acid and nutrient-nitrogen deposition in the United Kingdom has recently received more attention. The focus for future studies of modelling emissions and deposition of nitrogen and sulphur in the United Kingdom will therefore increasingly be on shipping emissions and ammonia emissions, as land based emissions of SO₂ and NO_x become relatively less important.

Sulphur and nitrogen compounds can be removed from the atmosphere by direct turbulent deposition to vegetation (dry deposition) which is an important pathway for deposition of gaseous species, SO₂, NO₂ and NH₃. For ammonia the deposition rate is particularly sensitive to the vegetation type, with high deposition rates to forest and moorland. For aerosols, as well as soluble gases (SO₂, HNO₃, NH₃) removal by precipitation (wet deposition) is an important pathway for deposition. Transport distances of chemicals may be several thousand km from their emissions source before they are deposited, depending on the chemical reactions and dry and wet removal rates of individual chemical species. Numeric atmospheric transport models are increasingly being used as a key tool to estimate the transport and deposition of nitrogen and sulphur.

The model currently used by DEFRA to estimate sulphur and nitrogen deposition in the United Kingdom is the **Fine Resolution Atmospheric Multi-pollutant Exchange model (FRAME)**. Estimates of present day S and N deposition may be derived from measurements, for example as shown for the UK by the **National Expert Group on Transboundary Air Pollution (NEG-TAP, 2001)**. The use of a canopy compensation point to generate maps of gaseous deposition to vegetation for the United Kingdom is described in Smith *et al.* (2000). Smith and Fowler (2001) describe a technique to generate maps of wet deposition for the United Kingdom by interpolation of measured concentrations of ions in precipitation. The combination of these two measurement-based data sets is referred to as **CBED (Concentration Based Estimated Deposition)** and is used to inform DEFRA about current levels of nitrogen and sulphur deposition in the United Kingdom.

The importance of protecting sensitive ecosystems from environmental damage has led to several international and European agreements. These include the 1999 Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, under the UNECE **Convention on Long-Range Transboundary Air Pollution (CLRTAP)** and the European Community **National Emissions Ceiling Directive (NECD)**. These agreements lay down targets for nation states to achieve reductions of

emissions of SO₂, NO_x and NH₃ by the year 2010. The UK Government and the devolved administrations published an **Air Quality Strategy** for England, Scotland, Wales and Northern Ireland (AQS) in 2000 (DETR, 2000) in January 2000. It sets air quality standards and objectives for eight key pollutants to be achieved between 2003 and 2008. For seven of these pollutants local authorities are charged with the task of working towards the objectives in a cost effective way. The standards and objectives are subject to regular review to take account of the latest information on the health effects of air pollution and technical and policy developments. Assessment of the environmental impact of the strategy is given in Stedman *et al.* (2006) and Hall *et al.* (2006).

Measurement-based estimates have been used successfully as an environmental assessment tool for past or present conditions. Assessment of future scenarios, however, requires the application of models linked to atmospheric emission changes. Measurements also have a limited spatial resolution, and uncertainty arises in the interpolation of concentrations and deposition between measurement sites. The spatial resolution of model estimates is limited either by the resolution of input data such as land use and emissions (which are available at a 1 km resolution for the United Kingdom) or by computational restrictions. Furthermore, for the assessment of the terms in mass-consistent budgets (emissions, deposition, import and export), atmospheric transport models are invaluable. Models are necessary for the establishment of source–receptor relationships for integrated assessment modelling and for estimating the contribution to S and N deposition from international shipping and from import from European sources.

The EMEP Eulerian Unified model (Tarrasón, *et al.*, 2003) is used to estimate sulphur and nitrogen deposition across Europe. Calculations are driven by HIRLAM, a Numerical Weather Prediction Model (NWP). The model incorporates emissions of SO₂, NO_x, NH₃, NMVOC, CO and PM_{2.5} and PM₁₀. The EMEP model includes a detailed treatment of three-dimensional transport and diffusion of air pollutants, as well as atmospheric chemical reactions and particle size distribution. Due to the continent scale size of the EMEP domain, it is restricted to operating on a 50 km grid with a vertical resolution in the lowest layer of 92 m. For national scale assessments, a 50 km scale is insufficient to resolve the finer scale distribution of land use, precipitation and emissions of pollutant gases. For accurate estimation of ammonia concentrations and dry deposition of ammonia, a model with a fine vertical resolution is essential. Increasingly there is a need to apply atmospheric transport models to estimating the relative roles of different emissions sources in contributing to acid and nutrient nitrogen deposition. The results of such simulations may be used as input to integrated assessment calculations in order to derive the most cost efficient means of abating pollutant emissions and protecting environmental and human health. The **United Kingdom Integrated Assessment Model, UKIAM** (Oxley *et al.*, 2003) has been developed to estimate the relative cost efficiency of abating emissions from different regions, at a county level, and point sources using sulphur and nitrogen deposition footprints from the FRAME model. Based on the above considerations, the requirements for a model capable of accurately estimating ground level gas and particulate concentrations, capturing the fine scale features of emissions of NO_x and NH₃ and of wet deposition in upland regions, as well as performing multiple simulations (of up to 100) for source-receptor applications may be specified simply as:

- (i) Fine horizontal resolution
- (ii) Fine near-surface vertical resolution
- (iii) Fast run time
- (iv) Good comparison with measurements of gas and aerosol concentrations and wet deposition

FRAME is well suited to fit these needs. It is important however to consider this work in the context of parallel developments with Eulerian models driven by real time meteorology. United Kingdom versions of both the EMEP model EMEP4UK (Vieno *et al.*, 2007) and the US EPA model, CMAQ (Byun and Schere, 2006) are currently under development. These models use detailed meteorological data to simulate atmospheric transport, including the effects of curved movement of air trajectories and lateral dispersion. They are therefore have the capability of achieving a better

representation of nitrogen and sulphur deposition than FRAME following their successful application. The time scale for the Eulerian models to surpass FRAME in accuracy of representing wet and dry deposition, as well as gas and particle concentrations, is not known, but can realistically be expected to occur within the few years. It is important to note, however, that a Eulerian model is unlikely to entirely replace FRAME in the short term. Future parallel development and regular inter-comparison of these modelling systems will be important. The following points emphasise the need for parallel development of modelling applications:

- (1) In the Eulerian chemical transport models, wet deposition is calculated using precipitation generated from a Numerical Weather Prediction Model (NWP). In a Lagrangian trajectory model such as FRAME, wet deposition is calculated using measurements of precipitation. Significant improvements in NWP models may therefore be necessary before the Eulerian models are capable of estimating wet deposition as effectively as FRAME.
- (2) The execution time for a full year by a Eulerian model, such as EMEP4UK run on a similar horizontal grid to FRAME, is estimated at approximately 8 hours using the CEH Nemesis parallel supercomputer. This compares with 20 minutes for a FRAME simulation. Eulerian models are therefore unsuitable for source-receptor calculations involving approximately 100 model runs with current computer technology.
- (3) The development of a 1 km version of FRAME is currently been undertaken. This fine scale resolution is currently an unrealistic aspiration for a Eulerian model with a UK domain due to computational considerations.

Simple models such as FRAME, HARM (Metcalf *et al.*, 2001) and TRACK (Lee *et al.*, 2000) are therefore expected to continue to play an important role in regulation and policy concerning emissions of air pollutants. Their fast run time is of particular importance for source attribution studies (Oxley *et al.*, 2003), uncertainty studies (Page *et al.*, 2004) and fine resolution national scale modelling studies (Hallsworth *et al.*, 2009 ; Dore *et al.*, 2006b).

2. Description of FRAME

2.1 History

The **FRAME** (**F**ine **R**esolution **A**tmospheric **M**ulti-pollutant **E**xchange) model is a Lagrangian atmospheric transport model used to assess the long-term annual mean deposition of reduced and oxidised nitrogen and sulphur over the United Kingdom. A detailed description of the FRAME model is contained in Singles *et al.* (1998). Fournier *et al.* (2003) describe the development of a parallelised version of the model with an extended domain that includes Northern Ireland and the Republic of Ireland. The model was developed from an earlier European scale model, **TERN** (**T**ransport over **E**urope of **R**educed **N**itrogen, ApSimon *et al.* 1994). FRAME was developed initially to focus, in particular, on transport and deposition of reduced nitrogen and was named the **F**ine **R**esolution **A**Mmonia **E**xchange model. Subsequently, FRAME was developed to improve the representation of sulphur and oxidised nitrogen (Fournier *et al.*, 2004). The developments included: the introduction of a fine angular resolution of 1° between trajectories; the generation of a point source database including stack parameters (stack height, stack diameter, exit temperature, exit velocity); the introduction of shipping emissions of SO₂ and NO_x. Following these changes, a robust multi-chemical species tool was developed. The new name reflects these changes whilst preserving the familiar acronym. The current version of FRAME is 5.8

2.2 FRAME Model Domain

The domain of FRAME covers the British Isles with a grid resolution of 5 km and grid dimensions of 172 x 244. Input gas and aerosol concentrations at the edge of the UK FRAME domain are calculated using **FRAME-EUROPE**, a larger scale European simulation which was developed from TERN to run a statistical model over the entirety of Europe with a 150 km scale resolution.

While FRAME is usually referred to as a Lagrangian model, strictly speaking it combines elements of both Lagrangian and Eulerian approaches: the lateral dispersion is Lagrangian, so that the model simulates an air column moving along straight-line trajectories over the UK. However, the model atmosphere is divided into 33 separate layers extending from the ground to an altitude of 2500 m, and the diffusion between these layers (using the finite volume approach) is effectively Eulerian in nature. FRAME is unique in regional scale dispersion models in having an extremely detailed vertical resolution: Layer thicknesses vary from 1 m at the surface to 100 m at the top of the domain. Separate trajectories are run at a 1° resolution for all grid edge points. Wind frequency and wind speed roses (Dore *et al.* 2006a) are used to give the appropriate weighting to directional deposition and concentration for calculation of total deposition and average concentration.

2.3 Emissions

Emissions of ammonia are estimated for each 5 km grid square using the AENEID model (Atmospheric Emissions for National Environmental Impacts Determination) that combines data on farm animal numbers (cattle, poultry, pigs, sheep and horses), with land cover information, as well as fertiliser application, crops and non-agricultural emissions (including traffic and contributions from human sources, wild animals etc). The AENEID model is described in Dragosits *et al.* (1998) and is now updated as a contribution of CEH to the National Atmospheric Emissions Inventory (NAEI, <http://www.naei.org.uk/>) and the National Ammonia Reduction and Strategies Evaluation System (NARSES). NH₃ is input to the lowest layer for emissions from sheep, fertiliser application and non-agricultural sources. Emissions from cattle, poultry and pigs are input to deeper surface layers depending on the relative time spent grazing and in housing. Emissions of SO₂ and NO_x are taken directly from the **N**ational **A**tmospheric **E**missions **I**nventory (**NAEI**, www.naei.org.uk). 900 individual point sources are included with detailed information on stack parameters from 250 of these. SO₂ and NO_x background emissions are divided into SNAP code emissions sector with the depth of

surface layer into which emissions are input selected according to emissions source. This division of emissions in FRAME directly into the SNAP codes allows ready exchange of information with the NAEI, and smooth running of scenarios based on emission controls applied to particular source sectors.

2.4 Plume Rise

Point source emissions of SO₂ and NO_x are treated individually with a plume rise model which uses stack height, stack diameter, exit temperature and exit velocity to calculate an 'effective emissions height'. The plume reaches its maximum height when its temperature is equal to that of the surrounding environment and its momentum is dissipated. Buoyancy forces dominate the plume rise, which is parameterised separately for stable conditions and for neutral and unstable conditions according to the Pasquill-Gifford stability classes. The incorporation of this parameterisation into FRAME has led to a substantial improvement in model performance for predicted SO₂ concentrations in relation to measurements from the rural SO₂ network (Vieno, 2005, 2009)

2.5 Diffusion

Diffusion of gaseous and particulate species in the vertical is calculated using K-theory eddy diffusivity and solved with a Finite Volume Method (Vieno, 2005). The vertical diffusivity K_Z has a linearly increasing value up to a specified height H_Z and then remains constant (K_{max}) to the top of the boundary layer. During daytime, when diffusivity depends on a combination of mechanical and convective mixing, H_Z is taken as 200 m and K_{max} is a function of the boundary layer depth and the geostrophic wind speed. At night time these values depend on the Pasquill stability class.

2.6 Chemistry

The chemical scheme in FRAME is similar to that employed in the EMEP Lagrangian model (Barrett and Seland, 1995). The prognostic chemical variables calculated in FRAME are: NH₃, NO, NO₂, HNO₃, PAN, SO₂, H₂SO₄, as well as NH₄⁺, NO₃⁻ and SO₄⁻ aerosol. For oxidised nitrogen, a suite of gas phase reactions is considered. These include photolytic dissociation of NO₂, oxidation of NO by ozone, formation of PAN (peroxyacetyl nitrate) and the creation of nitric acid by reaction with the OH free radical. NH₄NO₃ aerosol is formed by the equilibrium reaction between HNO₃ and NH₃. A second category of large nitrate aerosol is present and simulates the deposition of nitric acid on to soil dust or marine aerosol. The formation of H₂SO₄ by gas phase oxidation of SO₂ is represented by a predefined oxidation rate. H₂SO₄ then reacts with NH₃ to form ammonium sulphate aerosol. The aqueous phase reactions considered in the model include the oxidation of S(IV) by O₃, H₂O₂ and the metal catalysed reaction with O₂.

2.7 Wet Deposition

The FRAME model employs a constant drizzle approach using precipitation rates calculated from a climatological map of average annual precipitation for the British Isles. Wet deposition of chemical species is calculated using scavenging coefficients based on those used in the EMEP model. An enhanced washout rate is assumed over hill areas due to the scavenging of cloud droplets by the seeder-feeder effect. The washout rate for the orographic component of rainfall is assumed to be twice that calculated for the non-orographic component (Dore *et al.*, 1992). The model incorporates the directional dependence of orographic rainfall by considering two components of rainfall: non-orographic precipitation, which has no directional dependence, and orographic precipitation, which is directionally dependent and stronger for wind directions associated with humid air masses. The directional orographic rainfall model is described in detail by Fournier *et al.* (2005a).

2.8 Dry Deposition

Dry deposition of SO₂, NO₂ and NH₃ is calculated individually to five different land categories (arable, forest, moor-land, grassland and urban). For ammonia, dry deposition is calculated individually

at each grid square using a canopy resistance model (Singles *et al.*, 1998). The model includes an optional bi-directional canopy compensation point parameterisation (Vieno 2005) which is used in combination with monthly emissions and meteorological data. In the standard model version, the NH₃ deposition velocity is generated from the sums of the aerodynamic resistance, the laminar boundary layer resistance and the surface resistance. Dry deposition of SO₂ and NO₂ is calculated using maps of deposition velocity derived by the CEH ‘big leaf’ model, CBED (Smith *et al.* 2000), which takes account of surface properties as well as the geographical and altitudinal variation of wind-speed. Other species are assigned constant values of deposition velocity.

2.9 Diurnal Cycle

The depth of the boundary layer in FRAME is calculated using a mixed boundary layer model with constant potential temperature capped by an inversion layer with a discontinuity in potential temperature. Solar irradiance is calculated as a function of latitude, time of the year and time of the day. At night time, a single fixed value is used for the boundary layer depth according to Pasquill stability class and surface wind speed.

2.10 Wind Rose

The wind rose now employed in FRAME uses 6-hourly operational radiosonde data from the stations of Stornoway, Hillsborough, Camborne and Valentia spanning a ten-year period (1991-2000) to establish the frequency and harmonic mean wind speed as a function of direction for the British Isles. This is illustrated in Figures 2(a) and 2(b) for data averaged over the ten year period. The radiosonde wind frequency rose was found by Dore *et al.* (2006a) to have close agreement with the Jenkinson objective classification for a 120-year data set.

2.11 Computational Performance

The FRAME model code is written in High Performance FORTRAN 90 and executed in parallel on a Linux Beowulf cluster comprising of 60 dual processors, (i.e. 120 processors in total). Run time for a simulation employing 100 processors is approximately 25 minutes.

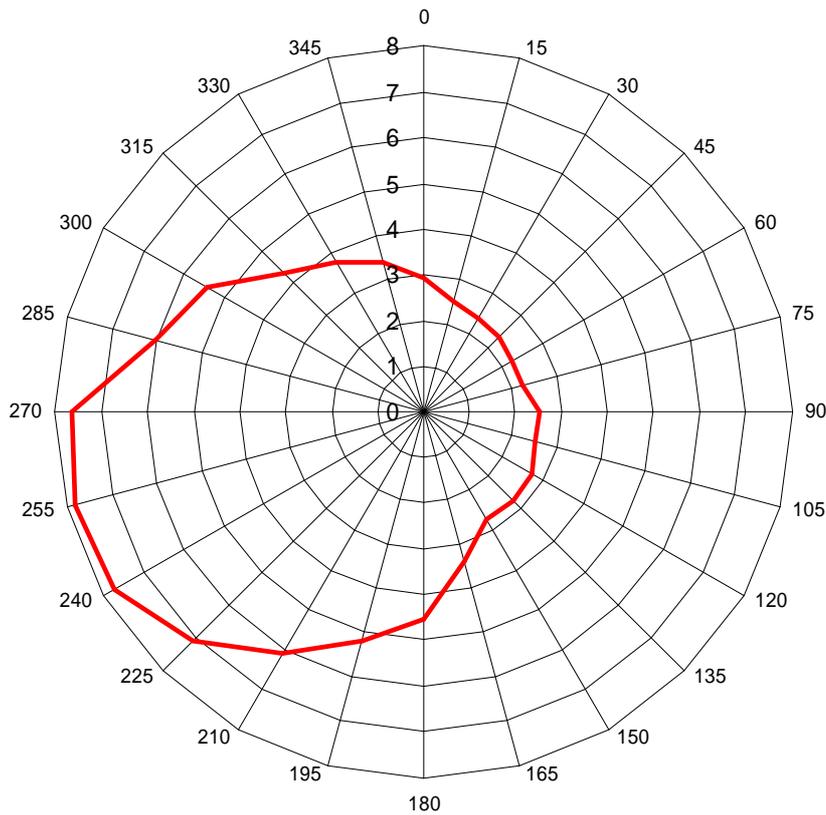


Figure 2(a) Wind frequency rose derived from radiosonde data (Dore *et al.* 2006a) as used in FRAME. Radial units are percent per 15° directional band.

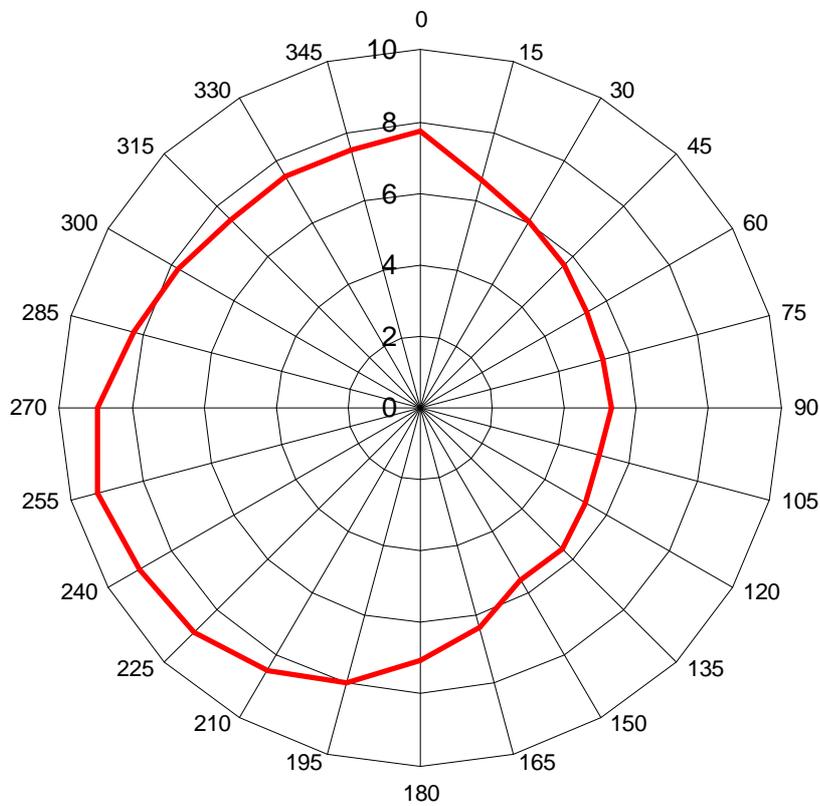


Figure 2(b) Wind speed rose (m s^{-1}) derived from radiosonde data (Dore *et al.* 2006a) as used in FRAME.

Box 1: Key features of the FRAME model.

- * 5km x 5km resolution over the British Isles (incorporating the Republic of Ireland) with grid dimensions: 244 x 172 and a 1° angular resolution in the trajectories.
- * Input gas and aerosol concentrations at the edge of the model domain are calculated with FRAME-Europe, using European emissions and running on the EMEP 150 km scale grid.
- * 33 layer Lagrangian model with an air column moving along straight-line trajectories. Layer thickness varies from 1 m at the surface to 100 m at the top of the mixing layer.
- * Emissions of SO₂ and NO_x, from 900 major point sources input at height dependent on plume rise calculation. SNAP code dependent area SO₂ and NO_x sources mixed into appropriate lower layers of the atmosphere. Source-dependent NH₃ emissions mixed into lowest surface layers.
- * Diffusion in the vertical is calculated using K-theory eddy diffusivity and solved with the Finite Volume Method.
- * Wet deposition calculated using a diurnally varying scavenging coefficient depending on mixing layer depth. A precipitation model is used to calculate wind-direction-dependent orographic enhancement of wet deposition.
- * Dry deposition for NH₃ is ecosystem specific, including a version with bi-directional NH₃ exchange. Dry deposition of NO₂ and SO₂ is derived from the CEH deposition model and is ecosystem dependent.
- * The model chemistry includes gas phase and aqueous phase reactions of oxidised sulphur and oxidised nitrogen and conversion of NH₃ to ammonium sulphate and ammonium nitrate aerosol.
- * The chemical species treated include: NH₃, NH₄⁺ aerosol, NO, NO₂, HNO₃, PAN, NO₃⁻ aerosol, SO₂, H₂SO₄ and SO₄²⁻ aerosol.
- * Current model run time: 20 minutes on CEH Edinburgh Beowulf cluster using 24 cores.

3 Inter-comparison of FRAME with EMEP and CBED deposition

Objective (ii) To compare the model with results from other UK and European models.

The mapped deposition of sulphur, oxidised nitrogen and reduced nitrogen calculated by FRAME for emissions year 2005 (using meteorology averaged over the three year period 2004-06) is shown in Figures 3.1, 3.2 and 3.3, respectively. These maps are compared to the equivalent deposition data for CBED (averaged over years 2004-2006) and for EMEP with emissions year 2005. Wet and dry nitrogen and sulphur deposition budgets for the UK for the three models are shown in table 3.1

In general, the spatial patterns of wet deposition for FRAME and CBED show close agreement. Deposition is highest in the hill areas of the Pennines and Wales, due to a combination of heavy precipitation and orographically enhanced concentrations in precipitation due to the seeder-feeder effect. The main difference in wet deposition between FRAME and CBED occurs in the north of Scotland where FRAME gives much lower estimates. This could be either due to an underestimate in concentrations of secondary particulate matter advected to the north caused by the straight line trajectory approximation in FRAME or an overestimate of orographic enhancement of deposition by the CBED procedure in the mountainous terrain. The pattern of wet deposition with the EMEP model is quite different. The EMEP model is run at a 50 km scale over Europe. The spatial distribution for wet deposition is quite different to FRAME. With FRAME, wet deposition is closely linked to the high rainfall areas whereas with EMEP wet deposition is highest in areas nearer the emissions sources. These differences occur partly due to the enhanced washout coefficient for orographic precipitation which is incorporated in FRAME and CBED but not included in EMEP. Another difference is that a constant drizzle approximation is used in FRAME whereas precipitation in EMEP is explicitly process based and can wash out material closer to its source during heavy precipitation. Wet deposition budgets with EMEP are significantly lower than FRAME.

In preliminary results from the EMEP4UK model (figure 3.4) the spatial pattern reproduces well the higher wet deposition over mountainous terrain, similar to that obtained with FRAME. This illustrates that the key challenge is to be able to capture the spatial scale of orographic precipitation. Orographic features are not well resolved when the EMEP model is run with a 50 x 50 km² grid resolution. By contrast, using the scale of 5 x 5 km² in EMEP4UK, the main features of UK orography and their influence on airflow, cloud formation, precipitation and wet deposition are resolved.

Dry deposition of sulphur (Figures 3.1(d)-(f)) shows different deposition patterns for the three data sets. With FRAME the highest deposition is closely linked to the large point sources and major industrial areas of north England as well as ports and coastal areas due to the influence of emissions from international shipping. The EMEP data show a strong SE-NW gradient in sulphur dry deposition, which is due to the strong influence of air imported from Europe. CBED generally gives lower deposition than FRAME and does not feature the point sources and ports as the data is interpolated from a rural monitoring network.

The advantages of running a fine scale trajectory model are clearly illustrated in Figure 3.2(d) for FRAME. Dry deposition of NO_y is closely correlated to road transport, and the large urban areas of Greater London, Birmingham, Manchester and the major motorways are clearly visible in this map. Overall, FRAME gives significantly lower estimates of NO_y deposition than CBED (as discussed below). An important factor in the dry deposition of oxidised nitrogen is nitric acid which contributes approximately 70% of the total NO_y deposition in CBED. The comparison of modelled HNO₃ concentrations with measurements is discussed below. This suggests that there is some underestimation of HNO₃ concentrations (and therefore deposition) in FRAME. However uncertainty in dry deposition with CBED also occurs due to interpolation of HNO₃ concentrations from a sparse monitoring network

The EMEP model gives a similar spatial distribution of NH_x dry deposition to FRAME but does not capture the fine scale resolution of deposition associated with local variation in ammonia emissions from livestock. CBED and FRAME give very similar reduced nitrogen deposition maps. This, however, is not surprising since CBED uses spatial output of ammonia concentrations from FRAME,

compensated by a measurement-model correlation to derive its fine scale spatial pattern in NH₃ dry deposition. One significant difference between FRAME and CBED is the presence of negative deposition with the CBED data in eastern England. This occurs due to the canopy compensation point parameterisation incorporated in CBED, which may result in net emissions from fertilised fields in agricultural areas.

