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Evidence Project Final Report

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Project identification

1. Defra Project code: AQ0719
2. Project title: Modelling the Deposition and Concentration of Long Range Air Pollutants
3. Contractor organisation(s):
   CEH Edinburgh
   Bush Estate
   Penicuik
   Midlothian EH26 OQB
4. Total Defra project costs (agreed fixed price): £ 230,895
5. Project: start date 1/4/2009

   end date 31/12/2012

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Executive Summary

7. The executive summary must not exceed 2 sides in total of A4 and should be understandable to the intelligent non-scientist. It should cover the main objectives, methods and findings of the research, together with any other significant events and options for new work.

- Application of the FRAME model for future emissions scenarios forecast major reductions in sulphur and oxidised nitrogen deposition of 44% and 39% respectively between the years 2008 and 2030. However the low level of ambition for reductions of ammonia emissions resulted in a small reduction of only 5% for NH_x deposition. The percentage habitat area in the UK with exceedance of acid deposition was calculated to decrease from 54% in 2006-08 to 38% in 2030 using the CBED and calibrated FRAME deposition data. For nitrogen deposition, the percentage habitat areas exceeded were 71% and 59% for 2006-08 and 2030 respectively.

- A study was made to assess the influence of model grid resolution on nitrogen deposition in the UK using deposition data gridded at 1 km, 5 km and 50 km resolutions. The high resolution deposition data was found to give a more accurate spatial representation of NO_2 concentrations in the vicinity of major roads as well as NH_3 concentrations in agricultural areas. Wet deposition in upland areas was calculated using high resolution precipitation data. The area of exceedance of critical loads for all ecosystems in the UK using uncalibrated FRAME deposition data was found to be relatively insensitive to grid resolution (31.5%, 32.6% and 35.4%) for 1 km, 5 km and 50 km resolution data respectively). However the area of exceedance for individual ecosystems (i.e. montane) and regions (i.e. Scotland) was much more sensitive to model grid resolution than summary statistics.

- The Defra model inter-comparison was aimed at assessing the strengths and weaknesses of different atmospheric chemical transport models and their suitability for use as tools to support policy. Data on concentrations and deposition of sulphur and nitrogen compounds from the FRAME model was submitted to the Deposition group. The validation of the models against measurements from the UKEAP national monitoring network for annually averaged data for the year 2003 showed that the models satisfied the basic criteria of being 'fit for purpose'. FRAME was overall able to perform as well as more complex models and in particular obtained good correlation with measurements of gas concentrations. More complex models tended to have improved performance for aerosol concentrations and concentrations in precipitation.

- The FRAME model was run for an 11 year series from the year 2000 to 2010. Analysis of the modelled change in concentrations of acid gases and aerosols showed that the major reduction of

SO_2 emissions from the UK during this period resulted in decreases of 80% in SO_2 concentrations. This change in turn caused a slower rate of secondary inorganic aerosol formation causing reductions of 38% and 37% in concentrations of sulphate aerosol and ammonium aerosol. Preliminary comparison with measurements during this period shows broad agreement between modelled and measured reduction in particulate and gas concentrations.

- Source-receptor matrices were calculated with FRAME for use in the UK Integrated Assessment Model (UKIAM). These included 402 individual emissions sources with emissions of NO_x and SO_2 by sub-SNAP sector and region and NH_3 emissions according to livestock sector as well as individual point sources and contributions from international shipping and Europe. The source-receptor matrices were used to link emissions from individual sources with sulphur and nitrogen deposition and aerosol concentrations in the UKIAM. This information was used to calculate the most effective pollutant abatement strategies to protect natural ecosystems and human health.

- An emissions model was designed to represent emissions of base cations from the sea in the region of the UK. The emissions were calculated using wind data from the WRF model. The FRAME model was run using the emissions from marine sources as well as anthropogenic emissions from the NAEI and estimates of emissions from dust re-suspended by wind. The model showed strong gradients in the concentrations of base cations in air at coastal locations. Satisfactory agreement was found with measurements of Na^+ and Mg^{2+} in air and precipitation. The under-estimate in modelled concentrations of Ca^{2+} was attributed to uncertainty in the contribution of wind driven re-suspension of surface dust.

- Total PM_{10} concentration were estimated by combining secondary inorganic aerosol concentrations, primary PM concentrations and sea salt concentrations modelled with FRAME and secondary organic aerosol concentrations calculated with the EMEP model. The model showed reasonable agreement with measurements with a normalised mean bias of -0.2

- FRAME was adapted to simulate the concentration and deposition of heavy metals in the UK (As, Cd, Cr, Cu, Pb, Ni, Se, V and Zn). Wet deposition was found to be the dominant process in removing metals from the atmosphere, accounting for two thirds of the total deposition. The modelled concentrations showed good correlation with measurements but with very large underestimates (normalised mean biases in the range -0.64 to -0.93), indicating a major under-estimate in total atmospheric emissions. Poorer correlation was found with measurements of wet deposition. Inclusion of estimates of spatial re-suspension of wind-driven dust for the UK in the model simulation led to an improvement in agreement with measured concentrations but was insufficient to close the gap between modelled and measured concentrations..

- The FRAME source code was re-parallelised from High Performance FORTRAN to OpenMP. As HPF is now infrequently used and unsupported on some new clusters, this was necessary to future-proof the model for portage on to the new generation of High Performance computers. Tests showed that FRAME was able to run with OpenMP on a single 8 core node in approximately the same time as with HPF using 3 nodes.

- Further work is required on estimation of uncertainty in modelled sulphur and nitrogen deposition which will be undertaken as part of a new contract on integrated assessment modelling.

Project Report to Defra

8. As a guide this report should be no longer than 20 sides of A4. This report is to provide Defra with details of the outputs of the research project for internal purposes; to meet the terms of the contract; and to allow Defra to publish details of the outputs to meet Environmental Information Regulation or Freedom of Information obligations. This short report to Defra does not preclude contractors from also seeking to publish a full, formal scientific report/paper in an appropriate scientific or other journal/publication. Indeed, Defra actively encourages such publications as part of the contract terms. The report to Defra should include:

- the objectives as set out in the contract;
- the extent to which the objectives set out in the contract have been met;
- details of methods used and the results obtained, including statistical analysis (if appropriate);
- a discussion of the results and their reliability;
- the main implications of the findings;
- possible future work; and
- any action resulting from the research (e.g. IP, Knowledge Exchange).

References to published material

9. This section should be used to record links (hypertext links where possible) or references to other published material generated by, or relating to this project.

Dore, A.J., D. Carslaw, J. Hall, C. Braban, M.Cain, C. Chemel, C.Conolly, R.G. Derwent, B.E.A. Fisher, S.J. Griffiths, S. Lawrence, S.E. Metcalfe, A. Redington, D. Simpson, R. Sokhi, R.I. Smith, P. Sutton, M. Vieno, J.D. Whyatt (2012) Evaluation and inter-comparison of acid deposition models and application to calculate exceedance of critical loads in the UK (in prep)

Hallsworth, S., Dore, A.J., Dore, C.J., Vieno, M., Nemitz, N., McDonald, A.G., Kryza, M. and Fowler, D. (2012) Identifying missing sources of heavy metals in the United Kingdom with an atmospheric transport model (in prep).

Oxley, T., Dore, A.J., Kryza, M. & ApSimon, H (2012). Modelling future impacts of air pollution using the multi-scale UK Integrated Assessment Model (UKIAM). *IJ. Environmental Modelling & Software.* (under review)

Dore, A.J., Kryza, M., Hall, J. Hallsworth, S., Keller, V., Vieno, M. & Sutton, M.A. (2012) The Influence of Model Grid Resolution on Estimation of National Scale Nitrogen Deposition and Exceedance of Critical Loads *Biogesciences* **9**, 1597-1609

Werner, M., Kryza, M., Dore, A. J., Blaś, M., Hallsworth, S., Vieno, M., Tang, Y. S., and Smith, R. I. (2011) Modelling of marine base cation emissions, concentrations and deposition in the UK, *Atmos. Chem. Phys*., **11**, 1023-1037, doi:10.5194/acp-11-1023-2011

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

Defra contract AQ0719

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Contents

Executive Summary

The objectives of the contract were:

- Development of an operational multi-scale code (at resolutions of 1 km, 5 km and 50 km)
- Development of a base cation modelling facility
- Calculation of source-receptor matrices for the UK Integrated Assessment Model
- Assessment of the sensitivity of nitrogen and sulphur deposition and critical loads exceedance to model grid resolution
- Annual update of model results and maintenance of the FRAME web site
- Comparison of FRAME with other models
- Estimation of uncertainty in modelled calculations of nitrogen and sulphur deposition
- Undertaking assessment of adhoc emissions scenarios for policy support
- Attendance and presentation at international conferences
- Re-calculation of import to UK from European emissions sources
- Modelling trends in concentrations of acid gases and aerosols
- Modelling the concentration and deposition of heavy metals

These objectives were successfully completed.

- Application of the FRAME model for future emissions scenarios forecast major reductions in sulphur and oxidised nitrogen deposition of 44% and 39% respectively between the years 2008 and 2030. However the low level of ambition for reductions of ammonia emissions

resulted in a small reduction of only 5% for NH_x deposition. The percentage habitat area in the UK with exceedance of acid deposition was calculated to decrease from 54% in 2006-08 to 38% in 2030 using the CBED and calibrated FRAME deposition data. For nitrogen deposition, the percentage habitat areas exceeded were 71% and 59% for 2006-08 and 2030 respectively.

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- Further work is required on estimation of uncertainty in modelled sulphur and nitrogen deposition which will be undertaken as part of a new contract on integrated assessment modelling.

Introduction

Both national and international legislation have been effective in reducing emissions of sulphur and reactive nitrogen to the atmosphere. In the UK a 94% reduction in SO_2 emissions occurred between 1970 and 2010. This resulted in major decreases of sulphur concentrations measured in the atmosphere in both air and precipitation (RoTAP, 2012) and reductions in acidifying inputs to natural ecosystems in the UK. Major reductions in emissions of NO_x have also occurred. However non-linearities in atmospheric chemical reactions have meant that these reductions have not resulted in major decreases in wet deposition of oxidized nitrogen. Furthermore, reductions in emissions of ammonia in the UK have been more modest and have not resulted in significant decreases in concentrations of ammonia gas and the wet deposition of reduced nitrogen. As a result, reductions of inputs of nitrogen to natural ecosystems have been much more modest than those for acid deposition during recent decades.

The eutrophication of natural ecosystems occurs due to the deposition of both oxidized nitrogen (emitted primarily from vehicles) and reduced nitrogen (emitted mostly from agricultural sources). Eutrophication of fresh waters promotes excessive plant growth and decay, favouring simple algae and plankton over other more complicated plants, and can cause a severe reduction in water quality impacting on fish stocks and other plant and animal life. Deposition of sulphur and nitrogen to the surface can occur via the mechanisms of both ‘dry’ deposition, mostly due to gas compounds (SO_2, HNO_3, NH_3, NO_2) and ‘wet’ deposition’ due to the incorporation of aerosol particles (acting as cloud condensation nuclei) in cloud droplets which fall to ground as precipitation, as well as below cloud scavenging of soluble gases.

The reaction of acidic gases with ammonia in the atmosphere leads to the formation of fine particulate matter (ammonium sulphate and ammonium nitrate), referred to as ‘secondary inorganic aerosol.’ Studies of human health have shown a correlation between particulate matter levels (PM) and increased respiratory and cardiovascular diseases, and mortality (i.e. Pope *et al.* 2002). In addition total PM also includes components of sea salt, organic carbon (of both anthropogenic and biogenic origin) and mineral dust (due to wind driven re-suspension of bare surface soil). These physical and chemical processes all need to be represented numerically in order for total particulate mass to be calculated using atmospheric transport models. Heavy metals (As, Cd, Cr, Cu, Pb, Hg, Ni, Se, V and Zn) make a minor contribution to total PM but are known to be hazardous to human health as well as being damaging to the natural environment.

Chemical Transport Models (CTMs) have been used in the UK during the last two decades to calculate acid deposition and provide advice to policy makers. The advantages of models include their ability to:

(i) Estimate the concentration and deposition of air pollutants at a large number of model grid cells in the UK (typically ~ 10,000 for a model with a 5 km grid resolution).
(ii) Estimate the future changes of impacts on ecosystems based on projections for pollutant emissions.
(iii) Correlate pollutant deposition to individual emissions sources through 'source attribution' studies.

A summary of the main features of the FRAME model used in this study is given below:

- 5 x 5 km or 1 x 1 km resolution over the British Isles (incorporating the Republic of Ireland);
- Input gas and aerosol concentrations at the edge of the model domain are calculated with FRAME-Europe, using European emissions and run on the EMEP 50 km scale grid. (Cooperative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe http://www.emep.int/UniDoc/index.html).
- Air column divided into 33 layers moving along straight-line trajectories in a Lagrangian framework with a 1^{o} angular resolution. The air column advection speed and frequency for a given wind direction is statistically derived from radio-sonde measurements (Dore *et al.*, 2006a). Variable layer thickness from 1 m at the surface to 100 m at the top of the mixing layer.
- Emissions are gridded separately by SNAP (Selected Nomenclature for Air Pollution) sector for SO_2 and NO_x using emissions data from the National Atmospheric Emissions Inventory (http://naei.defra.gov.uk/) gridded at a 1 km resolution. NH_3 emissions are input by agricultural sector and injected into vertical model layers which are source dependent.
- Vertical diffusion in the air column is calculated using K-theory eddy diffusivity and solved with the Finite Volume Method.
- Wet deposition is calculated using a scavenging coefficient dependent on the gas and aerosol species and a 'constant drizzle' approximation driven by an annual rainfall map. A

precipitation model is used to calculate wind-direction-dependent orographic enhancement of wet deposition (Fournier *et al.*, 2005)

- Five land classes: forest, moorland, improved grassland, arable, urban & water are considered. A vegetation specific canopy resistance parameterisation is employed to calculate dry deposition of SO_2, NO_x and $NH_{3.}$
- The model chemistry includes gas phase and aqueous phase reactions of oxidised sulphur and oxidised nitrogen and conversion of NH_3 to ammonium sulphate and ammonium nitrate aerosol.

This report illustrates developments and application of the FRAME chemical transport model. The range of pollutants modelled has been expanded to include heavy metals and base cations. An improved correlation with measurements of PM_{10} was achieved. A study was undertaken to investigate the sensitivity of nitrogen deposition and the exceedance of critical loads on model grid resolution. The FRAME source code was successfully re-parallelised from High Performance FORTRAN to Open MP, providing future-proofing for the model to be migrated onto new generation High Performance Computers. Participation was undertaken in the Defra model inter-comparison exercise and a simulation of changes in concentrations of gases and aerosols during the last decade was made. The model was applied to assess future changes in deposition of sulphur and nitrogen and the exceedance of critical loads for the years 2020 and 2030.

1. Sulphur and Nitrogen Deposition: Estimates of Future Changes

One of the most important applications of the FRAME model is calculating spatially distributed maps of sulphur and nitrogen deposition and estimating how these are expected to change in the future according to projections of reductions in emissions of SO_2, NO_x and NH_3. For this study, the UEP43 emissions projections for SO_2 and NO_x emissions for the years 2020 and 2030 for the UK were supplied by Anne Misra, AEA-Ricardo. The emissions of SO_2 and NO_x from the UK are forecast to fall by 41% and 47% respectively between 2010 and 2030. More modest reductions in NH_3 emission of 8% between 2008 and 2020 are predicted. European emissions were based on estimates from GAINS using the EMEP gridded emissions for the year 2008 and applying scaling factors by country to obtain spatially distributed emissions for 2020 and 2030.

A 2008 FRAME simulation was undertaken as a baseline year. Distributed emissions for the years 2020 and 2030 were calculated using emissions maps for the year 2008 and scaling these forward in time using SNAP sector scaling factors. The sulphur and nitrogen deposition for the future scenarios was calibrated relative to the reference measurement-based CBED 2006-08 deposition data. The exceedance of critical loads was calculated using CBED 2006-08 (based on measurement and interpolation of sulphur and nitrogen compounds in air and precipitation) and the calibrated FRAME 2020 and 2030 data.

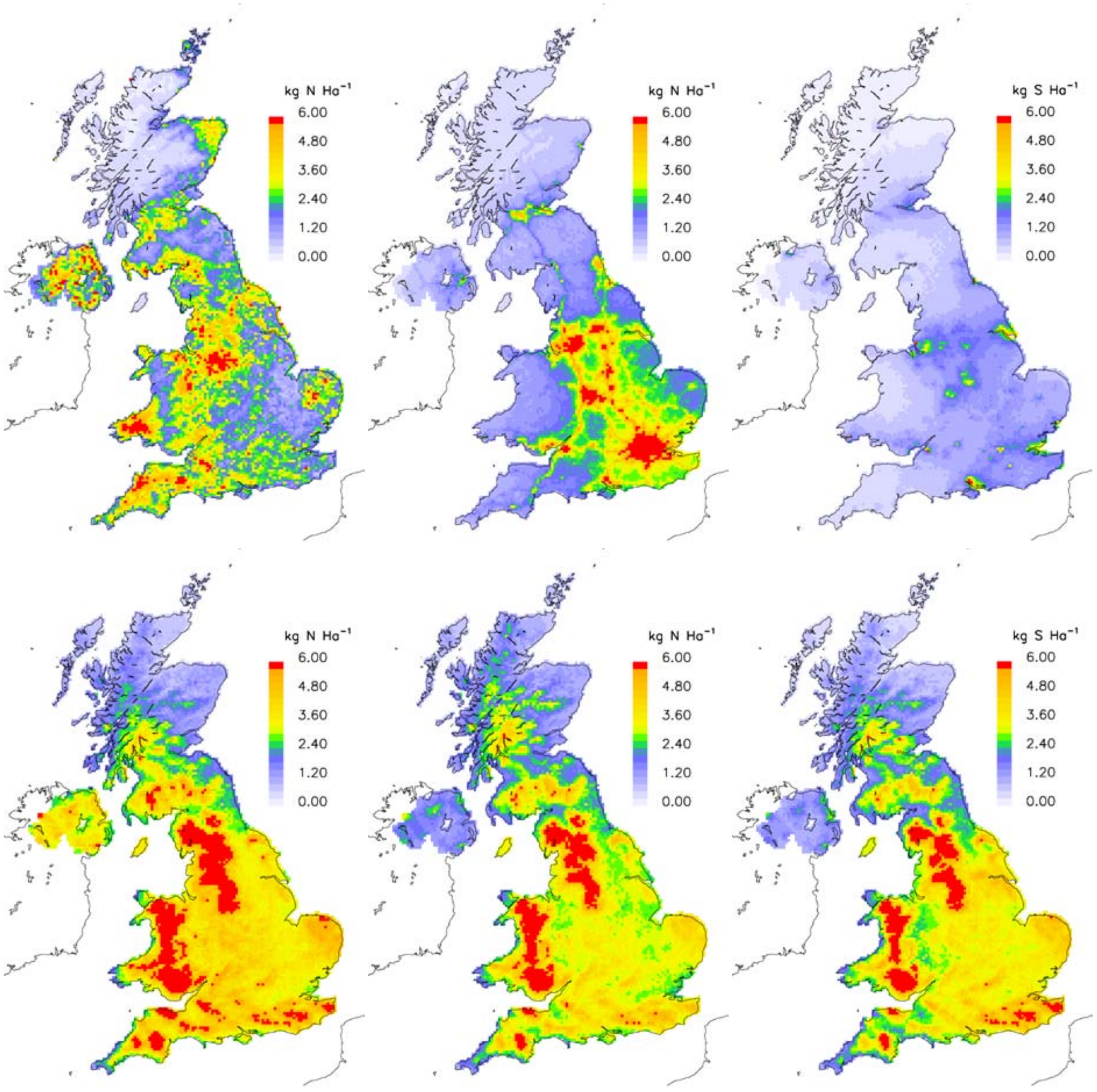


Figure 1.1 Sulphur and Nitrogen deposition modelled with FRAME for the year 2008: NH_x dry (upper left) ; NO_y dry (upper middle) ; SO_y dry (upper right) ; NH_x wet (lower left) ; NO_y dry (lower middle) ; SO_y dry (lower right)

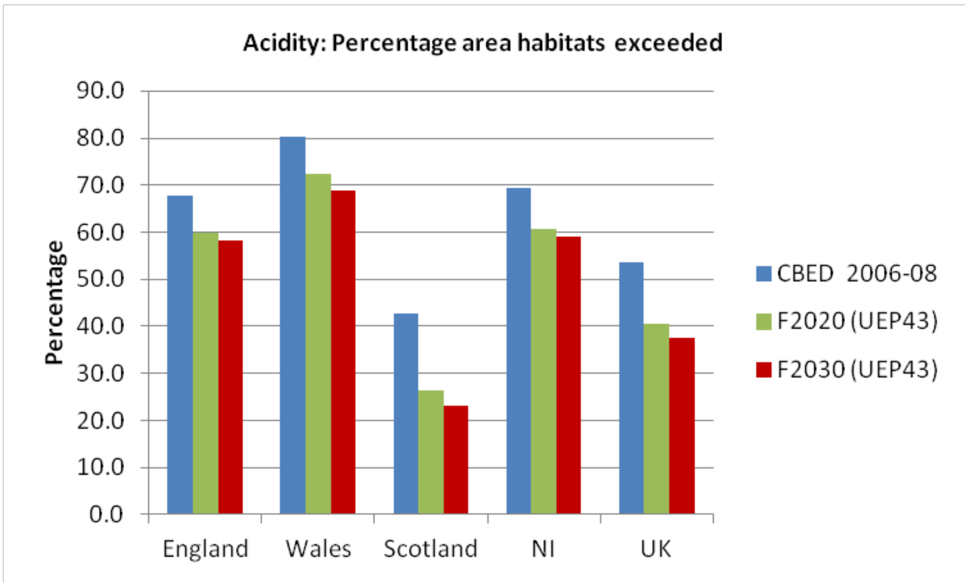
Wet and dry deposition of SO_x, NO_y and NH_x for the year 2008 is illustrated in Figure 1.1. Dry deposition of NH_x is highest in agricultural areas, principally in the west of the country. NO_y dry deposition is highest close to large urban areas and major roads and motorways, notably in England. Following major reductions in emissions during recent years, dry deposition of SO_2 has been significantly decreased. Areas of high deposition remain in the vicinity of major point sources (i.e. power stations) and ports, due to emissions from international shipping. Wet deposition is highest in the upland areas (i.e. Wales and the Lake District) due to a combination of long range transport of aerosol particles, the high precipitation in hill areas and the influence of the seeder-feeder effect (Dore *et al.*, 2006b).