Table 3.1: UK annual deposition budgets for FRAME, CBED and EMEP

Budget	FRAME 2005	CBED 04-06	EMEP 2005
SO_x wet (Gg S)	106	112	71
SO_x dry (Gg S)	51	30	65
SO_x total (Gg S)	157	142	136
NO_y wet (Gg N)	82	98	56
NO_y dry (Gg N)	66	87	49
NO_y total (Gg N)	148	185	105
NH_x wet (Gg N)	105	121	71
NH_x dry (Gg N)	66	62	67
NH_x total (Gg N)	171	183	138

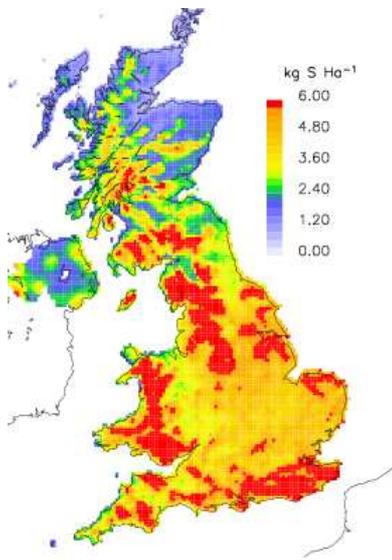


Fig. 3.1(a) FRAME 2005 SO_x wet deposition [kg S ha⁻¹ yr⁻¹]

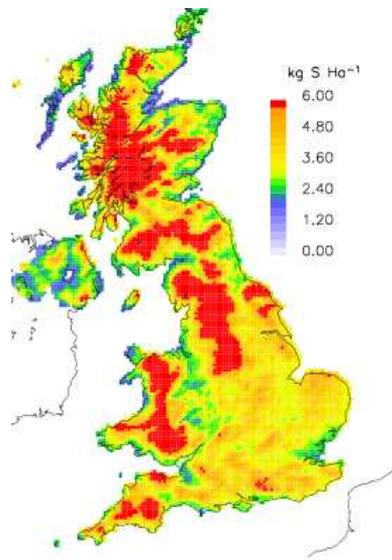


Fig. 3.1(b) CBED 2004-6 SO_x wet deposition [kg S ha⁻¹ yr⁻¹]

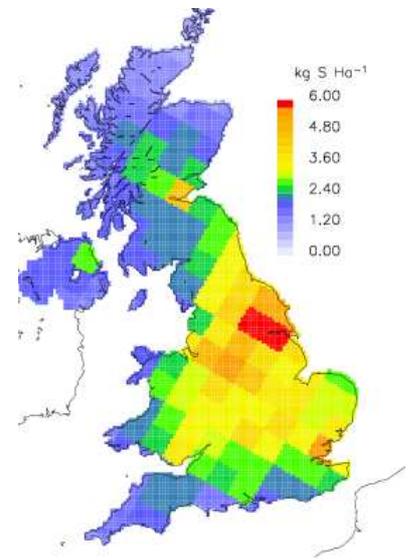


Fig. 3.1(c) EMEP 2005 SO_x wet deposition [kg S ha⁻¹ yr⁻¹]

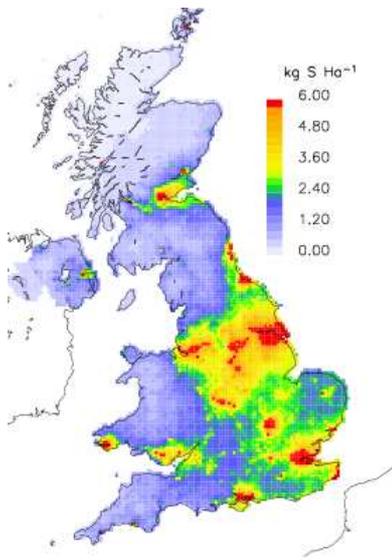


Fig. 3.1(d) FRAME 2005 SO_x dry deposition [kg S ha⁻¹ yr⁻¹]

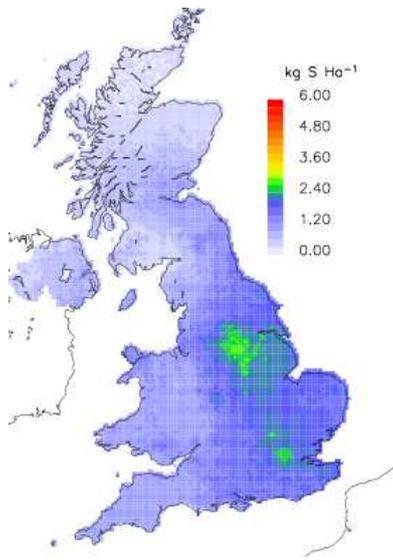


Fig. 3.1(e) CBED 2004-6 SO_x dry deposition [kg S ha⁻¹ yr⁻¹]

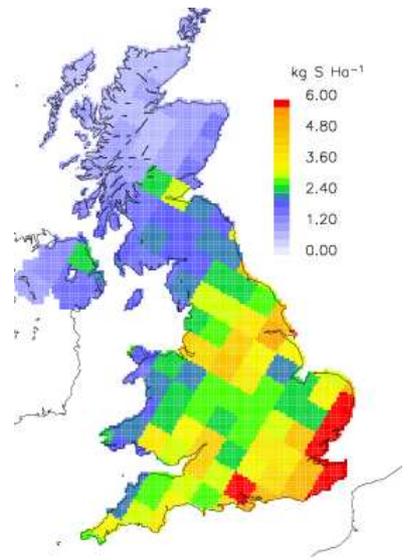


Fig. 3.1(f) EMEP 2005 SO_x dry deposition [kg S ha⁻¹ yr⁻¹]

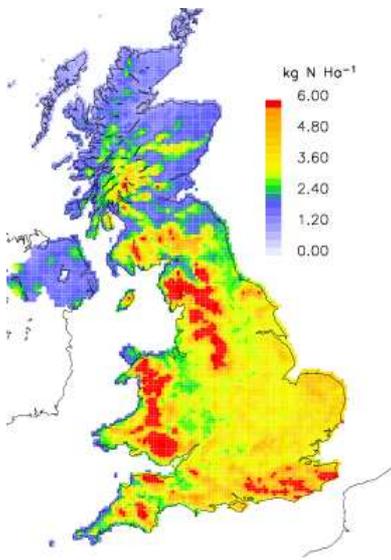


Fig. 3.2(a) FRAME 2005 NOy wet deposition [kg N ha⁻¹ yr⁻¹]

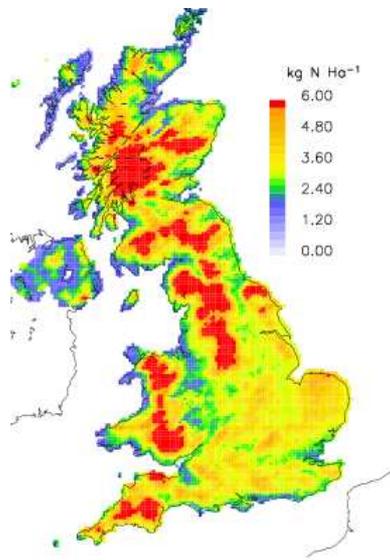


Fig. 3.2(b) CBED 2004-6 NOy wet deposition [kg N ha⁻¹ yr⁻¹]

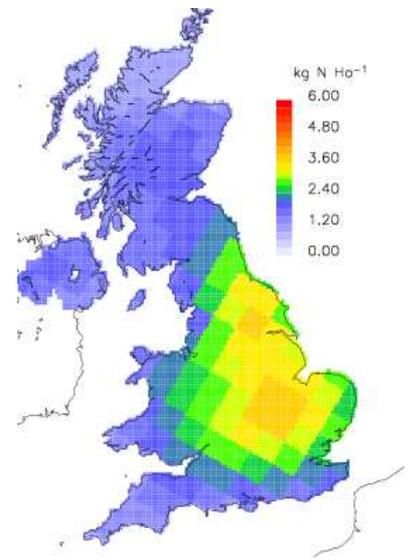


Fig. 3.2(c) EMEP 2005 NOy wet deposition [kg N ha⁻¹ yr⁻¹]

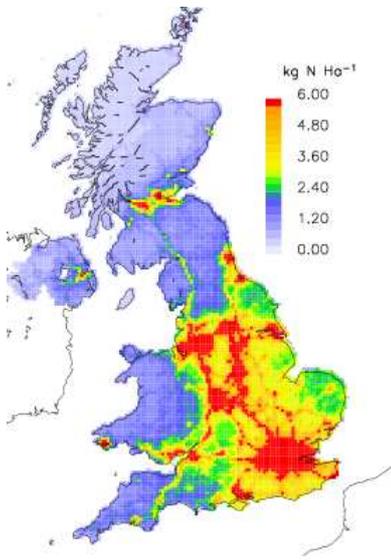


Fig. 3.2(d) FRAME 2005 NOy dry deposition [kg N ha⁻¹ yr⁻¹]

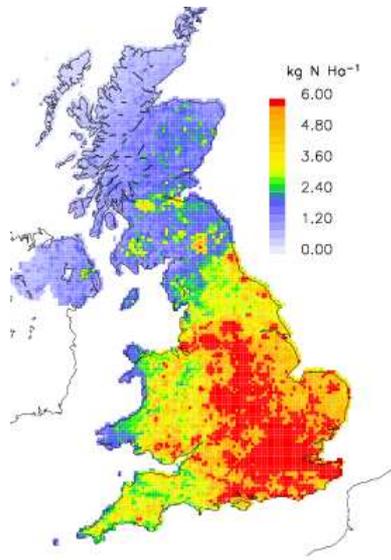


Fig. 3.2(e) CBED 2004-6 NOy dry deposition [kg N ha⁻¹ yr⁻¹]

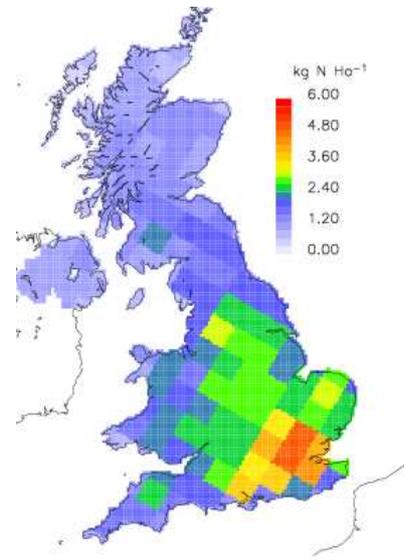


Fig. 3.2(f) EMEP 2005 NOy dry deposition [kg N ha⁻¹ yr⁻¹]

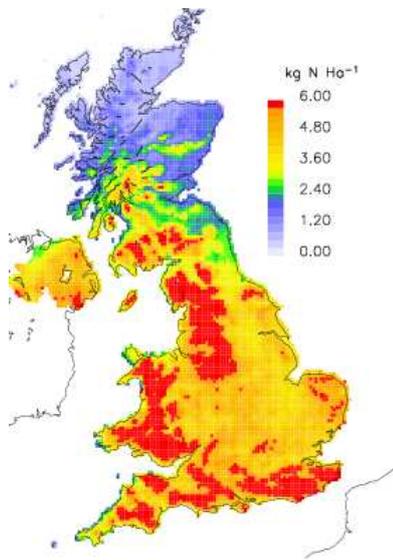


Fig. 3.3(a) FRAME 2005 NH_x wet deposition
[kg N ha⁻¹ yr⁻¹]

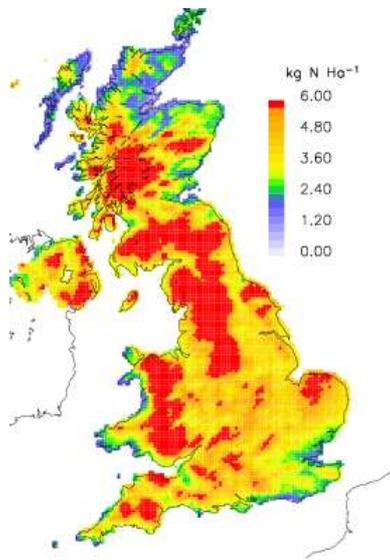


Fig. 3.3(b) CBED 2004-6 NH_x wet deposition
[kg N ha⁻¹ yr⁻¹]

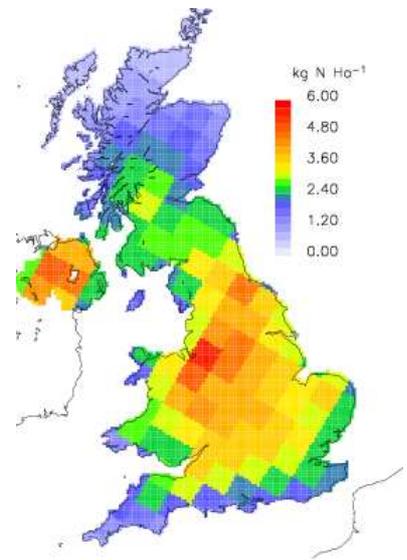


Fig. 3.3(c) EMEP 2005 NH_x wet deposition
[kg N ha⁻¹ yr⁻¹]

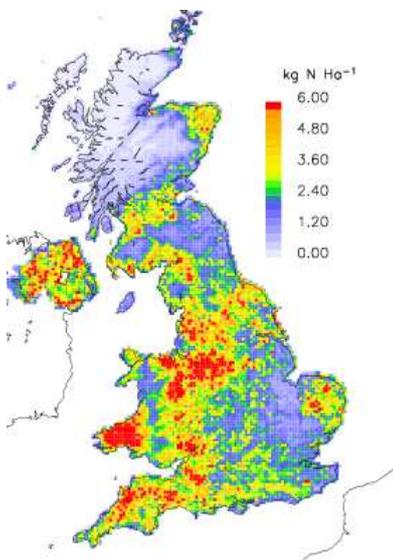


Fig. 3.3(d) FRAME 2005 NH_x dry deposition
[kg N ha⁻¹ yr⁻¹]

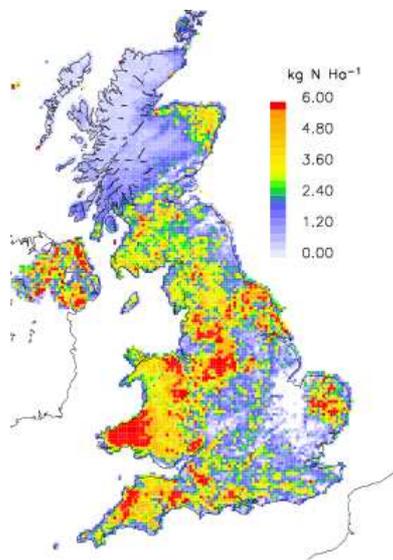


Fig. 3.3(e) CBED 2004-06 NH_x dry deposition
[kg N ha⁻¹ yr⁻¹]

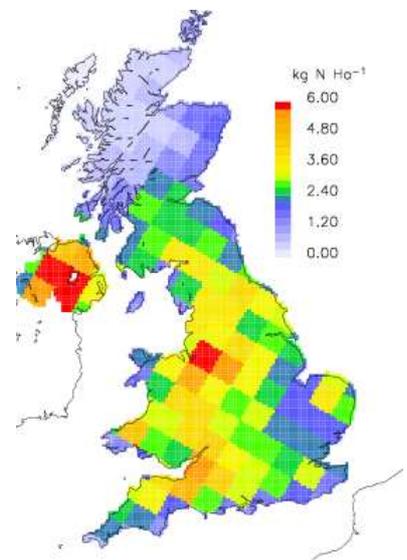


Fig. 3.3(f) EMEP 2005 NH_x dry deposition
[kg N ha⁻¹ yr⁻¹]

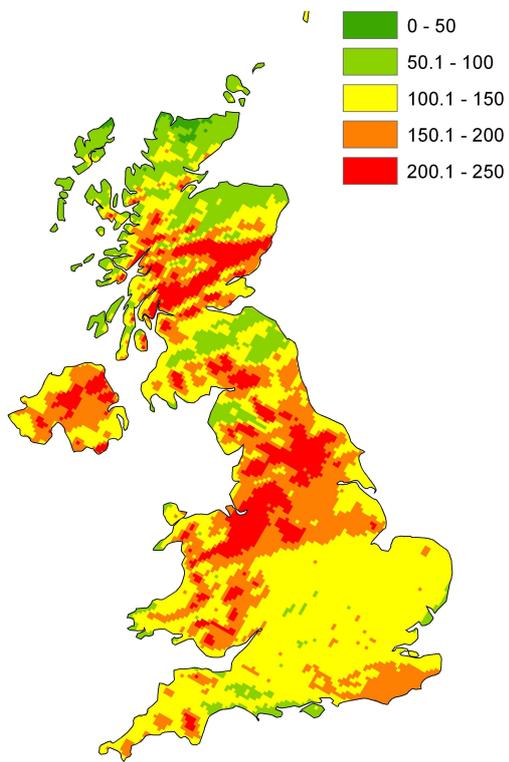


Figure 3.4: EMEP4UK annual NH_x wet deposition for the year 2003 ($\text{mg N m}^{-2} \text{yr}^{-1}$)

4 Correlation of FRAME with measurements from the national monitoring networks

Objective (iii) To compare the results of the model with measurements of gas and aerosol concentrations and wet deposition from the UK national monitoring networks.

A direct assessment of the accuracy of FRAME in estimating atmospheric concentrations and deposition rates of gaseous and particulate compounds of nitrogen and sulphur can be made by comparison with measurements. For this purpose, data from the National Ammonia Monitoring Network and the National Nitric Acid Monitoring Network using monthly sampling from **DELTA** samplers (**DE**nuder for **L**ong **T**erm **A**nalysis, Sutton *et al.*, 2001) were employed (gas phase and aerosol concentrations), together with results from the rural SO₂ and NO₂ networks and the UK wet deposition network. The modelled data for the year 2005 have been compared with measurements of gas and aerosol concentrations. Concentrations of NO₂ were taken from the rural monitoring network using diffusion tubes. Wet deposition was obtained from the secondary acid precipitation monitoring network, comprising fortnightly collections of precipitation from 38 sites with ion concentrations analysed by ion chromatography. All monitoring data were averaged over the three-year period 2004-2006 to smooth out inter-annual anomalies. The model was also driven with precipitation and wind statistics averaged over the same three year period.

The results of these scatter plots are illustrated in Figure 4(a)-(j) for the primary emitted gases (SO₂, NO₂, NH₃), wet deposition and aerosol concentrations for sulphate, nitrate and ammonium and nitric acid concentration. A summary of the correlation statistics is given in table 4.1. In general the model is able to well reproduce the measured concentrations of SO₂ and NO₂. A good correlation is found with measurements of sulphate, nitrate and ammonium aerosol concentrations, though there is some overestimate of sulphate and nitrate aerosol concentrations. Modelled wet deposition also shows a reasonable correlation with measurements. A considerable scatter is apparent in the correlation with measurements of ammonia concentration. This is caused by the very local scale variability in ammonia concentrations on a scale unresolved by the model 5 km grid. There is also considerable uncertainty in mapping ammonia emissions from certain livestock categories. Improvements to national scale modelling of dry deposition of reduced nitrogen will require the development of models with a higher horizontal resolution. A poor correlation and underestimation is also found with nitric acid concentrations. This secondary compound is reactive, soluble and readily deposited to vegetation and therefore presents a greater challenge to be well represented in atmospheric transport models.

Fig. 4(a) Modelled SO₂ concentration correlation with measurements

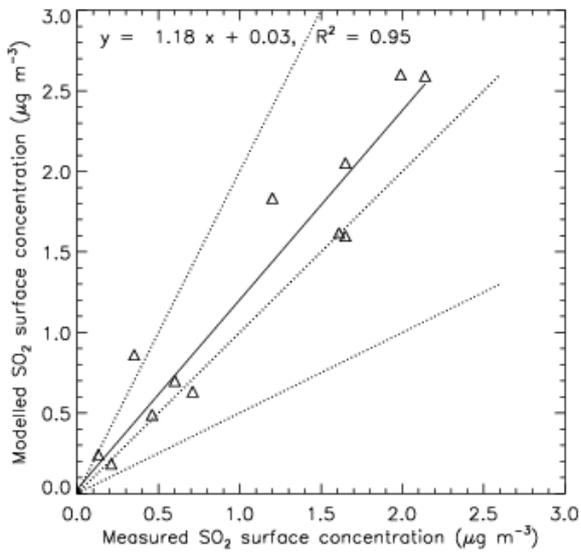


Fig. 4(b) Modelled SO₄⁻ concentration correlation with measurements

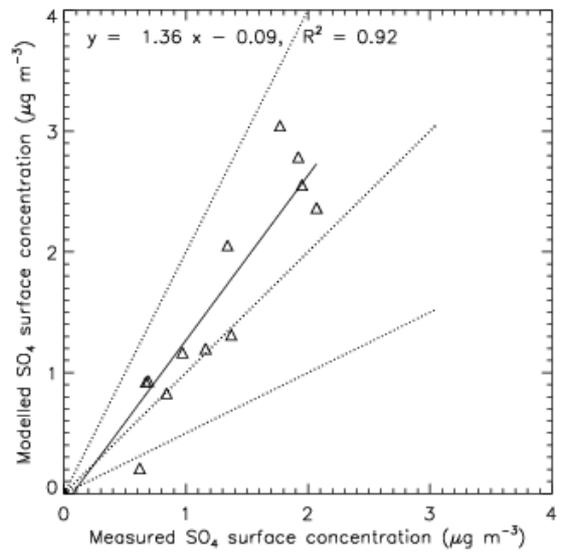


Fig. 4(c) Modelled NO₂ concentration correlation with measurements

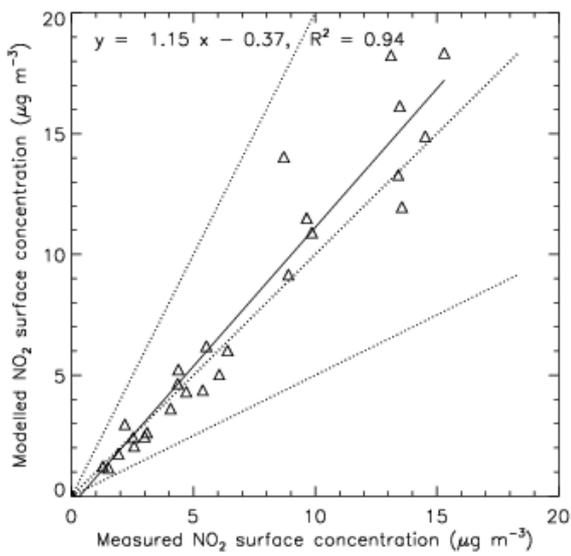
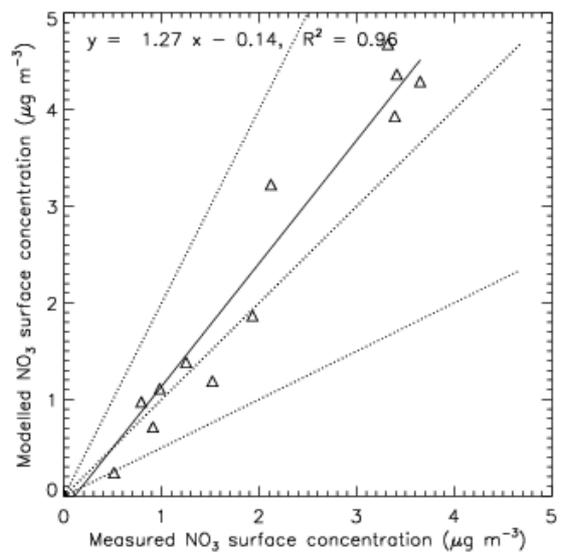


Fig. 4(d) Modelled NO₃⁻ concentration correlation with measurements



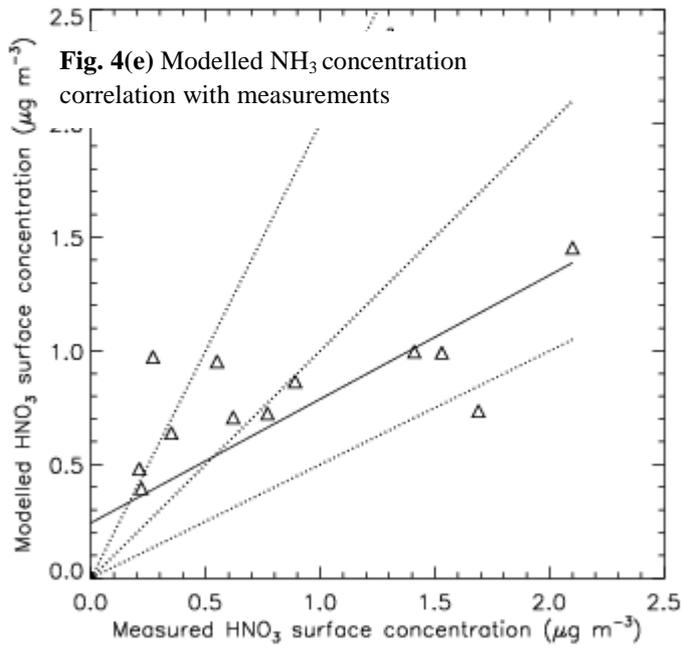


Fig. 4(e) Modelled NH_3 concentration correlation with measurements

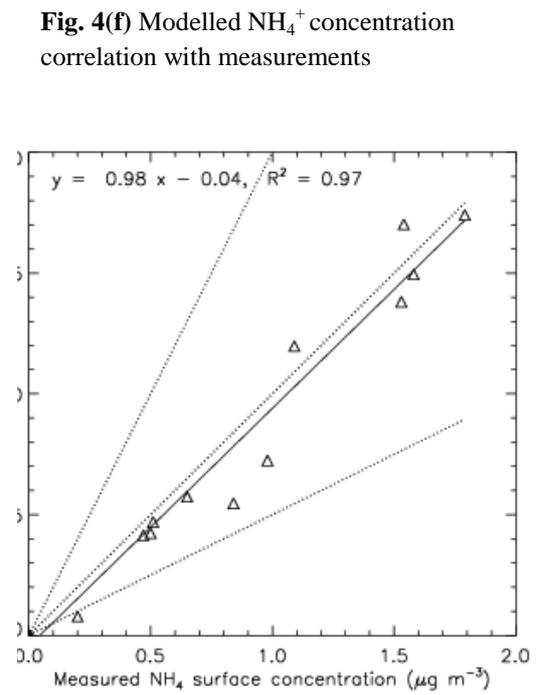


Fig. 4(f) Modelled NH_4^+ concentration correlation with measurements

Fig. 4(g) Modelled HNO_3 concentration correlation with measurements

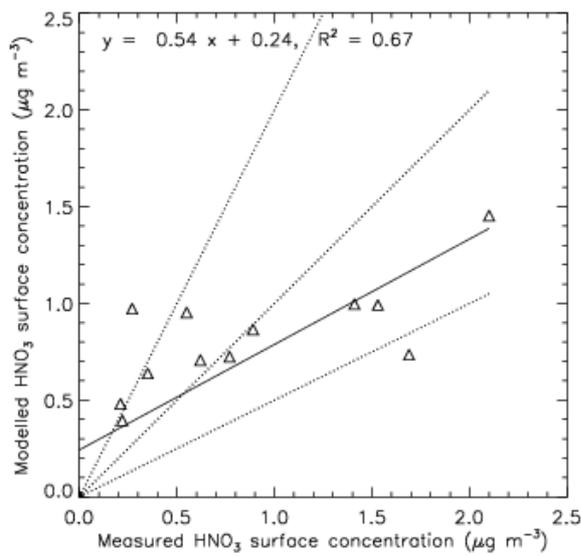
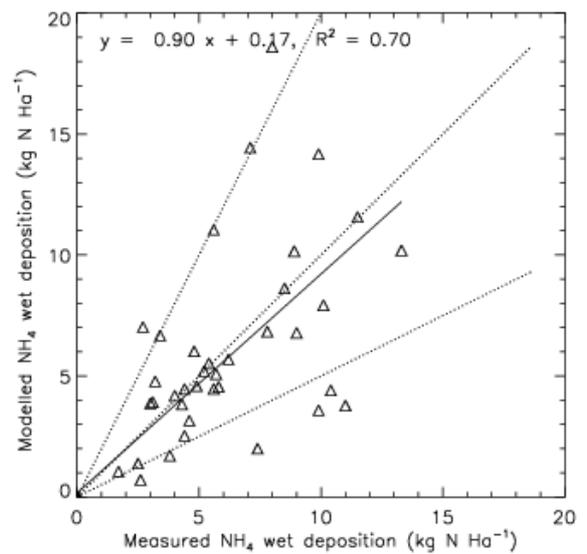


Fig. 4(h) Modelled NH_4^+ wet deposition correlation with measurements



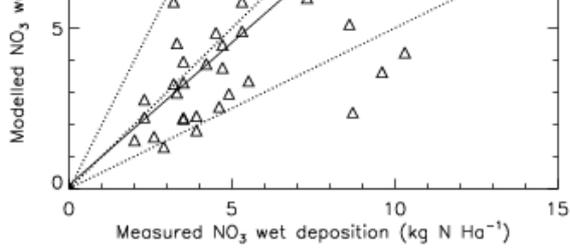


Fig. 4(i) Modelled NO_3^- wet deposition correlation with measurements

Fig. 4(j) Modelled SO_4^{2-} wet deposition correlation with measurements

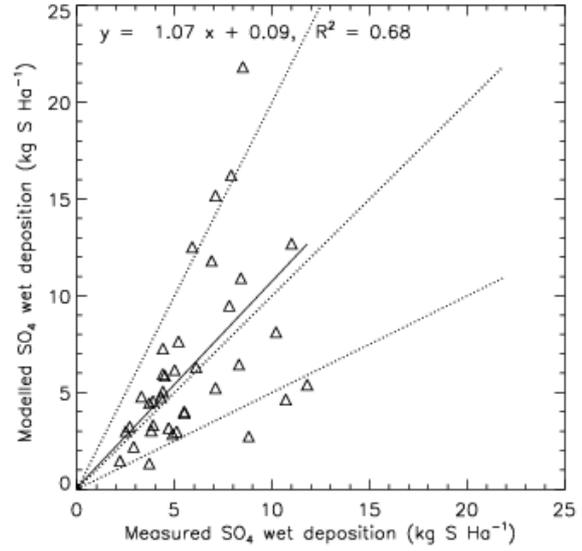
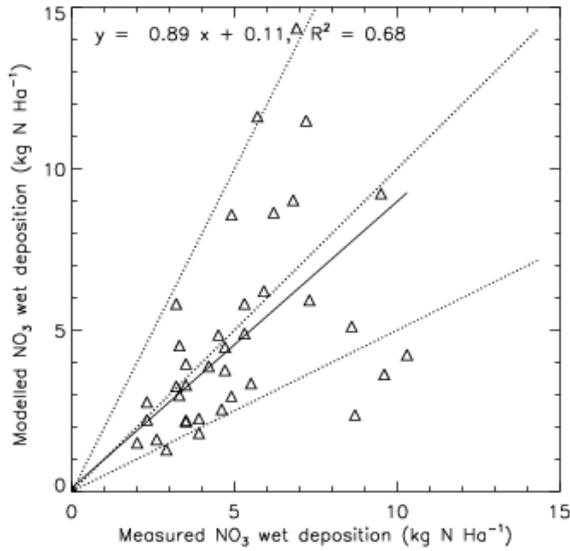


Table 4: Parameters for the linear regression $y_{(\text{modelled})} = m * x_{(\text{measured})} + c$, R^2 is the correlation coefficient and % is the per.centage of modelled values greater than half and less than twice the measured value

	m	C	R²	%
SO ₂ concentration	1.18	+0.03	0.95	92
SO ₄ ²⁻ concentration	1.36	-0.09	0.92	92
NO ₂ concentration	1.15	-0.37	0.94	100
NO ₃ ⁻ concentration	1.27	-0.14	0.96	92
NH ₃ concentration	0.90	+0.87	0.49	57
NH ₄ ⁺ concentration	0.98	-0.04	0.97	92
HNO ₃ concentration	0.54	+0.24	0.67	75
SO ₄ ⁻ wet deposition	1.07	+0.08	0.68	78
NO ₃ ⁻ wet deposition	0.89	+0.11	0.68	81
NH ₄ ⁺ wet deposition	0.90	+0.17	0.70	76

5. Source Receptor Matrices for the UKIAM

The National Atmospheric Emissions Inventory for the year 2003 was processed for use in FRAME model simulations to generate source-receptor matrices for the UKIAM. Area emissions sources were gridded at a 5 km resolution separately for each SNAP code for SO₂ and NO_x (and according to livestock category for NH₃). Individual point source emissions were gridded separately, including stack parameters, for use in the plume rise module. A new addition to this data set was the separation of NH₃ industrial point source emissions from the area sources (Figure 1(e)). Although the contribution of point source emissions of NH₃ (3.1 kT N) is small, and only comprises approximately 1% of total NH₃ emissions, this development allows more detailed treatment of sources which contribute to exceedance of the critical level for NH₃ with use of the plume rise parameterisation.

The footprints of concentration and deposition considered in this project included 99 simulations for the years 2003 and 2010 representing emissions from:

- 74 counties
- 22 large point sources
- remaining small point sources
- shipping
- European import

The emissions for the year 2003 were formatted for input to FRAME and the future emissions scenario for the year 2010 was generated according to the latest emissions forecasts (uep21). The FRAME code was modified to permit a batch execution of 99 simulations, with each corresponding to a different emissions abatement scenario. A post processing routine was developed to calibrate the modelled deposition and concentration footprints from each of the 99 sources according to the CBED deposition standard and to normalise the footprints of concentration and deposition to ensure that their sum matches the official total deposition for the appropriate year. A new development for this data set was the introduction of calibration of concentrations of gases (SO₂, NO_x & NH₃) and aerosols (sulphate, nitrate and ammonium) according to the linear regression for the comparison of air concentrations measured with the UK monitoring networks with FRAME modelled concentrations.

Very different spatial patterns in deposition resulting from emissions of different pollutants from different sources are evident from figures 1.5(a)-(d). Dry deposition of sulphur from shipping emissions (figure 1.5(a)) is highest in the coastal regions of south-east England. Emissions of ammonia from the county of Kent result in dry NH_x deposition restricted to the county of origin and the areas of the county border (figure 1.5(b)). Wet deposition of NO_y relates to the slower formation of HNO₃ and nitrate aerosol from its insoluble precursors, NO and NO₂. Consequently, larger transport distances are associated with this footprint (figure 1.5(c)). Further work will focus on attribution of deposition and concentrations according to emissions source by region (England, Scotland, Wales and northern Ireland) and sub-SNAP sector as well as international shipping and European sources. These are pollutant sources which can be more directly targeted by policy directives and therefore will represent a data set that is more relevant to integrated assessment modelling.

Figure 5(a) SO_y dry deposition from shipping for 2003 (Kg S Ha⁻¹)

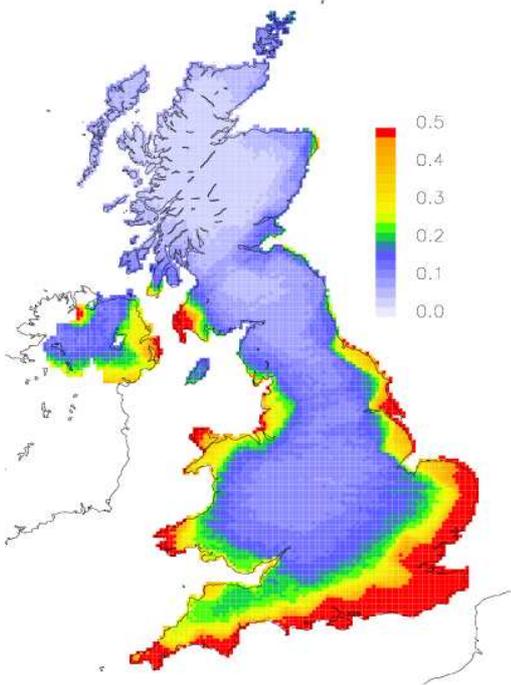


Figure 5(b) NH_x dry deposition from Kent for 2003 (Kg N Ha⁻¹)

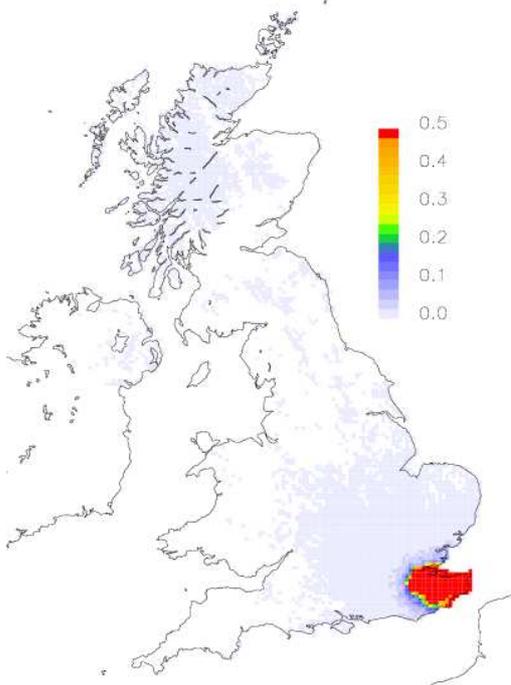
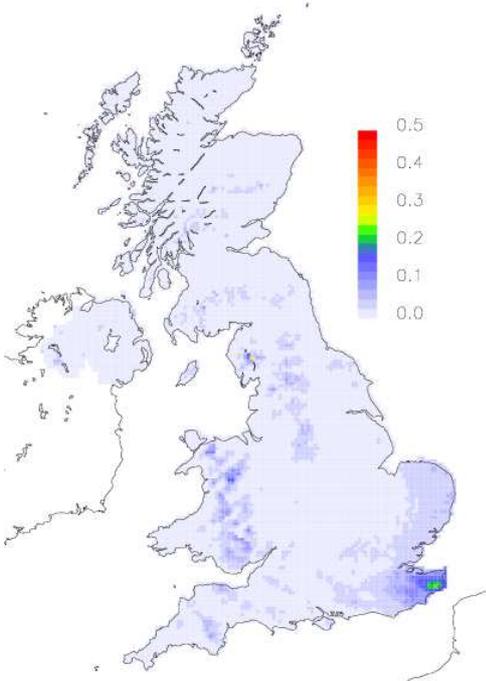


Figure 5(c) NO_y wet deposition from Kent for 2003 (Kg N Ha⁻¹)



6. Comparison of FRAME with a local dispersion model

FRAME has been used to attribute deposition of nitrogen and sulphur to individual point sources. It is therefore useful to compare the concentration and deposition generated from FRAME for a single source with the results of a local scale dispersion model, ADMS which is specially adapted to fine scale modelling of point source emissions. Two cases are considered: (i) a low level source of ammonia (a theoretical intensively farmed poultry unit); (ii) a high level source of SO₂ (Didcot power station).

6.1 NH₃ low level point source

ADMS 3 is an industry standard atmospheric dispersion model developed to estimate the impact of existing and proposed industrial installations. Emission sources can be represented as either point, line, area, volume or jet sources and the dispersion of emission plumes is assumed to be Gaussian for neutral and stable conditions with a smooth transition to non-Gaussian dispersion as the atmosphere becomes more unstable. The spread of the plumes in the vertical and cross-wind directions is determined by the vertical component of the turbulence and the standard deviation of the wind direction respectively. ADMS 3 has the ability to take into account building-induced turbulence and the effects of variable terrain. The model can also simulate both wet and dry deposition of gases and particles as well as a range of atmospheric chemical reactions.

For this study a volume source extending from the ground to a height of 1.5 m was used to simulate the ammonia emissions from a side-ventilated poultry unit. A simple scenario was used which did not take into account the effects of buildings or terrain or chemical reactions and only simulated dry deposition. This was done by manually entering a dry deposition velocity for ammonia (0.005 and 0.04 m s⁻¹ for improved grassland and woodland land covers respectively). Long term averaged wind speed and wind direction data were used in the form of a wind rose for the Midlands, as used in the SCAIL (Simple Calculation of Ammonia Impact Limits) model. This wind rose is reproduced in Figure 6.1.

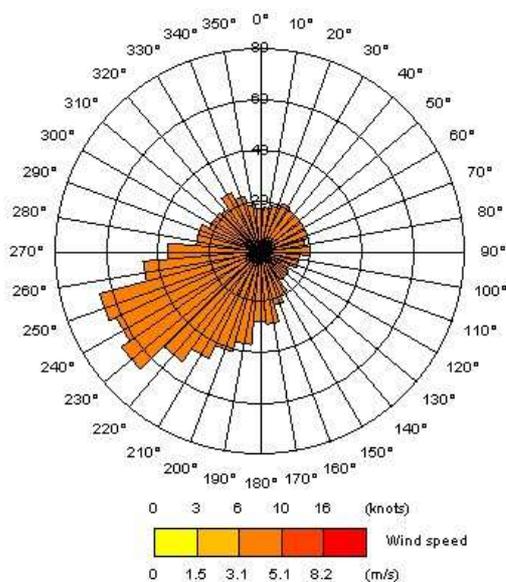


Figure 6.1 Long term Surface wind rose for the Midlands

FRAME was run with the model set up to consider only emissions of NH₃ from a theoretical typical poultry farm. The poultry unit was assumed to contain 40,000 birds, each with an annual emission of 0.5 kg NH₃, comprising a total of 2 Mg NH₃ per year. The unit was assumed to be side ventilated with emissions in the height range 1-2 m. The simulation was reduced to one of simple transport, diffusion and dry deposition by switching off both the model chemical scheme and washout from precipitation. A neutral atmospheric thermal stratification was assumed. The results from FRAME were compared with those obtained from ADMS, a local dispersion model. Two model runs were undertaken with both FRAME and ADMS, firstly with local land cover assumed to be grassland and secondly with land cover assumed to be forest. Both models assumed a deposition velocity of 5 mm s⁻¹ for grassland and 40 mm s⁻¹ for forest. For the ADMS simulation representing grassland, the model was run both with emissions evenly distributed across a 5km x 5km area, similar to FRAME, and with emissions located in a single 200 m grid square, more typical of a real poultry unit. The results of inter-comparing FRAME with ADMS for evenly distributed emissions are illustrated in Table 6.1.

Table 6.1. Comparison of ammonia concentration and NH_x dry deposition modelled with FRAME for a single 5 km grid square and ADMS modelled with a distributed 5km x 5km source.

	FRAME	ADMS
Average concentration ($\mu\text{g m}^{-3}$)	0.044	0.039
Average deposition (kg N ha^{-1})	0.056	0.050

Close agreement in estimates of concentration and deposition between the two models was found despite the very different approaches adopted in calculating vertical diffusion. For poultry farms and other intensive farming techniques, the even distribution of NH₃ emissions over a 25 km² area is clearly physically unrealistic. In reality, emissions may be confined to a single building or group of buildings. This is better represented with the local dispersion model by allocating emissions to a single 200m * 200 m grid square as illustrated in Figures 2.1(a) and 2.1(b) for grass and forest land cover respectively.

The use of the fine scale local dispersion model shows that the areas of high concentration are restricted mostly to the 1x1 km square at the centre of which is located the point of emissions. Higher concentrations are located to the north east of emissions source due to the predominance of south-westerly winds. The presence of forest land cover (Figure 2.1(b)) and its associated higher deposition velocity is clearly seen to restrict the area of high concentrations to a smaller area. Across the 5 x 5 km² domain, in the presence of forested vegetation, average concentrations with ADMS were found to 3.3 times lower and NH_x deposition 4.3 times higher than with the grassland scenario.

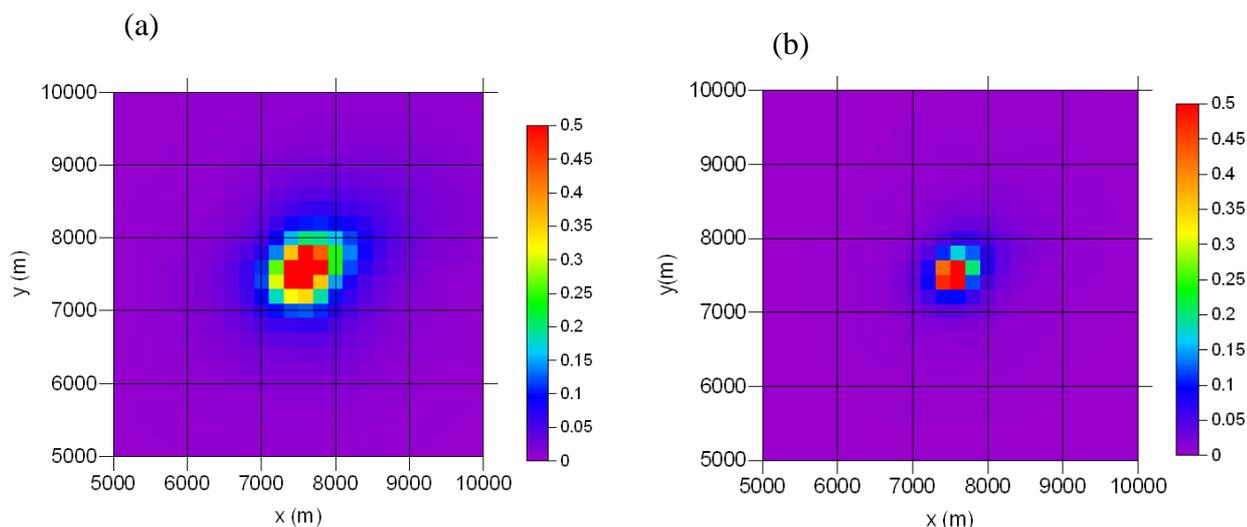


Figure 6.2: Ammonia concentration from a single point source ($\mu\text{g m}^{-3}$) modelled with ADMS: (a) grassland ; (b) forest

With the local dispersion model, it is clearly seen that ammonia concentrations associated with a single point source emitter vary by over an order of magnitude on the scale associated with a single 5 km FRAME grid cell. This gives the clear message that the current 5km resolution of national scale assessment of nitrogen deposition will have major uncertainties associated with it and in some circumstances may result in an overestimation of ammonia concentrations at sites away from the immediate proximity of point sources. This emphasises the need to develop national modelling capabilities at a finer 1 km resolution. Further comparison between the rates of vertical diffusion in FRAME and ADMS will be undertaken, as well as the inter-comparison between simulations of an elevated point source with the two models.

6.2 SO₂ Elevated point source

FRAME was compared with the results of a simulation of the ADMS local dispersion model for sulphur emissions from Didcot Power station (data supplied by Anna Theodorou and Helen ApSimon, Imperial College). The emissions characteristics of the point source are given in Table 2.2 For this simulation chemical reactions and wet deposition were switched off in FRAME in order to use a similar scenario to that with ADMS. Dry deposition of SO₂ is illustrated in Figure 2.2

Table 2.2: Emissions characteristics for sulphur dioxide source, Didcot A

Source Name	Didcot A
X(m)	451300
Y(m)	191900
Height (m)	198
Diameter (m)	12
Temperature / Density (kgm⁻³)	150
Exit Velocity (ms⁻¹)	20.6
Pollution Emission Rate (kT S-SO₂ yr⁻¹)	21

Figure 6.2 SO_y dry deposition from a single point source (Didcot A)

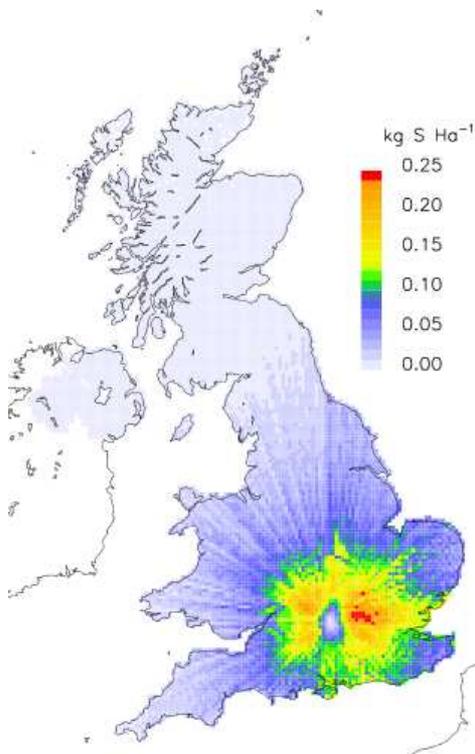


Figure 6.3(a) SO₂ concentration ($\mu\text{g m}^{-3}$) for Didcot power station modelled with ADMS