The influence of reductions in emissions of SO_2, NO_x and NH_3 on the total deposition of sulphur and nitrogen to the UK is illustrated in Table 1. Major reductions in total deposition of SO_2 and NO_y between 2008 and 2030 are forecast (by 44% and 39% respectively). However the low level of ambition for reductions of ammonia emissions results in a small reduction of only 5% for NH_x dry deposition. Despite a reduction in NH_3 emissions between 2008 and 2020, NH_x deposition shows only a very small reduction and was found to increase between 2020 and 2030. This can be attributed to greater reductions in acidifying gas concentrations (H_2SO_4 and HNO_3) and the resulting slower conversion rate of ammonia gas to ammonium aerosol.

Table 1: UK deposition budgets modelled with FRAME for the years 2008, 2020 and 2030**.**

Deposition (Gg N/S)	**2008**	**2020**	**2030**
NH_x dry	59.5	59.4	60.1
NO_y dry	50.0	31.3	27.4
SO_x dry	21.7	13.0	11.0
NH_x wet	92.6	85.3	84.5
NO_y wet	79.9	57.2	51.4
SO_x wet	77.0	49.1	44.3
NH_x total	152.1	144.7	144.6
NO_y total	129.9	88.5	78.8
SO_x total	98.6	62.1	55.3

The calibrated deposition data was used to calculate future changes in the exceedance of critical loads (Figure 1.2). The percentage habitat area in the UK with exceedance of acid deposition was calculated to decrease from 54% in 2006-08 to 40% in 2020 and 38% in 2030. For nitrogen deposition, the percentage habitat areas exceeded were 71%, 61% and 59% for 2006-08, 2020 and 2030 respectively. The UEP43 results gave broadly similar exceedance results to those for the earlier UEP30 calculations for 2020. There was evidence of greater reduction in percentage area exceeded in more remote regions (i.e. Scotland) whereas high pre-existing values of percentage area exceedance in England were less sensitive to the emissions changes. When exceedance statistics were presented as average accumulated exceedance, a greater impact of emissions reductions was apparent (i.e. changes from 0.39 to 0.19 keq $ha^{-1}yr^{-1}$ for acidity and 0.56 to 0.39 keq/ha/yr for nitrogen for the UK between 2006-08 and 2030)



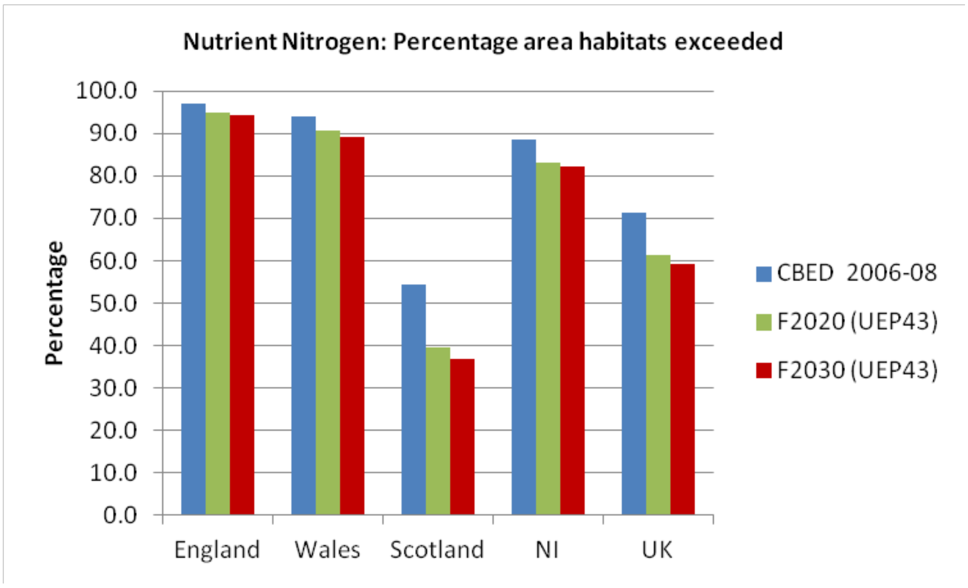


Figure 1.2: The exceedance of critical loads for acid deposition (upper) and nitrogen deposition (lower) for the regions of the UK for 2006-08 (CBED) and using forecast emissions for 2020 and 2030 (calibrated FRAME).

2. The sensitivity of the concentration and deposition of nitrogen and exceedance of critical loads to model grid resolution

2.1 Introduction

The spatial resolution at which calculations can be made with an atmospheric transport model depends on a number of factors. These include the size of the model domain, available computational power and the degree of complexity of the model. Inevitably, highly complex model simulations over large spatial domains will have limits imposed on grid resolution by the available computer facilities. Furthermore, fine spatial scale assessment of nitrogen deposition requires high resolution input data for meteorology as well as maps of land use and reactive nitrogen emissions. The OPS model represents a combination of a Gaussian plume model for local-scale application and a trajectory model for long-range transport operating on grid scales of 5 km and 500 m (Van Pul et al., 2004). The model was used to simulate concentrations, deposition and budgets of NH_3 gas and NH_4^+ aerosol for the Netherlands. The Danish Ammonia Modelling system (DAMOS) uses a combination of a long range transport model and a Gaussian local scale transport-deposition model for dry deposition. The model operates on a variety of scales with two-way nesting, from 150 km for the northern hemisphere, 50 km for Europe and 16.7 km for Denmark. Ammonia emissions are computed with high spatial and temporal resolution at a single farm and field level (Gyldenkaerne *et al.*, 2005). Vogt et al (2011) calculated ammonia concentrations and deposition at a 25 m resolution in an agricultural landscape. Fine resolution model simulation was demonstrated to be necessary to reproduce measured ammonia concentrations. A detailed discussion of modelling nitrogen deposition at a local scale is presented in Hertel *et al.*, (2006). The high resolution in the inventories was shown to be important for the model performance.

The Fine Resolution Atmospheric Multi-pollutant Exchange model is a Lagrangian Atmospheric Transport Model. Its relatively simple dynamic framework and chemical schemes result in fast run times. The model is therefore well suited to high resolution national scale simulations, which are currently too computationally demanding for more complex Eulerian models. The aim of this work is to investigate the influence of spatial averaging of modelled air concentrations and deposition on the exceedance of critical loads for nitrogen deposition.

The development of the FRAME model at a 1 km resolution over the UK and application to assess exceedance of the critical level for ammonia concentration in air over Natura 2000 sites (Special Protection Areas and Special Areas of Conservation) is described in Hallsworth *et al.* (2010). The study showed that a 1 km model simulation generated significantly lower values for the percentage of land surface area in nature sites with concentrations of ammonia in air exceeding the critical levels of 1 and 3 $\mu g\ m^{-3}$ when compared to 5 km resolution model data. This was attributed to the better spatial separation of agricultural source emissions areas for ammonia from sink nature reserve areas with the fine resolution study. For the present study the results of a 1 km model simulation have been mapped at resolutions of 1 km, 5 km and 50 km. This ensures that total national scale deposition is conserved. The three data sets have been compared spatially and assessed by validation with measurements of NO_2 gas concentrations. The different resolution data have been used to assess the sensitivity of model grid resolution on the exceedance of critical loads for nitrogen deposition in the UK. The influence of model grid resolution on NO_2 concentrations near a Site of Special Scientific Interest (SSSI) and on wet deposition of nitrate in a high precipitation upland region is considered.

2.2 High Resolution Precipitation Data

An annual precipitation map of the UK at a 1 km resolution was generated using data from 6000 daily measurement sites and 13100 monthly measurement sites in the UK Met Office national precipitation monitoring network. (Keller *et al.*, 2006). The triangular planes methodology (Jones, 1983) was used to generate daily 1 km^2 rainfall grids using a weighted average based upon the inverse distance of the three nearest rain gauges. The gridded rainfall data was then normalised and the daily rainfall totals were summed to give annual precipitation. The technique was successfully validated by comparison of the calculated rainfall data with site measurements (not included in the calculation) both for specific precipitation events and for monthly totals. In this study we focus on nitrogen deposition in the UK as a whole as well as a region of highly variable precipitation in Snowdonia in North Wales. Figures 2.1(a) and 2.1(b) illustrate the topography of the region and gridded precipitation data at a resolution of 1 km. The Snowdonia region is located near the west coast of North Wales and contains steep peaks of altitude exceeding 1000 m separated by broad valleys. The orography in the region has a strong influence on annual precipitation which varies from 1200 m near the west coast to approximately 4000 m in the region of Mt. Snowdon and varies significantly at a 1 km resolution scale. Precipitation in this region is strongly influenced by the seeder-feeder effect (Fowler *et al.*, 1988). The ascent and cooling of moist boundary layer air in prevailing winds frequently leads to the formation of low-level hill clouds. Whilst these clouds are generally too short lived to form into rain, their cloud droplets can be efficiently washed out by rain drops falling from higher level frontal rain clouds. A study of precipitation and wet deposition in this region using a simple model of the seeder-feeder effect is described in Dore *et al.* (2006b). The high precipitation resulted in high levels of deposition of sulphur and nitrogen and exceedance of critical loads for acid deposition and nitrogen deposition.

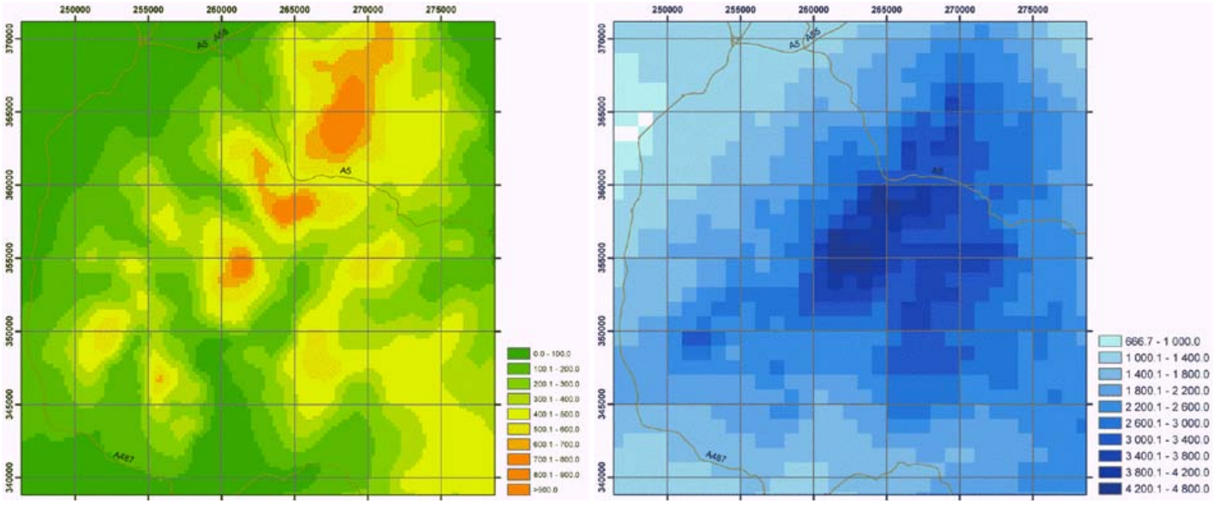


Figure 2.1: Terrain elevation in the region of Snowdonia, North Wales (m.a.s.l.) (left)
Annual precipitation (mm) gridded at a 1 km resolution for Snowdonia. (right)

2.3 Results

Figure 2.2 shows comparisons of NO_x concentrations generated with FRAME and gridded at both 1 km and 5 km resolutions at Stanford Park Site of Special Scientific Interest which is located approximately one km away from a major road. With the 1 km data, the NO_x concentrations are more closely correlated with the locations of the roads, in a more physically realistic manner. This resulted in lower NO_x concentrations being assigned to the grid square containing the SSSI.

Validation of the modelled NO_2 concentrations by comparison with measurements from rural sites in both the AURN and rural monitoring networks demonstrated an improved correlation using the higher resolution 1 km data. Analysis of modelled NO_y wet deposition in Snowdonia showed hot spots in wet deposition which are captured by 1 km resolution data but less evident with 5 km resolution data due to spatial smoothing over wider areas incorporating both hill peaks and lowlands.

The 1 km gridded data therefore represents an improved spatial distribution of air pollutant concentrations. However, even with 1 km data, strong spatial gradients in air concentrations may occur as a result of the physical limitations of the specified model grid. For focused local scale studies, dedicated local scale dispersion models are preferable. However the 1 km resolution simulation of nitrogen deposition data represents an improved reference national data set for sites where data from local scale dispersion studies are not available.

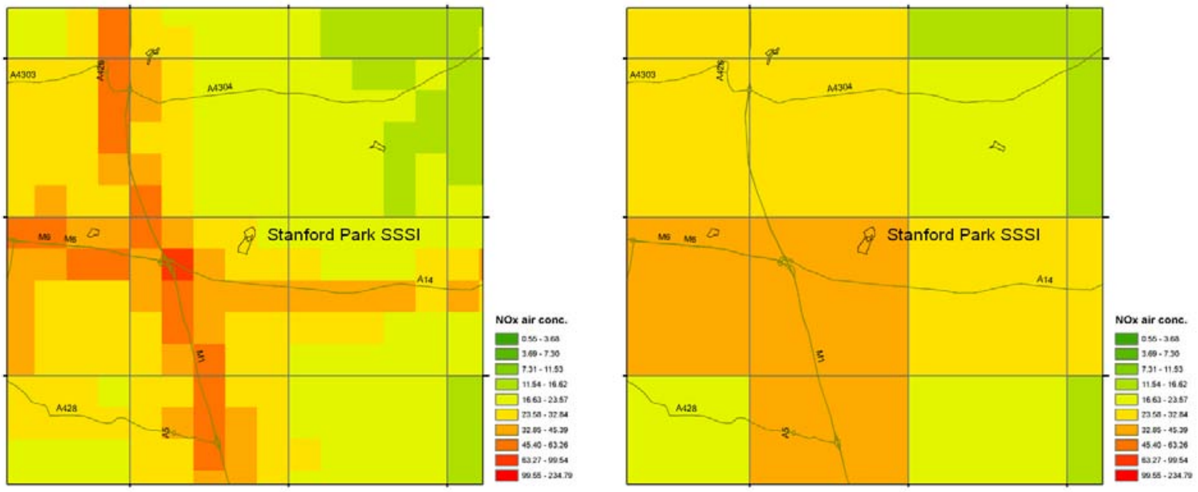


Figure 2.2: NO_x air concentrations at Stanford Park SSSI (µg m^{-3}) with 5 km grid resolution (left) and 1 km grid resolution (right)

The calculation of the exceedance of critical loads for nitrogen deposition is described in detail in Hall *et al.* (2003), Hall *et al.* (2011), and RoTAP (2011). Exceedances were calculated separately for each habitat type using 1km critical loads data and ecosystem-specific deposition (i.e., moorland deposition for the grassland, heath, bog and montane habitats, and woodland deposition for the woodland habitats). The results of calculating exceedance of the critical load for nutrient nitrogen deposition for each habitat across the UK are summarised in Tables 2.1 and

2.2. The influence of aggregating 1 km deposition data to a 5 km resolution grid is not manifested in a very large change in the percentage habitat area with exceedance of the critical load. The reason for this is the quasi-random distribution of source areas (i.e. industry, roads and agriculture) and sink areas (sensitive ecosystems). However, overall the exceedance of critical loads for nitrogen deposition is higher using the 5 km resolution data due to mixing of source areas (agriculture for reduced ammonia and road transport for oxidised nitrogen) with sensitive ecosystems in the same model grid square. With deposition data gridded at a 50 km resolution, the national scale area of ecosystem with exceedance is higher (35.4%) than for 1 km data (31.5%). This occurs because at the coarse 50 km resolution, nitrogen sources emitted from major industrial and urban areas are effectively co-located with natural ecosystems. Although the area exceeded was higher when using the 50 km deposition data, the magnitude of exceedance was lower. Use of 50 km resolution deposition resulted in spreading the exceedance wider, but with smaller resulting magnitude.

For regions with lower percentage area exceedance (Scotland and Northern Ireland), the influence of spatial averaging of nitrogen deposition over the larger 50 km grid cells resulted in more significant changes in total area with exceedance (i.e. from 5.1% for 1 km data to 7.5% for 50 km data for Scotland). For countries with higher percentage area exceedance (England and Wales) spatial averaging of deposition resulted in relatively small changes in the percentage in total area with exceedance (i.e. from 71.4% for 1 km data to 73.8% for 50 km data for England).

When percentage area exceedance is considered for the UK as a whole according to habitat type (Table 2.2), the general trend for increased percentage area exceedance using data with larger grid spacing is apparent. However for certain habitats (notably montane) the opposite is true. For this vegetation type, lower exceedances were obtained with the 50 km data. This is due to the fact that this habitat is associated with upland high precipitation areas located predominantly in the Scottish Highlands and that spatial averaging over 50 km in these regions leads to reduced wet deposition of nitrogen at the high elevation sites.

Furthermore it should be noted that the importance of spatial resolution inevitably depends on the nature of the landscape and the level of spatial mixing between source areas of nitrogen emissions (agriculture, roads and urban areas) and sink areas (natural ecosystems). In regions where emissions are densely concentrated in areas of intense agriculture and urban agglomerations which are distinctly separated from natural ecosystems, high grid resolution is of lower importance. However, for regions such as that illustrated in Figure 2.2 (a site of Special Scientific Interest with a nearby strong source of active nitrogen emissions), spatial resolution will be of greater significance.

Table 2.1: National scale summary statistics for habitat areas with exceedance of the critical load for nutrient nitrogen deposition by region.

Country	Habitat Area (km^2)	Percentage area habitats exceeded using FRAME deposition for 2007 at the following resolutions: 1 km	5 km	50 km
England	20299	71.4	72.5	73.8
Wales	7101	76.8	79.9	84.9
Scotland	43530	5.1	5.6	7.5
Northern Ireland	3500	37.3	40.3	58.0
UK	74430	31.5	32.6	35.4

Table 2.2: National scale summary statistics for habitat areas with exceedance of the critical load for nutrient nitrogen deposition by habitat type.

Broad Habitat	Habitat Area (km^2)	Percentage area habitats exceeded using FRAME deposition for 2007 at the following resolutions: 1 km	5 km	50 km
Acid grassland	15247	27.8	29.3	32.0
Calcareous grassland	3578	24.1	23.9	18.2
Dwarf shrub heath	24826	9.6	10.2	11.6
Bog	5537	25.7	26.9	35.8
Montane	3129	7.3	5.8	0.6
Coniferous woodland (managed)	8383	44.4	48.0	60.7
Broadleaved woodland (managed)	7482	89.7	89.9	89.1
Unmanaged woods (ground flora)	3297	85.8	86.0	86.2
Atlantic oak (epiphytic lichens)	822	40.9	40.9	45.3
Supralittoral sediment	2129	34.3	37.8	43.8
All habitats	74430	31.5	32.6	35.4

3. The Defra Model inter-comparison exercise

3.1 Introduction

The Defra model inter-comparison exercise was undertaken to assess the strengths and weaknesses of both simple and complex chemical transport models and their suitability for use in answering policy related questions concerning control of air pollution and the protection of human health and natural ecosystems. A protocol to evaluate the performance of air quality models is described in Derwent *et al.* (2010). Of the three different model groups (urban models, surface ozone and acid deposition) results from the FRAME model were submitted to the acid deposition group. A detailed analysis of these results is included in Carslaw (2011).

Modelling acid deposition in the UK was initially undertaken using ‘simple’ models such as HARM (Metcalfe *et al.*, 2001), FRAME and TRACK (Lee *et al.*, 2000). These Lagrangian models use straight line trajectories and operate in an annual average mode, assuming constant drizzle to drive wet deposition (based on maps of precipitation for the UK) and annual wind frequency roses to represent general circulation patterns of air trajectories. Lagrangian models independently perform calculations along pre-defined trajectories whilst Eulerian models simultaneously perform calculations at all points in the model domain. Major advances in High Performance Computer (HPC) technology have both driven a move to the use of complex Eulerian models during recent years. Such models include the US Environmental Protection Agency Community Multi-scale Air Quality (CMAQ) modelling system (Byun *et al*., 2006) and the European Modelling and Evaluation Programme (EMEP) model (Simpson *et al.*, 2012). These systems use a meteorological model to generate 3-dimensional temporally evolving meteorological data on wind speed, temperature, humidity, cloud and precipitation. These data are used to drive the chemical transport model.

The benefits of complex models include: a more detailed representation of meteorology and its influence on the deposition and concentrations of air pollutants and simultaneous multi-pollutant simulation (i.e. representation of acid deposition, surface ozone and particulate matter in one model). In contrast, simple models benefit from a fast simulation time. This allows: multiple simulation applications including source-receptor and integrated assessment studies (i.e. Oxley *et al.*, 2003; uncertainty studies (Page *et al.*, 2008) ; high spatial resolution studies (Hallsworth *et al*., 2010 ; Dore *et al.*, 2012).

3.2 Results

Monitoring data from the Department for the Environment, Food and Rural Affairs (Defra) United Kingdom Eutrophying and Acidifying atmospheric Pollutants (UKEAP) network was used to evaluate the models. The network data used for the evaluation included measurements of:

- Precipitation chemistry (SO_4^{--}, NO_3^-, NH_4^+) using bulk sample collections and analysis by ion chromatography at 37 sites.

- HNO_3, SO_2, NH_3 gas and aerosol (SO_4^{--}, NO_3^-, NH_4^+) concentrations at 12 sites using Delta samplers
- SO_2 gas concentrations at 37 sites using bubbler samplers
- NH_3 gas concentrations at 87 sites using both active (Delta) samplers and passive (Alpha) samplers
- NO_2 gas concentrations at 32 sites using diffusion tubes

All monitoring sites used in this study are based at rural locations. Further details are available at: http://uk-air.defra.gov.uk/networks/network-info?view=ukeap. The models were evaluated by comparison with annually averaged measurements of gas concentrations (SO_2, NO_2, NH_3, HNO_3) and aerosol concentrations (sulphate, nitrate and ammonium) in air as well as ion concentrations in precipitation for the year 2003. The evaluation was generated with the Openair software using the R statistical language (Carslaw et al., 2011).

Example plots of the correlation of the models with a gas concentration (NO_2), a particulate concentration (sulphate) and a concentration in precipitation (ammonium) are illustrated in Figure 3.1, 3.2 and 3.3 respectively. For this study the criteria for a model to be considered ‘fit for purpose’ were set by the model evaluation protocol as: $FAC2 > 0.5$ and $-0.2 < NMB < 0.2$ (where FAC2 is the fraction of modeled data points less than twice and greater than a half of the measured value ; NMB is the normalized mean bias). The first of these criteria was generally satisfied by the models, but the second condition was not satisfied for all variables by the models.

Analysis of statistics for all chemical species for all models indicated that whilst simple models were able to obtain good correlation with measured gas concentrations, the more advanced chemical schemes and detailed dynamics in complex models resulted in improved correlation with measured concentrations in precipitation and with aerosol concentrations. The overall results for model statistics, averaged for all models, are illustrated in Table 3.1 and for the FRAME model in Table 3.2. Compared to other more complex models, FRAME performed particularly well for comparison with measurements of NH_3, NO_2 and SO_2.

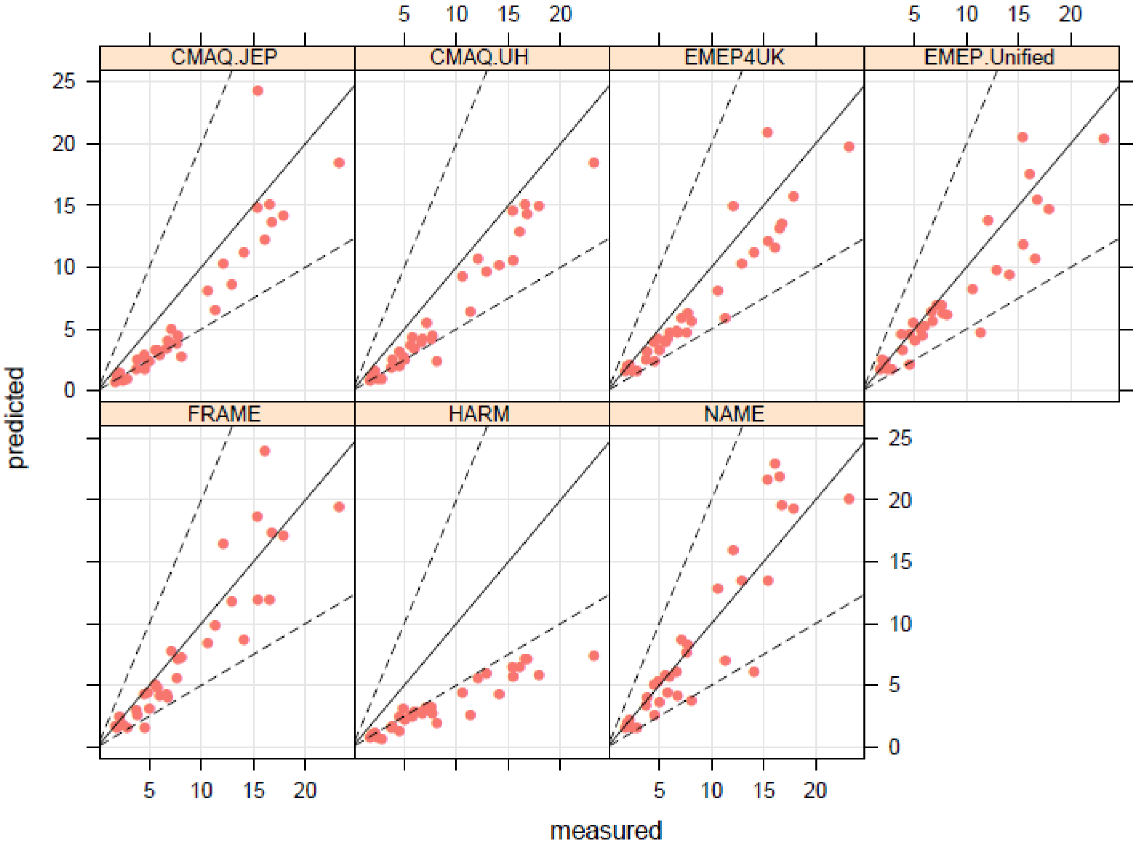


Figure 3.1: Correlation of the annual average modeled concentrations of NO_2 with measurements from the national monitoring network

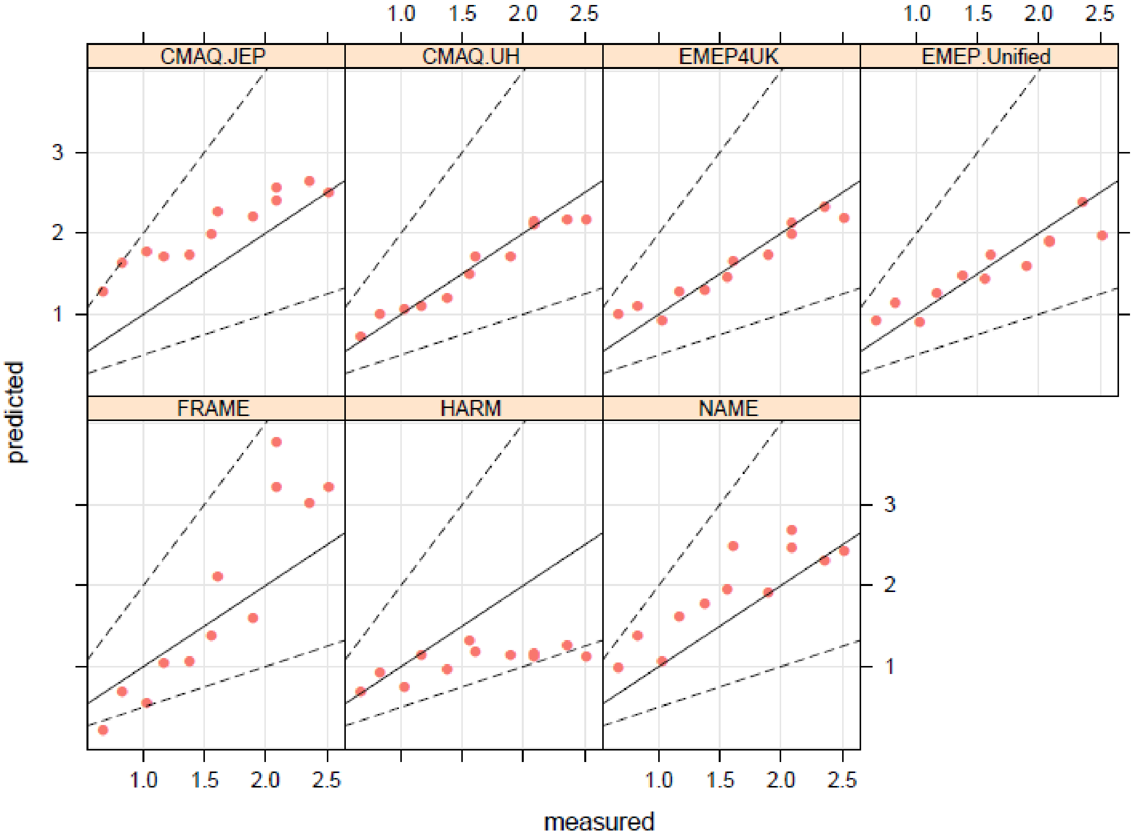


Figure 3.2: Correlation of the annual average modeled concentrations of sulphate aerosol with measurements from the national monitoring network.

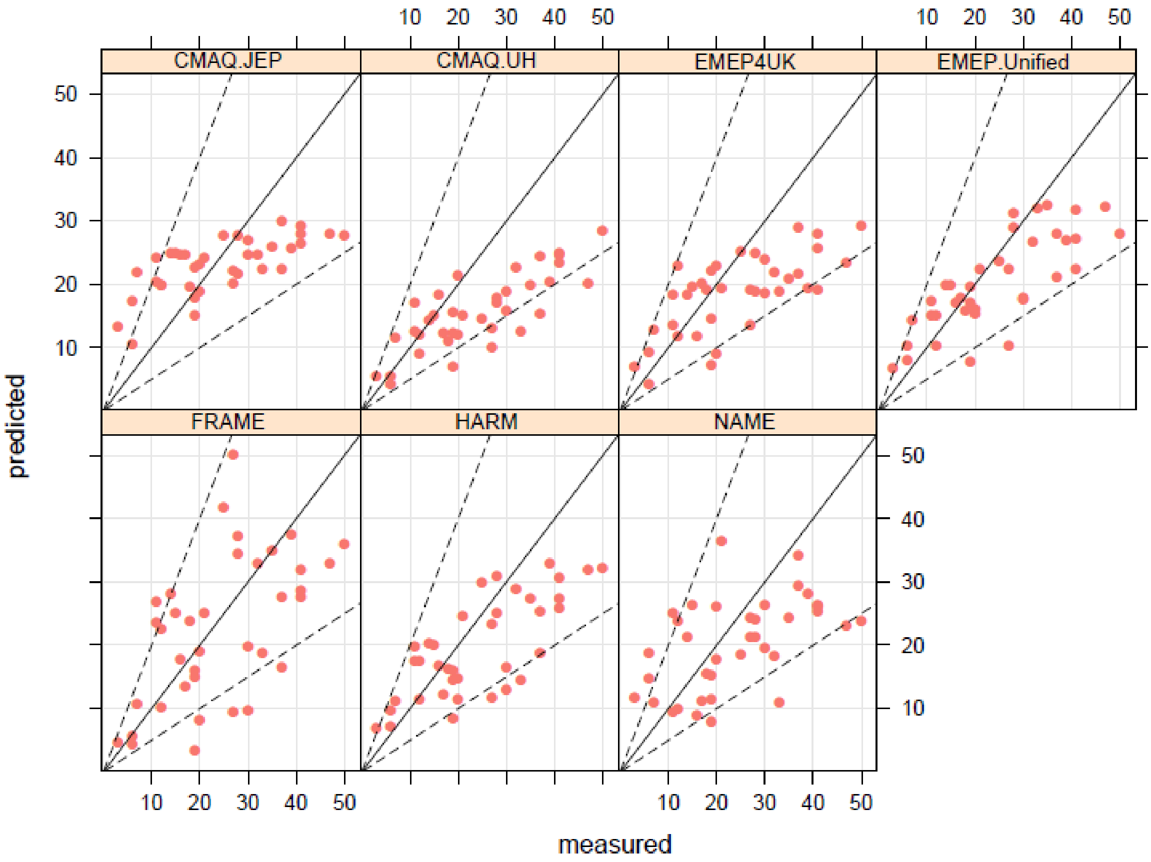


Figure 3.3: Correlation of the annual average modeled concentrations of ammonium in precipitation with measurements from the national monitoring network

By grouping the statistical outputs from all models for each of the measured pollutants, it may be possible to obtain some general understanding of the relative ability of transport models to represent concentrations of sulphur, oxidized and reduced nitrogen in the gas, particulate and aqueous phases as illustrated in Table 3.1

The scatter in correlation of the models with ammonia gas concentrations appears to generally be higher than for SO_2 and NO_2. This does not necessarily reflect a difficulty in the models to simulate the behaviour of ammonia. It is more likely to be caused by the high spatial variability in ammonia emissions in rural locations which results in changes in ammonia concentrations on scales not captured by atmospheric transport models with grid spacing typically of approximately 5 km. The ammonia concentration measured at an individual site may not be representative of the surrounding area as represented in a 5 km model grid cell. This issue has been studied in detail by Hallsworth *et al.* (2010).

Nitric acid makes a significant contribution to nitrogen deposition in the UK (RoTAP, 2011). However, as a chemically reactive vapour which is both soluble and rapidly deposited to vegetation, it may be expected to present problems for accurate representation in atmospheric transport models. The development of national monitoring networks to measure HNO_3 concentrations has occurred more recently than for NO_2 and SO_2. The performance of atmospheric transport models for HNO_3 is therefore historically less well known. The UK monitoring network has however established a 10 year series of continuous monitoring. It is therefore encouraging to see reasonable performance from all models for HNO_3 concentrations (FAC2 >= 0.75, -0.38<= NMB <= 0.12). The majority of the models show some underestimation, though this occurs in particular at two specific sites. Furthermore, recent evidence indicates that measurements of HNO_3 concentrations by Delta samplers may be elevated by the influence of HONO (nitrous acid) on the denuders.

There is clear evidence that the complex models (EMEP4UK, CMAQ, NAME) achieve better correlation with measurements of aerosol concentrations than the simple models (FRAME, HARM). This may be due to the difficulty of the simple models to capture the full magnitude of import of particulate matter from Europe during 2003. In general all models show some underestimate of ammonium aerosol concentrations. Model performance for sulphate aerosol is generally very good.

There is considerable scatter in the correlation of all the models for ammonium concentrations in precipitation. None of the models is able to achieve FAC2 > 0.9. All the models have a negative NMB which may indicate too low a rate of washout. As both ammonia gas and ammonium aerosol are soluble, this uncertainty / underestimate could be caused by either ammonia gas washout or ammonium aerosol washout. The average value of r for all the models for ammonium concentration in precipitation is 0.69, compared to 0.76 and 0.78 for sulphate and nitrate respectively. The models generally exhibited negative values of NMB for aqueous phase concentrations (average values of -0.08, -0.28 and -0.18 for sulphate, nitrate and ammonium respectively). This result is expected due to the fact that bulk precipitation collectors are used in the monitoring network and will be subject to dry deposition contamination, principally by gaseous deposition (i.e. Cape, 2009). Due to the significant regional variation in concentrations of gases as well as the turbulent properties of airflow driving their deposition to surfaces, it is not feasible to correct measured concentrations of ions from bulk collectors for dry deposition.

Table 3.1: Model performance statistics, averaged for all models, for comparison with measurements: **FAC2**: fraction of points greater than 0.5x and less than 2x the measured value ; **NMB**: normalised mean bias ; **NMGE**: normalised mean gross error ; **RMSE**: root mean square error ; **r**: correlation coefficient.

Group	Phase	FAC2	NMB	NMGE	RMSE	R
SO_2	Gas	0.65	0.80	0.88	2.13	0.79
NO_2	Gas	0.79	-0.19	2.87	3.28	0.93
NH_3	Gas	0.57	-0.24	0.53	1.49	0.63
HNO_3	Gas	0.88	-0.20	0.36	0.63	0.78
Sulphate	Aerosol	0.98	0.03	0.21	0.42	0.90
Nitrate	Aerosol	0.76	-0.24	0.31	1.10	0.93
Ammonium	Aerosol	0.80	-0.29	0.31	0.51	0.95
Sulphate	Aqueous	0.90	-0.08	0.32	9.58	0.76
Nitrate	Aqueous	0.87	-0.26	0.33	9.15	0.78
Ammonium	aqueous	0.84	-0.18	0.35	10.41	0.69

Table 3.2: Model performance statistics for FRAME, for comparison with measurements: **FAC2**: fraction of points greater than 0.5x and less than 2x the measured value ; **NMB**: normalised mean bias ; **NMGE**: normalised mean gross error ; **RMSE**: root mean square error ; **r**: correlation coefficient.