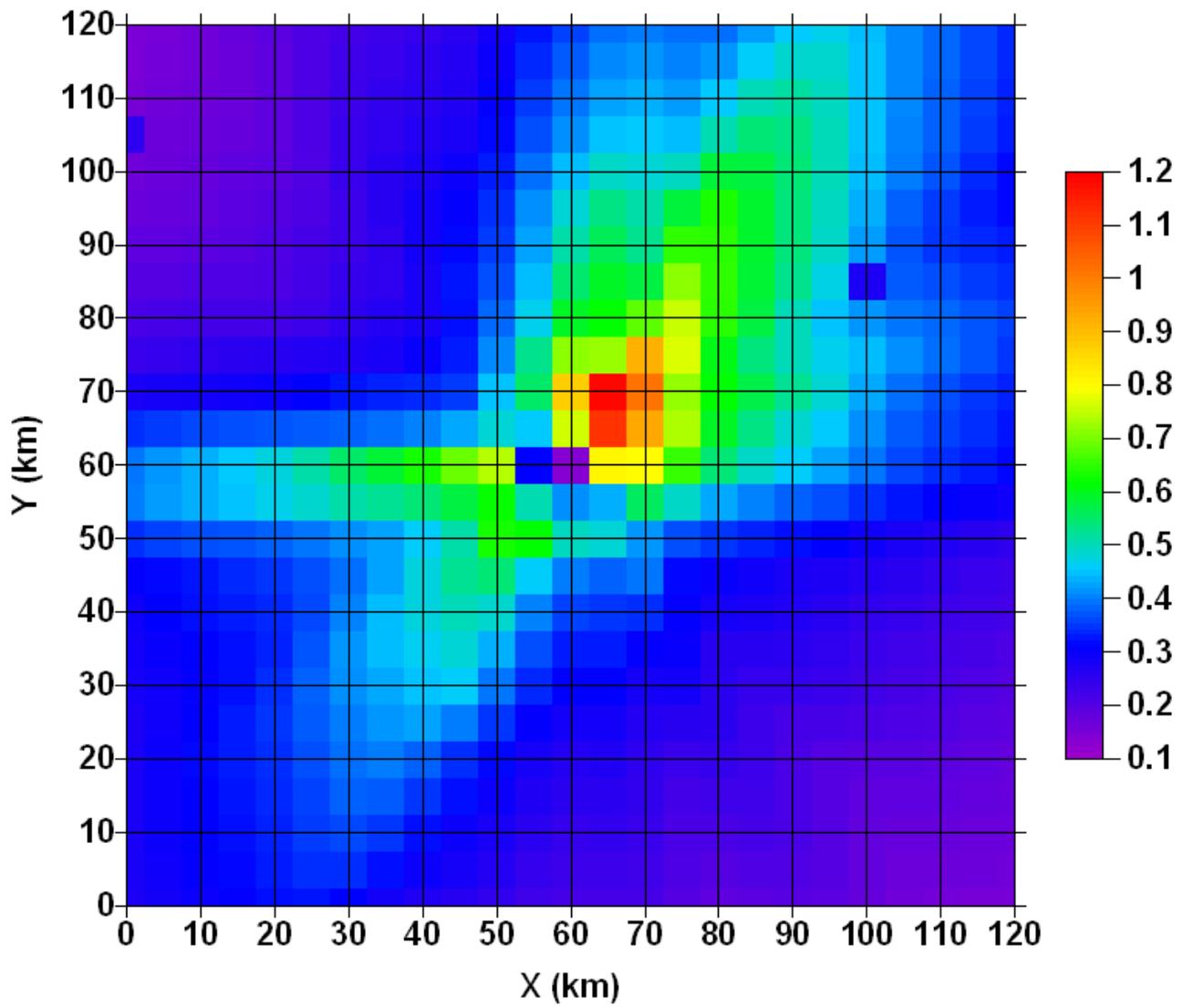
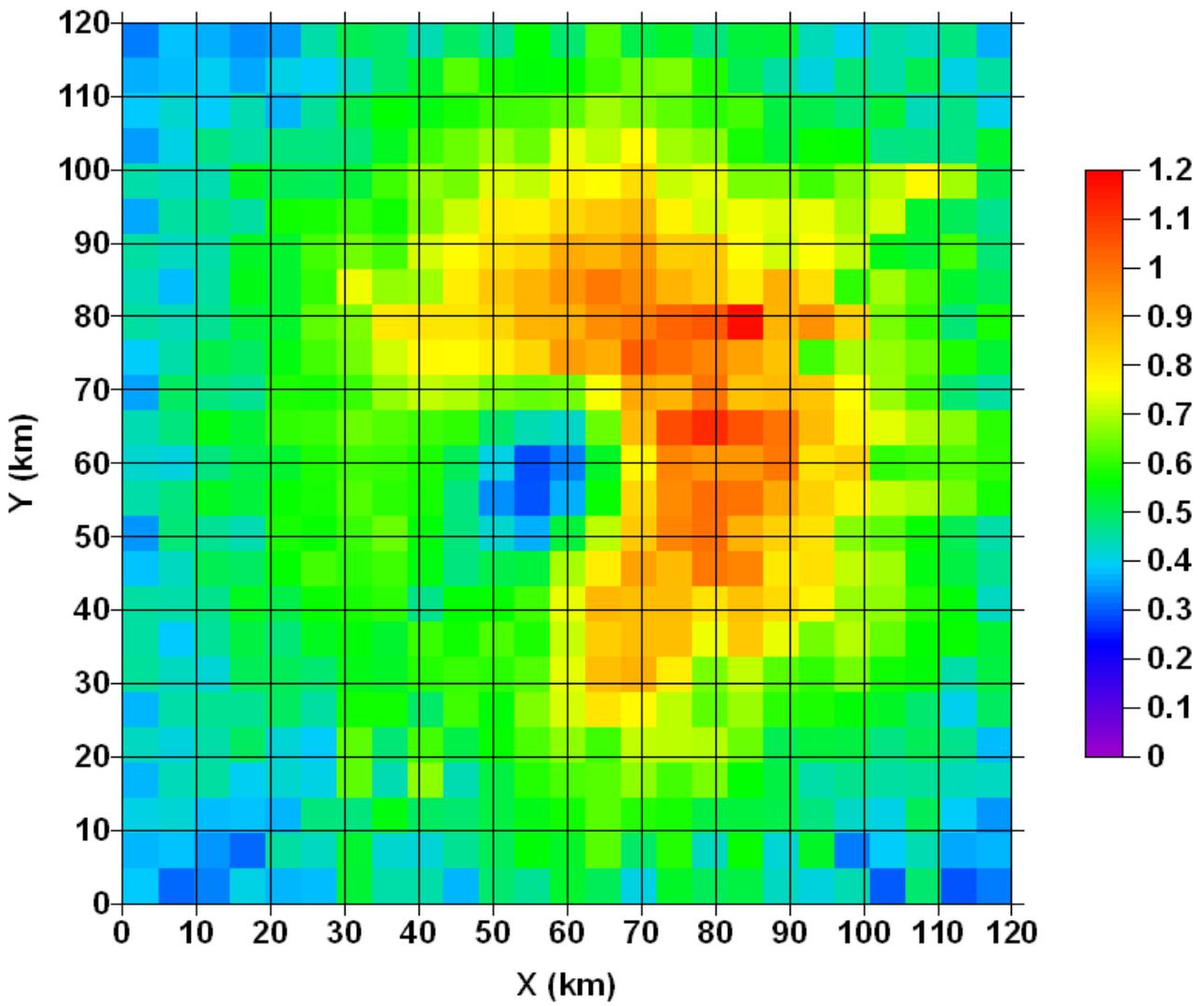


Figure 6.3(b) SO₂ concentration ($\mu\text{g m}^{-3}$) for Didcot power station modelled with FRAME



The ADMS simulation (figure 2.3(a)) shows that the peak concentration of SO₂ occurs 10-15 km to the north-east of the point source. In the FRAME simulation the peak concentration is approximately 20-25 km away from the source, somewhat further than with ADMS. The peak SO₂ concentration was 1.2 µg m⁻³ with both ADMS and with FRAME. However it is noticeable that the area of high SO₂ concentrations (> 0.8 µg m⁻³) is spread over a greater area with FRAME than with ADMS. This may be due to the absence of horizontal diffusion in FRAME. The parameterisation of horizontal diffusion in a local scale dispersion model leads to the rapid decrease of concentrations with increasing distance from a point source.

6.3 Improvement to parameterisation of plume rise

Subsequent to the study described in section 6.2, tests were undertaken to investigate the representation of plume rise from point sources in FRAME. In previous source attribution studies, plume rise was restrained to the boundary layer. This was enforced to generate physically realistic patterns for footprints of deposition and concentration from single point sources. It was recognised that in a model with statistically averaged meteorology and a diurnally variable boundary layer height, emissions could be injected into the free troposphere for certain trajectories but not for others, leading to problems with a 'wheel spoke effect' in deposition patterns. However, plume rise into the free troposphere is known to occur and should be represented in the model. The solution to this problem was found to be use of distributed vertical emissions layers. With emissions distributed into four vertical model layers, plume rise was permitted to penetrate the free troposphere. This led to a more physically realistic distribution of sulphur deposition from a single point source, as illustrated in figure 6.4 for Didcot power station.

Further comparison of point source footprints of air concentrations and deposition with other models (i.e. CMAQ) will be undertaken through the **CREMO** project (**C**omparison of **RE**gional **MO**del) funded by the Environment Agency.

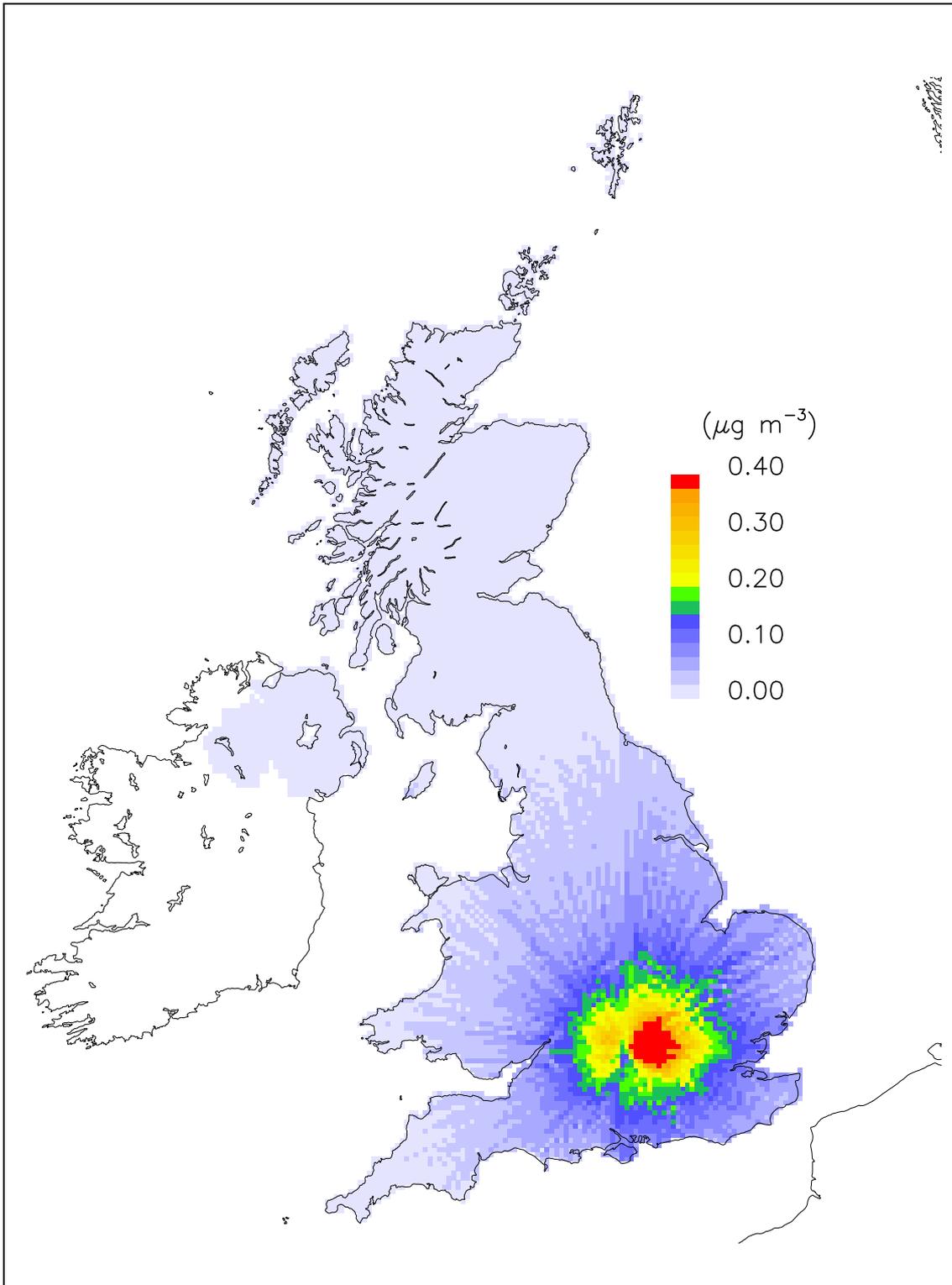


Figure 6.4 Didcot power station footprint of SO₂ simulated by the modified model with the plume distributed over four vertical layers but allowed to rise above the mixed layer into the free troposphere.

7. Treatment of import of pollutants in FRAME at the model boundaries

Import in FRAME version 5.9 was previously treated using the output from FRAME-Europe, a European scale model with a 150 km grid spacing, similar in concept to FRAME. The EMEP source-receptor data for the concentration of aerosols imported from European countries other than the UK was supplied by Imperial College for the year 2010. This was compared with the FRAME-Europe imported deposition footprint for the UK. Significant differences are apparent. The results of calculations of the average aerosol concentration from European sources over the United Kingdom suggested that the import of aerosol from Europe calculated with FRAME-Europe was underestimated by a factor of approximately 3.3.

Improved representation of import to the FRAME UK was undertaken involving further development of a European-scale modelling capacity. In order to meet this requirement, FRAME version 6.1 was developed to allow variable grid size and grid spacing. Whilst FRAME-Europe (150 km) and FRAME-UK were previously separate computer codes, the new version of FRAME has been developed with the aim of having one model allowing simulations at a European scale (on the EMEP 50 km grid), at a UK scale (on the OS 5 km grid) and at a regional 1 km scale. The first simulations of FRAME on the EMEP 50 km grid have been completed successfully. Following the successful FRAME-Europe 50 km simulation, the next step involved interfacing the directionally dependent concentrations into a FRAME-UK simulation at a 5 km resolution. Three FORTRAN routines have been developed to:

- (i) Regrid 8 directionally dependent (45° resolution) concentration data files output from the EMEP simulation to the OS grid.
- (ii) Read in the directionally dependent concentration data to a FRAME-UK 5 km simulation.
- (iii) Initialise the trajectories in a FRAME-UK simulation with the new directionally dependent concentration data.

These routines were successfully tested.

7.1 Input data to FRAME-Europe

Emissions data for FRAME-Europe were taken from the EMEP Expert Emission Inventory (Vestreng *et al.* 2006). Data for years 2005 and 2020 were prepared as FRAME formatted *.csv text files. Plots of total emissions for NH_3 , NO_x and SO_2 are illustrated in figures 7.1(a) to (c) respectively.

Annual precipitation data for FRAME-Europe were taken from the CRU Global Climate Dataset. These are gridded long term mean annual precipitation sums (1961-1990, $0.5^\circ \times 0.5^\circ$ resolution; New *et al.* 1999) as illustrated in figure 7.2. for the European and Mediterranean part of the FRAME-Europe domain. A default precipitation rate of 600 mm hr^{-1} was used for maritime areas.

	NH_3	SO_2		NO_2	
		Land	Shipping	Land	Shipping
2005	538.0	734.7	866.8	451.5	563.7

Table 7.1 Total emissions from land and shipping for the EMEP model domain for 2005.

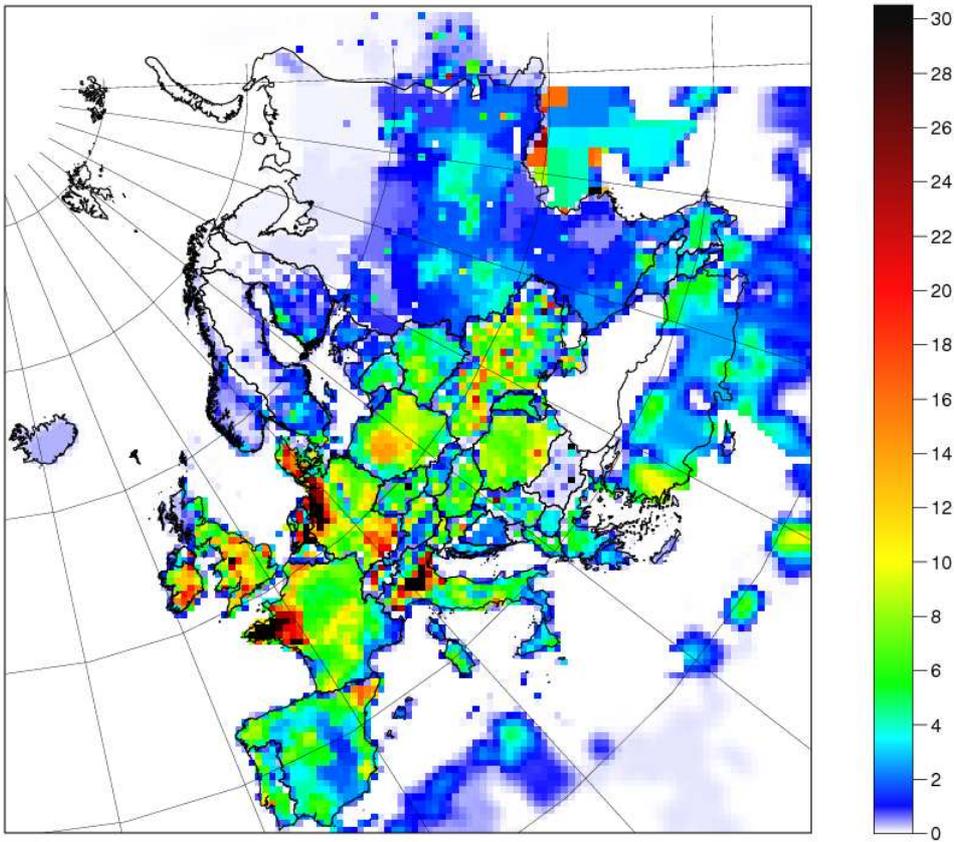


Fig. 71(a) FRAME-Europe 2005 NH₃ emissions

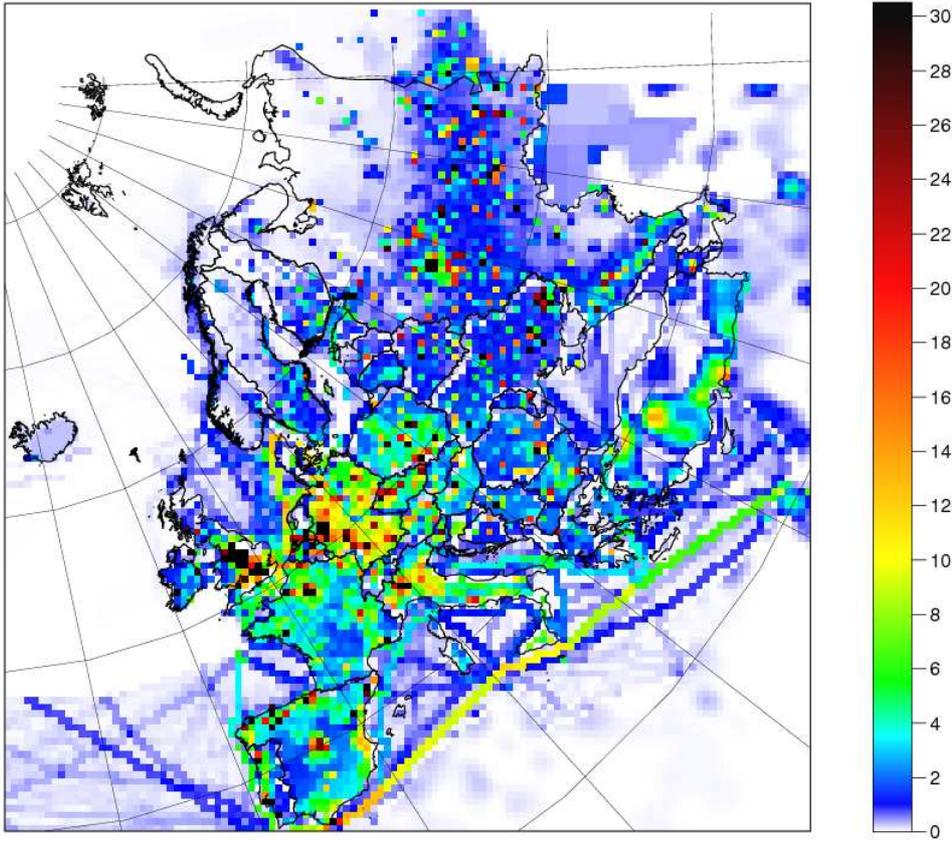


Fig. 7.1(b) FRAME-Europe 2005 NO_x emissions

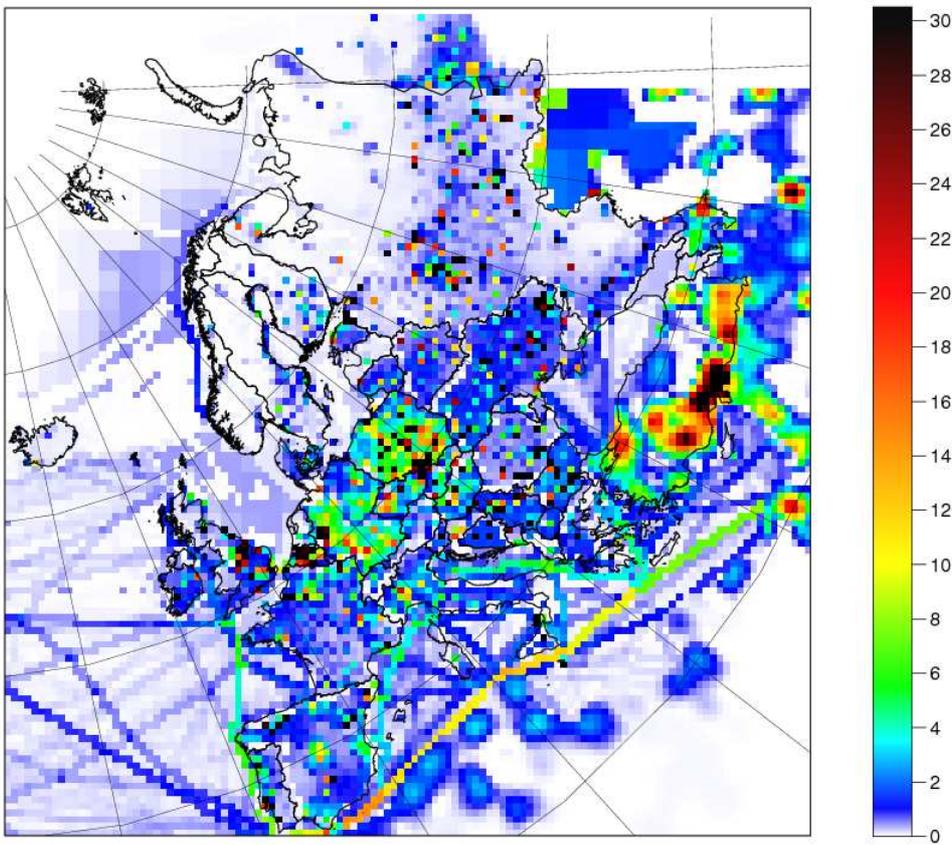


Fig. 7.1(c) FRAME-Europe 2005 SO₂ emissions

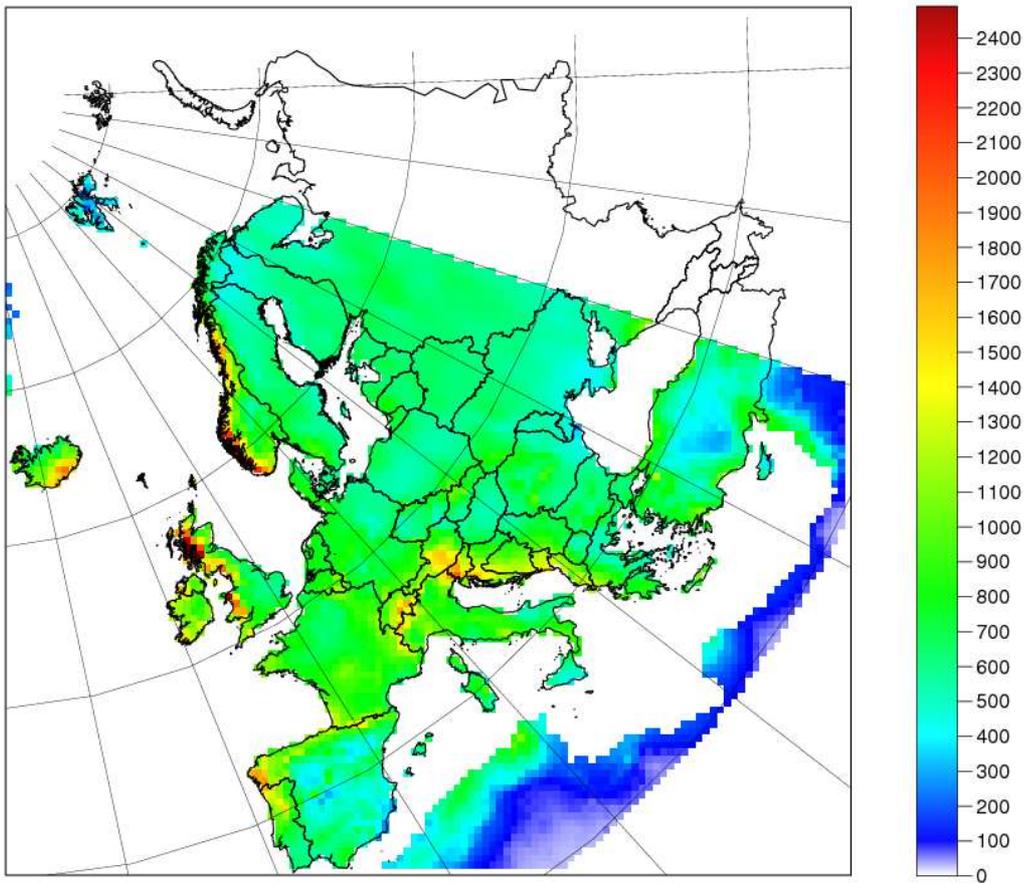


Fig. 7.2 Annual precipitation (1961-1990) for FRAME-Europe

7.2 Comparison of FRAME-Europe and EMEP gas and aerosol concentrations

FRAME-Europe (50 km) was used to initialize the gas and aerosol concentrations at the boundaries of the FRAME-UK domain. The performance of a preliminary simulation of FRAME on the European domain was assessed by comparison with air concentrations generated with the EMEP model. Gas concentrations (NH_3 , SO_2 , NO_x , NHO_3 and aerosol concentrations (NH_4^+ , NO_3^- , SO_4^{2-}) for FRAME-Europe for the year 2005 were compared with EMEP concentrations. A sub-set of these is illustrated for NH_3 , NO_3^- aerosol and SO_2 in figures 7.3(a) – (e). Ammonia concentrations are somewhat higher in FRAME than in EMEP. SO_2 concentrations are higher in EMEP than in FRAME with both models showing the strong influence of international shipping on SO_2 concentrations in the English Channel and the Mediterranean. The general patterns of gas and aerosol concentrations and their magnitude show encouraging agreement. In particular the formation of secondary inorganic aerosol, which is an important component of long range transport of air pollutants is well represented by FRAME-Europe despite the simplicity of the modeling approach on a European scale.

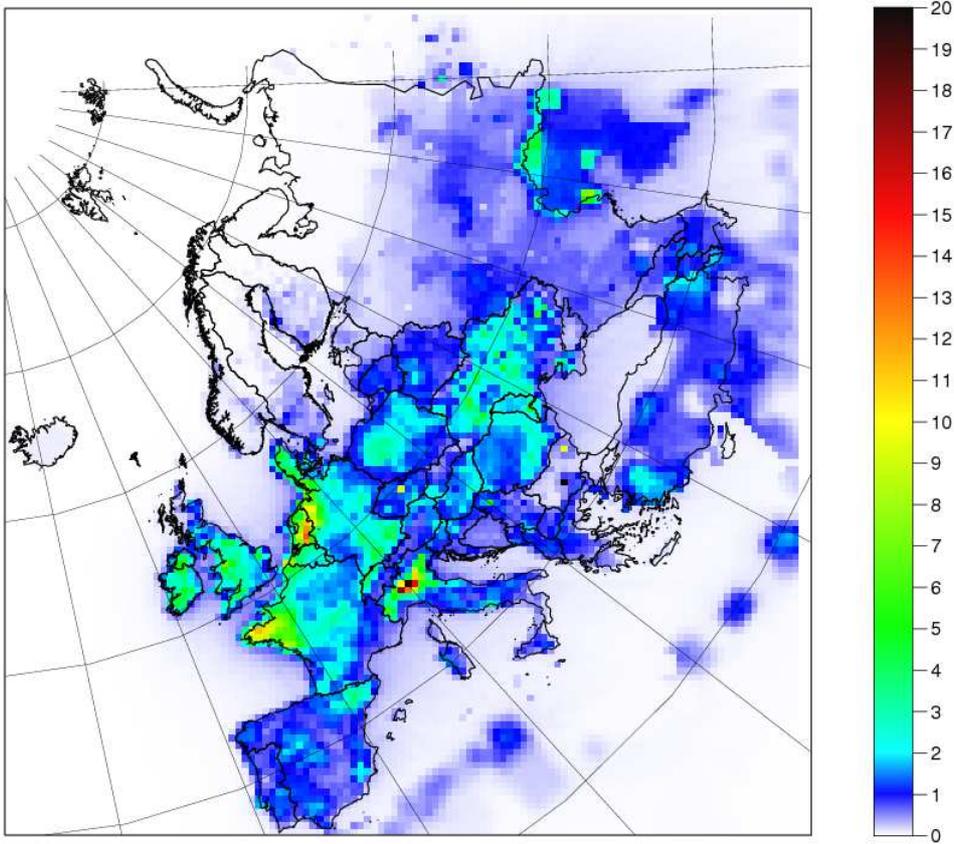


Fig. 7.3(a) FRAME-Europe NH_3 concentration ($\mu\text{g m}^{-3}$)

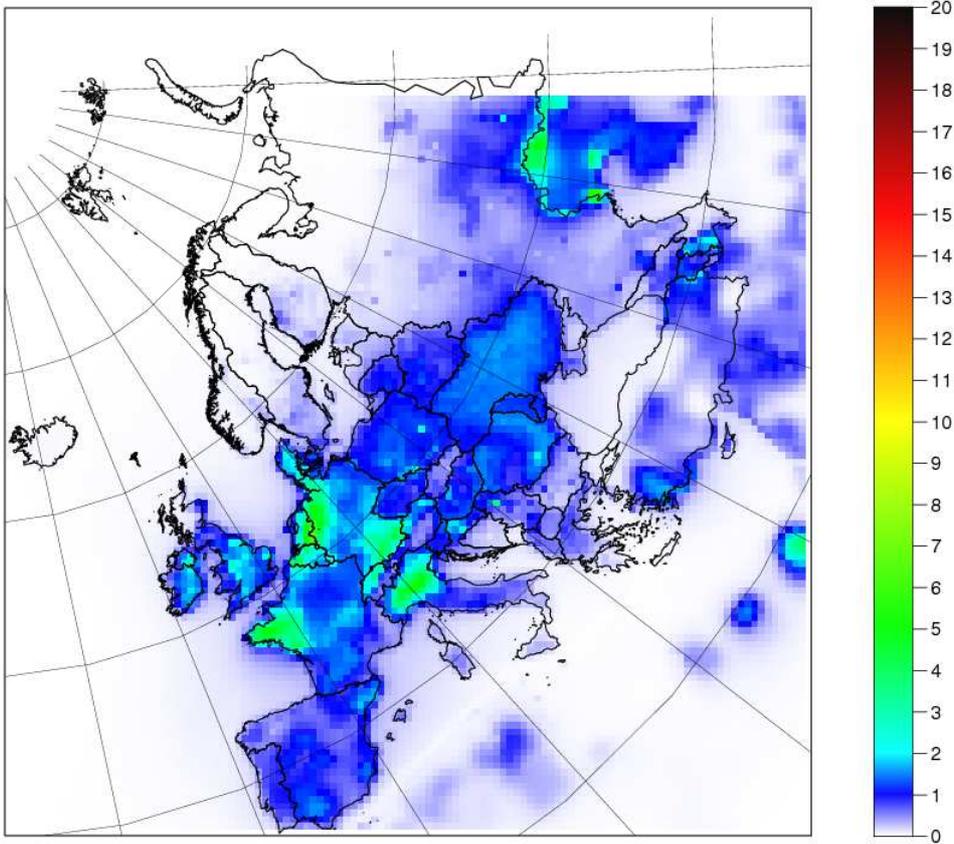


Fig. 7.3(b) EMEP NH_3 concentration ($\mu\text{g m}^{-3}$)

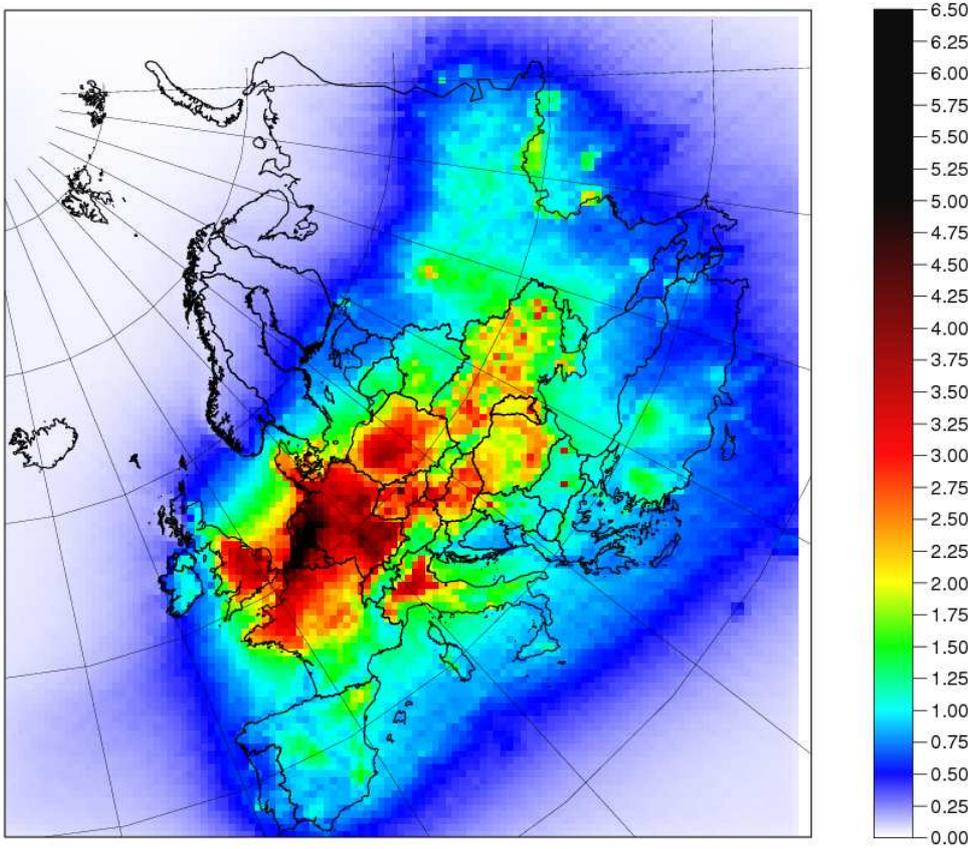


Fig. 7.3(c) FRAME-Europe NO_3^- aerosol concentration ($\mu\text{g m}^{-3}$)

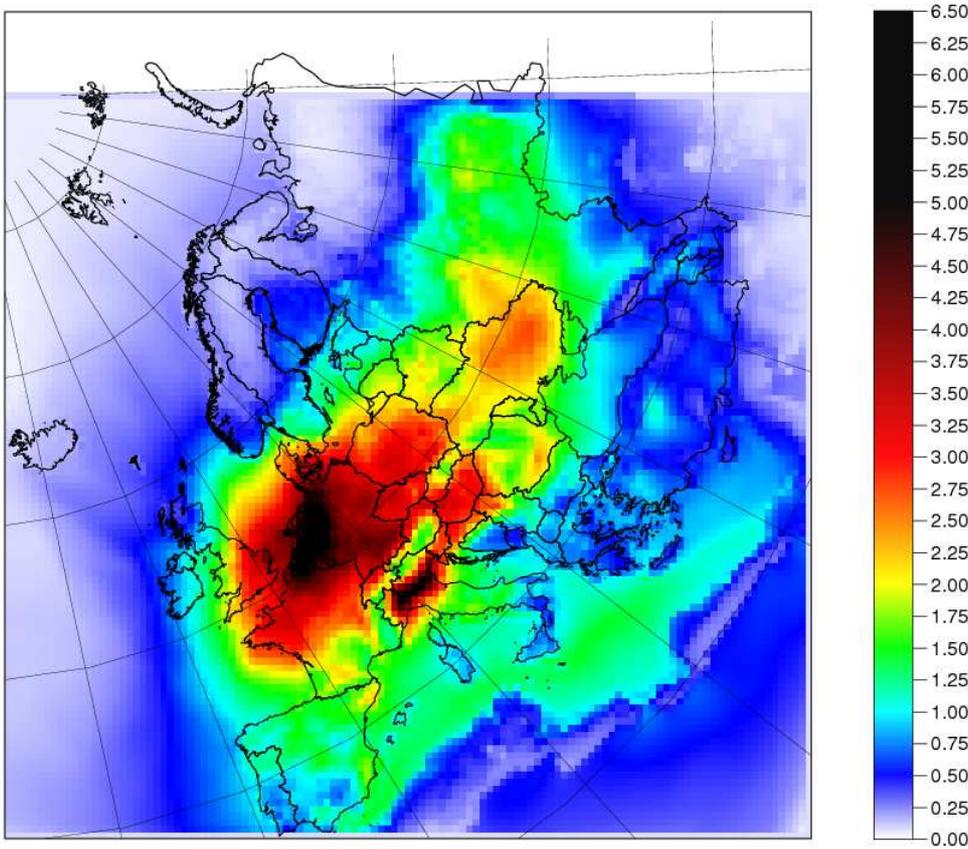


Fig. 7.3(d) EMEP NO_3^- aerosol concentration ($\mu\text{g m}^{-3}$)

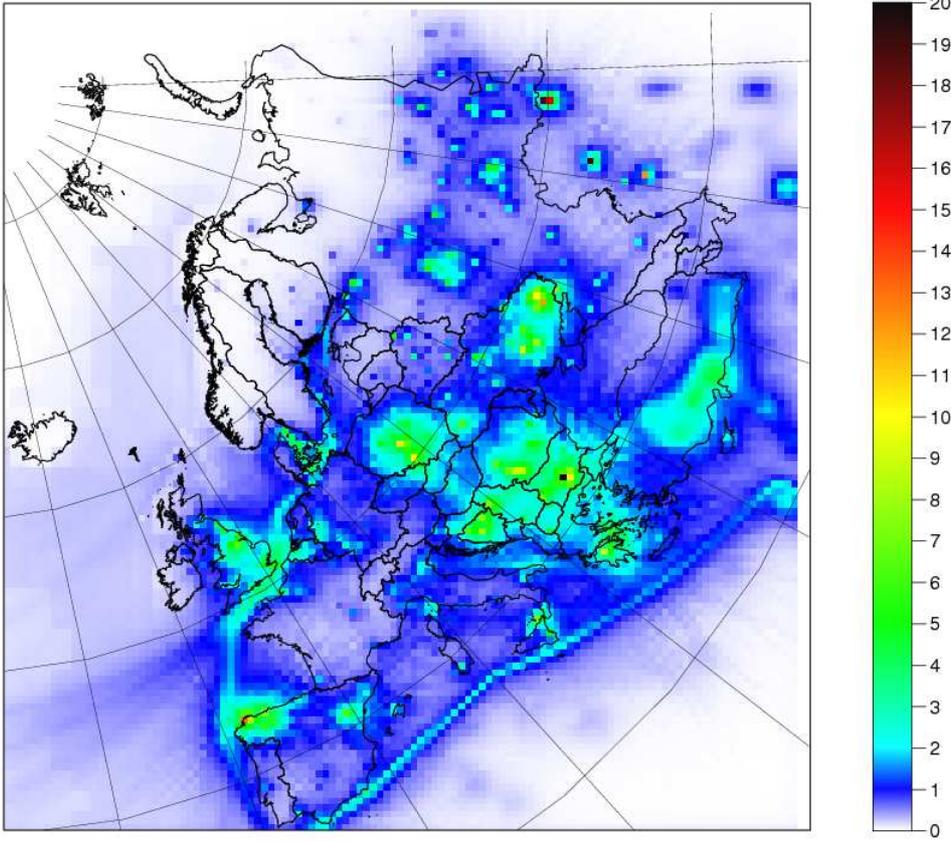


Fig. 7.3(e) FRAME-Europe SO₂ concentration ($\mu\text{g m}^{-3}$)

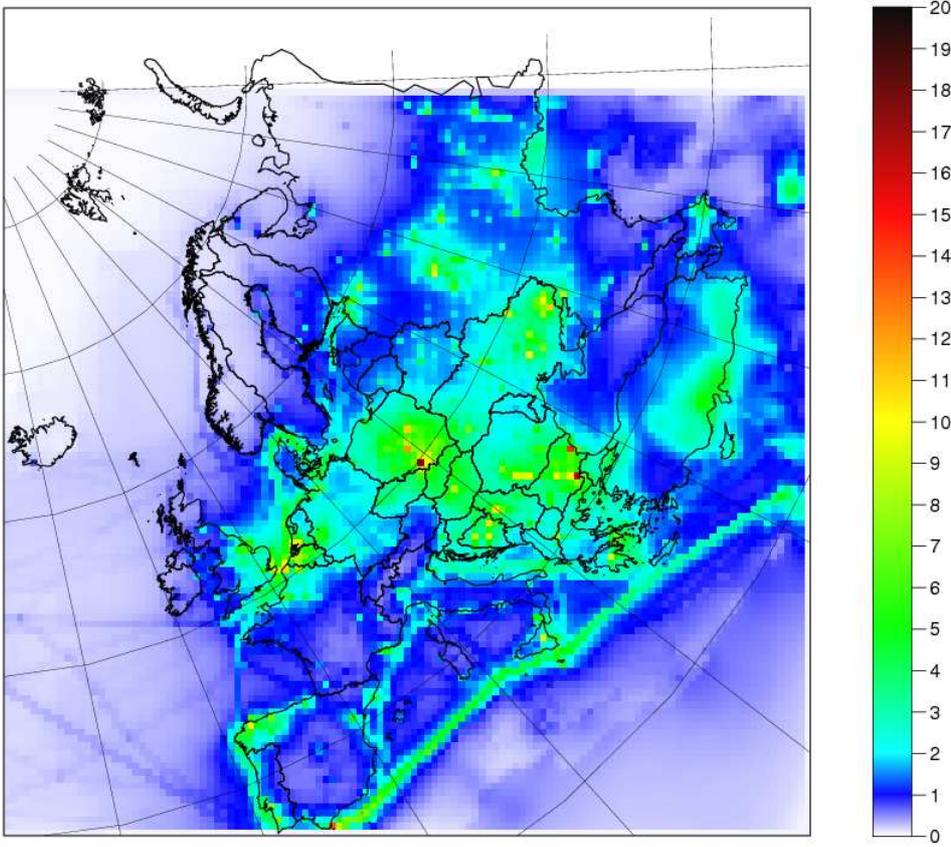


Fig. 73(f) EMEP SO₂ concentration ($\mu\text{g m}^{-3}$)

The deposition budgets to land in the FRAME-Europe domain for the year 2005 are illustrated in Table 7.2.

Table 7.2 FRAME-Europe deposition budgets [kt N/S]

	NH_x-N	NO_y-N	SO_x-S
Dry	1636	1503	1630
Wet	2624	1913	3481
Total	4260	3416	5111

7.3 Comparison with EMEP source receptor matrices

The aim of interfacing FRAME-Europe (50 km) with FRAME-UK (5 km) was to obtain compatibility with the EMEP grid in order to facilitate European emissions input to FRAME as well as allowing inter-comparison between FRAME-Europe and the well established EMEP model on the same model grids. One of the major applications of the EMEP model is the generation of country source-receptor data which permits the calculation of the contribution of pollutant emissions from all 'source' countries in the domain to pollutant deposition and air concentration of each of the 'receptor' countries in the domain. The contributions of emissions from international shipping in the Atlantic and North Sea are included as separate sources. This data provides a useful standard against which to assess the contributions from European emissions and shipping emissions to nitrogen and sulphur deposition in the UK calculated with FRAME. Figures 7.4(a) – (e) illustrate the contribution to deposition of NH_x, NO_y and SO_x with FRAME-Europe and with EMEP. For EMEP the contributions are broken down according to individual country (FR: France, ES: Spain, DE: Germany, NL: the Netherlands as well as BIC: boundary and initial conditions and NOS: International shipping in the North Sea and ATL: International shipping in the Atlantic). For FRAME a more basic distribution of three sources has been considered which includes the UK, international shipping and European sources (non-UK land sources). The pie charts illustrate that with FRAME-Europe interfaced to FRAME-UK, a source apportionment is obtained which gives close agreement to EMEP for NH_x and SO_x. For NO_y, FRAME estimates a greater contribution from UK sources (55%) than with EMEP (42%).

Fig. 7.4(a) FRAME source allocation for SO_x deposition in the UK

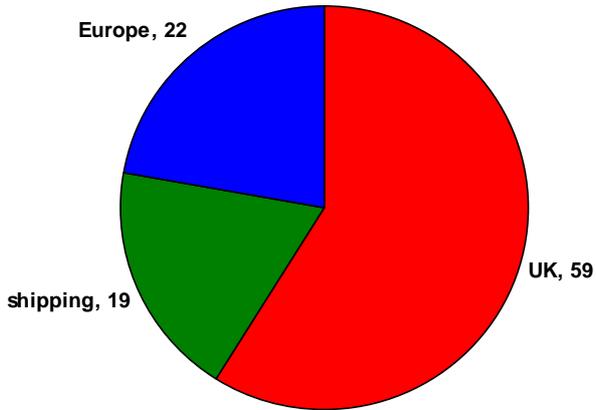


Fig. 7.4(b) EMEP source allocation for SO_x deposition in the UK

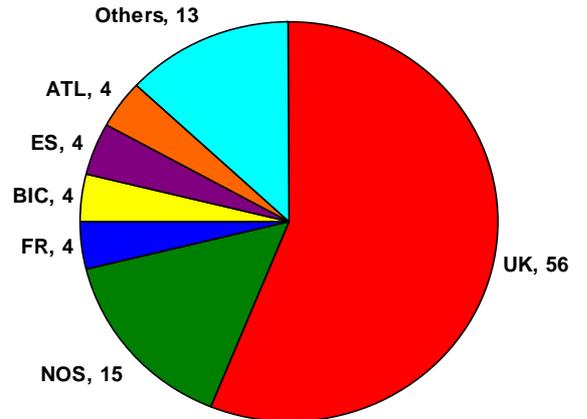


Fig. 7.4(c) FRAME source allocation for NO_y deposition in the UK

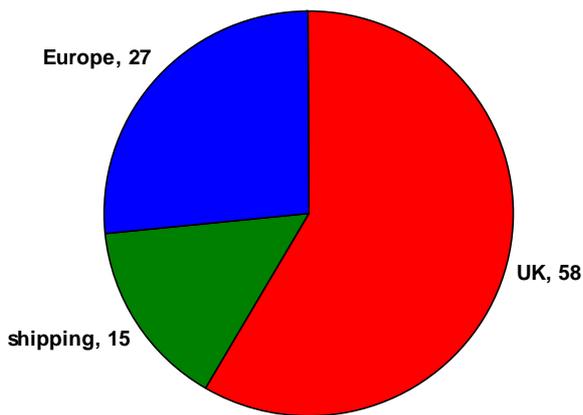


Fig. 7.4(d) EMEP source allocation for NO_y deposition in the UK

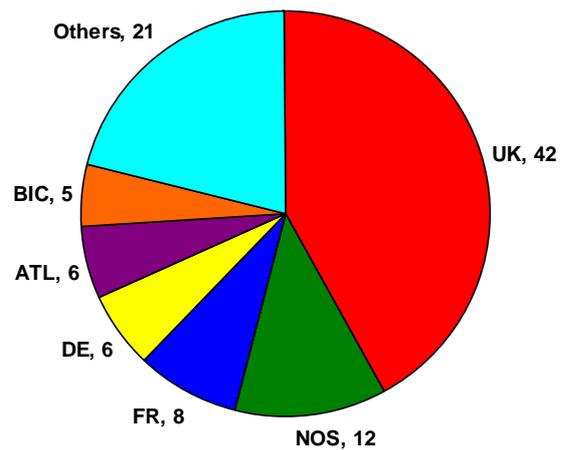


Fig. 7.4(e) FRAME source allocation for NH_x deposition in the UK

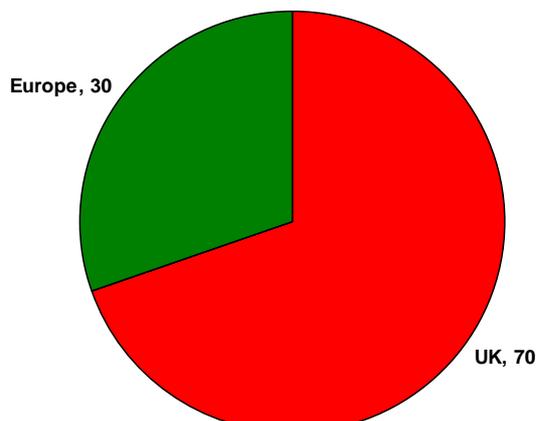
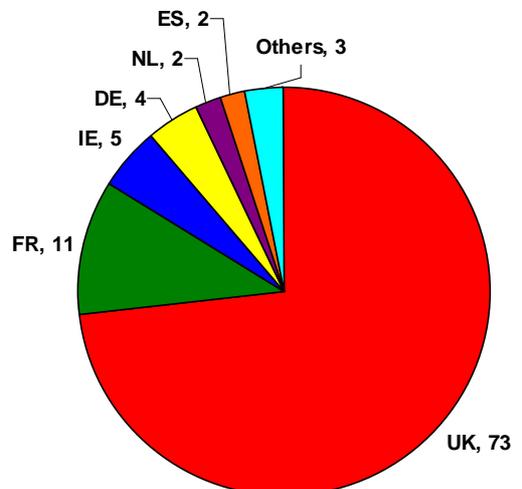


Fig. 7.4(f) EMEP source allocation for NH_x deposition in the UK



7.4 Application of the to model assessment of the role of shipping emissions

Emissions of SO₂ from international shipping in the region of the FRAME-UK and FRAME-Europe model domains are illustrated in Figures 7.5(a) and 7.5(b) respectively, gridded at a 50 km resolution (ENTEC, 2002; data available from: www.emep.int). The intensity of emissions is highest in the busy shipping lanes of the English Channel and in the vicinity of major ports. The relative contribution of shipping emissions to sulphur and oxidised nitrogen deposition in the United Kingdom was assessed by conducting two sets of model simulations. The first simulation included all sources (UK national emissions, long range transport of pollutants from Europe and shipping emissions). In the second set, shipping emissions of SO₂ and NO_x were set to zero in both the regional scale (5km resolution) and the European scale (50 km resolution) simulations. The difference in modelled sulphur and nitrogen deposition between the two simulations represents the contribution from shipping emissions alone. The significant contribution to sulphur dry deposition in the south-east of England (Figure 2(a)) and in other coastal regions is apparent. This close-to-source contribution is principally due to the dry deposition of SO₂ gas to vegetation. However, a long range transport component of sulphur deposition due to shipping can also be seen in the form of high wet deposition in the hill regions of Wales and northern England. This occurs due to the oxidation of SO₂ to sulphate aerosol, which is removed from the atmosphere principally by washout from precipitation and results in high deposition in the high rainfall upland regions (Figure 7.6(b)). This procedure was applied for both the year 2005 and for a future scenario for the year 2020. The future scenario included the significant forecast increase in shipping emissions. The results of the model simulations, illustrated in Table 7.3, suggest that, in the absence of emissions controls on international shipping, the relative contribution of shipping emissions to sulphur and oxidised nitrogen deposition in the United Kingdom will increase from 19% to 37% and 15% to 28% respectively over the period 2005-2020 (although total deposition will decrease due to the reductions in land-based emissions).

The significance of shipping emissions in contributing to oxidised nitrogen and sulphur deposition over land lends strong support to the need for international legislation to constrain emissions from shipping. The IMO has recently made an agreement to reduce the sulphur content in marine fuel to 0.5% by 2020, a significant reduction from currently much higher levels of 2.7% on average. An additional model scenario was run with emissions of SO₂ assumed to fall corresponding to the reduction in sulphur content. The result of this policy gives a clear benefit with the total UK sulphur deposition budget in 2020 falling from 122 to 85 Gg S. This can be expected to result in a significant decrease in exceedance of critical loads for acid deposition to ecosystems. It is important to note however that increases in shipping emissions based on the assumed growth of traffic of 2.5% per year between 2005 and 2020 are based on global estimates. The real influence of shipping emissions to the UK will depend on future changes of traffic through the English channel. Future work will include higher resolution (5 km) shipping emissions and detailed estimates of future emissions including the influence of application of the MARPOL convention.