Group	Phase	FAC2	NMB	NMGE	RMSE	R
SO_2	Gas	0.96	0.07	0.31	0.79	0.77
NO_2	Gas	0.97	-0.1	0.22	2.60	0.92
NH_3	Gas	0.78	0.07	0.39	1.08	0.75
HNO_3	Gas	0.83	-0.32	0.42	0.78	0.61
Sulphate	Aerosol	0.92	0.14	0.34	0.71	0.92
Nitrate	Aerosol	0.92	-0.19	0.19	0.70	0.97
Ammonium	Aerosol	0.58	-0.36	0.36	0.55	0.95
Sulphate	Aqueous	0.84	0.28	0.42	13.94	0.75
Nitrate	Aqueous	0.89	-0.06	0.32	9.60	0.54
Ammonium	Aqueous	0.78	-0.07	0.38	11.17	0.57

4. Trends in acid gases and aerosols

The FRAME model was run for an 11 year period from the year 2000 to 2010. This coincides with the timescale of continuous operation of 12 Delta samplers in the UK Acid Gases and Aerosols (AGA) monitoring network, measuring concentrations of SO_2, HNO_3, NH_3 as well as sulphate, nitrate and ammonium aerosol. Emissions were taken from the NAEI for the UK, from EMEP for Europe and from AMEC for shipping. The trends in total emissions during 2000-2010 from these three regions are shown for SO_2, NO_x and NH_3 in figures 4.1(a) – 4.1(c)

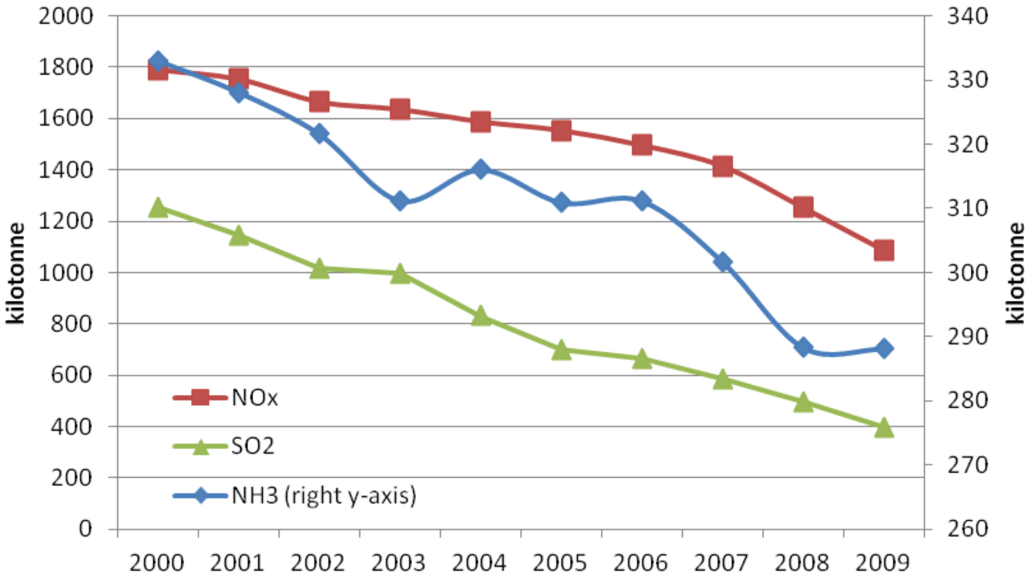


Figure 4.1(a): Total annual emissions of SO_2, NO_x and NH_3 from the UK.

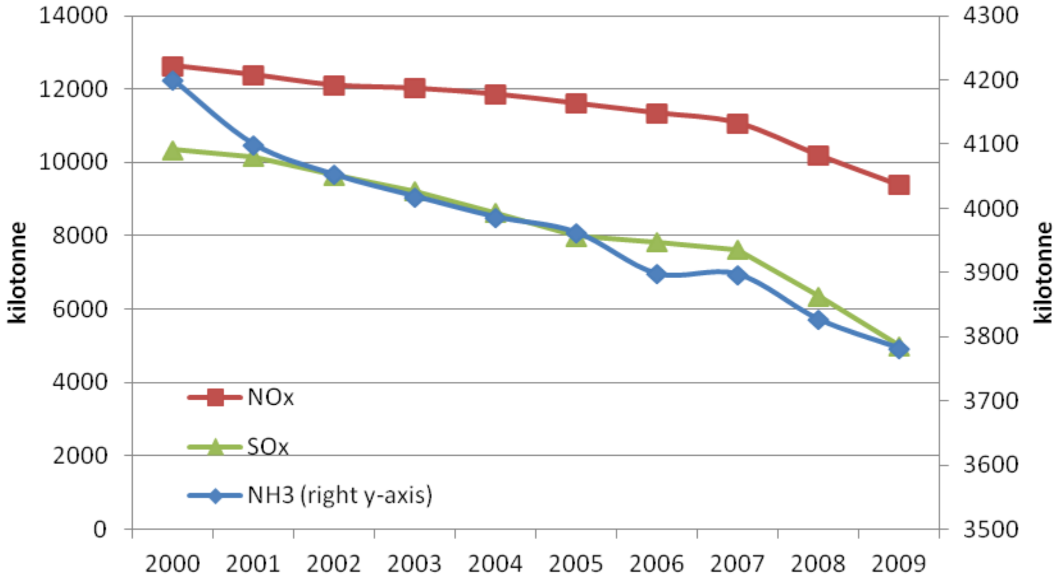


Figure 4.1(b): Total annual emissions of SO_2, NO_x and NH_3 from the European Union.

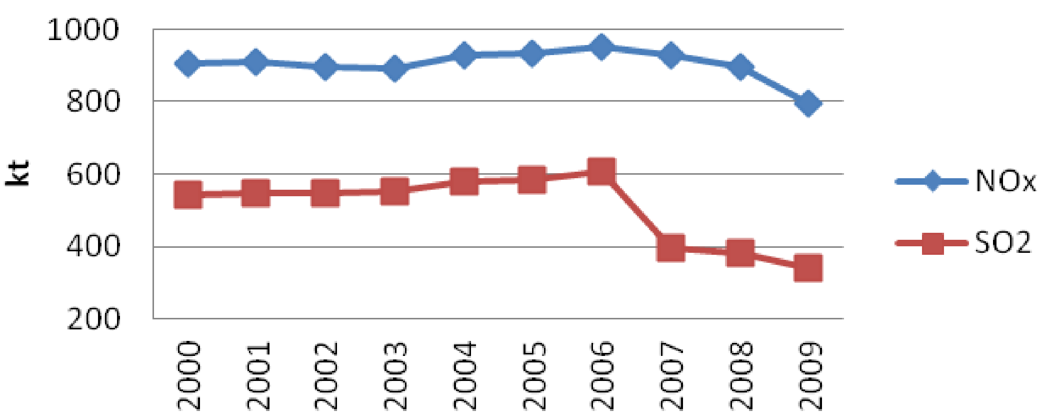


Figure 4.1(c) Annual shipping emissions from UK waters.

Annual concentrations of aerosol particles (i.e. sulphate, nitrate and ammonium) are subject to inter-annual variability due to both changes in meteorology. The variation in average annual precipitation for the UK and in wind direction frequency are illustrated in figures 4.2(a) and 4.2(b) respectively. The precipitation data was calculated from the UKMO annual gridded precipitation data. Wind roses were derived from 6-hourly operational radiosonde data from the stations of Aberporth, Camborne, Herstmonceux West End, Larkhill, Lerwick and Nottingham Watnall. The wind data from the radiosondes was taken from a layer at 950-900 hPa or about 500m -100m altitude.

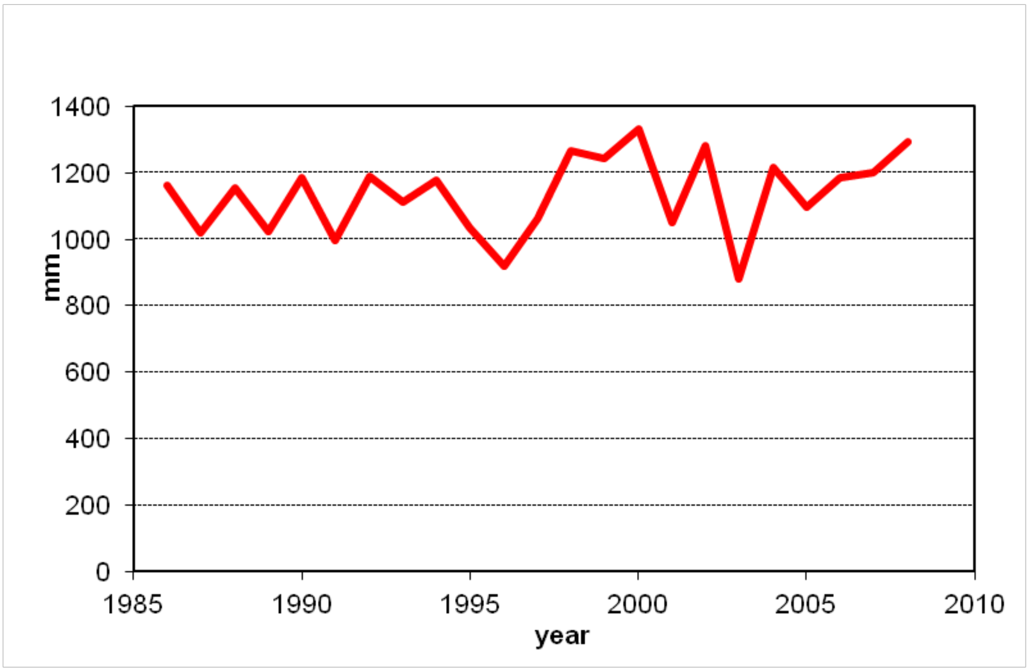


Figure 4.2(a) Average annual precipitation in the UK for 1986-2009

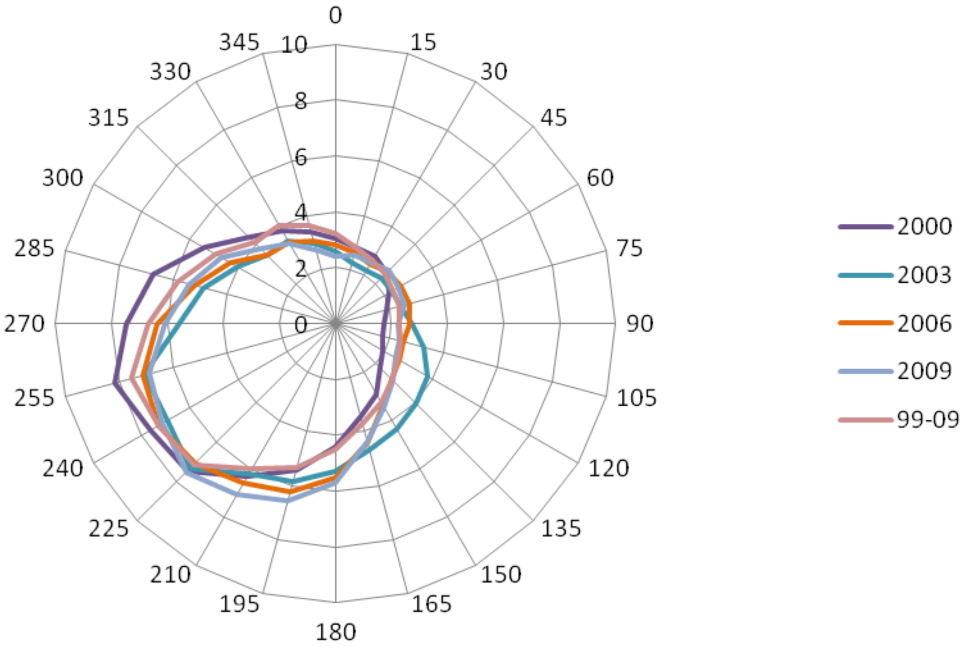


Figure 4.2(b) Annual UK wind roses for selected years

The annual average gas and aerosol concentrations across the UK calculated with FRAME for the years 2000-2010 are illustrated in Figure 4.3 and reductions of both emissions of gases from the UK and the EU and concentrations of gases and aerosols are illustrated in Table 4. A peak in concentrations of all aerosols (sulphate, nitrate and ammonium) is evident for the year 2003 due to high import of air from Europe resulting from a high level of south-westerly flow. Modelled SO_2 concentrations responded to the large decrease in emissions during this period with an average decrease of 80% over the UK. This also led to a significant reduction in concentrations of both sulphate (38%) and ammonium aerosol (37%) during this period. This illustrates that ammonium aerosol concentrations have largely been controlled by the reaction of H_2SO_4 with NH_3 during the last decade. Preliminary comparison with measurements show that the model was generally able to reproduce the observed changes in concentrations of SO_2 and aerosols during the 10 year period.

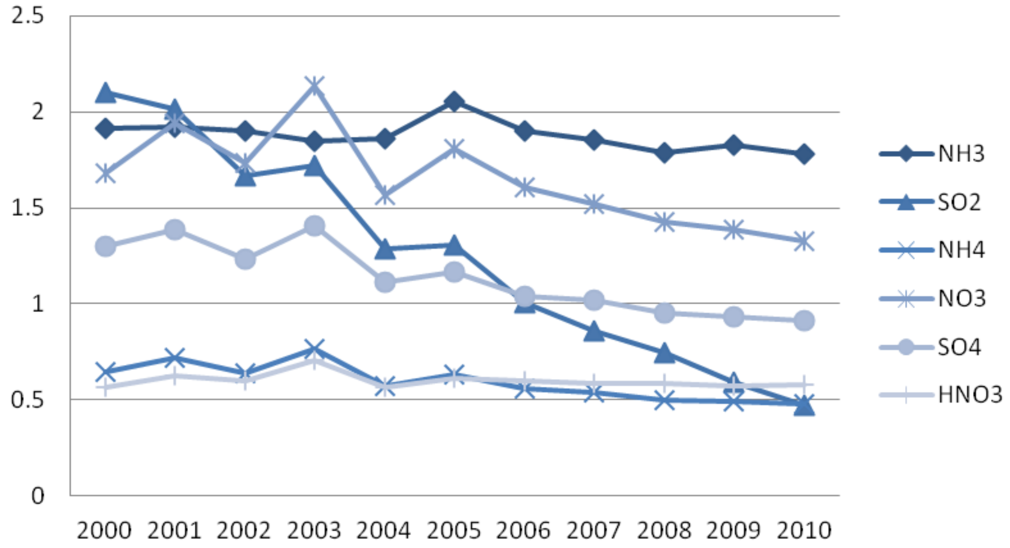


Figure 4.3 Annual average gas and aerosol concentrations for the UK calculated with FRAME for the years 2000-2010.

Table 4: Changes in emissions from the UK and the EU (2000-2009) and in modelled concentrations of gases and aerosols for the UK (2000-2010)

Emissions EU 2000-2009		FRAME 2000-2010	
NH3	-10%	SO4	-38%
NOx	-26%	NO3	-33%
SOx	-52%	NH4	-37%
Emissions UK 2000-2009		SO2	-80%
		HNO3	-7%
NH3	-14%	NH3	-6%
NOx	-39%		
SO2	-68%		

5. Modelling Source-Receptor matrices for the United Kingdom Integrated Assessment Model

5.1 Application of FRAME

FRAME was applied to generate source-receptor matrices for input to the United Kingdom Integrated Assessment Model (UKIAM). Following discussion with Tim Oxley (Imperial College), the following list of 402 emissions sources was generated with which to calculate deposition and concentration data for the UKIAM. These include 31 sub-SNAP sector sources for SO_2 and NO_x, 9 sectors for NH_3 (dairy, beef, pigs, layers, other poultry, sheep, other livestock, fertiliser, non-agricultural) and 5 regions (England, Scotland, Wales, Northern Ireland, London). Additional emissions sources were off-shore sources, European sources and international shipping. Three gaseous pollutants (SO_2, NO_x and NH_3) were abated individually. The list of sources abated is illustrated in Table 2.1.

Table 2.1: list of FRAME simulations to generate source-receptor matrices for the UKIAM

No. of simulations	Type of emissions abatement
1	No source abatement (baseline case)
155	SO_2 area emissions (5 regions x 31 sub-SNAP sectors)
155	NO_x area emissions (5 regions x 31 sub-SNAP sectors)
45	NH_3 area emissions (5 regions x 9 sectors)
20	major SO_2 point sources
20	major NO_x point sources
2	Off-shore sources (SO_2 and NO_x)
2	Shipping emissions (SO_2 and NO_x)
3	European emissions (SO_2, NO_x and NH_3)

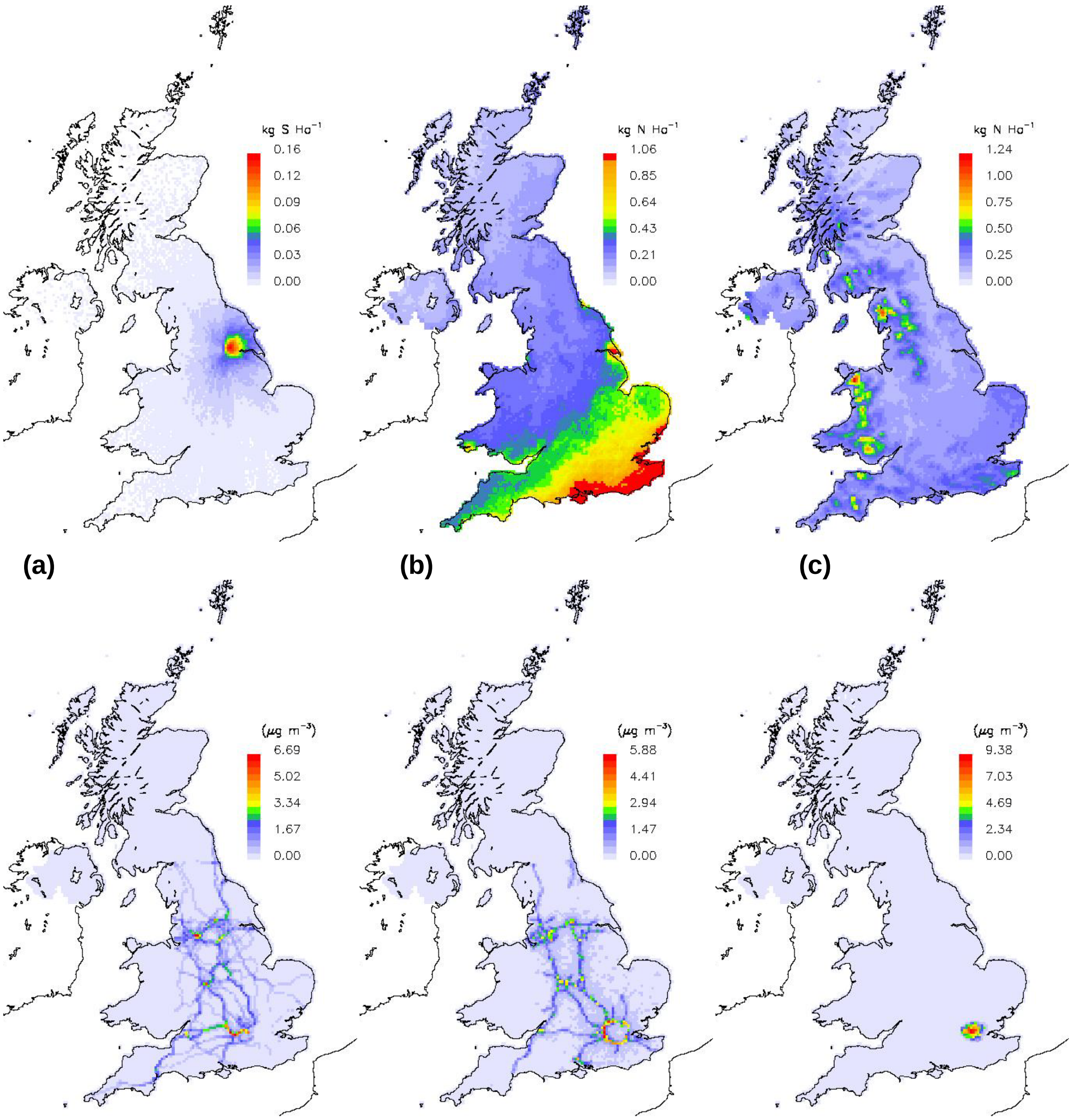
This approach to targeting emissions sources marks a significant change from previous data sets generated for the UKIAM (reported under contract CPEA34). Previously emissions sources were chosen according to county and included simultaneous abatement of different pollutants (SO_2, NO_x and NH_3). The changes reflect the need to select emissions sources which can be targeted directly by policy. Thus whilst country source-receptor matrices (SRMs) generated by the EMEP model are appropriate for Europe, county source-receptor matrices for the UK had limitations on their use in integrated assessment modelling because policy on pollutant emissions is not controlled at a county level. However with the devolution of the regions of the UK, the generation of SRMs by country (England, Scotland, Wales and Northern Ireland) has become relevant. Similarly, greater London was treated as a specific case and assigned as a fifth region.