Table 7.3: The modelled total sulphur and oxidised nitrogen deposition budgets to the United Kingdom originating from international shipping emissions. Three scenarios are considered: (i) for the year 2005, (ii) for the year 2020 assuming a Business As Usual scenario (BAU) and (iii) assuming application of the IMO agreement for the year 2020.

	2005		2020 BAU		2020 IMO	
	SO _x	NO _y	SO _x	NO _y	SO _x	NO _y
Deposition from shipping emissions (Gg S/N)	35	26	45	32	8	32
% contribution to total deposition from shipping emissions	19	15	37	28	9	28

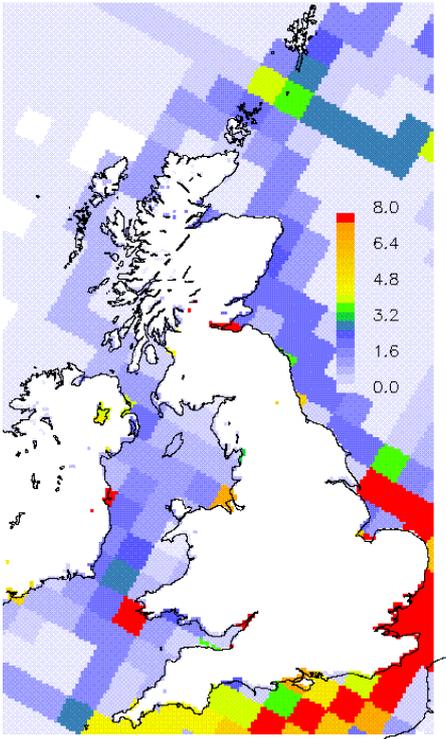


Figure 7.5(a). Emissions of SO₂ from international shipping in the FRAME-UK domain (kg S Ha⁻¹)

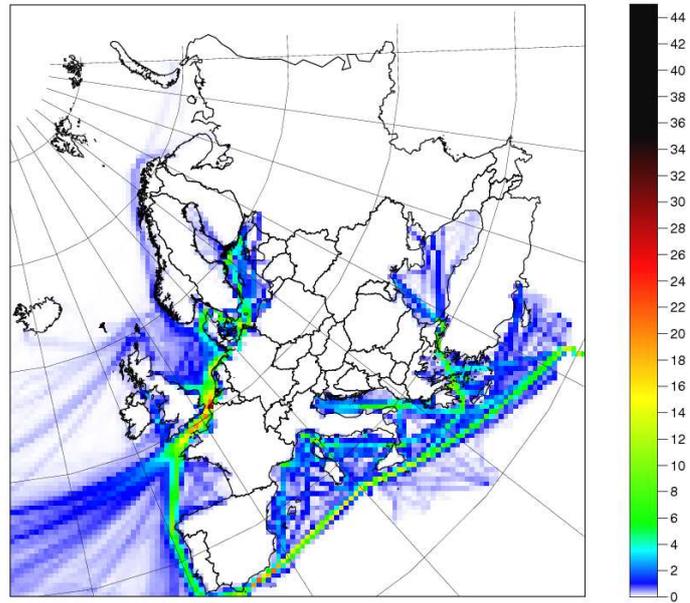


Figure 7.5(b). Emissions of SO₂ from international shipping in the FRAME-Europe domain (kg S Ha⁻¹)

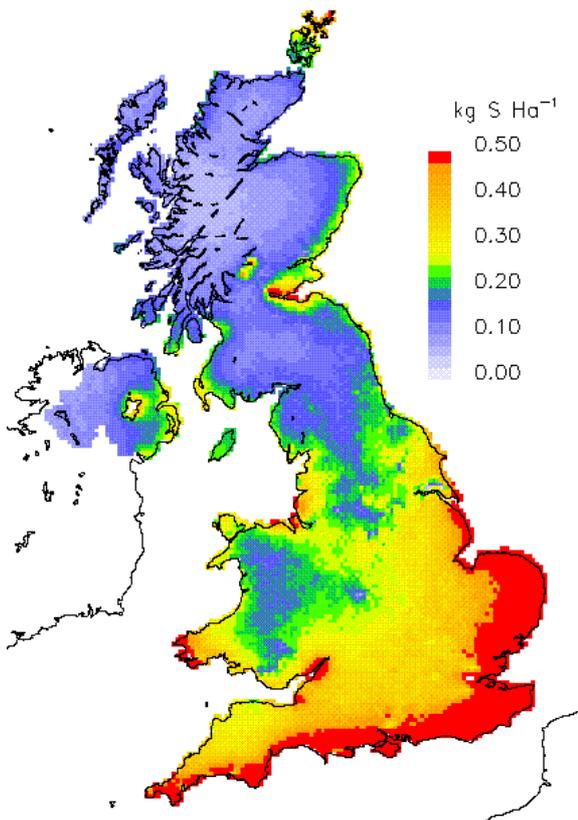


Figure 7.6(a). Dry deposition of SO_x due to emissions from international shipping (kg S Ha⁻¹)

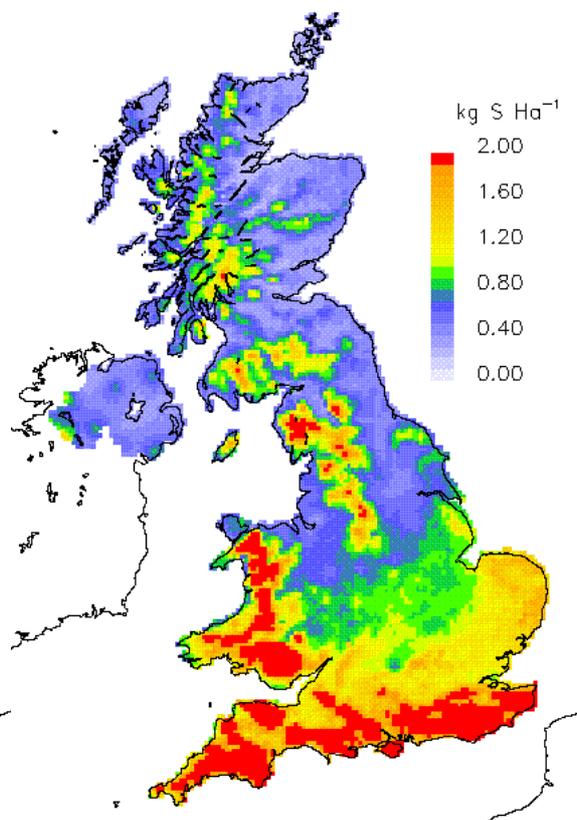


Figure 7.6(b). Wet deposition of SO_x due to emissions from international shipping (kg S Ha⁻¹)

8. Development of a 1 km version of FRAME

FRAME was re-coded to allow flexibility in the domain shape and size and in the horizontal spacing of the model grid and incorporate the option of national simulations at a 1 km resolution. This improvement implies a 25 fold increase in the number of grid squares over the domain. To enable this advance, the FRAME code was optimised with specific regard to efficient use of computer memory. As FRAME has evolved into a multi-species model, the demands on memory have increased considerably because each species requires space within a large 4-dimensional emissions array (three spatial dimensions and one species dimension). Not all of the species are required simultaneously and for this study, only three are necessary for the modelling of ammonia, including the chemistry. The 4 dimensional emissions array was split into several 3-dimensional arrays to enable de-allocation of the unused arrays for simulations at a horizontal resolution of 1 km. Common blocks of variables (a FORTRAN 77 feature) were updated to the FORTRAN 90 style using modules. The model was also adapted to accept higher resolution inputs such as emissions, rainfall and land use.

The model has an adaptive time step to ensure that at least one iteration of the diffusion is carried out over every grid square that a trajectory passes over. However, a single iteration may not be sufficient for the proper mixing and deposition to be calculated. It was necessary to reduce the model time step from 120 seconds for the 5 km model to 20 seconds for the 1 km model. This reduction allows sufficient calculations of vertical diffusion to be carried out for proper mixing and deposition over each grid square. No significant difference in distribution or total concentration of NH₃ was found between a 20 second time step and 10 second time step. Therefore, 20 seconds was chosen as an optimum time step for the 1 km model.

The following input files were generated for the UK at a 1 km resolution in a format suitable for input to FRAME:

- Annual precipitation (generated by extrapolation of data from the Met Office automatic precipitation monitoring network).
- Land use (classifications: moorland, forest, grassland, arable, urban, water)
- Area and point source SO₂ emissions (for year 2003)
- Area and point source NO_x emissions (for year 2003)
- Area and point source NH₃ emissions (for year 2003)

Maps of NH₃ and NO_x concentrations generated with FRAME at 5 km and 1 km resolution are illustrated in figures 8.1 and 8.3 respectively. The higher resolution maps are shown to give an improvement with correlation of NO_x concentrations from the rural monitoring network and with NH₃ concentrations from non-agricultural sites (figures 8.2 and 8.4 respectively). It is important to note that, whilst more accurate results can be generated with a model employing higher resolution grids, the quality of the modelled air concentrations relies on accurate emissions maps and uncertainty in mapping emissions increases as the resolution of the emissions increases. None-the-less there can be little doubt that the step to 1 km resolution simulation marks a significant improvement in the ability to disaggregate the locations of nitrogen emissions from roads and agricultural areas with the location of nitrogen deposition to sensitive ecosystems.

During 2007 new 'critical levels' (CLe) for assessing the effects of atmospheric ammonia on sensitive ecosystems were adopted by the United Nations Economic Commission for Europe (UNECE). The new critical levels are 1 and 3 [2-4] µg NH₃ m⁻³, according to habitat sensitivity ([2-4] indicates the uncertainty bounds on the latter level). Based on these new values, the modelled ammonia concentrations were applied to estimate stock-at-risk in the EU 'Natura 2000' network of Special Areas of Conservation (SAC) and Special Protection Areas (SPA), illustrated in the map in figure 8.5. Table 8.1 illustrates the area of SAC with exceedance of the different critical levels for ammonia for the regions of the UK. These results are clearly highly dependent on model resolution. The high resolution

data more successfully separates sources of agricultural emissions from the location of SACs, whereas at a 5 km resolution SACs are more likely to be co-located (unrealistically) in a model grid square containing agricultural emissions. As a result the 1 km data set shows 21% of SAC area in the UK with exceedance of the $1 \mu\text{g m}^{-3}$ critical level for ammonia concentrations compared to 40% with the 5 km data set. Future work will involve comparison of exceedance of critical loads calculated with the FRAME 1 km and 5 km resolution deposition data.

Table 8.1: Summary statistics for percentage area of UK Natura 2000 SAC network of 1, 2 and $3 \mu\text{g NH}_3 \text{ m}^{-3}$ exceeded for England, Wales, Scotland, Northern Ireland and the UK as a whole (uncalibrated 5 km and 1 km models).

FRAME application	Critical level /model	England	Wales	Scotland	Northern Ireland	UK
5 km model	$1 \mu\text{g m}^{-3}$	79.0%	39.5%	3.3%	77.0%	39.6%
5 km model	$2 \mu\text{g m}^{-3}$	19.8%	9.0%	0.6%	23.3%	9.9%
5 km model	$3 \mu\text{g m}^{-3}$	4.0%	2.1%	0.0%	10.0%	2.2%
1 km model	$1 \mu\text{g m}^{-3}$	40.9%	21.3%	2.4%	31.7%	20.8%
1 km model	$2 \mu\text{g m}^{-3}$	6.3%	6.1%	0.4%	11.1%	3.7%
1 km model	$3 \mu\text{g m}^{-3}$	1.6%	1.6%	0.0%	2.9%	0.9%

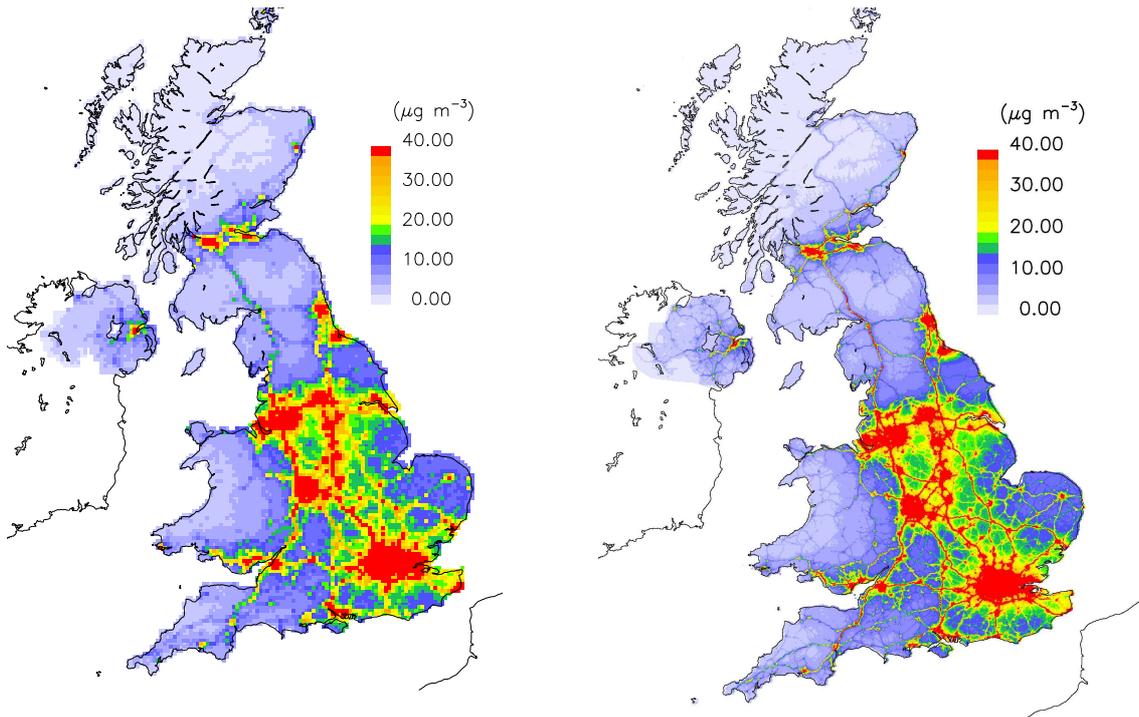


Figure 8.1 2003 NO_x concentration at 5 km resolution (left) and 1 km resolution (right)

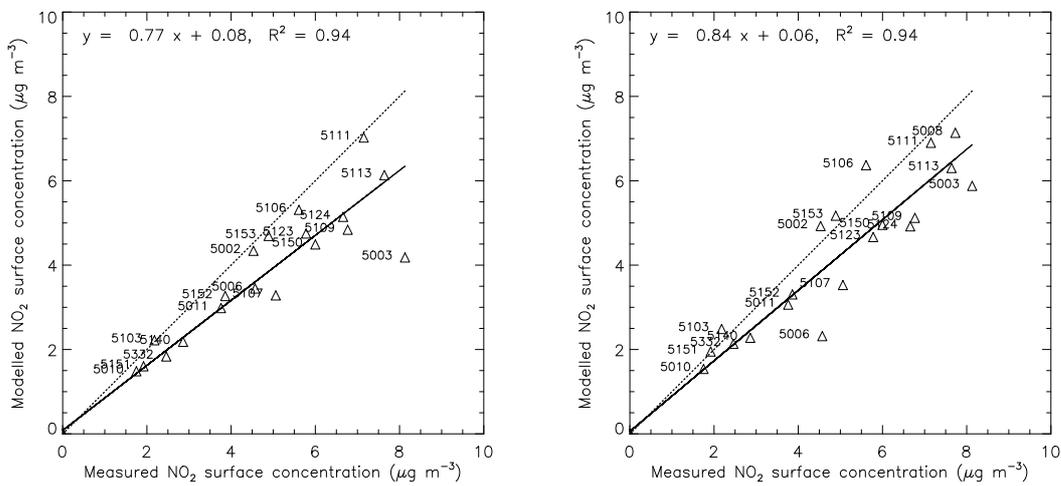


Figure 8.2: 2003 Correlation of model with measurements of NO₂ concentration at 5 km resolution (left) and 1 km resolution (right)

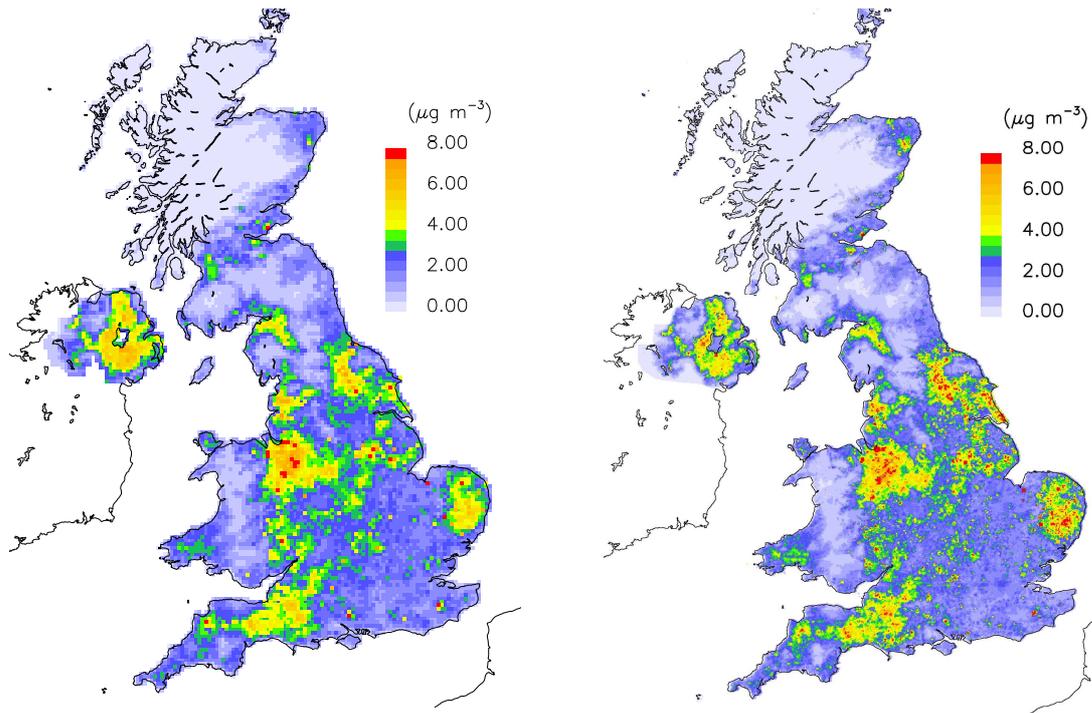


Figure 8.3 2003 NH₃ concentration at 5 km resolution (left) and 1 km resolution (right)

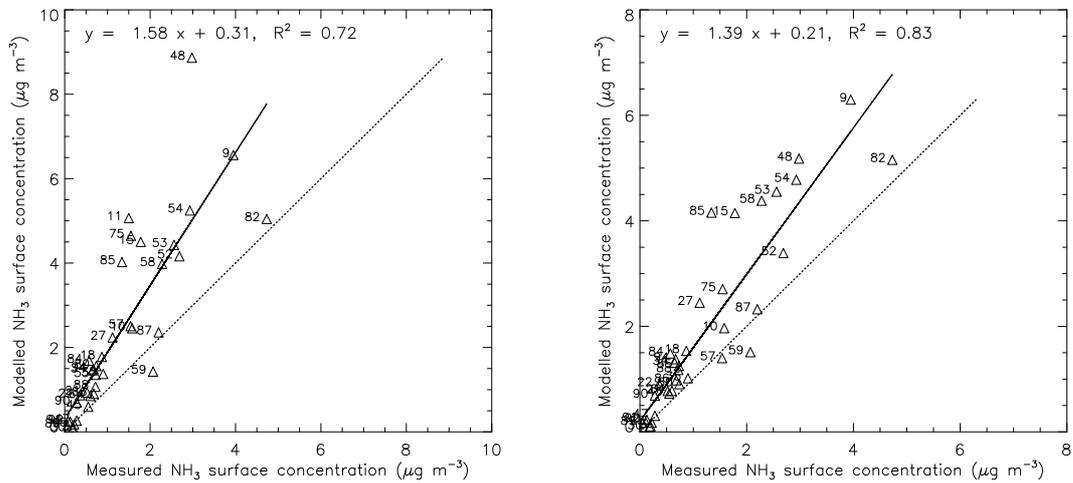


Figure 8.4 2003 Correlation of model with measurements of NH₃ concentration at non-agricultural sites for 5 km resolution (left) and 1 km resolution (right)

Surface
concentration of NH_3
exceedance ($\mu\text{g m}^{-3}$)

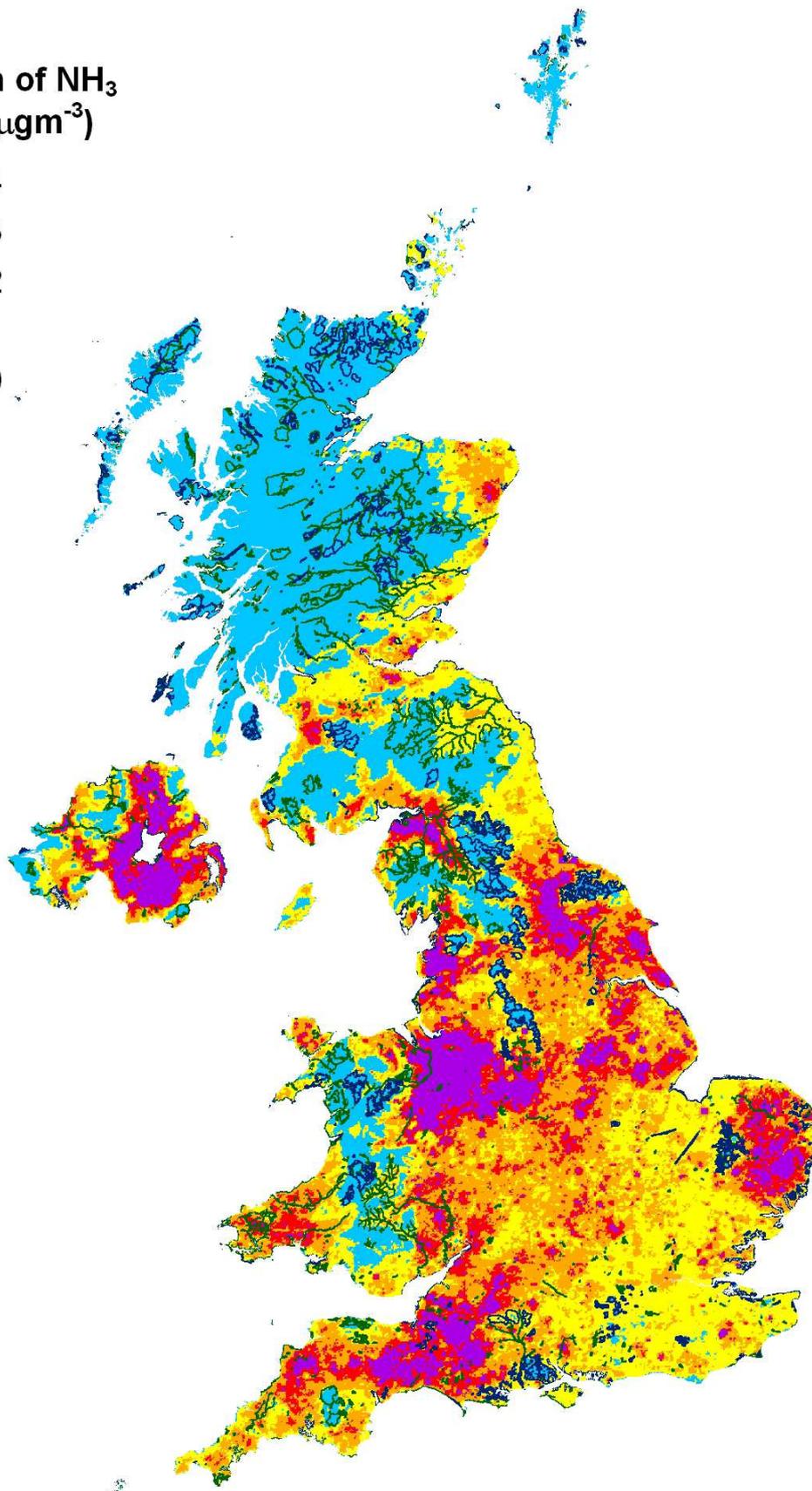
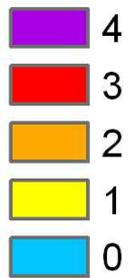


Figure 8.5: National map of ammonia concentrations at 1 km resolution with SAC and SPA boundaries indicated by green and blue borders respectively.

9. Development of primary particulate modelling with FRAME

Previously modelling of PM₁₀ concentrations was undertaken with a separate stand alone version of FRAME developed from FRAME version 1.0. The disadvantage with this approach was that the PM₁₀ FRAME model did not contain many of the improvements to the code which were subsequently implemented including FORTRAN 90 standardisation, parallelisation, fine angular resolution of trajectories, plume, directional orographic rainfall and operationalisation of the code. A separate version of FRAME has been developed to include detailed representation of the size distribution of PM₁₀ and the dependence of deposition velocity on size. These parameterisations are described in detail in McDonald *et al.* (2007).

A new variable to represent PM₁₀ was introduced to FRAME version 6.5 to allow simultaneous calculation of nitrogen and sulphur deposition as well as PM₁₀ concentrations with a single model. A simulation was performed using PM₁₀ emissions for the year 2004. Maps of UK emissions of PM₁₀ for the year 2004 are illustrated in figures 9.1 (a) – (b). Total emissions of PM₁₀ from the UK for 2004 are illustrated in Table 9.1.

Table 9.1 UK emissions of PM₁₀ for 2004

	Area	Point source	Total
2004 UK emissions of PM₁₀ (Gg)	76.9	29.5	106.4

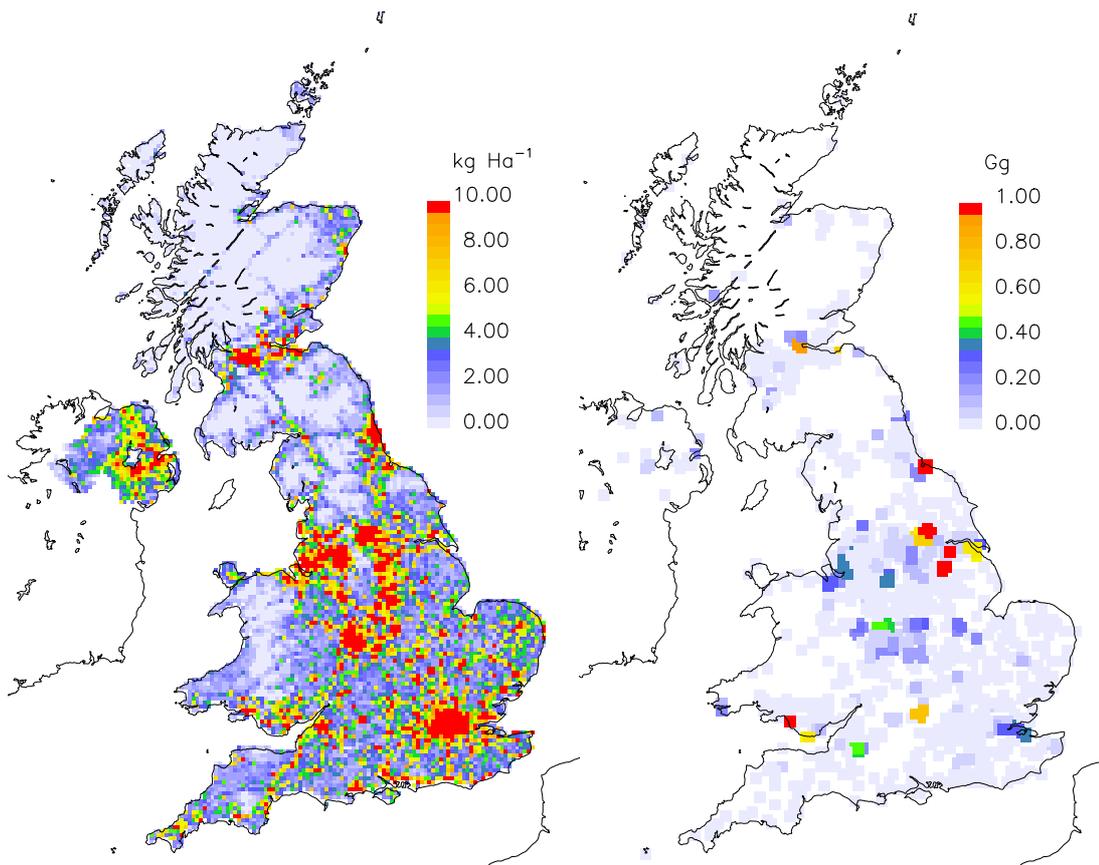


Figure 9.1(a) 2004 area emissions of PM₁₀

Figure 9.1(b) 2004 point source emissions of PM₁₀

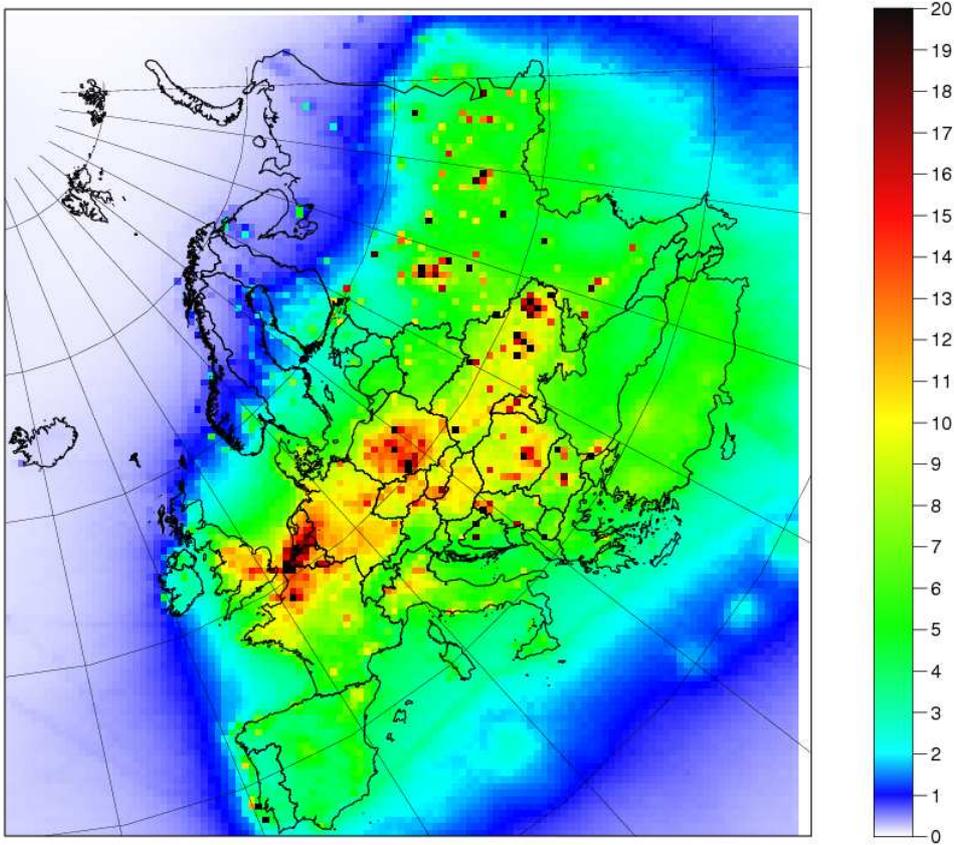


Fig. 9.2(a) FRAME-Europe PM₁₀ concentration ($\mu\text{g m}^{-3}$)

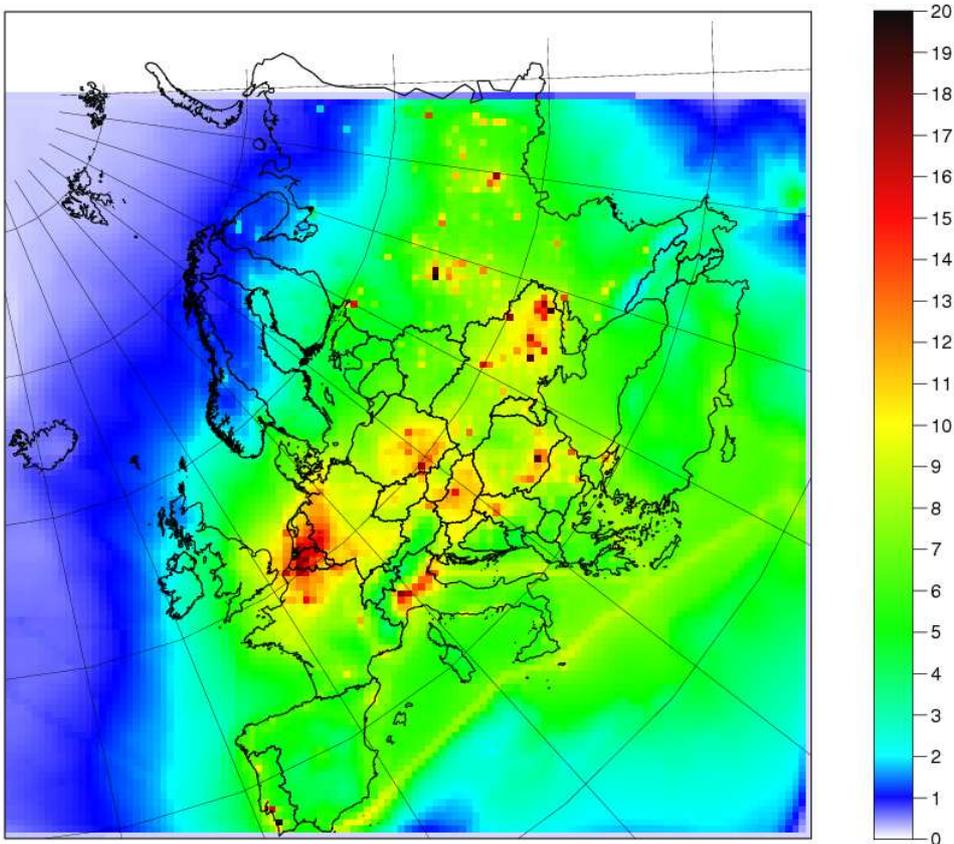


Fig. 9.2(b) EMEP PM₁₀ concentration ($\mu\text{g m}^{-3}$)

Emissions of PM₁₀ from European sources have been incorporated into FRAME-Europe. The primary PM₁₀ concentrations generated by FRAME-Europe were compared with those generated by the EMEP European model (figures 9.2(a) and 9.2(b) respectively). Inter-comparison of the maps shows reasonable agreement as regards the distribution and magnitude of primary PM₁₀ concentrations across Europe. This suggests that the long range transport of PM₁₀ is well represented in FRAME. A preliminary map of PM₁₀ concentrations for the UK generated with FRAME for the year 2005 is illustrated in figure 9.3. Inter-comparison with measurements from the UK PM₁₀ monitoring network is illustrated in figure 9.4. The model significantly underestimates total PM₁₀ concentration due to missing sources. In addition, the use of the 5 km resolution model for verification by a monitoring network which is based mostly in urban areas close to large sources may also lead to underestimates.

Future work will consider missing sources. These include base cations and secondary organic aerosol. The latter involves complex chemical reactions which are too detailed to be incorporated directly into FRAME. However via mutual cooperation with EMEP, it will be possible to obtain this data from a different source (i.e. Simpson *et al.*, 2007). In addition the possibility that particle-bound water may explain the difference between modelled and measured PM₁₀ concentrations should be investigated (Tsyro, 2005). Further work will focus on obtaining mass closure by inclusion of the missing components of PM₁₀ and developing a 1 km resolution modelling facility for particulate matter.

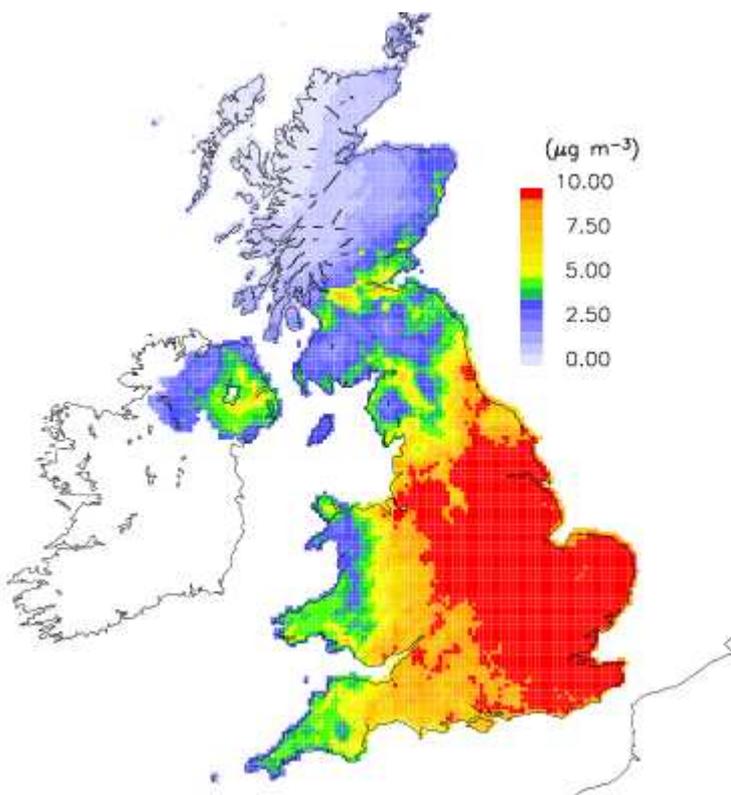


Figure 9.3 Total inorganic (primary and secondary) PM₁₀ concentrations ($\mu\text{g m}^{-3}$)

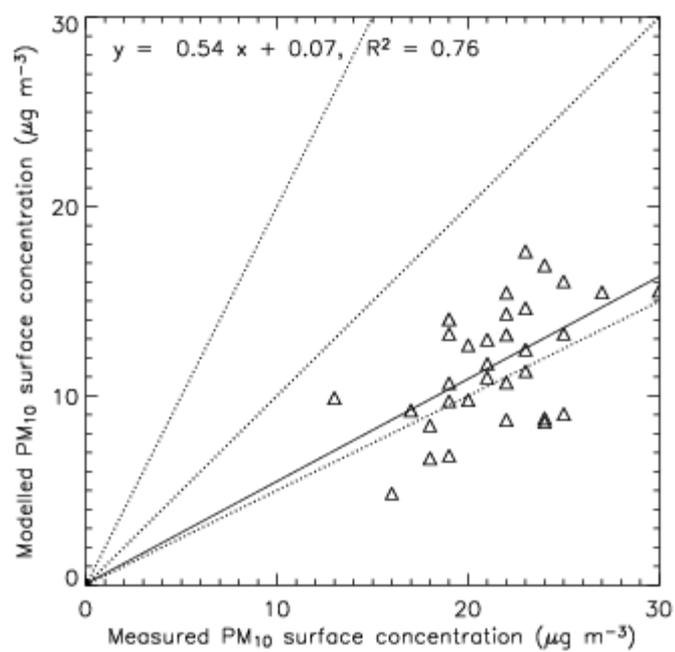


Figure 9.4 Comparison of modelled PM₁₀ concentrations with measurements from the national monitoring network (excluding kerbside measurement sites).

10. Modelling recent trends in acid deposition

The success of FRAME in estimating acid deposition is routinely checked by comparison with measurements of gas and aerosol concentrations and wet deposition from the UK national monitoring networks. For this purpose, measurement data averaged over the three year period 2004-06 has been selected. In addition however, it is important to assess how well FRAME can estimate changes in acid deposition over time, driven by reductions in emissions. In order to achieve this, the model has been run for each of the years 1990-2005 by preparing the appropriate input files (gaseous emissions, precipitation and wind frequency rose).

10.1 Model inputs

During the last two decades, emissions of SO₂, NO_x and NH₃ from the UK and Europe have changed significantly. However in addition to the general downward trend in emissions during the period 1990 to 2005, significant variations in both annual precipitation and wind direction frequency have occurred. It is necessary to consider the annual variation in meteorology in modelling studies in order to make a detailed comparison between modelled and measured trends.

10.1.1 EMISSIONS DATA

The trends in emissions of SO₂, NO_x and NH₃ since 1970 and projected ahead till 2020 are shown in figure 10.1 For SO₂ there have been significant reductions in emissions since 1970, the emission in 2005 representing an 89% reduction on the 1970 value. These have been caused by fuel switching from coal to gas, and the installation of abatement equipment (flue gas desulphurisation) at power stations. Emission projections for 2020 indicate a 50% reduction on the 2005 emission total.

For NO_x there have been significant reductions in emissions from a number of sources, the decrease from 1970 to 2005 representing a reduction of 48%. The largest emission reduction has been from Passenger Cars. This is due to the introduction of three-way-catalysts in the late 1990's and subsequently a number of increasingly stringent emission standards. Emission estimates for 2020 indicate a 51% reduction on the 2005 UK emissions total.

Emissions of NH₃ are available from 1990. These are dominated by agricultural activities, and cattle manure management in particular. There are numerous national policies in place to manage nitrogen emissions from the agricultural sector. However, it has proved difficult to have any significant impact on NH₃ emissions from this politically sensitive source sector. There was an 18% reduction from 1990 to 2005. This has primarily been driven by a decrease in livestock numbers, changes to animal diet and improvements to manure management.

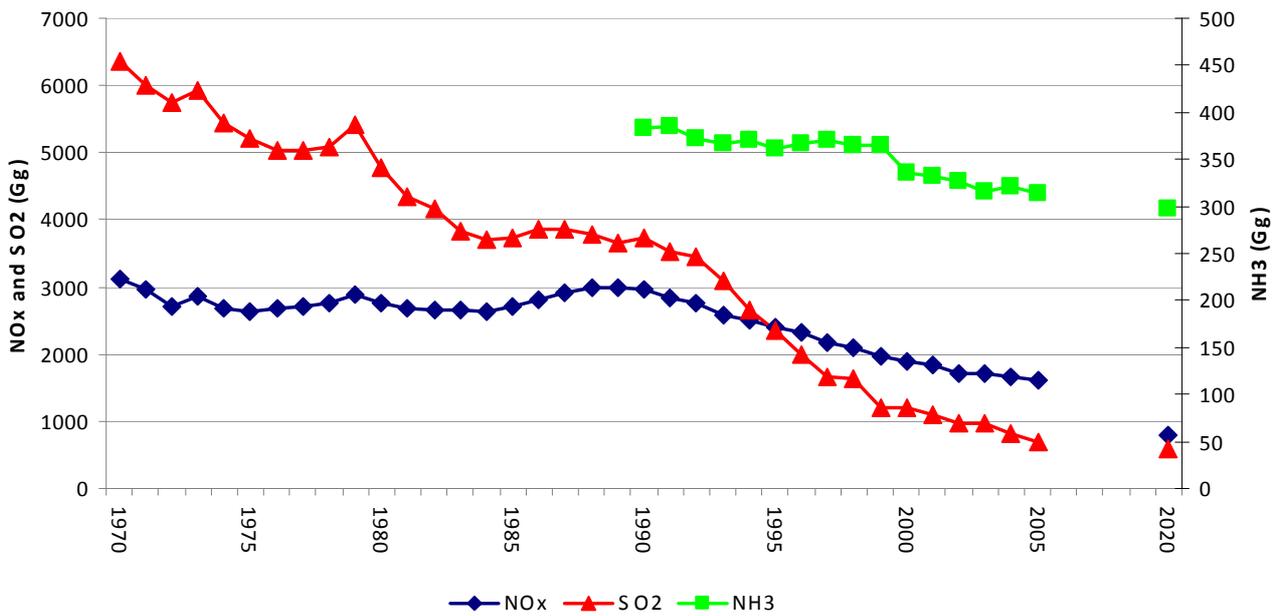


Figure 10.1 Trend in emissions of SO₂, NO_x and NH₃ in the UK during the period 1970-2020

10.1.2 METEOROLOGICAL DATA

The average annual precipitation in the UK during the period 1990 – 2004 is illustrated in figure 10.2. The data was generated from the UKMO official maps of precipitation for the UK gridded at a 5 km resolution. The average annual precipitation (1990-2004) for the UK was 1130 mm. The wettest years were 2000 (1331 mm), 2002 (1281mm) and 1998 (1261 mm). The driest years were 2003 (881 mm), 1996 (920 mm) and 1991 (995 mm).

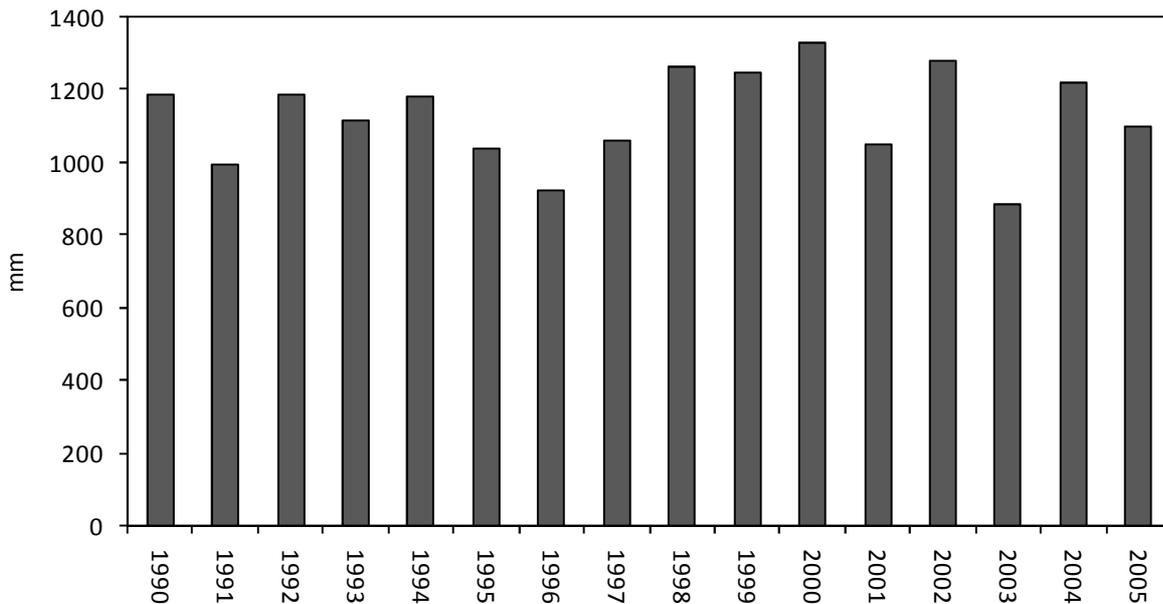


Figure 10.2 Trend in UK average annual precipitation between 1990 and 2005

The statistical distribution of wind direction for each of the years 1990-2005 was generated both from Jenkinson data (Jenkinson, 1977) and from radiosonde data. Jenkinson data assigns a circulation type and wind direction for each day of the year. The analysis showed that 1996 was a year with circulation weighted more towards the polluted south-east whilst 2004 was associated with circulation weighted more towards the cleaner maritime north-west.

10.2 Results of model simulations and comparison with measurements

The trends in wet deposition budgets generated by FRAME have been compared with those from the CBED measurement based data for the years 1990-2005 (figure 10.5). These show that the model is able to reproduce the observed trends in wet deposition. With CBED, inter-annual variations in meteorology dominate the year to year changes making a consistent trend difficult to detect for reduced nitrogen and oxidised nitrogen. The model is able to capture some of the inter-annual variation in deposition (notably the low deposition for the driest year, 2003) though this is somewhat restricted by the simple statistical representation of meteorology in the model.

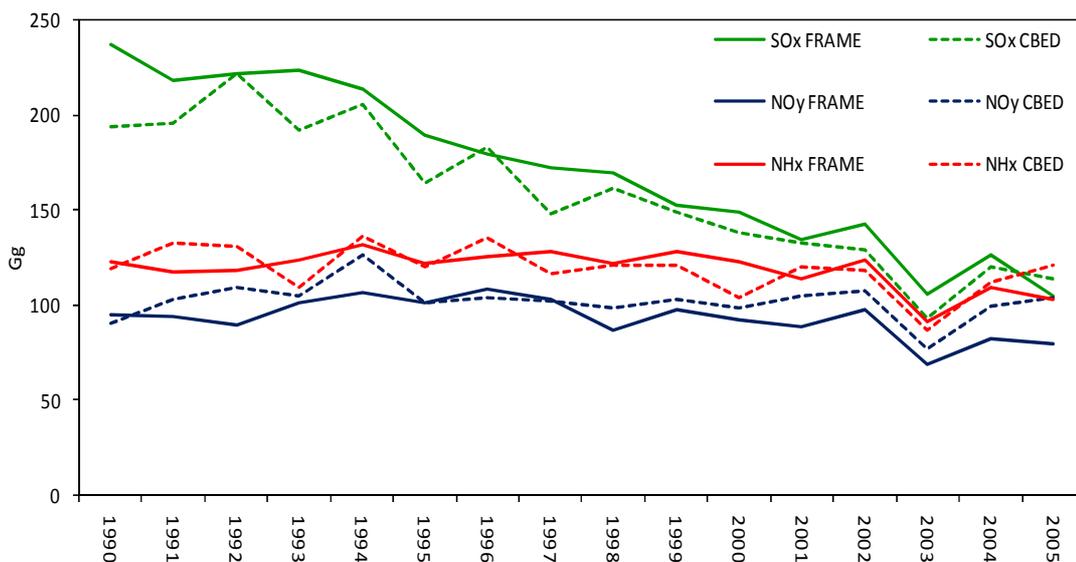


Figure 10.5 Modelled and measured UK national wet deposition budget for: S-SO_x, N-NO_y, N NH_x (Gg).