The change to calculating SRMs individually for different pollutants is in line with changes made by EMEP to calculate country SRMs on a European scale. This allows inclusion of 'cross terms' in the data set and permits assessment of questions such as: "What is the influence of abatement of SO_2 emissions on concentrations of NH_3?" or "What is the influence of abatement of NH_3 emissions on formation of nitrate aerosol?" The reduction of emissions of SO_2 for example may slow the formation of ammonium sulphate aerosol, resulting not only in decreases in wet and dry deposition of sulphur but also in a decrease in wet deposition of reduced nitrogen. However this reduction will be off set by increased concentrations of ammonia and dry deposition of reduced nitrogen, as has been observed in the Netherlands. The consequence of this is that emissions of primary pollutants may be correlated to negative concentrations of secondary pollutants. The concept of negative concentrations and deposition may be intuitively difficult to grasp but it is important to include this data in integrated assessment modelling if we are to consider the full range of effects (both environmentally beneficial and detrimental) associated with emissions reductions.

It is important to note however that model calculation of 'footprints' of concentration and deposition from individual sources are subject to relatively high uncertainty (because these are calculated based on the difference between two model simulations with often only very small differences in total input emissions). In the case of footprints for cross terms, we can expect even higher uncertainties.

5.2 Results

Example plots of the source-receptor data generated by FRAME are illustrated in figures 5(a)-(j). Figure 5(a) illustrates SO_x dry deposition from a power station in northern England with high deposition occurring within a few tens of km of the source. The contribution of international shipping emissions to NO_y dry deposition is illustrated in figure 5(b). This is highest in south-east England and near to major ports due to the heavy traffic of international shipping in the English Channel. Figure 5(c) shows the wet deposition of oxidised nitrogen associated with European emissions. Deposition is highest in the upland regions of England and Wales where precipitation is highest. NO_x concentrations associated with emissions from railways in England, heavy goods vehicles in England and cars in London are illustrated in figures 5(d), 5(e) and 5(f) respectively. High concentrations are associated with the rail traffic on the London-Bristol railway line, heavy goods vehicles on the M25 orbit motorway around London and cars in the centre of London. Figure 5(g) shows NH_x dry deposition from ‘other poultry’ (not layers) in England. A feature of this map is ‘hot spots’ in East Anglia, north-east and west England due to high emissions of ammonia from intensive farming at a small number of locations. This pattern contrasts strongly with NH_x dry deposition from beef in Scotland (figure 5(h)). The emissions from grazing animals are more widely distributed and deposition occurs in the lowland pasture areas of Ayrshire and Dumfries, the central belt and Aberdeenshire. NH_x dry deposition associated with emissions from sheep in Wales (figure 5(i)) is also widely distributed but the distribution includes the upland regions of central and northern Wales. Figure 3(j) illustrates nitrate aerosol concentrations from European NO_x emissions. Aerosol is associated with long range transport but the map generally illustrates a pattern with decreasing concentrations towards the north-west of the country.


kg S Ha^{-1}
0.16
0.12
0.09
0.06
0.03
0.00
kg N Ha^{-1}
1.06
0.85
0.64
0.43
0.21
0.00
kg N Ha^{-1}
1.24
1.00
0.75
0.50
0.25
0.00
(μg m^{-3})
6.69
5.02
3.34
1.67
0.00
(μg m^{-3})
5.88
4.41
2.94
1.47
0.00
(μg m^{-3})
9.38
7.03
4.69
2.34
0.00

(a) **(b)** **(c)**

(d) **(e)** **(f)**

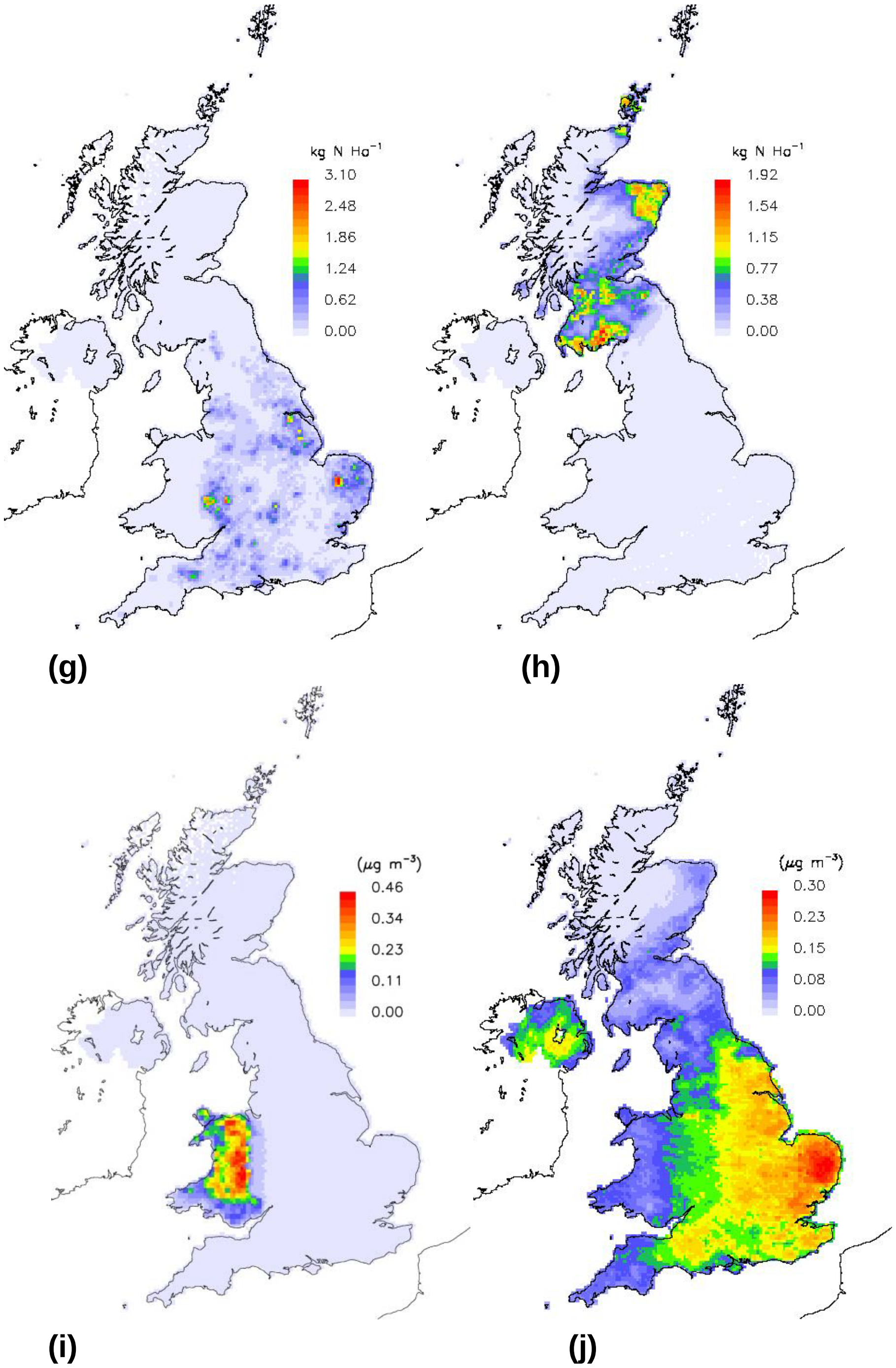


Figure 5: Examples of concentration and deposition footprints **(a)** SO_x dry deposition from a power station ; **(b)** NO_y dry deposition from international shipping ; **(c)** NO_y wet deposition from Europe ; **(d)** NO_x concentrations from railways in England ; **(e)** NO_x concentrations from heavy goods vehicles in England ; **(f)** NO_x concentrations from cars in London ; **(g)** NH_x dry deposition from 'other poultry' in England ; **(h)** NH_x dry deposition from beef cattle in Scotland ; **(i)** NH_x dry deposition from sheep in Wales ; **(j)** NO_3^- aerosol concentrations from Europe.

6. Modelling Base Cation emission, concentration and deposition

6.1 Introduction

Marine particles are one of the most important natural aerosol systems globally. They modify the Earth's radiative budget, and impact on both natural ecosystems and regional air quality (Colin *et al.* 2007). Aerosols influence radiative transfer directly, by scattering solar radiation and are also important as a source of cloud condensation nuclei (CCN) in the maritime environment. They are involved in the regulation of global climate through their influence upon the albedo of marine clouds and their impact upon the global atmospheric sulphur cycle (Foltescu et al. 2005). Sea salt aerosol particles can also change cloud properties and lifetime and provide media for chemical reactions (e.g.; Gong et al. 1997, Murphy et al. 1998, Behnke et al. 1997).

6.2 Production mechanisms.

Sea spray droplets come in three varieties: film droplets, jet droplets, spume droplets. Film (0.5-5.0 μm) and jet droplets (3-50 μm) derive from the same process: the bursting of air-entrained bubbles from oceanic whitecaps formed during the breaking of wind-induced waves (Martensson *et al.* 2003, Zhanga *et al*. 2005). Spume droplets (>20 μm) derive from the wind shear which tears the droplets directly from the wave crests (Andreas 1998). Emissions of drops from breaking wave whitecaps and sea foam has been established from laboratory studies (Wu, 1973 ; Monahan *et al.*, 1982 ; Petelski *et al.*, 2006). The existing empirical equations of drop emission from the sea surface are based on laboratory studies (Monahan *et al.* 1986; Monahan and Van Patten, 1989; Martensson *et al.* 2003) or on measurements of aerosol size distributions under an assumption that flux of the particles falling out of the near water atmospheric layer is equal to drop emission from the sea surface (Smith *et al.* 1993). The Marine aerosol consists of primary and secondary components. The primary marine aerosol is emitted from the water surface into the atmosphere directly as droplets with the composition of seawater enriched with chemical compounds, bacteria and viruses occurring in the upper water column and in the film covering the water surface.

There are several parameterizations for the sea spray generation function (dF/dr_0), which describes the surface flux of sea-spray aerosol, i.e. the number of droplets produced per unit surface area and per unit of time. Mostly, the source functions are presented as a power-law function and hence, at higher wind speeds, the source of sea spray increases in greater proportions than the wind speed increases. The generation functions for sea salt aerosols are primarily based on the relation between whitecap coverage and wind speed, although other variables such as sea surface temperature and salinity may also influence the flux (Martensson et al 2003). Studies presented by de Leeuw et al. (2000) show that the source function of Monahan et al. (1986) applies best to particles with diameters < 10 μm at formation, whereas the formulation offered by Smith et al., (1993) gives better results for larger particles.

6.3 Estimation of sea salt aerosol production for the UK domain.

It should be noted that the particle radius may be given as a:

- radius the sea salt particle would have at relative humidity RH = 0%, (r_{dry})
- radius the sea-salt particle would have when normalized to RH = 80%, (r_{80})
- radius at formation, RH~ 97%, (r_0)

The last one is also understood as a particle with the composition of seawater. The formulation depends on the way the source function has been derived. As a rule, it is assumed that $r_0 = 2r_{80} = 4r_{dry}$ (Gong et al. 1997).

To calculate the sea salt aerosol production (PM_{10}) emitted to the atmosphere, different parameterizations for three radii range are used. All formulations were calculated with a 0.1 μm radius size step for particles. The WRF modelled wind speed data, with a three hourly time resolution and 5 km x 5 km grid were used in the calculations. The number of particles produced from the domain in the range 0 – 10 μm was calculated with:

- **Martensson et al. (2003)**

The source function was determined from bubble-mediated laboratory studies to determine the flux as a function of whitecap coverage and then incorporated Monahan's wind speed and whitecap relationship to produce estimates. The parameterization was used in our work for particle radius below 0.8 μm.

$$\frac{dF}{dlogD_p} = 3.84 \times 10^{-6} V_{10}^{3.41} (A_k T_w + B_k)$$
$$A_k = c_4 D_p^4 + c_3 D_p^3 + c_2 D_p^2 + c_1 D_p^1 + c_0$$

$$B_k = d_4 D_p^4 + d_3 D_p^3 + d_2 D_p^2 + d_1 D_p^1 + d_0$$

F – particle flux (m^{-2} s^{-1})

V_{10} – mean horizontal wind speed at 10 m height (m s^{-1})

T_w – water temperature (K)

Dp- dry particle diameter (μm)

Ak, Bk – the polynomials for given size ranges with coefficients c0 to c4 and d0 to d4 reported in Martensson et al., (2003)

- **Monahan et al. (1986)**

This formulation is based on laboratory observations of dF/dr_0 and empirical relations for the whitecap cover (W in percent) as the function of the wind speed. The Monahan parameterization is used for the particles with radius (at 80% humidity) larger than 0.8 μm and lower than 4 μm radius.

$$\frac{\Delta F_i^{spume}}{\Delta r_i} = 1.373 \left| v_{h,10} \right|^{3.41} \left(1 + 0.057 r_i^{1.05}\right) 10^{1.19 e^{-B^2}} r_i^{-3}$$

$$B = (0.38 - \log_{10} r_i)/0.65$$

F – particle flux (m^{-2} s^{-1})
$V_{h,10}$ – mean horizontal wind speed at 10 m height (m s^{-1})
r_i – droplet radius (µm) at a reference relative humidity of 80%

- **Smith and Harrison (1998)**

This formulation is used for particles with radius above 4 µm.

$$\frac{\Delta F_i^{spume}}{\Delta r_i} = 0.2\left|v_{h,10}\right|^{3.5} e^{1.5\ln\left(\frac{r_i}{3}\right)^2} + 0.0068\left|v_{h,10}\right|^{3} e^{-\ln\left(\frac{r_i}{30}\right)^2}$$

F – particle flux (m^{-2} s^{-1})
$V_{h,10}$ – mean horizontal wind speed at 10 m height (m s^{-1})
r_i – droplet radius (µm) at a reference relative humidity of 80%

It is assumed that at formation, the density of particles is the same as the density of sea water and the particles have the same ion composition as ocean water. The Monahan and Smith & Harrison equations used in the present work give results for 80% humidity. Therefore the chemical composition was recalculated with the assumption that water has evaporated and that radius in 80% humidity is equal half of the radius at formation. To count the mass of PM_{10} sea salt particles it was assumed that they are spherical in shape. The salt mass of wet particles in the fine mode (radius <= 4 µm) and coarse mode (4 µm < radius <10 µm) is presented in Figure 6.1. To get the dry mass of base cations (Na^+, Mg^{2+}, Ca^{2+}, K^+) the total mass of PM_{10} particles (ions, other species contained in the sea water, and water) is multiplied by the percentage content of the given ion. The information on base cations (Na^+, Mg^{2+}, Ca^{2+}, K^+) emissions have been prepared for years 2003 and 2006.

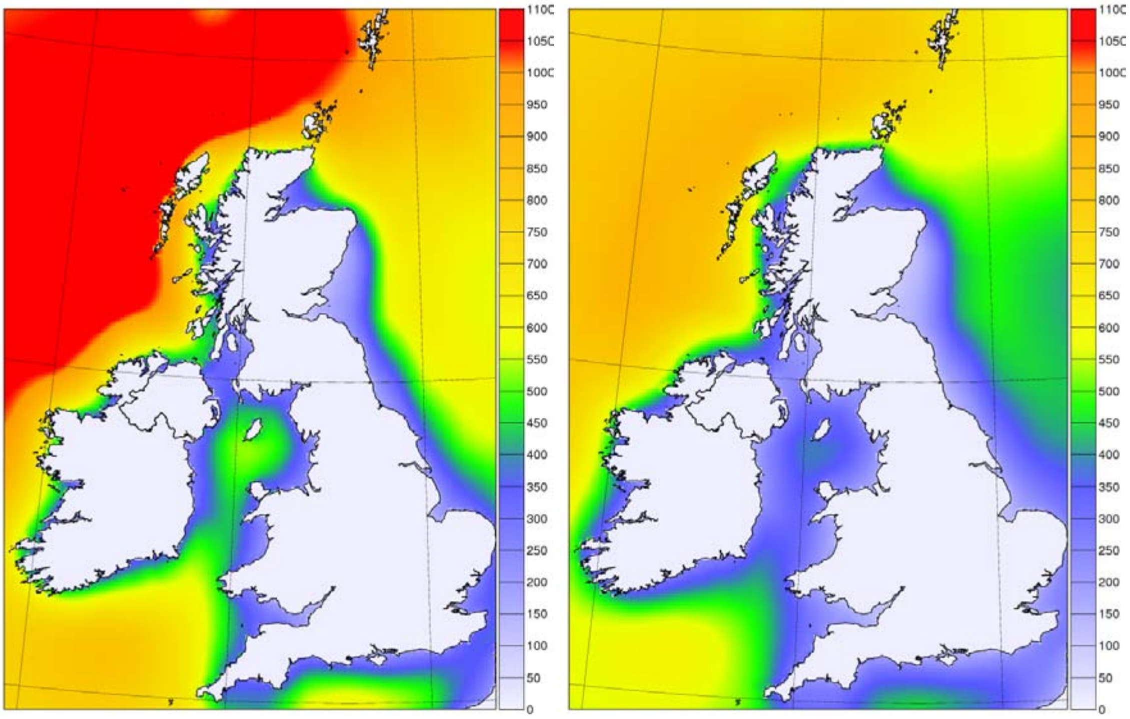


Fig. 6.1: Sea salt aerosol production of wet PM_{10} for the year 2003: fine fraction (r < 4 µm) – left and coarse fraction (r > 4 µm) – right (kg ha^{-1} $year^{-1}$).

6.4 FRAME simulations.

The FRAME model was run for the year 2003 and 2006 using the following emissions input data:

- Base cation (Na^+, Mg^{2+}, Ca^{2+}, K^+) emissions from the sea calculated using the method described above
- Calcium natural emission from the land: PM_{10} natural emission from the NatAir project (http://natair.ier.uni-stuttgart.de/) combined with a soil map
- NAEI base cation anthropogenic emissions of Na^+, Mg^{2+}, Ca^{2+}, K^+,
- The boundary conditions calculated with FRAME-Europe.

Additionally, to assess the importance of individual sources for the year 2006, two more simulations were run: first, with land emission only ; second with sea emission only.

The model results for each year were evaluated by comparing modelled values with measurements of concentrations in air and wet deposition of Na^+, Mg^{2+}, and Ca^{2+} from the UKEAP AGA-net and precip-net monitoring networks (http://pollutantdeposition.defra.gov.uk/ukeap). For the year 2006, in addition, the FRAME national budget of Mg^{2+} and Ca^{2+} dry and wet deposition was compared with CBED estimates, based on interpolation of measurements from the monitoring networks. There were 12 stations with validated measurements of Na^+ and Mg^{2+} concentrations in air and 10 stations for Ca^{2+} for the year 2003 and 21 stations for all ions for the year 2006. Fig. 6.2 illustrates the correlation with measurements of modelled Na^+, Mg^{2+} and Ca^{2+} concentrations for the year 2003 and 2006. For both years most points are located above/ below the 2:1 and 1:2 reference lines. The best correlation with measurements is evident for sodium, with R=0.6 for the year 2006, and the worst for Ca^{2+} for the same year.

The spatial distribution of concentration errors (C_e) for the year 2003 is presented in fig. 3. The C_e values are calculated in following way:

$$C_e = (\text{FRAME conc} - \text{Measured conc})/\text{Measured conc} * 100\%$$

The error values for all presented base cation concentrations have a similar spatial distribution. The model overestimates concentration on the west coast as well as in Scotland and underestimates in the center of the land (England). For sodium overestimates on the west coast are lower and underestimates in the England somewhat higher than for other species.

Wet deposition calculated with FRAME has also been compared with measurements. Some changes in the location of monitoring stations occurred between the years 2003 and 2006. Wet deposition was represented particularly well for sodium and magnesium, with correlation coefficients R=0.8 for both years (Fig. 6.4). Overestimation generally occurs for higher values of deposition, which are connected with sites close to the western coast, and underestimation occurs in hilly region (Fig. 6.5).

Considerable scatter is evident for Ca wet deposition. This could be connected with underestimation of Ca land emissions as well as with uncertainty in measurements.

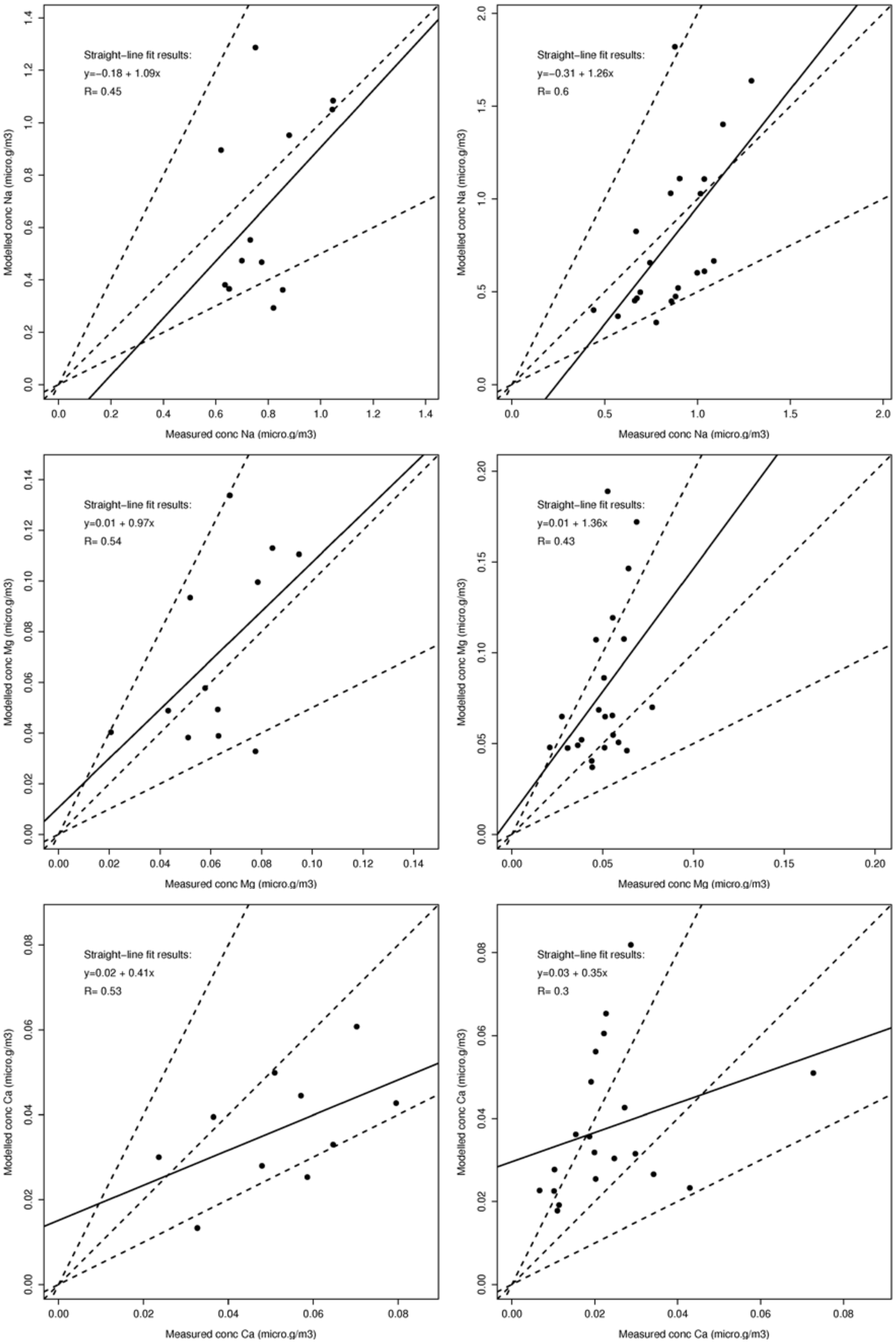


Figure 6.2: Correlation of modelled and measured air concentrations of Na^+, Mg^{2+} and Ca^{2+} for the years 2003 (left) and 2006 (right).

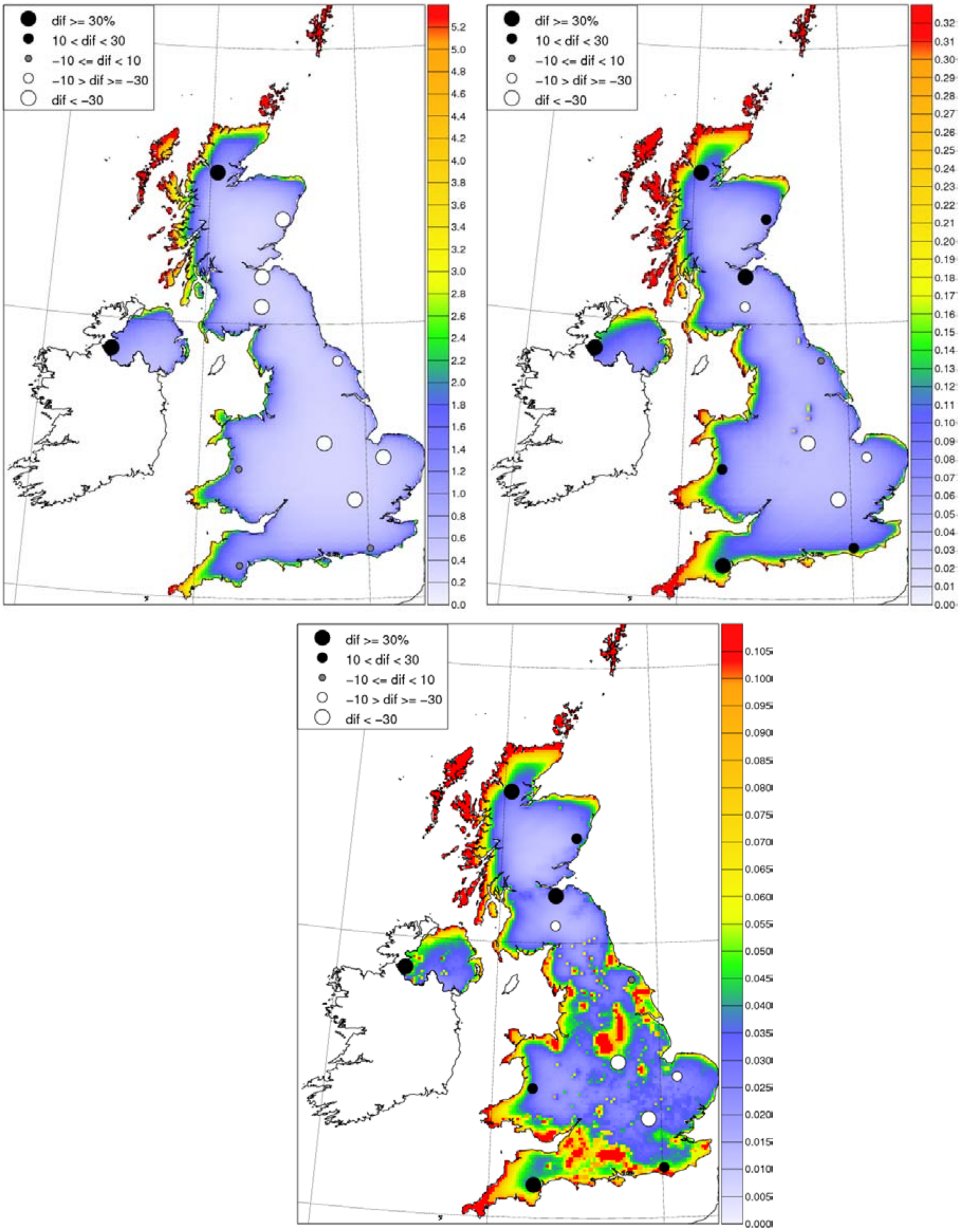


Fig. 6.3 Spatial distribution of base cation concentrations in air for the year 2003 (µg m^{-3}) – Na^{+} (upper left), Mg^{2+} (upper right) and Ca^{2+} (bottom) with errors for sites (%).

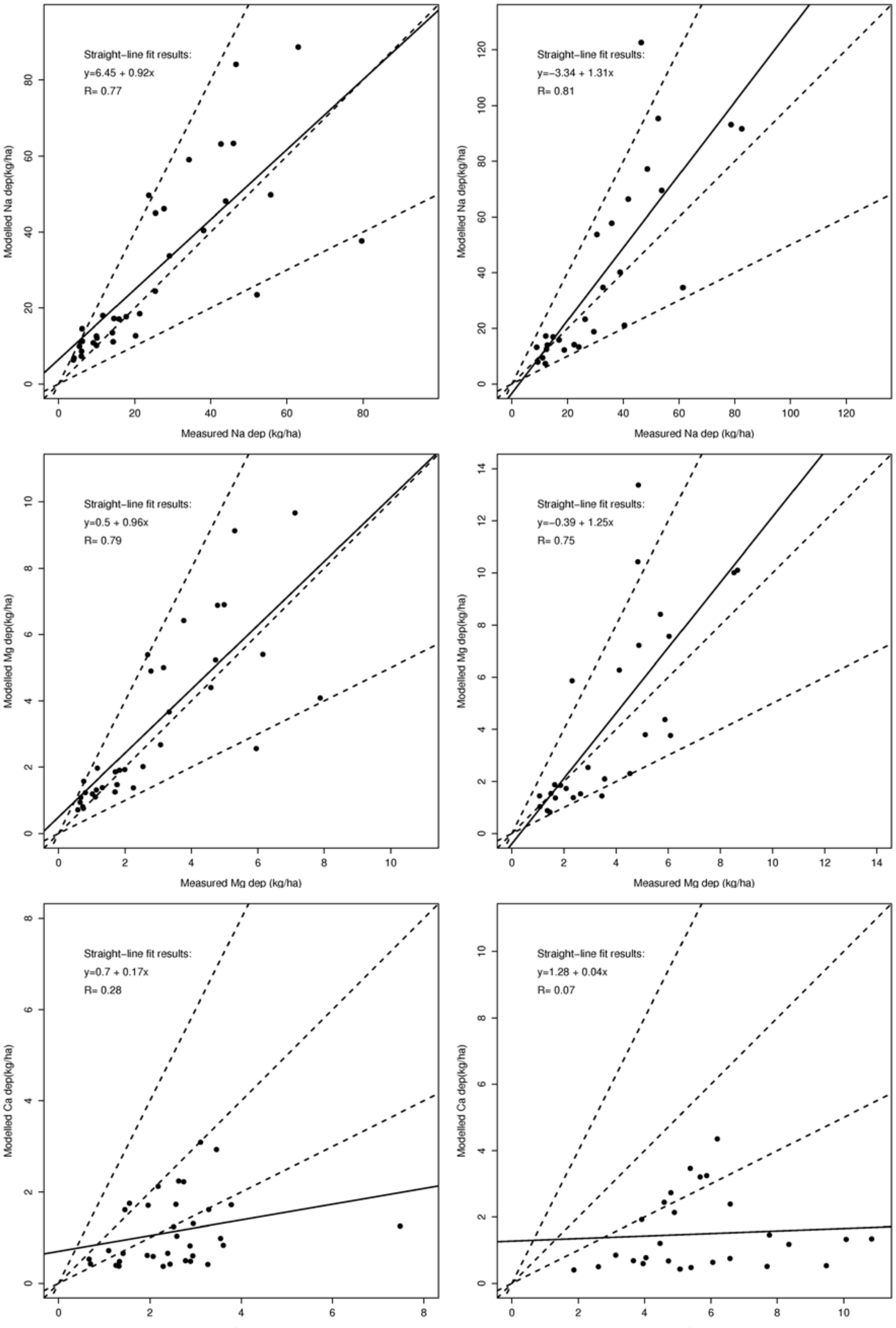


Figure 6.4: Correlation of modelled and measured wet deposition of Na^{+}, Mg^{2+} and Ca^{2+} for the year 2003 (left) and 2006 (right).

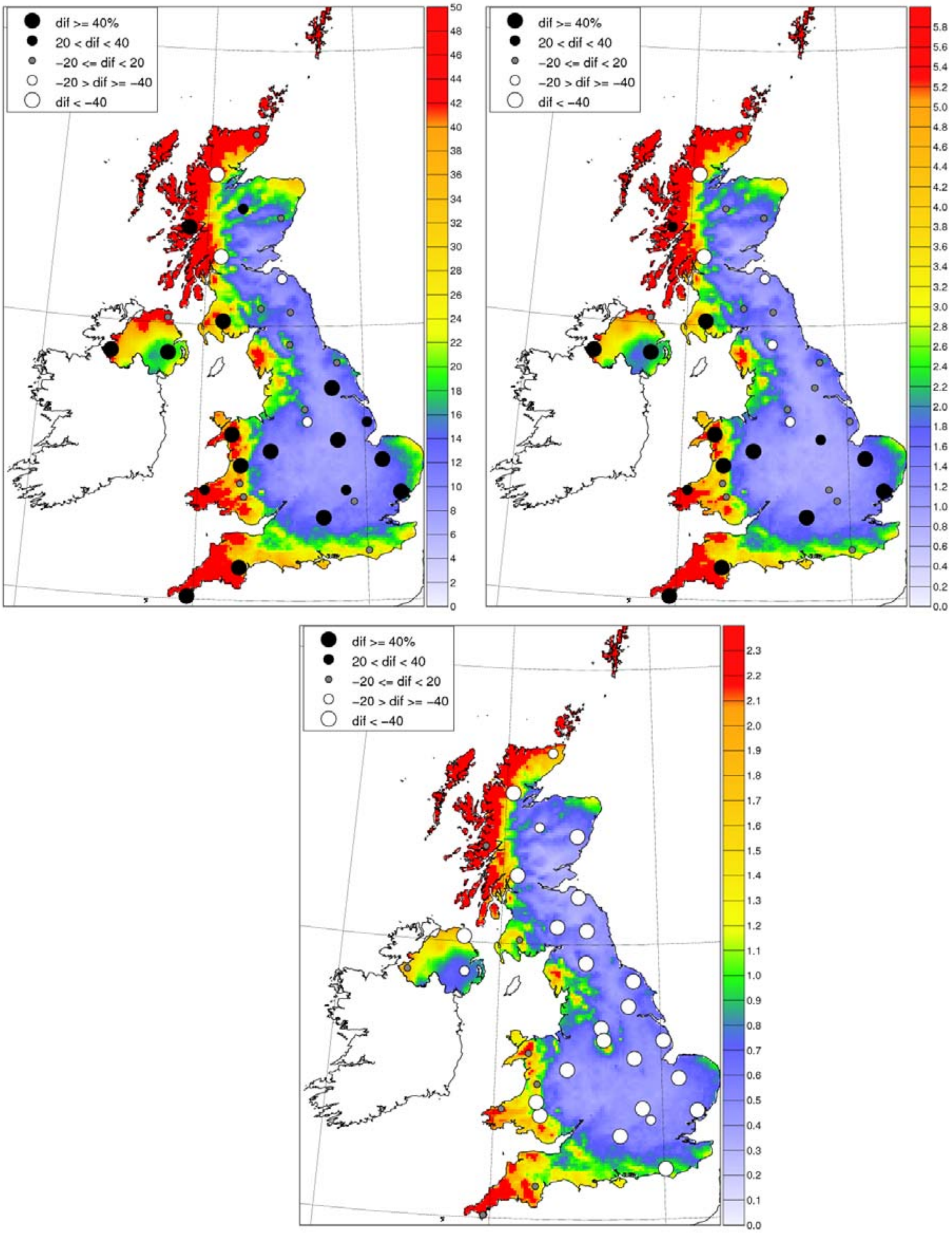


Figure 6.5: Spatial distribution of base cation wet deposition for the year 2003 (kg ha^{-1}) – Na^{+} (upper left), Mg^{2+} (upper right) and Ca^{2+} (bottom) with errors for sites (%).

Table 6.1: Comparison of the FRAME national deposition budget (Gg) of sea salt and non sea salt base cations (Mg and Ca) with CBED estimations for the year 2006.

land only			**sea only**		
Gg	Mg	Ca	Gg	Mg	Ca
FRAME					
Dry	0.14	1.85	dry	30.2	9.6
Wet	0.37	2.6	wet	99.4	31.8
CBED					
Dry	0.14	9.7	dry	12.0	4.2
Wet	0.45	58.0	wet	130.1	47.4

The FRAME wet and dry deposition budget for sea salt and non sea salt particles has been compared with CBED estimations for 2006. It is evident that for Ca we have large underestimations of the non sea-salt contribution to both dry and wet deposition, which could be caused by an underestimation of anthropogenic or wind re-suspended emissions. It is also noted that FRAME sea salt regional budget of Mg and Ca is higher for dry deposition and lower for wet deposition than the CBED estimations.

6.5. Maps of Concentration and Deposition

The highest values of base cation concentrations are observed close to the coastal zone, especially in the western part of UK (Fig. 6.3). In these regions, concentrations of Na^+, Mg^{2+}, and Ca^{2+} can even exceed 5 μg m^{-3}, 0.32 μg m^{-3}, 0.1 μg/m^3, respectively. For most areas of the UK the concentrations are in the range 1.0 to 2.0 μg/m^3 for Na^+, 0.05 to 0.12 μg m^{-3} for Mg^{2+}, and 0.03 to 0.04 μg m^{-3} for Ca^{2+}. Higher BC concentrations are also observed in some industrial areas. This is especially evident for calcium in the region of Northern England and South-west England. Wet deposition of BC reaches the highest values on the western coast, and in hilly regions, where deposition of Na^+, Mg^{2+} and Ca^{2+} exceeds 50 kg ha^{-1} $year^{-1}$, 6 kg ha^{-1} $year^{-1}$ and 2.5 kg ha^{-1} $year^{-1}$ respectively (Fig. 6.5).

Additional work (not shown here) included an update of base cation emissions for the year 2010.

7. Deposition and Concentration of Heavy Metals

7.1 Introduction

Trace metals of primary concern for human health and the environment include Arsenic (As), Cadmium (Cd), Chromium (Cr), Copper (Cu), Lead (Pb), Mercury (Hg), Nickel (Ni), Selenium (Se), Vanadium (V) and Zinc (Zn). Hg is not included in this study due to its complex chemical behaviour. The metals of concern for natural ecosystems include Cd, Pb, Cu, Ni and Zn. These metals have been shown to be detrimental to soil microbes and vegetation when critical limits are exceeded (RoTAP 2012). Estimates in the UK have indicated areas of both managed and unmanaged woodland where critical load exceedance occurs for Cu, Pb and Zn. Pb is toxic at very low exposure levels and has acute and chronic effects on human health. It is a multi-organ system toxicant that can cause neurological, cardiovascular, renal, gastrointestinal, haematological and reproductive effects. Cadmium is a toxic element for humans which can result in kidney and bone damage and is carcinogenic by inhalation.

A survey of mosses at 170 sites in the UK revealed a decrease in heavy metal concentrations between 1995 and 2005 which was consistent with reductions in emissions (Harmens et al., 2009). Assessment of the impact of atmospheric metal deposition on natural ecosystems is made using ‘critical loads’: the rate of deposition which at steady state leads to the metal concentrations in soils and water reaching a threshold for adverse effects. Critical loads in the UK have been mapped for Cd, Pb. Cu, Ni and Zn for a number of different ecosystems by Hall et al. (2006). For the year 2005 it was estimated that over 50% of forests were subject to deposition exceeding the critical loads for Cu, Pb and Zn (RoTAP, 2012). Exceedance of the critical loads was not evident for Cd and Ni.

The UNECE protocol on heavy metals (www.unece.org/env/lrtap/) was signed in 1998. This committed the UK to reducing the emissions of Pb, Cd and Hg to levels below those of 1990 as well as phasing out leaded petrol and requiring the use of the best available technology to reduce emissions from stationary sources. The sources of emissions of heavy metals to the atmosphere are quite diverse. Whilst the primary source of Pb was previously road transport, since the introduction of lead-free fuel in the 1990s, national emissions have fallen significantly and the iron and steel industry is now the main emissions source. A detailed breakdown of emissions sources for heavy metals in the UK is presented in the National Atmospheric Emissions Inventory (NAEI: http://www.naei.org.uk/). During the period between 1990 and 2006, emissions of heavy metals from the UK have fallen by 70%, 85%, 79%, 58%, 63%, 97%, 53%, 44%, and 61% for As, Cd, Cr, Cu, Ni, Pb, Se, V and Zn respectively.