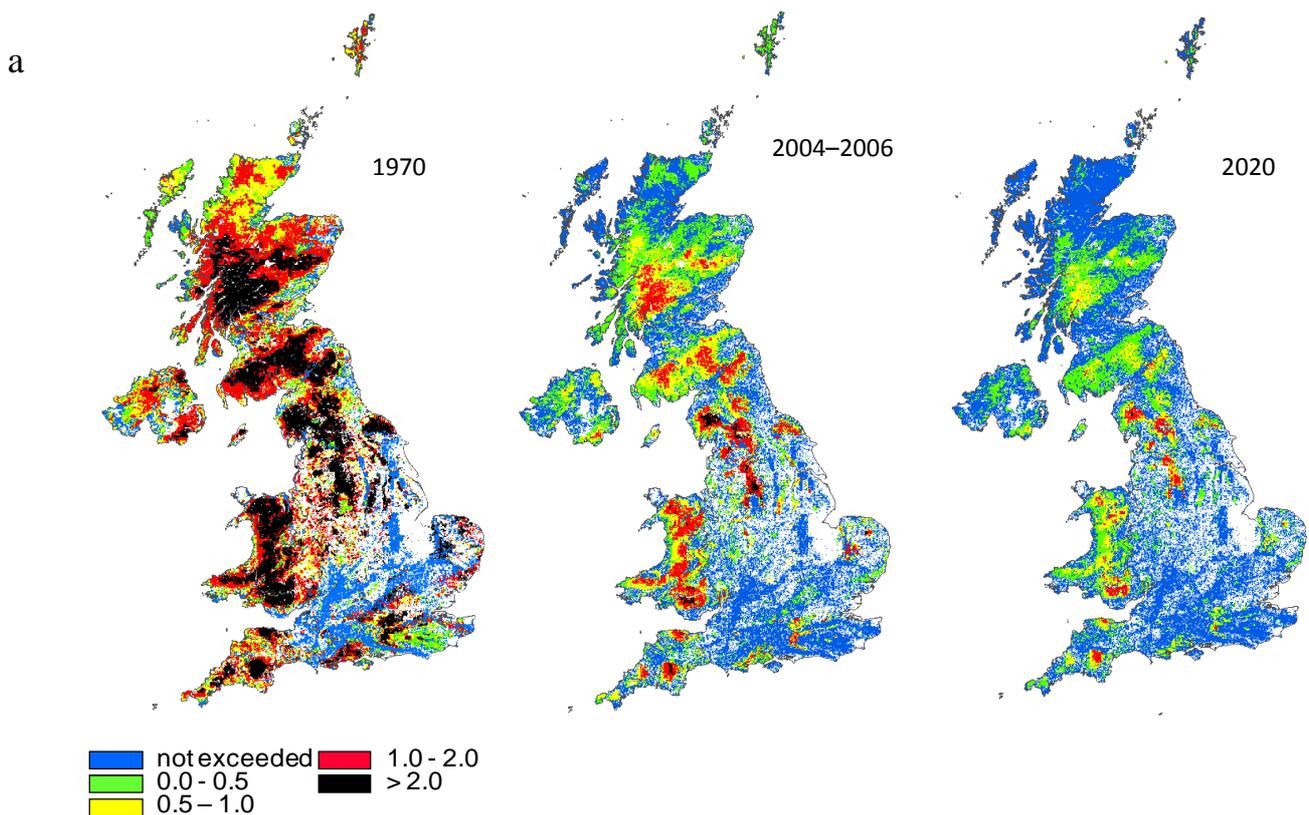
The model was also run with constant meteorology during the period 1990-2005. The resultant decreases in wet deposition were: 56%, 20% and 14% for SO_x, NO_y and NH_x respectively. These decreases in deposition are significantly lower than the decreases in emissions during the same period. Two factors may contribute to this. Firstly, whilst emissions from land sources in the UK during this period decreased significantly, emissions of NO_x and SO₂ from international shipping increased. Secondly, due to emissions reductions, the depletion of atmospheric oxidants became less of a controlling factor in determining the rate of conversion of pre-cursor gases to sulphate and nitrate aerosol (which make a major contribution to wet deposition).

10.3 Long term trends in exceedance of critical loads

To assess long term trends in deposition of sulphur and nitrogen, the model was run using historical emissions for 1970 and projected emissions for 2020.

A description of the methods used to derive and calculate critical loads is given in Hall et al. (2004). The significant reduction in the areas with exceedance is mapped in Fig. 10.6 (a) and (b). Large changes in exceedance of critical loads are noticed close to the emission sources, whereas in hilly regions, large exceedances remain in 2020. For acidity, the habitat areas with deposition exceeding critical loads are seen to fall significantly between 1970 and 2020 (from 94% to 22% for dwarf shrub heath). However, for nutrient nitrogen, the percentage area of unmanaged forest exceeded fell only marginally, from 99% to 95% between 1970 and 2020. This is due to the dominant role of dry deposition of ammonia to tall vegetation. The total area of sensitive UK habitats exceeded fell from 85% to 37% for acidity and from 73% to 49% for nutrient nitrogen.

Reductions in acid deposition and total nitrogen deposition may provide the conditions in which chemical and biological recovery of sensitive habitats can begin, but the timescales of these processes are often very long relative to the timescales for reductions in emissions. The study demonstrates the increasing relative importance of ammonia emissions in contributing to eutrophication and acidification. Efforts to further reduce deposition of sulphur and nitrogen to the natural environment must include measures to control emissions of ammonia.



b

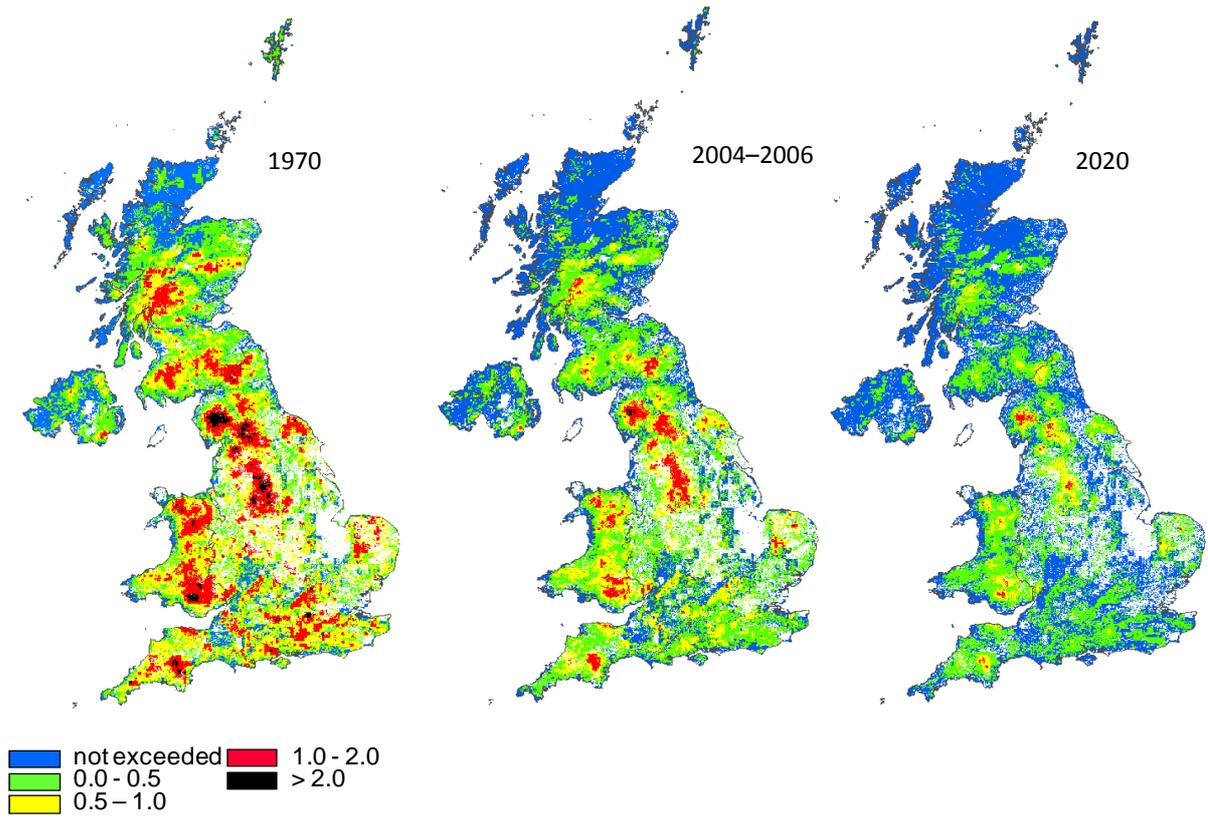


Figure. 10.6 Exceedance of 5th-percentile acidity critical loads by a) acid deposition b) nitrogen deposition.

11. Uncertainty Study

A large number of variables are incorporated into the FRAME model, including gaseous emission rates, chemical transformation rates, diffusion and advection rates, dry deposition velocities and washout coefficients. The uncertainty in setting these parameters will influence the accuracy with which the model can estimate sulphur and nitrogen deposition. An estimate of the uncertainty in acid deposition modelling was made by Abbott *et al.* (2003) using the TRACK, FRAME and HARM models. Both a Monte Carlo analysis (with parameter values sampled from within the range of uncertainty) and a first order analysis (with single parameters varied individually) were carried out. The results suggested that the uncertainty in acid deposition might broadly be described as a 'factor of two'. Page *et al.* (2004) applied a generalised likelihood uncertainty estimation methodology to the Hull Acid Rain Model. Two data sets of wet deposition from sites in Wales were used and the uncertainty prediction bounds were found to span the observed data satisfactorily. Detailed uncertainty studies require large numbers (typically a minimum of one thousand) of model simulations in order to obtain statistically significant results.

To quantify the uncertainty about parameter values in the form of a prior probability distribution, 23 parameters were selected from the FRAME model. A summary of a literature review of the parameter ranges is given in Table 11.1, including previous studies on the FRAME model, the review of Abbott *et al.*, (2003) and the selection of parameter ranges used by Page *et al.* (2004). Initially, a sensitivity study was undertaken to determine which of the 23 parameters were most significant in influencing wet deposition. The 12 most important parameters (meteorological, physical and chemical) were subsequently selected for the uncertainty study (Table 11.2).

The New CEH High Performance Computer Nemesis was used to undertake 2000 individual FRAME model runs in order to assess the uncertainty in wet deposition of sulphate and nitrate at the monitoring stations of the UK acid deposition network. The model was set up to run only trajectories which targeted the 38 'receptor' sites of model grid squares corresponding to locations of monitoring sites. This reduced the number of model trajectories required from 108,000 to 12,000. Tests showed that in this mode a simulation could run efficiently on a single node (comprising 8 cores) with a run time of 11 minutes. Use of two nodes or three nodes did not significantly decrease the simulation time. It was therefore decided that the most efficient use of the machine would be to run 5 sets of 400 simulations in parallel with a run time of 72 hours (three days).

Latin hypercube sampling of parameter values from a skewed triangular probability density distribution was undertaken to generate a set parameter values for each model run. The two most important model parameters in contributing to uncertainty in wet deposition were found to be the emissions of primary gases and the washout coefficients for aerosols. The next most important parameter was the import of boundary aerosol concentrations. Of subsequent and approximately equal importance were the parameters for wind speed, washout coefficients for gases and the seeder-feeder enhancement factor.

Figure 11.1 illustrates the modelled range of uncertainty, calculated from the standard deviation of the 2000 model runs which passed the acceptance criteria. Uncertainty in the measured wet deposition was assumed to be +/- 10% (Smith and Fowler, 2001) Uncertainty in modelled site-based wet deposition was found to range between 11% and 23% (mean 16%) with the higher ranges of uncertainty found at sites located more to the south of the country nearer to the national and European emissions sources. From figure 11.1, it is evident that the calculated model uncertainty is for most sites insufficient to explain the difference between model and measurements. The reason for this is the use of a skewed triangle distribution to sample parameter values, which are weighted close to the mean value. Future uncertainty studies with FRAME will be undertaken with a broader distribution in parameter values and will also consider in greater detail the geographical distribution of uncertainty in deposition.

Table 11.1. Literature review of parameter ranges (nominal parameter value is normalised to 1.0)

	Parameter name	Parameter	Parameter implementation ¹	Scale parameters from FRAME report		Scale parameters from AEA report		Scale parameters from HARM/GLUE paper	
				Minimum	Maximum	Minimum	Maximum	Minimum	Maximum
1	<i>VdVegNO2</i>	dry deposition velocity of NO ₂	land use dependent	0.8	1.3	0.3	1.7	0.7	1.3
2	<i>VdVegSO2</i>	dry deposition velocity of SO ₂	land use dependent	0.5	2.0	0.2	1.8	0.7	1.3
3	<i>Ddry</i>	dry deposition velocity of other species	Species dependent	0.7	1.5	0.5	2.0	0.7	1.3
4	<i>Rc</i>	Canopy resistance for ammonia deposition	land use dependent	0.5	2.0	0.5	2.0	0.7	1.3
5	<i>Δ_iSO₂</i>	scavenging ratio for wet deposition for SO ₂	chemical variable dependent	0.5	2.0	0	6.0	0.5	1.5
6	<i>Δ_iHNO₃</i>	scavenging ratio for wet deposition for HNO ₃	chemical variable dependent	0.5	2.0	0.3	10.0	0.5	1.5
7	<i>Δ_iNH₃</i>	scavenging ratio for wet deposition for NH ₃	chemical variable dependent	0.5	2.0	0.2	1.0	0.5	1.5
8	<i>Δ_iaerosol</i>	scavenging ratio for wet deposition for aerosol	chemical variable dependent	0.5	2.0	0.3	10.0	0.5	1.5
9	<i>RrNOO3</i>	reaction rate: NO+O ₃ →NO ₂ +O ₂	$2.1 \times 10^{-12} \times e^{-1450/T}$	0.8	1.2	0.8	1.2	0.5	1.5
10	<i>rrNO₂O₃</i>	reaction rate: NO ₂ +O ₃ →NO ₃ +O ₂	$1.2 \times 10^{-13} \times e^{-2450/T}$	0.8	1.3	0.7	1.3	0.5	1.5
11	<i>OxSO2</i>	reaction rate: SO ₂ + OH ⁻ → SO ₄	2 [daytime] ; 1 [night time]	0.5	2.0	0.4	2.2	0.5	1.5
12	<i>EquilC</i>	equilibrium constant: NH ₃ +HNO ₃ ↔NH ₄ NO ₃	temperature dependent	0.5	2.0	0.5	2.0	0.5	1.5
13	<i>Fphot</i>	reaction rate: NO ₂ +hv → NO+O	$1 \times 10^{-2} \times e^{(0.39 \text{sec}(zen))} \times (1-6/16)$	0.7	1.4	0.5	2.0	0.5	1.5
14	<i>FGToP</i>	reaction rate: HNO ₃ → NO ₃ ⁻ + H ⁺	1×10^{-5}	0.5	2.0	0.2[marine] ; 0.1[rural]	4.8[marine] ; 9.4[rural]	0.5	1.5
15	<i>rrNO2OH</i>	reaction rate: NO ₂ +OH ⁻ → HNO ₃	1.1×10^{-11}	0.6	1.7	0.6	1.6	0.5	1.5
16	<i>PeroxD</i>	daytime H ₂ O ₂ production rate	0.08333	0.7	1.4	0.5	2.0	0.5	1.5
17	<i>Sff</i>	Seeder feeder enhancement factor	2	0.5	2.0	0.5	1.5		
18	<i>emitNH₃</i>	NH ₃ emissions	spatially variable	0.8	1.3	0.7	1.3	0.4	1.6
19	<i>EmitNOX</i>	NO _x emissions	spatially variable	0.8	1.2	0.7	1.3	0.6	1.4
20	<i>EmitSOX</i>	SO ₂ emissions and H ₂ SO ₄ emissions	spatially variable	0.7	1.4	0.9	1.1	0.7	1.3
21	<i>Wspeed</i>	Optimised wind speed	directionally variable (5-9 ms ⁻¹)	0.9	1.1	0.8	1.2	0.5	1.5
22	<i>K_{max}</i>	Maximum vertical diffusivity	diurnally variable	0.5	2.0				
23	<i>hmix24</i>	Diurnally variable mixing layer height	diurnally variable	0.8	1.2	0.8	1.2	0.8	1.2

Table 11.2 Final parameter ranges for uncertainty study (nominal parameter value is normalised to 1.0)

	Parameter name	Parameter	Parameter implementation ¹	Final	
				Minimum	Maximum
1	$A_{i,gas}$	scavenging ratio for wet deposition of gas	chemical variable dependent	0.5	2.0
2	$A_{i,aerosol}$	scavenging ratio for wet deposition of aerosol	chemical variable dependent	0.5	2.0
3	$rrNO_2O_3$	reaction rate: $NO_2+O_3 \rightarrow NO_3+O_2$	$1.2 \times 10^{-13} \times e^{-2450/T}$	0.8	1.3
4	$OxSO_2$	reaction rate: $SO_2 + OH \cdot \rightarrow SO_4$	2 [daytime] ; 1 [night time]	0.5	2.0
5	$DDry$	Dry deposition velocity	chemical variable dependent	0.6	1.67
6	$import$	Import of aerosol at model boundary	Initial trajectory concentrations	0.6	1.67
7	$rrNO_2OH$	reaction rate: $NO_2+OH \cdot \rightarrow HNO_3$	1.1×10^{-11}	0.6	1.7
8	Sff	Seeder feeder enhancement factor	2	0.5	2.0
9	$emit$	NH_3 , NO_x , SO_2 and H_2SO_4 emissions	spatially variable	0.7	1.3
10	$Wspeed$	optimised wind speed	directionally variable (5-9 ms^{-1})	0.8	1.2
11	K_{max}	maximum vertical diffusivity	diurnally variable	0.5	2.0
12	$hmix24$	Diurnally variable mixing layer height	diurnally variable	0.8	1.2

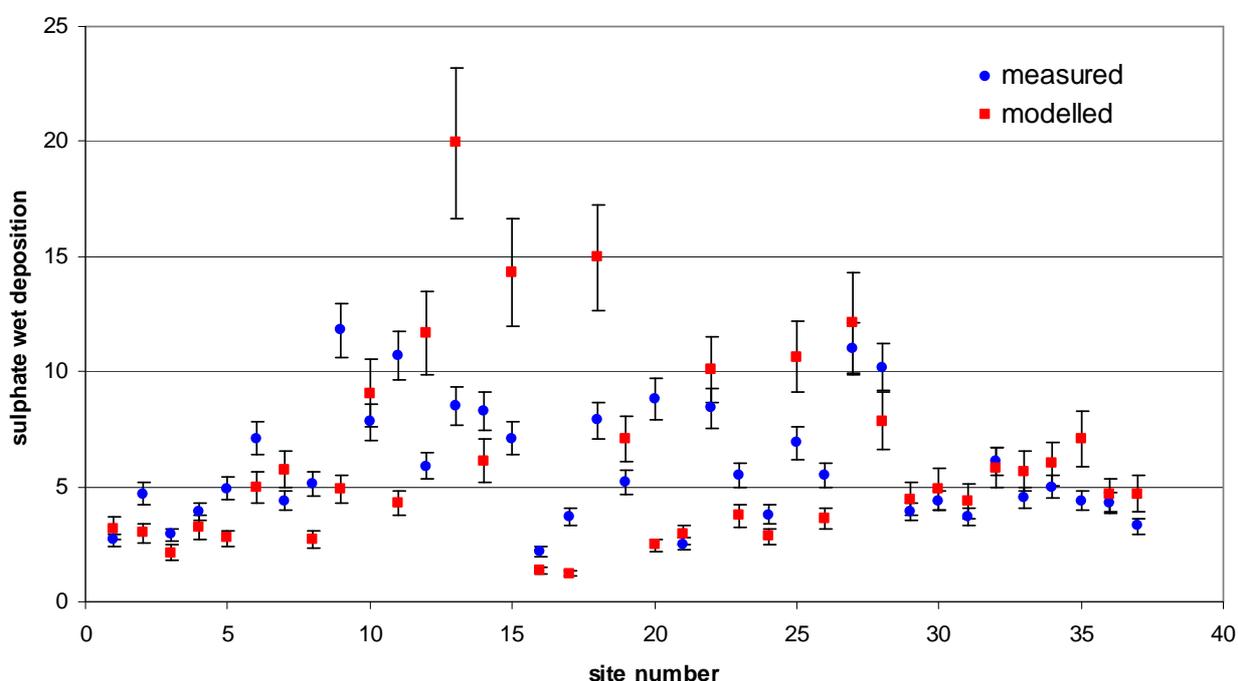


Figure 11.1 Uncertainty in modelled sulphate wet deposition compared to measurements from the acid deposition monitoring network

12. Assessment of the influence of climate change on sulphur and nitrogen deposition

Changes in general circulation, boundary layer height, temperature, cloud cover and precipitation resulting from climate change will lead to changes in air quality and pollutant deposition. The atmospheric oxidation rates of sulphur and nitrogen compounds are dependent on temperature and may also be influenced by climate driven changes in biogenic emissions (Hedegaard *et al.*, 2007). Some earlier studies have considered climate scenarios for the years 2080 and 2100. However the extensive time scales of such studies are well beyond the range of interest for air quality (and are of purely theoretical interest) when one considers that sulphur emissions in the UK have fallen by 90% in a 35 year period. Changes in air quality over future multiple decades will depend strongly on future emissions which are currently highly uncertain. High resolution model projections of the net

impacts of potential future changes in climate on UK air quality do not currently exist. It should be noted that the UK is close to the latitude where precipitation trends change from being generally drier in Southern Europe to being predominantly wetter in Northern Europe (Christensen *et al.*, 2007), so future trends in precipitation are highly uncertain.

A simple model such as FRAME employs statistical annually averaged meteorology comprising a wind direction frequency rose and an annual map of precipitation. The natural inter-annual variation in meteorology may be used to assess the potential magnitude of systematic climate change on sulphur and nitrogen deposition by setting emissions constant and employing meteorology from years with characteristic extreme values for annual precipitation and wind direction frequency.

FRAME was run using emissions for the year 2005 and with wind data and annual precipitation averaged over the years 1990-2005. The model was then run changing only the precipitation data or the wind direction frequency. Precipitation data from the wettest year (2000) and driest year (2003) during the 15 years series was selected (figure 10.2). Wind data from the year with strongest flow from the polluted continental south east direction (1996) and with cleaner maritime air with enhanced westerly flow (2004) was selected. The changes in deposition associated with these changes in precipitation and wind direction frequency (whilst keeping emissions constant) are illustrated in figure 11.1. The driest year (2003) resulted in decreases in wet deposition of sulphur and nitrogen deposition of 13-14% and small increases in dry deposition and the wettest year (2000) was associated with an increase of 7% in wet deposition. With enhanced flow from the south-east (year 2006) wet deposition is higher by about 22%, 14% and 12% for NO_y, SO_x and NH_x, respectively, with smaller increases in dry deposition. In general it was found that extreme inter-annual variation of precipitation and circulation could result in changes of +/- 10% in sulphur and nitrogen deposition.

Further work to investigate the influence of climate change on sulphur and nitrogen deposition in the UK will use a more integrated approach between detailed meteorology and atmospheric processes by employing the WRF model coupled to EMEP4UK.

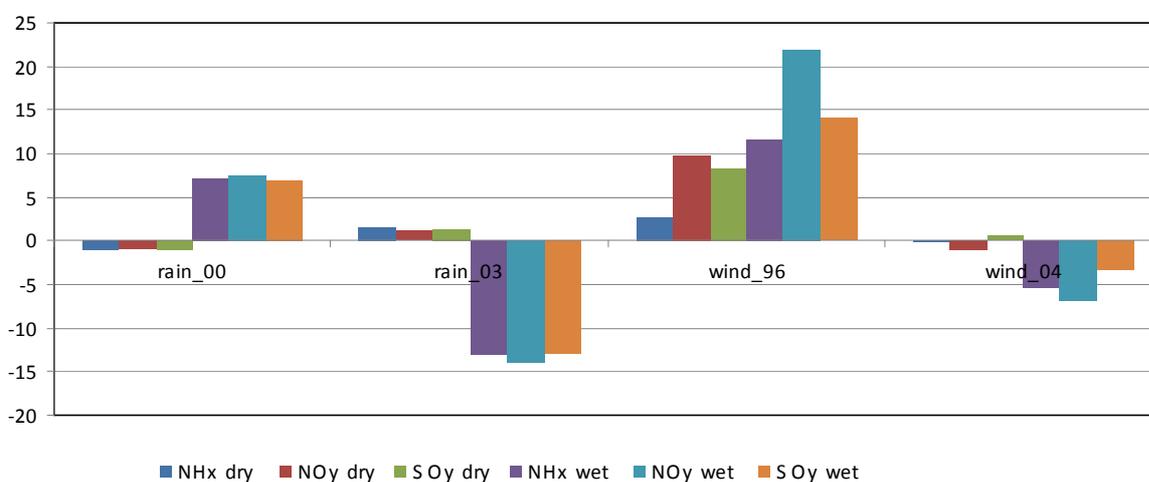


Figure 11.1 The percentage change in wet and dry deposition of sulphur and nitrogen in the UK using meteorology from the wettest (2000) and driest (2003) years and with enhanced south-easterly flow (1996) and westerly flow (2004).

Conclusion and Recommendations

Modelling the concentration and deposition of air pollutants provides important information which can be used to support of policy to control pollutant emissions and their effects. These include:

- (i) Estimation of concentration and deposition at a large number of modelled grid cells, providing more detailed spatial coverage than is possible with a monitoring network
- (ii) Quantitative attribution of concentrations and deposition of pollutants to their emissions sources
- (iii) Assessment of past and future changes in atmospheric chemical composition and its influence on the environment based on use of historical and projected pollutant emissions scenarios

The development of a fine scale (1 km resolution) version of FRAME over the UK represents an important step forward in improved spatial representation of emissions and concentrations of sulphur and nitrogen compounds. Future work should consider the influence of model resolution on wet and dry deposition of nitrogen and sulphur compounds and exceedance of critical loads.

Emissions from international shipping currently make a major contribution to the deposition of oxidised nitrogen and sulphur in the UK. Considerable uncertainty surrounds the magnitude of shipping emissions, spatial location and rate of change. Accurate high resolution maps of emissions from international shipping in the coastal waters of the UK and future forecasts of future changes in emissions are required to support further modelling studies.

Complex Eulerian models (such as EMEP4UK and CMAQ) are currently being applied to estimate sulphur and nitrogen deposition over the UK. These models include a detailed representation of meteorological processes and atmospheric chemistry. Their future application to answer policy related questions is therefore recommended. As with FRAME, the performance of complex models should be assessed by comparison with measurements of concentrations and deposition from the national monitoring networks. Furthermore, meteorological models should demonstrate that they can adequately model precipitation, particularly in upland regions. Complex models should be compared with the results from simple models and mapping techniques. They should also be applied to estimate both future and historical deposition of sulphur and nitrogen as well as the attribution of deposition to different emissions sources (including national, European and shipping emissions).

Simple models such as FRAME will continue to be useful, in particular concerning source-receptor calculations and uncertainty studies (which require large numbers of model simulations) and for high resolution (1 km) national scale modelling studies.

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