FRAME was adapted to include the emissions, transport and deposition of heavy metals in the UK at a 5 km resolution. The boundary conditions were initialised with concentrations generated from a FRAME-Europe simulation at a 50 km resolution on the EMEP grid. The European emissions were taken from ESPREME (http://espreme.ier.uni-stuttgart.de/) and the UK emissions from the NAEI. The deposition and concentrations of heavy metals are calculated simultaneously with base cations and are part of the same suit of FORTRAN routines as acid-FRAME but have a separate main routine. Calculation of concentration and deposition of sea salts and heavy metals is simpler than with sulphur and nitrogen as no chemical reactions are involved.

FRAME was used to calculate the concentrations in air and deposition of heavy metals from the national atmospheric emissions inventory. Comparison of the model results with measurements of metal concentrations in air and precipitation allow us to assess the magnitude of missing emissions sources which are needed to explain the measured metal concentrations.

7.2 Results and Discussion

The modelled concentration in air and dry and wet deposition for the year 2006 over the UK are illustrated in figures 7.1 for Cd and 7.2 for Pb. In general a strong gradient is evident with the higher concentrations found in the central and southern part of the country due to both long range transport of pollutants from European sources as well as the greater intensity of emissions sources in the southern part of the UK. The influence of emissions from major urban areas and the road network is most pronounced for air concentrations and dry deposition of Cd. Furthermore high values for wet deposition occur in more remote areas with lower air concentrations but high annual precipitation, such as the Highlands of Scotland.

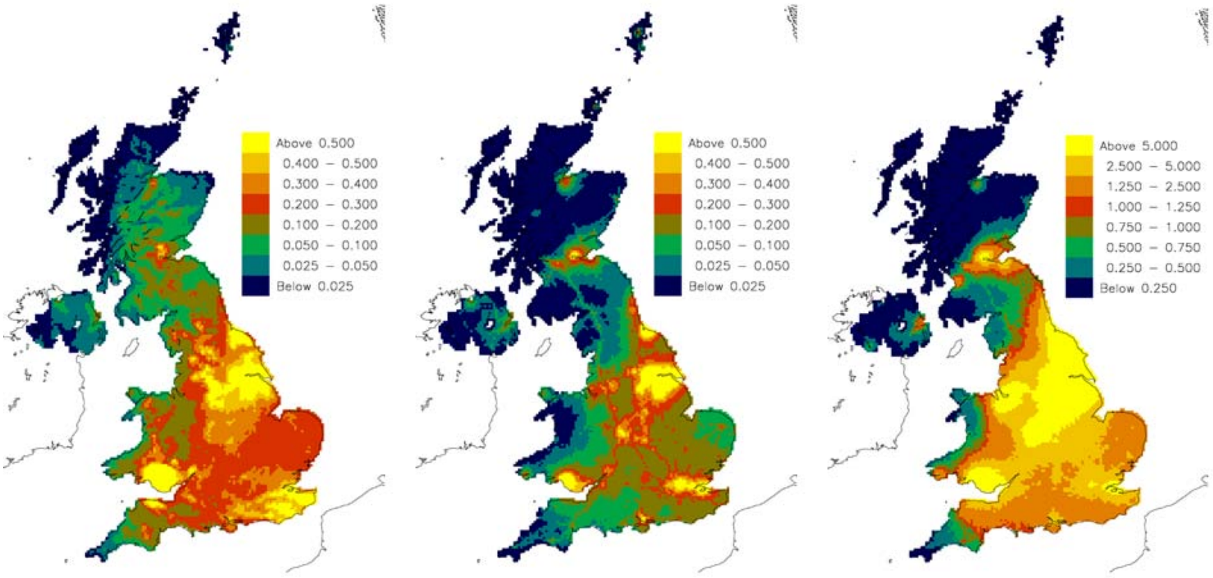


Figure 7.1: Modelled concentration of Cd in air (left; ng m^{-3}) ; dry deposition of Cd (centre ; g ha^{-1}) ; wet deposition of Cd (right ; g ha^{-1})

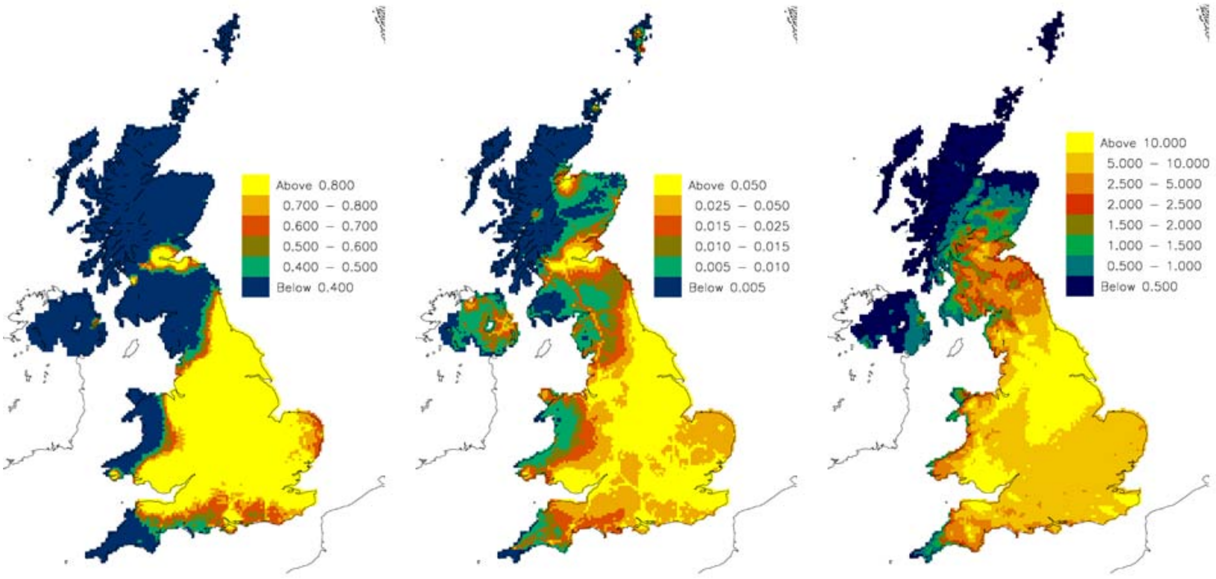


Figure 7.2: Modelled concentration of Pb in air (left; ng m^{-3}) ; dry deposition of Pb (centre ; g Ha^{-1}) ; wet deposition of Pb (right ; g Ha^{-1})

The annual average air concentration and wet deposition for all metals has been compared with the values obtained by measurement at the monitoring networks. Figure 7.3 and 7.4 illustrate the correlation with measurements for Cd and Pb respectively. In general, air concentrations and wet deposition of both these metals are significantly under-estimated by the model. For both metals there is evidence of a much stronger correlation with measured air concentrations (R^2 of 0.84 for Cd and 0.89 for Pb) than with wet deposition (R^2 of 0.42 for Cd and 0.67 for Pb). This may reflect both the complexity of the wet deposition process which is not fully captured by the simple modelling technique. Secondly there could be greater uncertainty in measured metal wet deposition than in measured air concentrations, possibly due to contamination by dry deposition of metals to the surface of the collectors. The low slope of the Pb correlation plots (0.08 for air concentration ; 0.17 for wet deposition) illustrates that overall Pb concentrations in both air and precipitation are greatly under-estimated by the model. This is a clear indication of missing or under-estimated emissions sources.

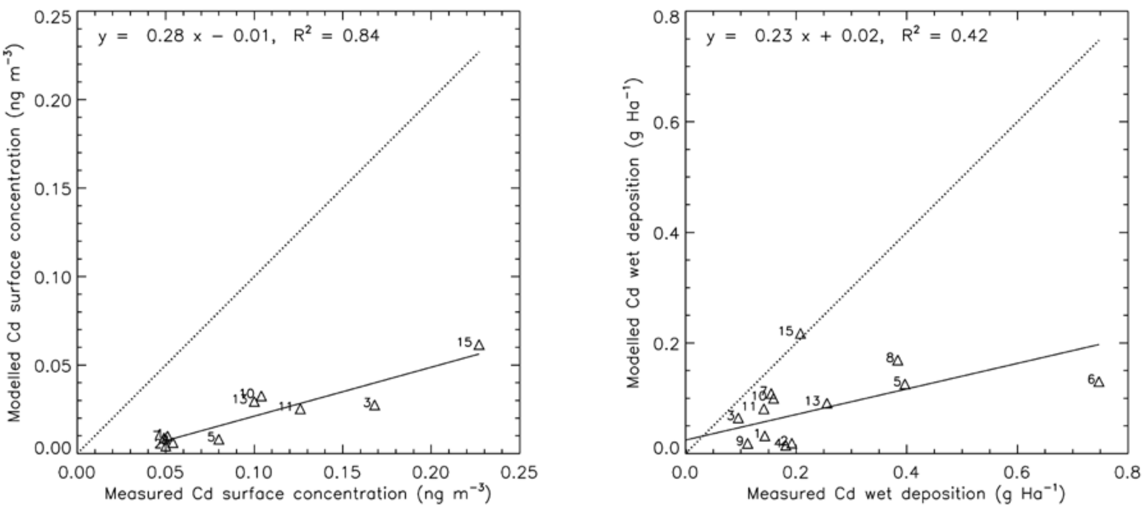


Figure 7.3: Correlation of modelled concentrations of Cd in air with measurements (left); Correlation of modelled wet deposition of Cd with measurements (right)

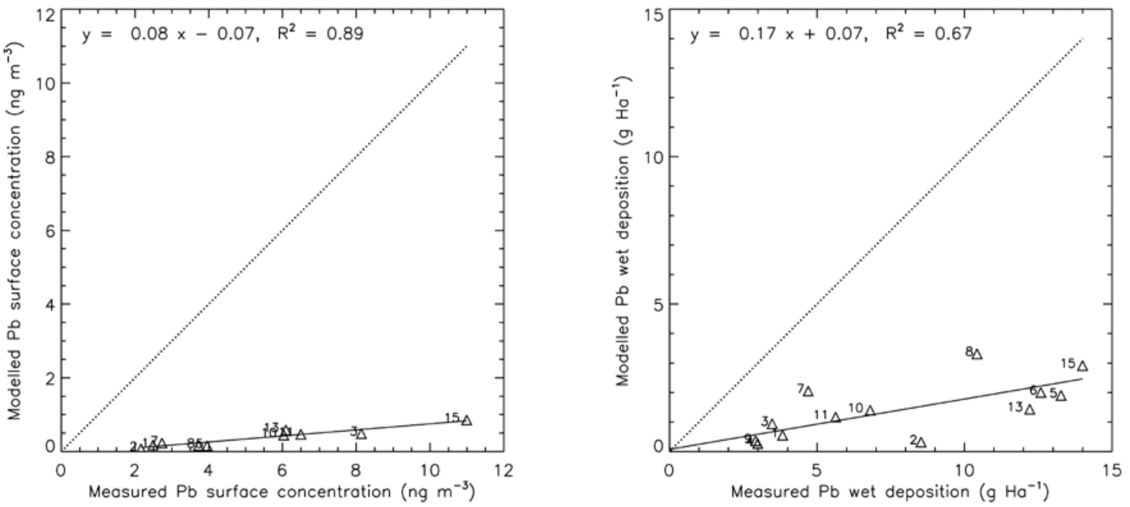


Figure 7.4: Correlation of modelled concentrations of Pb in air with measurements (left) ; Correlation of modelled wet deposition of Pb with measurements (right)

A rural network for monitoring the concentrations of heavy metals in air and precipitation has been in operation since the year 2004 (Malcolm *et al.*, 2010). For the year 2006 the network consisted of 13 sites at which samples of precipitation were collected for analysis of concentrations. Measurements of the concentration of heavy metals in air were also made at ten of these sites.

Analysis of the correlation with measurements of concentrations in air and wet deposition has been considered for all the metals included in the study. As with Cd and Pb the modelled metal concentrations generally correlated well with the measured air concentrations (with r^2 of 0.77 averaged for all metals except Se). A poorer correlation with wet deposition was evident for all metals (with an average r^2 of 0.48 for all metals except Se). For Vanadium there is evidence of over-estimated emissions in the NAEI as both air concentrations and wet deposition were significantly overestimated by the model (Normalised Mean Biases of 4.2 and 8.5 respectively). The poorest correlation was for Se wet deposition where the model showed no correlation with measurements. With the exception of V, all the modelled data show significant negative NMBs for both concentration and wet deposition. These results suggest that the official NAEI emissions estimates are insufficient to account for observed concentrations of As, Cd, Cr, Cu, Ni, Pb, Se and Zn by factors ranging from 2 – 10. Calculation of the total dry and wet deposition budgets for the UK showed that wet deposition is the dominant process for transferring heavy metals from the atmosphere to the surface. On average, for all the metals, wet deposition accounted for 64% of total deposition and dry deposition for 36%.

The historical legacy of significantly higher metal emissions during the previous few decades means that these pollutants are still present in the environment and can be re-suspended from agricultural areas and bare soils by wind erosion and from roads by vehicle turbulence. Estimates of the magnitude and spatial distribution of annual emissions of lead, cadmium, nickel and arsenic in the UK have been undertaken by Abbott (2008). The methods employed follow those developed by Mansell *et al.* (2006) in the United States and applied to Europe by the European Modelling and Evaluation Programme (EMEP Ilyin *et al.*, 2007; Travnikov *et al.*, 2012).These methods were applied to the UK using measured meteorological data, high resolution land cover maps and data on the metal content in soils. The total re-suspended mass of heavy metals was estimated to be approximately one third of that from the NAEI for As, Ni and Pb and 14% for Cd respectively. The contribution from soils was more than an order of magnitude higher than that from vehicles. It was noted that these estimates were based on metal concentrations taken from 15 cm surface soil core samples. The concentrations in the re-suspended surface layer of dust are largely unknown but are likely to be considerably higher.

A number of additional emissions scenarios have been undertaken with the FRAME model including estimates of re-suspension from both Abbott (2008) and EMEP as well as consideration of underestimated primary emissions from both point sources and vehicles. These results are analysed in greater detail in Hallsworth *et al.* (2012). These results suggest that a major increase in estimates of heavy metals to the atmosphere is needed to explain the difference between the model and the measurements. A combination of a significant increase in primary emissions as well as re-suspension with a greater magnitude than primary emissions would be needed to explain the measured values of metals in air and precipitation.

Additional work (not shown here) included an update of the heavy metal emissions for the year 2010.

8. Concentration of total PM

The FRAME model was run for secondary inorganic aerosols (SIA), primary particulate matter (PPM, both for land sources and shipping), and sea salt aerosol (SSA) to calculate the total concentration of PM_{10}. The emission and meteorology input data was for the year 2007. Two simulations were run for PPM - simUKa (only anthropogenic emission) and simUKan (anthropogenic and natural emissions from land) to show the individual contributions of emission sources. To include the role of marine emissions in primary particulate matter concentration, SSA concentration was added to the simUKan simulation (simUKans). In order to get the total concentration of PM_{10}, a spatial distribution of secondary organic aerosols (SOA) was needed. This map was obtained from the EMEP model, provided by David Simpson (Simpson *et al.* 2007, Bergström *et al*., 2012). The results were validated by the comparison of modelled concentrations with PM_{10} measurements. The spatial distribution of PPM_{10} concentration for simUKa, simUKan and simUKans is shown in figure 8.1.

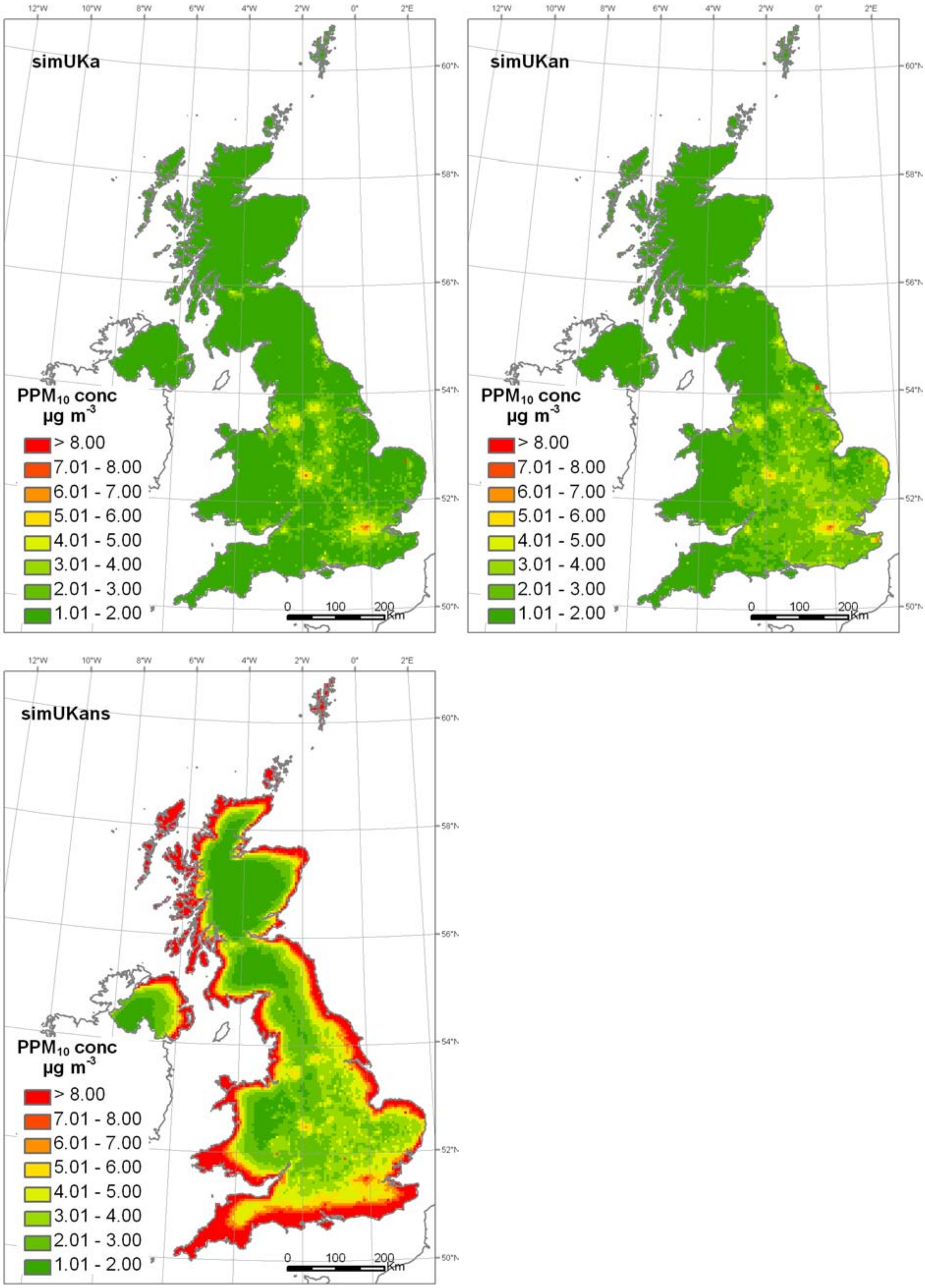


Figure 8.1: Primary particulate matter concentration (PPM_{10}). Simulation with anthropogenic emissions only (upper left), anthropogenic and land natural emissions (upper right), and anthropogenic, land natural and SSA (lower).

The national average concentration of PM_{10} is 12.0 µg m^{-3} (figure 8.2). The total PM_{10} concentration has a dominant contribution from particles from natural sources (54%). SSA contributes 95% of natural particles. Increased values of PM_{10} concentration are evident in the area of several kilometres along the coast. Higher concentrations also occur in the south-east part of the country. The contribution of chemical components (SIA, PPM, SOA) to the total concentration of PM_{10} is shown in figure 8.3. The contribution of PPM_{10} in PM_{10} varies from 30-40% in the central part of the UK to 90% at the coast. The spatial distribution for SIA is different – the lowest contribution is at the coast (10-20%) and the highest in the centre of England. The SOA contribution is low for the all UK, generally lower than 5%

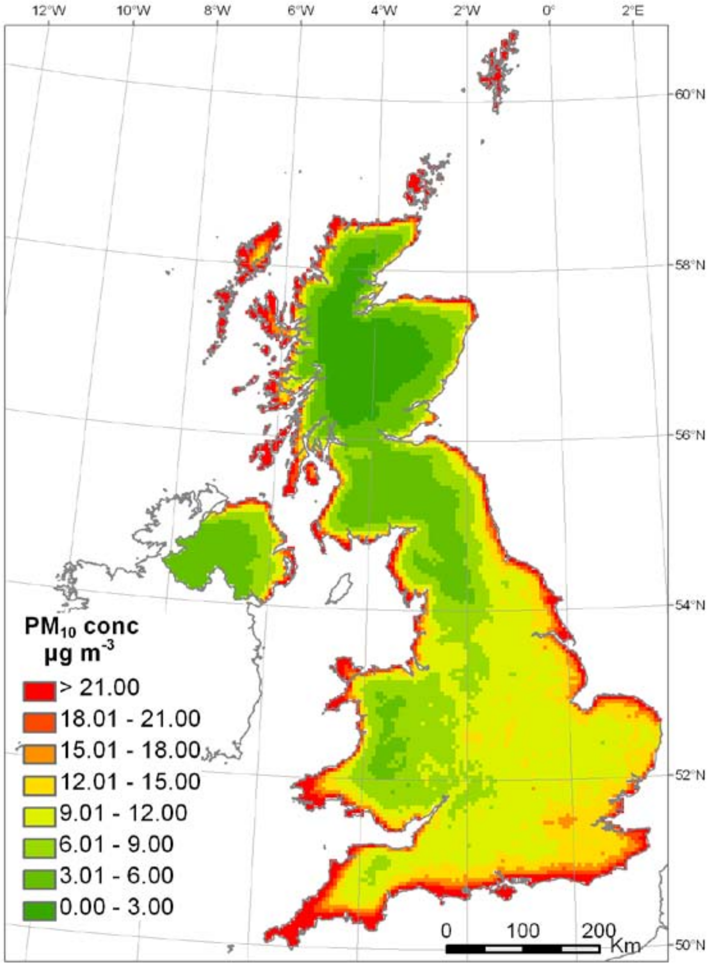


Figure 8.2: PM_{10} total concentration (FRAME results – dry particles)

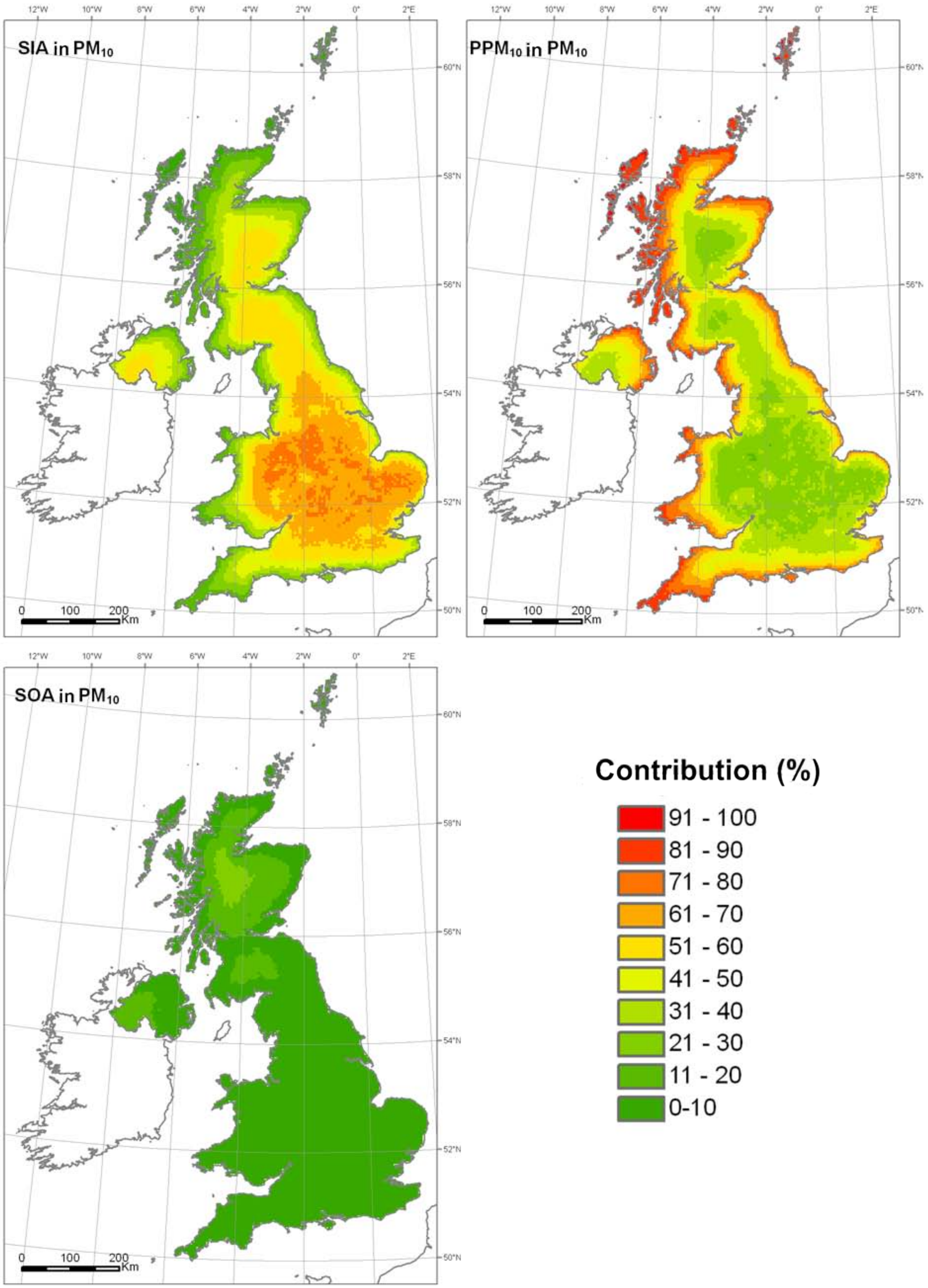


Figure 8.3 Contribution of SIA, PPM and SOA in total PM_{10} concentration.

The FRAME model results were validated against measurements of PM_{10} air concentration. For the validation process background stations were used. The FRAME model calculates results for dry particles. However, in reality particles in the natural environment are deliquescent and contain a component of water. A scaling factor of 1.3 was therefore used for the model data in line with recommendations from AQEG (2005), shown in figure 8.4.

Following data were included for the model validation (figure 8.5):

- 1) FRAME PM_{10} concentration without SSA (SIA+PPM+SOA),
- 2) FRAME PM_{10} concentration with SSA (SIA+PPM+SOA+SSA),
- 3) FRAME PM_{10} concentration with SSA; modelled concentration corrected for water content

The spatial distribution of relative errors is presented in figure 5 and measures of the average error are summed up in Table 8.1 (both according to the data set 3 above).

The validation process indicates the model tendency to slight underestimation of measured values (MB<0). Only one point is out of the area marked out by reference lines (dashed line in scatter plots, FAC2=0.98). Relative errors in the range of (-0.26) – (-0.50) appear in central England; for other areas errors are in the range (-0.25) – (+0.25). A larger error occurs for only one station (Lough Navar) in Northern Ireland, with RE = -0.60.

Table 8.1: Measures of the error (MB – mean bias ; MAGE – Mean Average Gross Error ; RMSE – Root Mean Square Error ; MNAE – Mean Normalised Absolute Error ; NMB – Normalised Mean Bias ; MFB - Mean Fractional Bias ; MFE - Mean Fractional Error ; IOA – Index of Agreement ; FAC2 – Factor of Two. *MB, MAGE, MAGE* in µg m^{-3}, remaining statistics are dimensionless.

MB	***MAGE***	***RMSE***	***MNAE***	***NMB***	***MFB***	***MFE***	***IOA***	***FAC2***
-4.098	4.874	5.793	0.231	-0.197	-0.235	0.275	0.64	0.97

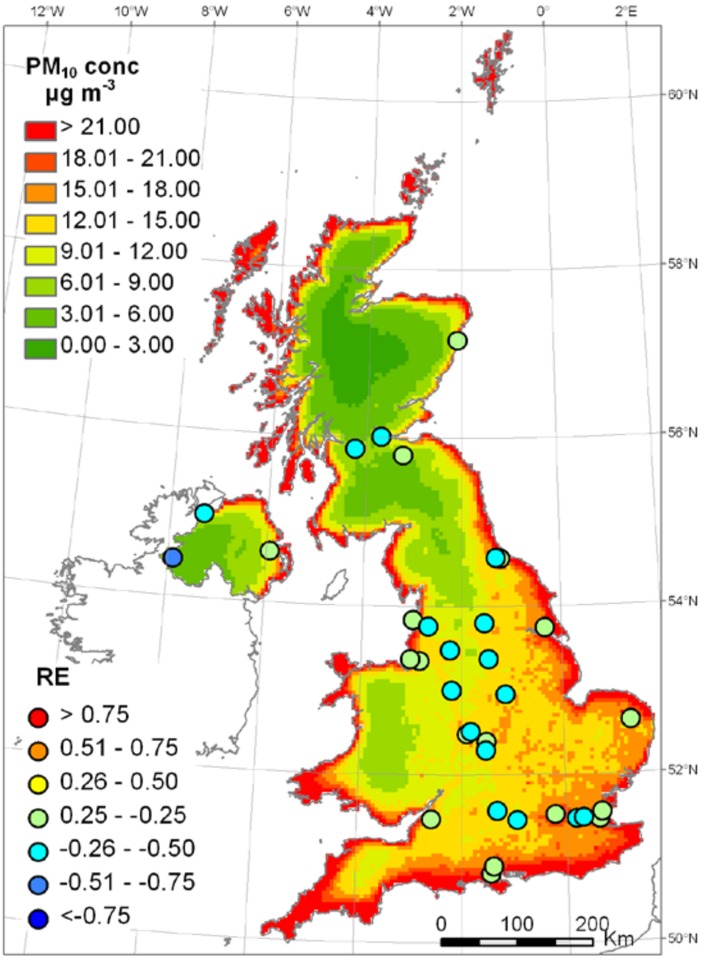
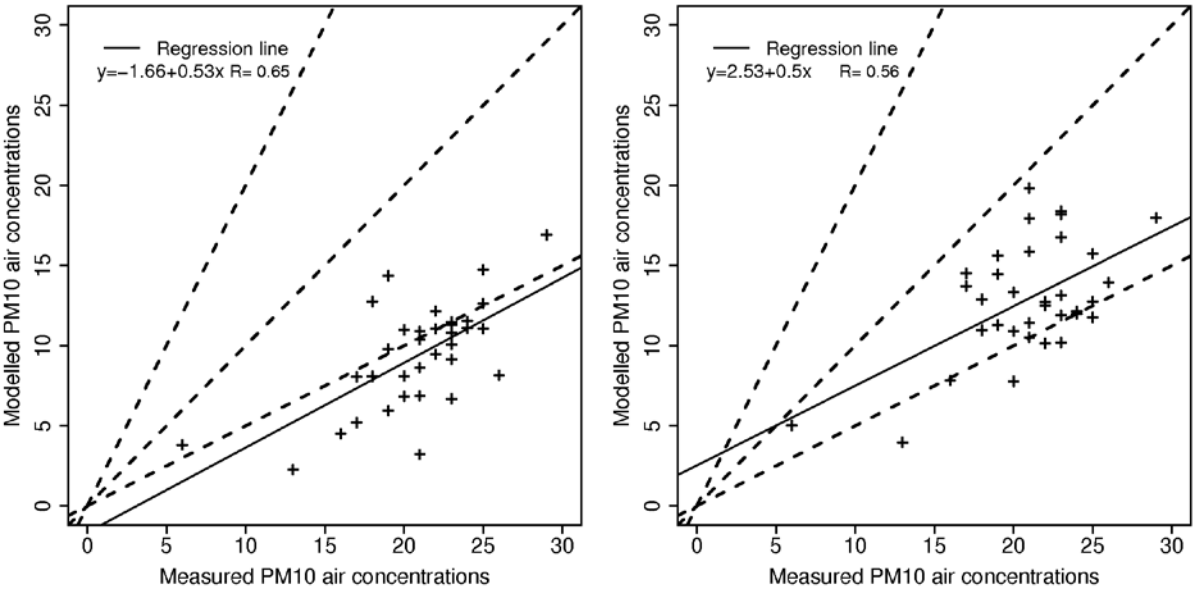


Figure 8.4: Modelled PM_{10} concentration with correction for water component including the spatial distribution of relative error (RE) for comparison with measurements.



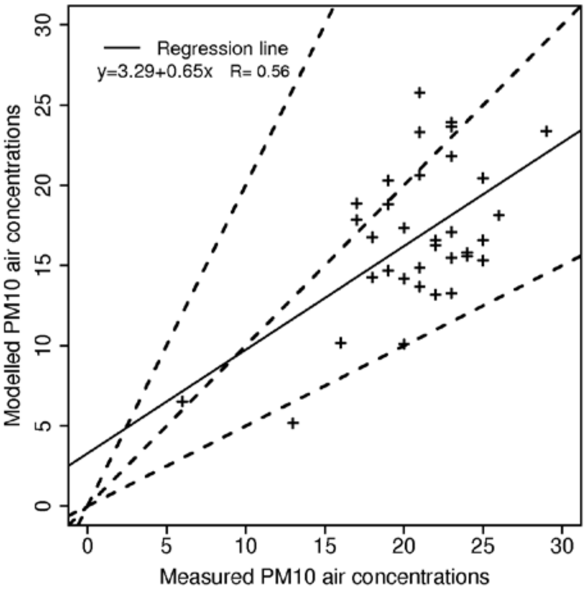


Figure 8.5: Scatter plots for PM_{10}. PM_{10} modelled concentration: without SSA (top left), with SSA added (top right), with addition of water component (bottom).

9. Re-parallelisation of the FRAME source code

Atmospheric transport models generally make use of High Performance Computers to reduce simulation times. To benefit from the multiple processing power of these computers requires the source code to be 'parallelised'. Essentially this involves splitting the calculations amongst different processors which are executed simultaneously. This contrasts with 'serial code' where calculations are performed consecutively on a single processor. A fundamentally different approach must be adopted to the parallelisation of Lagrangian and Eulerian atmospheric transport models. In Lagrangian models (i.e. FRAME, HARM, TRACK, NAME) calculations are performed along trajectories which are independent from another. Consequently such models are suitable for parallelisation with **H**igh **P**erformance **F**ORTRAN (**HPF,** a Data Parallel model) or OpenMP (Open Multiprocessing - a Shared Memory model). In Eulerian models, calculations are co-dependent and information must be continually dynamically passed between adjacent grid squares. Such models (i.e. WRF, CMAQ, EMEP, EMEP4UK) are parallelised with **M**essage **P**assing **I**nterface (**MPI**). Parallelisation of the FRAME code was initially undertaken by Fournier *et al.* (2002) using HPF. However during the last decade, HPF has become less frequently used and has generally been replaced by OpenMP, although some High Performance Computers continue to support HPF. Certain job schedulers (i.e. Grid Engine, CONDOR) are known to be incompatible with HPF. Therefore To future-proof FRAME (i.e. allow portability on to new High Performance Computers) it was necessary to re-parallelise the code to OpenMP. This work was undertaken as part of an MSc project (Tsilkos, 2011) at the Edinburgh Parallel Computing Centre.

A FRAME simulation comprises of 100,000 trajectories for a 5 km resolution simulation or 500,000 trajectories for a 1 km simulation. The High Performance Computer used for this work was

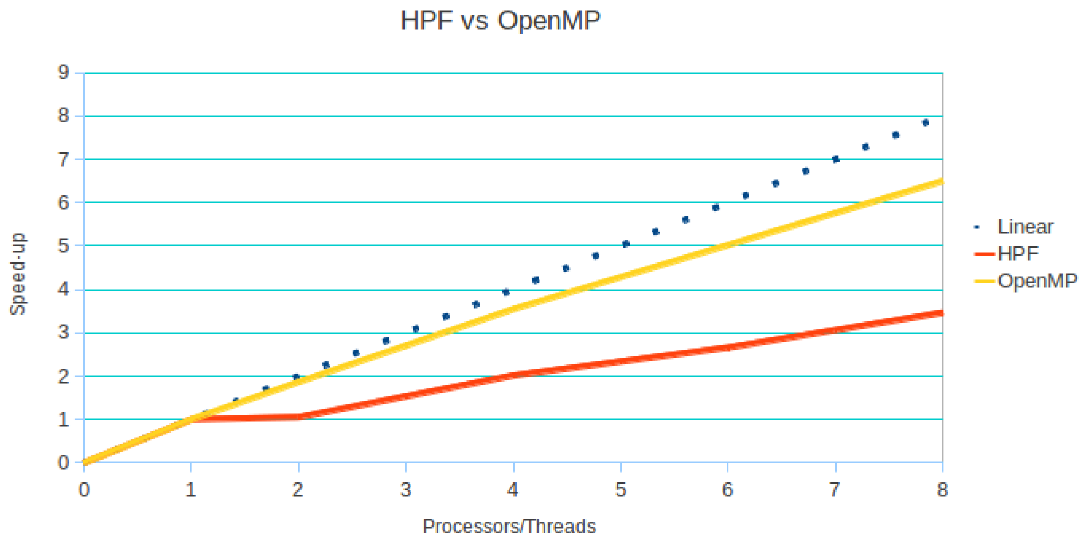
Nemesis based at CEH Edinburgh. Nemesis comprises of **26 nodes** each with **8 cores** (208 cores in all). The system includes 24 TB of disk storage and Infiniband inter-connectivity to ensure rapid communication between processors. The latter is important for MPI simulations but less relevant for HPF and OpenMP. FRAME 9.0 was re-parallelised and coded to optionally allow compilation: (i) in serial (ii) with HPF (iii) with OMP. Version 9.0 of the code was tested and found to give identical results for versions 8.5, 9.0 (HPF), 9.0 (OpenMP) for 5 km resolution simulations. Compilation with OpenMP permits simulation with a single 8 core node whilst HPF simulations can be distributed across multiple cores. In practice FRAME simulations perform fastest with HPF using 3 nodes. Table 9.1 illustrates the run times for OpenMP and HPF. It can be seen that whilst the run times are similar (~ 20 minutes for 5 km resolution simulations and 12 hours for 1 km resolution simulations) OpenMP is more efficient as it achieves these run times with a single node. OpenMP is now the parallelisation model of choice for FRAME simulations, benefitting from the requirement of a single processor to avoid queues on the Nemesis job scheduler. 1 km resolution OpenMP simulations have been used in Defra projects SAMBA and Ammonia for Future Patterns, achieving good operational turn-around times. FRAME-Europe (running on the 50 km resolution EMEP grid) has also been tested successfully with OpenMP. Heavy Metal and Base Cation FRAME (which use a different main routine) require further work for migration from HPF to OpenMP.

Table 9 Dependence of FRAME model performance on complier choice:
Model run time using HPF and OMP

	HPF	**OMP**
Number of cores (nodes)	24 (3)	8 (1)
5 km resolution run time	21 mins	27 mins
1 km resolution run time	12 hrs	12 hrs

The advantage of OMP is clearly illustrated in Figure 9 which shows the speed-up factor (i.e. relative increase in simulation time) for a 5 km FRAME simulation with OMP and HPF. The OMP simulation speed-up increases efficiently (nearly directly in proportion to the number of processors used).

Figure 9: Speed up in simulation time with processor number for HPF and OMP



Web site

A web site has been maintained illustrating output from the FRAME model and including maps of deposition and concentrations and plots of correlation with measurements as well as a list of peer reviewed publications: http://pollutantdeposition.defra.gov.uk/frame

Acknowledgement

This work was supported by the Department for the Environment, Food and Rural Affairs under contract AQ0719 ‘Modelling the Deposition and Concentration of Long Range Air Pollutants’. The authors are grateful to David Simpson (EMEP) for provision of modelled data on organic aerosol concentration, to Anne Misra, AEA-Ricardo for provision of data on future estimates of UK emissions, to John Abbott, AEA-Ricardo for provision of data on re-suspension of heavy metals and to Tim Oxley, Imperial College for provision of emissions data and the regional land mask used for calculating source-receptor matrices.

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